SYNTHESIS OF CHELATING IONOPHORES AND THEIR ELECTROANALYTICAL STUDIES AS CHEMICAL SENSORS

Ph.D. THESIS

by

MANOJ KUMAR SAHANI

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE - 247667 (INDIA)
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A THESIS

Submitted in partial fulfilment of the
requirements for the award of the degree
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CANDIDATE’S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled, “**SYNTHESIS OF CHELATING IONOPHORES AND THEIR ELECTROANALYTICAL STUDIES AS CHEMICAL SENSORS”** in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy and submitted in the Department of Chemistry of the Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out during a period from August, 2010 to December, 2015 under the supervision of Dr. A. K. Singh, Professor and Dr. A. K. Jain, (Retd) Professor, Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other Institute.

(MANOJ KUMAR SAHANI)

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

(A. K. Singh) Supervisor	(A. K. Jain) Supervisor

Date:

ABSTRACT

Environmental pollution is defined as the undesirable changes in physical, chemical and biological characteristics of ecosystem. It is therefore important to study the adulteration caused by pollution and its consequences on the ecosystem. Although, increased urbanization and rapid industrialization has improved the standard of life, but associated pollution has adversely affected the quality of life. Some adverse health effects because of metal toxicity are many nutritional deficiencies, neurological disorders, cancer and other debilitating chronic diseases. Monitoring of environmental pollution caused by toxic metals has been one of the primary concern of researches in present time. In view of metal toxicity, attempts have been made to quantify them in environmental samples. Numerous analytical techniques have been developed for quantifying analytes and these includes AAS (atomic absorption spectrometry), ICP-MS (inductive coupled plasma-mass spectrometry), ion chromatography, flame photometry, cyclic voltammetry, isotopic dilution, radiometric activation analysis, fluorescence, chemiluminescence phosphorescence techniques and high performance liquid chromatography *etc.* Although, these techniques provide accurate results but their widespread use in the analysis of large number of environmental sample is limited due to fact that their operation require expertise and large infrastructure backup. Thus, there is a need to develop a better method which involves simple instrumentation, inexpensive and fast method of analysis with minimum chemical manipulation. Such requirements are generally met with ion-selective electrodes (ISEs), which have emerged as promising tools for direct measurement of various species because of the advantages offered in terms of better selectivity and sensitivity, easy handling and cheap. The technique is generally non-destructive, adaptable to small sample volume with possible application in real-time analysis. Moreover, analysis of colored and viscous samples can also be carried out easily. The ISEs are routinely used not only for the analysis of clinical, industrial, agricultural and environmental samples but are also used as detectors in HPLC and capillary electrophoresis. The development of potentiometric membrane-based ion sensor with high selectivity remains a formidable challenge. The present work is aimed to design and synthesize new ligands and their complexes for use as electroactive components (ionophore) in the preparation of membranes for determination of various cations. The work embodied in the thesis has been organized in seven chapters. A brief report on the text of various chapters is described below.

First chapter is on ***"General introduction to the thesis"***. A review of literature on various sensors used for quantification of metal ions and anions is incorporated in this chapter. It also presents briefly classification of ISEs, methods of preparation of membranes and theory of membrane potential. The determination of selectivity coefficient of ISEs is described in this chapter and the significance of selectivity coefficient is also critically discussed. Besides this, the objective of present research activity is also presented at the end of this chapter.

The Second Chapter of the thesis entitled **"*Membranes of Macrocyclic Chelating ligand as Cd^{2+} Ion-Selective Sensors*"** deals with the synthesis and characterization of a macrocycle *viz.* 5,11,17-trithia-1,3,7,9,13,15,19,20,21-nonaazatetracyclo-[14.2.1.1^{4,7}.1^{10,13}]-henicosa-4(20),10(21),16(19)-triene-6,12,18-trithione (L_1) and their use as ionophores application in the preparation of Cd^{2+} selective ISEs. Preliminary studies on L_1 have showed that it has more the affinity towards Cd^{2+} ion. Thus, L_1 was used as an ionophore for the preparation of PVC-membrane sensor for Cd^{2+} ion. Three electrodes polymeric membrane electrode (PME), coated graphite electrode (CGE) and coated pyrolytic graphite electrode (CPGE) were prepared and investigated as Cd^{2+} sensor. Their performance characteristics were compared and it was found that of three electrodes CPGE gives the best performance. The best CPGE was found to exhibit quick sensing (10 s) and long durability (4 months), useful pH range of 2.5-8.5. This electrode exhibits low detection limit of 7.58×10^{-9} mol L^{-1} and a Nernstian slope of 29.6 mV decade^{-1} of activity. Applicability of the sensor was evaluated for Cd^{2+} quantification in numerous samples (water, soil and medicinal plants) and also as a potentiometric indicator electrode.

The Third Chapter of the thesis entitled ***"Diaminopyrimidin Based Chelating Ionophore as Ni^{2+} Ion-Selective Sensors"*** deals with the synthesis and characterisation of ligand 5,5'-((3-nitrophenyl)methylene)bis(2,6-diaminopyrimidin-4(3*H*)-one) (L_2). The L_2 prepared shows high affinity for Ni^{2+} ion and thus can be used for the preparation of Ni^{2+} sensor. CGE and CPGE were prepared using L_2 as an ionophore. A number of solvent mediators were used to improve the performance of Ni^{2+} sensor and it was found that the solvent mediator *o*-NPOE produces best effect. CPGE with the membrane of optimized composition (L_2: PVC: NaTPB : *o*-NPOE ≡ 7:33:2:58) was found to display linearity (2.04×10^{-8} - 1.0×10^{-1} mol L^{-1}), Nernstian slope (29.4±0.2 mV decade^{-1} of activity) and LOD (lower detection limit) of 8.12×10^{-9} mol L^{-1}and independent of pH (3.0 to 9.0.) This sensor exhibits fast response time of 8 s. The sensor was found to exhibit high selectivity over a number of metal ions and that`s why quantification of Ni^{2+} ion in analytical samples (water, soil and plant leaves) reflect the utility of sensor and has also been used as potentiometric indicator electrode in the titration (Ni^{2+} *vs* EDTA).

The Fourth Chapter entitled ***"Polydentate Heterocyclic Chelating Ionophores as Cu^{2+} Ion- Selective Sensors"*** deals with synthesis and characterization of a number of ligands *viz.*, L_3 (1,3-bis[2-(1,3-benzothiazol-2-yl)-phenoxy]propane) and L_4 (1,2'-bis[2-(1,3-benzothiazol-2-yl)-phenoxy]-2-ethoxy ethane) and their analytical application as Cu^{2+} selective electrodes. Preliminary study have shown that two ligands *viz.*, L_3 and L_4 show high affinity for Cu^{2+} and hence can be used for the preparation of Cu^{2+} selective electrode. A number of PVC-based electrodes were prepared. A comparative study of several polymeric membrane electrodes show that the electrodes with the membrane composition (w/w, mg) L_4: PVC: NaTPB: 1-CN≡ 6:53:2:39 is found to exhibit detection limit as low as 6.30×10^{-9} mol L^{-1}, Nernstian slope (29.5 mV $decade^{-1}$ of activity) and fast response time of 9 s. It also has sufficient life time of 5 months and can be used over a pH range of 2.0-8.5.The electrode show good selectivity over a number of metal ions and could therefore be employed in quantification of Cu^{2+} in analytical samples (water and soil). Cu^{2+} was also estimated in medicinal plant samples and besides this the sensor was also used as potentiometric indicator electrode in the estimation of Cu^{2+}.

The Fifth Chapter entitled "***N_3O_2 Chalcone Ligand as Ce^{3+} Ion-Selective Sensors"*** deals with the synthesis and characterisation of novel ligand L_5 (1,1'-(pyridine-2,6-diyl)bis(3-(1*H*-pyrrol-2-yl)prop-2-en-1-one)) and explored as ion carrier for the selective monitoring of Ce^{3+} ion in various samples. Colorimetric and conductometric studies performed on the L_5 show that it has high affinity for the Ce^{3+} ion and therefore, L_5 was used in the fabrication of poly (vinyl chloride) based membrane sensors PME, CGE and CPGE were prepared and investigated. Best performance was observed with CPGE having optimized membrane of composition (w/w, mg) L_5: PVC: *o*-NPOE: NaTPB≡7:31:59:3. The CPGE exhibits linearity of 1.9×10^{-8} mol L^{-1} and detection limit down to 5.0×10^{-9} mol L^{-1} with Nernstian slope of 19.4±0.2 $mVdecade^{-1}$ of activity. The sensor response is independent of pH in the range of 3.0-8.5 and show quick sensing (9 s). The sensor applicability in partially non-aqueous mixture (water-acetonitrile and water-ethanol) was examined and found that sensor could tolerate about 20% (v/v) of non- aqueous content. The utility of sensor is shown in quantification of Ce^{3+} in various samples. Further, the sensor was employed as potentiometric indicator electrode (Ce^{3+} *vs* F^- and $C_2O_4^{2-}$ titration).

The Sixth Chapter entitled ***"Multidentate Schiff Bases of Isonicotinohydrazide as Mn^{2+} Ion-Selective Sensors"*** deals with synthesis and characterization of two Schiff bases *viz.*, L_6 (N'(N',N'''E,N',N'''E)-N',N'''-((((oxybis(ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene))bis(methanylylidene))di(isonicotinohydrazide)) and L_7 ((N',N'''E,N',N'''E)-N',N'''-(((propane-1,3-diylbis-(oxy))bis(2,1-phenylene))bis(methanylylidene))di(isonicotino-hydrazide)). Preliminary study on the two Schiff bases L_6 and L_7 have shown that they have strong affinity for Mn^{2+}. Therefore, two Schiff bases have been selected as ionophores for the fabrication of Mn^{2+} selective sensors. The electrodes prepared are based on PME of L_6 and L_7. Three electrodes PME, CGE and CPGE were prepared and investigated. The CPGE with optimized membrane of composition (L_7: PVC: *o*-NPOE: NaTPB≡6:34:58:2) display broad working concentration 1.23×10^{-8}-1.0×10^{-1} mol L^{-1}, detection limit as low (4.78×10^{-9} mol L^{-1}) and Nernstian performance (29.5±0.4 mV decade^{-1} of activity). The useful working pH range has been found 3.5-9.0 and response of the electrode is quite fast (9 s). The sensor can be used for long duration (4 months) without any considerable divergence in its property. In view of good selectivity of the sensor for Mn^{2+} over large number of metal ions, the electrode could be used to monitor Mn^{2+} quantitatively in a number of samples and was employed as potentiometric indicator electrode (titration of Mn^{2+} against EDTA).

The Seventh Chapter entitled ***"Multidentate Schiff Bases of Hydrazinecarbothioamide as Co^{2+} and Zn^{2+} Ion-Selective Sensors"*** deals with synthesis and characterization of a number of Schiff bases *viz.*, L_8, L_9, L_{10}, L_{11}, L_{12} and L_{13}. Preliminary study have shown that L_8 (2,2'-(((ethane-1,2-diylbis(oxy))bis(3-methoxy-4,1-phenylener))bis(methanylylidene))bis(hydrazinecarbothioamide)), L_9 (2,2'-(((propane-1,3-diylbis(oxy))bis(3-methoxy-4,1-phenylene))bis(methanylylidene))bis(hydrazinecarbo-thioamide)) and L_{10} (2,2'-((((oxybis(ethane-2,1-diyl))bis(oxy))bis(3-methoxy-4,1-phenylene))bis(methanylylidene)bis(hydrazinecarbothioamide)) show higher affinity for Co^{2+}. Thus, they have been used as ionophores for the preparation of membrane electrodes for Co^{2+} determination. While preparing the membranes the effects of different plasticizers *viz.*, dioctylphthalate (DOP), dibutylphthalate (DBP), benzylacetate (BA), and 1-choronaphthelene (1-CN) and anion excluders potassium tetrakis-p-(chlorophenyl)borate (KTpClPB) and sodium tetraphenylborate (NaTPB) have also been seen. Polymeric membrane CGE and CPGE were prepared and investigated. A comparative study of all the membrane electrodes have shown that CPGE with membrane composition of L_9: PVC: 1-CN: KTpClPB≡6:35:56:3 (w/w, mg) gives the best performance. It shows good linearity (1.4×10^{-8}-1.0×10^{-1} mol L^{-1}) and detection limit as low (6.1×10^{-9} mol L^{-1}) with Nernstian compliance (29.4±0.6 mV $decade^{-1}$ of activity) and fast response time of 7 s. This electrode (CPGE) shows high selectivity over a number of metal ions and could therefore be used successfully for the quantification Co^{2+} in electroplating waste, medicinal plant and water aliquots and also was employed potentiometric indicator electrode in the titration of Co^{2+} ion against EDTA.

The remaining three Schiff bases L_{11} (2,2'-(((ethane-1,2-diylbis(oxy))bis(2,1-phenylene))bis(methanylylidene))bis(hydrazinecarbothioamide)), L_{12} (2,2'-(((propane-1,3-diylbis(oxy))bis(2,1-phenylene))bis(methanylylidene))bis(hydrazinecarbothioamide)) and L_{13} (2,2'-((((oxybis(ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene))bis(methanylylidene))bis-hydrazinecarbothioamide)) have been found to show higher affinity for Zn^{2+} and therefore membranes were fabricated using these ligands as ionophores. Several electrodes of these ionophores were prepared and investigated. A comparison of performance of various electrodes has shown that CPGE with the membrane composition of L_{13}: PVC: DBP: NaTBP≡6:34:58:2 (w/w, mg) exhibit best response of all ISEs performance parameters. For example, this sensor works over range of working concentration (1.1×10^{-8}-1.0×10^{-1} mol L^{-1}), detection limit of 8.1×10^{-9} mol $L^{-1}$and display Nernstian slope (29.6±0.2 mV $decade^{-1}$ of activity of Zn^{2+} ion) with quick sensing (10 s). The electrode exhibited self life time of about 4 months and was found independent of pH (3.0-9.0). The grater selectivity of the sensor for Zn^{2+} ion in presence of interfering ions permits the use of this electrode to determine Zn^{2+} in water, medicinal plant and soil samples and as potentiometric indicator electrode.

The performance characteristics of the sensor for the determination of Cd^{2+}, Ni^{2+}, Cu^{2+}, Ce^{3+}, Mn^{2+}, Co^{2+} and Zn^{2+} ions have been found to be not only comparable but better in some respects over reported sensors. Thus, the present work adds to our knowledge in the field of chemical sensors.

List of Abbreviations:

ISEs: Ion Selective Electrodes

PVC: Poly(vinyl chloride)

PME: Polymeric Membrane Electrode

CGE: Coated Graphite Electrode

CPGE: Coated Pyrolytic Graphite Electrode

DBP: Dibutylphthalate

DOP: Dioctylphthalate

BA: Benzylacetate

1-CN: 1-Chloronaphthalene

NaTPB: Sodium tetraphenylborate

KTpClPB: Potassiumtetrakis-p-(chlorophenyl)borate

o-NPOE: *o*-Nitrophenyloctylether

LOD: Limit of detection

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LIST OF PUBLICATIONS

1. A.K. Singh*, **Manoj Kumar Sahani**, K.R. Bandi, A.K. Jain, "*Electroanalytical studies on Cu(II) ion-selective sensor of coated pyrolytic graphite electrodes based on* $N_2S_2O_2$ *and* $N_2S_2O_3$ *heterocyclic benzothiazol ligands*", **Material science and engineering C**, **41**, (2014) 206-216.
2. **Manoj Kumar Sahani**, A.K. Singh*, A.K. Jain, A. Upadhyay, A. Kumar, Udai P. Singh, S. Narang, "*Fabrication of novel coated pyrolytic graphite electrodes for the selective nano-level monitoring of* Cd^{2+} *ions in biological and environmental samples using polymeric membrane of newly synthesized macrocycle*", **Analytica Chimica Acta**, **860** (2015) 51-60.
3. **Manoj Kumar Sahani**, A.K. Singh*, A.K. Jain, "*Nano-level monitoring of* Mn^{2+} *ion by fabrication of coated pyrolytic graphite electrode based on isonicotinohydrazide derivatives*", **Material science and engineering C**, **50**, (2015) 124-132.
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6. **Manoj Kumar Sahani**, A.K. Singh*, A.K. Jain, "*Quantification of* Zn^{2+} *ion in environmental and biological samples by fabrication of pyrolytic graphite electrode based on newly synthesized Schiff's bases*", **Communicated.**
7. **Manoj Kumar Sahani**, A.K. Singh*, A.K. Jain, "*Electrochemical sensor for the nano-scale monitoring of* Ni^{2+} *ion in environmental and biological samples by the fabrication of coated pyrolytic graphite electrode based on a novel pyrimidine derivative*", **Communicated.**

PARTICIPATED IN CONFERENCES

1. Participated in “International Conference on Material Science and Technology (ICMST-2012)”, organized by Department of Physics, St. Thomas College Pala, Kottayam, Kerela; 10-14, June, 2012.
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Chapter 1

“General Introduction”

1.1 INTRODUCTION

In last few years environmental pollution has raised to such a higher level that it has become primary global concern to take care of our environment before it ruin us. Anthropogenic activities performed in terms of rapid industrialization and urbanization although have improved the standards of life, but simultaneously have adverse effects on the quality of life. The World Health Organization (WHO) estimates that about 25% of the diseases facing humans today occur because of long-term exposure to environmental pollution, including air, soil, and water pollution [1, 2]. Metal contamination has become an imperative hazard and can have dramatic impact on our well-being. A metal is regarded as toxic if it injures the growth or metabolism of cells when it is present above a given concentration. Almost all metals are toxic at high concentrations and some are severe poisons, even at very low concentrations. Metals interacted to O, S and N of oganic compound as these are the group involved in ligand formation and therefore, it is accountable that exposer of heavy metals to organic moiety result in metal-organic speices formation which alter the functioning of biological molecules and causes cells decay. The accumulation of various heavy and toxic elements in the environment constitutes an important group of pollutants which produce toxicity above a threshold level and thus their determination has become a challenge to the researchers as it poses a serious problem to living ones. Therefore, it is necessary to quantify them in various environmental, industrial and biological samples for assurance against acute intoxication or prolonged exposure that may lead to many diseases or death [3, 4].

In view of metal toxicity, importance of healthy environment is being increasingly recognized and it has become essential for various agencies to monitor the adulteration caused by the pollutants in the environment so as to keep the level of pollution below permissible limits. As a result of environmental pollution, the field of environmental science has evolved to study the effects of pollutant on the ecosystem. Therefore, a number of techniques and instruments came in light to achieve the goal in the field of environmental science.

Various instrumental techniques such as flame atomic absorption spectrometry (FAAS), ETAAS (electrothermal atomic absorption spectrometry), AFS (atomic fluorescence spectrometry), ICP-AES (inductively coupled plasma-atomic emission spectrometry), ICP-MS (inductively coupled plasma-mass spectrometry), HPLC (high performance liquid chromatography spectrophotometry), ASV (anodic stripping voltammetry) and many more has become available for determining the concentration of metal ions in aqueous solutions [5-13]. Although these techniques provide accurate results but their widespread use in the analysis of large number of environmental samples is limited due to fact that their operation require expertise and large infrastructure backup. Thus, there is a need to develop a better method which involves simple instrumentation, inexpensive and fast method of analysis with minimum chemical manipulation. Such requirements are generally met with ion-selective electrodes (ISEs), which have emerged as promising tools for direct measurement of various species because of the advantages offered in line with high selectivity and sensitivity, reproducible and cheap. The most attractive features of this technique are insensitive to sample colour, viscosity or suspended solids, rapid response to changes in determinant concentration and possible use in a very wide concentration range. Moreover, their fabrication in the laboratory is quite easy and so they have been widely used for the quantification of many ionic and non-ionic species present in aqueous samples. As a result of analytical requirements, a number of commercially available ISEs have been developed as convenient tools for analysis which can be directly used for metal ion determination in soil, wastewater, medicinal plants, biological fluids, food products, effluents, fertilizers etc. [14, 15]. ISEs are routinely used not only for the analysis of clinical, industrial, agricultural and environmental samples but are also used as detectors in HPLC and capillary electrophoresis.

Ion-selective electrode consists of a semipermeable membrane that separates two different solutions of an appropriate electrolyte and responds selectively to a particular ion in presence matrix. The membrane constitutes an active ion-exchanger ingredient generally called an ionophore or electroactive material. Ionophore plays a key role in the sensitivity of an ion-selective electrode. The creation of cavities and cleft in the ionophore are complementary to the size and charge of a particular ion leading to selective interactions. Selectivity for a specific analyte over other is the most important features of an ISE and altered by the interaction of ionophore within the membrane with other ions in solution. The ion-ionophore interactions based on their ion-exchange property or size-exclusion of the ionophore, determine selectivity of an ion sensor and its proper functioning towards a specific ion. Stability and selectivity of M^{n+}-L complex, cavity size of the ligand and structure, extractabilty and solubility are the important parameters for designing and functioning of synthetic ionophores. The wide use of ion-selective potentiometry in routine analysis is accompanied by a search for more selective membrane materials and also on theoretical studies of the mechanism of functioning of these sensors [16-18].

Ion-selective electrodes are also of obvious interest because they help to translate the chemistry of new substrate-binding systems into tools that can be used to selectively monitoring of analyte even in matrix containing highly interfering ions. The design of host molecules capable of binding selectively to an ionic species in presence of interfering ions is a notoriously challenging area and consequently has given rise to a plethora of imaginative and ingenious systems designed to tackle the problem [19, 20]. Research aimed at expanding the application of ISEs is still flourishing with the goal of improving their performance, reaching better understanding of their response mechanism and finding new chemical or physical configurations. Thorough evaluation of the response is essential to forecast the chances of success of novel ISEs that are proposed at constant rate in the current literature.

1.2. HISTORICAL DEVELOPMENT OF ION-SELECTIVE ELECTRODES

It was Luigi Galvani who first was able to observe the bioelectric phenomenon while dissecting a frog in 1791. Later on, in 1848, du Bois-Reymond also concluded that living cell membranes show properties similar to an electrode of galvanic cell. However, it was understood until in 1890 when W. Ostwald brought the concept of semi-permeability of the membrane which was considered as the main cause of potential difference across a membrane [21]. The first success in the history of ISEs was pioneered by Cremer, who discovered glass electrode selective for sensing of hydrogen ions in 1906. Initially the potential response was interpreted in terms of Donnan equilibrium but in 1930s, Nicolsky suggested that electrode response is dependent on the active sites of the glass capable of ion exchange and the concept enabled the selectivity coefficient of an electrode to be calculated.

With the passage of time not only glass, but other materials were also explored in the fabrication of ISEs and it was Kolthoff and Sanders in 1937, who made first silver halide disk sensors [22] by using materials other than glass and thus initiated the use of new materials in the field of ISEs. In the early 1960s, E. Pungor [23] published his work on Ag-I based heterogeneous membrane electrodes which were the basis for first commercial solid state ISEs. These electrodes exhibited good selectivity, Nernstian response and were the first truly selective electrodes (non-glass) to be developed, which gave a thermodynamically reversible response with respect to the primary ion. Many workers continued their research towards the preparation of various ISEs of heterogeneous membranes consisting of an active material supported in an inert matrix of silicone rubber [24, 25]. The commercial development of ISEs began when Frant and Ross [26] developed calcium and fluoride electrodes. The fluoride selective electrode, based on lanthanum fluoride doped with europium fluoride, is the second best electrode developed after glass electrode.

Concepts from medicines and physiology also spurred the development of ISEs. In 1970, Higuchi *et al*. [26] introduced a liquid membrane electrode which responds both to organic and inorganic ions. The intuitive and systematic work of Buck and Linder group in designing new, highly selective ionophores made the ionophore-based liquid membrane sensors the most successful class among the ISEs [27]. The most important procedures for compounding, casting, drying and mounting PVC membranes were put forward by Moody and coworkers [28]. Finally, the birth of host-guest chemistry [29-31] played an important role to explore different materials in developing ISEs for various cations and anions. Therefore, the PVC based ion-selective membranes have attracted much attention and have been used in the construction of chemical sensors.

1.3. LITERATURE SURVEY

Ever since the discovery of glass electrode for pH determination, ion-selective electrodes have aroused a great deal of interest from both theoretical and practical points of view and their role in analytical chemistry has been steadily increasing. In recent years, the field of ISEs is perhaps one of the most eminent examples for interdisciplinary research in analytical chemistry. A number of books [32-41] and some significant papers [42-47] have appeared in the recent past. Progress in this field including theory, methodology, and applications of ISEs has been described in the periodic reviews [48-59]. The list is quite extensive and it is not possible to report the total bibliography on ISEs. Thus, only significant publications, which highlight various aspects of ISEs developed for various ions, are presented here.

1.3.1. Alkali Metal Ion-Selective Electrodes

There has been appreciable interest in the development of ISEs for alkali metal ions as the determination of Li^+, Na^+, K^+ is important in biological fluids. In eighties and nineties, the materials used for preparing the membranes of ISEs for alkali metal ions were generally neutral carriers of different types. Gadzekpo and coworkers [60, 61] have reported a review, which summarizes different types of Li^+ selective sensors, gives their applications and highlights the problems encountered in the determination of lithium in serum and other biological fluids. Fiedler *et al.* [62] introduced the first Li^+-selective electrodes based on *N,N′*-diheptyl-*N,N′*-5,5-tetramethyl-3,7-dioxanonanediamide. This electrode worked in the range of 1.0 M to 0.01 mM and showed high selectivity over sodium, potassium, magnesium and calcium. In 1981, Zhulov *et al.* [63] developed an important Li^+-selective sensor using neutral carrier *N,N,N′,N′*-tetra-isobutylcyolohexaneo-1,2-dicarboxamide with PVC as binder. This sensor display range of working concentration (1.0×10^{-5} to 1.0×10^{-1} mol L^{-1}) and was found selective for Li^+ over other interfering ions.

Later on, some other neutral carriers, *N,N′*-dicyclohexyl-*N′,N′*-diisobutyl-cis-cyclo hexanedicarbonylamide [64], 6,6-dibenzyl-1,4,8,11-tetraoxacyclotetradecane [65], l-phenyl-3-methyl-4-benzoyl-5-pyrazolone [66], crown ether derivatives [67, 68] and 1,10-phenanthroline derivatives [69], macrocycles [70] were also investigated as suitable ionophores to develop Li^+-selective sensors. All these sensors were of comparable performance. Gupta *et al.* [71] reported a Li^+-selective sensor based on a carbosiloxane dendrimer. The sensor showed a working concentration range of 2.5×10^{-5}-1.0×10^{-1} mol L^{-1} of Li^+ with a slope of 52.0 mV decade^{-1} of $a_{Li}{}^+$ and was used for the determination of Li^+ in blood serum.

A major interest for Na^+ analysis with ISEs comes from clinical chemistry. Most of the reported Na^+ selective sensors developed are based on neutral carriers. The sensors prepared by Wu *et al.* [72] based on triglycollic bisdiamides in PVC matrix performed well and showed good selectivity for Na^+ over other alkali and alkaline earth metals and could be used for the determination of sodium in water with high magnesium content. The sensors based on the membranes of crown ethers such as bis-[(3n+l)-crown-n]ether derivatives [73], dibenzo-16-crown-5 derivatives [74], 16-crown-5-derivatives [75], bis-(12-crown-4)methylmalonates [76], benzyloxymethyl-l1-crown-3 [77] and azo- and azoxycrown compounds with sulphur atoms in long side chains [78] were also found to be Na^+ selective. Calixarenes have also been extensively used as carriers for the fabrication of sodium selective sensors. Prominent among these are the sensors developed by symmetrical, unsymmetrical and bridged *p*-tert-butylcalix[4]arylacetate [79], calix[4]arene derivatives [80], triestermonoacid derivative of p-tert-butylcalix[4]arene [81]. All these sensors show high selectivity for Na^+ as calix[4]arene compounds exhibit an optimum cavity size for complexation with Na^+ and have been used for Na^+ determination in biological fluids. Recently, Kimura *et al.* [82] designed several sol-gel derived membranes selective to Na^+

which encapsulate valinomycin and bis-(crownether) as well as calix[4]arene ester and amide derivatives electroactive materials, while Kim *et al.* [83] tried lipophilic trimesters of calix[4]arene and calix[4]quinine to develop Na^+ selective sensors. These membranes showed good sensitivity, selectivity and low response time.

A major interest for K^+ analysis comes from clinical chemistry because changes in K^+ concentration in human serum bring along the risk of acute cardiac arrhythmia. A number of ISEs have been developed for K^+ in view of its importance in clinical chemistry. Fiedler and Ruzika [84] developed the first successful and commercially available sensor for potassium ion by using valinomycin, an electroneutral carrier. Since then many researchers [85-88] have developed neutral carrier based ISEs for K^+. A number of K^+ selective sensors based on crown ethers viz., cis- and trans-bis-(crown ethers) [89], bis-(15-crown-5) [90], 4'-picrylamino-5'-nitrobenzo-18-crown-6 [91] and 4-acryloylamidobenzo-15-crown-5 and 4-acryloylamidobenzo-18-crown-6 [92] have been prepared. All these sensors show high selectivity for K^+ over other alkali and alkaline earth metals and have been used for determining potassium in biological fluids. Yan *et al.* [93] used calix[6]arene hexaester for the preparation of membranes and investigated its applicability to determine K^+ in human serum. Recently, Katsu *et al.* [94] reported K^+ selective sensor based on macrocyclic metacyclophanes analogous to calixarenes which showed linear response down to 7.0×10^{-6} mol L^{-1} of K^+ but suffer serious interference from Na^+. Bobacka *et al.* [95, 96] introduced solid state potassium ion selective electrodes using carbon nanotubes as ion-to-electron transducer in polymer membranes.

The development of ISEs for Rb^+ has received relatively less attention mainly because of their conspicuous absence in biological systems. However, still some sensors have been reported. Cosgrove *et al.* [97] reported a valinomycin based sensor selective for Rb^+ and used it to determine rubidium in yeast cells. Singh and co-workers [98] used epoxy resin based membranes of rubidium tungustoarsenate to develop Rb^+-selective sensor. The sensors prepared were not highly selective but could be used for its determination by potentiometric titration procedure. A solid membrane electrode for the determination of Rb^+ selectively in the concentration range 4.0×10^{-5} - 1.0×10^{-1} mol L^{-1} was reported by Shrivastava and co-workers [99]. Another Rb^+ selective sensor was developed by Saleh *et al.* [100] using indanopyrazalo[l, 5-a] pyrimidines as electroactive material which showed Nernstian response in the narrow concentration range of 1.0×10^{-4} - 1.0×10^{-1} mol L^{-1}. Yang *et al.* [101] used decylidenebis-(4-benzo-15-crown-5) ether to develop Rb^+ selective sensor. It exhibited a near Nernstian response in the concentration range of 5.0×10^{-5} - 1.0×10^{-1} mol L^{-1} with detection limit down to 2.0×10^{-5} mol L^{-1}. Hyun *et al*. [102] explored binaphthyl-based crown ether derivatives as ionophores in the preparation of Rb^+- selective polymeric membrane electrodes which worked in the linear concentration range 1.0×10^{-5} - 1.0×10^{-1} mol L^{-1}.

Cesium has also received much attention during the last two decades and various ionophores were reported for the development of Cs^+-selective electrodes. Wang *et al*. [103] found 15-crown-5-phosphotungustic acid precipitate selective for Cs^+. It showed Nernstian response in the concentration range of 1.0×10^{-4} - 1.0×10^{-1} mol L^{-1}. Several crown ether derivatives *viz*., 14 and 15-crown formazans [104] and calix[4]crown ether-ester [105] showed good selectivity for Cs^+ over a number of ions. Cs^+-selective electrodes based on several calixarenes *viz*., calix[6]arene tetraester derivatives [106], bridged bis-calix[4]arenes [107], 1,3-bis-bridged cofacial-calix[6]crowns [108], crown bridged thiacalix[4]arenes [109], have also been reported. Shamsipur *et al*. [110] reported a 16-membered macrocylic diamide as a Cs^+-selective ionophore while Ganjali and co-workers [111] used a cavitand as Cs^+- selective ionophore. Saleh *et al*. [112] developed a Cs^+-selective sensor using cephalexin antibiotic drug as ionophore and a new Cs^+-selective graphite rod electrode based on Cs-Molybdophosphate was reported by Arida *et al*. [113]. Recently, a Cs^+-selective electrode, having longest lifetime of nine months, based on 5-(4'-nitrophenylazo)25,27-bis-(2-propyloxy)26,28-dihydroxycalix[4]arene has been reported by Ramanjaneyulu and co-workers [114] while Sadeghi *et al*. [115] fabricated a Cs^+-selective polymeric membrane coated graphite electrode based on 4',4"(5') di-tert-butyl di-benzo-18-crown-6.

1.3.2. Alkaline Earth Metal Ion-Selective Electrodes

Considerable efforts have been made by researchers to develop selective sensors for alkaline earth metal ions due to their occurrence in diverse samples. As such, a large number of sensors for these ions have been reported. A brief review on ISEs for these metals is given in the following paragraphs.

Among alkaline earth metal ions, beryllium has received less attention inspite of its wide industrial uses. This may be due to high charge density on Be^{2+} ion leading to its excessive hydration, as a result of which the hydrated Be^{2+} ion is poorly sensed by ionophores. Fleet and Rechnitz [116] used phosphate ester ionophores to prepare Be^{2+} selective sensors. Ganjali *et al*., employed 2,4-dinitrophenylhydrazine-benzo-9-crown-3 [117], naphtho-9-crown-3 [118], 2,3,5,6,8,9-hexahydro-1,4,7,10-benzotetraoxacyclododecine-12-carbaldehyde-12-(2,4-dinitrophenyl)hydrazine [119] and 4-nitrobenzo-9-crown-3-ether [120] to develop Be^{2+} ion-selective sensors. The sensor have 4-nitrobenzo-9-crown-3-ether as electroactive material showed Nernstian response to Be^{2+} ion and reported with concentration range of 1.0×10^{-10} - 1.0×10^{-4} mol L^{-1} with a limit of detection 3.5×10^{-11} mol L^{-1} (≈ 350 pg/L). Shamsipur *et al.*, [121] developed coated graphite sensors for selective determination of Be^{2+} ion with macrocyclic diamide, 15-diaza-3,4:12,13-dibenzo-5,8,11-trioxabicyclo[13,2,2]heptadecane-2,14-dione and compared its potentiometric performance was compared with polymeric membrane electrode. Recently Gupta *et al.*, fabricated Be^{2+} ion–selective electrodes using dibenzo(perhydrotriazino)aza-14-crown-4 ether [122].

The major challenge in the design of Mg^{2+} ion-selective electrode, ionophores lies in the discrimination of Ca^{2+} ion. A Mg^{2+} ion-selective sensor was prepared by Saleh *et al.*, [123] using phenylene bis-(ditolyl phosphineoxide) in PVC matrix which showed high selectivity for Mg^{2+} ion over Ca^{2+} ion and reported with working concentration range of 6.0×10^{-5}-1.0×10^{-1} mol L^{-1}. Further, Mg(II)oxinate [124] and 1-(*N*,*N*-dicyclohexylcarbamoyl)-2-(*N*,*N*-dioctadecylcarbamoyl)ethyl phosphonic acid monomethyl ester [125] were also used as ionophores for Mg^{2+} ion-selective sensors. These sensors exhibited linear potential response towards Mg^{2+} ion with reasonably good selectivity. Gupta *et al.*, reported Mg^{2+} ion-selective sensors with benzo-15-crown-5 [126] and magnesium-tetrazaporphyrin complex [127]. Both the sensors exhibited excellent selectivity for Mg^{2+} ion over other cations. Agarwal *et al.*, [128] carried out studies on zirconium(IV) selenomolybdate gel based Mg^{2+} ion-selective heterogeneous membrane sensor. A new method was developed for the selective determination of Mg^{2+} ion in erythrocytes by Malon *et al.*, [129].

Development of a convenient method for the determination of Ca^{2+} ion has been an area of extensive research because of its widespread occurrence in biological and environmental system. Initial attempts to develop a Ca^{2+} ion-selective sensor were not successful. The useful Ca^{2+} ion–selective sensors were developed by Khalil and coworkers [130] by incorporating Ca-bis-(2,6-dinitro-4[l,l,3,3-tetramethyl(butyl)])phenoxide and Ca-bis-(di[l,l,3,3-tetramethyl(butylphenyl)])phosphate in PVC. Later on, various organophosphates, such as di(2-ethylhexyl) phosphate [131], Ca-di(n-octylphenyl) phosphate [132] and polyaniline functionalized with bis-[4-(l,1,3,3-tetramethyl(butyl phenyl)]phosphate [133] were employed as electroactive material for Ca^{2+} ion-selective sensors. Some of these sensors respond to Ca^{2+} ion over a wide concentration range (down to 1.0×10^{-9} mol L^{-1}) with a fast response time but the selectivity of these sensors was not good. Kumar *et al.*, [134] developed Ca^{2+} ion-selective membrane sensor using dibenzo-18-crown-6. Singh *et al*., [135] developed highly selective Ca^{2+} ion potentiometric sensor with furildioxime as neutral carrier while Jain *et al*., [136] reported p-isopropylcalix[6]arene based sensor for the selective determination of Ca^{2+} ion. Recently Park *et al*., fabricated a solid contact Ca^{2+} ion-selective electrode in a microchannel [137] and reported with lower detection limit 10^{-9} mol L^{-1} and high selectivity towards K^{+} ion.

Determination of Ba^{2+} is important as it is present in various drugs. In the begining, non- ionic Antrarox CO-880 and its barium complex [138] were used to construct Ba^{2+} ion-selective sensors. Gupta *et al*., [139] used dibenzo-24-crown-8 to develop a highly selective sensor for Ba^{2+} ion, which exhibited linear response in the range of 1.4×10^{-5}-1.0×10^{-1} mol L^{-1}. Saleh [140] reported a Ba^{2+} ion-selective sensor using neutral bidentate organo phosphorous compounds. Singh *et al*., [141] reported 2,3,4-pyridine-1,3,5,7,12-pentaazacyclopentadeca-3-ene as ion for Ba^{2+} ion-selective sensor. Othman *et al*., [142] used complex ion associate of barium(II)-Rose Bengal as an ionophore for preparing Ba^{2+} ion-selective PVC membrane sensor which exhibited fast linear potential response for Ba^{2+} ions over the concentration range 5.0×10^{-5}-1.0×10^{-1} mol L^{-1} with a Nernstian slope of 28.5±0.4 mV $decade^{-1}$ of activity. Recently, Zamani *et al*., [143] constructed a Ba^{2+} ion-selective sensor based on 3-deoxy-erythro-hexos-2-ulosebis-(thiosemicarbazone) which showed high selectivity for Ba^{2+} ion over concentration range 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} with a lower detection limit of 5.6×10^{-7} mol L^{-1}.

The first Sr^{2+} ion-selective sensor was developed by Baumann [144] using strontium complex of nonylphenoxypoly(ethyleneoxy)ethanol as electroactive material but it exhibited higher selectivity for Ba^{2+} ion over Sr^{2+} ion. Qian *et al*., [145] reported a Sr^{2+} ion-selective sensor with tetracyclohexyl-2,6-pyridine-bis(methyleneoxyacetamide) as ionophore which showed strong interference to Pb^{2+} and Ag^{+} ions. While Ganjali *et al*., reported using dibenzo-30-crown-10 [146] as neutral carrier and Gupta *et al*., [147] used 5,11,17,23,9,35-hexakis(1,1,3,3-tetramethylbutyl)-37,38,39,40,41,42-hexakis-(carboxymethoxy)-calix[6]-arene to prepare Sr^{2+} ion-selective sensors. Potentiometric membrane sensor based on 6-(4-nitrophenyl)-2-phenyl-4,4-dipropyl-3,5-diaza-bicyclo[3,1,0]hex-2-ene was developed by Zanjanchi *et al*., [148] for trace level detection of Sr^{2+} ions. Zamani and co-workers [149] used 2,3-diphenylquinoxaline-4',4''-dioxytriethylene glycol as a suitable ionophore for preparing Sr^{2+} ion-selective sensor which exhibited a linear dynamic range 1.0×10^{-6}-1.0×10^{-2} mol L^{-1} with a Nernstian slope of 29.9 mV $decade^{-1}$ of $a_{Sr^{2+}}$ and a detection limit of 6.7×10^{-7} mol L^{-1}. Guo *et al*., [150] explored 1-benzothiazol-3-benzoyl-thiocarbamide as neutral carrier for the fabrication of fast response Sr^{2+} ion-selective polymeric membrane sensor which exhibits Nernstian response to Sr^{2+} ion over working concentration range 4.0×10^{-7}-1.0×10^{-1} mol L^{-1} with a detection limit of 2.5×10^{-7} mol L^{-1} and a slope of 30.1±0.1 mV decade^{-1} of $a_{Sr}{}^{2+}$.

1.3.3. Transition Metal Ion-Selective Electrodes

The determination of transition metals in pharmaceutical, clinical, environmental and other samples is important in view of their toxicity above certain concentration level. As such efforts have been made by many researchers in the field of ISEs to develop selective sensors for heavy metals, which may permit quick and reliable quantification. As a result of extensive investigations, a large number of sensors have been reported for the estimation of a number of transition metals. A detailed literature survey on various ISEs for Mn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} is presented in the subsequent Chapters of the thesis. Here a brief review of recently developed ISEs for various transitions elements *viz*., V^{3+}, Cr^{3+}, Fe^{3+}, Hg^{2+}, Ag^{+}, Au^{3+} etc. has been presented.

Among transition metal ions, vanadium has received less attention. Very few attempts have been reported for determination of vanadyl ions. PVC based membrane sensors using ion carriers such as 1,8-diaminonaphthlene [151], vanadyl phosphate [152] have been reported for the fabrication of vanadyl ions. Recently schiff's base has been explored successfully for determination of vanadyl ions by Ganjali and coworkers [153].

Determination of chromium is of considerable concern as it is used in chrome plating, pigment manufacturing, refractory industries, leather processing, and wood treatment, making steel and other alloys. A number of potentiometric sensors based on a variety of ionophores have been reported in the past three decades. In 1989, Chattopadhyaya reported precipitate based chromium selective electrode utilizing chromium dithizonate as an ionophore [154]. Several chromium selective electrodes based on asymmetrical Schiff bases [155], 5-amino-1-phenyl-1*H*-pyrazole-4-carboxamide [156], 1-(2-(1*H*-imidazole-1-yl)-1-(4-methoxyphenyl)ethylidene)-2-phenylhydrazine [157] and crown ether [158] have also been reported.

Iron is essential nutrient as it provides a fundamental structure to haemoglobin, myoglobin, haemeenzymes and many cofactors involved in enzyme activities. It is considered as being a moderately toxic element, but medical research studies have shown that the toxic doses of iron and its compounds can lead to serious problems, including depression, rapid and shallow respiration, coma, convulsions and cardiac arrest. Therefore, its determination is necessary in environmental and biological samples. There are only few reports of Fe(III) selective sensors in the literature. Pejcic and coworkers reported Fe(III) selective sensor based on chalcogenide glass system [159]. Ekmekci *et al.* [160] reported Fe(III) selective sensor based on benzo-18-crown-6 crown ether as an ionophore. In addition to these, various compounds [161-165] have been incorporated as an electroactive material in the fabrication of Fe(III) selective electrodes.

Amongst heavy metal ions, the determination of mercury is probably most important to analysts in view of its acute toxicity. Hg^{2+} ion-selective sensor based on 1-(2′-aminoaryl)-4,4,6-trimethyl-1,4,5,6-tetrahydro-6-hydroxy pyrimidine-2-thiol [166] and 2-amino-6-purinethiol and 5-amino-1,3,4-thiadiazole-2-thiol [167] as a chelating ionophores exhibited better performance characteristics. Saleh *et al*., [168] developed a highly selective Hg^{2+} ion sensor using ethylenediamine-bis-(thiophenecarboxaldehyde), it showed Nernstian response with a low detection limit 7.0×10^{-8} mol L^{-1}. Hosseini *et al*., [169] reported a calix[4]arene derivative as an ionophore in the preparation of Hg^{2+} ion-selective sensor which exhibited Nernstian response in the linear range of 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} and detection limit of 4.0×10^{-7} mol L^{-1}. Recently, Afkhami *et al*., fabricated Hg^{2+} ion-selective sensor using schiff base, N,N′-bis(3(2-thenylidenimino)propyl)piperazine [170].

Fast and selective determination of trace quantities of Ag^{+} ion is of critical importance due to its multi-purpose nature and its widespread use in dentistry, electronic and photographic film production industry. Lai and coworkers [171] reported the first neutral carrier Ag^{+}-selective electrode based on dithiacrown ether. Since then a number of electrodes have been reported for Ag^{+} ion and calixarene derivatives remain the most extensively used compounds in the construction of Ag^{+}-selective electrodes [172-176]. Besides calixarenes, crown ethers [177, 178], schiff bases [179, 180] and sulphur donor neutral and macrocyclic ligands [181, 182] have also been used as ionophore in the fabrication of Ag^{+}-selective sensors. Firooz *et al*., developed Ag^{+}-selective sensor using 7-(1*H*-indol-3-ylmethyl)-5,6,7,8,9,10-hexahydro-2*H*-1,13,4,7,10-benzodioxatriazacyclopeantadecine 3,11(4*H*,12*H*)-dione, as an ionophore [183].

Relatively less attention has been focused on the development of Au^{3+} ion-selective sensor as compared to other transition metal ions. Zhang and coworkers explored benzyldimethyloctadecylammoniumaurichloroaurate [184] for the determination of gold in minerals. The electrode showed Nernstian response to $AuCl_4^-$ in the concentration range 3.5×10^{-7} mol L^{-1} to 7.0×10^{-3} mol L^{-1}. Hassan *et al*., proposed Au^{3+} ion-selective electrode based on nitron tetrachloroaurate(III) as an electroactive material which exhibited fast response time over the working concentration range of 1.0×10^{-5} - 1.0×10^{-1} mol L^{-1} [185].

1.3.4. Rare Earth Metal Ion-Selective Electrodes

Rare-Earths also called lanthanides are an important group of 15 chemically active mainly trivalent metals. They usually have magnetic, catalytic and optic properties therefore they are widely used in industry. Rare-Earths have a low toxicity rating but it has been found that intraperitoneal administration of these elements affect metabolic processes. Industrial sources of lanthanides are hence potentially hazardous to human health, and therefore there is a growing demand for determination of these metal ions. A detailed literature on Ce^{3+}-selective sensors is presented in the subsequent Chapters of this thesis, while a brief review on ISEs for other rare-earths is given in the following paragraphs.

The determination of La^{3+} ion has become necessary because of the increasing interest in bioinorganic and coordination chemistry, as well as in the increased industrial use of lanthanum compounds and their enhanced discharge, toxic properties and other adverse effects. There are only a few reports on La^{3+} ion-selective electrodes till date. Akhond *et al*., fabricated a La^{3+} ion-selective sensor using 2,2′-dithiodipyridine [186]. Amarchand *et al*., [187] reported a PVC membrane and coated graphite electrode based on bis(2-mercaptoanil)diacetyl. But the above reported electrodes possessed narrow working concentration range and suffered serious interferences from various cations including Cu^{2+}, Ni^{2+} and Ce^{3+} ions. In addition to these, PVC based La^{3+} ion-selective electrodes based on other neutral carriers *viz*., 4-methyl-2-hydrazinobenzothiazole [188], $Bzo_2Me_2Pyo_2$(16)-hexaeneN_6 [189] and benzo-15-crown-5 [190] have also been reported.

In 1996, Chowdhury and coworkers reported the first Sm^{3+} selective sensor, by using bis(thiaalkylxanthato)alkanes as an ion carrier [191]. Later on Mittal and coworkers reported samarium(III) selective sensors based on tin(IV) boratophosphate [192] and zirconium(IV) boratophosphate [193] but these sensors showed super Nernstian slope. In addition to these, Sm^{3+} selective sensor based on 2-((2-thioxothiazo-lidin-4-one)methyl)phenol [194], 2-ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline [195], 2-[(E)-1-(1*H*-pyrrol-2-yl)methylidene]-1-hydrazinecarbothioamide [196] and N_2,N_4-bis((3*H*-indol-3-

yl)methylene)-6-phenyl-1,3,5-triazine-2,4-diamine [197] have also been reported have also been reported.

Although REEs, including Yb^{3+} ion, have a low acute toxicity rating, in some studies it has been found that intraperitoneal administration of this element in concentration of 0.01, 0.1 and 1% in the diet for 90 days, produced liver damage, which was more prominent in males than females. Few sensors are reported for Yb^{3+} ion determination and these are based on cefixime [198], N-(2-pyridyl)-N'-(2-methoxyphenyl)-thiourea [199], 3-hydroxy-*N*-[(2-hydroxyphenyl)methylene]-2-naphthohydrazide [200], 6-methy-4-{[1-(1H-pyrrol-2-yl)methyl-idene]amino}-3-thioxo-3,4dihydro-1,2,4-triazin-5(2*H*)-one [201], N-(6-picolyl)-N'-(4-methoxyphenyl)-thiourea [202], 2,5-bis(5-tert-butyl-benzoxazol-2-yl)thiophene [203]. The electrode sensors reported for Yb^{3+} ion exhibits narrow working concentration range and show interferences to various cations such as Ce^{3+}, Nd^{3+}, Gd^{3+}, and Pb^{2+}. Thus there is still a need for having good sensors for Yb^{3+} ion determination and further efforts are required to develop it. Singh *et al*., reported macrocyclic ligands 2,12-(2-methoxyaniline)$_2$-4,14-Me$_2$-[20]-1,4,11,14-tetraene-1,5,8,11,15,18-N$_6$ and 2,12-(2-methoxyaniline)$_2$-4,14-Me$_2$-8,18-dimethylacrylate-[20]-1,4,11,14-tetraene-1,5,8,11,15,18-N$_6$ as electroactive material in the fabrication of polymeric membrane electrode and coated graphite electrode for selective determination of Yb^{3+} ion [204]. Zamani *et al*., developed a PVC-membrane based Yb^{3+} ion-selective electrode using 4-Methoxybenzyl carbazate as electroactive material [205].

There have been few reports on Gd^{3+}-selective sensors. Zamani and coworkers used 6-methyl-4-{[1-(2-thienyl)methylidene]amino}3-thioxo-3,4-dihydro-1,2,4-triazin-5-(2*H*)-one [206] as an ionophore for fabrication of Gd^{3+} selective sensor. Singh *et al.*, explored 2,6-bis-[1-*{N*-cyanopropyl,*N*-(2-methylpridyl)}aminoethyl] pyridine as an ionophore for the determination of Gd(III) ions in waste water and rock samples [207]. Schiff bases N,N′-bis(methylsalicylidene)-2-aminobenzylamine have been used as an ionphore for the selective monitoring of Gd^{3+} in various samples by Zamani *et al*., [208].

In 2004, Agarwal and coworkers reported Nd(III) selective sensor using inorganic ion exchange resin [209] but this sensor showed long response time. Norouzi *et al.* explored N-(2-furylmethylene)pyridine-2,6-diamine for determination of Nd(III) ion [210] while in recent year Singh *et al.* reported Nd(III) selective sensor incorporating lariat ethers as an ionophore [211].

Zamani *et al.*, [212] explored 4-amino-3-{2-[4-amino-6-methyl-5-oxo-4,5-dihydro-1,2,4-triazin-3(2*H*)-yliden]hydrazono}-6-methyl-3,4-dihydro-1,2,4-triazin-5(2*H*)-one (ATO) as a suitable ionophore for determination of terbium ions. The sensor performed satisfactorily in the concentration range of 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} with Nernstian slope 19.4±0.5 mV $decade^{-1}$ of $a_{Tb}{}^{3+}$ and detection limit 8.6×10^{-7} mol L^{-1}. Singh *et al.*, [213] reported macrocyclic pendant ligands for development of Tb^{3+}-selective electrodes. Coated graphite electrode based on 3,4,5:12,13,14-dipyridine-2,6,11,15-tetramethyl-1,7,10,16-tetramethylacrylate-1,4,7,10,13,16-hexaazacyclooctadeca-3,13-diene showed fast linear response with a detection limit of 5.7×10^{-9} mol L^{-1}. Gupta *et al.*, [214] a new terbium selective sensor based on N-(2-hydroxyphenyl)-3-(2-hydroxyphenylhydroxyphenylimino)-N-phenylbutanamidine.

A number of ion-selective sensors for some other rare-earth metal ions *viz.*, Eu^{3+} ion [215-217], Tm^{3+} ion [218, 219], Dy^{3+} ion [220-222], Ho^{3+} ion [223-225], Pr^{3+} ion [226, 227] UO^{2+} ion [228, 229], *etc.*, have also been reported. All these sensors exhibited good selectivity for the ion of interest, sufficiently wide working concentration range and low response time.

1.3.5. Anion-Selective Sensors

In recent years, intensive research has been directed in the preparation of a variety of selective receptors for anions [230-240]. The most successful and important anion-selective sensor is for F^- anion which is based on the crystal of LaF_3. Another F^- selective sensor incorporating CaF_2 or LaF_3 or mixture of both has been reported by Newman *et al.*, [241]. The sensor exhibited working concentration range of 1.0×10^{-5}-1.0×10^{-2} mol L^{-1} and detection limit up to 0.6×10^{-6} mol L^{-1} F^- ion. Nakamura *et al.*, [242] used membranes of phthalocyanine cobalt(III) for preparing F^- sensors and used them for fluoride estimation in non-aqueous medium and pharmaceuticals. In recent years, various ionophores *viz.*, aluminum(III) porphyrins [243], complexes of Zr(IV) and Al(III) with 2,7,12,17-tetra-tert-butyl-5,10,15,20-tetraazaporphine [244], Al(III)- and Zr(IV)-salophens [245] and poly(3,4-ethylenedioxythiophene) [246] have been used in the preparation of F^- ion-selective electrode. Similarly, attempts have also been made to prepare Cl^- ion-selective sensor by using different ionophores such as lanthanide tris(b-diketonates) [247], 2,5-dihydroxy-p-benzoquinone [248], polypyrrole-graphite-epoxy composite [249] and derivatives of 2,2′-binaphthalene [250]. Havas *et al.*, first time used Br^- ion-selective membrane electrode [251] and Weiss *et al.*, utilized Br^- ionic electrodes in waters which were sensitive to poisoning by I^- and S^{2-} [252], later on Zhu *et al*., studied on the benzalkonium Br^- ion-selective electrode [253]. PVC based membrane sensors incorporating different ionophores such as tetrakis(4-N,N-dimethylaminobenzene)porphyrinatomanganese(III) acetate [254], Cd chelates of schiff bases, N,N'-bis(salicylidene)-1,4-diaminobutane and N,N'-bis(salicylidene)-3,4-diaminotoluene [255], 3-amino-5-mercapto-1,2,4-triazolecobalt(II) [256], meso-tetrakis(2-alkoxyphenyl)-porphyrincobalt(II) [257], bis-(o-phenylenediamine)Cu(II) [258] and poly(3-aminophenylboronic acid) [259] electro active materials in fabrication of I^- ion-selective electrodes.

After halide determination, the next important ion determined is nitrate due to its presence in soil, ground water and various other samples. Schwarz *et al*., [260] prepared NO_3^- selective sensor by using tridodecylmethyl ammonium nitrate as an electroactive material and applied it for in-situ determination of NO_3^- in ground water and drinking water. Some other membrane sensors were developed by using tris(2-aminoethyl)amine [261], 1,8-bis(salicylaldiminato)-3,6-dioxaoctane Ni(II) complex [262], bis-thiourea [263] and nanocomposite 3,6-bis(2-[2-sulfanyl-ethylimino-methyl]-4-(4-nitro-phenylazo)-phenol)pyridazine coated $SiO_2@Fe_3O_4$ [264] as ionophore in the construction of NO_3^- ion-selective electrodes.

Carbonate compounds are used extensively in the manufacturing of glass, paper, rayon, soaps, and detergents and for dyeing processes in textile industries. Although, carbonate is slightly toxic, but exposer causes corrosive to the gastro-intestinal tract and severe abdominal pain, diarrhea and vomiting are the symptoms of it. In view of its widespread occurrence, the accurate and rapid determination of CO_3^{2-} is important. Herman and Rechnitz reported first CO_3^{2-} ion-selective membrane sensors based on the trifluoroacetyl-*p*-butylbenzene derivatives [265]. However, the applicability of these sensors has often been limited because of interference caused by lipophilic anions such as salicylate, perchlorate, and thiocyanate. Later on, Scott *et al*., employed an anion-binding complex one such as mercuric EDTA in the buffer solution to decrease salicylate interference of the carbonate responsive membrane [266]. The change of cationic site (*e.g*., tridodecylmethylammonium chloride) in the trifluoroacetophenone based membranes was examined by Sokalski *et al*., to improve their CO_3^{2-} ion selectivity [267]. Asymmetric membrane technology was utilized to prevent salicylate from responding to CO_3^{2-} ion sensitive membranes in serum carbon dioxide measurements [268]. It was observed that association of acceptor group into phenyl ring of TFA (trifluoroacetyl-group) in paraposition enhances the selectivity of sensors [269, 270] and increase in the acidity of the TFA is responsible for CO_3^{2-} ion sensing. Tthe interferences from high concentrations of chloride and salicylate is still hinder wider application of CO_3^{2-} ion sensors.

A sulphate selective sensor based on a derivative of imidazole as neutral carrier was reported by Li *et al.*, [271] which showed strong interference to Br^- and NO_3^- ions. Hydrotalcites based sulphate selective sensor was reported by Morigi *et al.*, [272] which showed improved selectivity for sulphate over a number of anions. Recently, Sathyapalan and co-workers [273] designed a sulphate ISE based on a hydroxyl Schiff base which showed remarkable selectivity to SO_4^{2-} ion.

A few other anion selective sensors have also been reported. Messick *et al.*, [274] reported salicylate selective sensor with lutetium(III)porphyrin. Blikova *et al.*, [275] prepared salicylate selective sensors using complexes of Sn(IV) with 8-hydroxyquinoline and tetrakis(tert-butyl)phthalocyanine and used them to determine acetylsalicylic acid in medical preparation. Recent literature reveals that various ionophores have been proposed which show high selectivity to salicylate ion [276-279].

Arsenite selective sensor was prepared by Gupta *et al.*, [280] by the fabrication of cobalt(III)*p*-tertrmethoxy porphyrin as an electroactive material which showed linear range of concentration (0.79×10^{-6}-1.0×10^{-1} mol L^{-1}) AsO_2^- and Nernstian slope (28.8 mV $decade^{-1}$ of activity). The sensor worked satisfactorily in non-aqueous medium and showed good selectivity for arsenite over a large number of anions.

1.3.6. Miscellaneous Ion-Selective Sensors

Besides inorganic ions, efforts have also been made to develop sensors for gases and organic species. Ueda *et al.*, [281] made use of p-1,1,3,3-tetramethylbutyl calix[6]arenehexaacetic acid hexaethyl ester embedded in PVC matrix to develop sensor for methylammonium ion. The sensor displays a near Nernstian slope (58.5 mV $decade^{-1}$ of activity) and linear range of concentration (1.0×10^{-5}-1.0×10^{-2} mol L^{-1}). Mohammad *et al.*, [282] developed histamine selective sensors using iron(III) and manganese(II) porphyrins and applied to determine histamine in synthetic serum samples. Varga *et al.*, [283] documented a newely approach for the fabrication of anionic surfactant–selective sensors. The sensors thus developed showed Nernstian response, fast response time and good stability. Cocaine, caffeine, penicillin-G, diclofenac, atropine, viagra, ibuprofen and some chiral drugs selective sensors have been developed and applied for their estimation in pharmaceutical analysis [284-290]. A nicotine-selective sensor [291] has been prepared by adding silicotungstic acid and di(2-ethylhexyl)phthalate in PVC matrix which showed Nernstian response (1.0×10^{-6}-0.1×10^{-3} mol L^{-1} nicotine). In addition to organic species, a number of gas sensors for NH_3, CO_2, SO_2, NOx, H_2S and O_2 have been reported [292]. The NH_3 gas sensors have been used in the analysis of fresh water, effluents and sewage, CO_2 sensor for blood analysis, SO_2 sensor for food and beverages and NOx for the measurement of nitrite in soil extracts and water samples. Similarly, biosensors for a number of biomolecules have been prepared and some of them are commercially available [293-299].

1.4. THE PROBLEM

An overview of literature revealed that an intensive research have been done on ISEs for the estimation of ions such as alkali, alkaline earth, heavy metals and anions. In the journey of researchers on ISEs to improve the sensitivity and selectivity of the electrode, a large number of ISEs were reported for every single ion using different newer materials. However, for most of the ions, even the best sensor so far developed is not the final word and can always be improved in some respect with the availability of newer selective materials. Further, literature survey shows that the most of the sensors reported for Co^{2+}, Mn^{2+}, Nd^{3+}, Cu^{3+} and Fe^{3+} metal ions are not of very high selectivity and generally show high response time and limited working concentration range. As the determination of these ions is important, attempts have been made to develop new ISEs for these metal ions which show improved performance compared to the existing ones.

The performance of any ISEs depends mainly on the selectivity of the ionophore (electroactive component) present in the membrane. It is important and essential that ionophore used should have high affinity for a particular cation/anion and poor for others. Such ionophores are likely to act as a selective sensor for the ion to which they show high affinity. The high affinity of an ionophore for a particular ion may be due to various processes such as selective ion exchange, sorption, ion–ionophore complexation or hydrogen bonding. The problem is that very few materials are available which show high affinity to a particular ion as a result of either of these processes. However, the newer materials such as calixarenes, porphyrins, dendrimers, schiff base, macrocyclic compounds various types of metal chelates and hydrogen bonding receptors are being continually synthesized and few of them have shown selective response to only a limited number of cations/anions. In the present investigations, some of such materials have been explored as ionophores for the fabrication of PME CGE and CPGE for Cu^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} Cd^{2+} and Ce^{3+} metal ions. The efforts have been successful to a significant extent as evident from the results reported in the following chapters. The efforts have been successful to a significant extent as evident from the results reported in the following chapters.

- Polydentate macrocyclic ligands are cyclic molecules consisting of an organic framework interspersed with heteroatoms that are capable of interacting with a variety of species. They display unique and exciting chemistry as they can function as receptors for substrates of widely differing physical and chemical properties and can drastically alter these properties upon complexation. The most intriguing characteristic of the macrocyclic compounds is their ability to selectively bind certain cations in preference to others that may be present in solution. They are a class of compounds known for their remarkable selectivity for various transition and non-transition metal ions. Therefore, polydentate macrocyclic ligand *viz*., 5,11,17-trithia-1,3,7,9,13,15,19,20,21-nonaazatetracyclo-[14.2.1.$1^{4,7}$.$1^{10,13}$]henicosa-4(20), 10(21),16(19)-triene-6,12,18-trithione (L_1) was synthesized, characterized and explored as ionophores in the fabrication of Cd^{2+}-selective sensors. Thus, polymeric membrane electrode (PME), coated graphite electrode (CGE) and coated pyrolytic graphite electrode (CPGE) were prepared and investigated as Cd^{2+}-selective sensors. The Results obtained are described in the Second Chapter of this thesis which clearly demonstrates that efforts have been highly successful of using L_1 as ionophore in the fabrication of Cd^{2+}-selective sensors.

- Diaminopyrimidine based chelating ligand 5,5'-((3-nitrophenyl)methylene)bis(2,6-diaminopyrimidin-4(3*H*)-one) (L_2) was synthesized and characterized. Preliminary studies showed that L_2 has high affinity for Ni^{2+} ion and thus it was used in the fabrication of Ni^{2+}-selective sensors. The coated pyrolytic graphite electrode (CPGE) reflects improved performance over coated graphite electrode (CGE) and results of several studies are reported in the Third Chapter of this thesis and it was concluded that developed Ni^{2+} selective sensor showed better performance than many of the previously reported Ni^{2+} selective sensors and hence the effort was successful to a significant extent.

- Polydentate heterocyclic chelating ionophores namely L_3 (1,3-bis[2-(1,3-

benzothiazol-2-yl)-phenoxy]propane) and L_4 (1,2'-bis[2-(1,3-benzothiazol-2-yl)-phenoxy]-2-ethoxy ethane) were synthesized, characterized and investigated as Cu^{2+} selective sensors. A number of PVC-based electrodes were prepared and comparative study of several polymeric membrane electrodes showed that coated pyrolytic graphite electrode exhibited best performance. The results are described in the fourth chapter of this thesis which clearly states that efforts to made Cu^{2+} selective sensors was successful.

- Novel chalcone ligand L_5 (1,1'-(pyridine-2,6-diyl)bis(3-(1*H*-pyrrol-2-yl)prop-2-en-1-one)) was synthesized and characterized. Colorimetric and conductometric studies performed on the L_5 show that it has high affinity for the Ce^{3+} ion and therefore, L_5 was used in the fabrication of poly (vinyl chloride) based membrane sensors. The results of various studies are described in the fifth chapter of this thesis which demonstrates that efforts have been successful to a significant extent.

- Multidentate Schiff bases of isonicotinohydrazide namely, L_6 (N'(N',N'''E,N',N'''E)-N',N'''-((((oxybis(ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene))bis(methanylylidene))di(isonicotinohydrazide)) and L_7 ((N',N'''E,N',N'''E)-N',N'''-(((propane-1,3-diylbis(oxy))bis(2,1-phenylene))bis(methanylylidene))di(isonicotinohydrazide)) were investigated as Mn^{2+} selective sensors. In view of good selectivity of the sensor for Mn^{2+} over other metal ions, the efforts to develop Mn^{2+}- selective sensors have been achieved successfully and results have been described in the sixth chapter of this thesis.

- Multidentate Schiff bases of hydrazinecarbothioamide namely, L_8 [2,2'-(((ethane-1,2-diylbis(oxy))bis(3-methoxy-4,1-phenylener))bis(methanylylidene))bis(hydrazineecarbothioamide)], L_9 [2,2'-(((propane-1,3-diylbis(oxy))bis(3-methoxy-4,1-phenylene))bis(methanylylidene))bis(hydrazinecarbothioamide)], L_{10} [2,2'-((((oxybis(ethane-2,1-diyl))bis(oxy))bis(3-methoxy-4,1-phenylene))bis(methanylylidene)bis(hydrazinecarbothioamide)], L_{11} [2,2'-(((ethane-1,2-diylbis(oxy))bis(2,1-phenylene)) bis(methanylylidene))bis(hydrazinecarbothioamide)], L_{12} [2,2'-(((propane-1,3-diylbis(oxy))bis(2,1-phenylene))bis(methanylylidene))bis(hydrazineecarbothioamide)] and L_{13} [2,2'-((((oxybis(ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene))bis(methanylylidene))bis(hydrazinecarbothioamide)] have been synthesized and characterized. The preliminary studies performed on L_8, L_9 and L_{10} showed higher affinity for Co^{2+} while L_{11}, L_{12} and L_{13} showed higher affinity for Zn^{2+}. Results of several studies are reported in the last chapter of this thesis and it was concluded that efforts to develop Co^{2+} and Zn^{2+} selective sensors were successful to a significant extent.

1.5. CLASSIFICATION OF ION SELECTIVE ELECTRODES

ISEs have continued to be one of the most important developments in analytical chemistry. They have been used very successfully from decades in various areas of chemical analysis. While the initial era saw an intensive search for novel electrode materials and new constructions, this has given a way subsequently to more introspective studies on ion-selectivity and electrode mechanism. The rapid expansion of activity in the field of ion-selective electrodes makes them highly desirable to have an idea of their categories as well as their practical applications.

According to IUPAC [300] recommendations, in terms of the mode of operation, ion-selective electrodes are classified as primary, those respond to the species of interest directly, and sensitized, those response to some other species (not necessarily ionic) through the agency of a sensitizer.

1.5.1. Primary Ion-Selective Electrodes

Primary electrodes can be classified as follows:

1.5.1.1. Crystalline Membrane Electrodes

Membranes constructed by using crystalline material come under this heading and can further be divided into two sub-headings:

a. Homogeneous Membrane Electrodes

In this type of electrodes, membrane is constructd by incorporating crystalline material which is fabricated either a single or a homogeneous mixture of compounds. The active component of these electrodes consists of a solid material like LaF_3, AgCl, Ag_2S or a mixture such as $Ag_2Se + Cu_2Se$ or $Ag_2S + AgI$.

b. Heterogeneous Membrane Electrodes

Inert matrix like poly(vinyl chloride) or silicone rubber are the active substances which alone or in association with powdered active crystals are used for the preparation ofelectrodes on hydrophobized graphite. The flexible nature of the resulting membrane is advantageous as it resists breakage.

1.5.1.2. Non-Crystalline Membrane Electrodes

Under this category, ISE is usually imposed between two aqueous solutions and it is prepared from a support matrix which includes an ion exchanger (either cationic or anionic), a solvent mediator and an uncharged selectivity-enhancing group. Millipore filter, glass frit, etc. are porous which can be used as support. Also, glass or inert polymeric material like PVC, yielding with the ion-exchanger are non-porous can be used as a support. The response of the electrode is due to the presence of ion-exchange material in the membrane and the selectivity of the electrode is related to selective exchange behavior of the ion-exchanger. They may be rigid or non-rigid matrix electrodes:

a. Rigid Matrix (self-supporting electrodes)

This category involves mainly synthetic cross linked polymers *viz*. polystyrene sulfonate, sulfonated poly(tetrafluoroethylene), amino-poly(vinyl chloride) or silicate glass electrodes. A thin polymeric membrane with equipped sites or a thin piece of glass is used for the preaparation of ISE and selectivity of the membrane is dependent on chemical composition of polymer or glass.

These are mainly selective for hydrogen ion and monovalent (alkali metal cations) ions. These electrodes operate on the fact that when a glass membrane is immersed in a solution containing hydrogen ions, an ion-exchange mechanism with the fixed SiO^- groups in the glass membrane boundary region is initiated. The glass material is made up of a solid silicate matrix within which alkaline metal ions are mobile. When this glass membrane is brought in contact with an aqueous solution, its surface becomes hydrated to a depth of about 100 nm and the alkali metal cations from the glass matrix can be exchanged for other ions in solution, preferably H^+, creating a potential across the membrane that is a linear function of the pH of the solution.

b. Non-Rigid Matrix electrodes

They contain electrodes with mobile charged sites. This group of electrodes can further be divided into the following sub-headings based on the charge they bear:

(i) Positively charged mobile carrier electrodes

When positively charged hydrophobic cations like quaternary ammonium salts dissolved in a suitable organic solvent and kept in an inert support matrix like PVC or PPC (poly(propylene carbonate)) filter result in membranes which are susceptive to changes in the activities of anions. These electrodes contain a liquid ion-exchanger, a substance that has the ability to enter into heterogeneous equilibrium with the ion of interest, when dissolved in an organic solvent. A porous solid material is impregnated with the organic phase, thus forming a membrane separating inner and outer solutions. Extraction equilibrium replaces the solubility equilibrium of the crystalline membrane in determining the selectivity.

(ii) Negatively charged mobile carrier electrodes

Uncharged “carrier” electrodes incorporating solutions of molecular complexing agents of cations and anions could be employed in ion exchanger membrane formulation to allow selectivity and sensitivity to certain cations and anions. Ion-dipole formers such as macrocyclic compounds, antibiotics or other sequestering agents are well known molecular complexing agents of cations while adduct formers for example; porphyrins, organotin compounds and activated carbonyl compounds are regareded as molecular complexing agents of anions. These electrodes are based on a large neutral molecule that can complex the ion of interest to form an aggregate that is soluble in an organic solvent. The solution so formed is then located into a porous solid to constitute the ion-selective membrane. In these electrodes ion-dipole interactions between the donor atoms and the ion are responsible for the stability of the complex.

1.5.1.3. Ion-Selective Field-Effect Transistor Sensors (ISFET)

ISFET can be described as hybrid electronic devices consisting of an ion-selective membrane and a field effect transistor (FET) preamplifier in a single unit. They have the common features of processing central insulator of SiO_2 or Si_3N_4 surrounded by a doped semiconductor on one side, and ion exchanger (or other interfacial potential-developing membrane film or adsorption-promoting film) on the other. Only the latter side is exposed to the electrolyte solution under test.

1.5.1.4. Sensitized or Compound (Multiple Layer Membranes) Electrodes

It constitutes a very important group because of their inherent selectivity, as two membranes are used to generate the response, each with its own selectivity characteristics. This group of electrodes is further divided into the following two sub-headings:

1.5.1.4.1. Gas Sensing Electrodes

In gas sensing electrodes, a gas-permeable and water-impermeable membrane lies over the ISEs and this solution containing acidic/basic gaseous species (e.g. NH_3, CO_2, SO_3 and NO_2), diffuses through the membrane and indicates a change in pH, detected by the glass electrode. The alteration in pH is proportional to the partial pressure of the gaseous moiety present in the sample and measured by the ISE. An exception to this classification is the hydrogen gas electrode, which responds both to the partial pressure of hydrogen and to the pH. If it is amperometric and not potentiometric equipment, then oxygen electrode fits under this classification which is contrast to other sensors.

1.5.1.4.2. Enzyme Substrate Electrodes

ISE mounted by a coating incorporating an enzyme (between the solution and the glass electrode) is regarded as enzyme substrate electrodes. The enzyme associaed in electrode causes the reaction of substrate (an organic or inorganic substance) to produce a species which is then sensed by the electrode. As a matter of fact, the electrode can be capped with a layer of substrate which then reacts with the enzyme, co-factor or inhibitor to be analysed.

For example, a membrane containing immobilized urease, catalytically decomposes ambient urea to ammonium ions, which are sensed with a cation-sensing glass membrane electrode.

1.5.1.5. Metal Contact or Solid-State Ion-Selective Electrodes

There is no inner electrolyte solution in these electrodes and electronic conductor replaces the inner reference electrode. An anion sensor based on cation radical salts in contact with Pt or a bromide sensor film of AgBr reversibly contacted with Ag, are the considered as electronic conductor. This setup is in genral opposite to a common electrode functioning in which electrolyte solutions are in contact with opposite membrane sites.

1.6. MEMBRANE

A membrane is a phase, finite in space, which separates two other phases and exhibits individual resistance to the permeation of different species [301]. Ion selective sensors generally employ homogeneous/heterogeneous membranes of chemical compounds. The capability to differentiate between various permeating species is the principal characteristics of a membrane used in electrochemical sensors. This differentiation leads to the formation of an electrical double layer, which is the source of electric potential. The potential developed is basically due to two processes: (i) different mobilities of the ions through the membrane resulting in the generation of diffusion potential, (ii) Donnan or phase boundary potential arising from non-transport of one or more kind of ions. The potential developed is a function of activity ratios of the exchangeable ions on the two sides of the membrane.

Therefore, it can be used to determine the activity of an unknown solution. For the satisfactory performance of the membrane, the diffusion potential should be absent or be minimal. The membrane can play a critical role in the performance of the sensor in a particular environment. A successful membrane needs to be generally hydrophobic, have ion-exchanger properties and contain a lipophilic ionophore that provides selectivity to the sensor. The lack of ion-exchanger properties would lead to substantial uptake of sample cations as well as anions into the membrane, leading to effective breakdown of so-called perm selective behavior. In some instances membrane materials are susceptible to *in vivo* oxidative cleavage and hydrolysis. This would cause deterioration of the membrane and in the long term would render the sensor inoperative.

1.6.1. Membrane materials

In general, the polymeric membrane used in ISE consists of four components: Electroactive material (ionophore), lipophilic additive, plasticizer and the polymer matrix. The detailed description is described in subsequent sections.

1.6.1.1. Electroactive materials (Ionophore)

Selectivity and sensitivity of an ISE is highly controlled by the ionophore (e.g., ion carrier or ligand) and therefore it is the key component of polymeric membrane ion-selective electrodes.This is because of the binding between the ionophore and analyte which result signal to be responsed by ISE. Ionophore forms relatively strong complex and exhibit reversiblity with tast ion and not with the other ions. There are two kinds of ionophore, charged and neutral carrier. Various substances *viz*. inorganic and organic ion exchanger, solid electrolyte, salts of multivalent atoms, metal chelates, polyaza, polythia macrocycles, crown ethers, cryptands and calixarenes have been used as ion carriers for the preparation of ISEs. To be used as suitable ion carrier; the active sensor material should be physically compatible with the matrix, have a low solubility product, must exhibit some electrical conductivity, have balance between the free energies of ion-ligand interaction, ion-hydration and undergo rapid ion exchange at the membrane sample interface. In order to keep the membrane composition constant, the ionophore must retain within the membrane; therefore, aside from the binding centre it must contain numerous lipophilic groups. From a more mechanistic perspective, the potentiometric response of membrane-based ISEs containing a specific ionophore can be used to provide information about the mode of analyte binding as well as, at least potentially, molecular insights into the details of the relevant substrate receptor interactions.

1.6.1.2. Polymeric (inert) matrix

The matrix used provides an inert base that imparts physical-mechanical stability and elasticity to the membrane. As it was mentioned above, polymer membrane gives a unique opportunity to obtain a variety of electrodes selective towards particular ions by doping membrane with certain ionophore. Polymer matrixes are chemically inert, hydrophobic, tough, flexible, non-porous, crack resistant and should not swell in sample solutions. Silicon rubber [302], some methacrylates [303] polyurethanes [304] and polystyrene, polyamide or polyimide have been demonstrated as polymer matrices meeting this requirement, while the most commonly used polymer is poly(vinyl chloride) (PVC) due to simplicity of membrane preparation. Of the various binders used for preparing heterogeneous solid state membranes, PVC has been most widely used due to its relatively cheap cost, good mechanical properties, inertness and amenability to plasticization.

It also offers good resilience to mechanical and pressure damage as well as the electroactive materials is highly compatible with the matrix resulting in their reduced leaching from the membrane and the electrode life is increased to a substantial extent. Thomas and Moody are the pioneers in developing PVC based electrodes. Thomas *et al.* in 1986 recommended PVC as the most significant polymer support. A detailed comparative study of PVC with other polymeric materials in their response characteristics was provided by Moody *et al.* [305]. Buck *et al.* discussed the properties of PVC and found that the presence of dissociated fixed exchange sites contributes to the electrode response and selectivity [306, 307]. Further, Mikhelson also reviewed the advantages and disadvantages associated with the PVC matrix [308]. The incorporation of neutral carrier in a PVC matrix has provided an economical way of simplifying ISE construction.

1.6.1.3. Solvent Mediator or Plasticizer

The plasticizer to be used in membranes should exhibit high lipophilicity, high molecular weight, low tendency for exudation from the polymer matrix, low vapor pressure and high capacity to dissolve the substrate and other additives present in the membrane [309]. It is well documented that the addition of plasticizers not only improves the workability of the membranes but also contributes significantly towards the improvement in the detection limit, stability and shelf life of the sensor [310]. Additionally, its viscosity and dielectric constant should be adequate. It enhances the flexibility and softness of the fabricated membrane and provides mobility of membrane constituents within the membrane phase. Being a dominating component of PVC membranes, plasticizer acts as a membrane solvent, affecting membrane selectivity through both extraction of ions into organic phase and influencing their complexation with the ionophore [311].

In order to obtain a homogeneous organic phase, plasticizer must be compatible with the polymer and other membrane constituents have to be soluble in it. Polymeric membrane usually comprises of a matrix containing *ca.* 33 % (w/w) of PVC and 66 % of (w/w) solvent mediator. A number of organic solvents such as phthalates, sebacates, octyl ethers, acetophenone and benzyl acetate have been suitably and efficiently used as plasticizer to enhance the performance of ISE.

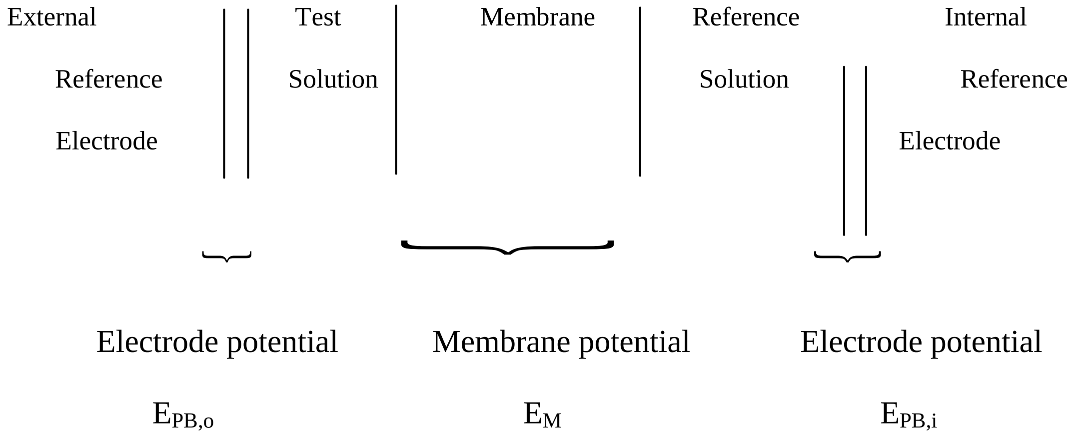
1.6.1.4. Lipophilic Additive or Lipophilic Ionic Sites

The prerequisite for obtaining a theoretical response with ISE membranes is their perm-selectivity, which means that no significant amount of counter ions may enter the membrane phase. Lipophilic ionic additive is a salt of non-exchangeable lipophilic anion/cation and an exchangeable counter ion. Their main function is to render the ion selective membrane perm selective, to optimize sensing selectivity (by defining the ratio of complexed to uncomplexed ionophore concentration in the membrane) and to reduce the bulk membrane impedance [312, 313]. The presence of lipophilic additive in ion selective membrane electrodes not only diminish the ohmic resistance and enhance the behavior but also in cases where the extraction capability is poor, increase the sensitivity of membrane electrodes. These additives may also catalyze the exchange kinetics at the sample membrane interface [314, 315].

Although the presence of the ionic sites is mandatory, membranes may function without deliberately incorporated ionic sites because of impurities in the polymer matrix or in other components. Their concentration relative to the ionophore has an important selectivity modifying effect due to the influence of the involved equilibrium. Various tetraphenylborate derivatives are currently used as anionic additives while tetraalkylammonium salts are used as cationic additives. The charge of the proper additive is tied directly to the response mechanism of the chosen ionophore.

1.7. POTENTIAL OF AN ION-EXCHNAGE MEMBRANE

Ion-selective electrodes are typically investigated under zero current condition by following cell set up.



The electromotive force (emf) across this cell is the sum of all individual potential contributions. Many of these are sample-independent, and the measured emf can usually be described as

$$emf = E_{const} + E_J + E_M \tag{1.1}$$

Liquid Junction potential E_J, originates from the different mobility of ionic species in the sample solution and in the bridge electrolyte of the reference electrode if ion-selective electrodes [316] can be kept constant by employing concentrated bridge electrolytes with similar mobilities of cations and anions (e.g. 1M KCl, NH_4NO_3 or LiOAc). The utility of membrane electrodes depends upon the determination of *membrane potential* E_{M}, which is ideally a function of the sample ion activity [317, 318]. So we will only focus on the membrane potential E_{M} of electrode.

Since the membrane is usually interposed between the sample and an inner reference electrolyte, it is commonly divided into three separate potential contributions, namely the phase boundary potential at both interfaces and the diffusion potential within the ion-selective membrane.

$$E_M = E_{PB} + E_{Diff} \tag{1.2}$$

The potential at the membrane/inner filling solution interface can be assumed to be independent of the sample, whereas the diffusion potential within the membrane may become significant if considerable concentration gradients of ions with different mobilities arise in the membrane. If no concentration gradients occur within the membrane, diffusion potential E_{Diff} is zero. This is often the case for membranes that show theoretical Nernstian response. Phase boundary potential E_{PB} arises from a charge separation caused by the non-uniform distribution of ionic species between the organic membrane and the aqueous phase. The phase boundary potential can be derived from basic thermodynamic considerations of chemical and electrical potential contributions. The electrochemical potential, $\bar{\mu}$ for species A in aqueous phase could be written as follows [319].

$$\bar{\mu}_{A(aq)} = \mu_{A(aq)} + Z_A F \phi_{(aq)}$$

$$\bar{\mu}_{A(aq)} = \mu^{\circ}_{A(aq)} + 2.303RT \log a_{A(aq)} + Z_A F \phi_{(aq)} \tag{1.3}$$

Similarly, the electrochemical potential for the analyte ion (A) in contacting organic phase is

$$\bar{\mu}_{A(org)} = \mu_{A(org)} + Z_A F \phi_{(org)}$$

$$\bar{\mu}_{A(org)} = \mu^{\circ}_{A(org)} + 2.303RT \log a_{A(org)} + Z_A F \phi_{(org)} \tag{1.4}$$

Where, μ is the chemical potential and μ^o is chemical potential under standard conditions, z_A is valency of analyte ion A and a_A is the activity of the uncomplexed ion A, ϕ is the electric potential and R, T and F are the universal gas constant, absolute temperature and Faraday constant respectively. It is assumed that the interfacial ion transfer and complexation processes are relatively fast and therefore, equilibrium holds at the interface so that the electrochemical potential for both phases are equal. This leads to a simple expression for the phase boundary potential, *i.e.*

$$E_{PB} = \Delta\phi = -\frac{\mu^o_{A(org)} - \mu^o_{A(aq)}}{Z_A F} + \frac{2.303RT}{Z_A F}\log\frac{a_{A(aq)}}{a_{A(org)}} \qquad (1.5)$$

Thus, equation (1.5) indicates that the phase boundary potential is a simple function of sample ion activity ($a_{A(aq)}$) particularly if $a_{A(org)}$ is not significantly altered by the sample. The complexation of analyte ion A with the ionophore inside the organic membrane phase influences free analyte activity $a_{A(org)}$ and therefore, also the phase boundary potential [320]. However, due to the strong complexation with the ionophore, concentration of the free ion in the organic membrane is small relative to that of the complexed ions. Consequently, the concentration of the complex is approximately equal to that of the anionic sites provided by the anion discriminator and remains unaltered if an excess of ionophore is added.

This is so because, in order to maintain electroneutrality of the membrane, only as many cations could enter the membrane phase as are the anionic sites provided by the anion excluder. By combining equations (1.2) and (1.5)

$$E_M = E_{const} + E_{PB}$$

$$E_{const} - \frac{\mu^o_{A(org)} - \mu^o_{A(aq)}}{Z_A F} - \frac{2.303RT}{Z_A F}\log a_{(org)} + \frac{2.303RT}{Z_A F}\log a_{A(aq)} \qquad (1.6)$$

Since $a_{A(org)}$ remains constant under the experimental conditions, it can be put together with all other sample-independent potential contributions, *i.e.* it could be included in a single term (E°). Thus, equation (1.6) is reduced to a well-known Nernst equation.

$$E_M = E^o + \frac{2.303RT}{Z_A F}\log a_{A(aq)} \qquad (1.7)$$

Thus, it is clear from equation (1.7) that the cell potential is directly proportional to the concentration or activity of the sample ions in aqueous solution under investigation. At 25°C, the value of 2.303 RT/ z_AF is 0.059/z_A volts. The membrane is said to exhibit

Nernstian response if the slope of a plot between cell potential and log activity comes out to be 0.059/z_A volts. These plots are then called Nernst plot and slope as Nernstian slope.

1.8. TERMS USED IN ISE

Before further discussion on the performance of ion-selective electrodes some of the terms used must be defined or explained. IUPAC compendium of nomenclature [321-323] is helpful in sorting out the terms.

1.8.1. Combination Electrode/ Cell Assembly

It is an electrochemical apparatus that incorporates an ion-selective electrode and a reference electrode in a single assembly, thereby avoiding the need for a separate reference electrode. This assembly is represented in Fig. 1.1.

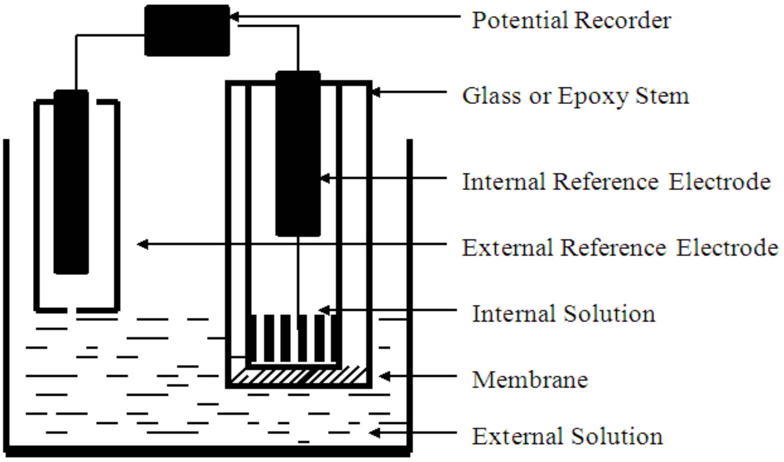


Fig. 1.1. Schematic representation of membrane electrode cell assembly

1.8.2. Calibration Graph

A calibration graph for an ion-selective electrode is defined as a plot of the potential difference between the ion-selective electrode and a reference electrode against the logarithm of the activity or concentration of the primary ion in the measurement cell. For a primary ion A, the logarithm of its activity or concentration is usually plotted along the abscissa of the graph and the cell potential is plotted along the ordinate. A calibration curve ordinarily has the shape shown in Fig. 1.2.

1.8.3. Limit of Detection

It may be defined as the lower activity of the target ion, A, at which the Nernstian plot of electrode potential against -log$_{10}$ a_A begins to depart from linearity. They fall into activity ranges where the electrode starts to loose sensitivity toward the primary ion.

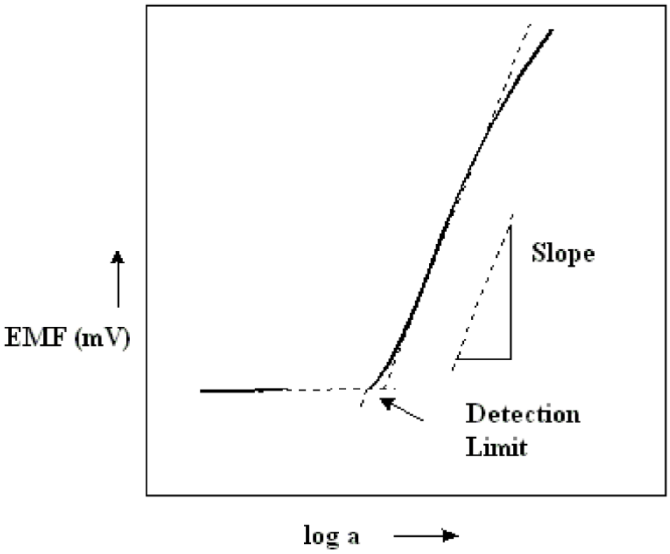


Fig. 1.2. Schematic representation of membrane electrode cell assembly

According to the IUPAC recommendation of 1976, the detection limit is defined by the cross-section of the two extrapolated linear parts of the calibration curves (Fig. 1.2). This Nernstian limit is the more important criterion of electrode performance as it specifies the lower limit of the most useful range of the electrode.

1.8.4. Measuring range/Linear Range/Working Concentration Range

The measuring range of ISE is defined as the activity ratio of upper and lower detection limit and approximately corresponds to the range where the electrode responds according to the Nernst equation. A maximum range will be achieved if the interfering ion is not complexed at all by the carrier. A typical linear range of the calibration curve of the ISE shown in Fig. 1.2 is considered to be its linear part between the two dashed lines.

1.8.5. Slope

Slope is defined as the gradient of the line formed by plotting the electrode response (E_M) in millivolts against the logarithm of the activity of the measured ion. Thus, according to Nernst equation (equation 1.8)

$$E_M = E^o + \frac{2.303RT}{Z_A F} \log a_{A(aq)} \tag{1.8}$$

Slope of the linear part of the calibration curve is 2.303 RT/ z_AF. This is a measure of the sensitivity of the electrode. If it is close to the Nernstian value of 59.1/z_k mV decade^{-1} activity (where, z_k is the charge of the ion) at 25^{o}C, then it points to the ideal electrode behavior. The theoretical values of the slope is 59.1 mV decade^{-1} activity at 298 K for monovalent ion, 29.5 mV decade^{-1} activity for divalent ion and 19.7 mV decade^{-1} activity for trivalent ion.

1.8.6. Response Time

The first Recommendations by IUPAC [324] defined the practical response time as “the length of time which elapses between the instant at which an ion-selective electrode and reference electrode are brought into contact with a sample solution and the first instant at which the potential of the cell becomes equal to its steady state value within ±1 mV”. In the ‘Recommendations for Publishing Manuscripts’ on Ion-Selective Electrodes issued shortly after, the response time was measured “as the first instant at which the potential of the cell has reached 90 % of the final value”. The corresponding symbol is t_{90}. However, a more recent version of recommendations with the same title reverted to t^* as the preferred expression of response speed. Finally, in 1994 recommendations for nomenclature of ion-selective electrodes [300] adopted a still different criterion.

According to it, the response time is the time elapses between the instant at which an ion-selective electrode and a reference electrode are brought into contact with a sample solution and the first instant at which emf/time slope ($\Delta E/\Delta t$) becomes equal to a limiting value on the basis of the experimental conditions and/or requirements concerning the accuracy.

The IUPAC recommendations outline two experimental procedures for measuring the response time. According to first method so called dipping method, the electrode is instantaneously immersed into a solution of known activity of the target ion; simultaneously the response time is recorded. The response time determined by this method is called as static response time. In second method response time is recorded by varying standard test solutions with different target ion concentrations. The measurement sequence is from lower to higher concentration [325]. To evaluate the reversibility of the electrodes, a similar procedure in the opposite direction can also be adopted.

1.8.7. Life Span of the Electrode/Electrode Life Time

The working life of an ISE can vary from a few days to a few months. After this time the slope and detection limit of the sensor get changed significantly. It will depend on factors such as the analysis technique used, the matrix of the samples analyzed, and the membrane composition. Loss of plasticizer, carrier, or ionic site from the polymeric film due to leaching into the sample is a primary reason for limited lifetime of the sensors. An important parameter to be considered during the active life of the electrode is how long the ISE can be used between calibrations without significant changes in the electrode parameters that will affect the accurate prediction of the target ion.

1.8.8. Drift

This is the slow, non-random change in the potential (emf) of an ion-selective electrode cell assembly with time, provided that the cell assembly is maintained in a solution of constant composition and temperature.

1.9. SELECTVITY OF ISE MEMBRANES

Selectivity is the most important characteristics of the ISE membrane, describing its specificity towards the primary ion in the presence of interfering ions.The ion for which the sensor is designed is called primary ion and all other ions are referred as interfering ions or foreign ions or secondary ions. In fact, no ISE responds exclusively to primary ion *i.e.*, specific to it, however, in practice it is more selective to primary ions than to interfering ions. This is a necessary parameter to determine as it indicates the commercial potential of any sensor. The degree of selectivity of the sensor for primary ions A, with respect to interfering ion B, is expressed in terms of potentiometric selectivity coefficient, $K_{A,B}^{Pot}$, which is defined by the semi empirical *Nicolsky-Eisenmann* equation

$$E = E^{o} \pm \frac{2.303RT}{z_A F} \log[a_A + \sum K_{A,B}^{Pot} a_B{}^{Z_A/Z_B}] \qquad (1.9)$$

Where z_A, z_B, a_A and a_B are the charges and activity of ions A and B, respectively. There are a number of different methods for the determination of potentiometric selectivity coefficient, among which three methods have been however, much more widely accepted [325, 326], which are namely:

- Separate Solution Method (SSM)

- Mixed Solution Method (MSM)
- Matched Potential Method (MPM)

1.9.1. Separate Solution Method (SSM)

In SSM method, the potential of the cell containing test solution of primary ion A of activity a_A is first determined. The curve is presented in Fig. 1.3. The emf of this cell E_A is related to the primary ion by the equation

$$E_A = E^0 + \frac{2.303RT}{z_A F} \log a_A \tag{1.10}$$

Next, the emf of a separate cell containing test solution of interfering ion B of activity a_B is determined. Its emf E_B is related to activity a_B by the equation

$$E_B = E^0 + \frac{2.303RT}{z_A F} \log \mathrm{K}_{A,B}^{Pot} (a_B)^{z_A/z_B} \tag{1.11}$$

From equations (1.10) and (1.11)   values are then calculated as:

$$\log K_{A,B}^{Pot} = \frac{z_A F(E_B - E_A)}{2.303\,RT} + \log\left(\frac{a_A}{a_B^{z_A/z_B}}\right) \tag{1.12}$$

The term 2.303 RT/z_AF is the slope of the Nernst plot. The separate solution method, although simple to perform, is not normally used for the determination of $K_{A,B}^{Pot}$ values, because it does not represent the actual conditions under which the sensors are used. This method is recommended only if the electrode exhibits a Nernstian response.

1.9.2. Mixed Solution Method (MSM)

This method involves measurement of the sensor potential in a range of solutions containing both A and B. Since in real conditions, analyte ion (primary ion) is present together with many other foreign ions (interfering ions). Thus, this method is preferred over separate solution method. There are two procedures for determining selectivity coefficient using MSM.

- Procedure I (Fixed Primary Method)

In this method, the potential of the cell containing test solution of primary ion A of activity a_A is first determined. The emf of this cell E_A is related to the primary ion by the equation (1.10). Then, the potential of the cell containing mixed solution of primary ion of activity a_A and interfering ion of activity a_B is determined. The emf of this cell E_{AB} is given by equation

$$E = E^\circ + \frac{2.303RT}{z_A F} \log \left[a_A + \mathrm{K}^{Pot}_{A,B} (a_B)^{z_A/z_B} \right] \tag{1.13}$$

From equations (1.10) and (1.13)

$$\mathrm{K}^{Pot}_{A,B} = \frac{a_A}{(a_B)^{z_A/z_B}} \left[\left(\frac{E_{A,B} - E_A}{10^{2.303RT/z_A F}} \right) - 1 \right] \tag{1.14}$$

Thus, knowing E_A and $E_{A,B}$ selectivity coefficient values can be calculated.

- Procedure II (Fixed Interference Method)

In this procedure, the potential of the cell is measured for a number of solutions containing interfering ion of constant activity a_B but varying values of activity of primary ion a_A. The plot of potential so obtained against activity a_A is shown in Fig. 1.4. This plot generally has three distinct regions. In the first region PQ, the linear response of the sensor indicates that it is responding only to primary ion, A, with no interference caused by B in this concentration range. In the second region QR, deviation from linearity is caused because now the sensor is also responding to the activity of B as the concentration of A decreases.

So in this region (QR), the response of the sensor is mixed and is due to both the ions A and B. The third region RS of the plot is linear and the potential is constant. Constancy in the potential indicates that the sensor is now only responding to interfering ion B with no contribution arising due to primary ion, A. This generally occurs at lower activity of A. As the activity of B is constant and A is not affecting the potential in this concentration range, the potential of the sensor remains constant. The linear portion PQ and RS are then extrapolated to point T. The potential corresponding to point T can be generated by constant activity of B or by the activity of A corresponding to point T. Thus, for point T, E_A is equal to E_B (E_A is generated by A of activity a_A and E_B by B of activity a_B). Under this condition of $E_A = E_B$, the $K_{A,B}$ can be calculated by the following equation

$$K^{Pot}_{A,B} = \frac{(a_A)}{(a_B)^{Z_A/Z_B}} \tag{1.15}$$

This procedure of mixed solution method is known as Fixed Interference Method (FIM) and is the most widely used procedure as per IUPAC recommendation for determining selectivity coefficient [327]. The reason behind this that the conditions prevailing at the membrane and solution interface in this method are similar to the one, which are prevalent while analyzing the sample.

1.9.3. Matched Potential Method (MPM)

The Matched Potential Method (MPM), which is independent of the Nickolsky-Eisenmann equation, was proposed by Gadzekpo and Christian [328] to overcome the difficulties for obtaining accurate selectivity coefficient when ions of unequal charge are involved. In this method, the selectivity coefficient $\mathrm{K}_{A,B}^{Pot}$ is given by the expression

$$\mathrm{K}_{A,B}^{Pot} = \frac{a'_A - a_A}{a_B} = \frac{\Delta a_A}{a_B} \qquad (1.16)$$

and is determined by measuring the change in potential upon increasing by a definite amount the primary ion activity from an initial value of a_A to a'_A and a_B represents the activity of interfering ion added to same reference solution of activity a_A which brings about same potential change. The curve is presented in Figure 2.5. This method provides practically realistic values of $K_{A,B}^{Pot}$. The characteristics of MPM are that the charge number on primary and interfering ions is not taken into consideration and Nernstian responses are assumed neither to the primary nor interfering ions. These characteristics lead to the following advantages: (i) the power term problem for ions of unequal charge disappears, and (ii) the method is applicable even to non-Nernstian interfering ions. However, as this method is independent of the Nicolsky-Eisenmann equation or its modified forms, and it is therefore difficult to correlate the values of $K_{A,B}^{Pot}$ obtained by this method with any particular phenomena such as ion exchange [329].

1.9.4. Significance of Selectivity Coefficient

The selectivity of a sensor depends on the selectivity coefficient values defined in terms of Nicolsky equation (equation 1.9). Ideally, it should be a constant value and called selectivity constant but it depends on the experimental conditions, usually the concentration of ions and the method of determination. It is for this reason $\mathrm{K}_{A,B}^{Pot}$ is not called selectivity constant but selectivity coefficient. The values of selectivity coefficient are higher if determined at higher concentration of interfering ions and vice-versa. Different methods give different values of selectivity coefficient, as the conditions prevailing at the membrane-solution interface are not same [330, 331]. It is apparent from equation (1.9) that a value of $K_{A,B}^{Pot}$ = 1 at $z_A = z_B$ indicates equal response to both A and B. Similarly, the value of $K_{A,B}^{Pot} < 1$ indicates that the electrode responds more to A in comparison to B *i.e.*, the electrode is selective to A over B. Smaller is the value of selectivity coefficient better is the selectivity. On the other hand $K_{A,B}^{Pot} > 1$ indicates that the electrode's response is more towards B rather than A and in such a case it is said that the ion B causes considerable interference. When the charges $z_A \neq z_B$, the values of selectivity coefficient $K_{A,B}^{Pot} \cong 1$ does not indicate equal response to primary and interfering ions as per equation (1.9), but now it depends on the values of z_A and z_B. In order to make it easy to appreciate the relative selectivity of the sensor when large number of ions of different charges are involved, it would be better to have only a single value $K_{A,B}^{Pot}$ that indicates equal response to A and B irrespective of their charges. Viteri and Diamond [332] have proposed a modification in the Nicolsky equation; they neglected the power term in the equation (1.9) while calculating the selectivity coefficient.

The modified form of equation (1.13) is

$$K_{A,B}^{Pot} = \frac{a_A}{a_B} \qquad (1.17)$$

In the present study, the selectivity coefficient values have been determined using the FIM and the MPM using equations (1.15) and (1.16), respectively.

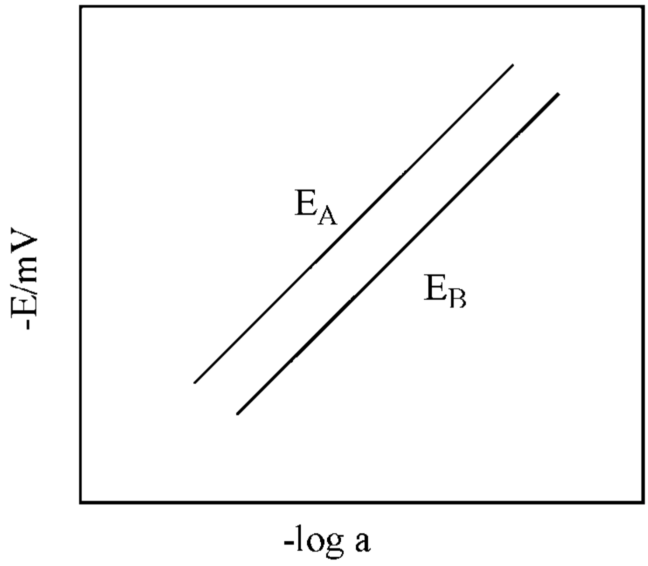


Fig. 1.3. Potential *vs*. log a_A plot illustrating the determination of selectivity-coefficient by Separate solution method (activity of B = a_B).

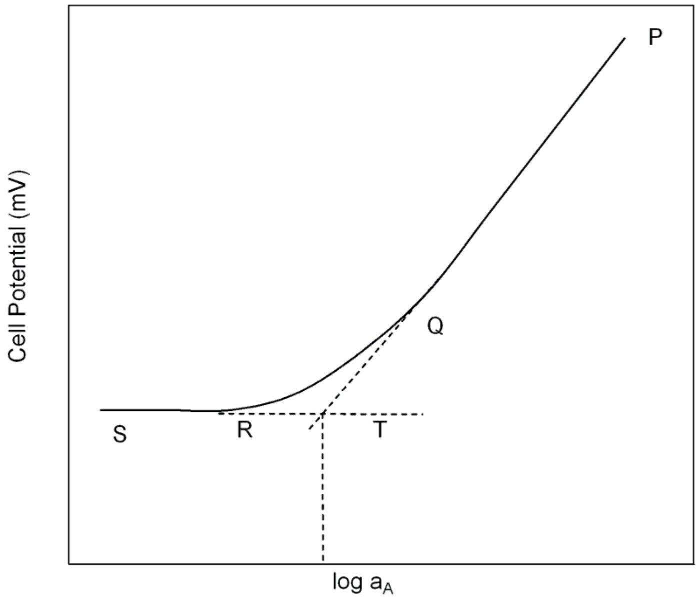


Fig. 1.4. **Schematic Potential vs. log a_A plot illustrating the determination of selectivity coefficient by fixed interference method.**

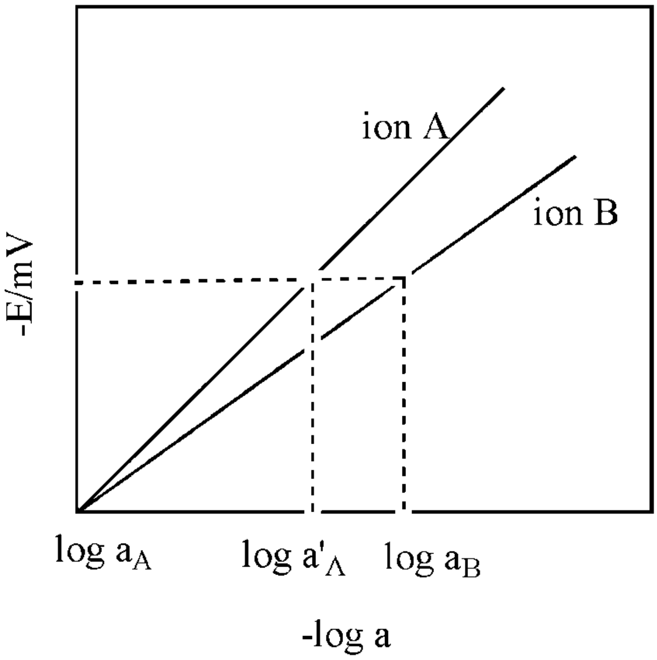


Fig. 1.5. **Potential *vs*. log a_A plot illustrating the determination of selectivity coefficient by Matched potential method (activity of B = a_B).**

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Chapter 2

"Membranes of Macrocyclic Chelating ligand as Cd^{2+} Ion-Selective Sensors"

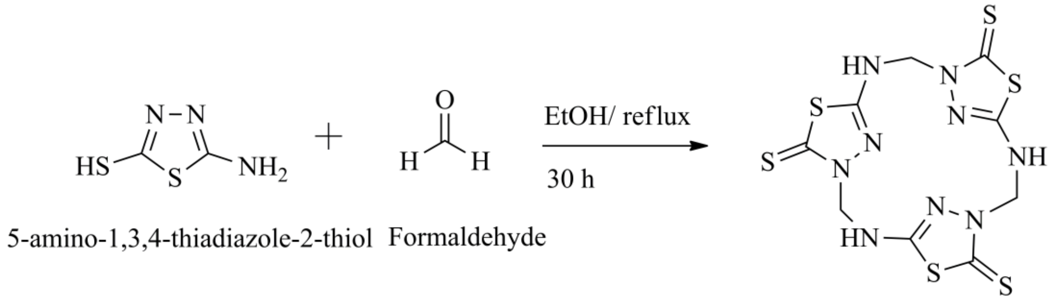
2.1. INTRODUCTION

The manifestation of cadmium in the environment is epidemic as it is being exploited for many industrial and agricultural intendments like metal plating, cadmium-nickel batteries, mining, stabilizers, alloys and phosphate fertilizers [1], which are few of the major sources of cadmium discharge in natural water and thereby aggravates the level of cadmium. The presence of cadmium as an impurity in the zinc of galvanized pipes or cadmium synoptic solders in fittings, water heaters and water coolers are of the principle causes of cadmium adulteration in drinking water. The admissible level of cadmium concentration in waste water and drinking water is 0.10 and 0.05 ppm, respectively [2]. The environmental examinations of cadmium are mainly concerned with its deleterious effect. Cadmium(II) is one of the 13 toxic metal species in the priority pollutant list of the Environmental Protection Agency [3(a),(b)] and is one of the sixth substances banned by the European Union's Restriction on Hazardous Substances directive [4]. Cadmium shows its toxicity by inhibiting the respiration for a-oxoglutarate and pyruvate [5] and by causing kidney problems, anemia and bone-marrow disorders [6]. Further, cadmium has been demonstrated to be a human carcinogen [7] and its exposure is attributed to renal dysfunction and calcium metabolic disorders [8]. The provisional tolerable weekly input for cadmium recommended by the World Health Organization-Food and Agriculture Organization, joint expert committee on food additives is 0.4-5.0 mg based on a tolerable intake of 1 mg kg^{-1} of body weight per day [9]. Thus in view of its hazardous effect on living species, there is a need to control the cadmium in the environment.

Numerous analytical methods have been reported for the monitoring of Cd^{2+} ion, such as, atomic fluorescence spectrometry (AFS) [10], electrothermal atomic absorption spectrometry (ETAAS) [11,12], flame atomic absorption spectrometry (FAAS) [13-15], the detection of radiolabel isotopes [16], electrochemical techniques[17], instrumental neutron activation analysis [18], inductively coupled plasma mass spectrometry (ICP-MS) [19] and diffusive gradient in thin films (DGT) [20]. However, these techniques have been employed successfully in the monitoring of cadmium but are not very convenient for the analysis of a large number of environmental samples as they demand of expertise, tedious sample preparation, time consuming and require good infrastructure. Therefore, there is a need to develop a method which involves simple instrumentation, cheap and should show fast response with minimum chemical manipulation. These specifications are generally met with ion selective electrodes (ISEs) which have proved its application in the determination of various species in a variety of samples. Potentiometric based ISEs exhibits superiority over other techniques in terms of selectivity, sensitivity, quick response and moreover, also suitable for online monitoring.

2.1.1. Cd^{2+} ion-selective electrodes

The literature survey reveal that varieties of neutral ion carriers have been used in the construction of Cd^{2+} ion selective electrodes [21-25]. Various types of electrodes have been applied for determination of different analytes. The solid contact electrodes have considerable advantages over conventional ones, such as their small size, lower cost of production and the ability to operate in high pressure [26-32]. Crown ether based polymeric memberaneelectrodes have proved to be an excellent choice due to their binding strength and selectivity [33-39]. The poly(4-vinyl pyridine) (P4VP) modified graphite pencil rod (GPR), especially of 2B pencil as ISE have become popular nowadays [40-43]. Carbon paste electrodes (CPEs) have attracted our attention due to their low ohmic resistance, renewability, no need for internal solution and stable response [44]. Ortuno J.A. *et al.*, have determined Cd^{2+}ion based on a flow-through bulk optode [45]. But the reported ISEs have suffered from narrow working concentration range, low pH range, substantial interferences from a variety of cations and high response time.



5,11,17-trithia-1,3,7,9,13,15,19,20,21-nonaazatetracyclo[$14.2.1.1^{4,7}.1^{10,13}$]henicosa-4(20),10(21),16(19)-triene-6,12,18-trithione (L_1)

Fig. 2.1. Synthesis of 5,11,17-trithia-1,3,7,9,13,15,19,20,21-nonaazatetracyclo-[$14.2.1.1^{4,7}.1^{10,13}$]henicosa-4(20),10(21),16(19)-triene-6,12,18-trithione (L_1).

Therefore, it is required to develop a better sensor for Cd^{2+} ions. Efforts have been made on the development of better sensor by the application of macrocyclicionophore as they provide suitable cavity size for binding with metal ions. Macrocycle exhibits better host-guest relationship as they function on the basis of chemical recognition principle and thereby, they help to translate the chemistry of new substrate binding systems. We have focused our attention in synthesisingmacrocyclic compounds and hence, their application as ISEs [46, 47]. Many macrocyclic compounds possessing heterocyclic constituents show unique chemical and biological properties with the potential for new drug discovery [48]. Cho *et al.*, in 2009 reported macrocyclic compounds containing two 5-mercapto-3*H*-1,3,4-thiadiazolin-2-one groups [49]. Incorporation of thiadiazole moieties in the macrocycle has showed potential biological and analytical interest [50]. Pappalardo*et al.* have reported the synthesis of macrocycle by the reaction of 2,5-dimercapto-1,3,4-thiadiazoles with 1,ω-dibromoalkanes [51]. The macrocycle reported by Pappalardo constitutes of three nitrogen (N) donating sites at its center and a tetradentate binding site with three N and one sulphur (S) at its periphery. We thought to produce the similar macrocycle with all the donating sites of N in order to make this ionophore suitable for binding with hard cations.

This is a novel and convenient strategy to synthesize the macrocycle (5,11,17-trithia-1,3,7,9,13,15,19,20,21-nonaazatetracyclo[14.2.1.1^{4,7}.1^{10,13}]henicosa-4(20),10(21),16(19)-triene-6,- 12,18-trithione (L_1)) and its application as Cd^{2+}selective sensors.

2.2. EXPERIMENTAL

2.2.1. Chemical and Reagents

Reagent grade sodium tetraphenylborate (NaTPB), dibutylphthalate (DBP), benzylacetate (BA), high molecular weight poly(vinyl chloride) (PVC) and THF were purchase from E. Merck (Mumbai, MH, India). Potassium tetrakis-p-(chlorophenyl) borate (KTpClPB) and *o*-nitrophenyloctylether (*o*-NPOE) were procured from Fluka and Sigma-Aldrich, respectively. Dioctylphthalate (DOP) and 1-chloronaphthlene (1-CN) was procured from Acros Organics and SD Fine-Chem Ltd., respectively. 5-Amino-1,3,4-thiadiazol-2-thiol was purchase from Sigma-Aldrich and formaldehyde were procured from Hi-Media. All of these chemicals and reagents were used as received. The nitrate and chloride salts of all the cations and solvents (methanol, ethanol, dimethylformamide (DMF) and acetonitrile) used were of analytical reagent grade and used without any further purification. Double distilled water was used throughout the experiment.

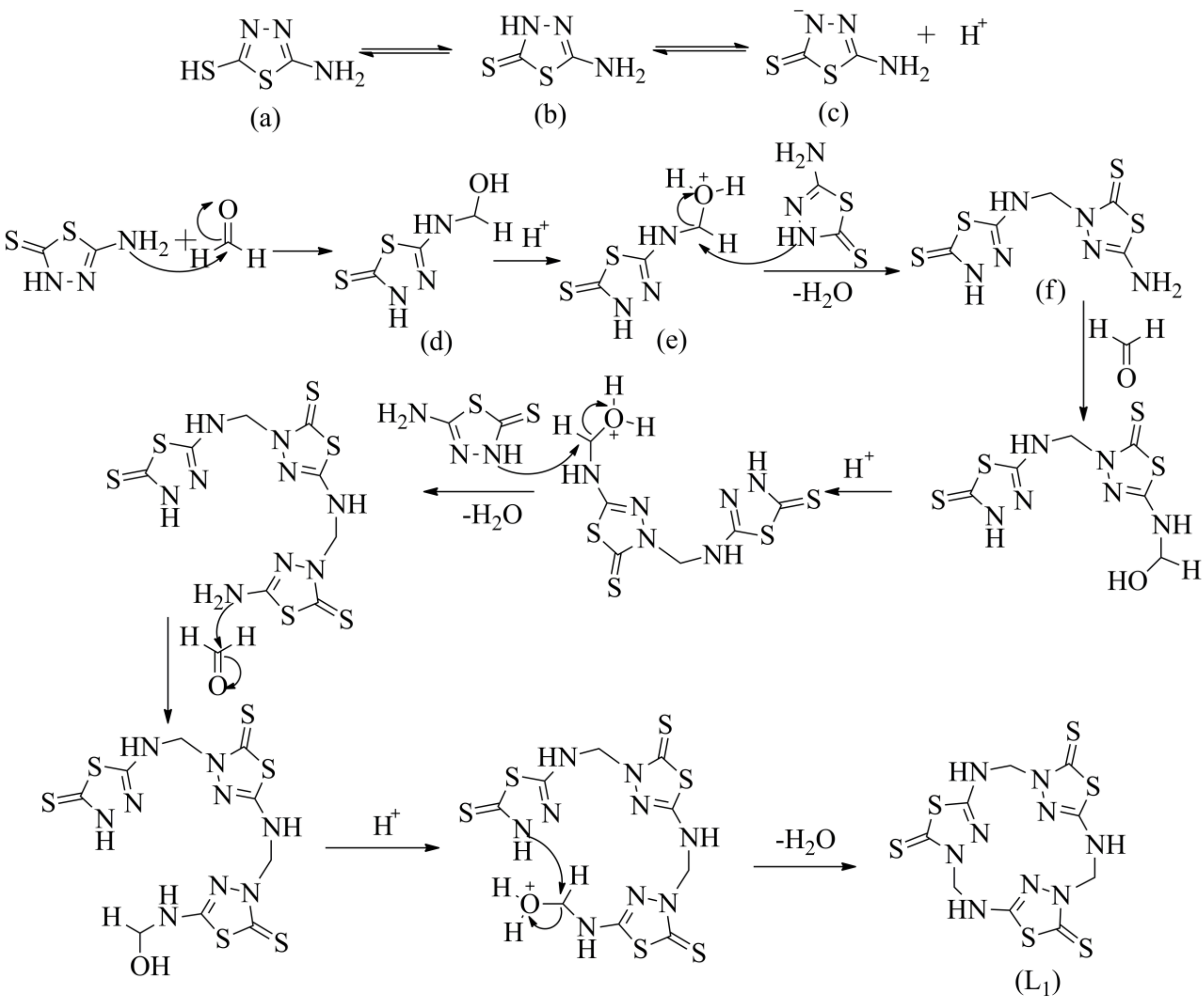


Fig. 2.2. **Mechanism of synthesis of L_1.**

2.2.2. Synthesis of macrocycle 5,11,17-trithia-1,3,7,9,13,15,19,20,21-nonaazatetracyclo[14.2.1.$1^{4,7}$.$1^{10,13}$]henicosa-4(20),10(21),16(19)-triene-6,12,18-trithione (L_1)

5-amino-1,3,4-thiadiazol-2-thiol with formaldehyde as shown in Fig. 2.1. 5-amino-1,3,4-thiadiazol-2-thiol (3 mM, 400 mg) was dissolved in 25 mL of ethanol by refluxing for half an hour and cooled it to room temperature. A solution of 37% formaldehyde (1.5 mM, 0.11 mL) dissolved in 5 mL of ethanol was added drop-wise to the previous solution with constant stirring and then this mixture was refluxed for 30 h. The precipitate that formed was filtered off and dried in air. A white powder obtained was then crystallized in DMSO solution by keeping it for 1 month asides. Fine suitable crystals were grown for single crystal XRD analysis.

Table 2.1. Crystal data and structure refinement parameters for L_1.

Chemical formula	$C_{15}H_{21}N_9O_3S_9$
Formula weight	664.04
Temperature	296 K
Wavelength	0.71070 Å
Crystal system	Monoclinic
Space group	*P 21/c*
Unit cell dimensions	a = 11.6822(12) Å, α = 90.0^o
	b = 26.736(3) Å, β = 101.285(5)^o
	c = 9.6727(9) Å, γ = 90.0^o
Volume	V = 2962.7(5) Å^3
Z, calculated density	4, 1.489 g cm^{-3}
Mu (Mo-Kα)	0.708 mm^{-1}
Theta (max)	26.390^o
Reflections measured	3763
R_1	0.0488
Goodness of fit	1.187

(5,11,17-trithia-1,3,7,9,13,15,19,20,21-nonaazatetracyclo[14.2.1.1.^{4,7}.1^{10,13}]henicosa-4(20),10(21),16(19)-triene-6,12,18-trithione (L_1)): yield: 34% analytically calculated for [$C_9H_9N_9S_6$] (%): C, 24.81; H, 2.08; N, 28.94; S, 44.16. Found: C, 24.76; H, 2.12; N, 28.81; S, 44.30. IR (KBr, cm^{-1}): 3247 (-NH), 1571 (-C=N), 1508, 1401, 1352, 1254, 1212, (Ar-). ^{1}H NMR (DMSO 500 MHz) δ (ppm):8.727-8.755 (3H, t, *J* =14 Hz, -NH), 5.417-5.431 (6H, d, *J* =7 Hz, -CH_2). ^{13}C NMR (DMSO 125 MHz) δ (ppm): 180.99 (-C=S), 154.79 (-C=N), 56.68 (-CH_2) (see appendix for spectra).

2.2.3. Single Crystal XRD

Single crystal suitable for X-ray diffraction of L_1 was grown in DMSO. The suitable single crystal were carefully chosen and its X-ray data collection were performed on a Bruker Kappa Apex four circle-CCD diffractometer using graphite monochromatedMoK radiation (λ= 0.71070 Å) at 296 K. In the reduction of data Lorentz and polarization corrections, empirical absorption corrections were applied [52]. Crystal structures were solved by direct method. Structure solution, refinement and data output were carried out with the SHELXTL program [53, 54]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions using a riding model. Images and hydrogen bonding interactions were created in the crystal lattice with diamond and mercury software [55, 56]. Crystal data and structure refinement parameters for L_1 are shown in Table 2.1.

Table 2.2. Selected hydrogen bonded parameters for L_1 (in Å).

D-H···A	d (D-H)	d (H-A)	d (D-A)	<(DHA)>	Symmetry code
N1-H1···O1	0.859(3)	2.020(3)	2.882(5)	155.0	-x+2, -y, -z+1
N7-H7···O2	0.861(3)	1.975(5)	2.762(6)	151.4	x, +y, +z-1
N4-H4···O3	0.860(3)	2.018(5)	2.810(6)	152.7	x+1, +y, +z

Crystallographic data for the macrocycle structure reported here have been deposited with the Cambridge Crystallographic Data Centre (deposition no. CCDC-963340). The data can be obtained free of charge via www.ccdc.cam.ac.uk/deposit or on application to the CCDC, 12 Union Road, Cambridge CB2 lEZ, U.K. (fax:+441223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

2.3. FABRICATION OF PVC MEMBRANES

2.3.1. Electrode Preparation

The membrane has been fabricated as suggested by Cragg [57]. Polymeric membrane based on high molecular weight PVC was prepared by dissolving appropriate amounts of membrane ingredients (ionophore (L_1), anion additives, PVC and plasticizers) in minimum amount of THF. Homogeneous mixture was obtained after complete dissolution of all the components and solvent was evaporated to obtain a concentrated solution. It was then poured into polyacrylate rings, which were placed on a smooth glass plates and THF was allowed to evaporate slowly at room temperature. The membrane, thus obtained, was detached from the glass plate and cut to suitable size and glued to one end of a ‘Pyrex’ glass tube with Araldite. It is known that the sensitivity, selectivity and linearity obtained for a given ionophore depends significantly on the membrane composition, time of contact and nature of plasticizer used.Thus, the ratio of membrane ingredients, time of contact and concentration of equilibrating membranes were optimized after a good deal of experimentation.

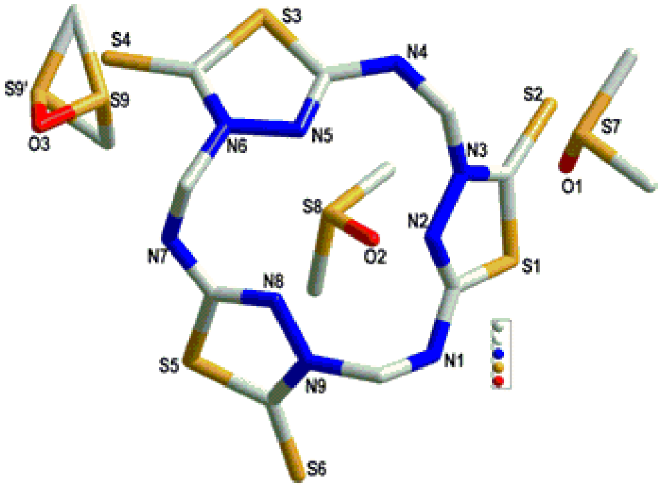


Fig. 2.3. **Crystal structure of L_1 (Colour code: C (Grey), O (Red), N (blue), S (yellow) and H (white).**

2.3.2. Preparation of Coated Pyrolytic Graphite Electrodes and Coated Graphite Electrodes

The concentrated solution of membrane ingredients were obtained as described above. Pyrolytic graphite electrode/graphite electrode of spectroscopic grade (6 mm long, 3 mm diameter) with copper wire glued at one end was dipped into the solution for few seconds and removed out and allowed the electrode to get dry. The process was repeated several times till homogeneous thickness of membrane was formed over pyrolytic graphite electrode/graphite electrode. Then it was glued (Araldite) to Pyrex glass keeping working area exposed.

2.3.3. Conditioning of Membrane and Potential Measurements

The PME were equilibrated for 3 days, while CGE and CPGE were conditioned for 1 day prior to potentiometric measurements in 1.0×10^{-1} mol L^{-1} and 1.0×10^{-3} mol L^{-1} $Cd(NO_3)_2$ solutions, respectively. The potential have been quantified by altering the concentration of $Cd(NO_3)_2$ solution in the range 1.0×10^{-1} to 1.0×10^{-9} mol L^{-1}. The standard solution had been obtained by gradual dilution of 1.0×10^{-1}mol L^{-1} $Cd(NO_3)_2$ solution. The potential measurements with the PME, CGE and CPGE were determined on a pH meter (Orion 4) at 25±0.1°C in which the reference electrode is Ag/AgCl (NaCl 3 mol L^{-1}) BASI 2056 with the following cell assemblies:

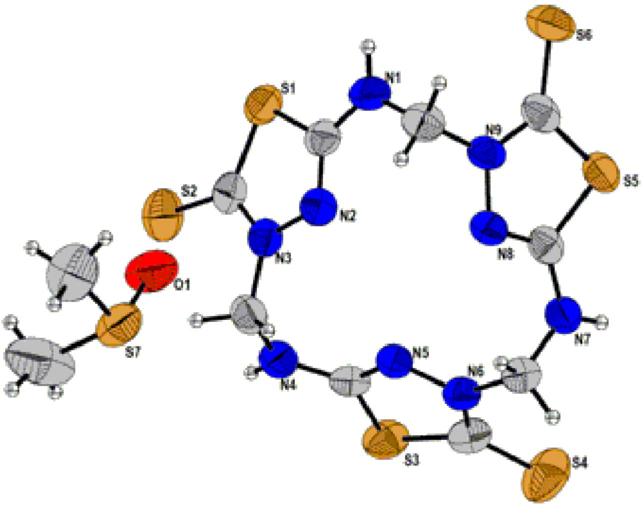


Fig. 2.4. **The ORTEP plot of L_1 is shown with 50% probability level.**

Ag/AgCl|NaCl (3 mol L^{-1})|internal solution (1.0×10^{-1} mol L^{-1} $Cd(NO_3)_2$)||PVC membrane||sample solution|Ag/AgCl, NaCl (3 mol L^{-1}).

CGE||Test solution||Ag/AgCl|NaCl (3 mol L^{-1}).

CPGE||Test solution||Ag/AgCl|NaCl (3 mol L^{-1}).

Activity coefficient was calculated according to Debye Huckel Procedure [58].

2.4. RESULTS AND DISCUSSION

2.4.1. Macrocyclic Scaffold and its Formation

A novel macrocyclicionophore was synthesised by 2:1 condensation reaction of 5-amino-1,3,4-thiadiazol-2-thiol with formaldehyde. The mechanism for L_1 formation is shown in Fig. 2.2. 5-Amino1,3,4-thiadiazol-2-thiol (a) is at equilibrium with its tautomeric form (b) which can get deprotonated and stay at equilibrium with its conjugate base (c) availing free protons in the solution.

We propose that reaction is triggered by the attack of amine on the formaldehyde to form the aminol (d) which can undergo protonation to form an intermediate cation (e). Subsequent attack of 1 on 5 can lead to release one equivalent of water and forming compound (f). Then, f, can be converted to the L_1 by following two rounds of reactions each consisting of attack on formaldehyde followed by protonation and then, dehydration.

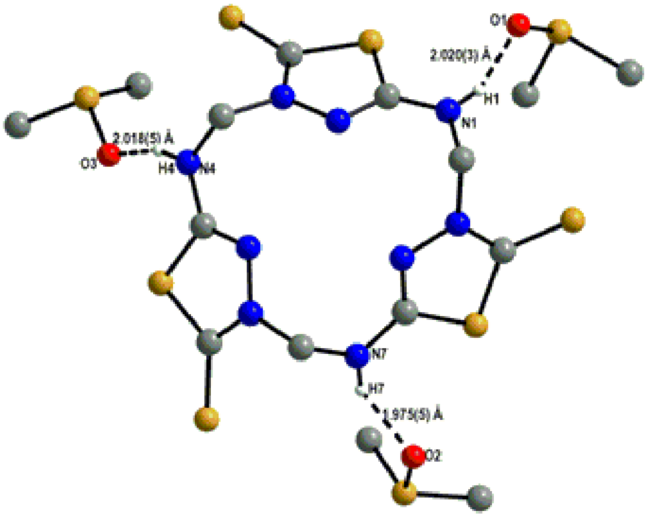


Fig. 2.5. **Intermolecular non-covalent interaction in L_1.**

2.4.2. Crystal Description of L_1

Single-crystal X-ray diffraction analysis revealed that L_1 is crystallized in to monoclinic space group *P21/c*. The asymmetric unit contains one cyclic molecule and three molecules of DMSO as shown in Fig. 2.3 and Fig. 2.4 represents the ORTEP plot of L_1 at 50% probability level. It was found that sulphur atom of one of the three DMSO is disordered and it was refined by giving PART instruction in 0.73232:0.26768 ratios.

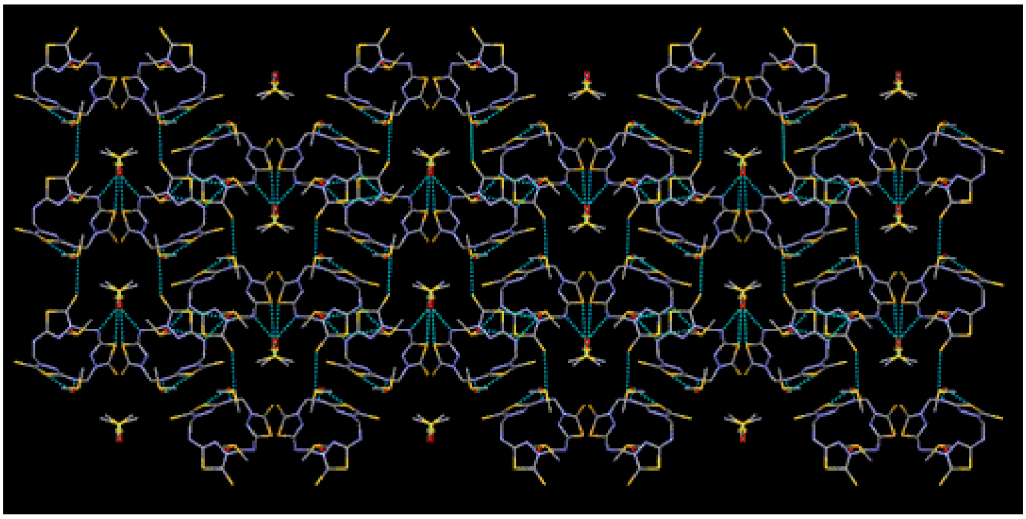


Fig. 2.6. **3-Dimensional packing of L_1 showing 1D channel along *c*-axis lining up the solvent molecules in it.**

Crystal packing shows that the organic cyclic molecule is stabilized by intermolecular non-covalent hydrogen bonding with the solvent molecule *via* N1-H1A--O1, 2.020(3) Å; N7-H7---O2, 1.975(5), N4-H4---O3, 2.018(5) see Fig. 2.5. The selected hydrogen bonded parameters for L_1 are shown in Table 2.2. Fig. 2.6 represents the 3-dimensional packing of L_1 showing 1D channel along *c*-axis lining up the solvent molecules in it.

2.4.3. Complexation Study

In order to know the affinity of L_1 toward heavier metal ions, conductometric titrations were carried out. The complexations of L_1 with a number of cations have been investigated conductometrically in DMF solution at 25±0.1°C. 25 mL of 1.0×10^{-4} mol L^{-1} cation solution was titrated against a 1.0×10^{-2} mol L^{-1} ionophore solution in DMF. The conductance of the solution was measured after each addition of L_1 and graph was drawn for various metal ions as a function of the $[L_1]/[M^{n+}]$ molar ratio (Fig. 2.7). It has been observed from Fig. 2.7 that, conductance variation of Cd^{2+} ion solution showed immense variation with the addition of L_1. Initially, the conductance falling off with the addition of L_1 which shows that Cd^{2+}ions are strongly interacting with the L_1 added and thus causes formingof Cd-L_1complex.

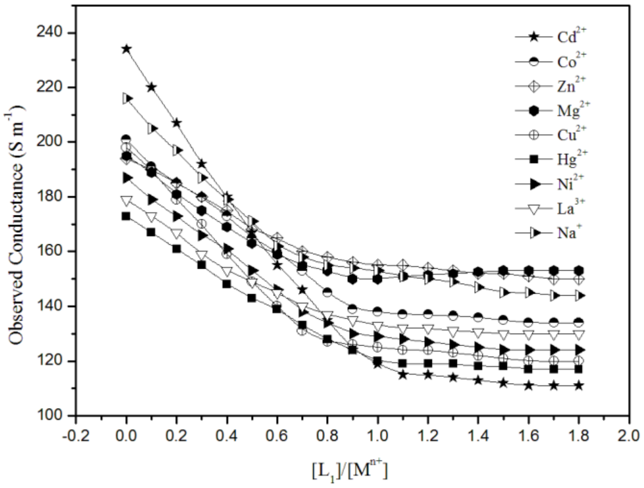


Fig. 2.7. Variation in the conductance of Cd^{2+} ion solution with the addition of L_1.

A stage is arrived when conductance of solutions nearly becomes constant and further addition of L_1 does not cause any appreciable change in the conductance which demonstrates that all of the metal ions have been consumed by the L_1 in forming complex.

The break in the conductance variation plot shows the stoichiometry of the resulting complex and from Fig. 2.7, it has been observed that the stoichiometry of metal to L_1 is 1:1.

2.4.4. Membrane Composition's Optimization and Potential Measurements

It is well known that membrane composition and ingredients broadly affect the selectivity and sensitivity of a given ionophore and also account the linearity in response of the sensor. Therefore, in the fabrication of polymeric membranes, a number of electrodes having different composition were prepared and studied. The potential of various electrodes were measured as a function of Cd^{2+} ion concentration in the range of 1.0×10^{-1}-1.0×10^{-9} mol L^{-1}. The potential responses of PME, CGE and CPGE were first investigated only with L_1 and PVC. The sensor of membrane of L_1 without plasticizer shows linear response over a linear range of 1.73×10^{-5} to 1.0×10^{-1} mol L^{-1} with a slope 26.4 mV decade^{-1} of activity. It is well known that the incorporation of plasticizer in the membrane phase enhances the performance characteristics of electrodes [59]. Thus, the electrodes were fabricated (Fig. 2.8) by the addition of various plasticizers (*viz.*, *o*-NPOE, BA, 1-CN, DBP and DOP) and the responses obtained with plasticized membranes were studied.

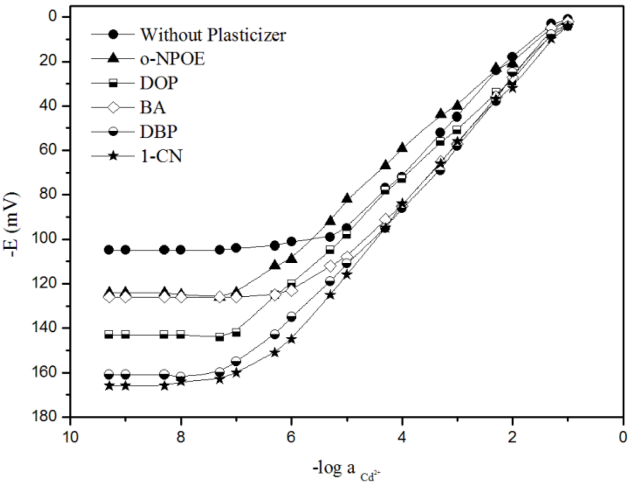


Fig. 2.8. Potentiometric characteristic graphs show the linearity of membrane potential as a function of Cd^{2+} ion concentration with different plasticizers.

Comparing the responses of plasticized and non-plasticized membranes, it has been observed that, membranes which were non-plasticized shows weak responses, linear and near-Nearnstian slope relative to plasticized membrane, which was found to be good in respect of its potentiometric characteristics. Plasticized membrane, thus shows, improved responses, linear and near Nernstian slope. The nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of ionophore molecules and the state of ionophore [60-62] and thus, it is expected to play an important role in determining the ion selective characteristics. Among all the membrane prepared so far, CPGE membrane having composition of L_1: PVC: 1-CN: NaTPB in the ratio of 7:37:54:2 (w/w; mg) performs best in all aspects of its potentiometriccharacteristics, and thus, further studies were performed with thesame.

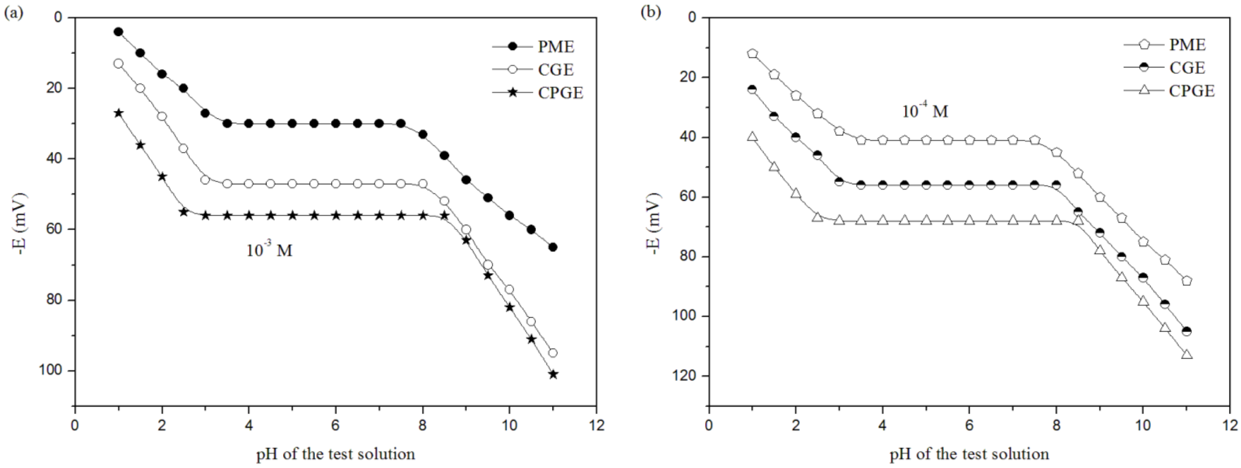


Fig. 2.9. **Effect of pH of the test solutions on the potential responses of the PME, CGE and CPGE with (a) 1.0×10^{-3} mol L^{-1} and (b) 1.0×10^{-4} mol L^{-1} Cd^{2+} ion solutions at different pH.**

2.4.5. Effect of pH on the Performance of Sensor

The effect of pH on the performance of the fabricated electrodes were examined by measuring their potentiometric responses for 1.0×10^{-3} mol L^{-1} and 1.0×10^{-4} mol L^{-1} solution of Cd^{2+} ion at different pH values ranging from 1.0 to 12.0. The pH was adjusted by the addition of 1.0×10^{-1} mol L^{-1}HCl/NaOH and the results are shown in Fig. 2.9. It is revealed from Fig. 2.9, that potential response for PME remains independent of pH over pH range 3.5-7.5, 3.0-8.0 for CGE and 2.5-8.5 for CPGE. Therefore, the same was regarded as the working range for these electrodes. The change in potential at higher pH may be attributed to the formation of metal hydroxides species in the matrix [63] and the deviation at low pH may be regarded as the effect of protonation of ionophore [64] and the electrodes start responding to H_3O^+ ions along with Cd^{2+} ion leading to an increase in potential.

2.4.6. Effect of Interfering Ions on the Performance of Sensor

The most important parameter which reflects the applicability of an ISE is its selectivity, which is measured in terms of selectivity coefficient. The potentiometric selectivity coefficient for CGE and CPGE based on L_1 were determined according to IUPAC recommended fixed interference method (FIM).

Table 2.3. Selectivity coefficient of Cd^{2+} ion sensor based on L_1 using CGE and CPGE.

Interfering ions	Selectivity coefficient ($K^{FIM}_{Cd^{2+},B}$)	
	CGE	CPGE
Ni^{2+}	4.87×10^{-3}	3.68×10^{-3}
Zn^{2+}	5.24×10^{-4}	2.53×10^{-4}
Co^{2+}	8.16×10^{-3}	5.27×10^{-3}
Cu^{2+}	9.25×10^{-3}	6.49×10^{-3}
Hg^{2+}	6.45×10^{-2}	5.75×10^{-2}
Mn^{2+}	5.91×10^{-3}	4.68×10^{-3}
Mg^{2+}	3.78×10^{-3}	1.92×10^{-3}
Ca^{2+}	2.63×10^{-3}	1.06×10^{-3}
Na^{+}	3.49×10^{-4}	1.85×10^{-4}
La^{3+}	4.37×10^{-3}	2.41×10^{-3}
Ce^{3+}	2.96×10^{-3}	1.57×10^{-3}

In this method, the selectivity coefficient was evaluated from the potential measurement on solutions containing a fixed concentration of interfering ion (1.0×10^{-2} mol L^{-1}) and varying amount of Cd^{2+} ion solution ranging from 1.0×10^{-1}-1.0×10^{-9} mol L^{-1}. The potentiometric selectivity coefficient was then determined using the following expression [65]:

$$K^{Pot}_{A,B} = \frac{(a_A)}{(a_B)^{Z_A/Z_B}} \qquad (1)$$

Where, a_A is the activity of primary ion A (Cd^{2+} ion) at the lower detection limit in the presence of interfering ion B, a_B, the activity of interfering ion B and z_A and z_B are their respective charges. The values of selectivity coefficient so obtained for CGE and CPGE are compiled in Table 2.3. From the selectivity coefficient given in Table 2.3, it has been observed that the electrodes are highly selective over a number of monovalent, divalent and trivalent cations.

Table 2.4. Determination of concentration (mol L^{-1}) of interfering ions in medicinal plant samples.

Sample	Interfering ions	ISE[a]±SD	AAS[a]±SD
Ocimum Sanctum (Tulsi)	Ca^{2+}	$(1.2±0.2)×10^{-3}$	$(1.3±0.3)×10^{-3}$
	Mg^{2+}	$(8.0±1.0)×10^{-4}$	$(8.2±1.1)×10^{-4}$
WithaniaSomnifera (Ashwagandha)	Ca^{2+}	$(1.6±0.2)×10^{-3}$	$(1.7±0.2)×10^{-3}$
	Mg^{2+}	$(1.0±0.4)×10^{-3}$	$(1.0±0.2)×10^{-3}$

[a]Mean value ± standard deviation (triplicate measurements).

However, selectivity coefficient obtained for Hg^{2+} is not very small and it caused some interference if present in eminent concentration. In general, the concentration of Ca^{2+} and Mg^{2+} ions are of several orders of magnitude higher than that of Cd^{2+} ion, hence, the selectivity coefficient against these ions can be not sufficient. Thus, it was thought to analyze the concentrations of these interfering ions (Ca^{2+}, Mg^{2+}) in the real samples by the sensor and the results obtained were compared with AAS experiment and found in close agreement with that of AAS (Table 2.4). The sensor can tolerate $1.6×10^{-3}$ and $1.0×10^{-3}$ mol L^{-1} of Ca^{2+} and Mg^{2+} ions, respectively. However, these ions interfere if present in higher concentration and thus, causes the shortening of working concentration range and Cd^{2+} ion could be determined in the reduced concentration range of $1.0×10^{-5}$-$1.0×10^{-1}$ mol L^{-1} in the presence of $1.0×10^{-2}$ mol L^{-1} solution of Ca^{2+} and Mg^{2+} ions. From Table 2.3, it has also been observed that CPGE based on L_1 performs comparably better than CGE. Thus, these electrodes can be used for the monitoring of Cd^{2+} ion in presence of rare earth metals, alkaline earth metals and lanthanides to a good extent.

2.4.7. Determination of Dynamic Response Time and life Time of Sensor

Dynamic response time is an important factor for an ISE. According to IUPAC recommendations, the response time of an ion-selective electrode is defined as the length of time between the instant at which the ion selective electrode and reference electrode are immersed in the solution and the moment at which the potential of the cell reaches its steady-state value within ±1 mV [66]. By gradually change in the concentration of the test solution from 1.0×10^{-6}-1.0×10^{-1} mol L^{-1} the response time of the sensor was measured.The required average time of the electrodes for reaching a potential response within ±1 mV of the final equilibrium value after consecutive immersion in a series of Cd^{2+} ion solution, each addition have a 10-fold difference in concentration was 14 s for PME, 12 s for CGE and 10 s for CPGE as shown in Fig. 2.10.

Table 2.5. Effect of partially non-aqueous medium on the working of Cd^{2+} sensor based on L_1 using CPGE.

Non-aqueous contents (%; v/v)	Working concentration range (mol L^{-1})	Slope (mV $decade^{-1}$ of activity)
0	2.18×10^{-8}-1.0×10^{-1}	29.6
Ethanol		
10	2.18×10^{-8}-1.0×10^{-1}	29.6
20	2.18×10^{-8}-1.0×10^{-1}	29.6
30	2.33×10^{-8}-1.0×10^{-1}	29.4
35	2.64×10^{-8}-1.0×10^{-1}	28.8
40	6.42×10^{-7}-1.0×10^{-1}	27.2
Methanol		
10	2.18×10^{-8}-1.0×10^{-1}	29.6
20	2.25×10^{-8}-1.0×10^{-1}	29.6
30	5.91×10^{-8}-1.0×10^{-1}	28.4
35	4.52×10^{-7}-1.0×10^{-1}	27.1
40	7.36×10^{-7}-1.0×10^{-1}	25.7
Acetonitrile		
10	2.18×10^{-8}-1.0×10^{-1}	29.6
20	2.18×10^{-8}-1.0×10^{-1}	29.6
30	2.47×10^{-8}-1.0×10^{-1}	29.4
35	3.69×10^{-8}-1.0×10^{-1}	28.0
40	5.31×10^{-7}-1.0×10^{-1}	27.5

CPGE has higher electrical conductivity of copper wire as compared to CGE and PME is expected to result in lower response time of CPGE in comparison with CGE and

PME. The PME, CGE and CPGE could be used over a period of 2-4 months, respectively without observing significant divergence in response time, slope and working concentration range.After this period, there was a slight change in potentiometric characteristics and this could be corrected by re-equilibrating the membrane with 1.0×10^{-1} mol L^{-1} solution of Cd^{2+} ion for 3 days.

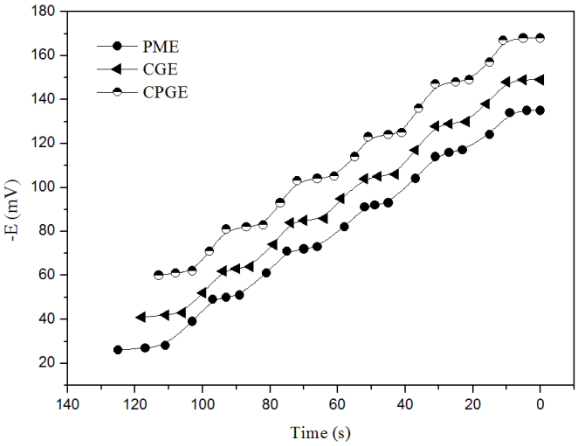


Fig. 2.10. Dynamic response time of the cadmium sensor based on L_1 for step changes in concentration of Cd^{2+} ion with PME, CGE and CPGE.

2.4.8. Effect of Non-Aqueous Medium on the Performance of Sensor

The non-aqueous content may be present in real samples; therefore, the functioning of the sensor was also enquiring in partially non-aqueous solutions in the range of 10-40% (v/v) non-aqueous content in methanol-water, ethanol-water and acetonitrile-water mixtures. The results are compiled in Table 2.5. The sensor did not display any remarkable change in the range of working concentration and slope in ethanol-water and acetonitrile-water mixtures up to 30% (v/v) non-aqueous contents, but drastic change has been observed in case of methanol-water mixture and it was found that only 20% (v/v) amount could be tolerated. Therefore, the sensor is not suitable for using in methanol-water mixture above 20% (v/v) concentration. This may be due to greater solubility of the ionophore in methanol which causes leaching of ionophore from the membrane phase.

2.4.9. Comparative Performance Characteristic of Polymeric Membrane Electrode (PME), Coated Graphite Electrode (CGE) and Coated Pyrolytic Graphite Electrode (CPGE)

The exploration on polymeric membrane based on L_1 has proved that it acts as suitable Cd^{2+} ion-selective sensor. The sensor based on L_1 containing 1-CN as plasticizer with the optimized membrane of composition L_1:PVC:1-CN:NaTPB ≡5:36:57:2 (w/w; mg) displays the widest range of working concentration (1.02×10^{-7} to 1.0×10^{-1} mol L^{-1}) and Nernstian compliance (29.0 mV $decade^{-1}$ of activity) with detection limit of 5.24×10^{-8} mol L^{-1}. The performance of this PME was compared with CGE and CPGE based on L_1 and the results are compiled in Table 2.6. The potential responses of the PME, CGE and CPGE are shown in Fig. 2.11, which reveals their Nernstian behaviour over a wide working concentration range. Comparative performance of the sensor is given in Table 2.6 shows that CPGE perform best potentiometric response characteristic in comparison to PME and CGE with respect to the wide working concentration range of 2.18×10^{-8} to 1.0×10^{-1} mol L^{-1}, the Nernstian slope 29.6 mV $decade^{-1}$ of activity with detection limit of 7.58×10^{-9} mol L^{-1}.

The improved performance behavior of CPGE, over those of PME and CGE presumably originated from the coated graphite technology, where the internal solution 1.0×10^{-1} mol L^{-1} $Cd(NO_3)_2$ in case of PME, has been exchanged by the copper wire for higher conductivity, in case of CGE and CPGE. The reason of higher LOD (limit of detection) of PME is because of deterioration of the internal solution to the analyte solution through polymeric membrane ia a well known fact [67].

2.5. ANALYTICAL APPLICATIONS

The potentiometric properties thus obtained revealed that the CPGE is better as compared to PME and CGE. Therefore, the CPGE was used for the further applications.

2.5.1. Potentiometric Titrations

The sensor was found to work well under laboratory conditions and it was used as an indicator electrode in the potentiometric titration of Cd^{2+} ion solution against EDTA solution. For this purpose, a potentiometric titration of 25 mL of 2.0×10^{-3} mol L^{-1} Cd^{2+} ion solution against 1.0×10^{-2} mol L^{-1} solution of EDTA at pH 5.5 was carried out using these electrodes and the titration plot obtained had sigmoid shapes which also supports that these electrodes are selective to Cd^{2+} ion and the inflexion point corresponds to 1:1 stoichiometry of Cd^{2+}-EDTA complex and therefore, these electrodes can be used as an indicator electrode for the potentiometric monitoring of Cd^{2+} ion.

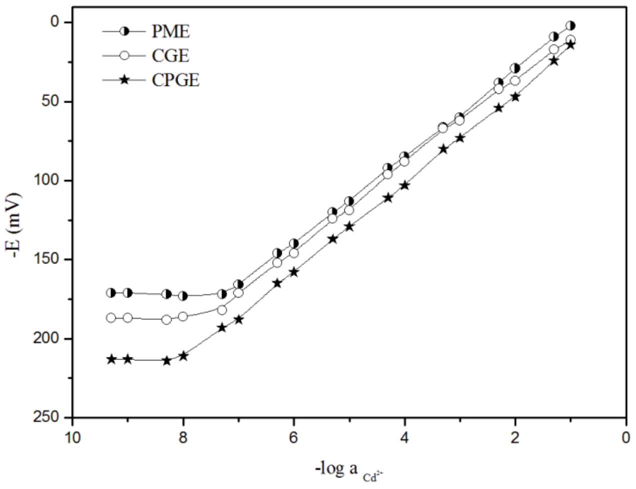


Fig. 2.11. Potentiometriccharacteristics calibration plot for Cd^{2+} ion-selective sensor with L_1.

The titration plots for electrodes PME, CGE and CPGE are shown in Fig. 2.12, from which we can accurately determine the amount of Cd^{2+} ion present in the sample.

2.5.2. Determination of Cadmium in Water samples

The sensor was used for the monitoring of Cd^{2+} ion in Ganga River (Roorkee) as well as waste water taken from the State Infrastructure and Industrial Development Corporation Uttaranchal (SIDCUL) Industrial area and Indian Institute of Technology-Roorkee, Chemistry Department. The samples were taken from different locations and digested with nitric acid (0.1 mol L^{-1}). The pH of these samples was adjusted to 5.5 by the addition of buffer solution of sodium acetate/acetic acid before the measurement. The potentiometry results are in good agreement with those obtained by AAS (Table 2.7).

2.5.3. Determination of Cadmium in Soil and Medicinal Plant samples

The sensor was successfully employed for the Cd^{2+} ion quantification in some medicinal plants and soil samples collected from Haridwar and Rishikesh regions. 2 g of dried powdered plant samples was digested with a 5:1 mixture of nitric acid (25 vol%) and perchloric acid, followed by controlled heating until the evolution of gases ceased. 15 mL of distilled water was added to this mixture and filtered through into a 25 mL volumetric flask.

Table 2.6. Potentiometric response characteristic of the Cd^{2+} ion sensor based on PME, CGE and CPGE.

Properties	Values/range		
	PME	CGE	CPGE
Optimized membrane composition	L_1(5 mg): PVC (36 mg): 1-CN (57 mg): NaTPB (2 mg)	L_1(6 mg): PVC (37 mg): 1-CN (55 mg): NaTPB (2 mg)	L_1(7 mg): PVC (37 mg): 1-CN (54 mg): NaTPB (2 mg)
Conditioning time	3 days in 0.1 M $Cd(NO_3)_2$	1 day in 1 mM $Cd(NO_3)_2$	1 day in 1 mM $Cd(NO_3)_2$
Working concentration range (mol L^{-1})	1.02×10^{-7}-1.0×10^{-1}	5.75×10^{-8}-1.0×10^{-1}	2.18×10^{-8}-1.0×10^{-1}
Detection limit (mol L^{-1})	5.24×10^{-8}	2.51×10^{-8}	7.58×10^{-9}
Slope (mV $decade^{-1}$ of activity)	29.0	29.8	29.6
Response time (s)	14	12	10
Life span (months)	2	3	4
pH range	3.5 to 7.5	3.0 to 8.0	2.5 to 8.5

The volume was adjusted to a final volume of 25 mL. The soil samples were digested in a cleaned Teflon beaker by treating 2 g of each soil sample with 10 mL of nitric acid. A 5:3:5 mixtures of nitric acid, perchloric acid and concentrated hydrofluoric acid were added, followed by controlled heating until white fumes evolved.

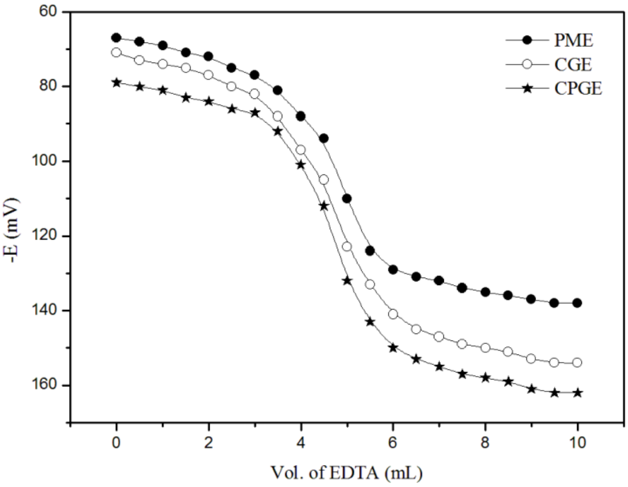


Fig. 2.12. Potentiometric titration curve of 25 mL of 2.0×10^{-3}mol L^{-1} solution of Cd^{2+} ion with 1.0×10^{-2}mol L^{-1} EDTA at pH 5.5.

The solution was filtered and diluted with distilled water to a final volume of 25 mL in a volumetric flask [68]. The results obtained by direct potentiometry were found in good agreement with those obtained by AAS and the results are compiled in Table 2.8.

Table 2.7. Determination of Cd^{2+} ion concentration (mg L^{-1}) in water samples.

Samples	ISE*±SD	AAS*±SD
Ganga water	03.68±0.17	03.92±0.35
Industrial waste water	11.14±0.38	11.45±0.24
Laboratory waste water	08.47±0.62	08.61±0.07

* Mean value ± standard deviation (triplicate measurements).

2.6. CONCLUSIONS

Novel PME, CGE and CPGE were fabricated with the ionophore (5,11,17-trithia-1,3,7,9,13,15,19,20,21-nonaazatetracyclo[14.2.1.$1^{4,7}$.$1^{10,13}$]henicosa-4(20),10(21),16(19)-triene-6,12,18-trithione (L_1)) along with different plasticizers and anionic excluders for selective determination of Cd^{2+} ion and its performance behavior was studied. It has been found that the CPGE showed superiority in terms of selectivity, sensitivity and detection limit as compared to PME and CGE. The composition of the membrane with the best performance indicators was found to be L_1: PVC: 1-CN: NaTPB in the ratio of 7:37:54:2, with detection limit of 7.58×10^{-9} mol L^{-1}. The potentiometric characteristic based on CPGE showed Nernstian slope of 29.6 mV decade^{-1} of activity and is independent of pH in the region 2.5-8.5. The response time of the sensor was found to be quite good (10 s) and can work satisfactorily in partially non-aqueous content up to 30% of acetonitrile-water and ethanol-water mixture and can tolerate 20% of methanol-water system.

Table 2.8. Determination of Cd^{2+} ion concentration (mg L^{-1}) in soil and medicinal plant samples.

Samples	ISE*±SD	AAS*±SD
Ocimum Sanctum (Tulsi)	0.84±0.04	0.90±0.16
WithaniaSomnifera (Ashwagandha)	1.47±0.11	1.42±0.12
Soil sample 1 (Haridwar)	4.72±0.09	4.87±0.05
Soil sample 2 (Rishikesh)	5.26±0.46	5.68±0.11

*Mean value ± standard deviation (triplicate measurements).

The sensor was successfully employed for the quantification of Cd^{2+} ion in real samples and besides this; the sensor was also used as an indicator electrode in potentiometric titration of Cd^{2+} ion with EDTA. A comparison of the performance characteristics with some of the previously reported sensors [25,33,35,36,39,40,44,46], as given in Table 2.9 revealed that the sensor is comparatively good to the existing Cd^{2+} ISEs in terms of selectivity, sensitivity and detection limit.

Table 2.9. Comparison of response characteristic of Cd^{2+} ion-selective sensor with previously reported electrodes.

Ref. no.	Selectivity coefficient ($K^{FIM}_{Cd^{2+},B}$)	Linear range (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mVdecade^{-1} of activity)	pH range	Response time (s)
[25]	Cu^{2+}(4.7×10^{-4}), Pb^{2+} (5.3×10^{-4}), Ag^{+} (0.12)	1.5×10^{-6}-1.0×10^{-1}	6.0×10^{-7}	29.8	2.0-8.0	12
[33]	Ni^{2+}(2.8×10^{-1}), Co^{2+}(2.8×10^{-1}), Zn^{2+}(2.5×10^{-1}), Mn^{2+}(3.2×10^{-1}), Mg^{2+} (1.6×10^{-1}), Hg^{2+}(3.2×10^{-1})	3.9×10^{-5}-1.0×10^{-1}	NM	30.0	3.2-7.5	25
[35]	Ni^{2+}(8.0×10^{-4}), Co^{2+}(1.0×10^{-3}), Zn^{2+} (4.0×10^{-4}), Mn^{2+}(1.1×10^{-4}), Mg^{2+} (2.5×10^{-4}), Ca^{2+} (1.9×10^{-4})	4.0×10^{-7}-1.0×10^{-1}	1.0×10^{-7}	29.0	2.5-8.5	10
[36]	Cu^{2+}(9.0×10^{-2}), Co^{2+} (8.5×10^{-2}), Zn^{2+} (6.2×10^{-2}), Hg^{2+}(1.9×10^{-2}), Mg^{2+} (3.9×10^{-2}), Ca^{2+} (5.1×10^{-2})	2.1×10^{-5}-1.0×10^{-1}	NM	29.0	1.9-7.0	17
[39]	Ni^{2+}(3.5×10^{-5}), Co^{2+}(6.0×10^{-5}), Zn^{2+} (1.6×10^{-4}), Mn^{2+}(4.3×10^{-3}), Cu^{2+} (4.5×10^{-3}), Hg^{2+} (4.2×10^{-4})	2.1×10^{-7}-1.0×10^{-1}	1.8×10^{-7}	30.0	5.0-7.0	50
[40]	Ni^{2+}(1.0×10^{-2}), Co^{2+} (3.1×10^{-3}), Zn^{2+} (4.2×10^{-3}), Cu^{2+}(1.7×10^{-3}), Mg^{2+} (6.3×10^{-3}), Ca^{2+} (3.3×10^{-3}), Hg^{2+}(1.0×10^{-4}),	1.0×10^{-7}-1.0×10^{-1}	2.5×10^{-8}	27.7	4.0-7.5	25
[44]	Ni^{2+}(4.8×10^{-6}), Co^{2+}(3.5×10^{-3}), Zn^{2+} (4.1×10^{-5}), Mn^{2+} (1.8×10^{-4}), Mg^{2+} (2.9×10^{-4}), Ca^{2+} (4.3×10^{-5}) Cu^{2+} (5.5×10^{-4})	3.0×10^{-8}-1.0×10^{-1}	7.5×10^{-9}	29.9	3.0-5.5	6
[47]	Cu^{2+}(6.6×10^{-2}), Co^{2+} (3.7×10^{-2}), Zn^{2+} (7.5×10^{-3}), Mg^{2+}(2.6×10^{-2}), Ca^{2+} (2.8×10^{-2}), Hg^{2+} (6.1×10^{-2})	1.6×10^{-6}-1.0×10^{-1}	NM	29.5	2.0-6.0	13
This work	Ni^{2+}(3.6×10^{-3}), Co^{2+} (5.2×10^{-3}), Zn^{2+} (2.5×10^{-4}), Mg^{2+}(1.9×10^{-3}), Ca^{2+} (1.0×10^{-3}), Hg^{2+} (5.7×10^{-2})	2.1×10^{-8}-1.0×10^{-1}	7.5×10^{-9}	29.6	2.5-8.5	10

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Chapter 3

“Diaminopyrimidin Based Chelating Ionophore as Ni^{2+} Ion-Selective Sensors”

3.1. INTRODUCTION

The occurrence of nickel in the environment is widespread and finds extensive industrial, agricultural and house hold applications. The major source of nickel distribution in aquatic systems is dissociation of rocks and soils, biological cycles and especially industrial processes and water disposal [1]. The tolerance limit of nickel in the drinking water has been reported as 2.5 ppm [2]. Above this threshold level, nickel exhibits toxicity and can cause acute pneumonitis, dermatitis, asthma, disorders of central nerve systems and cancer of the nasal cavity [3]. In view of its toxic effect, it is important to monitor nickel in various samples.

A number of sophisticated techniques have been reported for the monitoring of nickel and these includes atomic absorption spectrometry (AAS), flame atomic absorption spectrometry-electrothermal atomization (AAS-ETA), inductively coupled plasma-atomic emission spectrometry (ICP-AES), flame photometry and voltammetric techniques [4-9]. Though, these methods provide accurate results but are not very convenient for analysis of a large number of environmental samples as they require adequate expertise and large scale infrastructure back up. Hence, there is a need to develop a convenient and direct method for the assay of Ni^{2+} ion in environmental samples. Ion selective electrodes (ISEs) based on potentiometric monitoring of analyte offer several advantages over other techniques in terms of simple instrumentation, low cost, fast response, reasonable selectivity and wide dynamic range.

3.1.1 Ni^{2+} ion-selective electrodes

A number of Ni^{2+}-selective electrodes [10-32] have been reported. However, they are not very beneficial as many of reported sensors show narrow working concentration range, low pH range, substantial interferences from a variety of cations and high response time. Fabrication of new ISE is required with high selectivity and sensitivity, wide dynamic range, long lifetime and good reproducibility. Recently, we have prepared sensors of Cu^{2+}, Cd^{2+} and Mn^{2+} [33-35] by the fabrication of coated pyrolytic graphite electrodes with improved selectivity and sensitivity. Therefore, efforts have been made to develop a better sensor by the fabrication of coated pyrolytic graphite electrode based on ligand 5,5'-((3-nitrophenyl)methylene)bis(2,6-diaminopyrimidin-4(3*H*)-one) (L_2) for the determination of the Ni^{2+} ion in various environmental samples.

3.2. EXPERIMENTAL

3.2.1. Chemical and Reagents

Sodium tetraphenylborate (NaTPB), dibutylphthalate (DBP), benzylacetate (BA) and high molecular weight poly(vinyl chloride) (PVC) of reagent grade were obtained from E. Merck. Potassium tetrakis-p-(chlorophenyl)borate (KTpClPB) and *o*-nitrophenyloctylether (*o*-NPOE) were purchase from Fluka and Sigma Aldrich, respectively. Dioctylphthalate (DOP) and 1-chloronaphthlene (1-CN) were obtained from Acros Organics and s. d. fine-Chem Ltd., respectively. 3-Nitrobenzaldehyde and 2,4-diamino-6-hydroxypyrimidine were procured from Sigma Aldrich. All the cationic salts, ethylenediaminetetraacetic acid (EDTA) and solvents (ethanol, methanol, acetonitrile, tetrahydrofuran (THF), dimethylsulfoxide (DMSO), dimethylformamide (DMF), hexane and ethylacetate) used were of analytical reagent grade and used without any further purification. Double distilled water was used throughout the experiment.

3.2.2. Apparatus and Equipments

^{1}H NMR spectra was recorded in deuterated DMSO d_6 on a 500 MHz spectrometer (Bruker). IR was recorded on a NICOLET 6700 FTIR spectrometer. Elemental analysis was performed by using varioMICRO CHNS analyzer. Atomic absorption spectrometer (AAS) experiment was performed on a Perkin Elmer Analyst 800 at wavelength of 232 nm using air-acetylene as flame. The potential across the membranes were measured on an Orian 4 pH meter at 25±0.1°C in conjunction with Ag/AgCl (NaCl 3 Mol L^{-1}) BASI 2056 as reference electrodes. Conductance measurement was performed on an Orian 3 star pH bench top at 25±0.1°C. X-ray data collections were measured on a Bruker Kappa Apex four circle-CCD diffractometer using graphite monochromatedMoKα radiation (λ = 0.71070 Å) at 296 K.

3.2.3. Synthesis of ligand 5,5'-((3-nitrophenyl)methylene)bis(2,6-diaminopyrimidin-4(3*H*)-one) (L_2)

The L_2 was synthesised as shown in Fig. 3.1 while setting a reaction between amine and aldehyde in a 1:2 ratio which produces C-C coupled product (L_2). In a typical reaction setup, 2,4-diamino-6-hydroxypyrimidine (2 mM, 252.2 mg) was dissolved in 25 mL of DMF followed by drop wise addition of 3-nitrobenzaldehyde (4 mM, 604.5 mg) in 15 mL of DMF. The reaction mixture was stirred at room temperature for 3 hours and then it was

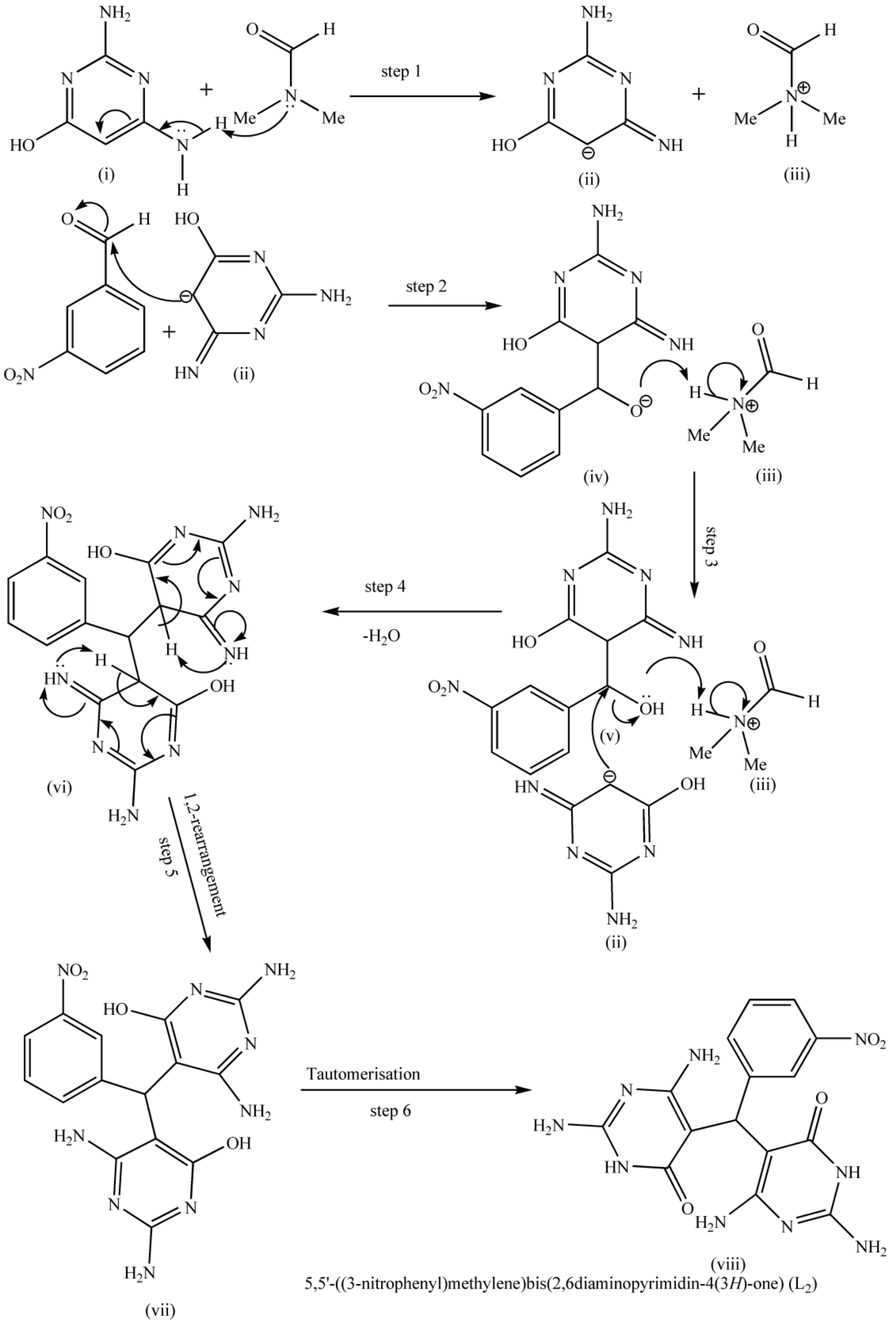

Fig. 3.1. Mechanism of Synthesis of (L$_2$).

refluxed for next 24 hours.The reaction mixture was cooled to room temperature and 200 mL distilled water was added to the reaction mixture which was then extracted with ethylacetate (50 mL × 3). The purity of product was checked by thin layer chromatography (hexane:ethylacetate, 1:1). The synthesised product was then kept for crystallization in a mixture of DMF and water asides for a month.

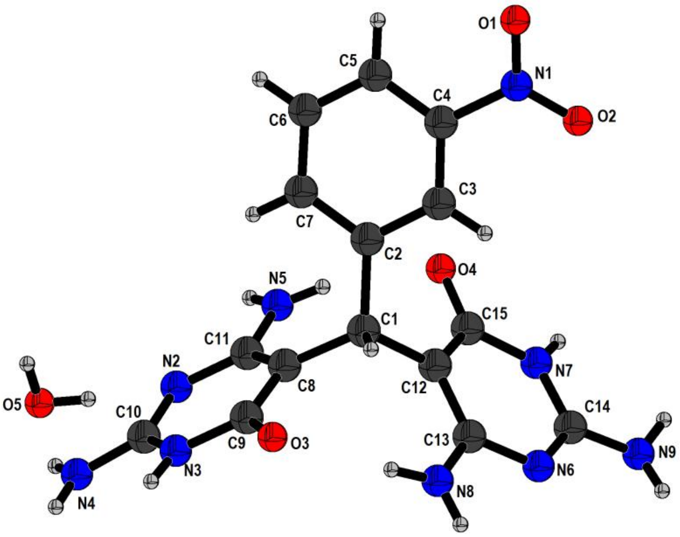

Fig. 3.2. Crystal Structure of L_2.

5,5'-((3-nitrophenyl)methylene)bis(2,6-diaminopyrimidin-4(3*H*)-one): Yield: 69% analytically calculated for [$C_{15}H_{15}N_9O_4$] (%):C, 46.75; H, 3.92; N, 32.71;. Found: C, 46.81; H, 3.84; N, 32.76. IR (KBr, cm^{-1}): 3405 (-NH), 1648 (-C=O), 1589 (-C=N), 1519, 1455, 1349, 1262, 1165, 1088, 1006 (Ar-). ^1H NMR (DMSO 500 MHz) δ (ppm): 5.442 (1H, s), 6.198 (8H, s), 7.466- 7.476 (2H, d), 7.814 (1H, s), 7.954-7.961 (1H, d), 10.046 (2H, s) (see appendix for spectra).

3.2.4. Single Crystal XRD of L_2

Single crystal suitable for X-ray diffraction of L_2 was grown in a mixture of DMF and water. The appropriate single crystal was carefully selected and its X-ray data collection were performed on a Bruker Kappa Apex four circle-CCD diffractometer using graphite monochromatedMoKα radiation (λ = 0.71070 Å) at 296 K. In the reduction of data Lorentz and polarization corrections, empirical absorption corrections were applied [36]. Crystal structures were solved by direct method. Structure solution, refinement and data output were carried out with the SHELXTL program [37, 38]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the parent molecule were placed in geometrically calculated positions using a riding model. DIAMOND and MERCURY software [39, 40]were used for making images and to show hydrogen bonding interactions present in the crystal lattice.

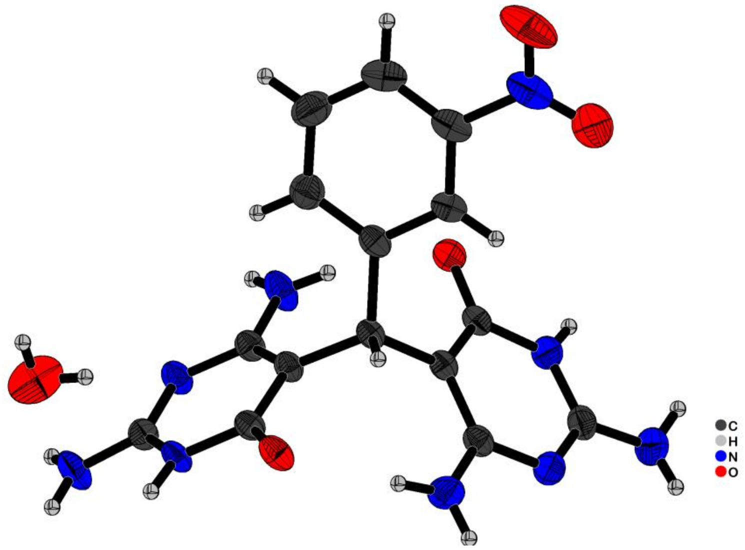

Fig. 3.3. The ORTEP plot of L_2 has shown with 50% probability level.

Table 3.1. Crystal data and structure refinement parameters for L_2.

Chemical formula	$C_{15}H_{17}N_9O_5$
Formula weight	403.38
Temperature	296 K
Wavelength	0.71070 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 9.7085 (9) Å, α = 90.0°
	b = 10.5325 (10) Å, β = 93.171(5)°
	c = 17.2763 (15) Å, γ = 90.0°
Volume	V = 1763.9 (3) Å^3
Z, calculated density	4, 1.519 g cm^{-3}
Mu (Mo-Kα)	0.118 mm^{-1}
Theta (max)	26.36°
Reflections measured	3593
R_1	0.0571
Goodness of fit	0.827

Crystal data and structure refinement parameters for the L_2 have been shown in the Table 3.1. Crystallographic data for the ligand structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-1003347). The data can be obtained free of charge via www.ccdc.cam.ac.uk/deposit or on application to the CCDC, 12 Union Road, Cambridge CB2 lEZ, U.K. (fax: + 44 (1223) 336 033; e-mail: deposit@ccdc.cam.ac.uk).

3.3. FABRICATIONOF PVC MEMBRANES

The membrane ingredients (ionophore, plasticizer and lipophilic additives) and their composition (plasticzer/PVC) ratio are known to considerably affect the performance of memerane as sensitivity and selectivity. All these influences the potential response of the membrane sensor, hence need to optimized for maximum efficiency of the sensor.

3.3.1. Preparation of Coated graphite Electrode (CGE) and Coated pyrolytic Graphite Electrode (CPGE)

The membrane has been fabricated as suggested by Cragg *et al.*, [41]. Polymeric membrane based on high molecular weight PVC was prepared by dissolving appropriate amount of membrane ingredients (ionophore (L_2), anionic excluders (NaTPB, KTpClPB), plasticizers (BA, DBP, DOP, 1-CN and *o*-NPOE) and PVC) in minimum amount of THF and the solvent was evaporated off to obtain a concentrated solution.

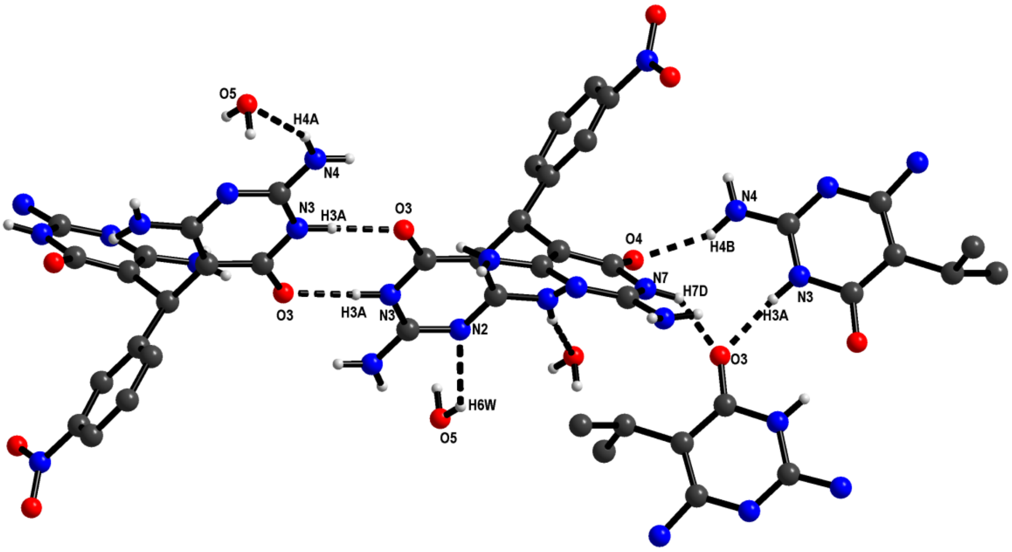

Fig. 3.4. **Intermolecular non-covalent interactions in L_2. Note: the molecule is not shown completely for clarity.**

The graphite electrode/pyrolytic graphite electrode of spectroscopic grade with copper wire glued at one end was dipped in to the above solution for few seconds and removed out and allowed the electrode to get dried. The process was repeated till the membrane was formed over graphite electrode/pyrolytic graphite electrode.

3.3.2. Conditioning of Membrane and Potential Measurements

The potential response of an ion selective electrode is a function of membrane composition. The CGE and CPGE were conditioned for one day prior to potentiometric measurements in 1.0×10^{-3} mol L^{-1} solution of $Ni(NO_3)_2$. The standard solution had been obtained by gradual dilution of stock solution 1.0×10^{-1} mol L^{-1} $Ni(NO_3)_2$. The potential measurements with the CGE and CPGE were carried out using Ag/AgCl (NaCl 3 mol L^{-1}) BASI 2056 as a reference electrode with the following cell assemblies;

CGE|Test solution||Ag/AgCl|NaCl(3 mol L^{-1})
CPGE|Test solution||Ag/AgCl|NaCl(3 mol L^{-1})
Activity coefficient were calculated according to Debye Huckel procedure [42].

3.4. RESULTSAND DISCUSSION

3.4.1. Mechanism of Synthesis of L_2

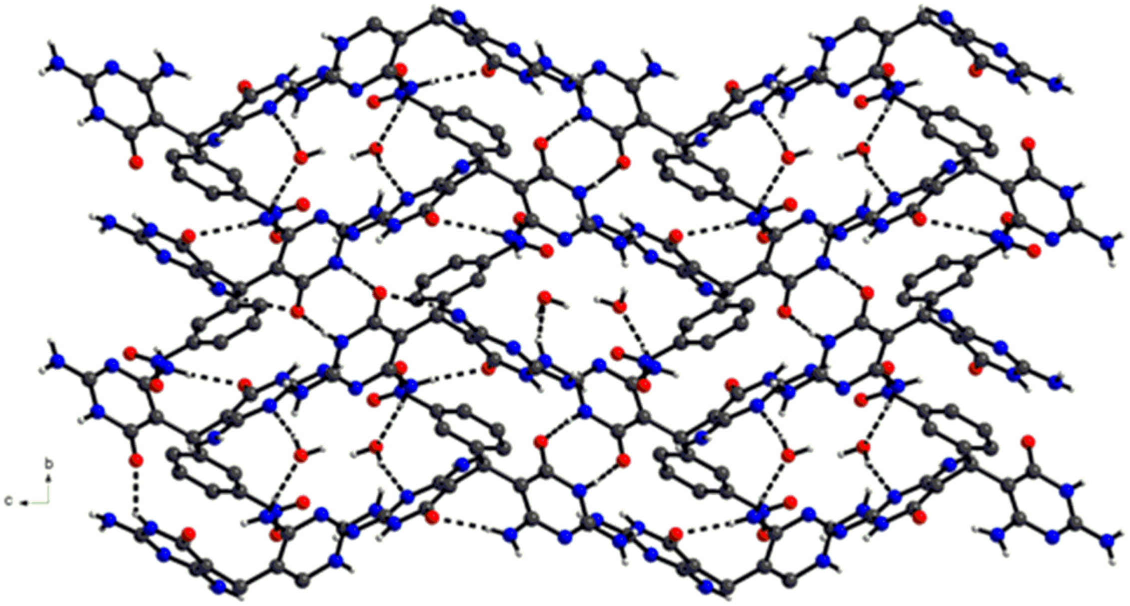

Fig. 3.5. 3-Dimensional packing of L_2 showing 1D channel along *a*-axis lining up the solvent molecules in it.

The reaction follows several steps to accomplish the final product (L_2) via a conjugate-acid, conjugate-base reaction as shown in Fig. 3.1. In the very first step, the dimethylformamide being a conjugate base in the reaction medium, abstracts a proton from the weak conjugate acid 2,6-diaminopyrimidine-4-ol (i) to form their corresponding weak conjugate acid, dimethylammoniumformamide (iii) and strong conjugate base, 2-amino-6-hydroxy-4-imino-4,5-dihydropyrimidin-5-ide (ii), respectively.

We propose that the reaction is triggered by the attack of (ii) on the more electrophilic C-centre of 3-nitrobenzaldehyde to form the intermediate compound (2-amino-6-hydroxy-4-imino-4,5-dihydro-pyrimidin-5-yl)(3-nitrophenyl)methanolate (iv) in the second steps of the reaction. The intermediate compound (iv) is a conjugate base and abstracts a proton from the dimethylammoniumformamide, which is a conjugate acid to give the compound 2-amino-5-(hydroxy(3-nitrophenyl)methyl)-6-imino-5,6-dihydro-pyrimidin-4-ol (v) in step 3. Step 4 involves a series of the reaction to give compound 5,5'-((3-nitrophenyl)methylene)bis(2-amino-6-imino-5,6-dihydropyrimidin-4-ol) (vi) by following one rounds of reaction each consisting of protonation and then, dehydration of water molecule followed by the nucleophilic attack of (ii) on the more electrophilic C-centre of (v).

Table 3.2. Selected hydrogen bonded parameters for L_2 (in Å).

D-H···A	d (D-H)	d (H-A)	d (D-A)	<(DHA)>	Symmetry code
N3-H3A···O3	0.860(3)	1.925(4)	2.775(7)	169.2	-x+2,-y+2,-z+1
N4-H4A···O5	0.861(3)	2.214(3)	3.014(4)	154.4	-
N8-H8A···O3	0.907(45)	2.148(45)	3.088(4)	165.9	-
N7-H7D···O3	0.860(2)	2.085(2)	2.795(3)	136.2	-x+1/2+1,+y-1/2,-z+1/2
N4-H4B···O4	0.860(3)	1.990(6)	2.797(8)	155.7	x+1/2,-y+1/2+1,+z+1/2
N5-H5B···O4	0.827(38)	2.013(38)	2.825(4)	165.6	-
O5-H5W···N6	0.830(48)	1.980(50)	2.790(4)	163.9	x-1/2,-y+1/2+1,+z+1/2

The next step is a 1,2-rearrangement of (vi) to give the compound 5,5'-((3-nitrophenyl)methylene)bis(2,6-diaminopyrimidin-4-ol) (vii) which then undergo tautomerisation to give the final product as 5,5'-((3-nitrophenyl)methylene)bis(2,6-diaminopyrimidin-4(3H)-one) (viii).

3.4.2. Crystal Description of L_2

Single-crystal X-ray diffraction analysis reveals that L_2 is crystallised in the monoclinic space group, $P2_1/n$. The asymmetric unit contains one condensed molecule formed from 3-nitrobenzaldehyde and 2,6-diaminopyrimidine-4-ol along with a water molecule as shown in Fig. 3.2 and its ORTEP plot has shown with 50% probability level in Fig. 3.3. It was found that the pyrimidine N of the heterocyclic group undergoes tautomerisation via the acidic proton of the hydroxyl group present on the same ring. Due to presence of number of hydrogen bonding moieties and water molecule, the molecule shows the propensity to form strong hydrogen bond as shown in Fig. 3.4 and lead to the formation of 3-D porous hydrogen bonded network with water molecules residing in it along *a*-axis via N-H···O interaction (Fig. 3.5). Crystal packing shows that the organic molecules are stabilized by intermolecular non-covalent hydrogen bonding with the water molecule via N4-H4A···O5, 2.214(3) Å; O5-H6W···N2, 2.507(68), N5-H5A···O5, 2.396(40). The selected hydrogen bonded parameters for L are shown in Table 3.2.

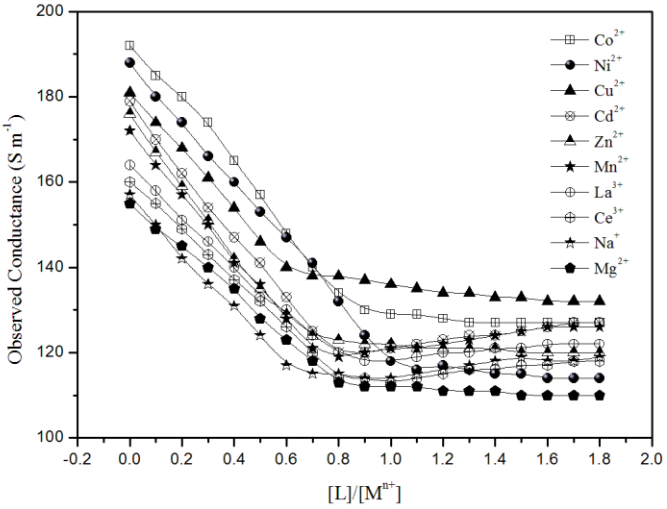

Fig. 3.6. Variation in the conductance of Ni^{2+} ion solution with the addition of L_2.

3.4.3. Complexation Study

In order to know the affinity of L_2 with various cations (M^{n+}), complexation study was setup by observing the conductance. The complexation of L_2 with M^{n+} was investigated conductometrically in a solution of DMF at 25±0.1°C. For this purpose, 25 mL of 1.0×10^{-4} mol L^{-1} solution of M^{n+} were titrated against 1.0×10^{-2} mol L^{-1} solution of L_2 in DMF. The conductance of M^{n+} were measured after each addition of L_2 and graph was drawn as a function of [L]/[M^{n+}] molar ratio and reported in Fig. 3.6. It is seen from the figure that Ni^{2+} ion shows the maximum variation in conductance with L_2. The break point in the conductance variation gives the stoichiometry of metal-ligand complex and thus Ni^{2+}-L_2 complex formed has a stoichiometry of 1:1.

3.4.4. Optimization of Membrane Composition and Potential Measurements

The optimization of membrane electrode is known to be largely influenced by the membrane ingredients and composition used for preparing the polymeric membrane. Therefore, in the fabrication of polymeric membrane with L_2 various compositions were prepared and studied. The potential of polymeric membranes of L_2 were measured as a function of Ni^{2+} ion concentration in the range of 1.0×10^{-1} to 1.0×10^{-9} mol L^{-1}. The potential responses of various fabricated electrodes were first investigated only with L and PVC and the results obtained are summarised in the Table 3.3. It can be seen from the Table 3.3 that membranes without plasticizer shows weak responses. The membrane incorporated with plasticizers showed improved performance [43] and the same was found true, if we compare the potentiometric responses of plasticized and non-plasticized membrane as shown in Table 3.3.

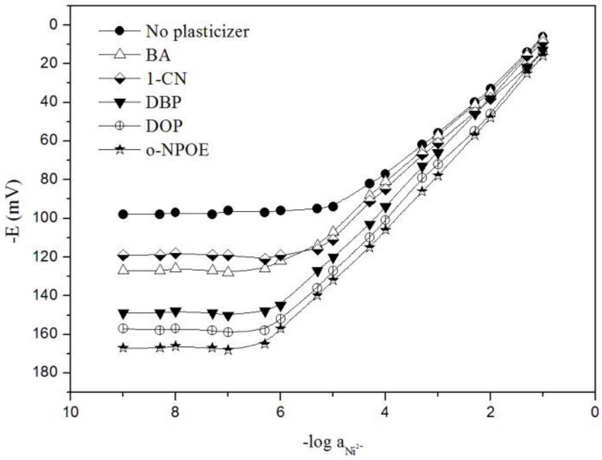

Fig. 3.7. Potential *vs* concentration of Ni^{2+} ion plots for membrane based on L_2 with various solvent mediators.

The plasticized membranes showed enhanced performance in terms of improved Nernstian slope, good linearity and low detection limits (Fig. 3.7).

Table 3.3. Membrane composition`s Optimization and their potentiometric charecteristic for Ni^{2+} ISE .

S. No.	Composition of membrane (% w/w; mg)									Working concentration range (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mVdecade^{-1} of activity)
	L_2	NaTPB	KTpClPB	DBP	DOP	BA	*o*-NPOE	1-CN	PVC			
1	7	-	-	-	-	-	-	-	93	9.3×10^{-5}-1.0×10^{-1}	1.3×10^{-5}	22.1±0.4
2	7	-	-	58	-	-	-	-	35	1.3×10^{-6}-1.0×10^{-1}	7.0×10^{-7}	26.3±0.5
3	7	-	-	-	58	-	-	-	35	1.2×10^{-6}-1.0×10^{-1}	6.6×10^{-7}	27.4±0.6
4	7	-	-	-	-	58	-	-	35	4.4×10^{-6}-1.0×10^{-1}	1.4×10^{-6}	25.3±0.6
5	7	-	-	-	-	-	58	-	35	5.3×10^{-7}-1.0×10^{-1}	3.8×10^{-7}	28.0±0.6
6	7	-	-	-	-	-	-	58	35	6.6×10^{-6}-1.0×10^{-1}	4.3×10^{-6}	27.1±0.3
7	7	2	-	-	-	-	58	-	33	7.6×10^{-8}-1.0×10^{-1}	5.1×10^{-8}	29.3±0.4
8	7	-	2	-	-	-	58	-	33	6.7×10^{-7}-1.0×10^{-1}	3.9×10^{-7}	30.6±0.4
9	8	2	-	-	-	-	58	-	32	5.9×10^{-6}-1.0×10^{-1}	2.7×10^{-6}	27.7±0.3
10	9	2	-	-	-	-	58	-	31	8.0×10^{-6}-1.0×10^{-1}	5.1×10^{-6}	32.4±0.4
11	6	2	-	-	-	-	58	-	34	7.8×10^{-7}-1.0×10^{-1}	6.2×10^{-7}	28.1±0.3
12	7	1	-	-	-	-	58	-	34	6.4×10^{-6}-1.0×10^{-1}	3.4×10^{-6}	26.4±0.6

The best performance was observed for the CPGE with optimized membrane of composition of L_2: PVC: *o*-NPOE: NaTPB ≡ 7:33:58:2 (w/w, mg) and thus, further studies were performed with the same.

3.4.5. Effect of pH on the Performance of Sensor

The effect of pH on the performance of the modified electrodes was examined by measuring their potentiometric responses for 1.0×10^{-3} mol L^{-1} and 1.0×10^{-4} mol L^{-1} solution of Ni^{2+} ion at different pH values ranging from 1-12. The pH was adjusted by the addition of 1.0×10^{-1} mol L^{-1} HCl/NaOH and the results obtained were reproduced in the Fig. 3.8.

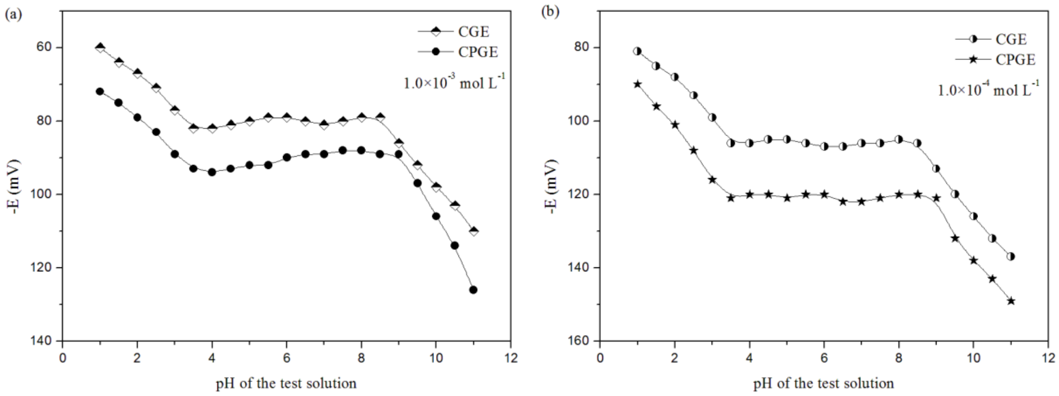

Fig. 3.8. Influences of pH of the test solution on the potential responses of CGE and CPGE in presence of (a) 1.0×10^{-3} mol L^{-1} and (b) 1.0×10^{-4} mol L^{-1} Ni^{2+} ion solutions.

It is from the Fig. 3.8, that potential response of CGE remains independent of pH over 3.5-8.5, while CPGE was found to remain unaffected in the pH range of 3.5-9.0 and hence, the same is considered as the working pH range of the electrode. The change in potential at higher pH may be attributed due to formation of metal hydroxides [44] and the deviation in the potential at lower pH may be regarded as the effect of protonation of ionophore [45] and therefore, electrode starts responding to H_3O^+ ions along with Ni^{2+} ion leading to an increase in potential.

3.4.6. Effect of Interfering Ions on the Performance of Sensor

Selectivity of an electrode is the most important parameter which reflects the applicability of an ISE and is measured in terms of selectivity coefficient. In present work, the IUPAC recommended fixed interference method (FIM) was employed for determining the potentiometric selectivity coefficient of these electrodes (CGE and CPGE). In this method, the selectivity coefficient was evaluated from the potential measurement on solutions containing a fixed concentration of interfering ion (1.0×10^{-2} mol L^{-1}) and varying amount of Ni^{2+} ion solution ranging from 1.0×10^{-1} to 1.0×10^{-9} mol L^{-1}. The potentiometric selectivity coefficient were then determined using the following expression [46]:

$$K_{A,B}^{Pot} = \frac{(a_A)}{(a_B)^{z_A/z_B}} \qquad (1)$$

Where a_A is the activity of primary ion A (Ni^{2+}) at the point of intersection, a_B, the activity of interfering ion B and z_A and z_B are their respective charges. The values of selectivity coefficient so obtained for CGE and CPGE are compiled in Table 3.4.

Table 3.4. Selectivity coefficient of various interfering ions for Ni^{2+} ion-selective sensor.

Interfering ions	Selectivity coefficient (-log $K_{Ni^{2+},B}^{FIM}$)	
	CGE*±SD	CPGE*±SD
Mn^{2+}	2.55±0.04	2.65±0.04
Zn^{2+}	2.38±0.03	2.46±0.05
Co^{2+}	1.11±0.02	1.19±0.02
Cd^{2+}	2.22±0.04	2.31±0.06
Cu^{2+}	1.16±0.03	1.22±0.06
Hg^{2+}	2.05±0.04	2.07±0.04
Mg^{2+}	3.76±0.02	3.92±0.02
Ca^{2+}	3.58±0.03	3.69±0.06
Na^{+}	2.34±0.06	2.40±0.05
La^{3+}	4.18±0.02	4.24±0.04
Ce^{3+}	4.15±0.02	4.20±0.02

From the Table 3.4 it has been observed that the electrodes are selective to Ni^{2+} ion over a number of monovalent, divalent and trivalent cations. However, the selectivity coefficient obtained for Co^{2+} and Cu^{2+} ions are not very small and it would cause some interference if present in higher concentrations. To estimate the extent of interference caused by the Co^{2+} and Cu^{2+} ions, mixed run studies were performed and the effect of the

Co^{2+} and Cu^{2+} ions concentration on the performance of the sensor was examined. The potential were measured in the presence of different concentrations (1.0×10^{-5}, 5.0×10^{-5}, 1.0×10^{-4} and 1.0×10^{-3} mol L^{-1}) of Co^{2+} and Cu^{2+} ions and the potential responses of the sensor to the mixtures are shown in Fig. 3.9. It is from Fig. 3.9 that Co^{2+} at $\leq1.0\times10^{-5}$ mol L^{-1} did not cause any deviation in the original plot obtained in pure Ni^{2+} ion. Thus, sensor can tolerate Co^{2+} at $\leq1.0\times10^{-5}$ mol L^{-1} over the entire working concentration range. However, when Co^{2+} ion present in higher concentration, significant interference was observed, which causes shorting of working concentration range and thus Ni^{2+} ion could be determined in the reduced working concentration range of 1.9×10^{-7}-1.0×10^{-1}, 3.2×10^{-7}-1.0×10^{-1} and 2.2×10^{-6}-1.0×10^{-1} mol L^{-1} in the presence of 5.0×10^{-5}, 1.0×10^{-4} and 1.0×10^{-3} mol L^{-1} of Co^{2+} ion, respectively. Similarly, it has been observed from Fig. 3.9 that sensor can tolerate Cu^{2+} ion at $\leq5.0\times10^{-5}$ mol L^{-1} over the entire working concentration range and the working concentration range reduces to 1.5×10^{-7}-1.0×10^{-1} and 6.6×10^{-6}-1.0×10^{-1} mol L^{-1} in the presence of 1.0×10^{-4} and 1.0×10^{-3} mol L^{-1} of Cu^{2+} ion, respectively.

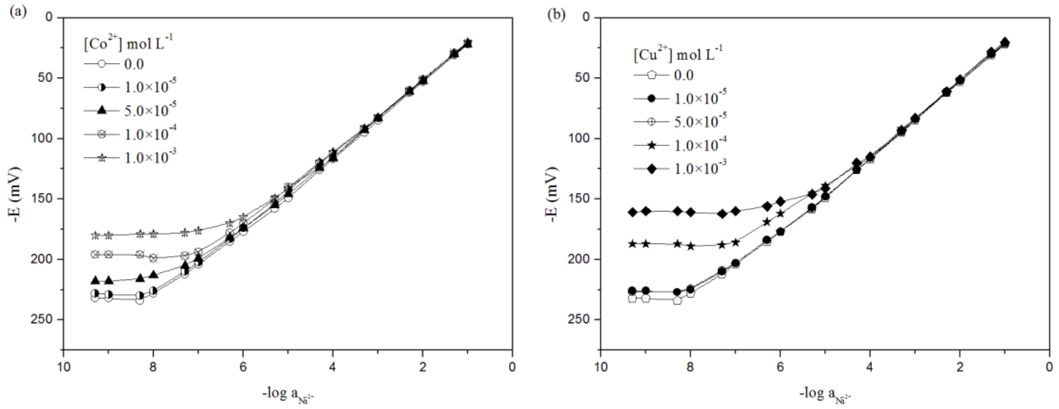

Fig. 3.9. Effect of different concentrations of (a) Co^{2+} ion and (b) Cu^{2+} ion on the performance of the sensor.

3.4.7. Determination of Dynamic Response Time and life Time of Sensor

Dynamic response time is an important factor for an ISE. According to IUPAC recommendations, the response time of an ISE is defined as the length of time between the instant at which the ion selective electrode and reference electrode are immersed in the solution and the moment when the potential of the cell reaches to its steady state value within ±1 mV [47].

The sesitivity (response time) of the sensor was estimated by altering concentration of the test solution, consecutively from 1.0×10^{-6} to1.0×10^{-1}mol L^{-1}.

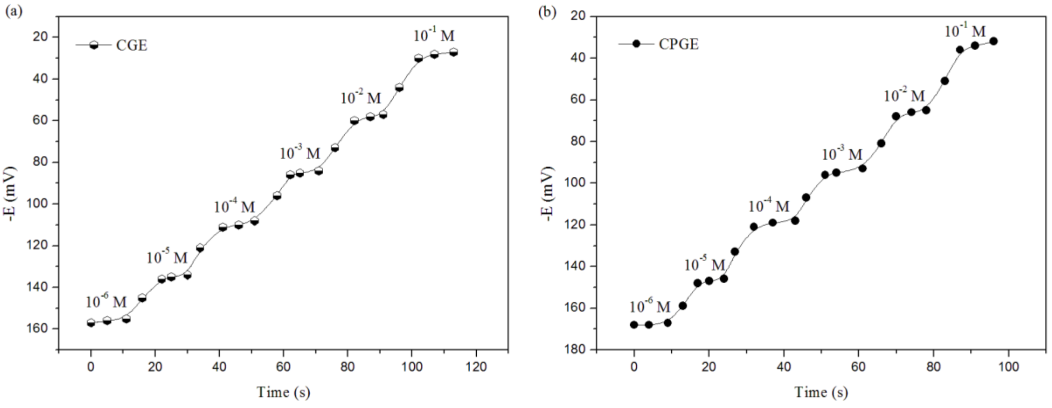

Fig. 3.10. Dynamic response time of Ni^{2+} ion sensor based on L_2 for step changes in concentration of Ni^{2+} ion with (a) CGE and (b) CPGE.

The average time needed to attain a potential response in the electrodes lies within ±1 mV range value of final equilibrium after immersing successively in a series of Ni^{2+} ion solution, each having a difference of 10-folds in concentration 11s for CGE and 8s for CPGE as shown in Fig. 3.10.

The life time of the electrode was measured by recording the potential at different time intervals and the results obtained are compiled in the Table 3.5. Thus, CGE and CPGE could be used over a period of 4 months, during which the slope of electrode showed only a slight change from 29.3±0.4 to 25.4±0.3 mV decade^{-1} of activity, the working concentration range shifted from 7.6×10^{-8}-1.0×10^{-1} to 6.7×10^{-7}-1.0×10^{-1} mol L^{-1} and the detection limit reduces from 5.1×10^{-8} to 3.8×10^{-7} mol L^{-1} for CGE and for CPGE the slope reduces from 29.4±0.2 to 26.3±0.2 mV decade^{-1} of activity, the working concentration range reduces from2.0×10^{-8}-1.0×10^{-1} to 3.3×10^{-7}-1.0×10^{-1} mol L^{-1} and the detection limit shifted from 8.1×10^{-9} to 1.2×10^{-7} mol L^{-1}.

3.4.8. Effect of Non-Aqueous Medium on the Performance of Sensor

The efficiency of the sensor was also estimated in partially non-aqueous solutions (as real sample may contain non-aqueous content) in range of 10- 40% (v/v) non-aqueous content in acetonitrile-water methanol-water and ethanol-water mixtures and the results are compiled in Table 3.6. It has been observed that membrane could tolerate 20% (v/v) of methanol water mixture, above this, sensor workability retarded probably due to leaching of ligand from the membrane phase. However, 30% of non-aqueous contents of acetonitrile-water and ethanol water solutions could be tolerated.

Table 3.5. Potential response of Ni^{2+} selective electrode based on L_2 using CGE and CPGE at different time intervals.

Time (Days)	Slope (mV decade^{-1} of activity)	Working concentration range (mol L^{-1})	Detection Limit (mol L^{-1})
CGE			
2	29.3±0.4	7.6×10^{-8}-1.0×10^{-1}	5.1×10^{-8}
10	29.3±0.4	7.8×10^{-8}-1.0×10^{-1}	5.3×10^{-8}
30	29.0±0.6	8.3×10^{-8}-1.0×10^{-1}	6.0×10^{-8}
45	28.7±0.3	8.8×10^{-8}-1.0×10^{-1}	6.4×10^{-8}
60	28.5±0.3	9.1×10^{-8}-1.0×10^{-1}	6.9×10^{-8}
75	28.4±0.2	9.8×10^{-8}-1.0×10^{-1}	7.3×10^{-8}
90	28.2±0.5	1.9×10^{-7}-1.0×10^{-1}	8.7×10^{-8}
110	28.0±0.6	3.1×10^{-7}-1.0×10^{-1}	9.6×10^{-8}
120	27.2±0.4	4.3×10^{-7}-1.0×10^{-1}	2.1×10^{-7}
130	25.4±0.3	6.7×10^{-7}-1.0×10^{-1}	3.8×10^{-7}
CPGE			
2	29.4±0.2	2.0×10^{-8}-1.0×10^{-1}	8.1×10^{-9}
10	29.4±0.2	2.0×10^{-8}-1.0×10^{-1}	8.1×10^{-9}
30	29.3±0.4	2.3×10^{-8}-1.0×10^{-1}	8.5×10^{-9}
45	29.0±0.2	2.5×10^{-8}-1.0×10^{-1}	9.0×10^{-9}
60	29.0±0.1	2.8×10^{-8}-1.0×10^{-1}	9.6×10^{-9}
75	28.8±0.3	3.3×10^{-8}-1.0×10^{-1}	1.8×10^{-8}
90	28.6±0.3	4.2×10^{-8}-1.0×10^{-1}	2.3×10^{-8}
110	28.3±0.5	5.5×10^{-8}-1.0×10^{-1}	3.4×10^{-8}
120	27.8±0.2	6.1×10^{-8}-1.0×10^{-1}	4.0×10^{-8}
130	26.3±0.2	3.3×10^{-7}-1.0×10^{-1}	1.2×10^{-7}

3.4.9. Comparative Performance Characteristic of Coated Graphite Electrode (CGE) and Coated Pyrolytic Graphite Electrode (CPGE)

The electroanalytical studies performed on PVC based polymeric membrane of L_2 has shown that it act as a suitable Ni^{2+}-selective sensor. The sensor number 7 based on L2 containing o-NPOE as the solvent mediator with the optimized membrane of compositionof L_2: PVC: *o*-NPOE: NaTPB ≡ 7: 33: 58: 2 (w/w; mg) exhibits widest working concentration range (7.6×10^{-8}-1.0×10^{-1} mol L^{-1}) and Nernstian slope (29.5±0.6 mV decade^{-1} of activity) with low detection limit (5.1×10^{-8} mol L^{-1}).

Table 3.6. Effect of partially non-aqueous medium on the performance of the sensor based on L_2 using CPGE.

Non-aqueous contents (%; v/v)	Working concentration range (mol L^{-1})	Slope (mV decade^{-1} of activity)
0	2.0×10^{-8}-1.0×10^{-1}	29.4±0.2
Ethanol		
10	2.0×10^{-8}-1.0×10^{-1}	29.4±0.2
20	2.0×10^{-8}-1.0×10^{-1}	29.4±0.3
30	2.7×10^{-8}-1.0×10^{-1}	29.2±0.6
35	4.8×10^{-8}-1.0×10^{-1}	28.4±0.3
40	7.2×10^{-7}-1.0×10^{-1}	27.6±0.4
Methanol		
10	2.0×10^{-8}-1.0×10^{-1}	29.4±0.2
20	2.0×10^{-8}-1.0×10^{-1}	29.4±0.4
30	5.3×10^{-8}-1.0×10^{-1}	28.4±0.7
35	6.7×10^{-7}-1.0×10^{-1}	27.6±0.4
40	8.4×10^{-7}-1.0×10^{-1}	26.4±0.4
Acetonitrile		
10	2.0×10^{-8}-1.0×10^{-1}	29.4±0.2
20	2.0×10^{-8}-1.0×10^{-1}	29.4±0.3
30	3.1×10^{-8}-1.0×10^{-1}	29.2±0.2
35	5.2×10^{-8}-1.0×10^{-1}	28.2±0.7
40	8.3×10^{-7}-1.0×10^{-1}	27.7±0.5

The CPGE was fabricated with the same composition as that of CGE and performance of the electrodes were summarised in the Table 3.7. The potential response of the CGE and CPGE are shown in Fig. 3.11 which reveals that slope is Nernstian and response is linear. A comparison of data as reported in Table 3.7 showed that CPGE exhibited best performance in terms of wide working concentration range of 2.0×10^{-8}-1.0×10^{-1} mol L^{-1}, the Nernstian slope of 29.4±0.2 mVdecade^{-1} of activity with detection limit of 8.1×10^{-9} mol L^{-1} to that of CGE.

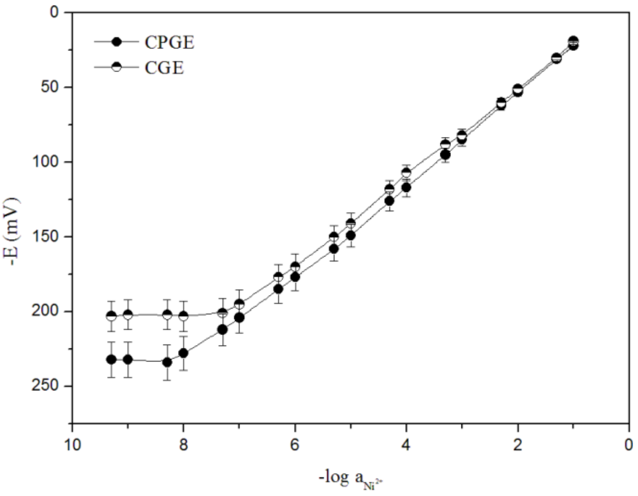

Fig. 3.11. Potentiometric characteristics calibration plot for Ni^{2+} ion selective sensor with L_2.

3.5. ANALYTICAL APPLICATIONS

The selectivity for Ni^{2+} ion exhibited by the sensor makes it potentially suitable for monitoring of Ni^{2+} ion in real samples and also the sensor was successfully employed as an indicator electrode in the potentiometric titration of Ni^{2+} ion with EDTA.

3.5.1. Potentiometric Titrations

The sensor could be used as indicator electrode in the potentiometric titration of Ni^{2+} ion by titrating against EDTA solution. For this purpose, a potentiometric titration of 25 ml of 2.0×10^{-3} mol L^{-1} Ni^{2+} ion solution against 1.0×10^{-2} mol L^{-1} solution of EDTA at pH 5.5 was carried out using these electrodes and the titration plot obtained (Fig. 3.12) had shows shapes which also supports that these electrodes are selective to Ni^{2+} ion. The inflexion point corresponds to 1:1 stoichiometry of Ni^{2+}-EDTA complex and therefore, these electrodes can be used as an indicator electrode for the potentiometric determination of Ni^{2+} ion by titration.

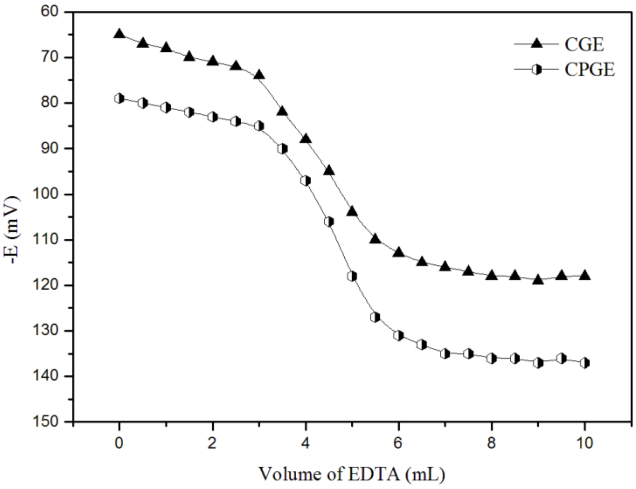

Fig. 3.12. Potentiometric titration curve of 25 mL of 2.0×10^{-3} mol L^{-1} solution of Ni^{2+} ion with 1.0×10^{-2} mol L^{-1} EDTA at pH 5.5.

3.5.2. Analysis of Ni^{2+} in Electroplating Waste and River Water Samples

The sensor was successfully employed for the monitoring of Ni^{2+} ion in the effluents discharged from electroplating works and river water samples. Three samples of local electroplating wastes and river water samples were collected, treated with diluted nitric acid, filtered and stored. The pH of the samples was adjusted to 5.5 before the measurement. The results obtained by potentiometry are in good agreement with those obtained for AAS experiment (Table 3.8).

3.5.3. Determination of Ni^{2+} in Soil and Medicinal Plant samples

The soil samples were digested in a cleaned Teflon beaker by treating 2 g of each soil sample with nitric acid. A 5:3:5 mixtures of nitric acid, Perchloric acid and concentrated hydrofluoric acid were added, followed by controlled heating until white fumes evolved. The filterate was make up to final volume of 25 mL in a volumetric flask by dilting with double distilled water [48]. Direct potentiometric measurement was performed at pH 5.5 and the results (Table 3.9) obtained are in close agreement with those of AAS experiment and thus, shows the utility of the sensor in the quantification of Ni^{2+} ion. The sensor was successfully employed for the Ni^{2+} ion quantification in some medicinal plants (*Ocimum sanctum*, *Cassia fistula* and *Withania somnifera*) and soil samples collected from Haridwar and Roorkee regions. 2 g of dried, powdered plant samples was digested with a 5:1 mixture of nitric acid and perchloric acid, followed by controlled heating until the evolution of gases ceased. Then double distilled water was added to this mixture and filtered through into a 25 mL volumetric flask.

Table 3.7. **Potentiometric response characteristics of Ni^{2+} sensor based on CGE and CPGE.**

Properties	Values/range	
	CGE	CPGE
Optimized membrane composition	L: PVC: *o*-NPOE: NaTPB ≡ 7: 33: 58: 2 (w/w, mg)	L: PVC: *o*-NPOE: NaTPB ≡ 7: 33: 58: 2 (w/w, mg)
Conditioning time	24 h in 1.0×10^{-3} mol L^{-1} $Ni(NO_3)_2$	24 h in 1.0×10^{-3} mol L^{-1} $Ni(NO_3)_2$
Working concentration range (mol L^{-1})	7.6×10^{-8}-1.0×10^{-1}	2.0×10^{-8}-1.0×10^{-1}
Detection limit (mol L^{-1})	5.1×10^{-8}	8.1×10^{-9}
Slope (mV $decade^{-1}$ of activity)	29.3±0.4	29.4±0.2
Response time (s)	11	8
Life span (month)	4	4
Working pH range	3.5-8.5	3.5-9.0

The volume was adjusted to a final volume of 25 mL. The pH of the sample was adjusted to 5.5 before direct potentiometric measurement was performed and the results (Table 3.10) obtained reflects the applicability of the sensor as the values obtained are in close agreement with those of AAS experiment.

Table 3.8. **Determination of Ni^{2+} ion in electroplating waste water and river water samples.**

Samples		ISE*±SD (mg L^{-1})	AAS*±SD (mg L^{-1})
Electroplating waste	Water sample 1	35.1±1.2	35.3±1.1
	Water sample 2	39.8±1.4	39.7±1.0
	Water sample 3	40.3±0.8	40.0±1.4
River Water	Water sample 1	09.6±0.8	09.7±1.2
	Water sample 2	09.0±0.5	08.8±1.5
	Water sample 3	10.6±0.7	10.3±1.0

*Mean value ± standard deviation (triplicate measurements).

Table 3.9. Determination of Ni^{2+} ion in soil samples.

Samples		ISE*±SD (mg kg^{-1})	AAS*±SD (mg kg^{-1})
Haridwar	Soil sample 1	11.4±0.8	11.3±0.4
	Soil sample 2	11.9±0.7	11.8±1.1
Roorkee	Soil sample 1	10.4±1.3	10.5±1.0
	Soil sample 2	10.1±0.2	09.8±1.5

*Mean value ± standard deviation (triplicate measurements).

Table 3.10. Determination of Ni^{2+} ion in medicinal plant samples.

Samples	ISE*±SD (mg kg^{-1})	AAS*±SD (mg kg^{-1})
Ocimum sanctum	5.64±0.60	5.63±0.56
Cassia fistula	6.26±0.43	6.27±0.53
Withaniasomnifera	8.98±0.52	9.07±0.24

*Mean value ± standard deviation (triplicate measurements).

3.6. CONCLUSIONS

The ionophore (L_2) showed maximum affinity for Ni^{2+} ion. Thus, L_2 was used as ionophore in the fabrication of PVC based membrane electrodes such as CGE and CPGE. A large number of electrodes with different compositions were prepared and studied. The performances of various fabricated sensor were examined and it was found that the solvent mediator *o*-NPOE significantly improve the performance of the sensor in comparison to other plasticizers. The CPGE based on L_2 found to be best in performance with the optimized membrane composition of L_2: PVC: *o*-NPOE: NaTPB ≡ 7:33:58:2 (w/w, mg). The CPGE shows wide working concentration range of 2.0×10^{-8}-1.0×10^{-1} mol L^{-1}, Nernstian slope of 29.4±0.2 mV decade $^{-1}$ of activity of Ni^{2+} ion. The sensor is independent of pH in the pH range of 3.5 to 9.0. The response time of the electrode was quite fast (8 s) and could work satisfactorily in partially non-aqueous content up to 30% of ethanol-water and acetonitrile-water mixtures and could tolerate about 20% of methanol-water mixtures. The sensor could be satisfactorily used for at least 4 months without observing any appreciable changes in working concentration range, slope and linearity. The sensor reflects its utility in the monitoring of Ni^{2+} ion in various environmental samples. The sensor has been successfully employed as an indicator electrode in the potentiometric titration of Ni^{2+} ion with EDTA. The sensor is compared with previously reported electrodes (Table 3.11) and found that sensor is superior in terms of wide working concentration range, detection limit, slope and sensitivity.

Table 3.11. Comparison of response characteristic of Ni^{2+} ion-selective electrode with previously reported electrodes.

Ref. no.	Ionophore	Linear range (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mVdecade^{-1} of activity)	pH range	Response time (s)
[14]	Heterogeneous membranes of macrocyclic compounds	$1.0\times10^{-6}-1.0\times10^{-1}$	NM	30.0	1.7-5.4	15
[15]	3,4:11,12-Dibenzo-2,5,10,13-tetraoxo-1,6,9,14-tetrazacyclohexane, Polystyrene	$3.1\times10^{-6}-1.0\times10^{-1}$	NM	30.7	2.5-7.0	10
[17]	5,7,12,14-Tetramethyldibenzotetraazaannulene	$7.9\times10^{-6}-1.0\times10^{-1}$	NM	30.0±1.0	2.7-7.6	15
[18]	2-Methyl-4-(4-methoxy phenyl)-2,6-diphenyl-2H-thiopyran	$2.0\times10^{-5}-5.0\times10^{-2}$	9.0×10^{-6}	29.5	3.0-6.0	10
[20]	1,3,7,9,13,15,19,21-Octaazapentacyclooctacosane	$1.0\times10^{-6}-1.8\times10^{-2}$	6.0×10^{-7}	30.5	3.0-6.0	5-40
[21]	Dibenzocyclamnickel(II)	$7.0\times10^{-6}-1.8\times10^{-2}$	NM	29.8±0.2	2.0-7.6	12
[23]	(2-Mercapto-4-methylphenyl)-2-benzamido-3-ethoxy-thiopropenoate	$1.0\times10^{-7}-1.0\times10^{-2}$	6.0×10^{-8}	29.0±1.0	5.0-8.5	15
[25]	N-(2-hydroxybenzylidene)- N'-(2-picolyl)-ethylenediamine	$3.2\times10^{-6}-5.0\times10^{-2}$	NM	29.0	2.2-5.9	10
[26]	Dibenzo-[e,k]-2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,5,7,9,11-hexaene.	$3.9\times10^{-6}-1.0\times10^{-1}$	2.9×10^{-6}	29.5	2.5-7.7	08
[27]	3-hydroxy-N-{2-[(3-hydroxy-Nphenylbutyrimidoyl)-amino]-phenyl}-N'-phenylbutyramidine	$1.6\times10^{-7}-1.0\times10^{-2}$	1.0×10^{-7}	30.0±0.2	2.5-9.5	10
[31]	Schiff base 3-aminoacetophenonesemicarbazone	$1.0\times10^{-7}-1.0\times10^{-2}$	5.1×10^{-8}	30.0±0.3	2.0-9.8	10
This work	5,5'-((3-Nitrophenyl)methylene)bis-(2,6-diaminopyrimidin-4(3*H*)-one)	$2.0\times10^{-8}-1.0\times10^{-1}$	8.1×10^{-9}	29.4±0.2	3.5-9.0	08

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Chapter 4

“Polydentate Heterocyclic Chelating Ionophores as Cu^{2+} Ion-Selective Sensors”

4.1. INTRODUCTION

The existence of copper in environment is widespread as it is used for many industrial, agricultural and household purposes. It has been perceived that copper is an essential element in many biological processes such as blood formation and function of many enzymes [1-4]. The tolerance limit for human being is 2 ppm of copper ions [5], however, enormous concentration of copper can be endured by human beings but inordinate intake of it manifests certain diseases in humans for examples, Menke's syndrome, Wilson's disease [6,7], gastrointestinal cattarch, hypoglycemia and dyslexia. Thus, monitoring of copper is important in view of its utility as well as deleterious effect.

Numerous analytical methods have been reported for low level monitoring of copper ions such as atomic absorption spectroscopy (AAS), inductively coupled plasma-optical emission spectroscopy (ICP-OES), fluorimetry, stripping voltammetry and inductively coupled plasma-mass spectrometry (ICP-MS) [8-12]. Although these methods provide accurate results, these methods are not very convenient for analysis of sophisticated, time consuming, and costeffectiveness. Potentiometry ISE have emerged as one of the most promising tools for direct determination of various species in environmental, biological and industrial analysis as they offer advantages such as selectivity, sensitivity, good precision, less time consumption, simplicity and low cost and even may also be suitable for online monitoring. Due to the vital importance of copper in industry [13] and in many biological systems [14, 15], efforts have been made for selective potentiometric monitoring of Cu^{2+} ions at lower concentration level.

4.1.1. Cu^{2+} ion-selective electrodes

In this regards, many ion-selective electrodes have been reported for the determination of Cu^{2+} ion in various environmental samples [16-31]. But many of these are suffering with some limitations in low linearity, low pH range, substantial interference from a variety of cations and high response time. Thus there is a need to develop a better sensor for copper ions. It has been observed that copper(II)-nitrogen-sulfur ligands frame provides significant contribution to determine Cu^{2+} ions in various samples [32]. Therefore in the present work, we tried to develop a better ion-selective electrode based on 1,3-bis[2-(1,3-benzothiazol-2-yl)-phenoxy]- propane (L_3) and 1,2'-bis[2-(1,3-benzothiazol-2-yl)-phenoxy]2-ethoxy ethane (L_4) as ionophores for selective and sensitive determination of Cu^{2+} ion.

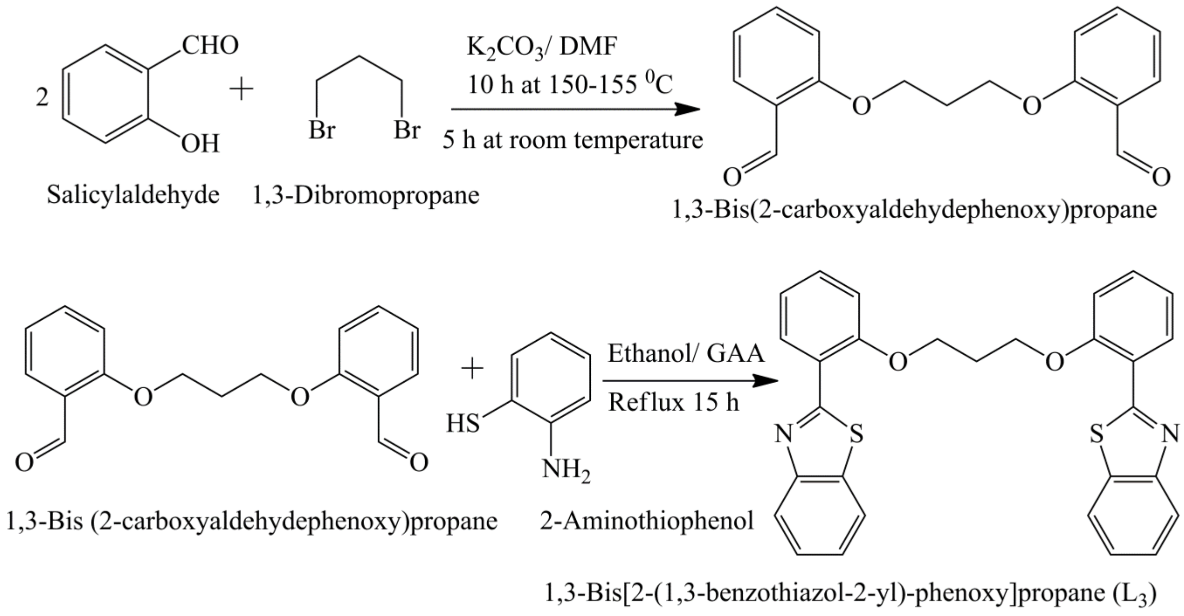

Fig. 4.1. Synthesis of ligand 1,3-bis[2-(1,3-benzothiazol-2-yl)-phenoxy]propane (L_3).

4.2. EXPERIMENTAL

4.2.1. Chemical and Reagents

Dibutylphthalate (DBP), NaTPB (sodium tetraphenylborate), , benzylacetate (BA) and high molecular weight poly(vinyl chloride) (PVC) were purchase from E. Merck (Mumbai, MH, India). Potassium tetrakis-p-(chlorophenyl)borate (KTpClPB) and *o*-nitrophenyl- octylether (*o*-NPOE) were procured from Fluka and Sigma Aldrich, respectively. Dioctylphthalate (DOP) and 1-chloronaphthlene (1-CN) were procured from Acros Organics and s. d. fine-Chem Ltd. Salicylaldehyde and 2-aminothiophenol was purchase from Sigma Aldrich, 1-chloro-2-(2-chloroethoxy) ethane and dibromopropane were procured from Hi-Media and used as received. The nitrate and chloride salts of all the cations used were of analytical grade and used without any further purification. Double distilled water was used throughout the experiment. The AAS experiments were performed on a Perkin Elmer Analyst 800 at a wavelength of 324.8 nm using air-acetylene as flame. The samples were extracted according to the described procedure. Standard solutions of copper were prepared and a calibration plot was drawn in the concentration range of 1-4 ppm. The samples with concentration higher than the maximum limit of the instruments were diluted and analysed. The concentration of the initial sample was estimated using the dilution factor.

4.2.2. Synthesis

The ligands L_3 and L_4 were synthesised by the reaction of precursor compounds (dialdehydes) with 2-aminothiophenol as shown in Fig. 4.1 and 4.2 by following a reported method [33]. Precursor compounds were synthesised by previously reported method [34]. Ligand L_4 have been reported somewhere else [35].

4.2.2.1. Synthesis of Ligand 1,3-Bis [2-(1,3-benzothiazol-2-yl)-phenoxy]propane (L_3)

A mixture of 1,3-bis (2-carboxyaldehydephenoxy) propane (284 mg, 1 mmol) and 2-amino- thiophenol (250 mg, 2 mmol) was refluxed in EtOH (15 mL) in the presence of glacial acetic acid (GAA) (0.5 mL) for 15 h. The precipitate that formed was filtered off and dried in air. A pale-yellow powder was obtained.

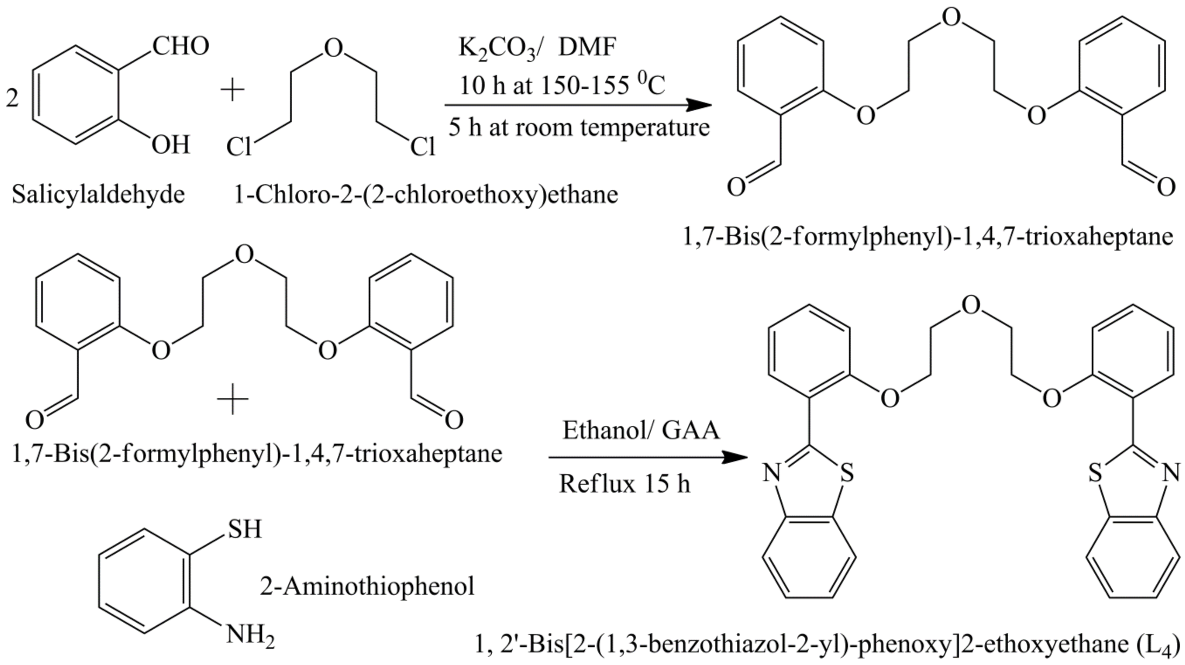

Fig. 4.2. **Synthesis of ligand 1,2′-bis[2-(1,3-benzothiazol-2-yl)-phenoxy]2-ethoxyethane (L_4).**

Yield: 78%, analytically calculated for [$C_{29}H_{22}N_2O_2S_2$] (%): C, 70.42; H, 4.48; N, 5.66; S, 12.97. Found C, 70.32; H, 4.54; N, 5.71; S, 13.02. IR (KBr, cm^{-1}): 1586 (-C=N), 1495, 1459, 1289, 1241 (Ar-). ^1H NMR ($CDCl_3$, 500 MHz) δ (ppm): 2.70-2.75 (2H, m), 4.59-4.61 (4H, t), 7.07-7.14 (4H, m), 7.35-7.43 (4H, m), 7.48-7.51 (2H, m), 7.87-7.89 (2H, d), 8.09-8.10 (2H, d), 8.54-8.55 (2H, dd). ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 29.57, 66.20, 112.73, 121.48, 121.60, 122.63, 123.10, 124.93, 126.24, 130.03, 132.10, 136.15, 152.40, 156.64, 163.17 (see appendix for spectra).

4.2.2.2. Synthesis of Ligand 1, 2’-Bis[2-(1,3-benzothiazol-2-yl)-phenoxy]2-ethoxyethane (L_4)

A mixture of 1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane (314 mg, 1 mmol) and 2-aminothio- phenol (250 mg, 2 mmol) was refluxed in EtOH (15 mL) in the presence of glacial acetic acid (0.5 mL) for 15 h. The precipitate that formed was filtered off and dried in air. A pale-yellow powder was obtained.

Yield: 68% analytically calculated for [$C_{30}H_{24}N_2O_3S_2$] (%): C, 68.68; H, 4.61; N, 5.34; S, 12.22. Found: C, 68.72; H, 4.54; N, 5.41; S, 12.16. IR (KBr, cm^{-1}): 1590 (C=N), 1496, 1447, 1294, 1249 (Ar). ^1H NMR ($CDCl_3$ 500 MHz) δ (ppm): 4.19-4.21 (4H, t), 4.40-4.42 (4H, t), 7.03-7.13 (4H, m), 7.29-7.32 (2H, t), 7.38-7.48 (4H, dt), 7.78-7.80 (2H, d), 8.06-8.08 (2H, d), 8.51-8.53 (2H, d). ^{13}C NMR ($CDCl_3$ 125 MHz) δ (ppm): 68.88, 70.06, 112.98, 121.39, 121.72, 122.85, 123.02, 124.84, 126.12, 129.96, 131.97, 136.31, 152.35, 156.65, 163.27 (see appendix for spectra).

4.3. FABRICATON OF PVC MEMBRANES

4.3.1. Electrode Preparation

The membrane has been fabricated as suggested by Craggs *et al.*, [36]. Polymeric membrane based on high molecular weight PVC was prepared by dissolving appropriate amounts of membrane ingredients [(ligands (L_3 and L_4), anionic excluders, PVC and plasticizers)] in minimum amount of THF (~5 mL). Homogeneous mixture was obtained after complete dissolution of all the components and solvent was evaporated to obtain a concentrated solution. It was then poured in to polyacrylate rings, which were placed on a smooth glass plates and THF was allowed to evaporate slowly at room temperature. The membrane thus obtained was detached from the glass plate and cut to suitable size and glued to one end of a “Pyrex glass” tube with Araldite. It is known that the sensitivity, selectivity and linearity obtained for a given ionophore depends significantly on the membrane composition, time of contact and nature of plasticizer used. Thus the ratio of membrane ingredients, time of contact and concentration of equilibrating membrane were optimized after a good deal of experimentation.

4.3.1.1. Preparation of Coated Graphite Electrodes (CGE) and Coated Pyrolytic Graphite Electrodes (CPGE)

Appropriate amounts of membrane ingredients [(L_3 and L_4, anionic excluders, plasticizer and PVC)] dissolved in THF (5 mL) and the solvent was evaporated off to obtain concentrated solution. Graphite electrode/pyrolytic graphite electrode of spectroscopic grade (6 mm long, 3 mm in diameter) with copper wire glued at one end was dipped in to solution for few seconds and removed out and allowed the electrodes to get dry.

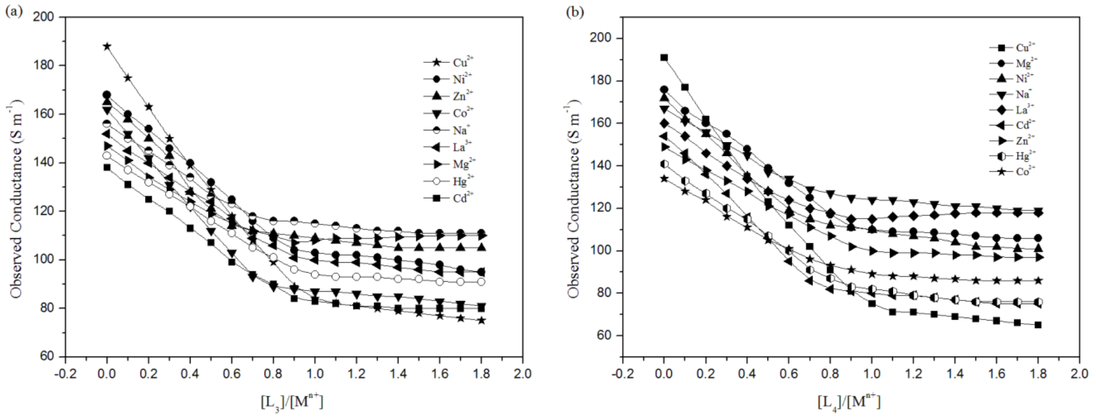

Fig. 4.3. Conductometric study of ion-ionophore complex with (a) ligand L_3 and (b) L_4.

The process was repeated several times till homogeneous thickness of the membrane was formed over graphite electrode/pyrolytic graphite electrode. Then it was glued to “Pyrex glass” keeping working area exposed.

4.3.2. Conditioning of Membrane and Potential Measurements

The potential response of ion selective electrode is largely affected by the nature and amount of membrane ingredients. The PME were equilibrated for 3 days, while CGE and CPGE were conditioned for 1 day prior to potentiometric measurements in 1.0×10^{-1} mol L^{-1} and 1.0×10^{-3} mol L^{-1} $Cu(NO_3)_2$ solutions, respectively. The potential have been measured by varying the concentration of $Cu(NO_3)_2$ solution in the range of 1.0×10^{-1}-1.0×10^{-9} mol L^{-1}. The standard solution had been obtained by gradual dilution of 1.0×10^{-1} mol L^{-1} $Cu(NO_3)_2$ solution. The potential measurements with the PME, CGE and CPGE were performed on a pH meter (Orion 4) at 25±0.1°C in conjunction of Ag/ AgCl (NaCl 3 mol L^{-1}) BASI 2056 as reference electrode. The cell can be repsented as given below:

Ag/AgCl|NaCl(3 mol L^{-1})|internal solution (1.0×10^{-1} mol L^{-1} $Cu(NO_3)_2$)||PVC membrane||sample solution|Ag/AgCl|NaCl (3 mol L^{-1})

CGE||Test solution||Ag/AgCl|NaCl (3 mol L^{-1})

CPGE||Test solution||Ag/AgCl|NaCl(3 mol L^{-1})

Activity coefficients were determined according to Debye-Huckel procedure [37].

4.4. RESULTS AND DISCUSSION

4.4.1. Complexation Study

In preliminary experiments, the complexations of L_3 and L_4 with a number of metal ions have been investigated conductometrically in DMF solutions in order to obtain a hint about the stoichiometry of the resulting complexes at 25±0.05°C. For this purpose, 25 mL of 1.0×10^{-4} mol L^{-1} cation solution was titrated against a 1.0×10^{-2} mol L^{-1} ionophore solution in DMF. The conductance of the solution was measured after each addition of ligand. The conductance variation plots with different metal ions as a function of the $[L]/[M^{n+}]$ molar ratio is shown in Fig. 4.3 (a) and (b). As it can be seen from the Fig. 4.3 (a) and (b) that conductance variation of copper solution showed greatest variation with the addition of ligand, initially the conductance falling off with the addition of ligand which shows that copper ions are strongly interacting with the ligands added and forming Cu-L_3 and Cu-L_4 complexes, respectively, with the ligands L_3 and L_4 and thus causes conductance to falls-off. A stage is arrived when conductance of the solutions nearly becomes constant and further addition of ligands does not cause any appreciable change in conductance which indicates that all of the metal ions have been consumed by the ligands in forming complexes. The break in the conductance variation plots shows the stoichiometry of the resulting complexes and from the Fig. 4.3 (a) and (b), it has been observed that the stoichiometry of metal to ligand is 1:1. Therefore, these ligands (L_3 and L_4) are explored as neutral ionophores for the fabrication of Cu^{2+} selective and sensitive sensors based on PME, CGE and CPGE.

4.4.2. Membrane's Composition Optimization and Potential Measurements

The selectivity, sensitivity and linearity estimated for a specified ionophore highly depends on the nature of plasticizer and membrane ingradients [38]. It has also been found that additives added [39, 40] influence the performance of the sensor. Therefore, to improve the performance of these polymeric membranes based on L_3 and L_4 a number of electrodes having different composition were prepared and studied. The potential response of PME, CGE and CPGE were first investigated only with the ionophore and PVC and the results are summarized in Tables 4.1-4.6.

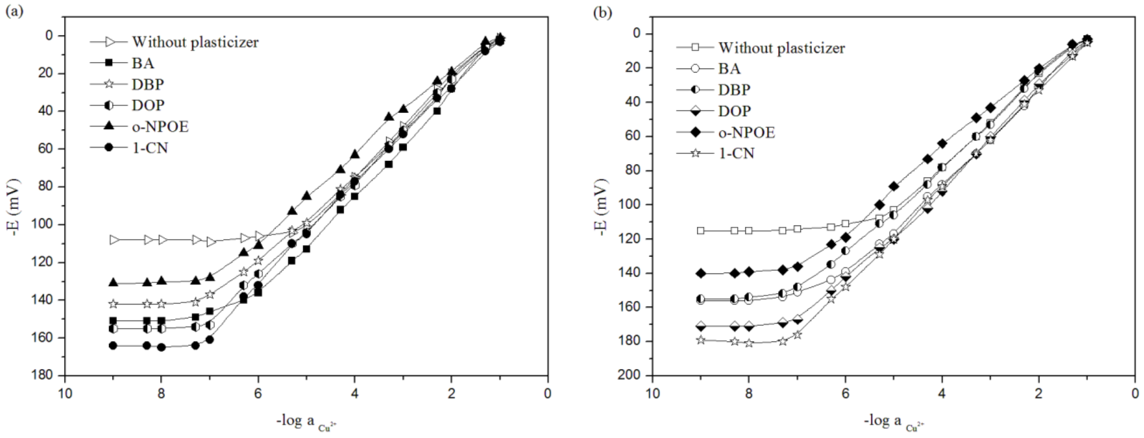

Fig. 4.4. Potentail vs. concentration graph of of sensor for Cu^{2+} ions incorporating (a) L_3 and (b) L_4 with different plasticizers.

Tables depicts that sensors number 1, A1 and B1 incorporating membrane of L_3 without solvent mediator shows linearity of 3.1×10^{-5}-1.0×10^{-1}, 1.68×10^{-5}-1.0×10^{-1} and 8.32×10^{-6}-1.0×10^{-1} mol L^{-1}, with a slope of 25.4, 26.8 and 26.8 mV decade^{-1} of activity, respectively. Similarly, sensor number 14, A14 and B14 having membrane of L_4 without plasticizer shows linear response over a working concentration range of 2.75×10^{-5}-1.0×10^{-1}, 1.47×10^{-5}-1.0×10^{-1} and 6.81×10^{-6}-1.0×10^{-1} mol L^{-1} with a slope of 25.7, 26.3 and 27.0 mV decade^{-1} of activity, respectively. The incorporation of plasticizer enhances the performance characteristics of electrodes, is a well known fact. Therefore in these study five plasticizers viz. *o*-NPOE, BA, DBP, DOP and 1-CN were checked into and the responses obtained with the plasticized membranes are shown in Fig. 4.4 (a) and (b). As expected the plasticized membrane electrodes observed to be good in its potentiometric characteristics in terms of large working range, linear and Nernstian slope. Since the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands [41-43], it is expected to play an important role in determining the ion selective characteristics. Among all the membranes prepared so far, CPGE membrane having composition of L_3: PVC: 1-CN: NaTPB in the ratio of 5:38:55:2 (w/w, mg) and L_4: PVC: 1-CN: NaTPB in the ratio of 6:39:53:2 (w/w, mg) perform best in all aspects of its potentiometric characteristics and thus, further studies were performed with the same.

Table 4.1. Optimization of membrane composition based on L_3 using PME and their potentiometric responses characteristics of Cu^{2+}.

S. No.	Composition of membrane (w/w; mg)									Working concentration range (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mVdecade^{-1} of activity)
	L_3	NaTPB	KTpClPB	DBP	DOP	BA	*o*-NPOE	1-CN	PVC			
1	5	-	-	-	-	-	-	-	95	3.10×10^{-5}-1.0×10^{-1}	7.50×10^{-6}	25.49
2	5	-	-	53	-	-	-	-	42	5.62×10^{-7}-1.0×10^{-1}	1.25×10^{-7}	24.28
3	5	-	-	-	53	-	-	-	42	6.02×10^{-7}-1.0×10^{-1}	1.23×10^{-7}	22.57
4	5	-	-	-	-	53	-	-	42	1.96×10^{-6}-1.0×10^{-1}	5.62×10^{-7}	27.71
5	5	-	-	-	-	-	53	-	42	3.85×10^{-5}-1.0×10^{-1}	5.20×10^{-6}	23.71
6	5	-	-	-	-	-	-	53	42	1.47×10^{-7}-1.0×10^{-1}	7.76×10^{-8}	28.95
7	5	2	-	-	-	-	-	53	40	9.00×10^{-8}-1.0×10^{-1}	6.30×10^{-8}	29.04
8	5	-	2	-	-	-	-	53	40	9.12×10^{-7}-1.0×10^{-1}	2.45×10^{-7}	26.66
9	6	2	-	-	-	-	-	53	39	8.56×10^{-7}-1.0×10^{-1}	4.04×10^{-7}	25.76
10	7	2	-	-	-	-	-	53	38	7.84×10^{-6}-1.0×10^{-1}	2.85×10^{-6}	24.98
11	4	2	-	-	-	-	-	53	41	5.89×10^{-7}-1.0×10^{-1}	2.03×10^{-7}	16.74
12	5	1.5	-	-	-	-	-	53	42.5	3.45×10^{-7}-1.0×10^{-1}	4.47×10^{-8}	28.32
13	5	1	-	-	-	-	-	53	41	6.18×10^{-6}-1.0×10^{-1}	1.55×10^{-6}	24.95

Table 4.2. Optimization of membrane composition based on L_4 using PME and their potentiometric responses characteristics of Cu^{2+}.

S. No.	Composition of membrane (w/w; mg)									Working concentration range (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mVdecade^{-1} of activity)
	L_4	NaTPB	KTpClPB	DBP	DOP	BA	*o*-NPOE	1-CN	PVC			
14	5	-	-	-	-	-	-	-	95	$2.75\times10^{-5}-1.0\times10^{-1}$	5.12×10^{-6}	25.71
15	5	-	-	58	-	-	-	-	37	$1.81\times10^{-7}-1.0\times10^{-1}$	6.60×10^{-8}	25.42
16	5	-	-	-	58	-	-	-	37	$2.88\times10^{-7}-1.0\times10^{-1}$	1.25×10^{-7}	31.94
17	5	-	-	-	-	58	-	-	37	$3.30\times10^{-6}-1.0\times10^{-1}$	6.02×10^{-7}	27.99
18	5	-	-	-	-	-	58	-	37	$5.62\times10^{-7}-1.0\times10^{-1}$	1.38×10^{-7}	22.13
19	5	-	-	-	-	-	-	58	37	$4.59\times10^{-7}-1.0\times10^{-1}$	9.85×10^{-8}	29.03
20	5	2	-	-	-	-	-	58	35	$1.04\times10^{-7}-1.0\times10^{-1}$	7.07×10^{-8}	29.43
21	5	-	2	-	-	-	-	58	35	$1.44\times10^{-7}-1.0\times10^{-1}$	7.41×10^{-8}	27.37
22	6	2	-	-	-	-	-	58	34	$3.93\times10^{-6}-1.0\times10^{-1}$	5.48×10^{-7}	28.36
23	7	2	-	-	-	-	-	58	33	$7.63\times10^{-6}-1.0\times10^{-1}$	3.49×10^{-6}	26.58
24	4	2	-	-	-	-	-	58	36	$9.27\times10^{-7}-1.0\times10^{-1}$	4.43×10^{-7}	24.50
25	5	1.5	-	-	-	-	-	58	35.5	$6.42\times10^{-7}-1.0\times10^{-1}$	2.59×10^{-7}	26.47
26	5	1	-	-	-	-	-	58	36	$8.78\times10^{-6}-1.0\times10^{-1}$	5.98×10^{-6}	27.95

Table 4.3. **Optimization of membrane composition based on L_3 using CGE and their potentiometric responses characteristics of Cu^{2+}.**

S. No.	Composition of membrane (w/w; mg)									Working concentration range (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mVdecade^{-1} of activity)
	L_3	NaTPB	KTpClPB	DBP	DOP	BA	*o*-NPOE	1-CN	PVC			
A1	5	-	-	-	-	-	-	-	95	1.68×10^{-5}-1.0×10^{-1}	8.07×10^{-6}	26.80
A2	5	-	-	54	-	-	-	-	41	6.54×10^{-7}-1.0×10^{-1}	2.56×10^{-7}	25.04
A3	5	-	-	-	54	-	-	-	41	3.84×10^{-6}-1.0×10^{-1}	9.58×10^{-7}	25.76
A4	5	-	-	-	-	54	-	-	41	5.47×10^{-7}-1.0×10^{-1}	1.84×10^{-7}	31.02
A5	5	-	-	-	-	-	54	-	41	8.36×10^{-7}-1.0×10^{-1}	4.92×10^{-7}	27.37
A6	5	-	-	-	-	-	-	54	41	2.75×10^{-7}-1.0×10^{-1}	8.32×10^{-8}	29.18
A7	5	2	-	-	-	-	-	54	39	7.41×10^{-8}-1.0×10^{-1}	2.75×10^{-8}	29.39
A8	5	-	2	-	-	-	-	54	39	4.23×10^{-7}-1.0×10^{-1}	1.63×10^{-7}	27.69
A9	6	2	-	-	-	-	-	54	38	9.19×10^{-6}-1.0×10^{-1}	6.41×10^{-6}	30.45
A10	7	2	-	-	-	-	-	54	37	8.46×10^{-6}-1.0×10^{-1}	4.83×10^{-6}	28.97
A11	4	2	-	-	-	-	-	54	40	3.58×10^{-7}-1.0×10^{-1}	9.45×10^{-8}	24.36
A12	5	1.5	-	-	-	-	-	54	39.5	6.73×10^{-7}-1.0×10^{-1}	2.78×10^{-7}	26.75
A13	5	1	-	-	-	-	-	54	40	7.92×10^{-6}-1.0×10^{-1}	3.69×10^{-6}	27.53

Table 4.4. **Optimization of membrane composition based on L_4 using CGE and their potentiometric responses characteristics of Cu^{2+}.**

S. No.	Composition of membrane (w/w; mg)									Working concentration range (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mVdecade^{-1} of activity)
	L_4	NaTPB	KTpClPB	DBP	DOP	BA	*o*-NPOE	1-CN	PVC			
A14	5	-	-	-	-	-	-	-	95	1.47×10^{-5}-1.0×10^{-1}	7.21×10^{-6}	26.34
A15	5	-	-	55	-	-	-	-	40	5.62×10^{-7}-1.0×10^{-1}	2.78×10^{-7}	25.83
A16	5	-	-	-	55	-	-	-	40	2.97×10^{-6}-1.0×10^{-1}	8.96×10^{-7}	27.29
A17	5	-	-	-	-	55	-	-	40	4.38×10^{-7}-1.0×10^{-1}	1.54×10^{-7}	30.56
A18	5	-	-	-	-	-	55	-	40	7.25×10^{-7}-1.0×10^{-1}	3.47×10^{-7}	28.72
A19	5	-	-	-	-	-	-	55	40	3.54×10^{-7}-1.0×10^{-1}	9.15×10^{-8}	29.02
A20	5	2	-	-	-	-	-	55	38	6.60×10^{-8}-1.0×10^{-1}	2.60×10^{-8}	29.49
A21	5	-	2	-	-	-	-	55	38	8.73×10^{-7}-1.0×10^{-1}	4.63×10^{-7}	24.97
A22	6	2	-	-	-	-	-	55	37	5.87×10^{-6}-1.0×10^{-1}	2.32×10^{-6}	28.32
A23	7	2	-	-	-	-	-	55	36	3.79×10^{-6}-1.0×10^{-1}	1.62×10^{-6}	31.28
A24	4	2	-	-	-	-	-	55	39	2.45×10^{-7}-1.0×10^{-1}	8.27×10^{-8}	26.85
A25	5	1.5	-	-	-	-	-	55	38.5	9.38×10^{-7}-1.0×10^{-1}	4.93×10^{-7}	27.65
A26	5	1	-	-	-	-	-	55	39	1.79×10^{-6}-1.0×10^{-1}	8.49×10^{-7}	28.16

Table 4.5. **Optimization of membrane composition based on L_3 using CPGE and their potentiometric responses characteristics of Cu^{2+}.**

S. No.	Composition of membrane (w/w; mg)									Working concentration range (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mVdecade^{-1} of activity)
	L_3	NaTPB	KTpClPB	DBP	DOP	BA	*o*-NPOE	1-CN	PVC			
B1	5	-	-	-	-	-	-	-	95	8.32×10^{-6}-1.0×10^{-1}	4.61×10^{-6}	26.84
B2	5	-	-	55	-	-	-	-	40	4.87×10^{-7}-1.0×10^{-1}	2.08×10^{-7}	25.98
B3	5	-	-	-	55	-	-	-	40	9.64×10^{-7}-1.0×10^{-1}	5.73×10^{-7}	28.36
B4	5	-	-	-	-	55	-	-	40	3.95×10^{-7}-1.0×10^{-1}	1.09×10^{-7}	29.87
B5	5	-	-	-	-	-	55	-	40	5.71×10^{-7}-1.0×10^{-1}	2.82×10^{-7}	30.12
B6	5	-	-	-	-	-	-	55	40	2.98×10^{-7}-1.0×10^{-1}	8.93×10^{-8}	29.16
B7	5	2	-	-	-	-	-	55	38	1.31×10^{-8}-1.0×10^{-1}	7.76×10^{-9}	29.39
B8	5	-	2	-	-	-	-	55	38	6.24×10^{-7}-1.0×10^{-1}	3.57×10^{-7}	25.78
B9	6	2	-	-	-	-	-	55	37	4.56×10^{-6}-1.0×10^{-1}	1.98×10^{-6}	28.57
B10	7	2	-	-	-	-	-	55	36	2.78×10^{-6}-1.0×10^{-1}	8.46×10^{-7}	30.97
B11	4	2	-	-	-	-	-	55	39	2.08×10^{-7}-1.0×10^{-1}	7.97×10^{-8}	28.37
B12	5	1.5	-	-	-	-	-	55	38.5	7.82×10^{-7}-1.0×10^{-1}	3.46×10^{-7}	26.23
B13	5	1	-	-	-	-	-	55	39	9.87×10^{-7}-1.0×10^{-1}	5.68×10^{-7}	28.85

Table 4.6. **Optimization of membrane composition based on L_4 using CPGE and their potentiometric responses characteristics of Cu^{2+}.**

S. No.	Composition of membrane (w/w; mg)									Working concentration range (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mVdecade^{-1} of activity)
	L_4	NaTPB	KTpClPB	DBP	DOP	BA	*o*-NPOE	1-CN	PVC			
B14	6	-	-	-	-	-	-	-	94	6.81×10^{-6}-1.0×10^{-1}	3.57×10^{-6}	27.05
B15	6	-	-	53	-	-	-	-	41	3.46×10^{-7}-1.0×10^{-1}	1.04×10^{-7}	26.76
B16	6	-	-	-	53	-	-	-	41	7.26×10^{-7}-1.0×10^{-1}	4.52×10^{-7}	25.46
B17	6	-	-	-	-	53	-	-	41	5.64×10^{-7}-1.0×10^{-1}	2.31×10^{-7}	24.67
B18	6	-	-	-	-	-	53	-	41	4.86×10^{-7}-1.0×10^{-1}	2.04×10^{-7}	28.93
B19	6	-	-	-	-	-	-	53	41	2.25×10^{-7}-1.0×10^{-1}	8.16×10^{-8}	29.20
B20	6	2	-	-	-	-	-	53	39	1.02×10^{-8}-1.0×10^{-1}	6.30×10^{-9}	29.58
B21	6	-	2	-	-	-	-	53	39	5.46×10^{-7}-1.0×10^{-1}	2.82×10^{-7}	26.72
B22	7	2	-	-	-	-	-	53	39	3.23×10^{-6}-1.0×10^{-1}	8.72×10^{-7}	27.18
B23	8	2	-	-	-	-	-	53	37	6.88×10^{-6}-1.0×10^{-1}	3.48×10^{-6}	30.24
B24	5	2	-	-	-	-	-	53	40	1.42×10^{-7}-1.0×10^{-1}	6.28×10^{-8}	27.64
B25	6	1.5	-	-	-	-	-	53	39.5	4.20×10^{-7}-1.0×10^{-1}	1.28×10^{-7}	28.87
B26	6	1	-	-	-	-	-	53	40	5.87×10^{-7}-1.0×10^{-1}	1.94×10^{-7}	31.42

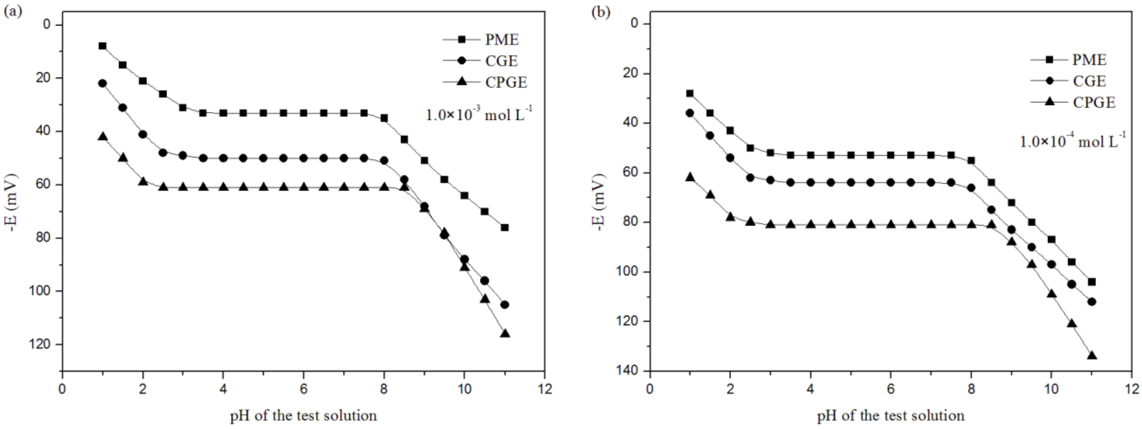

Fig. 4.5. **Potential vs. pH response of the PME, CGE and CPGE in presece of (a) 1.0 × 10^{-3} mol L^{-1} and (b) 1.0 × 10^{-4} mol L^{-1} Cu^{2+} ion solutions at different pH.**

4.4.3. Influence of pH on the Performance of the Sensor

In order to check the effect of pH on the proposed electrode, the potential of the membrane electrodes were collected at 1.0×10^{-3} mol L^{-1} and 1.0×10^{-4} mol L^{-1} Cu^{2+} ion solution by varying the pH of the solutions from 1.0 to 12.0. The pH was adjusted by the addition of 1.0×10^{-1} mol L^{-1} HCl/NaOH and from the obtained potential a graph was drawn for potential and pH of the solution (Fig. 4.5 (a) and (b)). It is revealed from the Fig. 4.5 that potential response for PME remains constant over pH range 3.0 to 7.5, 2.5 to 8.0 for CGE and 2.0 to 8.5 for CPGE. Therefore, the same was regarded as the working pH range for these electrodes. The change in potential at higher pH may be attributed to the formation of metal hydroxides species in the matrix [44] and the deviation at low pH may be regarded as effect of protonation of ionophore [45] and the electrodes start responding to H_3O^+ ions along with Cu^{2+} ions leading to an increase in the potential.

4.4.4. Effect of Interfering Ions on the Performance of the Proposed Sensor

The most important parameter which reflects the applicability of an ion selective electrode is its selectivity, which is measured in terms of the selectivity coefficients. The potentiometric selectivity coefficients for CPGE based on L_3 and L_4 were determined according to the IUPAC recommended fixed interference method (FIM). In this method, the selectivity coefficient was evaluated from the potential measurement on solutions containing a fixed concentration of interfering ion (1.0×10^{-2} mol L^{-1}) and varying the amount of Cu^{2+} ion solution ranging from 1.0×10^{-1}-1.0×10^{-9} mol L^{-1}. The potential values so obtained were then plotted versus activity of Cu^{2+}. The linear portion of potential response curve then extrapolated and the value of a_{Cu2+} was obtained from the intersection point. The potentiometric selectivity coefficients were then calculated using the following expression [46]:

$$K_{A,B}^{Pot} = \frac{(a_A)}{(a_B)^{z_A/z_B}} \qquad (1)$$

Where a_A is the activity of primary ion A (Cu^{2+}) at the lower detection limit in the presence of interfering ion B, a_B, the activity of interfering ion B and z_A and z_B are their respective charges. The values of selectivity coefficients so determined for CPGE are compiled in the Table 4.7. From the selectivity coefficients given in the Table 4.7 it has been observed that the electrodes are highly selective over a number of monovalent, divalent and trivalent ions. However, selectivity coefficients obtained for Cd^{2+} are not very modest and it caused some interference if present in eminent concentration. It has been observed that, CPGE (B20) with membrane composition L_4: PVC: 1-CN: NaTPB in the ratio of 6:39:53:2 (w/w, mg) performs comparatively better regarding selectivity than CPGE (B7) having membrane composition of L_3: PVC: 1-CN: NaTPB in the ratio of 5:38:55:2 (w/w, mg) which showed significant interferences for Cd^{2+}. Thus, these electrodes could be of importance even in sample containing rare earth metals, alkaline earth metals and lanthanides for the estimation of Cu^{2+} ion to a good extent.

4.4.5. Determination of Dynamic Response Time and Lifetime of the Sensor

Dynamic response time is also an important factor of an ISE. According to IUPAC recommendations, the response time of an ion selective electrode is defined as the length of time between the instant at which the ion selective electrode and reference electrode are immersed in the solution and the moment at which the potential of the cell reaches its steady- state value within ±1 mV [47].

Response time of the sensor can be measured by consecutively changing the concentration of the test solution from 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1}. The average time needed to attain a potential response in the electrodes lies within ±1 mV range value of final equilibrium after immersing successively in a series of Cu^{2+} ion solution, each having a 10-fold difference in concentration was 13 s for PME (20), 11 s for CGE (A20) and 9 s for CPGE (B20) as shown in Fig. 4.6. The good response of the CPGE as compared to CGE is may be due to the higher conductivity of pyrolytic graphite as compared to that of graphite rod. The PME, CGE and CPGE could be used over a period of 3, 4 and 5 months, respectively without observing significant divergence in response time, slope and working concentration range. After this period, there was a slight change in potentiometric characteristics and this could be corrected by re-equilibrating the membrane with 1.0 × 10^{-1} mol L^{-1} solution of Cu^{2+} ion for 3 days.

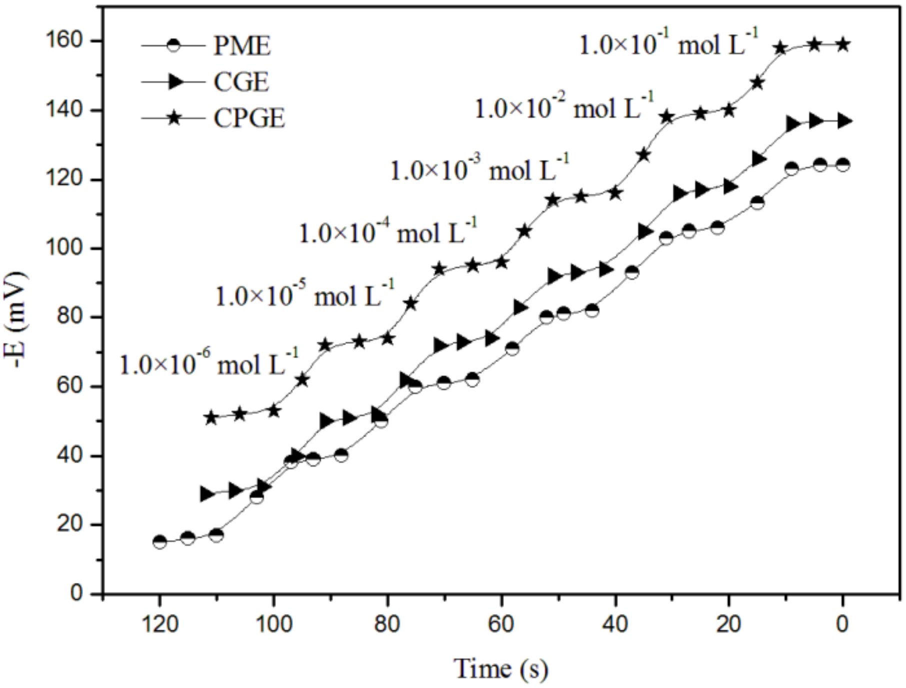

Fig. 4.6. Dynamic response time of the proposed copper sensor based on L_4 for step changes in concentration of Cu^{2+} ion with (a) PME, (b) CGE and (c) CPGE.

4.4.6. Effect of Non-Aqueous Media on the Performance of the Sensor

Non-aqueous content might be present in analytical samples; therefore the efficiency of the sensor was also estimated in partially non-aqueous solutions in range of 10-40% (v/v) non-aqueous content in methanol-water, ethanol-water and acetonitrile-water mixtures and the results are compiled in Table 4.8. Therefore, the electrode is not suitable for using in methanol-water mixture above 10% (v/v) concentration. This may be due to greater solubility of the ligand in methanol which causes leaching of ionophore from the membrane phase. However, the electrode can be satisfactorily used in ethanol-water and acetonitrile-water solutions up to 30%.

Table 4.7. Selectivity coefficients of Cu^{2+} selective electrodes based on L_3 and L_4 using CPGE.

Interfering ions (B)	Selectivity Coefficients ($K^{FIM}_{Cu^{2+},B}$)	
	CPGE B7 (L_3)	CPGE B20 (L_4)
Ni^{2+}	3.2×10^{-3}	1.8×10^{-3}
Zn^{2+}	6.4×10^{-3}	2.7×10^{-3}
Co^{2+}	5.8×10^{-3}	2.4×10^{-3}
Cd^{2+}	7.3×10^{-2}	3.6×10^{-2}
Hg^{2+}	9.7×10^{-3}	5.2×10^{-3}
Mg^{2+}	4.6×10^{-4}	1.3×10^{-4}
Ca^{2+}	8.5×10^{-3}	6.1×10^{-3}
Na^{+}	2.9×10^{-4}	1.4×10^{-4}
La^{3+}	6.1×10^{-3}	4.9×10^{-3}
Ce^{3+}	3.8×10^{-3}	1.5×10^{-3}

Table 4.8. Effect of partially non-aqueous medium on the working of Cu^{2+} sensor based on L_4 using CPGE.

Non-aqueous content (%; v/v)	Working concentration range (mol L^{-1})	Slope (mVdecade^{-1} of activity)
0	1.02×10^{-8} - 1.0×10^{-1}	29.58
Ethanol		
10	1.02×10^{-8}-1.0×10^{-1}	29.58
20	1.02×10^{-8}-1.0×10^{-1}	29.58
30	1.13×10^{-8}-1.0×10^{-1}	29.42
35	2.41×10^{-8}-1.0×10^{-1}	28.79
40	5.86×10^{-7}-1.0×10^{-1}	26.94
Methanol		
10	1.02×10^{-8}-1.0×10^{-1}	29.58
20	3.47×10^{-8}-1.0×10^{-1}	28.95
30	8.64×10^{-8}-1.0×10^{-1}	28.76
35	2.52×10^{-7}-1.0×10^{-1}	27.98
40	6.39×10^{-7}-1.0×10^{-1}	26.58
Acetonitrile		
10	1.02×10^{-8}-1.0×10^{-1}	29.58
20	1.02×10^{-8}-1.0×10^{-1}	29.58
30	1.58×10^{-8}-1.0×10^{-1}	29.56
35	4.26×10^{-8}-1.0×10^{-1}	28.83
40	7.96×10^{-7}-1.0×10^{-1}	27.46

4.4.7. Comparative Performance Characteristics of Polymeric Membrane Electrode (PME), Coated Graphite Electrode (CGE) and Coated Pyrolytic Graphite Electrode (CPGE)

High affinity shown by membrane of ligands (L_3 and L_4) have proved that, they act as suitable and selective Cu^{2+} ion-sensors. The sensor number 20 based on L_4 containing 1-CN as the solvent mediator with the composition of L_4: PVC: 1-CN: NaTPB in the ratio of 5:35:58:2 (w/w; mg) exhibits linear response (1.04×10^{-7}-1.0×10^{-1} mol L^{-1}) and Nernstian compliance (29.4 mV $decade^{-1}$ of activity) with detection limit of 7.07×10^{-8} mol L^{-1}.

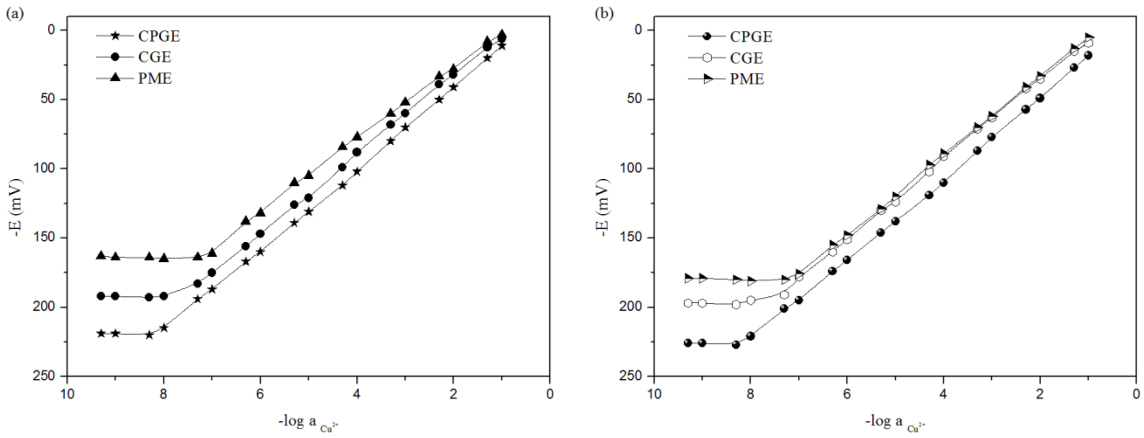

Fig. 4.7. Potentiometric characteristic calibration plot for Cu^{2+} ion-selective sensors with (a) L_3 and (b) L_4.

The performance of this PME was compared with CGE and CPGE based on ligand L_4 and the results are depicted in the Table 4.9. The performance of PME, CGE and CPGE are shown in Fig. 4.7 (a) and (b), which reveals their linearity and Nernstian slope. Comparison Table 4.9 showed that CPGE shows the better response characteristic in comparison to PME and CGE with respect to the wide working concentration range of 1.02×10^{-8}-1.0×10^{-1} mol L^{-1}, the Nernstian slope of 29.5 mV $decade^{-1}$ of activity and low detection limit of 6.30×10^{-9} mol L^{-1}. High LOD of PME is accountable because of deplation of membrane ingradients from internal solution into analyte solution through membrane [48].

4.5. ANALYTICAL APPILCATIONS

The selectivity for Cu^{2+} ions exhibited by the sensor makes it potentially suitable for monitoring of Cu^{2+} ion in real samples and besides this, the sensor was successfully employed as an indicator electrode for the potentiometric titration of Cu^{2+} ion with EDTA.

4.5.1. Potentiometric Titration

The sensor was found to work well under laboratory conditions and it was used as an indicator electrode in the potentiometric titration of Cu^{2+} ion solution against EDTA solution.

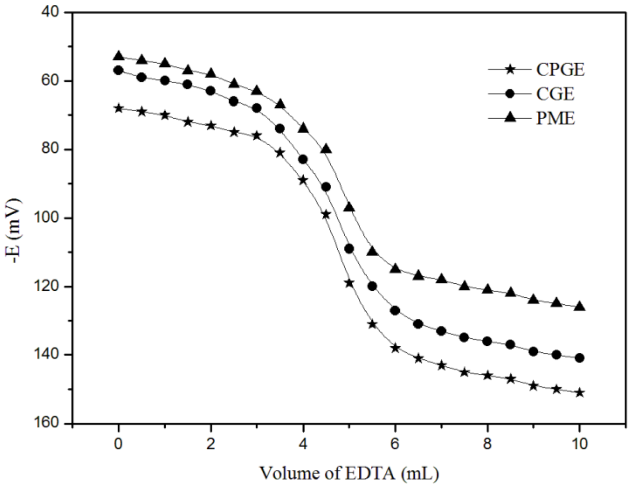

Fig. 4.8. Potentiometric titration curve of 25 mL of 2.0×10^{-3} mol L^{-1} solution of Cu^{2+} ion with 1.0×10^{-2} mol L^{-1} EDTA at pH 5.5.

For this purpose, a potentiometric titration of 25 ml of 2.0×10^{-3} mol L^{-1} Cu^{2+} ion solution against 1.0×10^{-2} mol L^{-1} solution of EDTA at pH 5.5 was carried out using these electrodes and the titration plot obtained had sigmoid shapes which also supports that these electrodes are selective to Cu^{2+} ion and the inflexion point corresponds to 1:1 stiochiometry of Cu^{2+}-EDTA complex and therefore, these electrodes can be used as an indicator electrode for the potentiometric estimation of Cu^{2+} ion. The titration plot for electrodes PME (20), CGE (A20) and CPGE (B20) are shown in Fig. 4.8, from which we can accurately determine the amount of Cu^{2+} ion present in the sample.

4.5.2. Determination of Cu^{2+} in Soil and Water Samples

The sensor (CPGE-B20) was used for the monitoring of Cu^{2+} in Ganga River (Roorkee) as well as waste water taken from the State Infrastructure and Industrial Development Corporation Uttaranchal (SIDCUL) Industrial area and Indian Institute of Technology-Roorkee, Chemistry Department. The samples collected were filtered through a Millipore membrane and the filtered solution was then treated with 1 mol L^{-1} nitric acid. The pH of these samples was adjusted to 5.5 before the measurement. The potentiometry results are in good agreement with those obtained by AAS in Table 4.10. The soil samples were collected from Haridwar, Risikesh and Institute Hospital (IITR) region. The soil samples were digested in a cleaned Teflon beaker by treating 2 g of each soil sample with 10 mL of nitric acid. A 5:3:5 mixture of nitric acid, perchloric acid and concentrated hydrofluoric acid was added, followed by controlled heating until white fumes evolved. The solution was filtered and diluted with deionised water to a final volume of 25 mL into a volumetric flask [49]. The results obtained by potentiometry were found in good agreement with those obtained by AAS and results are compiled in Table 4.11.

4.5.3. Determination of Cu^{2+} in Medicinal Plants

The plant samples were collected from Haridwar. An accurately weighed ~2.0 g of dried powdered plant samples was digested with a 5:1 mixture of nitric acid (25% v/v) and perchloric acids, followed by controlled heating until the evolution of gases ceased. A 15 mL of deionised water was added to this mixture and filtered through a Millipore membrane into a 25 mL volumetric flask [49]. The results obtained were then compiled in Table 4.12 which showed that potentiometric measurements of Cu^{2+} ions in medicinal plants are in good agreement with those obtained by AAS and thus, the proposed sensor (CPGE-B20) shows its utility in quantification of Cu^{2+} in real samples.

4.6. CONCLUSIONS

The studies on a large number of electrodes based on ligands L_3 and L_4 have shown that the plasticizer 1-chloronaphthalene (1-CN) enhances the performance characteristics of electrodes better than the rest of the plasticizers. CPGE based on ligand L_4 was found to be best in performance characteristics. The composition of the membrane with the best performance indicators was found to be L_4: PVC: 1-CN: NaTPB in the ratio of 6:39:53:2 (w/w, mg) with the detection limit of 6.30×10^{-9} mol L^{-1}. The potentiometric characteristics based on CPGE shows Nernstian slope of 29.5 mV decade^{-1} of activity and is independent of pH in regions 2.0 to 8.5. The response timeof the electrode was found to be quite good (9 s) and can work satisfactorily in partially non-aqueous content up to 30% of acetonitrile-water and ethanol-water mixture and can tolerate 10% of methanol-water system. Comparative studies of all these electrodes show that CPGE is superior over CGE and PME. The sensor was successfully employed for the monitoringof Cu^{2+} in real samples *viz.* water, soil and herbal medicinal plants. Besides this, the proposed sensor was successfully used in the potentiometric titration of Cu^{2+} ions with EDTA as an indicator electrode. A comparison of the performance characteristics with previously reported electrodes [19, 23, 25, 26, 28-31], as shown in Table 4.13 implies that the proposed sensor is superior to those listed in Table 4.13 in terms of sensitivity and detection limit. Therefore, we wish that present work is an improved addition to the existing set of copper selective ISEs.

Table 4.9. Potentiometric response characteristics of the Cu^{2+} selective electrodes based on PME, CGE and CPGE.

Properties	Values/range		
	PME	CGE	CPGE
Optimized membrane composition	(L_2)(5 mg): PVC (35 mg): 1-CN (58 mg): NaTPB (2 mg)	L_2 (5 mg): PVC (38 mg): 1-CN (55 mg): NaTPB (2 mg)	L_2 (6 mg): PVC (39 mg): 1-CN (53 mg): NaTPB (2 mg)
Conditioning time	3 days in 0.1 M $Cu(NO_3)_2$	1 day in 1 mM $Cu(NO_3)_2$	1 day in 1 mM $Cu(NO_3)_2$
Working concentration range (mol L^{-1})	1.04×10^{-7}-1.0×10^{-1}	6.60×10^{-8}-1.0×10^{-1}	1.02×10^{-8}-1.0×10^{-1}
Detection limit (mol L^{-1})	7.07×10^{-8}	2.60×10^{-8}	6.30×10^{-9}
Slope (mV decade^{-1} of activity)	29.43	29.49	29.58
Response time (s)	13	11	9
Life span (months)	3	4	5
pH range	3.0 to 7.5	2.5 to 8.0	2.0 to 8.5

Table 4.10. Determination of Cu^{2+} concentration (mg L^{-1}) in water samples.

Samples	CPGE(B7)*±SD	AAS*±SD
Ganga water	04.54±0.10	04.42±0.17
Industrial water	13.91±0.27	14.05±0.24
Laboratory waste water	12.69±0.37	12.72±0.15

*Mean value ± standard deviation (triplicate measurements).

Table 4.11. Determination of Cu^{2+} concentration (mg Kg^{-1}) in soil samples.

Samples	CPGE(B7)*±SD	AAS*±SD
Sample 1 (IITR Hospital)	3.29±0.31	3.45±0.25
Sample 2 (Haridwar)	4.12±0.34	4.10±0.15
Sample 3 (Rishikesh)	3.65±0.14	3.79±0.05

*Mean value ± standard deviation (triplicate measurements).

Table 4.12. Determination of Cu^{2+} concentration (mg Kg^{-1}) in medicinal plant samples.

Samples	CPGE(B7)*±SD	AAS*±SD
Adhatoda vasica	07.49±0.21	07.55±0.16
Ocimum sanctum	12.75±0.35	12.66±0.18
Withania somnifera	15.60±0.46	15.72±0.23

*Mean value ± standard deviation (triplicate measurements).

Table 4.13. Comparison of performance characteristic of Cu^{2+} selective electrode with previously reported electrodes.

Ref. No.	Slope (mVdecade^{-1} of activity)	Linear range (mol L^{-1})	Detection limit (mol L^{-1})	pH range	Response time (s)	Life span (months)
[19]	29.50	5.0×10^{-8}-1.0×10^{-1}	4.0×10^{-8}	2.5-5.5	10.0	2.0
[26]	29.80	1.8×10^{-7}-1.0×10^{-1}	5.7×10^{-8}	2.0-8.0	5.0	4.0
[34]	29.34	6.0×10^{-8}-1.0×10^{-1}	4.0×10^{-8}	2.0-5.0	10.0	1.0
[35]	28.90	1.0×10^{-7}-1.0×10^{-1}	3.0×10^{-8}	2.5-6.0	10.0	4.0
[37]	30.00	1.0×10^{-6}-1.0×10^{-1}	1.0×10^{-7}	3.0-9.0	15.0	5.0
[38]	30.00	1.9×10^{-6}-1.0×10^{-1}	NM	3.0-7.5	12.0	3.0
[39]	29.50	6.0×10^{-6}-1.0×10^{-2}	4.0×10^{-6}	4.0-7.0	30.0-70.0	3.0
[40]	31.76	NM	2.8×10^{-7}	5.0	15.0	NM
[41]	28.80	1.0×10^{-6}-1.0×10^{-1}	7.0×10^{-7}	1.3-6.0	10.0-40.0	2.0
[42]	29.50	8.7×10^{-7}-1.0×10^{-1}	1.1×10^{-7}	3.0-7.0	6.0	3.0
[43]	29.54	1.2×10^{-7}-1.0×10^{-1}	9.8×10^{-8}	4.0-6.0	9.0	3.5
[44]	30.00	3.0×10^{-7}-1.0×10^{-2}	2.5×10^{-7}	3.0-7.4	10.0	4.0
[45]	30.30	1.2×10^{-6}-1.0×10^{-2}	8.9×10^{-7}	4.5-8.5	5.0	NM
This work	29.58	1.0×10^{-8}-1.0×10^{-1}	6.3×10^{-9}	2.0-8.5	9.0	5.0

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Chapter 5

“N_3O_2 Chalcone Ligand as Ce^{3+} Ion-Selective Sensors”

5.1. INTRODUCTION

The rare earth`s elements (RRE) are widely distributed in low concentration throughout the earth crust and are considered slightly toxic. Cerium is traditionally referred to as one of the rare earths, however, in reality it is more plentiful in the earth`s crust than many other elements. It is the most widely distributed among the rare earths, averaging 22 mg kg^{-1} in the earth crust [1-3]. It is found in monazite, ceric bastnaesite and silicate rocks. It has many applications in the area of lightning and television, metallurgy, glass and ceramics and as one of the active components in catalytic converters in vehicles. It is widely used in the production of ductile iron, cast steel, stainless steel [4] and in some rare earth`s alloys. Cerium is also used in nuclear reactors, agriculture, forestry and animal husbandry. Inhalation exposure of cerium in human has been known to cause sensitivity to heat, itching and an increased awareness odor and test. The increasing exploitation of cerium and several reports of cerium toxicity [5] have attracted the researchers to monitor it in various environmental samples. Thus, the determination of cerium in different samples is of special interest.

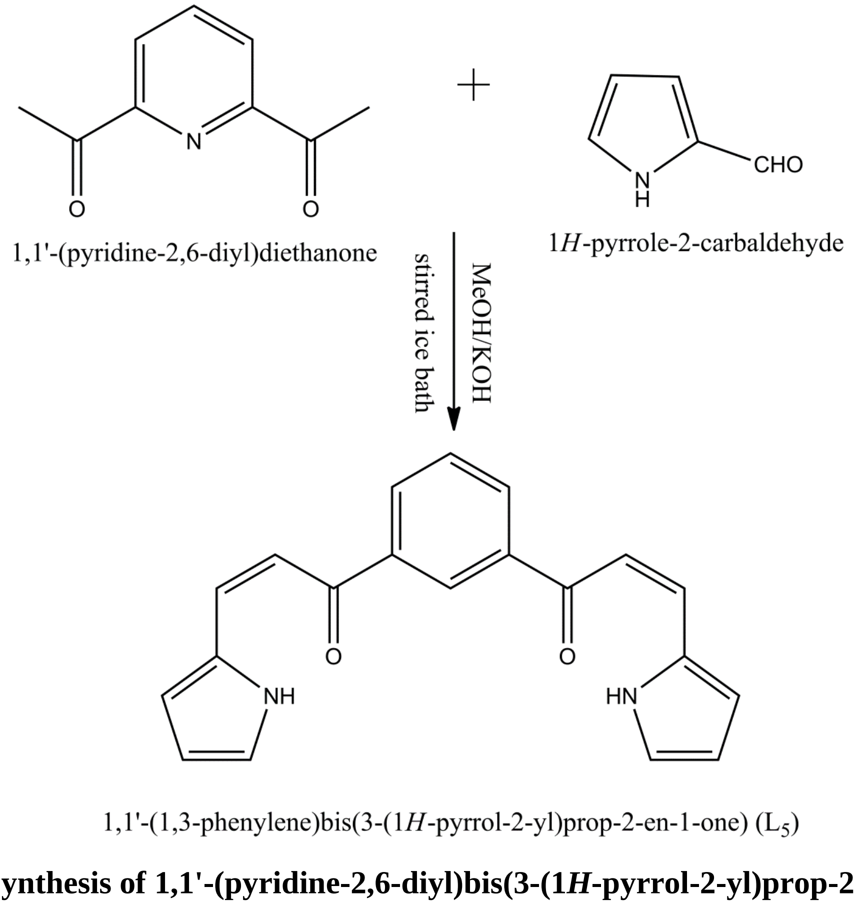

Fig. 5.1. Synthesis of 1,1'-(pyridine-2,6-diyl)bis(3-(1*H*-pyrrol-2-yl)prop-2-en-1-one) (L$_5$).

A number of sophisticated techniques such as inductively coupled plasma-atomic emission spectroscopy (ICP-AES) [6], inductively coupled plasma-mass spectrometry (ICP-MS) [7, 8], X-ray fluorescence (XRF) [9], neutron activation analysis (NAA) [10] and DPASV (differential pulse anodic stripping voltammetry) [11] have been described for the estimation of cerium in various samples. Although, these techniques have been employed for the determination of cerium but are not very convenient for the analysis of a large number of samples as they generally require of expertise and large infrastructure backup. Potentiometric sensors based on ISE are especially useful for direct measurement of analyte because of the advantages offerred in terms of sensitivity and selectivity, reproducibility and costeffectiveness [12-14].

5.1.1. Ce^{3+} ion-selective electrodes

Literature survey reveal that a number of ion carriers have been employed for the monitoring of Ce^{3+} ion [15-24]. However, the reported ISE have suffered from narrow working concentration range, poor selectivity, low pH and high response times. Fabrication of new ISE with high selectivity and sensitivity, wide working concentration range, long life time and good reproducibility is always in need. Therefore, it is required to develop a better sensor for Ce^{3+} ion. Recently, we have prepared sensors of Cu^{2+}, Cd^{2+} and Mn^{2+} [25-27] by the fabrication of coated pyrolytic graphite electrode with improved selectivity and sensitivity. Thus, the present communication describes the synthesis of a novel chalcone 1,1'-(pyridine-2,6-diyl)bis(3-(1*H*-pyrrol-2-yl)prop-2-en-1-one) and thereby its application in the determination of Ce^{3+} ion in various environmental and industrial samples.

5.2. EXPERIMENTAL

5.2.1. Chemical and Reagents

Diacetyl pyridine, pyrrole-2-carbaldehyde, high molecular weight poly(vinyl chloride) (PVC) and *o*-nitrophenyloctylether (*o*-NPOE) Aldrich (USA); sodium tetraphenylborate (NaTPB), 1-chloronaphthalene (1-CN) BDH (UK); dioctylphthalate (DOP) Renkem (India); dibutylphthalate (DBP) CDH (India);Benzylacetate (BA) and Potassium tetrakis-p-(chlorophenyl)borate (KTpClPB) Fluka (Switzerland) were used as obtained.The nitrate and chloride salts of all the cations, ethylenediaminetetraacetic acid (EDTA) and solvents (ethanol, methanol, acetonitrile (ACN), tetrahydrofuran (THF), dimethylsulfoxide (DMSO), dimethylformamide (DMF), hexane and ethylacetate) utilised were of analytical reagent grade and made use of with no further purification. All the solutions of metal salts were prepared in double distilled water and standardized by appropriate chemical methods. Solutions of different concentration were prepared by diluting the standard stock solution of 1.0×10^{-1}mol L^{-1}. Double distilled water was used throughout the experiment.

5.2.2. Apparatus and Equipments

NMR (^{1}H and ^{13}C) spectra were recorded in deuterated DMSO d_6 on a 500 and 125 MHz NMR spectrometer (Bruker), respectively. Elemental analysis was performed on a Perkin-Elmer 2400 series CHNS/O analyzer. Atomic absorption spectrometer (AAS) experiment was performed on a Perkin Elmer Analyst 800 at wavelength of 240.7 nm using air-acetylene as flame. The conductance study was performed on an Orion 4 conductometer at 25±0.1 °C. The potential across the membranes were measured on an Orian 4 pH meter at 25±0.1 °C in conjunction with Ag/AgCl (NaCl 3 Mol L^{-1}) BASI 2056 as reference electrodes.

5.2.3. Synthesis of 1,1'-(pyridine-2,6-diyl)bis(3-(1*H*-pyrrol-2-yl)prop-2-en-1-one) (L_5)

The ligand was synthesised as shown in Fig. 5.1. In a typical reaction setup, KOH (in excess) dissolved in methanol-water (8:2, v/v) was added to a methanolic solution of diacetyl pyridine (2 mM, 326.5 mg) and stirred at ice bath for half an hour. Then pyrrole-2-carbaldehyde (4 mM, 384.5 mg) dissolved in methanol was added drop-wise in to the above solution and stirred for 3 h. The yellow precipitate that formed was filtered and washed with cold methanol and recrystallised in ethanol.

1,1'-(pyridine-2,6-diyl)bis(3-(1*H*-pyrrol-2-yl)prop-2-en-1-one) Yield: 83% analytically calculated for [$C_{19}H_{15}N_3O_2$] (%):C, 71.91; H, 4.76; N, 13.24. Found C, 71.74; H, 4.93; N, 13.39. IR (KBr, cm^{-1}): 3366 (-NH), 2855, 1641 (-C=O), 1584, 1530, 1406, 1388, 1292, 1218, 1127, 1029 (Ar-). ^{1}H NMR (500 MHz) δ (ppm): 11.942 (s, 2H, -NH), 8.203-8.281 (m, 3H, *J*=39 Hz), 8.052-8.083 (d, 2H, *J*=15.5 Hz), 7.792-7.823 (d, 2H, *J*=15.5 Hz), 7.211 (s, 2H), 6.871 (s, 2H), 6.290-6.294 (d, 2H, *J*=2.0 Hz).^{13}CNMR (125 MHz) δ (ppm): 187.81, 153.62, 139.10, 135.17, 129.45, 125.22, 125.17, 117.05, 113.76, 111.12 (see appendix for spectra).

5.2.4. Fabrication of PVC Membranes

The quantity and nature of membrane ingredients such as plasticizer, ionophore, plasticizer/PVC ratio and especially lipophilic additives are known to significantly affect the selectivity and sensitivity. All these affect the potential response of the membrane sensor and hence need to optimize for maximum efficiency of the sensor.

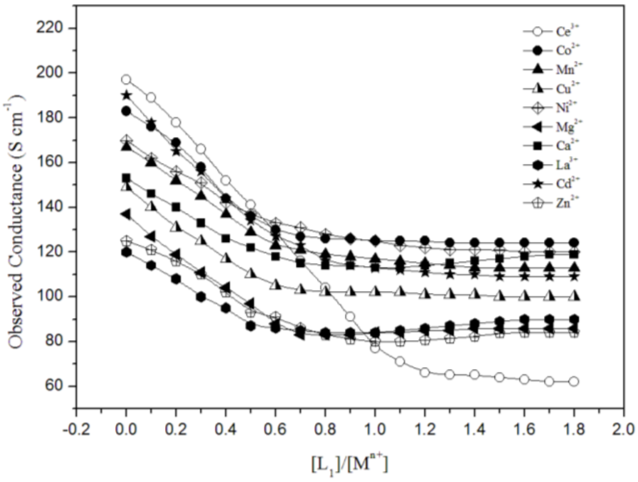

Fig. 5.2. Variation in the conductance of Ce^{3+} ion solution with the addition of L_5.

5.2.5. Preparation of Coated Graphite Electrode (CGE) and Coated Pyrolytic Graphite Electrode (CPGE)

The membrane has been fabricated as suggested by Craggs*et. al*, [28]. Polymeric membrane based on high molecular weight poly(vinyl chloride) (PVC) was prepared by dissolving appropriate amount of membrane ingredients (L_5, anionic excluders (NaTPB and KTpClPB), plasticizers (BA, 1-CN, DOP, DBP and *o*-NPOE) and PVC) in minimum amount of THF and the solvent was evaporated off to obtain a concentrated solution. Graphite electrode/pyrolytic graphite electrode of spectroscopic grade with copper wire glued at one end was dipped in to the above solution for few seconds and removed out and allowed the electrode to get dry. The process was repeated several times till the membrane was formed over graphite electrode/pyrolytic graphite electrode.

5.2.6. Conditioning of Membrane and Potential Measurements

The CGE and CPGE were conditioned for 1 day prior to potentiometric measurements in 1.0×10^{-3} mol L^{-1} $Ce(NO_3)_3$ solution. The potential have been measured by varying the concentration of $Ce(NO_3)_3$ solution in the range 1.0×10^{-1}-1.0×10^{-9} mol L^{-1}. The standard solution had been obtained by gradual dilution of stock solution 1.0×10^{-1} mol L^{-1} $Ce(NO_3)_3$. The potential measurements with the CGE and CPGE were performed on pH meter (Orion 4) at 25±0.1°C in conjunction of Ag/AgCl (NaCl 3 mol L^{-1}) BASI 2056 as reference electrode with the following cell assemblies;

CGE||Test solution||Ag/AgCl|NaCl(3 mol L^{-1})

CPGE||Test solution||Ag/AgCl|NaCl(3 mol L^{-1})

Activity coefficients were calculated according to Debye Huckel procedure [29].

5.3. RESULTS AND DISCUSSION

5.3.1. Complexation Study

In preliminary experiments, the complexation of L_5 with a number of cations has been investigated conductometrically in methanol solution in order to obtain an idea about the stoichiometry of the resulting complexes at 25±0.1°C. For this purpose, 25 mL of 1.0×10^{-4} mol L^{-1} cation solution was titrated against a 1.0×10^{-2} mol L^{-1} ligand solution in methanol. The conductance of the solution was measured after each addition of the titrant. The conductance variation plots with different metal ions as a function of the $[L_5]/[M^{n+}]$ molar ratio is depicted in Fig. 5.2. It is from the Fig. 5.2 that the conductance variation of Ce^{3+} ion solution showed maximum variation with the addition of L_5, initially the conductance falling off with the addition of L_5 which show that Ce^{3+} are strongly interacting with the L_5 added. A stage is arrived when conductance of solution nearly becomes constant and further addition of ligand does not cause any appreciable change in the conductance which demonstrates that all of the metal ions have been consumed by the L_5. The break point in the conductance variation plots gives the stoichiometry of the resulting complexes and it has been observed that the stoichiometry of Ce^{3+} to L_5 is 1:1.

5.3.2. Membrane's Composition Optimization and Potential Measurements

All the characteristics like linearity, selectivity and sensitivity obtained for a specified ionophore largely depends on the membrane ingredients, nature of plasticizer [30] and additives added [31, 32]. Therefore, to improve the performance of polymeric membranes based on L_5 a number of electrodes having different composition were fabricated and studied.

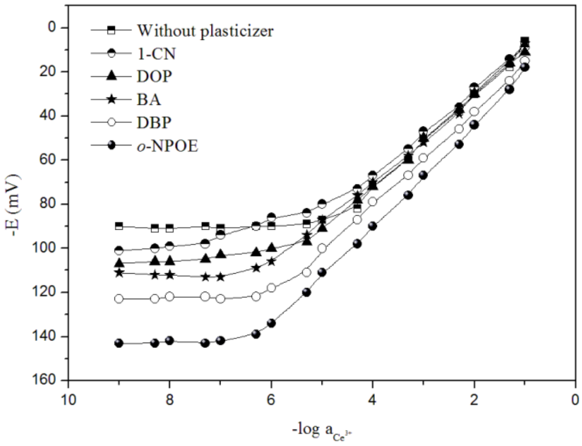

Fig.5.3. **Potentiometric characteristics graph showing changes of membrane potential as a function of Ce^{3+} ion concentration for the membranes incorporating L_5 as ionophore.**

The potential of various electrodes were measured as a function of Ce^{3+} ion concentration in the range of 1.0×10^{-1}-1.0×1^{9}mol L^{-1}. The potential response of CGE and CPGE were first investigated only with L_5 and PVC and it was found that membranes of L_5 without plasticizer show linear response over a working concentration range of 4.5×10^{-5}-1.7×10^{-5}mol L^{-1},with a slope of 16.6±0.3 mV decade^{-1} of activity. It is well known that the incorporation of plasticizer enhances the performance of the electrodes. Thus, effect of various plasticizers *viz*, BA, DOP, DBP, *o*-NPOE and 1-CN were investigated in to and the response obtained with plasticized membranes are shown in Fig. 5.3. It has been observed that the membranes which were plasticized showed improved response. The optimized membrane composition of L: *o*-NPOE: NaTPB: PVC≡7:59:3:31 (w/w, mg) exhibited the best performance in terms of wide working concentration range, low detection limit and Nernstian slope, respectively.

5.3.3. Effect of pH on the Performance of Sensor

The effect of pH on the performance of electrodes were examined by measuring their potentiometric response for 1.0×10^{-3} mol L^{-1} and 1.0×10^{-4} mol L^{-1} solutions of Ce^{3+} ion at different pH values ranging from 1.0-12.0. The pH was adjusted by the addition of 1.0×10^{-1} mol L^{-1} HCl/NaOH and the results are shown in Fig. 5.4.

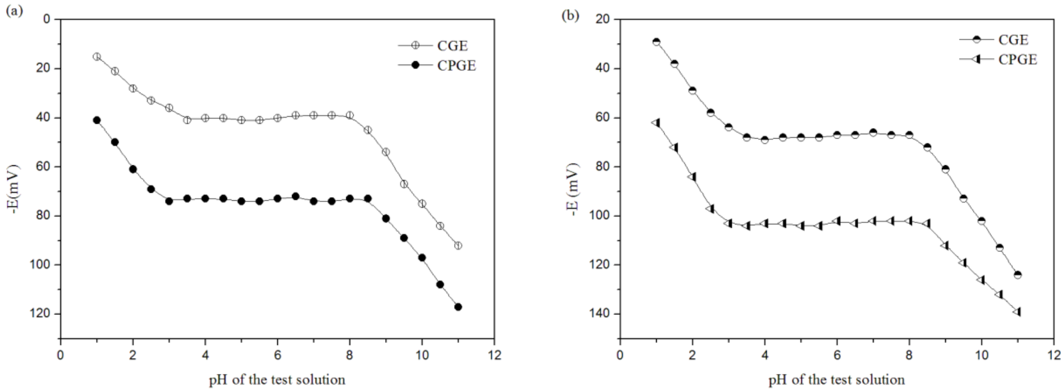

Fig. 5.4. **Effect of pH of the test solution on the potential response of CGE and CPGE with (a) 1.0×10^{-3}mol L^{-1} and (b) 1.0×10^{-4}mol L^{-1} Ce^{3+} ion solutions at different pH.**

It has been observed that potential response for the CGE remains independent of pH over pH range of 3.5-8.0 and 3.0-8.5 for the CPGE. Therefore, the same was regarded as the working pH range for these electrodes. The change in potential at higher pH may be attributed to formation of metal hydroxides species in the matrix [33] and the deviation at low pH may be regarded as the effect of protonation of ionophore [34] and the electrodes start responding to H_3O^+ ions along with Ce^{3+} ion leading to an increase in potential.

5.3.4. Effect of Interfering ions on the performance of the sensor

The most important parameter which reflects the applicability of an ISE is its selectivity, which is measured in terms of selectivity coefficient. The potentiometric selectivity coefficient for the CGE and CPGE based on L_5 were determined according to IUPAC recommended fixed interference method (FIM). In this method, the selectivity coefficient was evaluated from the potential measurement on solution containing a fixed concentration of interfering ion (1.0×10^{-2} mol L^{-1}) and varying amount of Ce^{3+} ion solution ranging from 1.0×10^{-1} to1.0×10^{-9} mol L^{-1}. The potential values so obtained were then plotted versus activity of Ce^{3+} ion.

$$K_{A,B}^{Pot} = \frac{(a_A)}{(a_B)^{Z_A/Z_B}}$$

The linear portion of potential response curve then extrapolated and the value of a_{Ce3+} was obtained from the intersection point. The potentiometric selectivity coefficients were then determined using the following expression [35]. Where a_A is the activity of primary ion

A (Ce^{3+}) at the point of intersection, a_B, the activity of interfering ion B and z_A and z_B are their respective charges. The values of selectivity coefficient obtained for the CGE and CPGE are compiled in the Table 5.1.

Table 5.1. Interfering ions and their selectivity coefficient for selectivity of Ce^{3+} ion sensor.

Interfering ions	Selectivity coefficients ($K^{FIM}_{Ce^{3+},B}$)	
	CGE	CPGE
Eu^{3+}	8.6×10^{-2}	6.4×10^{-3}
Sm^{3+}	9.3×10^{-3}	4.2×10^{-3}
Nd^{3+}	7.7×10^{-3}	2.9×10^{-3}
Tb^{3+}	4.3×10^{-3}	8.2×10^{-4}
La^{3+}	3.6×10^{-2}	4.0×10^{-3}
Ni^{2+}	8.9×10^{-2}	7.5×10^{-3}
Cu^{2+}	5.1×10^{-3}	2.2×10^{-3}
Co^{2+}	6.4×10^{-3}	3.0×10^{-4}
Hg^{2+}	7.1×10^{-3}	5.8×10^{-4}
Zn^{2+}	9.5×10^{-4}	1.7×10^{-4}
Cd^{2+}	4.2×10^{-3}	3.6×10^{-4}
Mg^{2+}	6.0×10^{-3}	2.3×10^{-3}
K^{+}	5.8×10^{-3}	9.8×10^{-4}
Na^{+}	3.4×10^{-4}	1.3×10^{-4}

From the selectivity coefficients given in the Table 5.1, it has been observed that the electrodes are highly selective over a number of monovalent, divalent and trivalent cations. However, selectivity coefficients obtained for La^{3+} ion wasnot very low and they caused some interference if present in eminent concentration. To estimate the extent of interference caused by the La^{3+} ion, mixed run studies was performed and the effect of the La^{3+} ion concentration on the performance of the sensor was examined. The potential were measured in the presence of different concentrations (1.0×10^{-5}, 5.0×10^{-5}, 1.0×10^{-4} and 1.0×10^{-3} mol L^{-1}) of La^{3+} ion and the potential responses of the sensor to the mixtures are shown in Fig. 5.5. It is revealed from the Fig.5.5 that La^{3+} ion at $\leq5.0\times10^{-5}$ mol L^{-1} did not cause any deviation in the original plot obtained in pure Ce^{3+} ion. Thus, the sensor can tolerate La^{3+} ion at $\leq5.0\times10^{-5}$ mol L^{-1} over the entire working concentration range. However, when La^{3+}

ion present in higher concentration, significant interference was observed which causes shorting of working concentration range and thus Ce^{3+} ion could be determined in the reduced concentration ranges of 7.9×10^{-7}-1.0×10^{-1} and 6.6×10^{-6}-1.0×10^{-1} mol L^{-1} in the presence of 1.0×10^{-4} and 1.0×10^{-3} mol L^{-1} of La^{3+} ion, respectively.

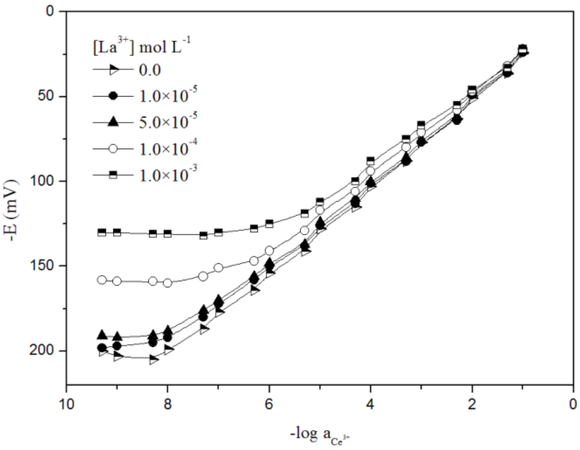

Fig. 5.5. **Effect of different concentrations of La^{3+} ion on the performance of the sensor.**

5.3.5. Determination of Life Time and Dynamic Span of the Sensor

Dynamic response time is an important factor for an ISE. According to IUPAC recommendations, the response time of an ion selective electrode is defined as the length of time between the instant at which the ion selective electrode and reference electrode are immersed in the solution and the moment at which the potential of the cell reaches its steady state value within ±1 mV [36]. The concentration of the undertaken solution was respectively changed from 1.0×10^{-6}-1.0×10^{-1} mol L^{-1} to amplify the response time of the sensor. The average time needed to attain a potential response in the electrodes lies within ±1 mV range value of final equilibrium after immersing successively in a series of Ce^{3+} ion solution, each having a 10-fold difference in concentration was 12 s for the CGE and 9 s for the CPGE as shown in Fig. 5.6. The life time of the electrodes were measured by recording the potential at different time intervals and results are tabulated in Table 5.2.

The CGE and CPGE could be used over a period of 3 and 4 months, respectively, a slight change was occur in slope of the electrode from 19.1±0.6 to 16.1±0.6 mV $decade^{-1}$ of activity, the working concentration range shifted from 3.1×10^{-7} to 9.3×10^{-6} mol L^{-1} and the detection limit reduces from 8.3×10^{-8} to 5.4×10^{-6} mol L^{-1} for the CGE and for the CPGE the slope reduces from 19.4±0.2 to 17.0±0.4 mV decade^{-1} of activity, the working concentration range reduces from 1.9×10^{-8} to 9.2×10^{-7} mol L^{-1} and the detection limit reduced to 5.0×10^{-9} - 4.5×10^{-7} mol L^{-1}.

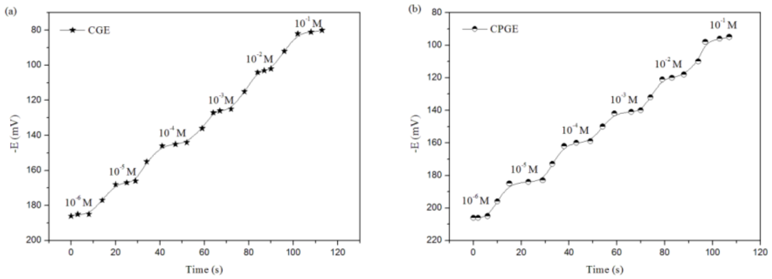

Fig. 5.6. Dynamic response time of Ce^{3+} ion-selective sensor based on L_5 for step changes in concentration of Ce^{3+} ion with (a) CGE and (b) CPGE.

5.3.6. Effect of Non-aqueous on the performance of the sensor

The working of the electrode was explored in partially non-aqueous media (the real samples may contain non-aqueous content) in range of 10-40% (v/v) non-aqueous content in methanol-water, ethanol-water and acetonitrile-water mixtures and the results are compiled in the Table 5.3. It was concluded that sensor did not show significant depletion in slope and linearity in mixtures containing 30% (v/v) of ethanol-water and acetonitrile-water solutions, but drastic change has been observed in case of methanol-water mixture and it was found that only 20% (v/v) amount could be tolerated. Therefore, the electrode is not suitable for using in methanol-water mixture above 20% (v/v) concentration. This may be due to greater solubility of the ionophore in the methanol which causes leaching of ionophore from the membrane phase.

5.3.7. UV-vis Study

The affinity of ligand towards Ce^{3+} ion was also confirmed by UV-vis study. The colorimetric studies were performed with equimolar concentrations (1.0×10^{-4} mol L^{-1}) of ligand and metal ions in methanolic solution and spectra were studied. It is observed from the UV-vis study that the free ligand gives three absorption peaks at 210.9, 268.8 and 391.5 nm (Fig. 5.7(a)). However, on addition of Ce^{3+} ion solution to ligand a new and prominent absorption peak appeared at 509.0 nm which is the indication of complexation reaction between metal and ligands. The complexation study reveals that ligand is more selective and sensitive for Ce^{3+} ion over other metal ions tested. The two absorption peaks at 268.8

and 391.5 nm of free ligand may be due to π-π^* and n-π^* transitions. Upon the addition of Ce^{3+} ion, a new and prominent absorption peak appeared at 509 nm.

Table 5.2. Potential response of Ce^{3+} ion-selective sensor.

Time (Days)	Slope (mV decade^{-1} of activity)	Working concentration range (mol L^{-1})	Detection limit (mol L^{-1})
CGE			
2	19.1±0.6	3.1×10^{-7}-1.0×10^{-1}	8.3×10^{-8}
10	19.1±0.6	3.1×10^{-7}-1.0×10^{-1}	8.3×10^{-8}
30	18.8±0.2	4.4×10^{-7}-1.0×10^{-1}	8.8×10^{-8}
45	18.5±0.4	5.6×10^{-7}-1.0×10^{-1}	9.4×10^{-8}
60	18.3±0.3	6.5×10^{-7}-1.0×10^{-1}	9.9×10^{-8}
75	17.7±0.5	8.2×10^{-7}-1.0×10^{-1}	5.8×10^{-7}
90	17.4±0.6	9.5×10^{-7}-1.0×10^{-1}	6.2×10^{-7}
95	16.1±0.6	9.3×10^{-6}-1.0×10^{-1}	5.4×10^{-6}
CPGE			
2	19.4±0.2	1.9×10^{-8}-1.0×10^{-1}	5.0×10^{-9}
10	19.4±0.2	1.9×10^{-8}-1.0×10^{-1}	5.0×10^{-9}
30	19.2±0.4	2.9×10^{-8}-1.0×10^{-1}	5.8×10^{-9}
45	19.0±0.3	3.7×10^{-8}-1.0×10^{-1}	6.4×10^{-9}
60	18.7±0.3	4.9×10^{-8}-1.0×10^{-1}	7.3×10^{-9}
75	18.4±0.4	5.6×10^{-8}-1.0×10^{-1}	8.0×10^{-9}
90	18.1±0.2	6.3×10^{-8}-1.0×10^{-1}	8.7×10^{-9}
110	17.9±0.5	7.4×10^{-8}-1.0×10^{-1}	9.7×10^{-9}
120	17.6±0.5	8.6×10^{-8}-1.0×10^{-1}	4.5×10^{-8}
130	17.0±0.4	9.2×10^{-7}-1.0×10^{-1}	4.2×10^{-7}

Table 5.3. Applicability of the sensor in partially non-aqueous medium.

Non-aqueous contents (%; v/v)	Working concentration range (mol L^{-1})	Slope (mV $decade^{-1}$ of activity)
0	1.9×10^{-8}-1.0×10^{-1}	19.4±0.2
Ethanol		
10	1.9×10^{-8}-1.0×10^{-1}	19.4±0.2
20	1.9×10^{-8}-1.0×10^{-1}	19.4±0.2
30	3.4×10^{-8}-1.0×10^{-1}	19.1±0.3
35	6.0×10^{-8}-1.0×10^{-1}	18.0±0.5
40	7.5×10^{-7}-1.0×10^{-1}	16.9±0.3
Methanol		
10	1.9×10^{-8}-1.0×10^{-1}	19.4±0.2
20	1.9×10^{-8} -1.0×10^{-1}	19.4±0.3
30	7.9×10^{-8}-1.0×10^{-1}	17.8±0.4
35	6.2×10^{-7}-1.0×10^{-1}	16.6±0.4
40	9.3×10^{-7}-1.0×10^{-1}	14.4±0.5
Acetonitrile		
10	1.9×10^{-8}-1.0×10^{-1}	19.4±0.2
20	1.9×10^{-8}-1.0×10^{-1}	19.4±0.2
30	2.9×10^{-8}-1.0×10^{-1}	19.0±0.5
35	4.1×10^{-8}-1.0×10^{-1}	18.3±0.4
40	6.2×10^{-7}-1.0×10^{-1}	17.2±0.4

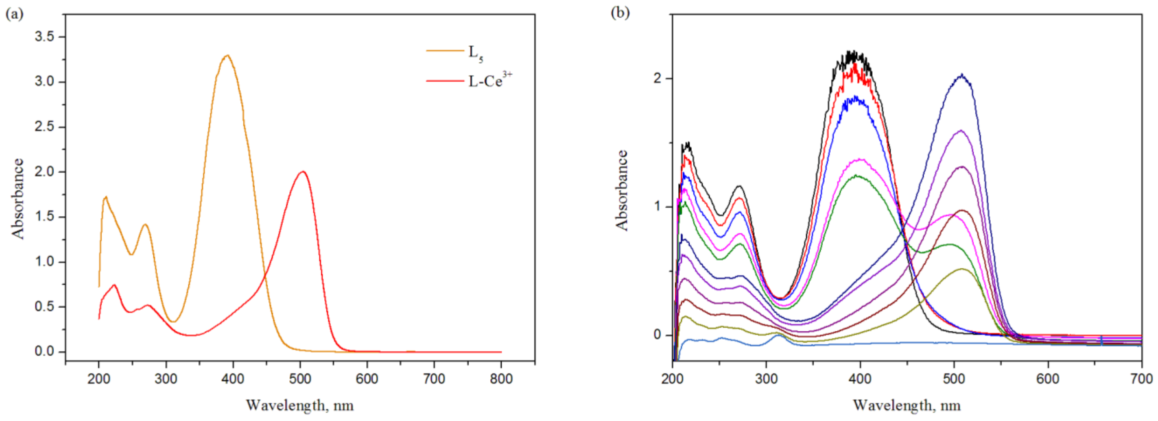

Fig. 5.7. UV-vis absorbance spectra of (a) L_5 with Ce^{3+} and (b) continuous variation in mole fractions of L_5 with Ce^{3+} ion.

This new absorption peak is probably due to complexation of metal ion with the ligand. In the complex, Ce^{3+} ion possibly coordinate with N- of the pyrolle ring and/or with the O- of the carbonyl group. On the basis of these interactions, ligand shows bathochromic shift with the addition of metal ion. The stoichiometry and the formation constants of the L_5 with Ce^{3+} were examined by the Job`s method.

5.3.8. Evaluation of Formation constant

Stability of the Ce^{3+}-L_5 complex has been demonstrated by the determination of the formation constant.

5.3.9. Job’s Method

In this method, equimolar solutions of ligand (1.0×10^{-4} mol L^{-1}) and metal ion were prepared in methanol. The absorption spectra were recorded for each of the different mole fraction of the ligand and metal ion [37, 38]. The stoichiometry of the ligand to metal ion has been found 1:1. The formation constants were calculated by the following expressions:

$$M + L \leftrightarrow ML \quad (1)$$

$$K_f = \frac{[ML]}{[M][L]} \quad (2)$$

$$K_f = \frac{[A_2 / A_1]}{[1 - A_2 / A_1][C_L - C_M \times A_2 / A_1]} \quad (3)$$

Where, A_1 is the absorbance at break point, A_2 is the actual absorbance, C_M is the metal ion concentration and C_L is the ligand concentration.

Fig. 5.7(b) shows the uv-vis absorbance spectra of L_5 with Ce^{3+} and continuous variation in mole fractions of L_5 with Ce^{3+} ion while Fig. 5.8 represent the Job`s plot with an equimolar concentration (1.0×10^{-4}mol L^{-1}) of L_5 and Ce^{3+} ion. The high intensity of new absorption band of ligand with metal ion is confirmed with the stability of Ce^{3+}-lignad complex and the formation constant value was evaluated as 6.06.

5.3.10. Comparative performance of CGE and CPGE

The investigations on polymeric membrane based on L_5 have proved that L_5 acts as suitable Ce^{3+} ion-selective sensor. The sensor based on L_5 containing *o*-NPOE as the solvent mediator with the composition L_5: PVC: *o*-NPOE: NaTPB≡7:31:59:3 (w/w, mg) perform best in terms of wide working concentration range of 3.1×10^{-7}-1.0×10^{-1} mol L^{-1} and

Nernstian compliance of 19.4±0.2 mV decade^{-1} of activity with the detection limit of 8.3×10^{-8} mol L^{-1}. Therefore, the same composition was used in the fabrication of pyrolytic graphite electrode and the responses obtained are shown in Fig. 5.9 and tabulated in Table 5.4. A comparison of the data given in the Table 5.4 showed that the CPGE exhibited best performance over the CGE in terms of wide working concentration range of 1.9×10^{-8}-10×10^{-1} mol L^{-1}, the Nernstian slope 19.4±0.2 mV decade^{-1} of activity with detection limit of 5.0×10^{-9} mol L^{-1}.

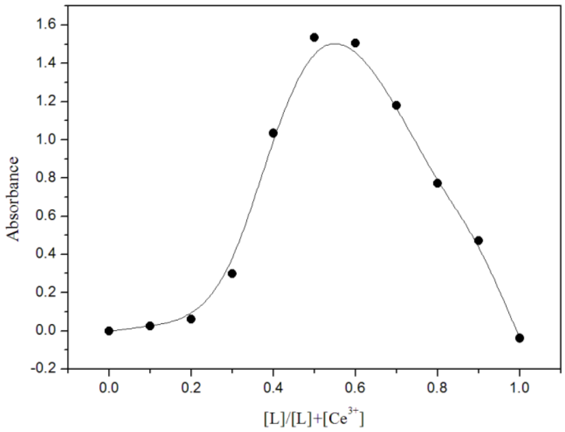

Fig. 5.8. Job's plot with an equimolar concentration (1.0×10^{-4} mol L^{-1}) of L_5 and Ce^{3+} ion.

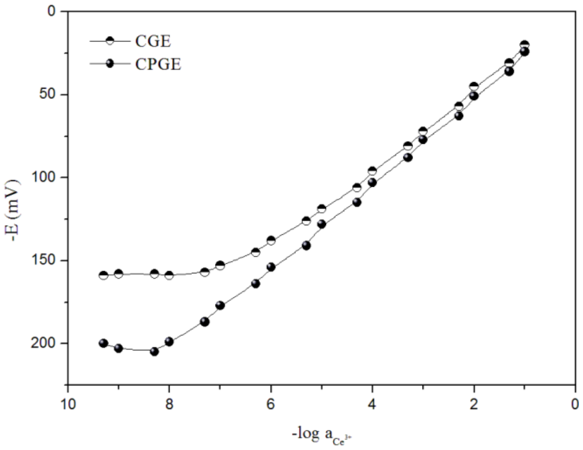

Fig. 5.9. Potentiometric characteristic calibration plot of Ce^{3+} selective sensor with CGE and CPGE based on L_5.

5.4. ANALYTICAL APPLICATIONS

The sensor show higher selectivity for Ce^{3+} ion and therefore, suitable for the recovery of Ce^{3+} ion in binary mixtures and determination of oxalate and fluoride in vegetable and mouthwash samples and beside this; the sensor was successfully employed as an indicator electrode in the potentiometric titration of Ce^{3+} ion with oxalate and fluoride ions.

5.4.1. Potentiomertic Titration

The sensor was found to work well under laboratory conditions andit was used as an indicator electrode in the potentiometric titration of 20.0 mL of 1.0×10^{-2}mol L^{-1} Ce^{3+} ion solution with 1.0×10^{-1}mol L^{-1} oxalate and fluoride anions at pH 5.5.

The exact amounts of oxalate and fluoride ions were then evaluated from the sharp inflection points of the resulting titration curve. Oxalates are found in a wide variety of foods such as spinach, mushroom, and beet leaves. The sensor was successfully applied in the determination of oxalate in vegetable samples viz. spinach and mushroom. The sample solution of spinach and mushroom were prepared as per procedure reported [39]. The fresh vegetables (spinach and mushroom) were cut into small pieces and pounded into paste in a mortar. The paste obtained was subsequently mixed with water in a 100 mL reflux flask and boiled for 45 min, and cooled to room temperature.

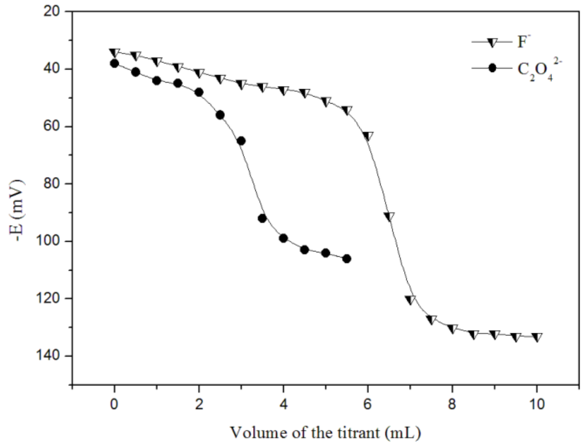

Fig. 5.10. Potentiometric titration of 1.0×10^{-2} mol L^{-1} Ce^{3+} ion solution with 1.0×10^{-1} mol L^{-1} oxalate and fluoride ions.

The suspension was filtered thrice through filter paper and the filtrate was diluted to 250 mL. The results are reported in the Table 5.5.

Table 5.4. Potentiometric response characteristic of Ce^{3+} ion selective sensor with L_5.

Properties	Values/range	
	CGE	CPGE
Optimized membrane composition	L: PVC: *o*-NPOE: NaTPB≡7:31:59:3 (w/w, mg)	L: PVC: *o*-NPOE: NaTPB≡7:31:59:3 (w/w, mg)
Conditioning time	24 h in 1.0×10^{-3} mol L^{-1} Ce^{3+}	24 h in 1.0×10^{-3} mol L^{-1} Ce^{3+}
Working concentration range (mol L^{-1})	3.1×10^{-7}-1.0×10^{-1}	1.9×10^{-8}-1.0×10^{-1}
Detection limit (mol L^{-1})	8.3×10^{-8}	5.0×10^{-9}
Slope (mV $decade^{-1}$ of activity)	19.1±0.6	19.4±0.2
Response time (s)	12	09
Life span (month)	3	4
Working pH range	3.5-8.0	3.0-8.5

Table 5.5. Determination of oxalate in vegetable samples.

Samples	Added (µg mL^{-1})	ISE*±SD (µg mL^{-1})	Recovery (%)
Spinach	-	0.75±0.05	-
	0.25	0.98±0.06	98
	0.50	1.22±0.02	97.6
Mushroom	-	0.85±0.04	-
	0.25	1.09±0.04	99
	0.50	1.33±0.02	98.5

Table 5.6. Determination of fluoride contents in various mouth wash samples.

Sampples	Labelled (%)	Found by the sensor (%)
Listerine mouthwash	0.022	0.020
Senquel AD	0.20	0.18
Colgate mouthwash	0.18	0.16

*Mean value ± standard deviation (triplicate measurement).

The sensor was employed in the determination of fluoride ion concentration in mouthwash preparations. Each sample of the sodium fluoride mouthwash solutions was diluted with distilled water in a 100 mL flask and titrated with Ce^{3+} ion solution (1.0×10^{-4} mol L^{-1}). The result of the triplicate measurements are presented in the Table 5.6. The sensor was also used for the recovery of Ce^{3+} ion from binary mixtures (Table 5.7).

5.5. CONCLUSIONS

UV-vis spectral studies and conductometric measurement reveal that the L_5 has high affinity for Ce^{3+} ion than rest of the other cations studied. Therefore, L_5 was used in the fabrication of Ce^{3+} ion-selective sensor.The studies on a large number of electrodes based on L_5 have shown that the plasticizer *o*-NPOE enhances the performance characteristics of the electrodes better than rest of the plasticizers. The composition of the membrane (CPGE) with the best performance indicator was found to be L_5: PVC: *o*-NPOE: NaTPB≡7:31:59:3 (w/w, mg) with the low detection limit of 5.0×10^{-9} mol L^{-1}.

The potentiometric characteristics based on the CPGE showed nice Nernstian slope of 19.4±0.2 mV $decade^{-1}$ of activity and is independent of pH in the region 3.0 to 8.5. The response time of the electrode was fast (9 s) and can work satisfactorily in partially non-aqueous content up to 30% of acetonitrile-water and ethanol-water mixture and can tolerate

Table 5.8. Comparison of performance characteristic of Ce^{3+} ion selective sensor with various reported sensors.

Ref.	Carrier name	Linear range (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mV decade^{-1} of activity)	pH	Response time (s)	Selectivity coefficients ($\log K_{A,B}^{Pot}$)
[15]	N-[(Z)-2-chloro-2-(1-hydroxy-1,1,1-triphenyl phosphoranyl)-1-ethenyl]-4-ethyl-1-benzene sulfonamide	6.6×10^{-7}-6.2×10^{-2}	2.3×10^{-7}	19.5±0.3	4.5-8.5	<10	Na^{+}(-3.85), K^{+}(-3.88), Ag^{+}(-4.00), Mg^{2+}(-2.39), Ca^{2+}(-2.30), Ba^{2+}(-2.50), Co^{2+}(-2.28), Ni^{2+}(-2.29), Sr^{2+}(-2.28), Mn^{2+}(-2.20), Cu^{2+}(-2.28), Zn^{2+}(-2.27), Cd^{2+}(-2.63), Hg^{2+}(-2.25), Pb^{2+}(-2.26), Fe^{3+}(-2.00), Al^{3+}(-1.67), Cr^{3+}(-1.69), Ga^{3+}(-1.92), La^{3+}(-1.37), Sm^{3+}(-1.49), Gd^{3+}(-1.58), Yb^{3+}(-1.65), Ce^{4+}(-2.03)
[16]	azomethine of piperonylidine-4-[2.2]paracyclophanylamine	2.5×10^{-5}-1.0×10^{-1}	1.2×10^{-5}	19.3±0.3	4.5-8.0	30	Li^{+}(-4.00), Na^{+}(-3.90), K^{+}(-2.65), Mg^{2+}(-4.20), Ca^{2+}(-4.30), Sr^{2+}(-3.65), Ba^{2+}(-3.70), Co^{2+}(-3.67), Ni^{2+}(-3.76), Cu^{2+}(-4.35), Zn^{2+}(-4.35), Cd^{2+}(-3.95), Hg^{2+}(-2.36), Al^{3+}(-3.67), Fe^{3+}(-2.77), Ru^{3+}(-3.47), La^{3+}(-3.88), Sm^{3+}(-3.40)
[17]	2-aminobenzothia- zole	2.0×10^{-6}-2.0×10^{-2}	1.8×10^{-6}	19.6±1.0	4.1-7.3	13	Na^{+}(-6.00), Ag^{+}(-2.85), Mg^{2+}(-6.00), Ca^{2+}(-6.00), Ba^{2+}(-6.00),Co^{2+}(-4.55), Cu^{2+}(-2.39),Zn^{2+}(-6.00), Pb^{2+}(-2.59), Cd^{2+}(-3.68),Hg^{2+}(-2.77), La^{3+}(-2.52), Fe^{2+}(-2.33), Al^{3+}(-2.49), Cr^{3+}(-3.92),Cs^{+}(-6.00), Rb^{+}(-6.00), NH$_4^{+}$(-6.00), Sr^{2+}(-6.00)
[18]	1,3,5-trithiane	2.5×10^{-8}-4.7×10^{-4}	2.0×10^{-8}	19.2±0.1	2.0-10-0	10	Co^{2+} (-1.49), Cu^{2+} (-1.42), Ni^{2+} (-1.88), Co^{2+} (-3.67), Zn^{2+} (-1.20), Mg^{2+} (-2.51), Ba^{2+} (-1.92), Ca^{2+} (-1.66), Pb^{2+} (-1.96), Cd^{2+} (-1.15),Na^{+} (-2.62), K^{+} (-2.20), La^{3+} (-1.30), Li^{+} (-2.79), Tl^{+} (-3.30), Ag^{+} (-1.49), Hg^{2+} (-4.00)
[19]	[4-(4-nitrobenzyl)-1-phenyl-3,5-pyrazolidinedion)] (NBPP)	2.5×10^{-6}-1.0×10^{-1}	1.6×10^{-6}	19.5±0.2	4.0-8.0	>10	K^{+}(-1.03), Na^{+}(-1.19), Li^{+}(-1.39), Cs^{+}(-1.34), Rb^{+}(-1.50), NH$_4^{+}$(-1.94), Cu^{2+}(-3.98), Cd^{2+}(-4.13), Ba^{2+}(-4.10), Zn^{2+}(-3.02), Hg^{2+}(-5.22), Ni^{2+}(-1.20),Co^{2+}(-4.44), Ca^{2+}(-1.33),

							Fe^{3+}(-3.10), Sm^{3+}(-2.65), Nd^{3+}(-2.81)
[20]	2,3,4:12,13,14-dipyridine-1,5,8,11,15,18-hexamethylacrylate1,3,5,8,11,13,15,18-octaazacycloicosa-2,12-diene (L_2)	1.0×10^{-8}-1.0×10^{-1}	7.7×10^{-9}	19.7±0.2	2.5-8.5	10	La^{3+}(-2.37), Dy^{3+}(-2.22), Sm^{3+}(-2.20),Gd^{3+}(-2.18), Nd^{3+}(-2.16),Pb^{2+}(-2.14), K^{+}(-2.13), Ba^{2+}(-2.11), Sr^{2+}(-2.10), Eu^{3+}(-2.07), Na^{+}(-2.06), Ca^{2+}(-2.04), Cd^{2+}(-2.00), Cu^{2+}(-3.58), Zn^{2+}(-3.53),Mg^{2+}(-3.45), Co^{2+}(-3.35), Ni^{2+}(-3.31), Hg^{2+}(-3.25)
[21]	N'-[(2-hydroxyphen-yl)methylidene]-2-furohydrazide	1.0×10^{-5}-1.0×10^{-1}	7.6×10^{-6}	19.4±0.3	3.5-10.0	<15	Co^{2+}(-2.51), Cu^{2+}(-2.52), Ni^{2+}(-2.34), Zn^{2+}(-3.00), Mg^{2+}(-2.55), Ba^{2+}(-3.07), Ca^{2+}(-3.24), Pb^{2+}(-2.32), Cd^{2+}(-2.74),Na^{+}(-2.58), K^{+}(-2.30), La^{3+}(-3.00), Gd^{3+}(-3.45), Sm^{3+}(-2.89), Eu^{3+}(-3.02), Nd^{3+}(-3.10), Dy^{3+}(-3.11)
[22]	N'N-bis[2-(salicylic-deneamino)ethyl]ethane-1,2-diamine	1.4×10^{-7}-1.0×10^{-2}	8.9×10^{-8}	20.0	3.0-8.0	<10	Co^{2+}(-3.24), Tb^{3+}(-3.14), Cu^{2+}(-2.34), Ni^{2+}(-2.31), Cd^{2+}(-2.31), Zn^{2+}(-2.57), Pb^{2+}(-3.20), Hg^{2+}(-3.12), Ag^{+}(-3.53), Sr^{2+}(-2.25), Tl^{+}(-2.30), Mn^{2+}(-2.18), La^{3+}(-1.45),Na^{+}(-3.87), Mg^{2+}(-2.17)
[23]	1,3,5-trithiane coated graphite electrode	2.5×10^{-8}-4.7×10^{-4}	2.0×10^{-8}	19.2±0.1	5.0-8.0	10	Co^{2+}(-4.29), Zn^{2+}(-4.16), Cu^{2+}(-4.22), Cd^{2+}(-3.09), Hg^{2+}(-4.08), La^{3+}(-2.39), Pb^{2+}(-2.08), Tl^{+}(-4.02), Ni^{2+}(-4.65), Ag^{+}(-3.95)
[24]	2,5-dioxo-4-imidazolidinyl	1.0×10^{-6}-1.0×10^{-1}	5.7×10-7	19.6±0.3	3.1-9.8	<10	Sm^{3+}(-3.00), Cr^{3+}(-3.21), Nd^{3+}(-3.03), Dy^{3+}(-3.08), La^{3+}(-2.07), Na^{+}(-3.33), K^{+}(-3.38), Mg^{2+}(-3.25), Ca^{2+}(-3.11), Zn^{2+}(-3.21), Ni^{2+}(-3.10), Co^{2+}(-3.19), Cd^{2+}(-3.12), Hg^{2+}(-3.49), Pb^{2+}(-3.59)
This work	1,1'-(pyridine-2,6-diyl)bis(3-(1H-pyrrol-2-yl)prop-2-en-1-one) (L)	1.9×10^{-8}-1.0×10^{-1}	5.0×10^{-9}	19.4±0.2	3.0-8.5	09	Eu^{3+}(-2.19), Sm^{3+}(-2.37), Nd^{3+}(-2.53), Tb^{3+}(-3.08), La^{3+}(-2.39), Ni^{2+}(-2.12), Cu^{2+}(-2.65), Co^{2+}(3.52), Hg^{2+}(-3.23), Zn^{2+}(-3.76), Cd^{2+}(-3.44), Mg^{2+}(-2.63), K^{+}(-3.00), Na^{+}(-3.88)

20% of methanol-water system. Comparative studies of the sensors reveal that the CPGE is superior over CGE.

Table 5.7. Recovery of Ce^{3+} from various binary mixtures.

Ce^{3+} (μg mL^{-1})	Cations added (μg mL^{-1})	Found by sensor* (μg mL^{-1})	Recovery (%)
12.0	La^{3+}, 12.0	11.4±0.4	95.0±0.6
12.0	Eu^{3+}, 12.0	11.8±0.4	98.3±0.4
12.0	Sm^{3+},12.0	11.5±0.2	95.8±0.2
12.0	Nd^{3+}, 12.0	11.8±0.3	98.3±0.5
12.0	Tb^{3+}, 12.0	11.9±0.3	99.2±0.2
12.0	Co^{2+}, 12.0	11.6±0.4	96.7±0.4
12.0	Cu^{2+}, 12.0	11.5±0.3	95.8±0.5
12.0	Ni^{2+}, 12.0	11.7±0.2	97.5±0.4

*Mean value ± standard deviation (triplicate measurement).

The applicability of the sensor is illustrated by determining Ce^{3+} ion in various real samples and as an indicator electrode in the potentiometric titration of Ce^{3+} ion with oxalate and fluoride ions. A comparison of the performance characteristics with previously reported electrodes [15-24], as shown in Table 5.8 implies that the sensor is comparably superior to those listed in Table 5.8 in terms of wide working concentration range, Nernstian slope, sensitivity, selectivity and low detection limit.

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Chapter 6

“Multidentate Schiff Bases of Isonicotinohydrazide as Mn^{2+} Ion-Selective Sensors”

6.1. INTRODUCTION

Manganese occurs widely in the nature and finds extensive industrial, agricultural and house hold applications. It is often used in battery, fertilisers, pesticides, and in dietary supplements [1]. Another important use of manganese is to prepare steel and alloy with improved hardness, stiffness and strength [2]. Not only these applications, but also manganese is an essential element for many physiological processes in human bodies [3-7]. In spite of many applications and its nutritional value [8] manganese shows enough toxicity at higher concentration level [9]. Its maximum permissible content is for domestic water 0.05 mg mL^{-1} and for irrigation water 2.0 mg mL^{-1} [10]. A form of neurodegeneration similar to Parkinson's disease called "manganism" has been linked to manganese exposure amongst miners and smelters since the early 19th century [11]. Some other harmful effects of manganese intake are impotence, loss of libido and adverse effect on the eye. In view of its toxic effect, it is important to determine manganese in various environmental samples.

Numerous analytical techniques have been reported for the low level monitoring of manganese such as atomic absorption spectroscopy (AAS) [12], inductively coupled plasma mass spectrometry (ICP-MS) [13], inductively coupled plasma atomic emission spectroscopy (ICP-AES) [14], X-ray fluorescence (XRF) [15], fluorimetry [16] and adsorptive cathodic stripping voltammetry (CSV) [17]. Though, these techniques have been employed successfully in the determination of manganese, but are not very convenient for the analysis of a large number of environmental samples as they require of expertise and large infrastructure backup. Therefore, there is a need to develop a better method which involves simple instrumentation, inexpensive and fast method of analysis with minimum chemical manipulation. Such requirements are generally met with ion selective electrodes (ISEs), which have emerged as promising tools for direct measurement of various species in the environmental, biological and industrial analysis because of the advantages offerd in terms of sensitivity and selectivity, reproducibility and cost effectiveness.

6.1.1. Mn^{2+} ion-selective electrodes

The literature survey reveals that a variety of ionophores have been used for the construction of Mn^{2+}-selective electrodes [18-28]. However, they exhibit some limitations such as narrow working concentration range, low pH range, poor selectivity and high response time. Thus, there is a need to develop better sensor for the monitoring of Mn^{2+} ion. To achieve the aim, we looked out to synthesise some novel compounds which have good affinity to bind with metal ions particularly Mn^{2+}. We have chosen isonicotinohydrazide derivative as a suitable ionophore to prepare Mn^{2+}-selective sensor. Thus, the present research describes the applications of isonicotinohydrazide derivatives (N',N'''E,N',N'''E)-N',N'''-((((oxybis(ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene))bis(methanylylidene))di-(isonicotinohydrazide) (L_6) and (N',N'''E,N',N'''E)-N',N'''-(((propane-1,3-diylbis(oxy))bis-(2,1-phenylene))bis(methanylylidene))di(isonicotinohydrazide) (L_7) as an ionophore in poly(vinyl chloride) based sensor for the monitoring of Mn^{2+} in various samples, viz., waste water, vegetables, soil samples and in medicinal plants.

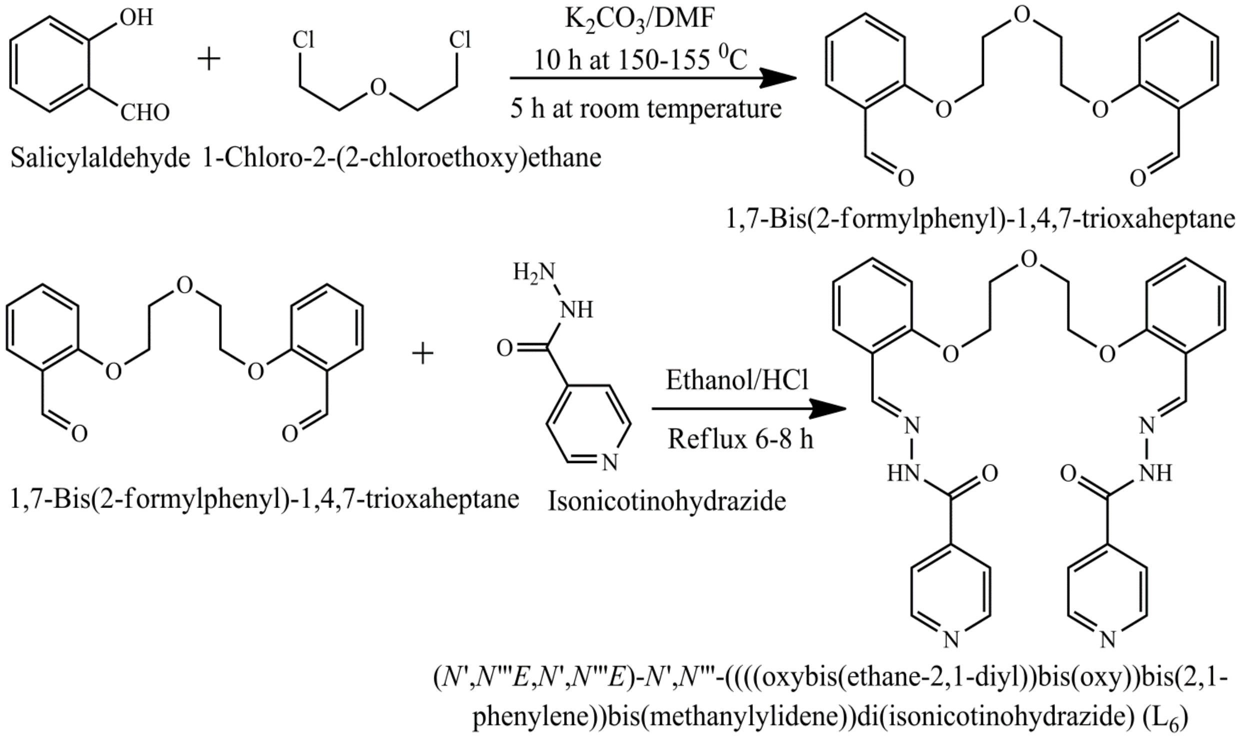

Fig. 6.1. Synthesis of chelating ionophore (N',N'''E,N',N'''E)-N',N'''-((((oxybis(ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene))bis(methanylylidene))di(isonicotinohydrazide) (L_6).

6.2. EXPERIMNTAL

6.2.1. Chemical and Reagents

NaTPB (sodium tetraphenylborate), dibutylphthalate (DBP), benzylacetate (BA) and high molecular weight poly(vinyl chloride) (PVC) were procured from E. Merck. Potassiumtetrakis-p-(chlorophenyl)borate (KTpClPB) and *o*-nitrophenyloctylether (*o*-

NPOE) were procured from Fluka and Sigma Aldrich, respectively. Dioctylphthalate (DOP) and 1-chloronaphthlene (1-CN) were procured from Acros Organics and s. d. fine-Chem Ltd., respectively. Salicylaldehyde and isonicotinohydrazide were obtained from Sigma Aldrich, and 1-chloro-2-(2-chloroethoxy) ethane and 1,3-dibromopropane were procured from Hi-Media and used as received. The nitrate and chloride salts of all the cations, EDTA and solvents (tetrahydrofuran (THF), methanol, ethanol, dimethylformamide (DMF), dimethylsulfoxide (DMSO) and acetonitrile) used were of analytical grade and used without any further purification. Double distilled water was used throughout the experiment.

6.2.2. Synthesis

The ionophores were synthesised as shown in Fig. 6.1 and 6.2. One of the ionophore (L_6) has been reported by O.N. Chupakhin *et. al*. [29].

6.2.2.1. Synthesis of Chelating Ionophore (N',N'''E,N',N'''E)-N',N'''-((((oxybis(ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene))bis(methanylylidene))di(isonicotinohydrazide) (L_6)

To a solution of isonicotinohydrazide (4.0 mM, 548.5 mg) in ethanol (20 mL), 1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane (2.0 mM, 628.6 mg) in ethanol (10 mL) was added drop-wise with constant stirring. Few drops of HCl (37%) was added in the above reaction mixture with constant stirring and then refluxed for 6-8 h. The completion of the reaction mixture was monitored by thin layer chromatography ($CHCl_3$: Methanol, 8:2). The reaction mixture was concentrated and the residue obtained was washed with water and dried. The crude product obtained on recrystallization from alcohol gave the pure hydrazones. The synthesized product was then characterized.

Yield: 69% analytically calculated for [$C_{30}H_{28}N_6O_5$] (%): C, 65.21; H, 5.11; N, 15.21; Found: C, 65.14; H, 5.17; N, 15.25. IR (KBr, cm^{-1}): 3211 (NH-), 1660 (-C=O), 1602 (C=N), 1553, 1486, 1452, 1409, 1360, 1298, 1252, 1142, 1062 (Ar-). ^{1}H NMR (DMSO 500 MHz) δ (ppm): 12.09 (2H, s), 8.81 (2H, s), 8.75-8.76 (4H, d, *J*=5 Hz), 7.86-7.88 (2H, d, *J*=10 Hz), 7.80-7.81 (4H, d, *J*=5 Hz),7.36-7.39 (2H, t, *J*=15 Hz), 7.11-7.13 (2H, d, *J*=10 Hz), 7.00-7.03 (2H, t, *J*=15 Hz), 4.24-4.26 (4H, t, *J*=10 Hz), 3.88-3.89 (4H, t, *J*=5 Hz). ^{13}C NMR (DMSO 125 MHz) δ (ppm): 161.53, 157.16, 150.24, 149.49, 144.46, 140.45, 131.79, 125.76, 122.38, 121.53, 121.01, 113.14, 69.05, 67.95 (see appendix for spectra).

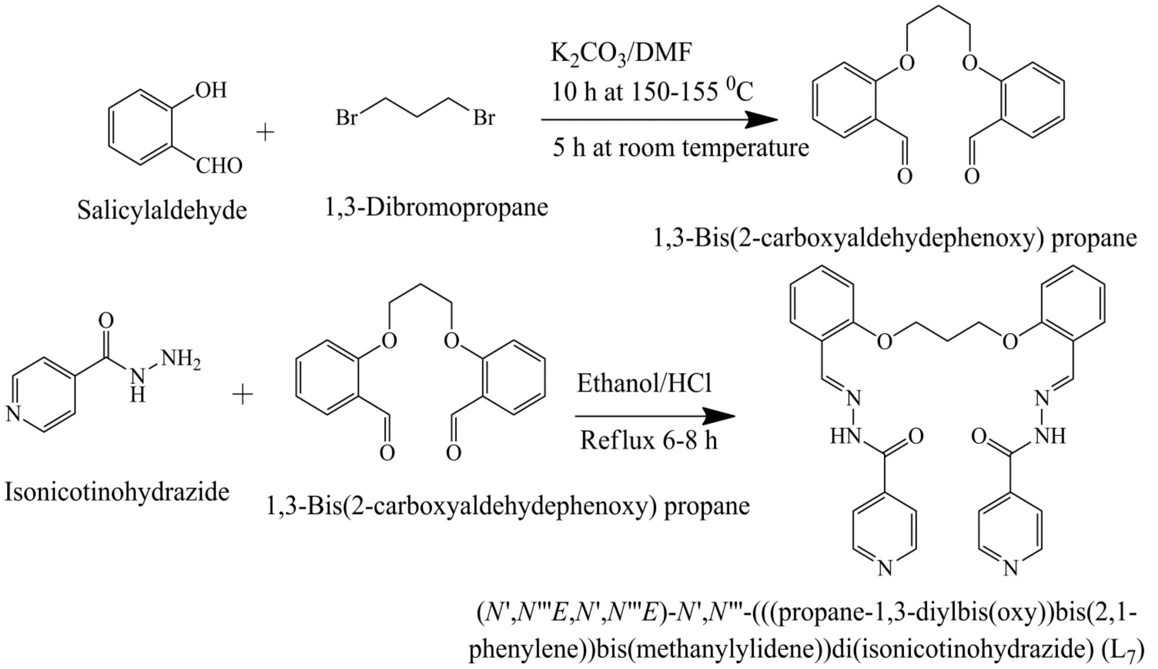

Fig. 6.2. Synthesis of chelating ionophore (N',N'''E,N',N'''E)-N',N'''-(((propane-1,3-diylbis-(oxy))bis(2,1-phenylene))bis(methanylylidene))di(isonicotinohydrazide) (L_7).

6.2.2.2. Synthesis of Chelating Ionophore (N',N'''E,N',N'''E)-N',N'''-(((propane-1,3-diylbis(oxy))bis(2,1-phenylene))bis(methanylylidene))di(isonicotinohydrazide) (L_7)

The ionophore was synthesized by following the same procedure as described above for L_6 and instead of 1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane, a (2.0 mM, 568.6 mg) solution of 1,3-bis(2-carboxyaldehydephenoxy)propane was used.

Yield: 76% analytically calculated for [$C_{29}H_{26}N_6O_4$] (%): C, 66.66; H, 5.02; N, 16.08. Found: C, 66.60; H, 5.07; N, 16.12. IR (KBr, cm^{-1}): 3224 (NH-), 1655 (-C=O), 1601 (-C=N), 1550, 1488, 1455, 1405, 1365, 1296, 1255, 1155, 1111, 1061 (Ar-). ^1H NMR (DMSO 500 MHz) δ (ppm): 12.04 (2H, s), 8.88 (2H, s), 8.77-8.78 (4H, d, *J*=5 Hz), 7.88-7.89 (2H, m, *J*=5 Hz), 7.80-7.81 (4H, m, *J*=5 Hz), 7.39-7.43 (2H, m, *J*=20 Hz), 7.15-7.17 (2H, d, *J*=10 Hz), 7.01-7.04 (2H, m, *J*=15 Hz), 4.30-4.32 (4H, t, *J*=10 Hz), 2.26-2.31 (2H, m, *J*=25 Hz). ^{13}C NMR (DMSO 125 MHz) δ (ppm): 161.55, 157.08, 150.28, 149.50, 144.38, 140.54, 131.87, 125.77, 123.09, 122.21, 121.52, 120.93, 112.80, 64.83, 28.77 (see appendix for spectra).

Table 6.1. Optimization of membrane composition and their potentiometric response for Mn^{2+} ion-selective membrane based on L_6.

S. No.	Composition of membrane (w/w; mg)									Working concentration range (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mVdecade^{-1} of activity)
	L_6	NaTPB	KTpClPB	DBP	DOP	BA	*o*-NPOE	1-CN	PVC			
1	6	-	-	-	-	-	-	-	94	5.49×10^{-6}-1.0×10^{-1}	1.99×10^{-6}	24.6±0.3
2	6	-	-	56	-	-	-	-	38	6.76×10^{-7}-1.0×10^{-1}	2.51×10^{-7}	27.1±0.5
3	6	-	-	-	56	-	-	-	38	7.41×10^{-7}-1.0×10^{-1}	2.34×10^{-7}	27.7±0.3
4	6	-	-	-	-	56	-	-	38	7.94×10^{-7}-1.0×10^{-1}	1.94×10^{-7}	27.4±0.6
5	6	-	-	-	-	-	56	-	38	6.02×10^{-7}-1.0×10^{-1}	1.34×10^{-7}	28.2±0.6
6	6	-	-	-	-	-	-	56	38	2.23×10^{-6}-1.0×10^{-1}	2.18×10^{-7}	25.1±0.3
7	6	2	-	-	-	-	56	-	36	5.62×10^{-7}-1.0×10^{-1}	1.73×10^{-7}	28.6±0.6
8	6	-	2	-	-	-	56	-	36	4.23×10^{-7}-1.0×10^{-1}	1.63×10^{-7}	27.7±0.5
9	7	2	-	-	-	-	56	-	35	9.19×10^{-6}-1.0×10^{-1}	6.41×10^{-6}	30.5±0.3
10	8	2	-	-	-	-	56	-	34	8.46×10^{-6}-1.0×10^{-1}	4.83×10^{-6}	28.9±0.7
11	5	2	-	-	-	-	56	-	37	5.85×10^{-7}-1.0×10^{-1}	3.29×10^{-7}	31.3±0.3
12	6	1	-	-	-	-	56	-	37	6.73×10^{-7}-1.0×10^{-1}	2.78×10^{-7}	26.7±0.4

Table 6.2. Optimization of membrane composition and their potentiometric response for Mn^{2+} ion-selective membrane based on L_7.

S. No.	Composition of membrane (w/w; mg)									Working concentration range (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mVdecade^{-1} of activity)
	L_7	NaTPB	KTpClPB	DBP	DOP	BA	*o*-NPOE	1-CN	PVC			
13	6	-	-	-	-	-	-	-	94	6.45×10^{-6}-1.0×10^{-1}	1.51×10^{-6}	25.3±0.3
14	6	-	-	58	-	-	-	-	36	7.07×10^{-7}-1.0×10^{-1}	3.80×10^{-7}	26.3±0.4
15	6	-	-	-	58	-	-	-	36	1.99×10^{-6}-1.0×10^{-1}	3.38×10^{-7}	25.4±0.3
16	6	-	-	-	-	58	-	-	36	2.34×10^{-6}-1.0×10^{-1}	4.46×10^{-7}	27.4±0.5
17	6	-	-	-	-	-	58	-	36	4.46×10^{-7}-1.0×10^{-1}	1.69×10^{-7}	28.6±0.4
18	6	-	-	-	-	-	-	58	36	5.12×10^{-7}-1.0×10^{-1}	2.24×10^{-7}	25.9±0.4
19	6	2	-	-	-	-	58	-	34	6.30×10^{-8}-1.0×10^{-1}	1.90×10^{-8}	29.4±0.3
20	6	-	2	-	-	-	58	-	34	6.42×10^{-7}-1.0×10^{-1}	3.87×10^{-7}	28.4±0.3
21	7	2	-	-	-	-	58	-	33	9.76×10^{-7}-1.0×10^{-1}	6.13×10^{-7}	28.0±0.6
22	8	2	-	-	-	-	58	-	32	3.79×10^{-6}-1.0×10^{-1}	1.62×10^{-6}	31.2±0.6
23	5	2	-	-	-	-	58	-	35	2.45×10^{-6}-1.0×10^{-1}	8.27×10^{-7}	26.8±0.3
24	6	1	-	-	-	-	58	-	35	9.38×10^{-7}-1.0×10^{-1}	4.93×10^{-7}	27.6±0.4

6.2.3. Fabrication of PVC Membranes

6.2.3.1. Preparation of Coated Graphite Electrode (CGE) and Coated Pyrolytic Graphite Electrode (CPGE)

The membrane has been fabricated as suggested by Craggs *et al.*, [30]. Polymeric membrane based on high molecular weight PVC was prepared by dissolving appropriate amounts of membrane ingredients (ionophore (L_6 and L_7), anionic additives (NaTPB and KTpClPB), and plasticizers (*o*-NPOE, DBP, DOP, 1-CN and BA) and PVC) dissolved in THF (5 mL) and the solvent was evaporated off to obtain concentrated solution. The graphite electrode and pyrolytic graphite electrode of spectroscopic grade (6 mm long, 3 mm diameter) with a copper wire glued at one end were dipped in to the solution and removed out and allowed the electrode to get dry. The process was repeated till the membrane was formed over graphite electrode/pyrolytic graphite electrode. Then it was glued (Araldite) to a “Pyrex glass tube" keeping working area exposed.

6.2.4. Conditioning of Membrane and Potential Measurements

The potential response of an ion selective electrode is a function of membrane composition. The CGE and CPGE were conditioned 1 day before the potentiometric measurements in 1.0×10^{-3} mol L^{-1} $Mn(NO_3)_2$ solution.

The EMF of cell was recorde by altering the concentration of $Mn(NO_3)_2$ solution in the range 1.0×10^{-1} to 1.0×10^{-9} mol L^{-1}. The standard solution had been obtained by gradual dilution of stock solution 1.0×10^{-1} mol L^{-1} $Mn(NO_3)_2$. The potential measurements with the CGE and CPGE were performed on a pH meter (Orion 4) at 25±0.1°C in conjunction of Ag/AgCl (NaCl 3 mol L^{-1}) BASI 2056 as reference electrode with the following cell assemblies;

CGE|Test solution||Ag/AgCl|NaCl (3 mol L^{-1})
CPGE|Test solution||Ag/AgCl|NaCl (3 mol L^{-1})
Activity coefficient were calculated according to the Debye-Huckel procedure [31].

6.3. RESULTS AND DISCUSSION

6.3.1. Complexation study

The important component of a membrane is the ionophore. The purpose of the ionophore is to facilitate the transport of some ions more as compared to all other ions.

Thus, such membrane shows selectivity for the ion which has been facilitated for transport to the membrane. The important criteria for a membrane to show discriminate response toward some ions is that it should have a strong affinity for some particular ions and poor for all other ions. Therefore, before establishing selectivity studies on some membranes it is important that affinity studies for the ionophores should be carried out. Thus, conductometric titration was carried out in order to know the affinity of these ionophores in DMF solutions at 25±0.1°C. For this purpose, 25 mL of 1.0×10^{-4} mol L^{-1} cation solution was titrated against a 1.0×10^{-2} mol L^{-1} ionophore solution in DMF. The conductance of the solution was measured after each addition of ionophores.

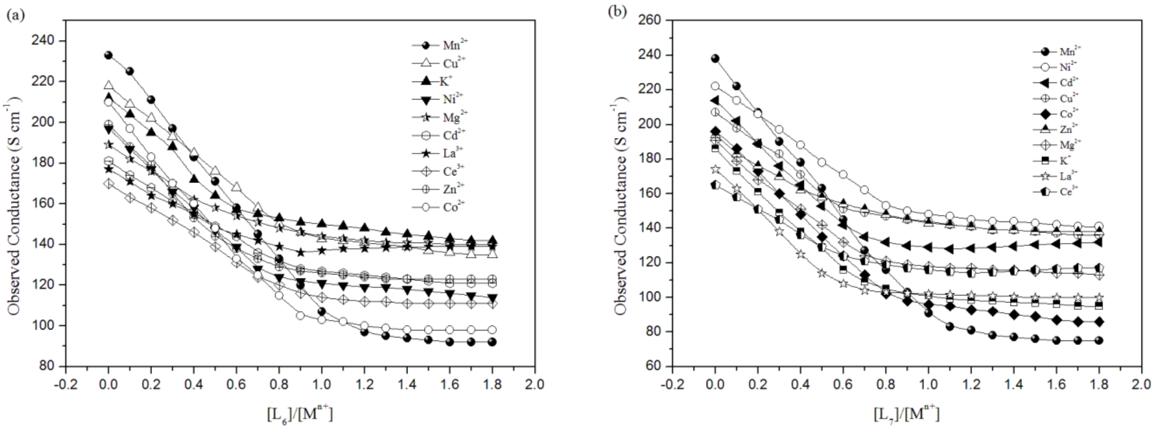

Fig. 6.3. Variation in the conductance of cationic solution with the addition of ionophores (a) L_6 and (b) L_7.

The conductance variation plots with different metal ions as a function of the [L]/[M^{n+}] molar ratio is shown in Fig. 6.3. It is observed from the Fig. 6.3 that conductance variation of Mn^{2+} solution shows maximum variation with the addition of ionophore, initially the conductance falling off with the addition of ionophore indicating that Mn^{2+} is strongly interacting with the ionophores. A stage is arrived when conductance of solutions nearly becomes constant and further addition of ionophores does not cause any appreciable change in the conductance which demonstrates that all of the metal ions have been consumed by the ionophores in forming complexes. The break point in the conductance variation plots gives the stoichiometry of the resulting complex. It is seen from Fig. 6.3, that the stoichiometry of metal to ionophore is found to be 1:1. Therefore, L_6 and L_7 are explored as neutral carrier in the fabrication of Mn^{2+} ion-selective sensor using CGE and CPGE.

6.3.2. Membrane's Composition Optimization and Potential Measurements

The selectivity, sensitivity and linearity estimated for a specified ionophore highly depends on the nature of plasticizer and membrane ingradients [32]. It has also been found that additives added [33, 34] influence the performance of the sensor. The potential of CGE (membranes containing L_6 and L_7) were recorded and performance of the electodes are documented in Tables 6.1 and 6.2, respectively. The sensor 1 (of L_6, Table 6.1) and 13 (of L_7, Table 6.2) having no plasticizer and additive were found to show working concentration range 5.49×10^{-6}-1.0×10^{-1} mol L^{-1} for L_6, 6.45×10^{-6}-1.0×10^{-1} mol L^{-1} for L_7 with the Nernstian slope 24.6±0.3 and 25.3±0.3 mV $decade^{-1}$ of activity, respectively.

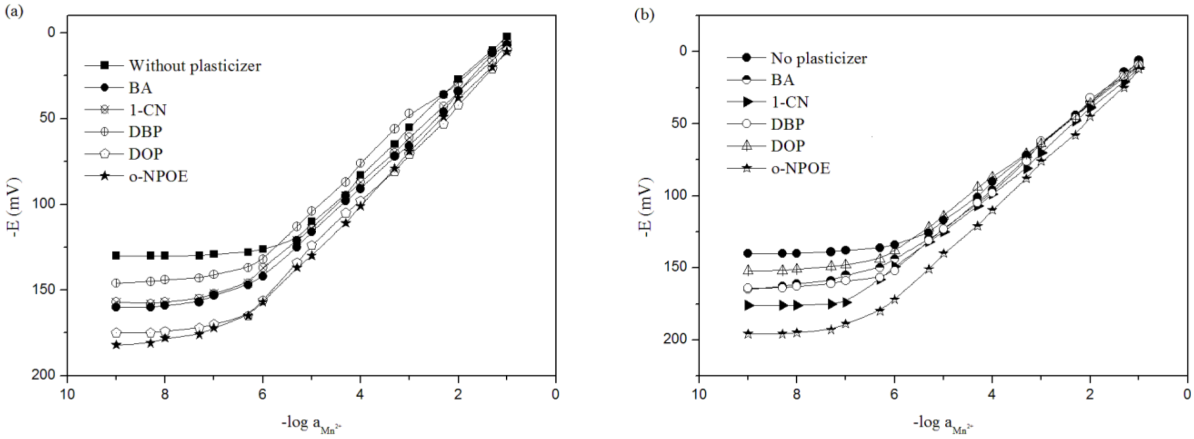

Fig. 6.4. Potential vs. concnentration graph displaying deviation of membrane potential for Mn^{2+} ion with different plasticizers.

The working concentration range is narrow and the slope is non Nernstian and hence, the performance of membrane needs to be improved. It is well known that the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of ionophore molecules [35-37]; therefore, it is expected to play an important role in determining the ion selective characteristics. Thus, in these studies five plasticizers viz., *o*-NPOE, BA, 1-CN, DBP and DOP were incorporated and the responses obtained are shown in Fig. 6.4 and reported in Tables 6.1 and 6.2. Comparing the responses of plasticized and non-plasticized membranes it is observed that the addition of plasticizer improves the performance of the electrode (electrode numbers 2-6 for L_6 and 14-18 for L_7) with respect to wide working concentration range and near Nernstian slope. It is further seen that the electrode nos. 5 and 17 having *o*-NPOE as plasticizer performs the best as they exhibit widest working concentration range and near Nernstian slope. The association of additives can significantly improve the selectivity of an ion-selective sensor is a well known fat [38]. Thus, effect of NaTPB and KTpClPB was studied as additives. The response shown in

Tables 6.1 and 6.2 reveals that NaTPB produces significant effects, electrode numbers 7 and 19 containing 2% (w/w) NaTPB performs best in terms of wide working concentration range with Nernstian slope and lower detection limit over the KTpClPB incorporating membrane.

It is observed from Tables 6.1 and 6.2 that electrode number 7 with membrane of composition of L_6: PVC: *o*-NPOE: NaTPB in the ratio of 6:36:56:2 (w/w, mg) and electrode number 19 with membrane of composition of L_7: PVC: *o*-NPOE: NaTPB in the ratio of 6:34:58:2 (w/w, mg) gives the best performance in terms of wide working concentration range, slope and lower detection limit. The alternation in response with varying quantity of ionophores and anionic excluders was also examined and reported in the Tables 6.1 and 6.2. It has been found that change in amount of ionophore and anionic excluder does not in any way improve the performance of the electrode (electrode numbers 9-12 and 21-24).

6.3.3. Effect of pH on the Performance of Sensor

The effect of pH on the performance of the modified electrodes was examined by measuring their potentiometric responses for 1.0×10^{-3} mol L^{-1} and 1.0×10^{-4} mol L^{-1} solution of Mn^{2+} ions at different pH values ranging from 1.0 to 12.0. The pH was adjusted by the addition of 1.0×10^{-1} mol L^{-1} HCl/NaOH and the results are shown in Fig. 6.5.

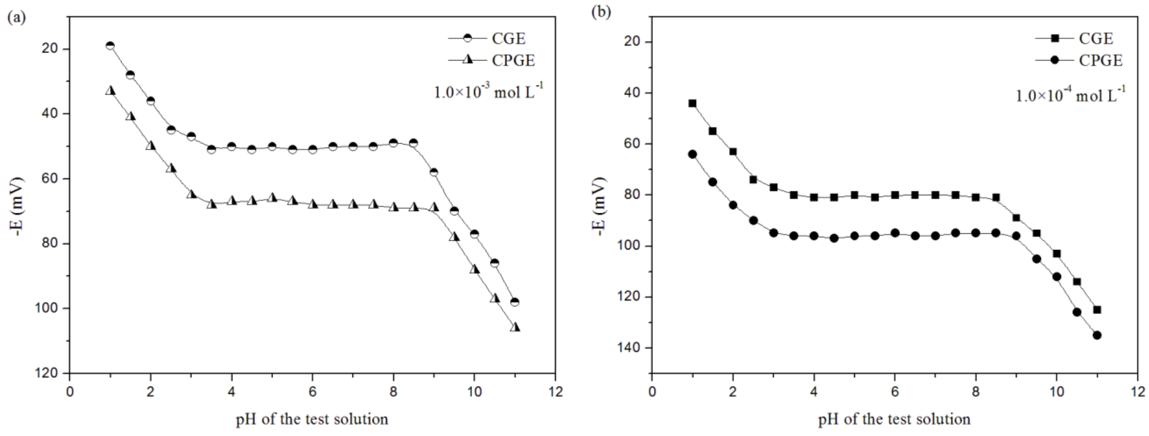

Fig. 6.5. Effect of pH of the test solution on the potential responses of CGE and CPGE with (a) 1.0×10^{-3} mol L^{-1} and (b) 1.0×10^{-4} mol L^{-1} of Mn^{2+} ion solutions at different pH.

The potential response for CGE is independent of pH in range 3.5-8.5 and CPGE can be used in pH range of 3.5-9.0. The deviation in performance at higher pH has been reported as a result of metal hydroxides accumulation in the matrix [39] and the deviation at low pH may be regarded as the effect of protonation of ionophore [40] and the electrodes start responding to H_3O^+ ions along with Mn^{2+} ion leading to an increase in potential.

6.3.4. Effect of Interfering Ions on the Performance of Sensor

The most important parameter which reflects the applicability of an ISE is its selectivity, which is measured in terms of selectivity coefficient. The potentiometric selectivity coefficient for the CGE and CPGE were determined according to IUPAC recommended fixed interference method (FIM) [41].

In this method, the selectivity coefficient was evaluated from the potential measurement on solutions containing a fixed concentration of interfering ion (1.0×10^{-2} mol L^{-1}) and varying amount of Mn^{2+} ion solution ranging from 1.0×10^{-1} to 1.0×10^{-9} mol L^{-1}. The potential values so obtained were then plotted versus activity of Mn^{2+} ion. The linear portion of potential response curve then extrapolated and the value of a_{Mn2+} were obtained from the intersection point. The potentiometric selectivity coefficient were then determined using the following expression:

$$K_{A,B}^{Pot} = \frac{(a_A)}{(a_B)^{Z_A/Z_B}} \qquad (1)$$

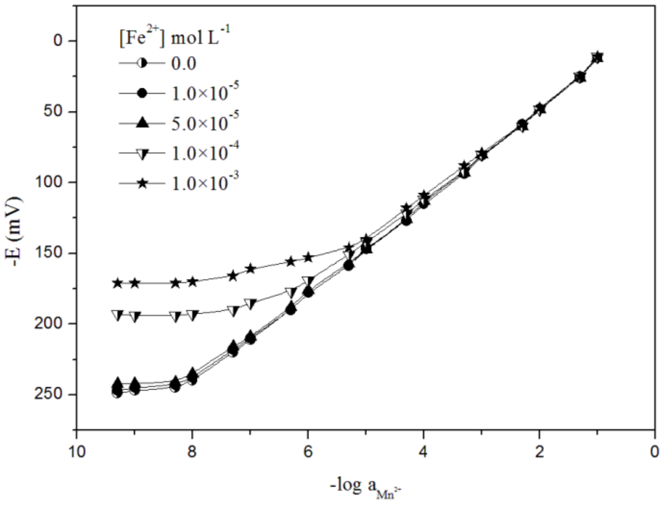

Fig. 6.6. Effect of different concentration of Fe^{2+} ion on the performance of the sensor.

Where a_A is the activity of primary ion A (Mn^{2+}) at the point of intersection, a_B is the activity of interfering ion B and z_A and z_B are their corresponding ionic charges. Selectivity coefficient value thus estimated for the CGE and CPGE are doccumented in the Table 6.3. From the selectivity coefficient given in the Table 6.3 it is observed that the electrodes are highly selective over a number of monovalent, divalent and trivalent cations. However, selectivity coefficient obtained for Fe^{2+} is not very low and it would cause some interference if present in higher concentration. Thus, it was thought to examine the tolerance limit of the sensor in the presence of Fe^{2+} and for this purpose, mixed run studies were performed and the effect of Fe^{2+} ion concentration on the performance of sensor was examined. The potential were measured in the presence of different concentrations (1.0×10^{-5}, 5.0×10^{-5}, 1.0×10^{-4} and 1.0×10^{-3} mol L^{-1}) of Fe^{2+} ion and the potential response of the sensor to the mixture is shown in Fig. 6.6.

It is seen from the figure that Fe^{2+} at $\leq5.0\times10^{-5}$ mol L^{-1} did not cause any deviation in the original plot obtained in pure Mn^{2+} ion. Thus, the sensor can tolerate Fe^{2+} at $\leq5.0\times10^{-5}$ mol L^{-1} over the entire working concentration range.

Table 6.3. Interfering ions and their selectivity coefficient for Mn^{2+} ion-selective sensor.

Interfering ions	Selectivity coefficient ($K^{FIM}_{Mn^{2+},B}$)	
	CGE	CPGE
Ni^{2+}	6.6×10^{-3}	5.2×10^{-3}
Zn^{2+}	4.8×10^{-3}	2.9×10^{-3}
Co^{2+}	4.4×10^{-3}	2.1×10^{-3}
Cd^{2+}	5.3×10^{-4}	3.4×10^{-4}
Fe^{2+}	5.5×10^{-2}	4.1×10^{-2}
Hg^{2+}	6.1×10^{-4}	3.8×10^{-4}
Mg^{2+}	5.8×10^{-4}	4.2×10^{-4}
Ca^{2+}	4.7×10^{-4}	3.5×10^{-4}
Na^{+}	7.9×10^{-4}	5.4×10^{-4}
La^{3+}	8.2×10^{-5}	6.3×10^{-5}
Ce^{3+}	5.2×10^{-4}	3.1×10^{-4}

However, when Fe^{2+} ion is present in higher concentration, significant interference was observed which causes shortening of working concentration range and thus Mn^{2+} ion could be determined in the reduced working concentration ranges of 8.70×10^{-7}-1.0×10^{-1} and 7.91×10^{-6}-1.0×10^{-1} mol L^{-1} in the presence of 1.0×10^{-4} and 1.0×10^{-3} mol L^{-1} of Fe^{2+} ion, respectively. From Table 6.3, it has also been observed that CPGE based on L_7 perform comparably better than CGE.

6.3.5. Determination of Dynamic Response Time and Life Span of Sensor

Dynamic response time is an important factor for an ISE. According to IUPAC recommendations, the response time of an ion selective electrode is defined as the length of time between the instant at which the ion selective electrode and reference electrode are immersed in the solution and the moment at which the potential of the cell reaches its steady-state value within ±1 mV [42].

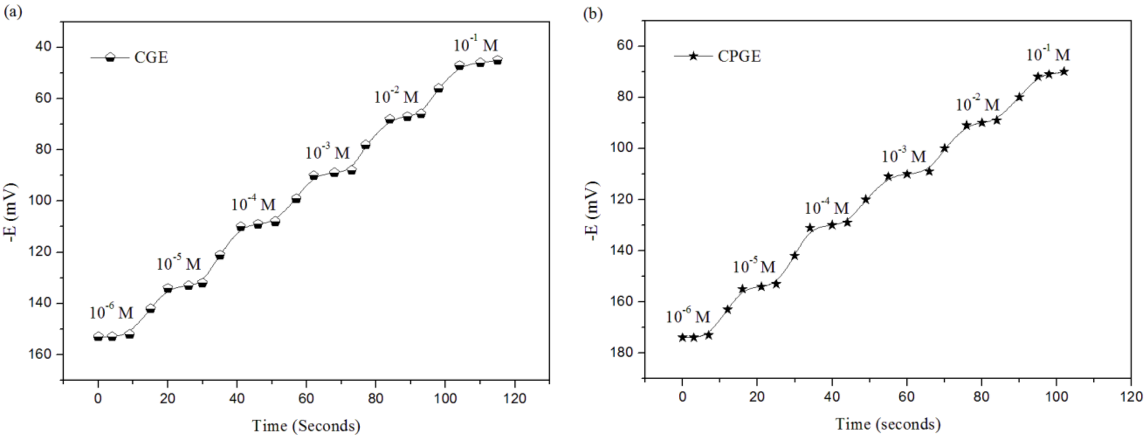

Fig. 6.7. Dynamic response time of the Mn^{2+} ion sensor based on L_7 for step changes in concentration of Mn^{2+} ion with (a) CGE and (b) CPGE.

Response time of the sensor can be measured by consecutively changing the concentration of the test solution from 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1}. The average time needed to attain a potential response in the electrodes lies within ±1 mV range value of final equilibrium after immersing successively in a series of Mn^{2+} ion solution, each having a 10-fold difference in concentration was 11 s for CGE and 9 s for CPGE as shown in Fig. 6.7.

The life time was determined by measuring the response of electrodes at different time intervals and results are compiled in the Table 6.4. Thus, CGE and CPGE could be used over a period of 4 months, and it was concluded that sensor show no remamrkable depletion from the Nernstian slope from 29.4±0.3 to 25.1±0.5 mV decade^{-1} of activity, the linearity shifted from 6.3×10^{-8}-1.0×10^{-1} to 4.2×10^{-7}-1.0×10^{-1} mol L^{-1} and the detection limit reduces from 1.9×10^{-8} to 1.7×10^{-7} mol L^{-1} for CGE and for CPGE the slope reduces from

29.5±0.4 to 25.6±0.2 mV decade^{-1} of activity, the working concentration range reduces from 1.2×10^{-8}-1.0×10^{-1} to 2.9×10^{-7}-1.0×10^{-1} and the detection limit shifted from 4.7×10^{-9} to 1.3×10^{-7} mol L^{-1}.

Table 6.4. Potential response of Mn^{2+} selective electrode based on L_7 using CGE and CPGE at different time intervals.

Time (Days)	Slope (mV decade^{-1} of activity)	Working concentration range (mol L^{-1})	Detection Limit (mol L^{-1})
CGE			
2	29.4±0.3	6.3×10^{-8}-1.0×10^{-1}	1.9×10^{-8}
10	29.3±0.4	6.5×10^{-8}- 1.0×10^{-1}	2.0×10^{-8}
30	29.3±0.6	7.0×10^{-8}-1.0×10^{-1}	3.6×10^{-8}
45	29.1±0.2	7.4×10^{-8}-1.0×10^{-1}	3.9×10^{-8}
60	28.7±0.2	8.0×10^{-8}-1.0×10^{-1}	4.3×10^{-8}
75	28.3±0.5	8.7×10^{-8}-1.0×10^{-1}	5.2×10^{-8}
90	28.0±0.4	9.4×10^{-8}-1.0×10^{-1}	6.8×10^{-8}
110	27.6±0.3	1.5×10^{-7}-1.0×10^{-1}	9.1×10^{-8}
120	27.1±0.5	2.4×10^{-7}-1.0×10^{-1}	7.6×10^{-8}
130	25.1±0.5	4.2×10^{-7}-1.0×10^{-1}	1.7×10^{-7}
CPGE			
2	29.5±0.4	1.2×10^{-8}-1.0×10^{-1}	4.7×10^{-9}
10	29.5±0.4	1.2×10^{-8}-1.0×10^{-1}	4.7×10^{-9}
30	29.4±0.2	1.5×10^{-8}-1.0×10^{-1}	5.0×10^{-9}
45	29.2±0.6	2.2×10^{-8}-1.0×10^{-1}	5.6×10^{-9}
60	29.0±0.3	3.6×10^{-8}-1.0×10^{-1}	7.2×10^{-9}
75	28.6±0.5	4.4×10^{-8}-1.0×10^{-1}	2.3×10^{-8}
90	28.2±0.2	5.1×10^{-8}-1.0×10^{-1}	2.8×10^{-8}
110	27.9±0.6	6.6×10^{-8}-1.0×10^{-1}	3.4×10^{-8}
120	27.4±0.3	8.4×10^{-8}-1.0×10^{-1}	5.9×10^{-8}
130	25.6±0.2	2.9×10^{-7}-1.0×10^{-1}	1.3×10^{-7}

6.3.6. Effect of Non Aqueous Medium on the Performance of Sensor

The efficiency of the sensor was also estimated in partially non-aqueous solutions (non-aqueous content might be present in analytical samples) in the range of 10-40% (v/v) non-aqueous content of methanol-water, ethanol-water and acetonitrile-water mixtures and the results are compiled in Table 6.5.

The electrodes did not reflect any considerable deviation from the linearity and Nernstian slope in solution containing 30% of non-aqueous content (ethanol-water and acetonitrile-water mixtures), but drastic change has been observed in the case of methanol-water mixture and it was found that only 20% (v/v) amount of methanol-water could be tolerated.

Table 6.5. Applicabilty of sensor in partially non-aqueous medium.

Non-aqueous contents (%; v/v)	Working concentration range (mol L^{-1})	Slope (mV $decade^{-1}$ of activity)
0	1.23×10^{-8}-1.0×10^{-1}	29.4±0.3
Ethanol		
10	1.23×10^{-8}-1.0×10^{-1}	29.4±0.3
20	1.23×10^{-8}-1.0×10^{-1}	29.4±0.5
30	1.87×10^{-8}-1.0×10^{-1}	29.2±0.5
35	3.91×10^{-8}-1.0×10^{-1}	28.8±0.4
40	6.47×10^{-7}-1.0×10^{-1}	27.9±0.3
Methanol		
10	1.23×10^{-8}-1.0×10^{-1}	29.4±0.6
20	1.23×10^{-8}-1.0×10^{-1}	29.4±0.4
30	4.61×10^{-8}-1.0×10^{-1}	28.6±0.4
35	8.47×10^{-7}-1.0×10^{-1}	27.9±0.3
40	9.12×10^{-7}-1.0×10^{-1}	26.8±0.6
Acetonitrile		
10	1.23×10^{-8}-1.0×10^{-1}	29.4±0.3
20	1.23×10^{-8}-1.0×10^{-1}	29.4±0.6
30	2.12×10^{-8}-1.0×10^{-1}	29.4±0.5
35	5.57×10^{-8}-1.0×10^{-1}	28.7±0.5
40	7.97×10^{-7}-1.0×10^{-1}	27.5±0.3

Therefore, the electrode is not suitable for using in methanol-water mixture above 20% (v/v) concentration. This may be due to greater solubility of the ionophore in methanol which causes leaching of ionophore from the membrane phase.

6.3.7. Comparative Performance Characteristic of Coated Graphite Electrode (CGE) and Coated Pyrolytic Graphite Electrode (CPGE)

The studies suggest that ionophores L_6 and L_7 show high affinity for Mn^{2+} ion. The sensor number 19 incorporating L_7 and containing *o*-NPOE as plasticizer with the optimized membrane of composition (w/w; mg) L_7: PVC: *o*-NPOE: NaTPB ≡ 6:34:58:2 exhibits the linearity (6.30×10^{-8}-1.0×10^{-1} mol L^{-1}) and Nernstian slope (29.4±0.3 mV $decade^{-1}$ of activity) with a detection limit of 1.90×10^{-8} mol L^{-1}. The CPGE was prepared with the same composition and thus obtained results were compared with the CGE.

Table 6.6. Potentiometric performance characteristic of Mn^{2+} sensor based on CGE and CPGE.

Properties	Values/range	
	CGE	CPGE
Optimized membrane composition	L_7: PVC: *o*-NPOE: NaTPB≡ 6:34:58:2 (w/w, mg)	L_7: PVC: *o*-NPOE: NaTPB≡ 6:34:58:2 (w/w, mg)
Conditioning time	24 h in 1.0×10^{-3} mol L^{-1} $Mn(NO_3)_2$	24 h in 1.0×10^{-3} mol L^{-1} $Mn(NO_3)_2$
Working concentration range (mol L^{-1})	6.30×10^{-8}-1.0×10^{-1}	1.23×10^{-8}-1.0×10^{-1}
Detection limit (mol L^{-1})	1.90×10^{-8}	4.78×10^{-9}
Slope (mV $decade^{-1}$ of activity)	29.4±0.3	29.5±0.4
Response time (s)	11	9
Life span (month)	4	4
Working pH range	3.5-8.5	3.5-9.0

The potential responses of the CGE and CPGE are shown in Fig. 6.8, which reveal their Nernstian behaviour over a wide working concentration range.

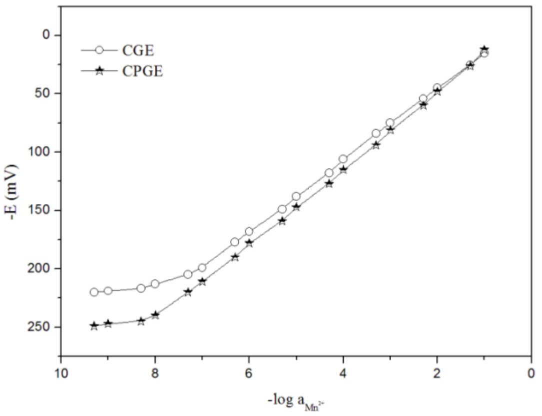

Fig. 6.8. Potentiometric characteristic calibration plots for Mn^{2+} ion selective sensor (CGE and CGPE) based on L_7.

Comparision Table 6.6 demonstrate that while both electrodes show a nice Nernstian behaviour with fast response, the wide working concentration range and the limit of detection of CPGE are significantly improved relative to that of CGE. The sensor is compared with previously reported electrodes (Table 6.7) and found that the sensor is superior in terms of selectivity, sensitivity and low detection limit.

6.4. ANALYTICAL APPLICATIONS

The sensor show high selectivity for Mn^{2+} ion and thus it is suitable for the monitoring of Mn^{2+} ion in various environmental samples.

6.4.1. Potentiometric titration

The sensor could be used as an indicator electrode in the potentiometric titration of Mn^{2+} ion solution by titrating against EDTA solution. For this purpose, a potentiometric titration of 25 ml of 2.0×10^{-3} mol L^{-1} Mn^{2+} ion solution against 1.0×10^{-2} mol L^{-1} solution of EDTA at pH 5.5 was carried out using the electrode and the titration plot obtained (Fig. 6.9) had shows shape which also supports that these electrodes are substantially selective to Mn^{2+} ion.

The inflexion point corresponds to 1:1 stoichiometry of Mn^{2+}-EDTA complex and therefore, these electrodes can be used as an indicator electrode for the determination of Mn^{2+} by titration.

Table 6.7. **Comparison of performance characteristic of Mn^{2+} sensor with previously reported sensors.**

Ref. no.	Ionophore	Linear range (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mVdecade^{-1} of activity)	pH range	Response time (s)
[1]	Dihydrogen[N, N',N", N'''-1,5,8,12-tetraazadodecane-bis(salicylaldominato)]	5.0×10^{-6}-1.0×10^{-1}	NM	30.0	3.0-6.5	10
[21]	N-(2-picolinamido ethyl)-picolinamide	1.0×10^{-5}-1.0×10^{-1}	8.0×10^{-6}	29.3±0.5	4.0-9.0	15
[22]	Pentaaza macrocyclic manganese complex	1.2×10^{-5}-1.0×10^{-1}	1.2×10^{-5}	29.5	3.0-8.0	20
[23]	5-[(4-nitrophenylazo)-N-hexylamine]salicylaldimine	4.0×10^{-7}-1.8×10^{-2}	1.0×10^{-7}	30.1±1.0	4.5-7.5	10
[24]	3-(6-Aminopyridin-2-ylimino)-1,3-diphenylpropylidene) pyridine-2,6-diamine	1.0×10^{-6}-1.0×10^{-1}	4.0×10^{-7}	29.6±0.5	4.0-8.0	15
[25]	Heterogeneous membrane of manganese dibenzyldithiocarbamate	1.0×10^{-8}-1.0×10^{-1}	NM	33.1	2.5-5.5	15
[26]	Polypyrrole Sn (IV) phosphate	1.0×10^{-6}-1.0×10^{-1}	1.0×10^{-6}	29.6	3.0-8.0	40
[27]	(E)-2-(hydroxyl-5-methoxybenzylideneamino)phenol	6.0×10^{-6}-2.0×10^{-2}	NM	29.0±1.0	4.0-9.5	11
[28]	N2,N4-di(cyanoethyl)-2,4-bis(2-acetoxybenzylamino)-6-phenyl-1,3,5-triazine	4.1×10^{-7}-1.0×10^{-1}	6.7×10^{-8}	29.5±0.3	3.0-9.0	12
This work	(N',N'''E,N',N'''E)-N',N'''-(((propane-1,3-diylbis (oxy))bis(2,1-phenylene))bis(methanylylidene))di-(isonicotinohydrazide) (L_7)	1.2×10^{-8}-1.0×10^{-1}	4.7×10^{-9}	29.5±0.4	3.5-9.0	9

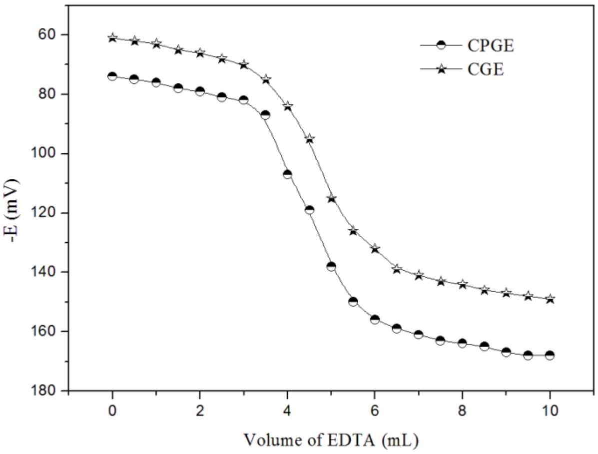

Fig. 6.9. **Potentiometric characteristic calibration plots for Mn^{2+} ion selective sensor (CGE and CGPE) based on L_7.**

6.4.2. Determination of Mn^{2+} ion in soil and water samples

The best electrode (CPGE) was used for the monitoring of Mn^{2+} ion in waste water taken from the State Infrastructure and Industrial Development Corporation Uttaranchal (SIDCUL) Industrial area as well as water taken from Ganga River, Haridwar and Indian Institute of Technology-Roorkee Chemistry Department. The samples were taken from different locations and treated with diluted nitric acid. The pH of these samples was adjusted to 5.5 before the measurement. The potentiometry results are in good agreement with those obtained by AAS (Table 6.8).

The soil samples were digested in a cleaned Teflon beaker by treating 2 g of each soil sample with 10 mL of nitric acid. A 5:3:5 mixtures of nitric acid, perchloric acid and concentrated hydrofluoric acid were added, followed by controlled heating until white fumes evolved. The solution was filtered and diluted with distilled water to a final volume of 25 mL in a volumetric flask [43]. The pH of these samples was adjusted to 5.5 before the measurement. The results (Table 6.8) obtained by potentiometry are in good agreement with those obtained by AAS.

6.4.3. Determination of Mn^{2+} ion in medicinal plants and vegetable samples

The sensor was successfully employed for the Mn^{2+} ion quantification in some medicinal plants (*Andrographis paniculata*, *Adhatoda vasica* and *Withania somnifera*) and soil samples collected from Haridwar and Roorkee regions. 2 g of dried powdered plant samples was digested with a 5:1 mixture of nitric acid (25 vol.%) and perchloric acid, followed by controlled heating until the evolution of gases ceased. 15 mL of double distilled water was added to this mixture and filtered through into a 25 mL volumetric flask. The volume was adjusted to a final volume of 25 mL. The pH of these samples was adjusted to 5.5 before the measurement. Then it was analysed by the sensor and the results obtained are in close agreement with those obtained for AAS (Table 6.9) experiment and showing the analytical utility of the electrodes.

Table 6.8. Determination of Mn^{2+} in water samples.

Samples		ISE*±SD (mg L^{-1})	AAS*±SD (mg L^{-1})
Haridwar	Water sample 1	04.8±0.4	05.0±0.1
	Water sample 2	04.1±0.2	04.2±0.2
Laboratory waste water	Water sample 1	09.4±0.6	09.3±0.5
	Water sample 2	09.9±0.3	09.8±0.6
Industrial waste water	Water sample 1	14.0±0.3	13.9±0.6
	Water sample 2	13.5±0.6	13.3±0.4
Mn^{2+} ion in Soil		ISE*±SD (mg kg^{-1})	AAS* ±SD (mg kg^{-1})
Haridwar	Soil sample 1	269.4±0.6	270.9±1.0
	Soil sample 2	261.8±3.6	263.1±1.9
Roorkee	Soil sample 1	249.8±1.2	247.2±1.8
	Soil sample 2	231.7±0.7	233.1±0.5

*Mean value ± standard deviation (triplicate measurements).

Fresh vegetables were washed with double distilled water thoroughly to remove soil from the surface and dried. These vegetables (2 g) were digested with 1:1 (v/v) HNO_3 and HCl solution and heated to 100 °C for 12 h. After digestion, the resulting solution was cooled to room temperature and filtered. The volume was adjusted to a final volume of 25 mL. The pH was adjusted to 5.5 before the measurement. The potentiometry results (Table 6.9) are in good agreement with those obtained by AAS.

6.5. CONCLUSION

The studies on a large number of electrodes based on ionophores L_6 and L_7 have shown that the plasticizer *o*-NPOE enhances the performance characteristics of electrodes are better than the rest of the plasticizers. The CPGE having composition L_7: PVC: *o*-NPOE: NaTPB ≡ 6:34:58:2 (w/w, mg) is found to be best with respect to lower detection limit (4.78×10^{-9} mol L^{-1}), wide working concentration range (1.23×10^{-8}-1.0×10^{-1} mol L^{-1}) and Nernstian slope (29.5±0.4 mV decade^{-1} of activity). The electrode is independent of pH in the regions 3.5 to 9.0. The response time (9 s) of the electrode was found to be quite fast and can work satisfactorily in partially non-aqueous content. Therefore, the sensor was successfully employed in the potentiometric titration of Mn^{2+} ion with EDTA as an indicator electrode and also used for the monitoring of Mn^{2+} ion in various real samples *viz*., water, soil, vegetables and medicinal plants samples.

Table 6.9. Determination of Mn^{2+} in medicinal plant samples.

Samples	ISE*±SD (mg kg^{-1})	AAS*±SD (mg kg^{-1})
Andrographis paniculata	46.1±1.3	48.7±0.8
Adhatoda vasica	35.9±1.8	36.2±1.7
Withania somnifera	62.4±2.6	63.7±1.0
Mn^{2+} ion in Vegetables	ISE*±SD (mg kg^{-1})	ISE*±SD (mg kg^{-1})
Solanum tuberosum (Potato)	10.5±0.5	11.6±1.3
Allium cepa (Onion)	13.2±0.8	12.8±0.6
Daucus carota (Carrot)	08.4±0.8	08.6±0.6

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Chapter 7

“Multidentate Schiff Bases of Hydrazinecarbothioamide as Co^{2+} and Zn^{2+} Ion-Selective Sensors”

7.1. INTRODUCTION

The increase of metal concentration in the environment caused by natural processes and human activities, poses hazards to human and animal life. Thus, the toxic effects of metals present in environment have made it imperative to determine them in environmental samples. The determination of metals in pharmaceutical, clinical, environmental and other samples is thus important. As a result of extensive investigations, a large number of sensors have been reported for estimation of a number of heavy metal ions.

7.1.1. Co^{2+} Ion-Selective Sensor

Monitoring of cobalt is relevent because of its free occurence in the environment (meteorites, sea and in fresh water, animals and plants) accounting for 0.001% of earth crust [1]. Cobalt is being used in electroplating industry, as prime material for the preparation of batteries, paints and as catalysts in the chemical and food industry [2]. Cobalt perform important role in the metabolism of iron and synthesis of haemoglobin. Cobalt is essential for living beings as an important co-factor in vitamin B_{12} [3, 4] and as a key component in a number of enzymes [5]. Cobalt deficiency may lead to retarded growth, loss of appetite and anaemia and if it is consumed in dose higher than a threshold value may exert toxicity in the form of irritation of gastrointestinal tract, vomiting and diarrhoea [6]. The subjection to cobalt may lead to severe dieseses like coughing, asthma, pulmonary edema and pneumonia [7, 8]. Cobalt intake above 10 ppm has been reported as toxic for genral livestock species [9]. Numerous advanced techniques have been developed for the monitoring of cobalt and these include graphite furnace atomic absorption spectrometry, flame atomic absorption spectrometry, differential pulse anodic stripping voltammetry, electrothermal-atomic absorption spectrometry, thin film sequential injection and electrochemiluminescence [10-15]. Although, above mentioned techniques have been employed for the determination of cobalt but are not very convenient for the analysis of a large number of samples as they generally require of expertise and large infrastructure backup. ISEs are considerably used for quantifying the analyte as they offer advantages in terms of selectivity and sensitivity, simplicity and low cost [16].

Studies on ISEs reveal that varieties of ion carriers have been used in the development of Co^{2+} ion-selective electrode and these include the application of organic resins [17], mercapto compounds [18], OXCDD (diamide) [19], isothiazole [20], thiazole based ligands [21], calixarenes [22, 23], macrocycles [24-29] and Schiff bases [30-32].

However, the reported ISE have suffered from narrow working concentration range, low pH range, poor selectivity and high response time. Fabrication of new ion-specific ISE with high selectivity and sensitivity, wide working concentration range, long lifetime and good reproducibility, is always in need. Therefore, it is required to develop a better sensor for Co^{2+} ion. Potentiometric sensors comprising Schiff base as ion carrier have been reported to exhibit good selectivity for specific metal ions [33-35] and almost most of the metals form 1:1 metal complexes with Schiff bases [36] and Schiff bases are very well known as potential antimicrobial and anticonvulsant agents [37-39].

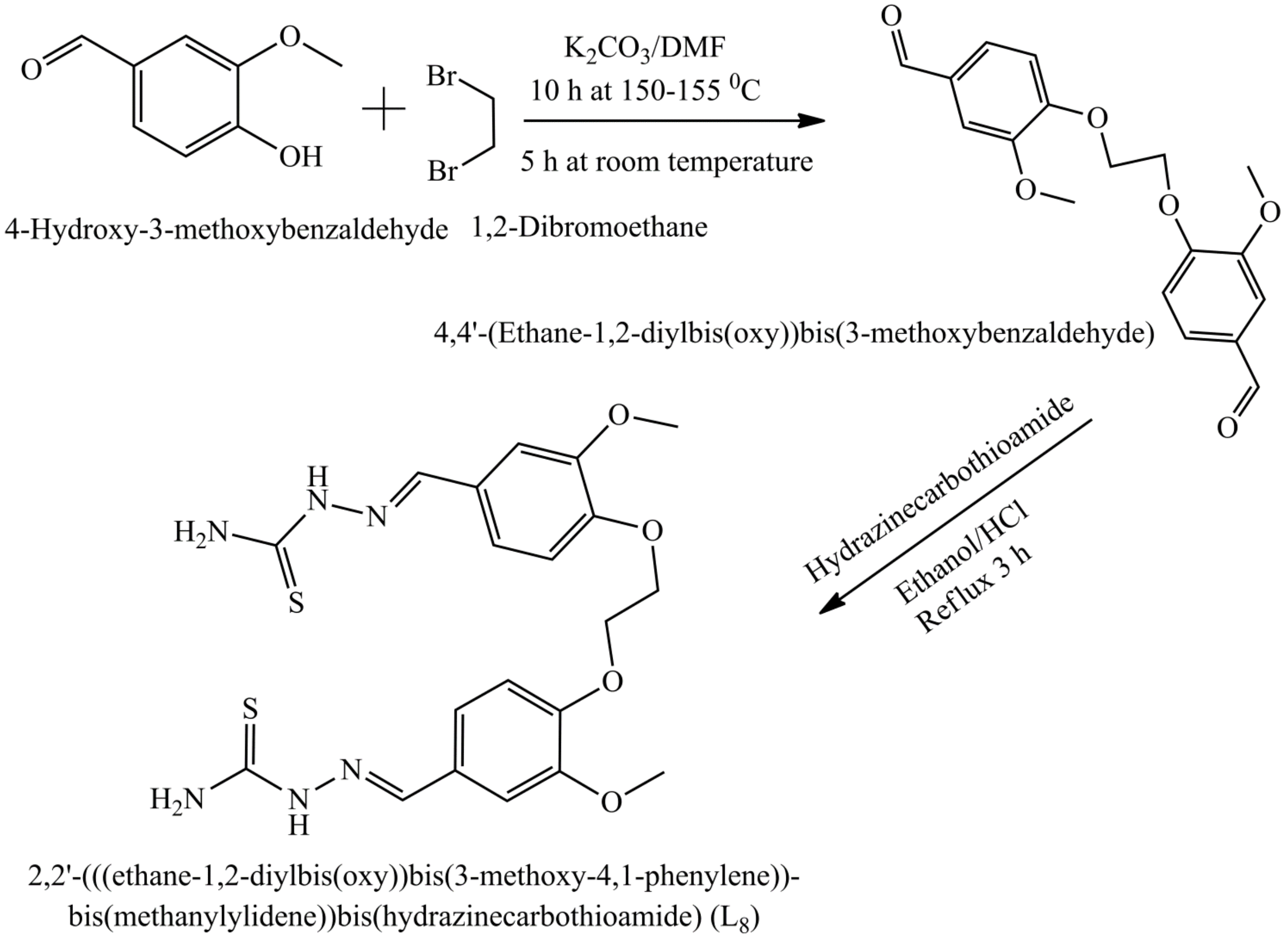

Fig. 7.1. **Synthesis of L_8.**

Therefore, much interest have been focused on the Schiff bases because they form selective and ideal complexes with transition and heavy metal ions and have been successfully used as ion carrier in the ISE [40, 41]. Recently, Singh *et al*., have prepared the ion-selective sensors of Cu^{2+}, Cd^{2+} and Mn^{2+} [42-44] by the fabrication of coated pyrolytic graphite electrode with improved selectivity and sensitivity. Thus, the present communication describes the application and comparative studies of three synthesised Schiff base ligands *viz*, L_8, L_9 and L_{10} as Co^{2+} ion-selective sensors.

7.1.2. Zn^{2+} Ion-Selective Sensor

Zinc is one of the most common element in Earth`s crust and also known as “essential trace element” as very small amount of it is necessary for human health and thereby monitoring of it assumes importance due to its widespread occurrence in industrial, environmental and biological samples. Zinc and its salts have numerous applications and are widely used in paints, in electrical devices, in rubber and tyre industries, ceramics, textiles, fertilizers, pigments, batteries, catalysts, corrosion control in drinking water and in medical supplements [45, 46].

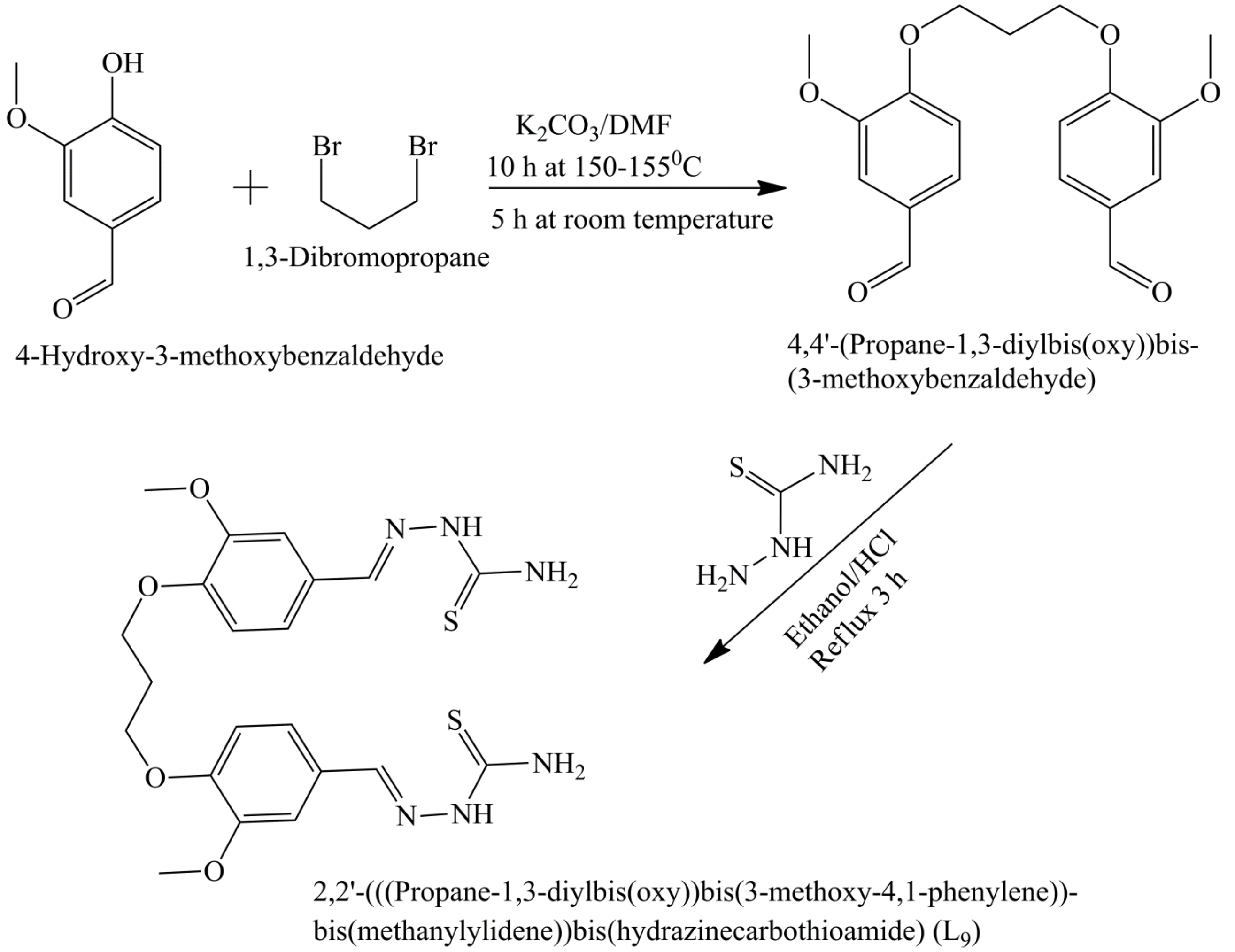

Fig. 7.2. Synthesis of L_9.

Zn^{2+} ion is an important bivalent cation in biological systems and performed vital roles in human body influencing DNA synthesis, gene expression, microtubule polymerization, immune system function and the activity of some enzymes such as carbonic anhydrase and matrix metalloproteinase [47]. Zinc is relatively non-toxic, but it may show toxicity if consumed in higher doses and may lead to variety of disorders such as systematic immunological, neurological, genotoxic, reproductive and carcinogenic effects [48-52]. Due to such a great diversity of zinc, monitoring of it needed and therefore efforts have made on the development of methods for its determination in various samples such as environmental, biological and industrial samples.

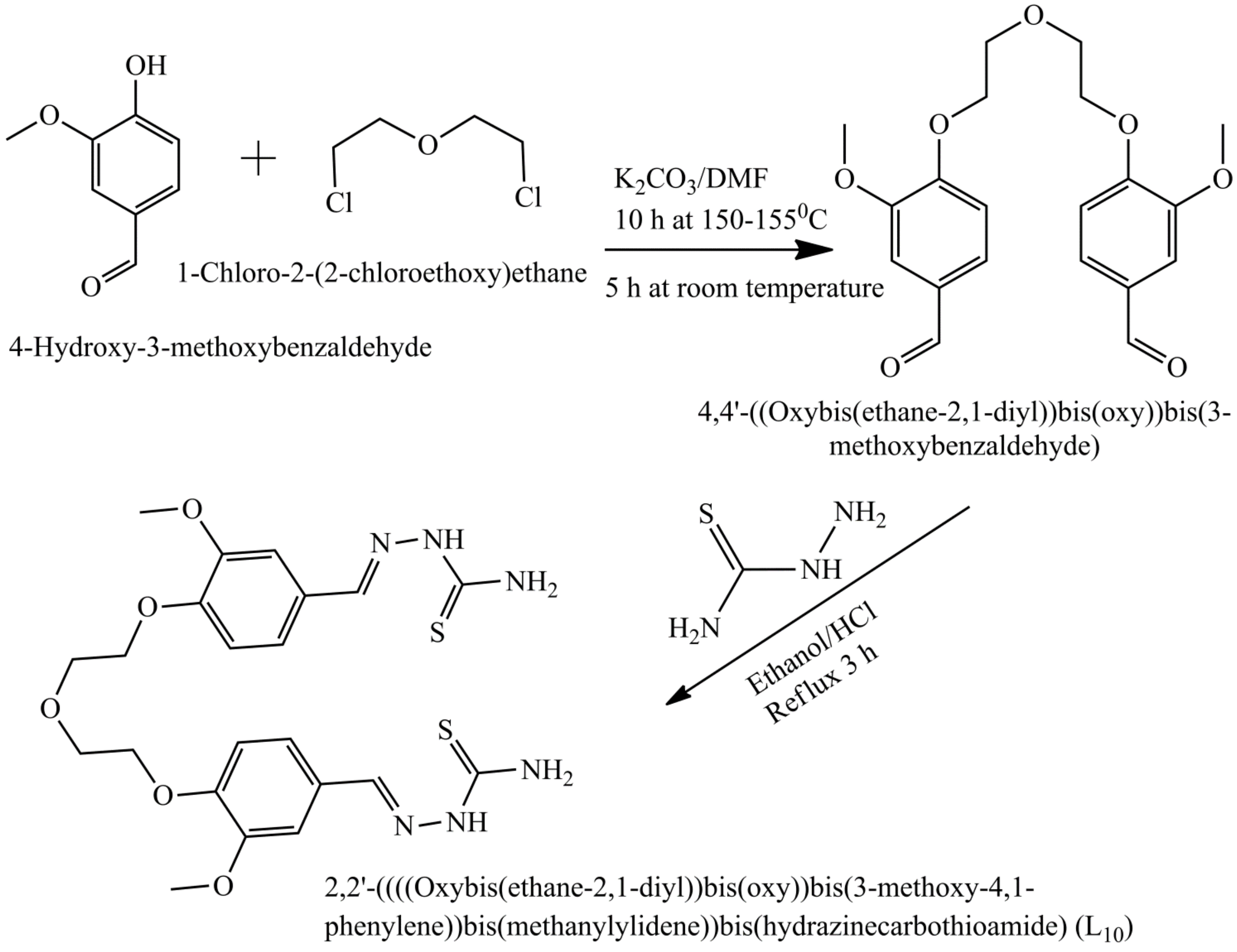

Fig. 7.3. Synthesis of L_{10}.

Literature survey revealed that attempts have been made for the monitoring of Zn^{2+} ion and these methods include UV-Vis spectroscopy [53], flame atomic absorption spectroscopy (FAAS) [54], inductively coupled plasma atomic emission spectroscopy (ICPAES) [55], voltammetric [56] and fluorescence spectroscopy methods [57, 58].

However, these methods provide accurate results, but are not very convenient for a large number of samples as they generally require adequate expertise and large scale infrastructure back-up. Therefore, there is a need to develop a convenient and direct method for the monitoring of Zn^{2+} ion in various samples. Ion selective electrodes (ISE) based on potentiometric monitoring of analyte ion in matrix offer several advantages over other techniques in terms of simple instrumentation, low-cost, fast response, reasonable selectivity and wide dynamic range.

Literature surveys have shown that varieties of ionophores have been used in the fabrication of Zn^{2+} ISE and these includes cryptands [59], sulipride drugs [60], chalcogenides [61], polypyrrole [60], porphyrins [62], bis(2-nitrophenyl)disulfide [64], crown ethers [65], thiazolidin-4-one [66], macrocycles [67, 68], N,N'-bis(acetylacetone)ethylenediamine [69], tripodal chelating ligand [70] and some more [71-74]. However, these efforts have not been very beneficial as most of the reported sensors have suffered from narrow working concentration range, low pH range, high response time

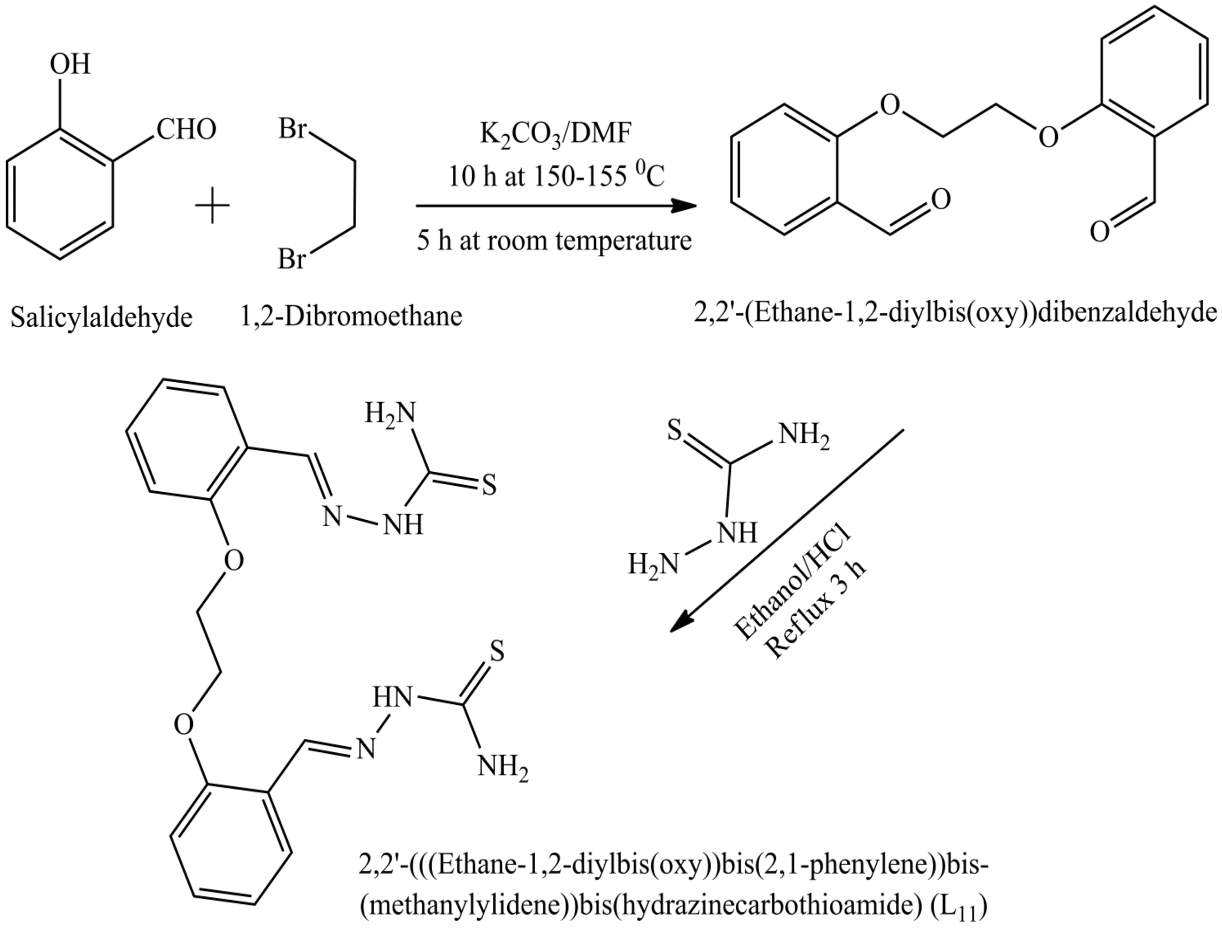

Fig. 7.4. Synthesis of L_{11}.

and substantial interferences from variety of cations. Fabrication of new ISE with high selectivity and sensitivity, wide dynamic range, long lifetime and good reproducibility, is always in need. Therefore, efforts have been made in present communication to develop a improved ion selective sensor by the fabrication of coated pyrolytic graphite electrode based on ligand 2,2'-(((ethane-1,2-diylbis(oxy))bis-(2,1-phenylene))bis(methanylylidene))-bis(hydrazinecarbothioamide) (L_{11}), 2,2'-(((propane-1,3-diylbis(oxy))bis(2,1-phenylene))-bis(methanylylidene))bis(hydrazinecarbothioamide) (L_{12}) and 2,2'-((((oxybis(ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene))bis(methanylylidene)bis(hydrazinecarbothioamide) (L_{13}).

7.2. EXPERIMENTAL

7.2.1. Chemical and Reagents

Salicylaldehyde, thiosemicarbazide, 4-hydroxy-3-methoxybenzaldehyde, 1,2-dichloroethane, 1,3-dibromopropane, 1-chloro-2-(2-chloroethoxy)ethane, high molecular weight poly(vinyl chloride) (PVC) and *o*-nitrophenyl octylether (*o*-NPOE) were procured from Aldrich (USA). Sodium tetraphenylborate (NaTPB) and 1-chloronaphthalene (1-CN) were procured from BDH (UK). Dioctylphthalate (DOP) and dibutylphthalate (DBP) were procured from Renkem and CDH (India), respectively. Benzylacetate (BA) and potassium tetrakis-p-(chlorophenyl)borate (KTpClPB) Fluka (Switzerland) were used as obtained. The nitrate and chloride salts of all the cations, ethylenediaminetetraacetic acid (EDTA) and solvents (ethanol, methanol, acetonitrile (ACN), tetrahydrofuran (THF), dimethylsulfoxide (DMSO), dimethylformamide (DMF), hexane and ethylacetate) utilised were of analytical reagent grade and made use of with no further purification. All the solutions of metal salts were prepared in double distilled water and standardized by appropriate chemical methods. Solutions of different concentration were prepared by diluting the standard stock solution of 1.0×10^{-1} mol L^{-1}. Double distilled water was used throughout the experiment.

7.2.2. Apparatus and Equipments

NMR (^{1}H and ^{13}C) spectra were recorded in deuterated DMSO-d_6 on a 500 and 125 MHz NMR spectrometer (Bruker). Elemental analysis was performed on a Perkin-Elmer 2400 series CHNS/O analyzer. Atomic absorption spectrometer (AAS) experiment was performed on a Perkin Elmer AAnalyst 800 at wavelength of 240.7 nm using air-acetylene as flame. The conductance study was performed on an Orion 4 conductometer at 25±0.1 °C.

The potentials across the membranes were measured on an Orian 4 pH meter at 25±0.1 °C in conjunction with Ag/AgCl (NaCl 3 Mol L^{-1}) BASI 2056 as reference electrodes.

7.2.3. Synthesis of Ligands

The ligands L_8, L_9, L_{10}, L_{11}, L_{12} and L_{13} were synthesised by the reactions of hydrazinecarbothioamoide (thiosemicarbazide) with dialdehydes D_1, D_2, D_3, D_4, D_5, and D_6 respectively. The dialdehydes were synthesised by following a reported method [75]. The ligand L_{10} has been reported somewhere else [76] while Fedorova, *et al.*, [77] have shown synthesis and *in vitro* tuberculostatic activity of L_{11} and L_{13}.

7.2.3.1. Synthesis of 4,4'-(ethane-1,2-diylbis(oxy))bis(3-methoxybenzaldehyde) (D_1)

To a stirred solution of 4-hydroxy-3-methoxybenzaldehyde (2 mM, 304 mg) and K_2CO_3 (in excess) in DMF (50 mL) was added drop wise 1,2-dichloroethane, (1 mM, 100 mg) in DMF (40 mL). The reaction was continued for 10 h at 150-155 °C and then 5 h at room temperature. After completion of the reaction, distilled water (200 mL) was added in the reaction mixture and was kept in a refrigerator. Then 1 hour later the precipitate was filtered and washed with distilled water. It was then dried in air, recrystallised from ethanol and filtered under vacuum.

4,4'-(ethane-1,2-diylbis(oxy))bis(3-methoxybenzaldehyde) Yield: 78% analytically calculated for [$C_{18}H_{18}O_6$] (%):C, 65.45; H, 5.49. Found C, 65.34; H, 5.58. IR (KBr, cm^{-1}): 3450, 1700 (-C=O), 1642, 1566, 1412, 1344, 1273, 1229, 1139, 1021 (Ar). ^1H NMR ($CDCl_3$, 500 MHz) δ (ppm): 9.847 (2H, s), 7.430-7.446 (2H, d, *J*=8 Hz), 7.404 (2H, s), 7.078-7.094 (2H, d, *J*=8 Hz), 4.527 (4H, s), 3.895 (6H, s). ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 191.09, 153.67, 150.24, 130.91, 126.65, 112.68, 109.88, 67.64, 56.23.

7.2.3.2. Synthesis of 4,4'-(propane-1,3-diylbis(oxy))bis(3-methoxybenzaldehyde) (D_2)

The dialdehyde (D_2) was synthesised by following the same procedure as described above for D_1 and instead of 1,2-dichloroethane, a solution of 1,3-dibromopropane (1 mM, 202 mg) was used.

4,4'-(propane-1,3-diylbis(oxy))bis(3-methoxybenzaldehyde) Yield: 86% analytically calculated for [$C_{19}H_{20}O_6$] (%): C, 66.27; H, 5.85. Found C, 66.15; H, 5.93. IR (KBr, cm^{-1}): 3437, 2958, 2825, 2725, 2358, 1684 (C=O), 1592, 1512, 1456, 1397, 1270, 1135, 1062, 1029 (Ar). ^1H NMR ($CDCl_3$, 500 MHz) δ (ppm): 9.843 (2H, s), 7.401-7.438 (4H, m, *J*=18.5 Hz), 7.018-7.034 (2H, d, *J*=8.0 Hz), 4.323-4.347 (4H, t, *J*=12 Hz), 3.909 (6H, s), 2.421-2.469 (2H, p, *J*=24 Hz). ^{3}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 191.16, 153.99, 150.10, 130.45, 126.97, 111.91, 109.50, 65.61, 56.22, 29.06.

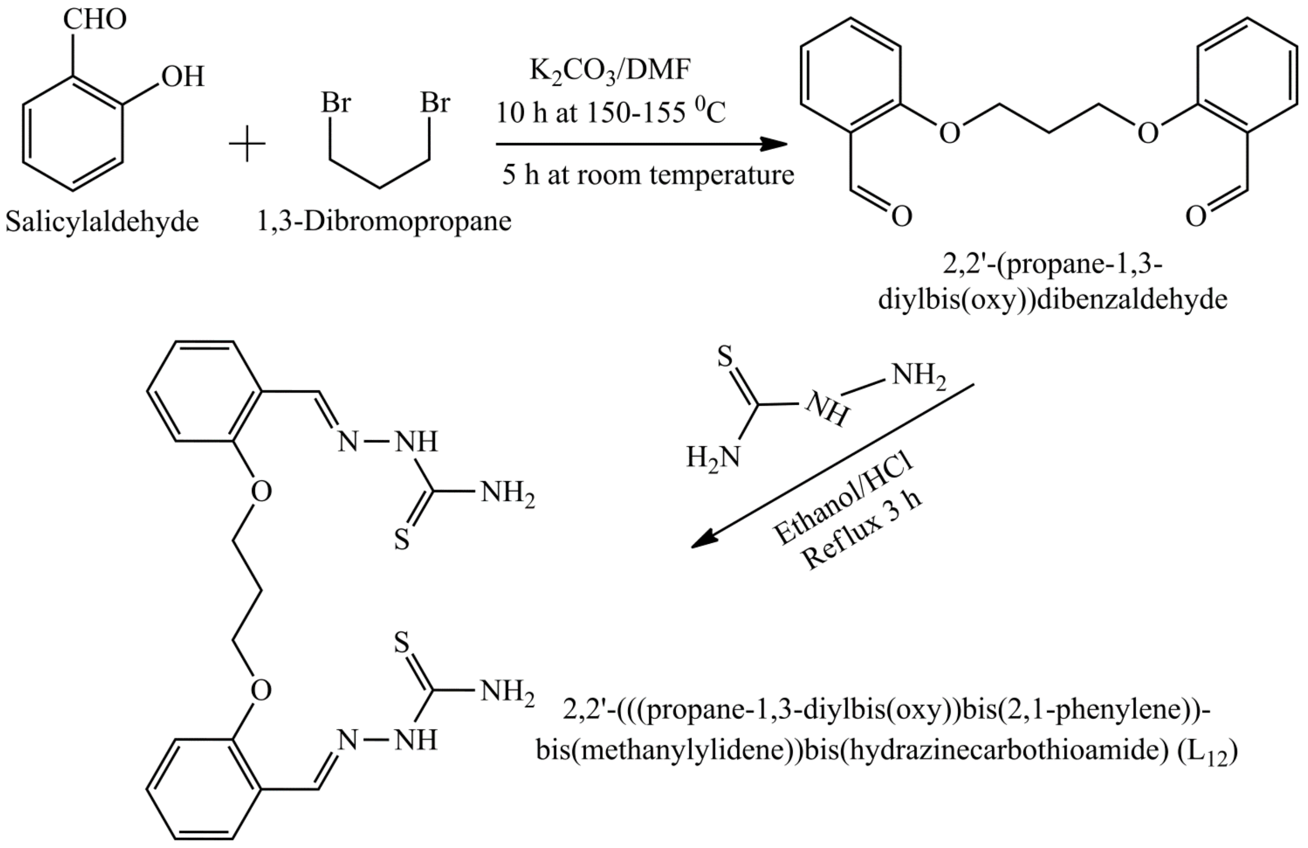

Fig. 7.5. Synthesis of L_{12}.

7.2.3.3. Synthesis of 4,4'-((oxybis(ethane-2,1-diyl))bis(oxy))bis(3-methoxybenzaldehyde) (D_3)

The dialdehyde (D_3) was synthesised by following the same procedure as described above for D_1 and D_2 and instead of 1,2-dichloroethane, a solution of 1-chloro-2-(2-chloroethoxy)ethane (1 mM, 143 mg) was used.

4,4'-((oxybis(ethane-2,1-diyl))bis(oxy))bis(3-methoxybenzaldehyde) Yield: 79% analytically calculated for [$C_{20}H_{22}O_7$] (%): C, 64.16; H, 5.92. Found: C, 64.07; H, 5.97. IR (KBr, cm^{-1}): 3440, 2360, 1685, 1643, 1565, 1415, 1345, 1277, 1130, 1024 (Ar). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 9.839 (2H, s), 7.396-7.425 (4H, m, *J*=14.5 Hz), 6.992-7.008 (2H, d, *J*=8.0 Hz), 4.277-4.297 (4H, t, *J*=10 Hz), 4.009-4.029 (4H, t, *J*=10 Hz), 3.905 (6H, s). ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 191.18, 154.00, 150.14, 130.57, 126.85, 112.14, 109.60, 69.95, 68.77, 56.21.

7.2.3.4. Synthesis of 2,2'-(((ethane-1,2-diylbis(oxy))bis(3-methoxy-4,1-phenylene))bis(methanylylidene))bis(hydrazinecarbothioamide) (L_8)

The L_8 was synthesised as shown in Fig. 7.1. To a solution of thiosemicarbazide (2.0 mM, 182 mg) in ethanol (25 mL), an ethanolic solution (40 mL) of D_1 (1.0 mM, 330 mg) was added drop-wise with constant stirring. Few drops of diluted HCl were added in the above reaction medium with stirring and then refluxed for 3 h. The completion of reaction was monitored by thin layer chromatography ($CHCl_3$: Methanol, 8:2). The reaction mixture was concentrated and the residue obtained washed with water and dried. The crude product obtained on recrystallisation from ethanol gave the pure hydrazinecarbothioamide. The synthesised product was then characterized.

2,2'-(((ethane-1,2-diylbis(oxy))bis(3-methoxy-4,1-phenylene))bis(methanylylidene)-)bis(hydrazinecarbothioamide): Yield: 73% analytically calculated for [$C_{20}H_{24}N_6O_4S_2$] (%): C, 50.40; H, 5.08; N, 17.63; S, 13.46. Found: C, 50.33; H, 5.13; N, 17.67; S, 13.18. IR (KBr, cm^{-1}): 3438 (NH-), 2937, 2357, 1642, 1598 (C=N-), 1514, 1459, 1418, 1356, 1270, 1177, 1135, 1029 (Ar). ^1H NMR (DMSO, 500 MHz) δ (ppm): 11.27 (2H, s), 7.97-8.07 (6H, d), 7.50 (2H, s), 7.03-7.15 (4H, d,), 4.32 (4H, s), 3.80 (6H, s). ^{13}C NMR (DMSO, 125 MHz) δ (ppm): 177.70, 149.78, 149.35, 142.93, 127.42, 122.34, 112.72, 109.02, 67.25, 55.86 (see appendix for spectra).

7.2.3.5. Synthesis of 2,2'-(((propane-1,3-diylbis(oxy))bis(3-methoxy-4,1-phenylene))-bis (methanylylidene))bis(hydrazinecarbothioamide) (L_9)

The L_9 was synthesised as shown in Fig. 7.2 and by following the same procedure as described above for L_1 and instead of D_1, an ethanolic solution of D_2 (1.0 mM, 344 mg) was used.

2,2'-(((propane-1,3-diylbis(oxy))bis(3-methoxy-4,1-phenylene))bis(methanylylidene))bis(hydrazinecarbothioamide): Yield: 73% analytically calculated for [$C_{21}H_{26}N_6O_4S_2$] (%): C, 51.41; H, 5.34; N, 17.13; S, 13.07. Found: C, 51.34; H, 5.40; N, 17.09; S, 13.12. IR (KBr, cm^{-1}): 3417, 3302, 3161 (-NH), 2913, 2357, 1671, 1596 (-C=N), 1506, 1463, 1421, 1336, 1268, 1136, 1094, 1000 (Ar-). ^1H NMR (DMSO, 500 MHz) δ (ppm): 11.315 (2H, s), 8.157 (2H, s), 8.022 (2H, s), 7.959 (2H, s), 7.516-7.534 (2H, dd, J=9.0 Hz), 7.114-7.133 (2H, dd, J=9.5 Hz), 6.989-7.006 (2H, d, J=8.5 Hz), 4.136-4.160 (4H, t, J=12 Hz), 3.811 (6H, s), 2.162-2.209 (2H, p, J=26.5 Hz). ^{13}C NMR (DMSO, 125 MHz) δ (ppm): 177.50, 149.72, 149.31, 142.47, 127.11, 122.14, 112.43, 108.74, 64.92, 55.73, 28.61 (see appendix for spectra).

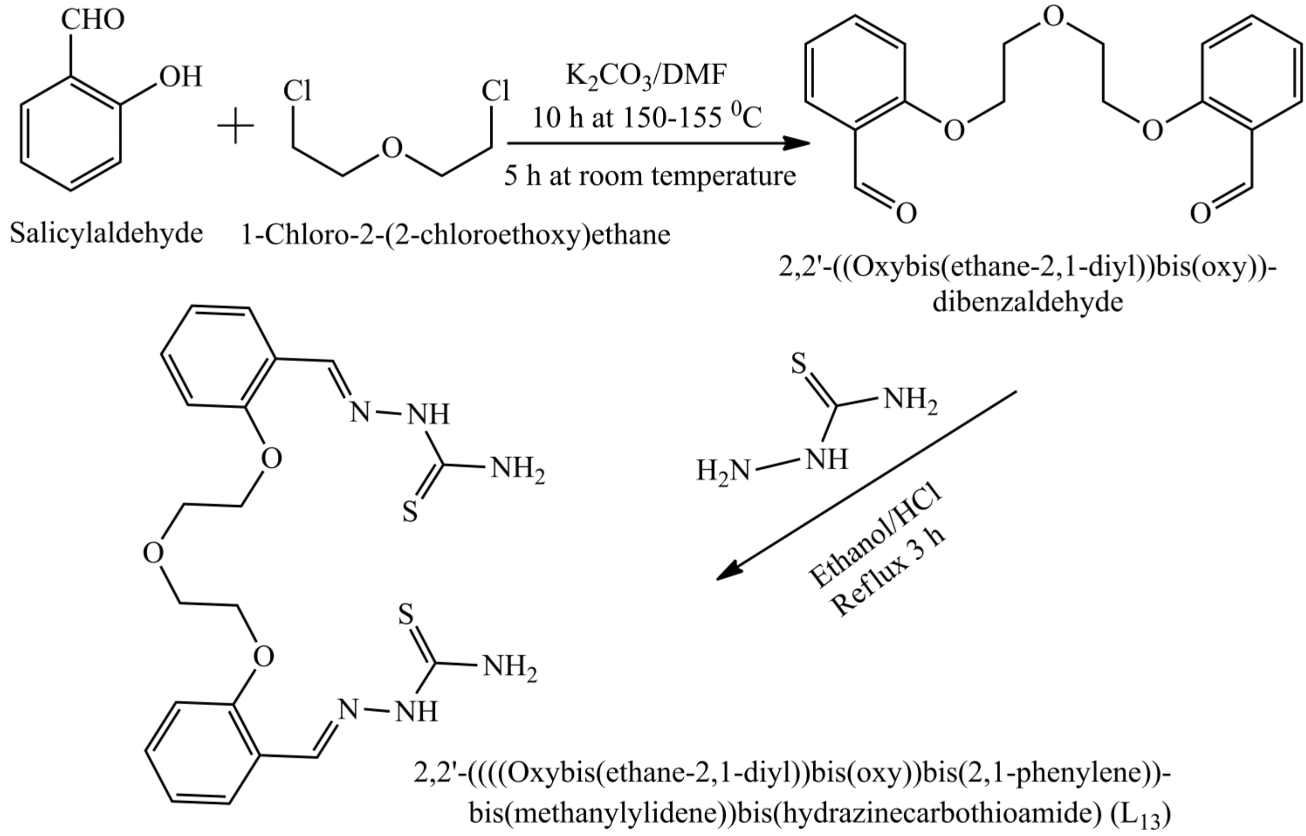

Fig. 7.6. Synthesis of L_{13}.

7.2.3.6. Synthesis of 2,2'-((((oxybis(ethane-2,1-diyl))bis(oxy))bis(3-methoxy-4,1-phenylenze))bis(methanylylidene))bis(hydrazinecarbothioamide) (L_{10})

The L_{10} was synthesised as shown in Fig. 7.3 and by following the same procedure as described above for L_1 and L_2 and instead of D_1, an ethanolic solution of D_3 (1.0 mM, 374 mg) was used.

2,2'-((((oxybis(ethane-2,1-diyl))bis(oxy))bis(3-methoxy-4,1-phenylene))bis-(methanylylidene))bis(hydrazinecarbothioamide): Yield: 76% analytically calculated for [$C_{22}H_{28}N_6O_5S_2$] (%): C, 50.75; H, 5.42; N, 16.14; S, 12.32. Found: C, 50.68; H, 5.48; N, 16.10; S, 12.36. IR (KBr, cm^{-1}): 3411, 3300, 3166 (-NH), 2990, 1683, 1599 (-C=N), 1506, 1463, 1417, 1336, 1267, 1169, 1136, 1093 (Ar-). ^{1}H NMR (DMSO, 500 MHz) δ (ppm): 11.313 (2H, s), 8.154 (2H, s), 8.019 (2H, s), 7.958 (2H, s), 7.514-7.518 (2H, d, *J*=2 Hz), 7.105-7.125 (2H, dd, *J*=10 Hz), 6.965-6.982 (2H, d, *J*=8.5 Hz), 4.120-4.138 (4H, t, *J*=9.0 Hz), 3.826-3.837 (4H, t, *J*=5.5 Hz), 3.813 (6H, s). ^{13}C NMR (DMSO (d_6), 125 MHz) δ (ppm): 177.51, 149.72, 149.24, 142.47, 127.11, 122.07, 112.40, 108.74, 68.99, 67.85, 55..65 (see appendix for spectra).

7.2.3.7. Synthesis of Schiff base 2,2'-(((ethane-1,2-diylbis(oxy))bis(2,1-phenylene))-bis(methanylylidene))bis(hydrazinecarbothioamide) (L_{11})

The Schiff base (L_{11}) was synthesised as shown in Fig. 7.4. To a solution of thiosemicarbazide (2.0 mM, 182 mg) in ethanol, 2,2'-(ethane-1,2-diylbis(oxy))dibenzaldehyde (D_4) (1.0 mM, 270 mg) in ethanol was added drop-wise with constant stirring. To this reaction mixture few drops of HCl were added drop-wise with constant stirring and then refluxed for 3 h. The completion of the reaction mixture was monitored by thin layer chromatography ($CHCl_3$:MeOH, 8:2). The reaction mixture was concentrated and the residue obtained was poured in ice cold water and filter through vacuum suction. The crude product obtained on recyrstallisation gave the pure thiosemicarbazones as white powder. The product was then characterised as follows;

2,2'-(((ethane-1,2-diylbis(oxy))bis(2,1-phenylene))bis(methanylylidene))bis-(hydrazinecarbothioamide): Yield: 72% analytically calculated for [$C_{18}H_{20}N_6O_2S_2$] (%): C, 51.90; H, 4.84; N, 20.18; S, 15.40. Found: C, 51.18; H, 5.16; N, 21.03; S, 16.11. FTIR (KBr, cm^{-1}): 3431, 3234, 3043, (-NH), 1663, 1600 (-C=N), 1558, 1487, 1362, 1295, 1250 (Ar) (see appendix for spectra).

7.2.3.8. Synthesis of Schiff base 2,2'-(((propane-1,3-diylbis(oxy))bis(2,1-phenylene))bis(methan- ylylidene))bis(hydrazinecarbo- thioamide) (L_{12})

The Schiff base (L_{12}) was synthesised as shown in Fig. 7.5 by following the same procedure as described above for L_{11} and instead of D_4, 4,4'-(propane-1,3-diylbis(oxy))bis(benzaldehyde) (D_5) (1.0 mM, 344 mg) in ethanol was added drop-wise with constant stirring. The product was then characterised as follows;

2,2'-(((propane-1,3-diylbis(oxy))bis(2,1-phenylene))bis(methanylylidene))-bis(hydrazinecarbothioamide): Yield: 81% analytically calculated for [$C_{19}H_{22}N_6O_2S_2$] (%): C, 53.00; H, 5.15; N, 19.52; S, 14.90. Found: C, 52.78; H, 5.03; N, 19.64; S, 15.03. FTIR (KBr, cm^{-1}): 3237, 3140, 2925, 2863, 2339, 1600 (-C=N), 1396, 1217, 1114 (Ar-). ^1H NMR (DMSO, 500 MHz) δ (ppm): 11.408 (2H, s, -NH), 8.499 (2H, s, -CH=N), 8.139 (2H, s), 8.066-8.085 (2H, q, *J*=9.5 Hz), 7.930 (2H, s), 7.350-7.385 (2H, p, *J*=17.5 Hz), 7.082-7.099

(2H, d, *J*=8.5 Hz), 6.938-6.968 (2H, t, *J*=15 Hz), 4.249-4.273 (4H, t, *J*=12 Hz), 2.212-2.259 (2H, p, *J*=23.5Hz) (see appendix for spectra).

7.2.3.9. Synthesis of Schiff base 2,2'-((((oxybis(ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene))bis(methanylylidene))bis(hydrazinecarbothioamide) (L_{13})

The Schiff base L_{13} was synthesised as shown in Fig. 7.6 by following the same procedure as described above for the synthesis of L_{11} and L_{12} and instead of D_5 an ethanolic solution of 4,4'-((oxybis(ethane-2,1-diyl))bis(oxy))bis(benzaldehyde) (D_6) (1 mM) was used.

2,2'-((((oxybis(ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene))bis(methanylylidene))-bis(hydrazinecarbothioamide) (L_{13}): Yield: 78% analytically calculated for [$C_{20}H_{24}N_6O_3S_2$] (%):C, 52.16; H, 5.25; N, 18.25; S, 13.92. Found: C, 52.03; H, 5.11; N, 18.38; S, 14.04. FTIR (KBr, cm^{-1}) 1602 (-C=N), 1502, 1359, 1288, 1236 (Ar-). ^{1}H NMR (DMSO, 500 MHz) δ (ppm): 11.476 (2H, s), 8.448 (2H, s), 8.134 (2H, s), 8.059-8.077 (2H, dd, *J*=9 Hz), 7.927 (2H, s), 7.330-7.364 (2H, p, *J*=17 Hz), 7.057-7.074 (2H, d, *J*=8.5 Hz), 6.938-6.968 (2H, t, *J*=15 Hz), 4.178-4.195 (4H, t, *J*=8.5 Hz), 3.892-3.909 (4H, t, *J*=8.5 Hz). ^{13}C NMR (DMSO, 125 MHz) δ (ppm): 177.82, 157.15, 138.30, 131.35, 126.24, 122.52, 120.84, 112.93, 69.53, 68.40 (see appendix for spectra).

7.3. FABRICATION OF PVC MEMBRANES

The nature and quantity of ionophore, plasticizer, plasticzer/PVC ratio and especially of lipophilic additives utilised considerably affect the selectivity and sensitivity. All these affect potential response of the membrane sensor hence need to optimized for sensor’s maximum efficiency.

7.3.1. Preparation of Coated Graphite Electrodes (CGE) and Coated Pyrolytic Graphite Electrodes (CPGE)

The membrane has been fabricated as suggested by Craggs *et. al*., [78]. Polymeric membrane based on high molecular weight poly(vinyl chloride) (PVC) was prepared by dissolving appropriate amount of membrane ingredients (ligands, anionic excluders (NaTPB and KTpClPB), plasticizers (BA, 1-CN, DOP, DBP and *o*-NPOE) and PVC) in minimum amount of THF and the solvent was evaporated off to obtain a concentrated solution. Graphite electrode/pyrolytic graphite electrode of spectroscopic grade with copper wire glued at one end was dipped in to the above solution for few seconds and removed out and allowed the electrode to get dry. The process was repeated several times till the membrane was formed over graphite electrode/pyrolytic graphite electrode. The well prepared electrodes were then kept in a 1.0×10^{-3} mol L^{-1} solution of test analyte when not in use.

7.3.2. Conditioning of Membrane and Potential Measurements

The fabricated electrodes were equilibrated with corresponding test analyte for which the electrode is made to be selective. The time of contact and concentration of equilibrating solution was optimized so that sensors generated stable and reproducible potential.

For Co^{2+} determination CGE and CPGE based on L_8, L_9, and L_{10} as ionophores were conditioned for 1 day prior to potentiometric measurements in 1.0×10^{-3} mol L^{-1} $Co(NO_3)_2$ solution. The potential has been measured by altering the concentration of solution of $Co(NO_3)_2$ in the range of 1.0×10^{-1}-1.0×10^{-9} mol L^{-1}. The standard solution had been obtained by gradual dilution of stock solution 1.0×10^{-1} mol L^{-1} $Co(NO_3)_2$.

For Zn^{2+} determination CGE and CPGE based on L_{11}, L_{12}, and L_{13} as ionophores were conditioned for 1 day prior to potentiometric measurements in 1.0×10^{-3} mol L^{-1} $Zn(NO_3)_2$ solution. The potential have been measured by altering the concentration of solution of $Zn(NO_3)_2$ in the range of 1.0×10^{-1}-1.0×10^{-9} mol L^{-1}. The standard solution had been obtained by gradual dilution of stock solution 1.0×10^{-1} mol L^{-1} $Zn(NO_3)_2$.

The potential measurements with the CGE and CPGE were performed on a 4 pH meter (Orion) at 25±0.1°C utilising Ag/AgCl (NaCl 3 mol L^{-1}) BASI 2056 as reference electrode with the following cell assemblies;

CGE||Test solution||Ag/AgCl|NaCl (3 mol L^{-1})
CPGE||Test solution||Ag/AgCl|NaCl (3 mol L^{-1})
Activity coefficients were calculated according to Debye Huckel procedure [79].

7.4. Results and Discussion

7.4.1. Membranes of L_8, L_9 and L_{10} as Co^{2+} Selective Sensors

Table 7.1. **Optimization of membrane composition and their potentiometric response for Co^{2+} ion sensor based on L_8.**

S. No.	Composition of membrane (w/w; mg)									Working concentration range (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mVdecade^{-1} of activity)
	L_8	KTpClPB	NaTPB	DBP	DOP	BA	*o*-NPOE	1-CN	PVC			
1	6	-	-	-	-	-	-	-	94	7.4×10^{-6}-1.0×10^{-1}	1.6×10^{-6}	22.3±0.6
2	6	-	-	56	-	-	-	-	38	6.7×10^{-7}-1.0×10^{-1}	3.9×10^{-7}	28.1±0.3
3	6	-	-	-	56	-	-	-	38	6.0×10^{-7}-1.0×10^{-1}	2.2×10^{-7}	28.6±0.3
4	6	-	-	-	-	56	-	-	38	1.9×10^{-6}-1.0×10^{-1}	4.5×10^{-7}	26.3±0.4
5	6	-	-	-	-	-	56	-	38	6.4×10^{-7}-1.0×10^{-1}	3.0×10^{-7}	26.8±0.4
6	6	-	-	-	-	-	-	56	38	1.7×10^{-7}-1.0×10^{-1}	9.5×10^{-8}	27.4±0.7
7	6	3	-	-	-	-	-	56	35	1.1×10^{-7}-1.0×10^{-1}	6.9×10^{-8}	28.8±0.6
8	6	-	3	-	-	-	-	56	35	8.4×10^{-7}-1.0×10^{-1}	6.8×10^{-7}	31.8±0.4
9	7	3	-	-	-	-	-	56	34	1.9×10^{-6}-1.0×10^{-1}	7.6×10^{-7}	28.4±0.6
10	8	3	-	-	-	-	-	56	33	4.0×10^{-7}-1.0×10^{-1}	2.7×10^{-7}	30.7±0.3
11	5	3	-	-	-	-	-	56	36	5.9×10^{-7}-1.0×10^{-1}	3.3×10^{-7}	27.9±0.4
12	6	2	-	-	-	-	-	56	36	8.9×10^{-6}-1.0×10^{-1}	4.6×10^{-6}	28.1±0.4

Table 7.2. Optimization of membrane composition and their potentiometric response for Co^{2+} ion sensor based on L_9.

S. No.	Composition of membrane (w/w; mg)									Working concentration range (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mVdecade^{-1} of activity)
	L_9	KTpClPB	NaTPB	DBP	DOP	BA	*o*-NPOE	1-CN	PVC			
A 1	6	-	-	-	-	-	-	-	94	5.7×10^{-6}-1.0×10^{-1}	1.7×10^{-6}	24.2±0.4
A 2	6	-	-	56	-	-	-	-	38	4.2×10^{-7}-1.0×10^{-1}	2.3×10^{-7}	26.6±0.6
A 3	6	-	-	-	56	-	-	-	38	4.8×10^{-7}-1.0×10^{-1}	1.6×10^{-7}	28.8±0.5
A 4	6	-	-	-	-	56	-	-	38	7.4×10^{-7}-1.0×10^{-1}	2.1×10^{-7}	27.1±0.4
A 5	6	-	-	-	-	-	56	-	38	5.6×10^{-7}-1.0×10^{-1}	2.5×10^{-7}	26.5±0.7
A 6	6	-	-	-	-	-	-	56	38	9.7×10^{-8}-1.0×10^{-1}	5.5×10^{-8}	28.1±0.4
A 7	6	3	-	-	-	-	-	56	35	3.8×10^{-8}-1.0×10^{-1}	1.9×10^{-8}	29.3±0.5
A 8	6	-	3	-	-	-	-	56	35	3.4×10^{-7}-1.0×10^{-1}	1.9×10^{-7}	28.5±0.2
A 9	7	3	-	-	-	-	-	56	34	6.4×10^{-7}-1.0×10^{-1}	4.8×10^{-7}	30.2±0.3
A 10	8	3	-	-	-	-	-	56	33	2.9×10^{-6}-1.0×10^{-1}	8.6×10^{-7}	31.8±0.4
A 11	5	3	-	-	-	-	-	56	36	8.7×10^{-7}-1.0×10^{-1}	5.4×10^{-7}	28.3±0.6
A 12	6	2	-	-	-	-	-	56	36	4.7×10^{-7}-1.0×10^{-1}	2.9×10^{-7}	27.5±0.5

Table 7.3. Optimization of membrane composition and their potentiometric response for Co^{2+} ion sensor based on L_{10}.

S. No.	Composition of membrane (w/w; mg)									Working concentration range (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mVdecade^{-1} of activity)
	L_{10}	KTpClPB	NaTPB	DBP	DOP	BA	*o*-NPOE	1-CN	PVC			
B 1	8	-	-	-	-	-	-	-	92	6.8×10^{-6}-1.0×10^{-1}	2.2×10^{-6}	23.9±0.3
B 2	8	-	-	54	-	-	-	-	38	7.9×10^{-7}-1.0×10^{-1}	4.1×10^{-7}	25.8±0.4
B 3	8	-	-	-	54	-	-	-	38	8.3×10^{-7}-1.0×10^{-1}	1.8×10^{-7}	28.8±0.4
B 4	8	-	-	-	-	54	-	-	38	8.5×10^{-6}-1.0×10^{-1}	1.3×10^{-6}	26.8±0.6
B 5	8	-	-	-	-	-	54	-	38	9.3×10^{-7}-1.0×10^{-1}	2.9×10^{-7}	27.7±0.5
B 6	8	-	-	-	-	-	-	54	38	1.8×10^{-7}-1.0×10^{-1}	6.4×10^{-8}	27.9±0.4
B 7	8	3	-	-	-	-	-	54	35	9.1×10^{-8}-1.0×10^{-1}	4.7×10^{-8}	28.5±0.6
B 8	8	-	3	-	-	-	-	54	35	2.5×10^{-7}-1.0×10^{-1}	1.2×10^{-7}	31.4±0.3
B 9	9	3	-	-	-	-	-	54	34	4.8×10^{-7}-1.0×10^{-1}	2.9×10^{-7}	26.9±0.6
B 10	10	3	-	-	-	-	-	54	33	6.2×10^{-6}-1.0×10^{-1}	4.3×10^{-6}	30.8±0.3
B 11	7	3	-	-	-	-	-	54	36	8.6×10^{-7}-1.0×10^{-1}	5.8×10^{-7}	28.4±0.4
B 12	8	2	-	-	-	-	-	54	36	5.3×10^{-7}-1.0×10^{-1}	3.6×10^{-7}	27.2±0.3

The PVC based polymeric membranes of L_8, L_9 and L_{10} were used as ionophores and studied on these electrodes has shown greater selectivity for Co^{2+} ion over other cations tested.

7.4.1.1. Complexation Study

In preliminary experiments, the complexation of ligand with a number of cations has been investigated conductometrically in DMF solutions in order to obtain an idea about the stoichiometry of the resulting complexes at 25±0.1°C. For this purpose, 25 mL of 1.0×10^{-4} mol L^{-1} cation solution was titrated against a 1.0×10^{-2} mol L^{-1} ligand solution in DMF. The conductance of the solution was measured after each addition of the titrant.

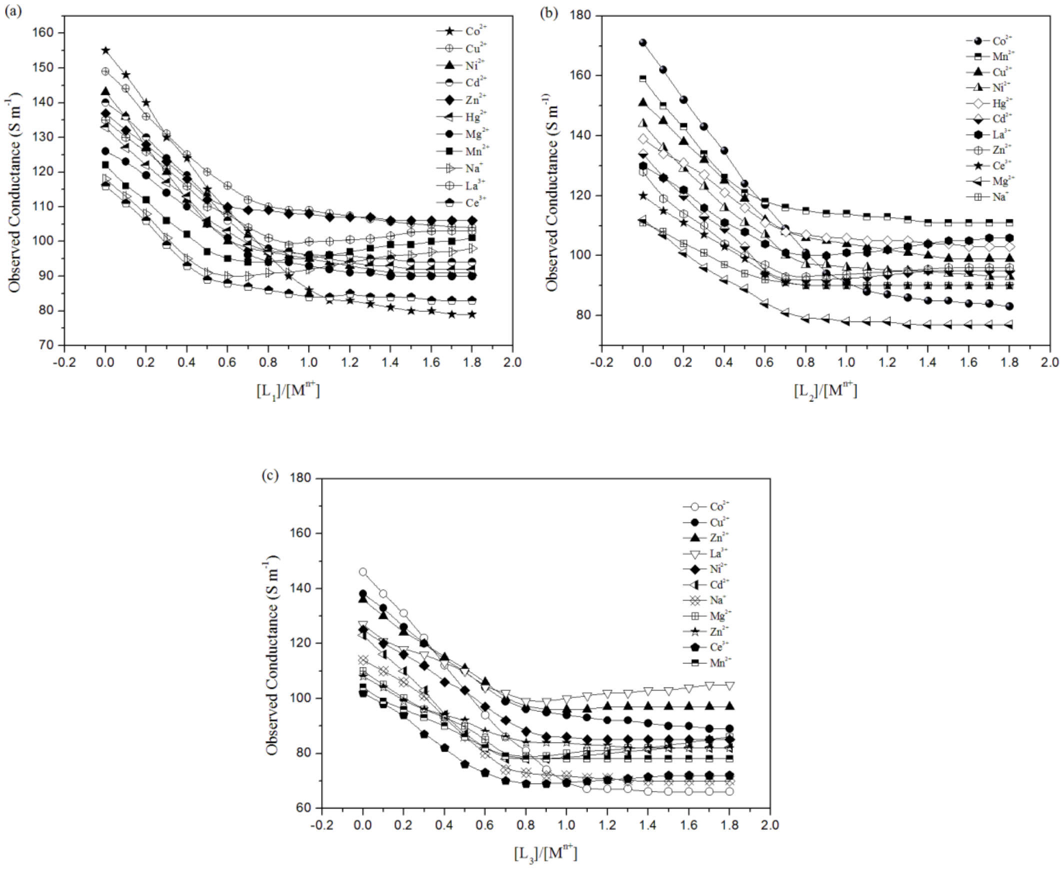

Fig. 7.7. Variation in conductance of Co^{2+} with the addition of Ligands (a) L_8, (b) L_9 and (c) L_{10}.

The conductance variation plots with different metal ions as a function of the $[L]/[M^{n+}]$ molar ratio is depicted in Fig. 7.7. It is observed from the figure that conductance variation of Co^{2+} ion solution showed maximum variation with the addition of ligand, initially the conductance falling off with the addition of ligand which show that Co^{2+} are strongly interacting with the ligand added. A stage is arrived when conductance of solution nearly becomes constant and further addition of ligand does not cause any appreciable change in conductance which demonstrates that all of the metal ions have been consumed by the ligand. The break point in the conductance variation plots gives the stoichiometry of the resulting complexes and it has been observed that the stoichiometry of metal to ligand is 1:1.

7.4.1.2. Optimization of membrane Composition and Potential Measurements

The selectivity, sensitivity and linearity estimated for a given ionophore largely depends on the membrane, the nature of plasticizer [80] and additives added [81, 82]. Therefore, to improve the performance of polymeric membranes based on L_8, L_9 and L_{10} a number of electrodes having different composition were fabricated and studied. The potentials of various electrodes were measured as a function of Co^{2+} ion concentration in the range of 1.0×10^{-1} to 1.0×10^{-9} mol L^{-1}. The potential responses of CGE and CPGE were first investigated only with ligand and PVC and the results are summarized in Tables 7.1-7.3. It is observed from the Tables that sensor number 1, A1 and B1 having membranes of L_8, L_9 and L_{10} without plasticizer showed linear response over a working concentration range of 7.4×10^{-6}-1.0×10^{-1}, 5.7×10^{-6}-1.0×10^{-1} and 6.8×10^{-6}-1.0×10^{-1} mol L^{-1}, with a slope of 22.3±0.6, 24.2±0.4 and 23.9±0.3 mV decade^{-1} of activity, respectively. The incorporation of plasticizer enhances the performance of the electrodes is a well known fact. Thus, effect of various plasticizers *viz*, BA, DOP, DBP, *o*-NPOE and 1-CN were investigated in to and the response obtained with plasticized membranes are shown in Fig. 7.8 and reported in the Tables 7.1-7.3.

It has been observed that the membranes which were plasticized showed improved response. It is from the Tables that the electrode number 7, A7 and B7 with optimized membrane composition of L_8: PVC: 1-CN: KTpClPB≡6:35:56:3, L_9: PVC: 1-CN: KTpClPB≡6:35:56:3 and L_{10}: PVC: 1-CN: KTpClPB≡8:35:54:3 (w/w, mg) exhibited the best performance in terms of wide working concentration range, low detection limit and Nernstian slope.

7.4.1.3. Effect of pH on the Performance of Sensor

The pH dependence of the sensor was also investigated at different pH values. For this purpose, the electrode potentials of CGE and CPGE were measured at two different concentrations of 1.0×10^{-3} and 1.0×10^{-4} mol L^{-1} Co^{2+} ion solution in the pH range of 1.0-12.0. The pH was adjusted by the addition of HCl/NaOH and the results are shown in Fig. 7.9. It is from the Fig. 7.9 that potential response remains independent of pH in the range of 3.5-7.5 and 2.5-8.5 for CGE and CPGE respectively. Therefore, the same was regarded as the working pH range of the electrodes.

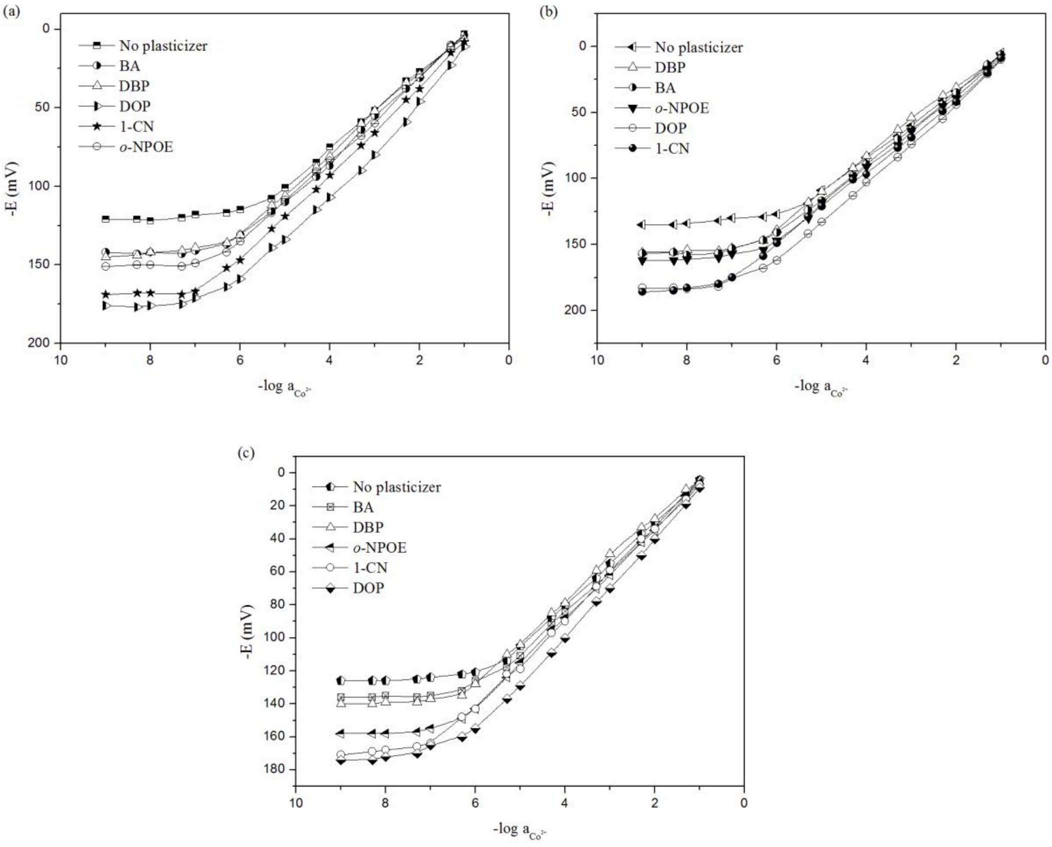

Fig. 7.8. Potentiometric characteristic plots showing variation of membrane potential with the concentration of Co^{2+} ion based on (a) L_8, (b) L_9 and (c) L_{10}.

The change in potential at higher pH may be attributed to formation of metal hydroxides species in the matrix [83] and the deviation at low pH may be regarded as the effect of protonation of ionophore [84] and the electrodes start responding to H_3O^+ ions along with Co^{2+} ion leading to an increase in potential.

7.4.1.4. Effect of Interfering Ions on the Performance of Sensor

The most important parameters which reflect the applicability of an ISE is its selectivity which is a measure of the influence of the interfering ions on the response behaviour of the ion-selective membrane sensor and it is usually described in terms of the selectivity coefficients. The potentiometric selectivity coefficients for CGE and CPGE based on L_9 were determined according to IUPAC recommended fixed interference method (FIM). In this method, the selectivity coefficient was evaluated from the potential measurement on solutions containing a fixed concentration of interfering ion (1.0×10^{-2} mol L^{-1}) and varying amount of Co^{2+} ion solution ranging from 1.0×10^{-1} to 1.0×10^{-9} mol L^{-1}.

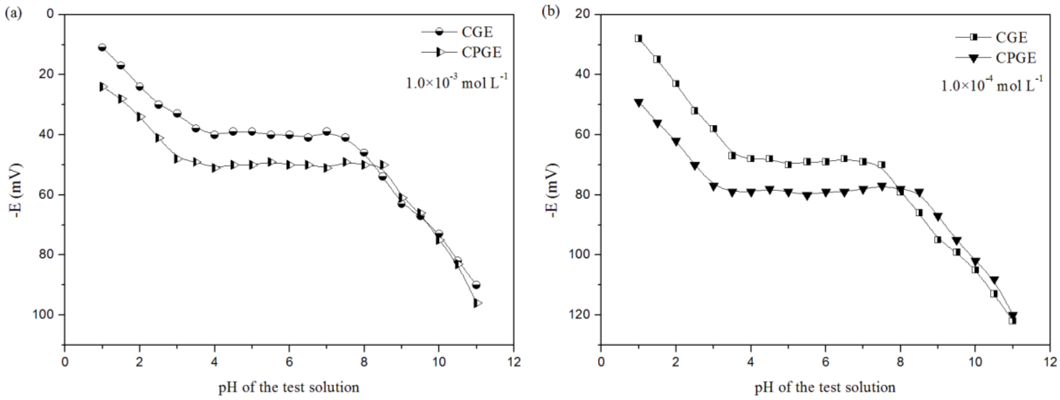

Fig. 7.9. Effect of pH of the test solution on the potential responses of CGE and CPGE with (a) 1.0×10^{-3} mol L^{-1} and (b) 1.0×10^{-4} mol L^{-1} Co^{2+} ion solutions at different pH.

The potential values so obtained were then plotted versus activity of Co^{2+} ion. The linear portion of potential response curve then extrapolated and the value of a_{Co2+} was obtained from the intersection point. The potentiometric selectivity coefficients were then determined using the following expression [85]:

$$K_{A,B}^{Pot} = \frac{(a_A)}{(a_B)^{z_A/z_B}} \quad (1)$$

Where a_A is the activity of primary ion A (Co^{2+}) at the point of intersection, a_B, the activity of interfering ion B and z_A and z_B are their respective charges. The values of selectivity coefficients so obtained for CGE and CPGE are compiled in the Table 7.4. It has been observed that the electrodes are highly selective over a number of monovalent, divalent and trivalent cations. However, selectivity coefficients obtained for Cu^{2+} and Ni^{2+} ions are not very low and they caused some interference if present in eminent concentration.

To estimate the extent of interference caused by the Cu^{2+} and Ni^{2+} ions, mixed run studies were performed and the effect of the Cu^{2+} and Ni^{2+} ions concentration on the performance of the sensor was examined. The potential were measured in the presence of different concentrations (1.0×10^{-5}, 5.0×10^{-5}, 1.0×10^{-4} and 1.0×10^{-3} mol L^{-1}) of Cu^{2+} and Ni^{2+} ions and the potential responses of the sensor to the mixtures are shown in Fig. 7.10.

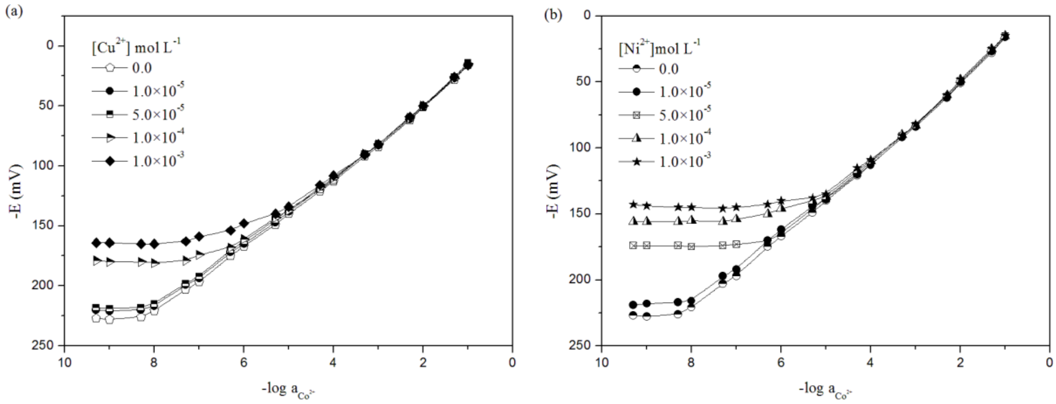

Fig. 7.10. Effect of different concentrations of (a) Cu^{2+} ion and (b) Ni^{2+} ion on the performance of the sensor.

It is revealed from Fig. 7.10 that Cu^{2+} at $\leq5.0\times10^{-5}$ mol L^{-1} did not cause any deviation in the original plot obtained in pure Co^{2+} ion. Thus, the sensor can tolerate Cu^{2+} at $\leq5.0\times10^{-5}$ mol L^{-1} over the entire working concentration range. However, when Cu^{2+} present in higher concentration, significant interference was observed and causes shorting of working concentration range and thus Co^{2+} ion could be determined in the reduced concentration ranges of 6.0×10^{-7}-1.0×10^{-1} and 7.4×10^{-6}-1.0×10^{-1} mol L^{-1} in the presence of 1.0×10^{-4} and 1.0×10^{-3} mol L^{-1} of Cu^{2+} ion, respectively. Similarly, it has been observed from the Fig. 7.10 that the sensor can tolerate Ni^{2+} at $\leq1.0\times10^{-5}$ mol L^{-1} over the entire working concentration range and the working concentration range reduces to 8.5×10^{-7}-1.0×10^{-1}, 9.1×10^{-6}-1.0×10^{-1} and 9.7×10^{-6}-1.0×10^{-1} mol L^{-1} in presence of 5.0×10^{-5}, 1.0×10^{-4} and 1.0×10^{-3} mol L^{-1} of Ni^{2+} ion, respectively.

Table 7.4. **Selectvity coefficient of various interfering ions for Co^{2+} ion-sensor.**

Interfering ions	Selectivity coefficients ($K^{FIM}_{Co^{2+},B}$)	
	CGE	CPGE
Cu^{2+}	7.8×10^{-2}	4.3×10^{-2}
Zn^{2+}	8.1×10^{-3}	6.3×10^{-3}
Mn^{2+}	5.5×10^{-3}	3.6×10^{-3}
Cd^{2+}	3.9×10^{-3}	3.1×10^{-3}
Hg^{2+}	4.7×10^{-4}	3.4×10^{-4}
Ni^{2+}	9.6×10^{-2}	6.2×10^{-2}
Na^{+}	6.8×10^{-3}	5.5×10^{-3}
Mg^{2+}	4.4×10^{-4}	3.9×10^{-4}
Ca^{2+}	7.6×10^{-3}	7.0×10^{-3}
Ce^{3+}	2.8×10^{-4}	2.4×10^{-4}
La^{3+}	4.3×10^{-4}	3.8×10^{-4}

7.4.1.5. Determination of Dynamic Response Time and Life Span of the Sensor

Dynamic response time is an important factor for an ISE. According to IUPAC recommendations, the response time of an ion selective electrode is defined as the length of time between the instant at which the ion selective electrode and reference electrode are immersed in he solution and the moment at which the potential of the cell reaches its steady-state value within ±1 mV [86]. Response time of the sensor was measured by successively changing the concentration of the test solution from 1.0×10^{-6}-1.0×10^{-1} mol L^{-1}.

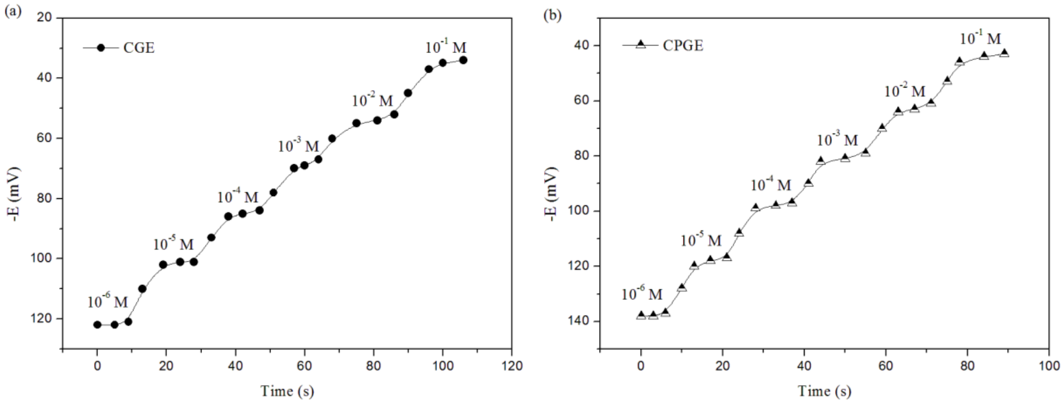

Fig. 7.11. **Dynamic response time of Co^{2+} ion sensor based on L_9 for step changes in concentration of Co^{2+} ion with (a) CGE and (b) CPGE.**

The average time needed to attain a potential response ranging between ±1 mV of the final equilibrium value for the electrodes after immersing successively in a series of Co^{2+} ion solution, each having a difference of 10-folds in concentration was 10 seconds for CGE and 7 seconds for CPGE as shown in Fig. 7.11.

The life time of the electrodes were measured by recording the potential at different time intervals and the results are compiled in the Table 7.5.

Table 7.5. Potential response of Co^{2+} ion sensor based on L_2 using CGE and CPGE at different time intervals.

Time (Days)	Slope (mV decade^{-1} of activity)	Working concentration range (mol L^{-1})	Detection Limit (mol L^{-1})
CGE			
2	29.3±0.5	3.8×10^{-8}-1.0×10^{-1}	1.9×10^{-8}
10	29.3±0.5	3.8×10^{-8}-1.0×10^{-1}	1.9×10^{-8}
30	29.1±0.4	4.1×10^{-8}-1.0×10^{-1}	2.2×10^{-8}
45	28.9±0.2	4.5×10^{-8}-1.0×10^{-1}	2.7×10^{-8}
60	28.4±0.2	5.0×10^{-8}-1.0×10^{-1}	3.1×10^{-8}
75	28.2±0.4	6.2×10^{-8}-1.0×10^{-1}	3.8×10^{-8}
90	28.0±0.5	7.6×10^{-8}-1.0×10^{-1}	6.4×10^{-8}
95	25.4±0.4	8.4×10^{-7}-1.0×10^{-1}	5.7×10^{-7}
CPGE			
2	29.4±0.6	1.3×10^{-8}-1.0×10^{-1}	6.1×10^{-9}
10	29.4±0.4	1.3×10^{-8}-1.0×10^{-1}	6.1×10^{-9}
30	29.3±0.2	1.7×10^{-8}-1.0×10^{-1}	6.4×10^{-9}
45	29.1±0.5	1.9×10^{-8}-1.0×10^{-1}	7.1×10^{-9}
60	29.1±0.2	2.4×10^{-8}-1.0×10^{-1}	8.3×10^{-9}
75	28.8±0.6	2.9×10^{-8}-1.0×10^{-1}	9.5×10^{-9}
90	28.5±0.5	3.7×10^{-8}-1.0×10^{-1}	1.6×10^{-8}
110	28.2±0.4	4.3×10^{-8}-1.0×10^{-1}	2.9×10^{-8}
120	28.1±0.3	5.2×10^{-8}-1.0×10^{-1}	4.2×10^{-8}
130	26.1±0.3	6.2×10^{-7}-1.0×10^{-1}	3.5×10^{-7}

Thus, CGE and CPGE could be used over a period of 3 and 4 months, respectively, in which the slope of electrode displayed only a small deviation from 29.3±0.5 to 25.4±0.4

mV decade^{-1} of activity, the working concentration range shifted from 3.8×10^{-8}-1.0×10^{-1} to 8.4×10^{-7}-1.0×10^{-1} mol L^{-1} and the detection limit reduces from 1.9×10^{-8} to 5.7×10^{-7} mol L^{-1} for CGE and for CPGE the

slope reduces from 29.4±0.6 to 26.1±0.3 mV decade^{-1} of activity, the working concentration range reduces from 1.3×10^{-8}-1.0×10^{-1} to 6.2×10^{-7}-1.0×10^{-1} and the detection limit shifted from 6.1×10^{-9}-3.5×10^{-7} mol L^{-1}.

7.4.1.6. Effect of Non Aqueous Medium on the Performance of Sensor

Non-aqueous content might be present in real samples; therefore the efficiency of the sensor was also estimated in partially non-aqueous solutions containing 10%, 20%, 30% and 40% (v/v) non-aqueous content in methanol-water, ethanol-water and acetonitrile-water mixtures and the results are compiled in Table 7.6. The sensor did not exhibit any considerable change in the range of working concentration and slope in 30% non-aqueous contents of acetonitrile-water and ethanol-water solutions. But drastic change has been observed in case of methanol-water mixture and it was found that only 20% amount could be tolerated. Therefore, the electrode is not suitable for using in methanol-water mixture above 20% concentration. This may be due to greater solubility of the ionophore in methanol which causes leaching of ionophore from the membrane phase. However, the sensor can be satisfactorily used in acetonitrile-water and ethanol-water solutions up to 30%.

7.4.1.7. Comparative Performance Characteristic of the Coated Graphite Electrode (CGE) and Coated Pyrolytic Graphite Electrode (CPGE)

The investigations on polymeric membrane based on L_8, L_9 and L_{10} have proved to be promising and selective to Zn^{2+} ion. The sensor number A7 based on L_9 containing 1-CN as plasticizer with the optimized membrane of composition L_9: PVC: 1-CN: KTpClPB ≡ 6:35:56:3 (w/w; mg) perform best in terms of wide working concentration range of 3.8×10^{-8}-1.0×10^{-1} mol L^{-1} and Nernstian compliance of 29.3±0.5 mV decade^{-1} of activity with low detection limit of 1.9×10^{-8} mol L^{-1}. Therefore, the same composition was used in the fabrication of pyrolytic graphite electrode and the responses obtained are shown in Fig. 7.12 and tabulated in Table 7.7. A comparison of data given in Table 7.7 showed that CPGE exhibited best performance in comparison to CGE with wide working concentration range of 1.4×10^{-8}-1.0×10^{-1} mol L^{-1}, the Nernstian slope of 29.4±0.6 mV $decade^{-1}$ of activity with low detection limit of 6.1×10^{-9} mol L^{-1}.

7.4.1.8. Analytical Applications

The selectivity for Co^{2+} ion revealed by the sensor makes it significantly suitable for the Co^{2+} ion monitoring in water, soil, medicinal plant and pharmaceutical samples.The sensor was also used as an indicator electrode in the potentiometric titration of Co^{2+} ion with EDTA.

Table 7.6. Effect of partially non-aqueous medium on the performance of Co^{2+} ion sensor.

Non-aqueous contents (%; v/v)	Working concentration range (mol L^{-1})	Slope (mV $decade^{-1}$ of activity)
0	1.4×10^{-8}-1.0×10^{-1}	29.4±0.6
Ethanol		
10	1.4×10^{-8}-1.0×10^{-1}	29.4±0.6
20	1.4×10^{-8}-1.0×10^{-1}	29.4±0.6
30	2.3×10^{-8}-1.0×10^{-1}	29.2±0.5
35	4.5×10^{-8}-1.0×10^{-1}	28.6±0.4
40	7.3×10^{-7}-1.0×10^{-1}	27.6±0.5
Methanol		
10	1.4×10^{-8}-1.0×10^{-1}	29.4±0.6
20	1.4×10^{-8}-1.0×10^{-1}	29.4±0.5
30	5.8×10^{-8}-1.0×10^{-1}	28.3±0.6
35	7.9×10^{-7}-1.0×10^{-1}	27.4±0.4
40	9.5×10^{-7}-1.0×10^{-1}	26.4±0.6
Acetonitrile		
10	1.4×10^{-8}-1.0×10^{-1}	29.4±0.6
20	1.4×10^{-8}-1.0×10^{-1}	29.4±0.6
30	2.6×10^{-8}-1.0×10^{-1}	29.4±0.5
35	4.9×10^{-8}-1.0×10^{-1}	28.5±0.5
40	8.1×10^{-7}-1.0×10^{-1}	27.2±0.6

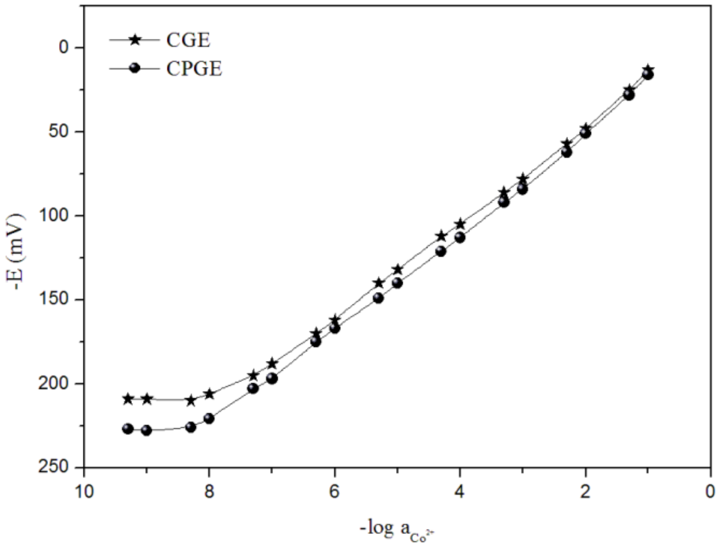

Fig. 7.12. Potentiometric characteristics calibration plot for Co^{2+} ion selective sensor with CGE and CPGE based on L_9.

7.4.1.8.1. Potentiometric titration

The sensor could be used as an indicator electrode in the potentiometric titration of Co^{2+} ion solution by titrating against EDTA solution. For this purpose, a potentiometric titration of 20 mL of 5.0×10^{-4} mol L^{-1} Co^{2+} ion solution against 1.0×10^{-2} mol L^{-1} solution of EDTA at pH 5.5 were carried out using the sensor (CGE and CPGE) and the titration plot obtained had showed sigmoid shapes Fig. 7.13 which also support that these sensors are selective to Co^{2+} ion.

The inflexion point corresponds to 1:1 stiochiometry of Co^{2+}-EDTA complex and therefore, these electrodes can be used as an indicator electrode for the potentiometric determination of Co^{2+} ion by titration.

7.4.1.8.2. Analysis of Co^{2+} ion in electroplating waste water and in river water samples

The sensor was successfully employed for the monitoring of Co^{2+} ion in the effluents discharged from electroplating works. Three samples of local electroplating wastes were collected, treated with dilute nitric acid filtered and stored. The pH of the sample was adjusted to 5.5 before the measurement. The results (Table 7.8) obtained by potentiometry are in good agreement with those obtained for AAS experiment.

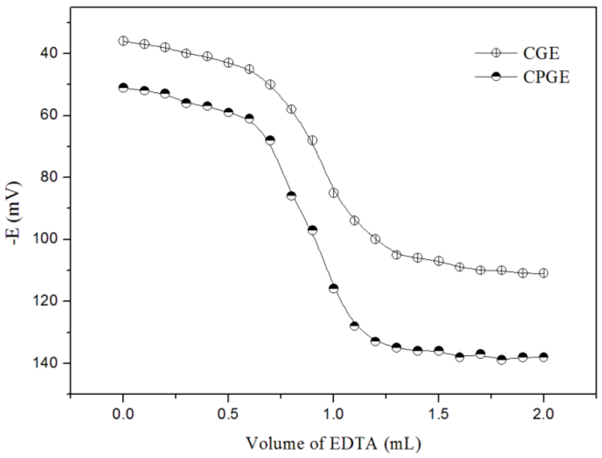

Fig. 7.13. **Potentiometric titration curve of 20 mL of 5.0×10^{-4} mol L^{-1} solution of Co^{2+} ion with 1.0×10^{-2} mol L^{-1} EDTA at pH 5.5.**

Similarly, Co^{2+} content of river water samples was determined by the sensor. The water samples collected were treated with dilute nitric acid, filtered and stored. The pH of the sample was adjusted to 5.5 before the measurement. The measurement was performed by direct potentiometry and the result obtained by the sensor was found in close agreement with those of AAS (Table 7.8).

7.4.1.8.3. Analysis of Co^{2+} ion in soil samples

The soil samples were digested in a cleaned Teflon beaker by treating 2 g of each soil sample with 10 mL of nitric acid. A 5:3:5 mixtures of nitric acid, perchloric acid and concentrated hydrofluoric acid were added, followed by controlled heating until white fumes evolved. The solution was filtered and diluted with distilled water to a final volume of 25 mL in a volumetric flask [87]. The pH of the sample was adjusted to 5.5 before the measurement. The results obtained by potentiometry were found in good agreement with those obtained by AAS and the results are compiled in Table 7.9.

7.4.1.8.4. Analysis of Co^{2+} ion in medicinal plants and pharmaceutical samples

The sensor was successfully employed for the Co^{2+} ion quantification in some medicinal plants (*Ocimum sanctum*, *Andrographis paniculata* and *Withania somnifera*) collected from Haridwar regions.

Table 7.7. Potentiometric response characteristics of Co^{2+} ion-selective electrodes based on L_9.

Properties	Values/range	
	CGE	CPGE
Optimized membrane composition	L_9: PVC: 1-CN: KTpClPB ≡ 6:35:56:3 (w/w, mg)	L_9: PVC: 1-CN: KTpClPB ≡ 6:35:56:3 (w/w, mg)
Conditioning time	24 h in 1.0×10^{-3} mol L^{-1} $Co(NO_3)_2$	24 h in 1.0×10^{-3} mol L^{-1} $Co(NO_3)_2$
Working concentration range (mol L^{-1})	3.8×10^{-8}-1.0×10^{-1}	1.4×10^{-8}-1.0×10^{-1}
Detection limit (mol L^{-1})	1.9×10^{-8}	6.1×10^{-9}
Slope (mV decade^{-1} of activity)	29.3±0.5	29.4±0.6
Response time (s)	10	7
Life span (month)	4	4
Working pH range	3.5-7.5	3.0-8.5

Table 7.8. Determination of Co^{2+} in electro-plating waste and river water samples.

Samples		**ISE*±SD (mg L^{-1})**	**AAS*±SD (mg L^{-1})**
Electroplating waste	Water sample 1	15.6±1.2	15.7±1.6
	Water sample 2	12.1±0.9	11.9±1.0
	Water sample 3	10.7±0.5	10.9±0.2
River water	Water sample 1	06.5±0.6	06.6±0.5
	Water sample 2	05.4±0.7	05.3±0.8
	Water sample 3	08.4±0.6	08.3±0.4

*Mean value ± standard deviation (triplicate measurements).

Table 7.9. Determination of Co^{2+} in soil samples.

Samples	**ISE*±SD (mg kg^{-1})**	**AAS*±SD (mg kg^{-1})**
Soil sample 1	09.80±1.31	09.77±1.22
Soil sample 2	10.45±0.50	10.47±0.35
Soil sample 3	09.92±0.30	09.91±0.25

*Mean value ± standard deviation (triplicate measurements).

Table 7.10. Determination of Co^{2+} in medicinal plant samples.

Samples	ISE*±SD (mg kg^{-1})	AAS*±SD (mg kg^{-1})
Ocimum sanctum	1.13±0.21	1.11±0.22
Andrographis paniculata	1.07±0.15	1.09±0.17
Withania somnifera	1.17±0.16	1.16±0.06

*Mean value ± standard deviation (triplicate measurements).

Table 7.11. Determination of Co^{2+} in pharmaceuticle samples.

Samples	Certified value (ppm)	Found value (ppm)	
		ISE*±SD	AAS*±SD
Neurobion Forte, Merck, India	15.00	14.96±0.06	14.97±0.05
Sioneuran (Inj.) Albert David Ltd., India	10.86	10.83±0.01	10.85±0.03

*Mean value ± standard deviation (triplicate measurements).

2.0 g of dried powdered plant samples was digested with a 5:1 mixture of nitric acid (25 vol. %) and perchloric acid, followed by controlled heating until the evolution of gases ceased. 15 mL of double distilled water was added to this mixture and filtered through into a 25 mL volumetric flask. The volume was adjusted to a final volume of 25 mL. Then it was analysed directly by the sensor at pH 5.5 and the results obtained were compared with the result obtained from AAS experiment and reported in the Table 7.10. The precision and utility of the sensor was accounted for cobalt quantificaation in pharmaceutical samples.

Nitric acid was used to digest sample apiece of injectable Neurobion (Merck, India) and Sioneuron (Albert David Ltd., India). The leaching of sample residue was done with diluted H_2SO_4. The preparation of working solutions was undertaken by taking an adequate amount of the sample and determination of its Co^{2+} content was done by the sensor at pH 5.5. The results (Table 7.11) obtained by potentiometry are in line with those of AAS experiment.

7.4.1.9. Conclusions

The investigation on PVC based fabricated membranes of Schiff bases (L_8, L_9 and L_{10}) show that they are Co^{2+} ion-selective sensor. The solvent mediator 1-chloronaphthalene (1-CN) enhances the performance characteristics of the sensor better than rest of the plasticizers. A comparative study showed that CPGE is superior over CGE (Table 7.7). The CPGE with the optimized membrane of composition of L_9: PVC: 1-CN: KTpClPB≡6:35:56:3 (w/w, mg) exhibits detection limit down to 6.1×10^{-9} mol L^{-1} to be low, selectivity for Co^{2+} ion to be high and. Nernstian slope of 29.4±0.6 mV $decade^{-1}$ of activity The sensor is independent of pH in the pH range of 3.0-8.5. The response time of the electrode is quick (7 s) and can work satisfactorily in partially non-aqueous content up to 30% of acetonitrile-water and ethanol-water mixture and can tolerate 10% of methanol-water system. Due to high selectivity and sensitivity, the sensor could be used for the determination of Co^{2+} ion in soil, water, medicinal plants and pharmaceutical samples and also as an indicator electrode in the potentiometric titration of Co^{2+} ion with EDTA. A comparison of the performance characteristics with previously reported sensors [18-20, 22, 23, 25, 29, 30, 32], (Table 7.12) revealed that the present sensor is superior in terms of wide working concentration range, low detection limit, Nernstian slope and selectivity is better than most of the other electrodes.

7.4.2. Membranes of L_{11}, L_{12} and L_{13} as Zn^{2+} Selective Sensors

The polymeric membranes fabricated with L_{11}, L_{12} and L_{13} as ionopohores have been used for selective monitoring of Zn^{2+}.

7.4.2.1. Complexation Study

In preliminary experiments, the complexation of Schiff bases (L_{11}, L_{12} and L_{13}) with a number of cations has been investigated conductometrically in DMF solution in order to obtain an idea about the stoichiometry of the resulting complexes at 25±0.1°C. Therefore, 25 mL of 1.0×10^{-4} mol L^{-1} cation solution was titrated against a 1.0×10^{-2} mol L^{-1} solution of $L_{11,}$ L_{12} and L_{13} in DMF. The conductance of the solution was measured after each addition of the titrant. The conductance variation plots with Zn^{2+} ion as a function of the $[L]/[Zn^{2+}]$ molar ratio is shown in Fig. 7.14.

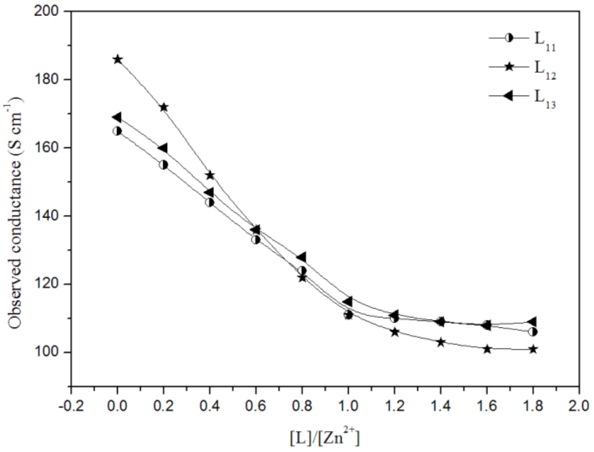

Fig. 7.14. Variation in conductance of Zn^{2+} ion solution with the addition of L_{11}, L_{12} and L_{13}.

It is from the Fig. 7.14 that conductance variation of Zn^{2+} ion solution showed immense variation with the addition of L_{12}, than with L_{11} and L_{13}. Initially the conductance falling off with the addition of ligands which depicts that Zn^{2+} are strongly interacting with the lignad added and forming Zn^{2+}-ligand complex and thus causes conductance to falls-off. A stage is arrived when conductance of solution nearly become constant and further addition of ligand does not cause any appreciable change in conductance which indicated that all of the Zn^{2+} ion have been consumed by the ligand in forming complex.

Table 7.12. Comparison of response characteristic of Co^{2+} ion-selective sensor with various reported electrodes.

Ref. no.	Ionophore	Linear range (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mVdecade^{-1} of activity)	pH range	Response time (s)
[18]	(2-mercapto-4-methylphenyl)-2-benzamido-3-phenyl-thiopropenoate	4.0×10^{-7} - 1.0×10^{-2}	1.0×10^{-7}	30.0 ± 1.0	5.0-8.0	5
[19]	OXCCD	1.0×10^{-6} - 1.0×10^{-1}	9.0×10^{-7}	29.8	3.5-8.0	25
[20]	5-amino-3-methylisothiazole	6.3×10^{-7} - 1.0×10^{-1}	3.9×10^{-7}	29.5 ± 0.2	3.3-9.0	12
[22]	modified calixarene	5.3×10^{-6} - 1.0×10^{-1}	3.0×10^{-7}	30.0	2.5-6.0	10
[23]	p-(4-n-butylphenylazo)calix[4]arene	9.2×10^{-6} - 1.0×10^{-1}	4.0×10^{-6}	29.0 ± 1.0	4.0-7.2	25
[25]	dibenzopyridino-substituted macrocyclic diamide	7.0×10^{-7} - 1.0×10^{-2}	2.0×10^{-7}	29.1 ± 0.1	3.0-8.5	10
[29]	Pendant armed macrocycle	1.3×10^{-8} - 1.0×10^{-1}	6.8×10^{-9}	29.5 ± 0.1	2.0-9.0	8
[30]	5-((4-nitrophenyl)azo)-N-(2′,4′-dimethoxyphenyl) salicylaldimine	9.0×10^{-7}- 1.0×10^{-2}	8.0×10^{-7}	29.0 ± 1.0	3.5-6.0	5-10
[32]	N_2O_2 Salen ligands	1.1×10^{-8}- 1.0×10^{-1}	7.0×10^{-9}	29.6	3.0-9.0	9
This work	2,2'-(((propane-1,3-diylbis(oxy))bis(3-methoxy-4,1-phenylene))bis(methanylylidene))bis-(hydrazinecarbothioamide) (L_9)	1.4×10^{-8} - 1.0×10^{-1}	6.1×10^{-9}	29.4 ± 0.6	3.0-8.5	7

The break in the conductance variation plots gives the stoichiometry of the resulting complex and from the Figure 7.14 it has been observed that the stoichiometry of metal to ligand is 1:1. Therefore, L_{12} was used for further study because of its maximum affinity toward Zn^{2+} ion.

7.4.2.2. Optimization of Membrane Composition and Potential Measurements

The selectivity, sensitivity and linearity estimated for a specified ionophore highly depends on the nature of plasticizer and membrane [80]. It has also been found that additives added [81, 82] influence the performance of the sensor. Therefore, to improve the performance of these polymeric membranes based on $L_{11,}$ L_{12} and L_{13} a number of electrodes having different composition were fabricated and studied. The potential of various electrodes were measured as a function of Zn^{2+} ion concentration in the range of 1.0×10^{-1}-1.0×10^{-9} mol L^{-1}. The potential response of CGE and CPGE were first investigated only with ligand and PVC and the results are summarized in Fig. 7.15. It has been concluded that sensors having membranes of L_{11}, L_{12} and L_{13} without plasticizer and containing only PVC 5% (w/w, mg) showed linear response over a working concentration range of 1.7×10^{-5}-1.0×10^{-1}, 5.5×10^{-6}-1.0×10^{-1} and 1.1×10^{-5}-1.0×10^{-1} mol L^{-1}, with a slope of 24.9±0.3, 25.7±0.2 and 23.5±0.3 mV decade^{-1} of activity, respectively. The working concentration range is narrow and the slope is non-Nernstian. Therefore, attempts were made to bring the detection limit low and slope to Nernstian by the incorporation of plasticizers as it is well known that the incorporation of plasticizer in the membrane phase enhances the performance characteristics of the electrodes. Therefore, in these studies five plasticizers *viz*., *o*-NPOE, BA, 1-CN, DBP and DOP were investigated in to and the response obtained with plasticized membranes is shown in Fig. 7.15. Comparing the responses of plasticized and non-plasticized membranes it has been observed that membranes which were plasticized imparts improved response in terms of working concentration range and near-Nernstian slope relative to non-plasticized membranes. Since the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of ionophore molecules [39, 88, 89], it is expected to play an important role in determining the ion selective characteristics. Effects of NaTPB and KTpClPB as suitable anionic excluders were studied with L_{11}, L_{12} and L_{13} on the potentiometric response of Zn^{2+} ion to improve the slope and it was found that NaTPB produced significant effects, and performed best in terms of wide working concentration range with Nernstian slope and lower detection limit over the KTpClPB incorporating membrane.

The optimized membrane composition of L_{11}: PVC: DOP: NaTPB ≡ 5:37:55:3, L_{12}: PVC: DOP: NaTPB ≡ 6:34:58:2 and L_{13}: PVC: DOP: NaTPB ≡ 6:34:58:2 % (w/w, mg) gives the best performance in terms of wide working concentration range, slope and lower detection limit. The potential variations with different quantity of ligands were also studied and it has been observed that change in amount of ligands does not in any way improve the performance of the electrodes.

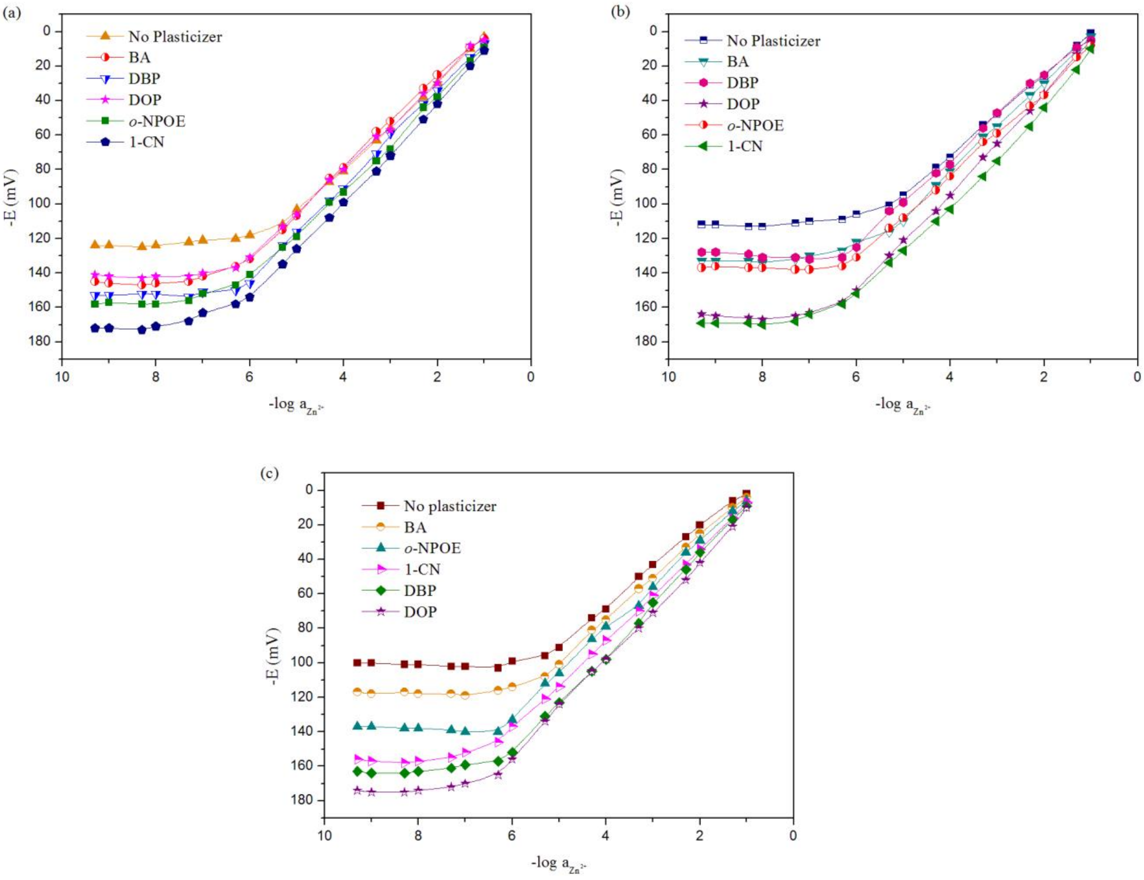

Fig. 7.15. Potentiometric characteristics plots showing variation of membranes potential with the concentration of Zn^{2+} ion based on (a) L_{11}, (b) L_{12} and (c) L_{13}.

7.4.2.3. pH-Potential Profile

The effect of pH on the performance of the fabricated electrodes were examined by measuring their potentiometric responses for 1.0×10^{-3} mol L^{-1} and 1.0×10^{-4} mol L^{-1} solution of Zn^{2+} ion at different pH values ranging from 1.0-12.0. The pH was adjusted by the addition of 1.0×10^{-1} mol L^{-1} HCl/NaOH and the results are shown in Fig. 7.16. It is revealed from the Fig. 7.16, that potential response for CGE remains independent of pH over pH range of 3.5 to 9.0 and 3.0 to 9.0 for CPGE. Therefore, the same was considered as the working range for pH for these electrodes. The potential change at higher pH may be attributed to formation of metal hydroxides species in the matrix [83] and the deviation at low pH may be regarded as the effect of protonation of ionophore [84] and the electrodes start responding to H_3O^+ ions along with Zn^{2+} ion leading to an increase in potentials.

7.4.2.4. Effect of Interfering Ions on the Performance of Sensor

The most important parameter which reflects the applicability of an ISE is its selectivity, which is measured in terms of selectivity coefficients. The potentiometric selectivity coefficients for CGE and CPGE based on Schiff base L_{11} were determined according to IUPAC recommended fixed interference method (FIM).

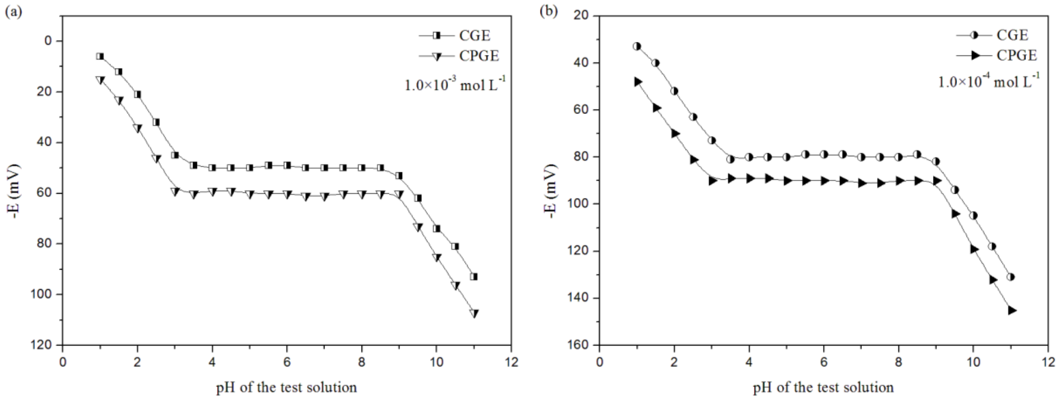

Fig. 7.16. Effect of pH of the test solution on the potential response of CGE and CPGE with (a) 1.0×10^{-3} mol L^{-1} and (b) 1.0×10^{-4} mol L^{-1} Zn^{2+} ion solutions at different pH.

In this method, the selectivity coefficient was evaluated from the potential measurement on solutions containing a fixed concentration of interfering ion (1.0×10^{-2} mol L^{-1}) and varying amount of Zn^{2+} ion solution ranging from 1.0×10^{-1} to 1.0×10^{-9} mol L^{-1}. The potential values so obtained were then plotted versus activity of Zn^{2+} ion. The linear portion of potential response curve then extrapolated and the value of a_{Zn2+} was obtained from the intersection point. The potentiometric selectivity coefficients were then determined using the following expression [85]:

$$K_{A,B}^{Pot} = \frac{(a_A)}{(a_B)^{z_A/z_B}} \qquad (1)$$

Where a_A is the activity of primary ion A (Zn^{2+}) at the lower detection limit in the presence of interfering ion B, a_B, the activity of interfering ion B and z_A and z_B are their respective charges. The values of selectivity coefficients thus obtained for CGE and CPGE are compiled in the Table 7.13. From the selectivity coefficients given in the Table 7.13, it has been observed that the electrodes are highly selective over a number of monovalent, divalent and trivalent cations. However, selectivity coefficients obtained for Cd^{2+} ion is not very low and they caused some interference if present in eminent concentration. To estimate the extent of interference caused by the Cd^{2+} ion, mixed run studies were performed and the effect of the Cd^{2+} ion concentration on the performance of the sensor was examined. The potentials were measured in the presence of different concentrations (1.0×10^{-5}, 5.0×10^{-5}, 1.0×10^{-4} and 1.0×10^{-3} mol L^{-1}) of Cd^{2+} ion and the potential responses of the sensor to the mixtures are shown in Fig. 7.17. It is revealed from Fig. 7.17 that Cd^{2+} at $\leq5.0\times10^{-5}$ mol L^{-1} did not cause any deviation in the original plot obtained in pure Zn^{2+} ion. Thus, the sensor can tolerate Cd^{2+} at $\leq5.0\times10^{-5}$ mol L^{-1} over the entire working concentration range.

Table 7.13. Selectivity coefficients of various interfering ions for Zn^{2+} ion-selective sensor.

Interfering ions	Selectivity coefficients ($K_{Zn^{2+},B}^{FIM}$)	
	CGE	CPGE
Na^+	3.1×10^{-3}	1.8×10^{-3}
K^+	2.9×10^{-3}	2.1×10^{-3}
Mg^{2+}	2.7×10^{-3}	1.9×10^{-3}
Cd^{2+}	2.2×10^{-2}	1.1×10^{-2}
Hg^{2+}	3.7×10^{-2}	2.8×10^{-2}
Ni^{2+}	2.6×10^{-4}	1.2×10^{-4}
Co^{2+}	4.3×10^{-4}	2.3×10^{-4}
Cu^{2+}	7.1×10^{-3}	5.2×10^{-3}
Mn^{2+}	5.7×10^{-4}	3.0×10^{-4}
Ce^{3+}	4.8×10^{-4}	3.3×10^{-4}
La^{3+}	6.3×10^{-4}	4.4×10^{-4}

However, when Cd^{2+} present in higher concentration, significant interference was observed and thus causes shorting of working concentration range and thus Zn^{2+} ion could be determined in the reduced concentration ranges of 6.4×10^{-7}-1.0×10^{-1} and 6.7×10^{-6}-1.0×10^{-1} mol L^{-1} in the presence of 1.0×10^{-4} and 1.0×10^{-3} mol L^{-1} of Cd^{2+} ion, respectively.

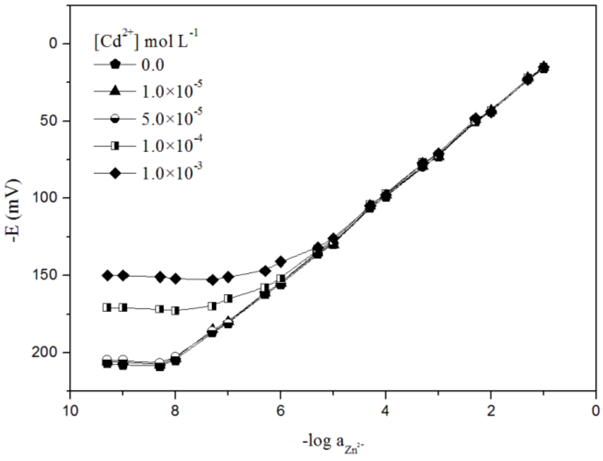

Fig. 7.17. Effect of different concentrations of Cd^{2+} ion on the performance of the sensor.

From Table 7.13, it has also been observed that CPGE based on L_{12} performs comparably better than CGE. Thus, these electrodes can be utilised for the estimating Zn^{2+} ion in existence of rare earth metals, alkaline earth metals and lanthanides to a good extent.

7.4.2.5. Determination of Dynamic Time and Life Span of the Sensor

Dynamic response time is an important factor for an ISE. According to IUPAC recommendations, the response time of an ion selective electrode is defined as the length of time between the instant at which the ion selective electrode and reference electrode are immersed in the solution and the moment at which the potential of the cell reaches its steady- state value within ±1 mV [86]. Response time of the sensor can be measured by consecutively changing the concentration of the test solution from 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1}. The average time needed to attain a potential response in the electrodes lies within ±1 mV range value of final equilibrium after immersing successively in a series of Zn^{2+} ion solution, each having a difference of 10-folds in concentration was 13 seconds for CGE and 10 seconds for CPGE as shown in Figure 7.18. The life time of the electrodes were estimated by soaking both CGE and CPGE in 1.0×10^{-1} mol L^{-1} of $Zn(NO_3)_2$ solution for interval range of 2 to 130 days till the Nernstian behaviour of the electrode was lost . The deviation from the ideal value is accredited to decomposition of the ionophore and depletion of other components in the membrane phase that was in contact with aqueous test solution containing Zn^{2+} ion.

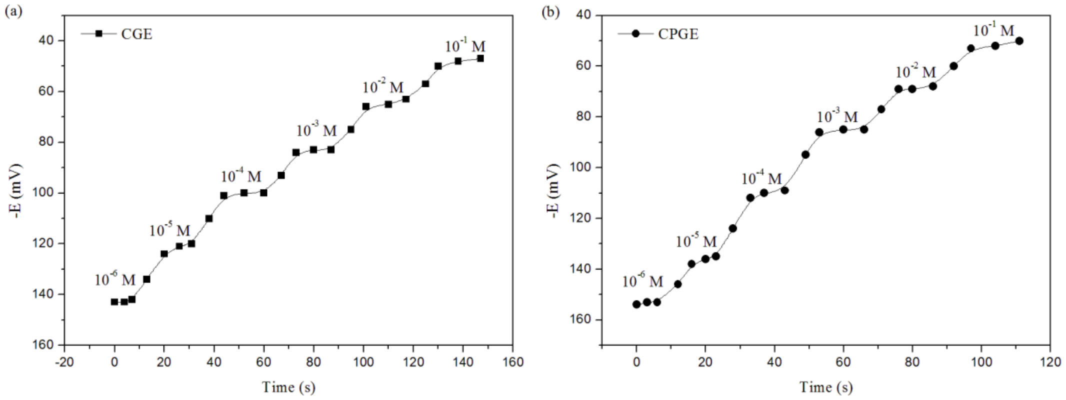

Fig. 7.18. Dynamic response time of Zn^{2+} ion sensor based on ligand (L_{12}) for step changes in concentration of Zn^{2+} ion with (a) CGE and (b) CPGE.

The response of both the electrodes has been measured by recording the potential at different intervals and the results are compiled in the Table 7.14. Thus, CGE and CPGE could be used over a period of 3 and 4 months, respectively, during which the slope of electrode showed only a slight change from 29.3±0.3 to 25.8±0.2 mV decade^{-1} of activity, the working concentration range shifted from 6.9×10^{-8}-1.0×10^{-1} to 6.7×10^{-7}-1.0×10^{-1} mol L^{-1} and the detection limit reduces from 2.8×10^{-8}-4.2×10^{-7} mol L^{-1} for CGE and for CPGE the slope reduces from 29.6±0.2 to 26.0±0.4 mV decade^{-1} of activity, the working concentration range reduces from 1.1×10^{-8}-1.0×10^{-1} to 7.7×10^{-7}-1.0×10^{-1} and the detection limit shifted from 8.1×10^{-9} to 5.4×10^{-7} mol L^{-1}.

7.4.2.6. Effect of Non-aqueous Medium on the Performance of the Sensor

Non-aqueous content might be present in analytical samples; therefore the efficiency of the sensor was also estimated in partially non-aqueous solutions containing 10%, 20%, 30% and 40% (v/v) non-aqueous content in acetonitrile-water methanol-water and ethanol-water mixtures. The sensor did not exhibit any considerable deviation in the range of working concentration and slope in 30% non-aqueous contents of acetonitrile-water and ethanol-water solutions. However, it was found that only 20% amount of methanol-water could be tolerated. Therefore, the sensor is not suitable for using in methanol-water mixture above 20% concentration. This may be due to greater solubility of the ionophore in methanol which causes leaching of ionophore from the membrane phase.

Table 7.14. Potential response of Zn^{2+} selective sensor based on L_{12} using CGE and CPGE at different time intervals.

Time (Days)	Slope (mV decade^{-1} of activity)	Working concentration range (mol L^{-1})	Detection Limit (mol L^{-1})
CGE			
2	29.3±0.3	6.9×10^{-8}-1.0×10^{-1}	2.8×10^{-8}
10	29.3± 0.3	6.9×10^{-8}-1.0×10^{-1}	2.8×10^{-8}
30	29.0±0.6	7.4×10^{-8}-1.0×10^{-1}	3.3×10^{-8}
45	28.8±0.5	7.9×10^{-8}-1.0×10^{-1}	3.8×10^{-8}
60	28.1±0.5	8.6×10^{-8}-1.0×10^{-1}	4.9×10^{-8}
75	27.8±0.6	9.5×10^{-8}-1.0×10^{-1}	5.6×10^{-8}
90	27.5±0.2	9.8×10^{-8}-1.0×10^{-1}	6.0×10^{-8}
95	25.8±0.2	6.7×10^{-7}-1.0×10^{-1}	4.2×10^{-7}
CPGE			
2	29.6±0.2	1.1×10^{-8}-1.0×10^{-1}	8.1×10^{-9}
10	29.6±0.2	1.1×10^{-8}-1.0×10^{-1}	8.1×10^{-9}
30	29.5±0.3	1.4×10^{-8}-1.0×10^{-1}	8.2×10^{-9}
45	29.3±0.2	1.8×10^{-8}-1.0×10^{-1}	8.5×10^{-9}
60	29.1±0.6	2.7×10^{-8}-1.0×10^{-1}	9.4×10^{-9}
75	28.7±0.5	3.6×10^{-8}-1.0×10^{-1}	9.7×10^{-9}
90	28.3±0.6	4.4×10^{-8}-1.0×10^{-1}	1.9×10^{-8}
110	28.0±0.2	5.3×10^{-8}-1.0×10^{-1}	2.6×10^{-8}
120	27.8±0.2	6.6×10^{-8}-1.0×10^{-1}	3.5×10^{-8}
130	26.0±0.4	7.7×10^{-7}-1.0×10^{-1}	5.4×10^{-7}

7.4.2.7. Comparative Performance of Coated Graphite Electrode (CGE) and Coated Pyrolytic Graphite Electrode (CPGE)

The explorations on polymeric membrane based on Schiff bases (L_{11}, L_{12} and L_{13}) have proved to be promising and selective to Zn^{2+} ion. The sensor with optimized membrane composition of L_{11}: PVC: DOP: NaTPB ≡ 5:37:55:3 (w/w; mg) performed best in terms of wide working concentration range (1.1×10^{-7}-1.0×10^{-1} mol L^{-1}) and Nernstian compliance (29.0±0.4 mV decade^{-1} of activity) with detection limit of 8.3×10^{-8} mol L^{-1}. On the other hand, sensor incorporating L_{12} as ionophore and dioctyl phthalate as plasticizer performed best with optimized membrane of composition L_{12}: PVC: DOP: NaTPB ≡ 6:34:58:2 (w/w; mg). The sensor (L_{12} as ionophore) display linear working concentration range (6.9×10^{-8}-1.0×10^{-1} mol L^{-1}) and Nernstian compliance (29.3±0.3 mV decade^{-1} of activity) with lower detection limit (2.8×10^{-8} mol L^{-1}).

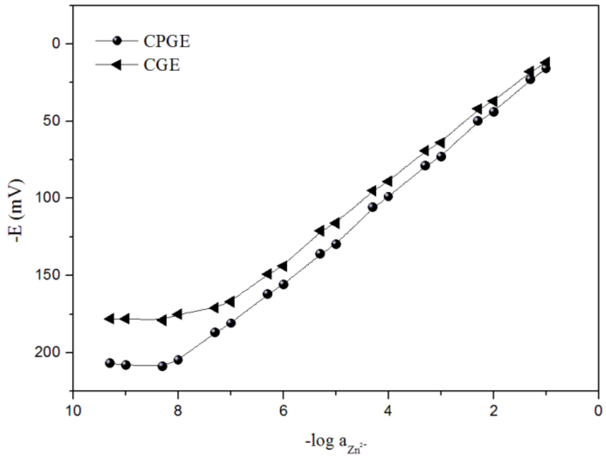

Fig. 7.19. Potentiometric characteristics calibration plot for Zn^{2+} ion selective sensor with ligand L_{12}.

While optimized membrane of L_{13}: PVC: DOP: NaTPB in the ratio of 6:34:58:2 % (w/w; mg) performed best in terms of wide working concentration range (8.2×10^{-8}-1.0×10^{-1} mol L^{-1}) and Nernstian slope (28.8±0.4 mV decade^{-1} of activity) with lower detection limit of 2.2×10^{-8} mol L^{-1}. Therefore, L_{12} was used for the fabrication of pyrolytic graphite electrode keeping the same composition as that of CGE and the response is shown in the Fig. 7.19 and tabulated in Table 7.15. A comparison of data given in the Table 7.15 showed that CPGE showed improved response in comparison to CGE. The CPGE exhibit wide working concentration range of 1.1×10^{-8}-1.0×10^{-1} mol L^{-1}, the Nernstian slope of 29.6±0.2 mV decade^{-1} of activity with detection limit of 8.1×10^{-9} mol L^{-1}.

7.4.2.8. Analytical Application

The sensor show higher selectivity for Zn^{2+} ion. Therefore, performace of the sensor was tested in water, soil and medicinal plant samples and Zn^{2+} ion was determined. Also, the sensor was successfully employed as an indicator electrode in the potentiometric titration of Zn^{2+} ion with EDTA.

Table 7.15. Potentiometric response characteristics of Zn^{2+} ion-selective sensor based on CGE and CPGE.

Properties	Values/range	
	CGE	CPGE
Optimized membrane composition	L_{12}: PVC: DOP: NaTPB ≡ 6:34:58:2 (w/w, mg)	L_{12}: PVC: DOP: NaTPB ≡ 6:34:58:2 (w/w, mg)
Conditioning time	24 h in 1.0×10^{-3} mol L^{-1} $Zn(NO_3)_2$	24 h in 1.0×10^{-3} mol L^{-1} $Zn(NO_3)_2$
Working concentration range (mol L^{-1})	6.9×10^{-8}-1.0×10^{-1}	1.1×10^{-8}-1.0×10^{-1}
Detection limit (mol L^{-1})	2.8×10^{-8}	8.1×10^{-9}
Slope (mV decade^{-1} of activity)	29.3±0.3	29.6±0.2
Response time (s)	13	10
Life span (month)	3	4
Working pH range	3.5-9.0	3.0-9.0

7.4.2.8.1. Potentiometric Titration

The sensor was found to work well under laboratory conditions and it was used as indicator electrode in the potentiometric titration of Zn^{2+} ion solution against EDTA solution. For this purpose, a potentiometric titration of 20 mL of 5.0×10^{-4} mol L^{-1} Zn^{2+} ion solution against 1.0×10^{-2} mol L^{-1} solution of EDTA at pH 5.5 were carried out using these electrodes and the titration plot obtained had sigmoid shapes which also supports that these electrodes are selective to Zn^{2+} ion and the inflexion point corresponds to 1:1 stoichiometry of Zn^{2+}-EDTA complex and therefore, these electrodes can be used as indicator electrode for the potentiometric estimation of Zn^{2+} ion.

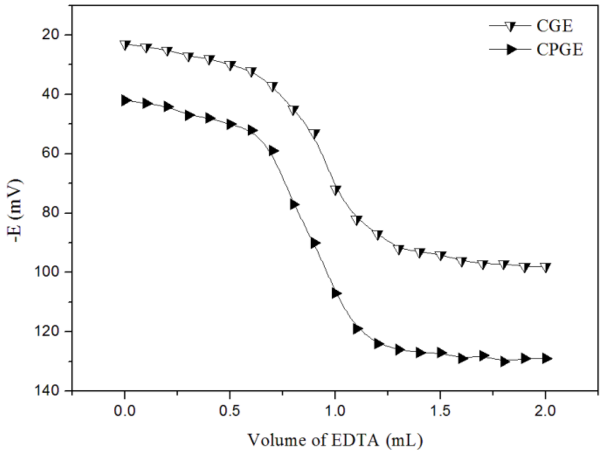

Fig. 7.20. **Potentiometric titration curve of 20 mL of 5.0×10^{-4} mol L^{-1} solution of Zn^{2+} ion with 1.0×10^{-2} mol L^{-1} EDTA at pH 5.5.**

The titration plot for electrodes CGE and CPGE are shown in Fig. 7.16, from which we can accurately determine the amount of Zn^{2+} ion present in the sample.

7.4.2.8.2. Analysis of Zn^{2+} ion in water and soil samples

The Zn^{2+} ion content of 50 mL river water and electroplating waste water samples were determined using CPGE. The water samples were treated with 7.5 mL of diluted nitric acid and 2.5 mL of hydrogen peroxide (30%). The mixture was stirred and its volume was reduced to half by heating, 2.5 mL dilute HNO_3 was added and the solution was filtered through a 0.45-μm membrane filter paper. After adjustment to pH ∼5.5 by addition of dilute HNO_3, Zn^{2+} ion was determined by the sensor and also the results obtained were found in close agreement with that of AAS as shown in the Table 7.16.

Table 7.16. Determination of Zn^{2+} in electroplating waste and water samples.

Samples		ISE*±SD (µg mL^{-1})	AAS*±SD (µg mL^{-1})
Electroplating waste	Water sample 1	19.4±2.8	19.1±2.6
	Water sample 2	19.0±1.9	19.5±1.0
	Water sample 3	18.7±2.5	19.0±0.8
River water	Water sample 1	06.9±1.6	06.6±1.5
	Water sample 2	07.3±2.7	07.3±0.8
	Water sample 3	06.4±0.3	06.3±0.5

*mean value ± standard deviation (triplicate measurements).

Table 7.17. Determination of Zn^{2+} contents in soil samples.

Samples	ISE*±SD (mg kg^{-1})	AAS*±SD (mg kg^{-1})
Soil sample 1	69.2±3.5	69.0±1.2
Soil sample 2	54.8±1.9	55.1±0.5
Soil sample 3	61.3±4.3	60.4±2.5

*mean value ± standard deviation (triplicate measurements).

The soil samples were digested in a cleaned Teflon beaker by treating 2.0 g of each soil samples with 10 mL of nitric acid. A 5:3:5 mixtures of concentrated nitric acid, perchloric acid and hydrofluoric acid were added, followed by controlled heating until white fumes evolved. The filteration and dilution of the solution was done with double distilled water to a final volume of 25 mL in a volumetric flask. The results obtained were found in close agreement with that of AAS and are compiled in Table 7.17.

7.4.2.8.3. Analysis of Zn^{2+} ion in medicinal plant samples

The sensor was successfully employed for the Zn^{2+} ion determination in some medicinal plants of importance namely, *Withania somnifera, Androgarphis paniculata* and *C. Fistula* collected from Haridwar regions. 2 g of dried powder plant samples was digested with a 5:1 mixture of nitric acid (25%) and perchloric acid, followed by controlled heating until the evolution of gases ceased. 15 mL of double distilled water was added and filtered through into a 25 mL volumetric flask. The volume was adjusted to a final volume of 25 mL. Then it was analysed directly by the sensor and the results obtained were found in close agreement with those of AAS experiments (Table 7.18).

Table 7.18. Determination of Zn^{2+} contents in medicinal plant samples.

Samples	ISE*±SD (mg kg^{-1})	AAS*±SD (mg kg^{-1})
Withania somnifera	39.8±1.1	39.4±1.5
Andrographis paniculata	28.2±1.4	28.4±0.5
C.fistula	47.8±2.6	48.2±1.3

7.4.2.9. Conclusions

The studies on a large number of electrodes based on Schiff bases L_{11}, L_{12} and L_{13} have shown that the plasticizer DOP enhances the performance characteristics of the electrodes better than rest of the plasticizers. CPGE based on L_{12} has been found to be the best in performance characteristics. The composition of the membrane with the best performance indicators was found to be L_{12}: PVC: DOP: NaTPB ≡ 6:34:58:2 % (w/w; mg). with the wide working concentration range of 1.1×10^{-8} mol L^{-1} and low detection limit of 8.1×10^{-9} mol L^{-1}. The CPGE shows Nearnstian slope of 29.6±0.3 mV decade^{-1} of activity and is independent in the pH range of 3.0-9.0. The response time of the electrode was found to be 10 s and can work satisfactorily in partially non-aqueous medium up to 30% of ethanol-water and acetonitrile-water mixtures and can tolerate 20% of the methanol-water mixture. The electrode reflects its utility in the monitoring of Zn^{2+} ion in various real samples and as well as an indicator electrode in the potentiometric titration of Zn^{2+} ion with EDTA.The performance of the sensor is good in terms of selectivity, sensitivity and detection limit.

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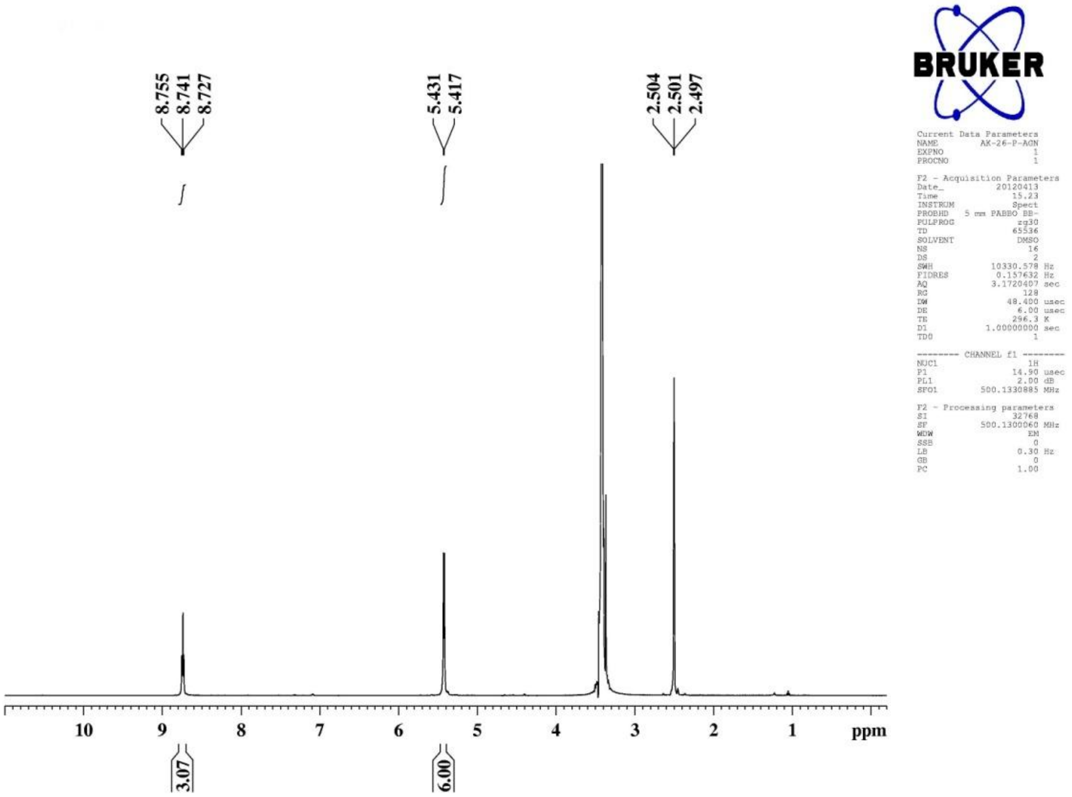
^{1}H NMR Spectra of L_1



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Current Data Parameters
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EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120413
Time               15.23
INSTRUM            Spect
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PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH          10330.578 Hz
FIDRES        0.157632 Hz
AQ           3.1720407 sec
RG                   128
DW              48.400 usec
DE                6.00 usec
TE               296.3 K
D1          1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1               14.90 usec
PL1               2.00 dB
SFO1       500.1330885 MHz

F2 - Processing parameters
SI                 32768
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WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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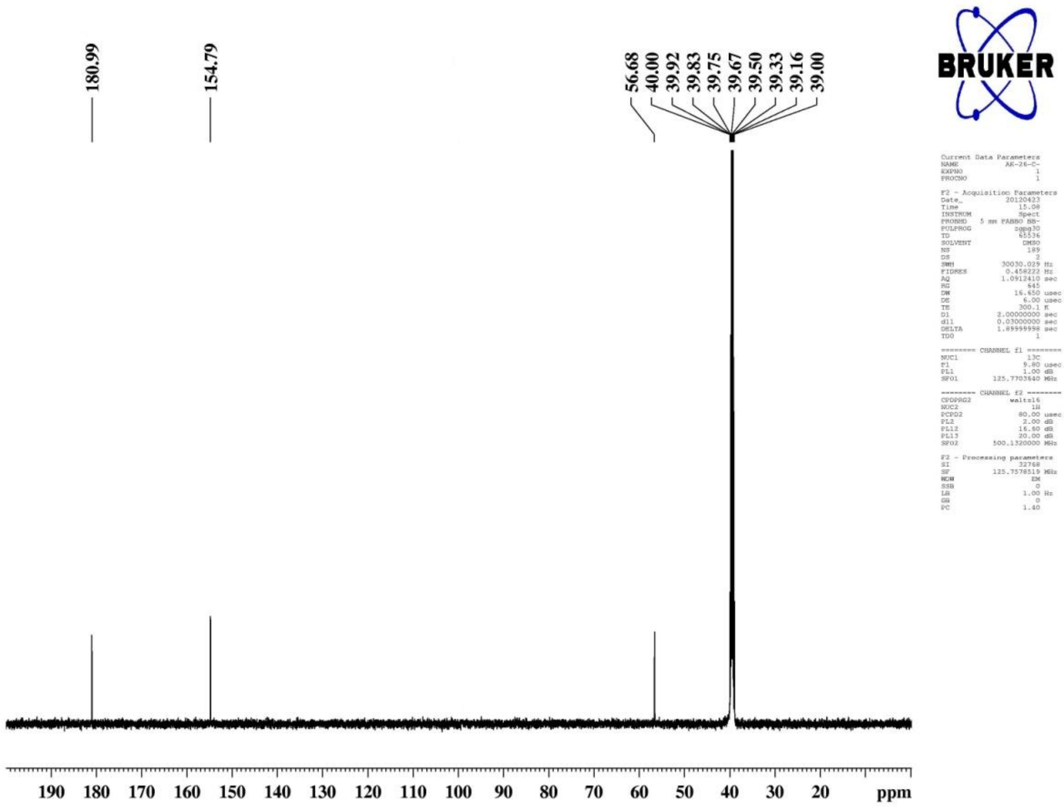
^{13}C NMR Spectra of L_1



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Current Data Parameters
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EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
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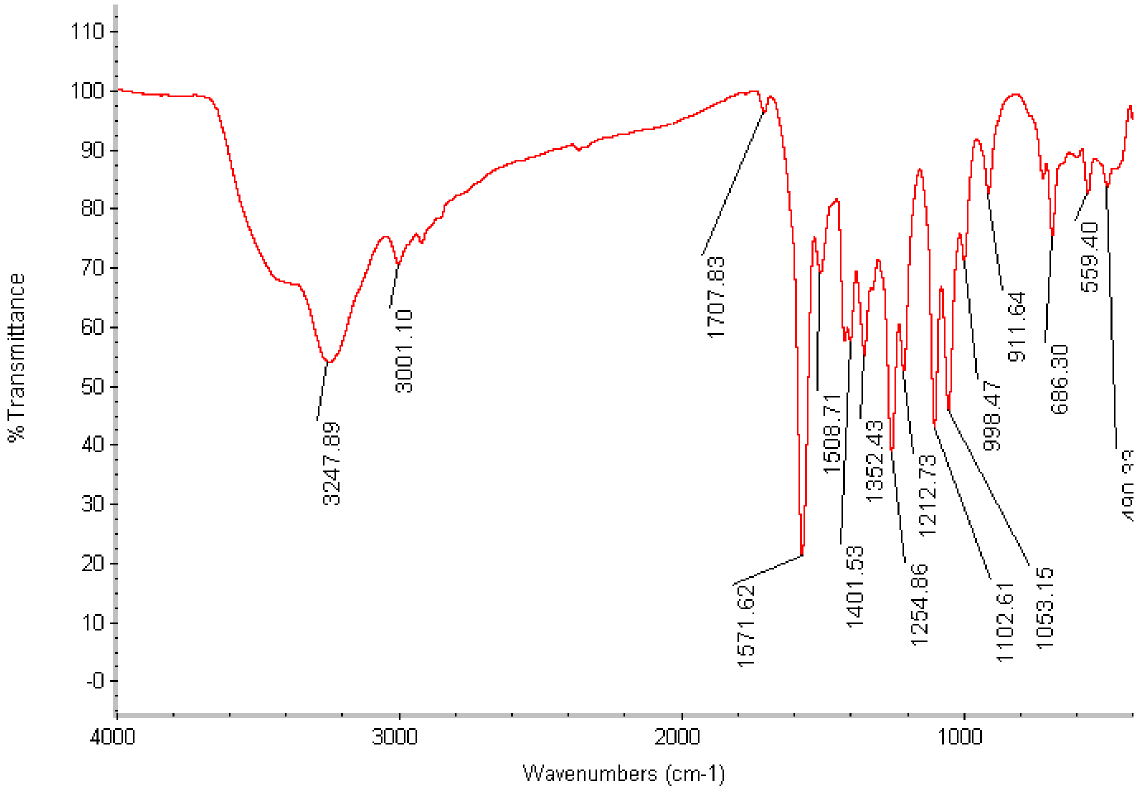
PULPROG           zgpg30
TD                 65536
SOLVENT             DMSO
NS                   189
DS                     2
SWH            30030.029 Hz
FIDRES          0.458222 Hz
AQ             1.0912410 sec
RG                   645
DW                16.650 usec
DE                  6.00 usec
TE                 300.1 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.80 usec
PL1                 1.00 dB
SFO1         125.7703640 MHz

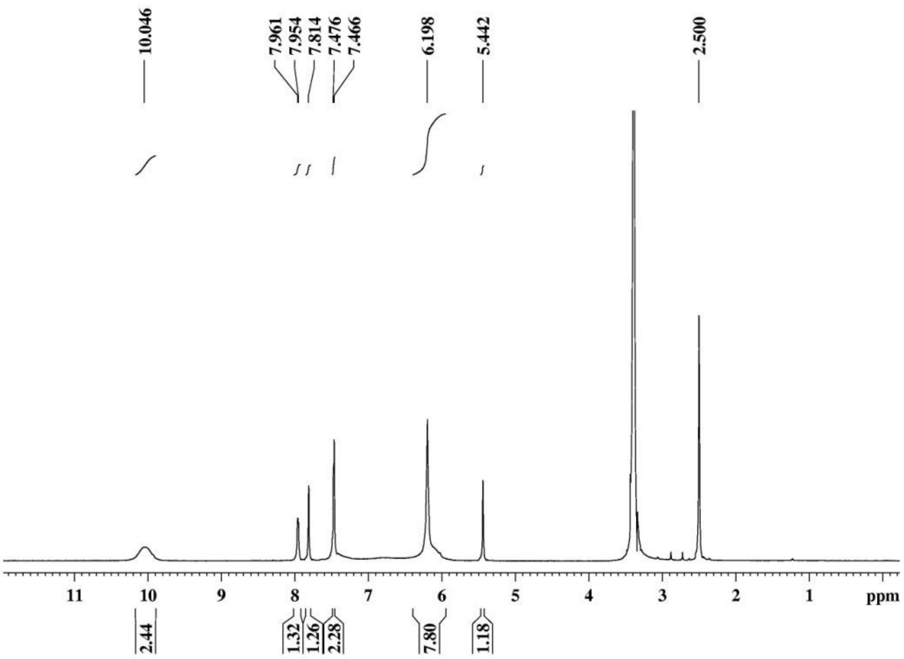
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 2.00 dB
PL12               16.60 dB
PL13               20.00 dB
SFO2         500.1320000 MHz

F2 - Processing parameters
SI                 32768
SF           125.7578519 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

FTIR Spectra of L_1



^{1}H NMR Spectra of L_2



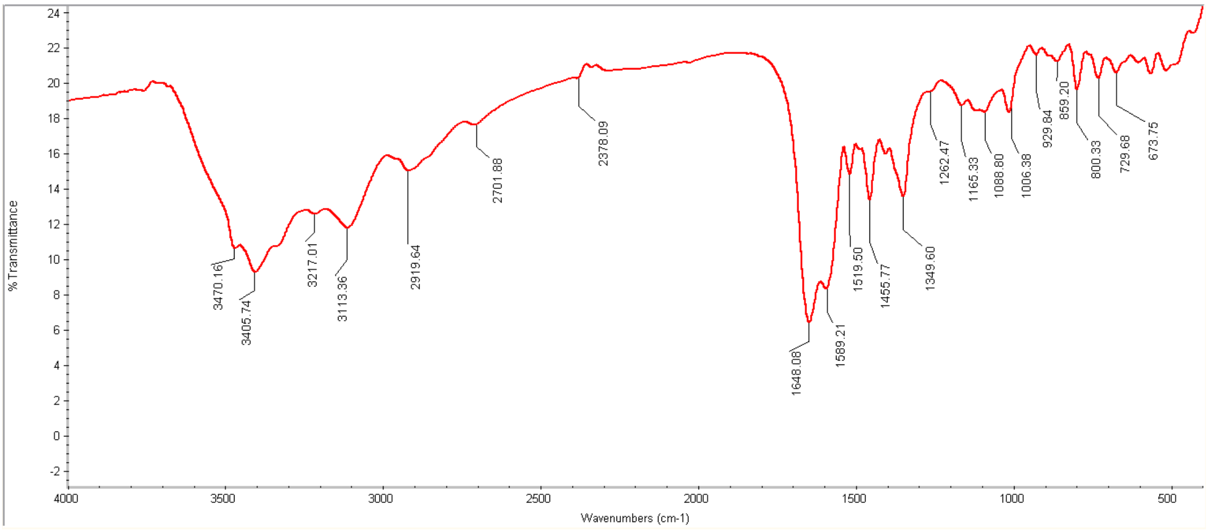
```
Current Data Parameters
NAME             SAH-CRY-4
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20140522
Time                 15.00
INSTRUM              Spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                      16
DS                       2
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1720407 sec
RG                     181
DW                  48.400 usec
DE                    6.50 usec
TE                   295.3 K
D1              1.00000000 sec
TD0                      1

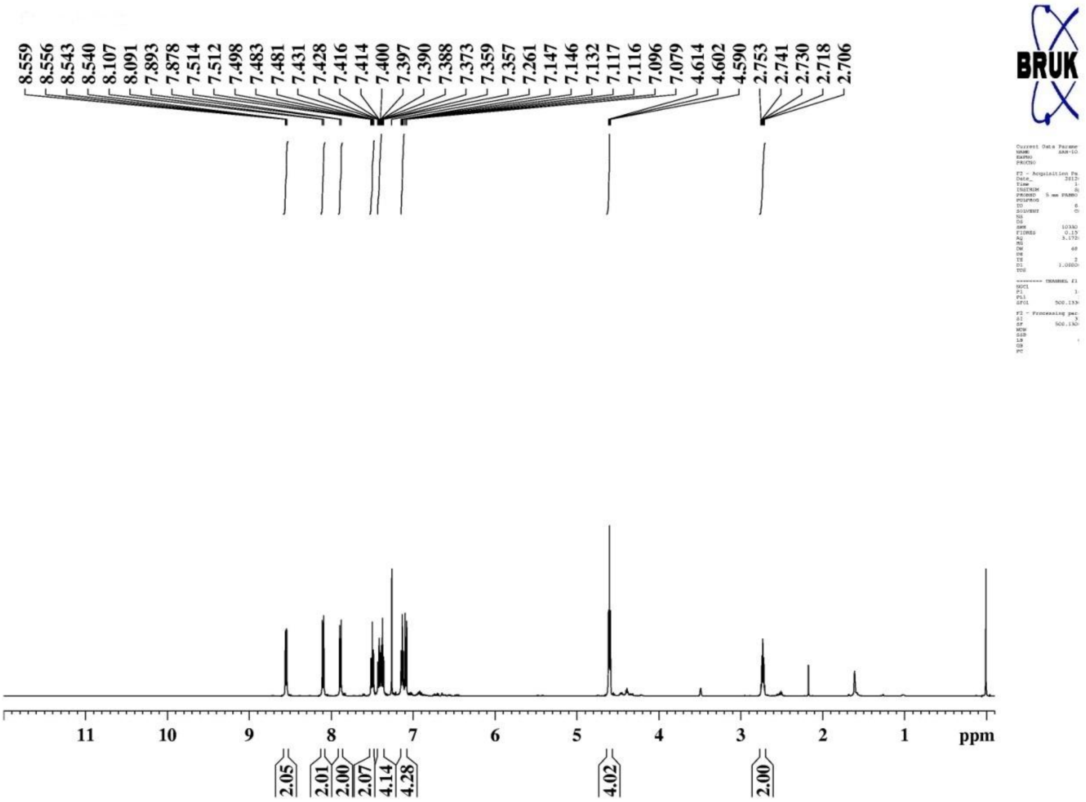
======== CHANNEL f1 ========
NUC1                    1H
P1                   14.90 usec
PL1                   2.00 dB
PL1W           14.97724056 W
SFO1           500.1330885 MHz

F2 - Processing parameters
SI                   32768
SF             500.1300047 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

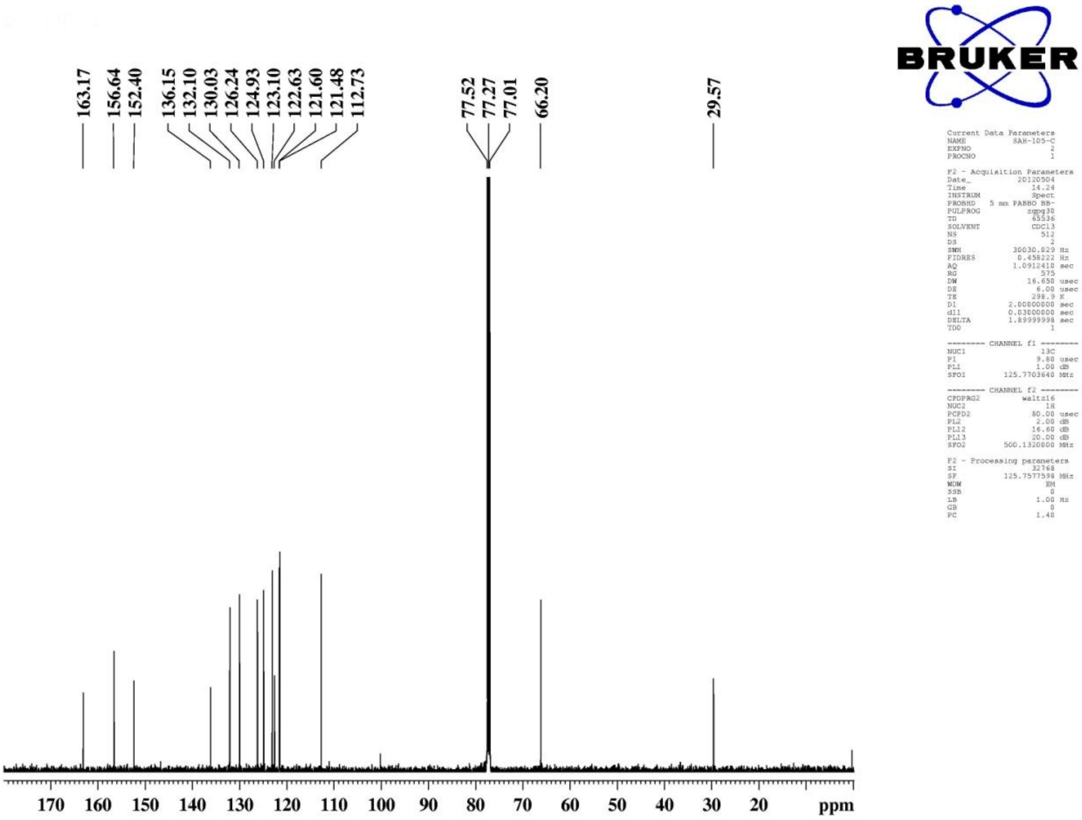
FTIR Spectra of L_2



^{1}H NMR Spectra of L_3



^{13}C NMR Spectra of L_3



```
Current Data Parameters
NAME          SAH-105-C
EXPNO                 2
PROCNO                1

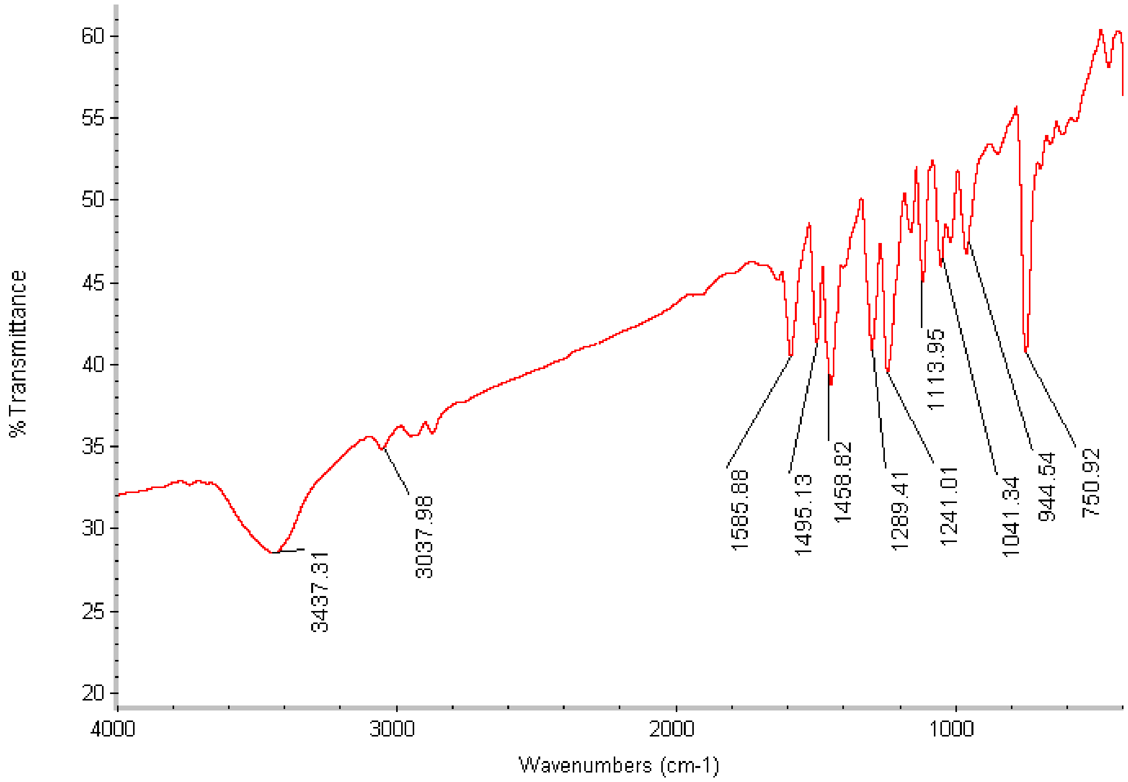
F2 - Acquisition Parameters
Date_          20120504
Time              14.24
INSTRUM           Spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  512
DS                    2
SWH           30030.029 Hz
FIDRES         0.458222 Hz
AQ            1.0912410 sec
RG                  575
DW               16.650 usec
DE                 6.00 usec
TE                298.9 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.80 usec
PL1                1.00 dB
SFO1        125.7703640 MHz

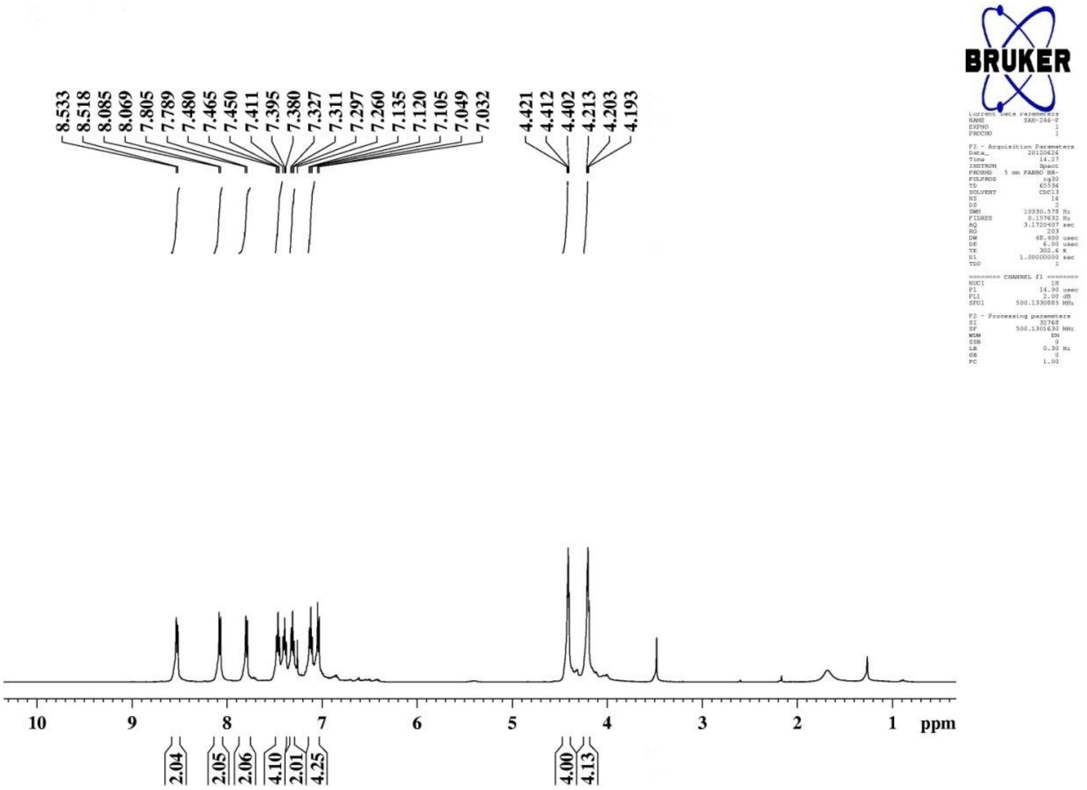
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                2.00 dB
PL12              16.60 dB
PL13              20.00 dB
SFO2        500.1320000 MHz

F2 - Processing parameters
SI                32768
SF          125.7577598 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

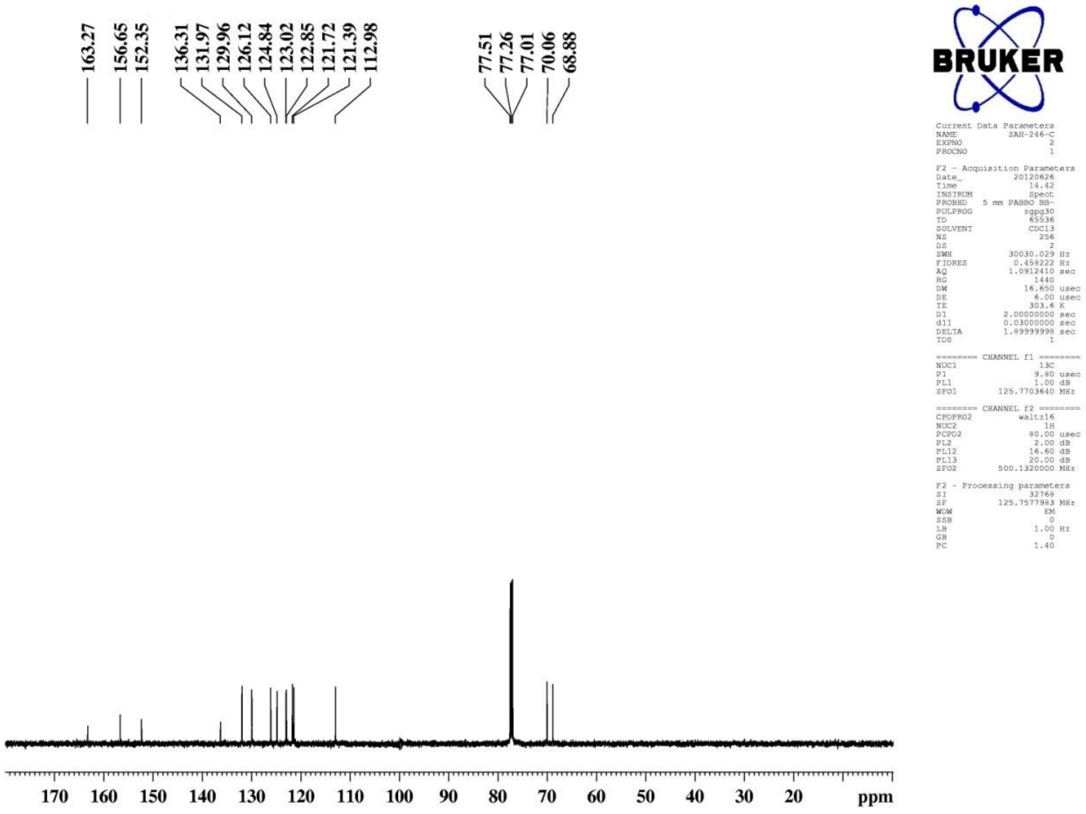
FTIR Spectra of L_3



^{1}H NMR Spectra of L_4



^{13}C NMR Spectra of L_4



```
Current Data Parameters
NAME            SAH-246-C
EXPNO                   2
PROCNO                  1

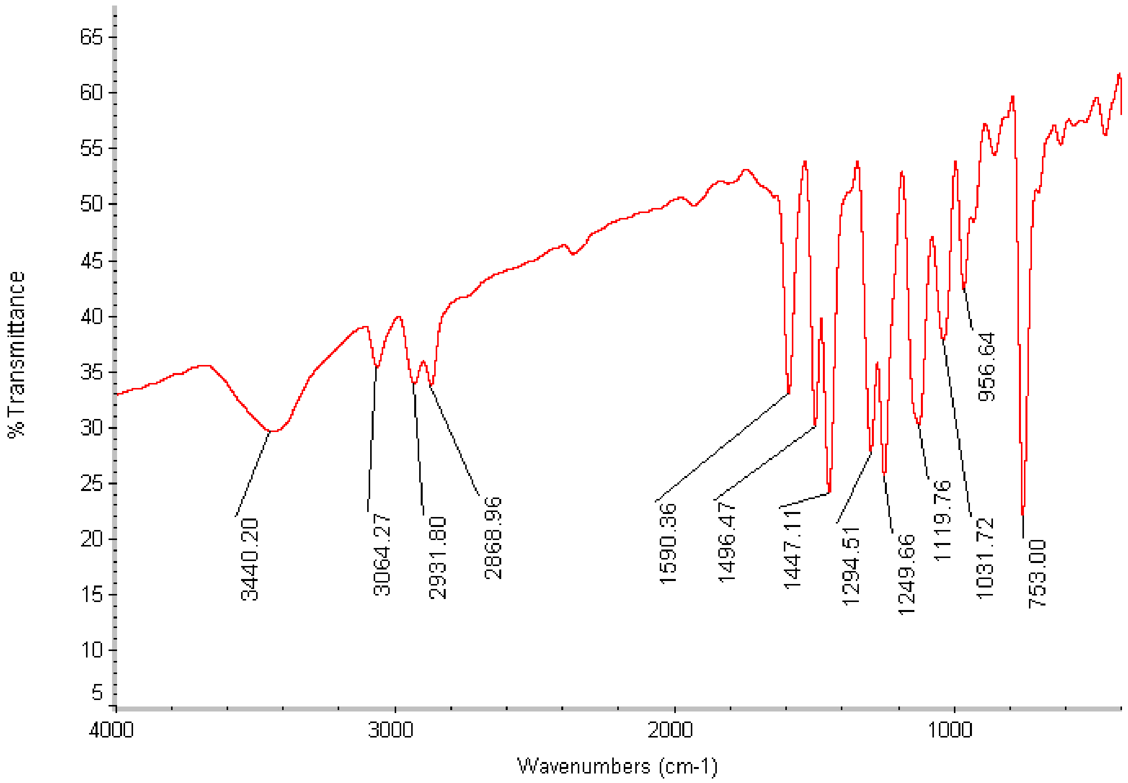
F2 - Acquisition Parameters
Date_            20120626
Time                14.42
INSTRUM             Spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      2
SWH             30030.029 Hz
FIDRES           0.458222 Hz
AQ              1.0912410 sec
RG                   1440
DW                 16.650 usec
DE                   6.00 usec
TE                  303.6 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.80 usec
PL1                  1.00 dB
SFO1          125.7703640 MHz

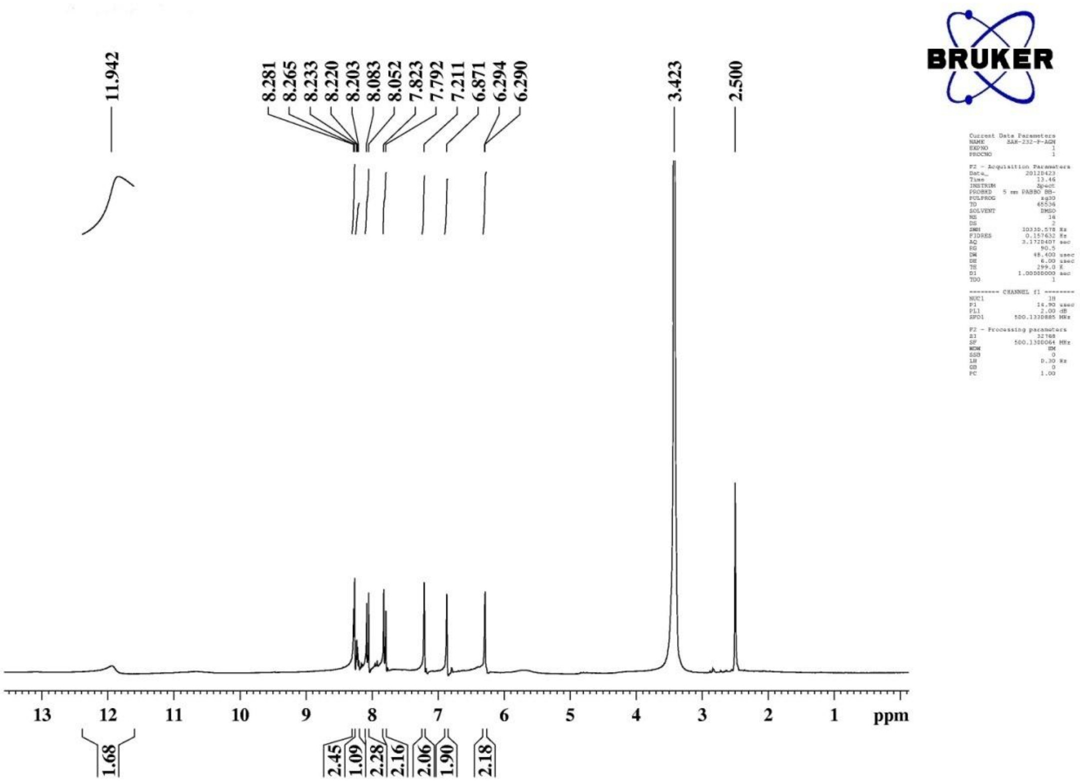
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  2.00 dB
PL12                16.60 dB
PL13                20.00 dB
SFO2          500.1320000 MHz

F2 - Processing parameters
SI                  32768
SF            125.7577983 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

FTIR Spectra of L_4



^{1}H NMR Spectra of L$_5$



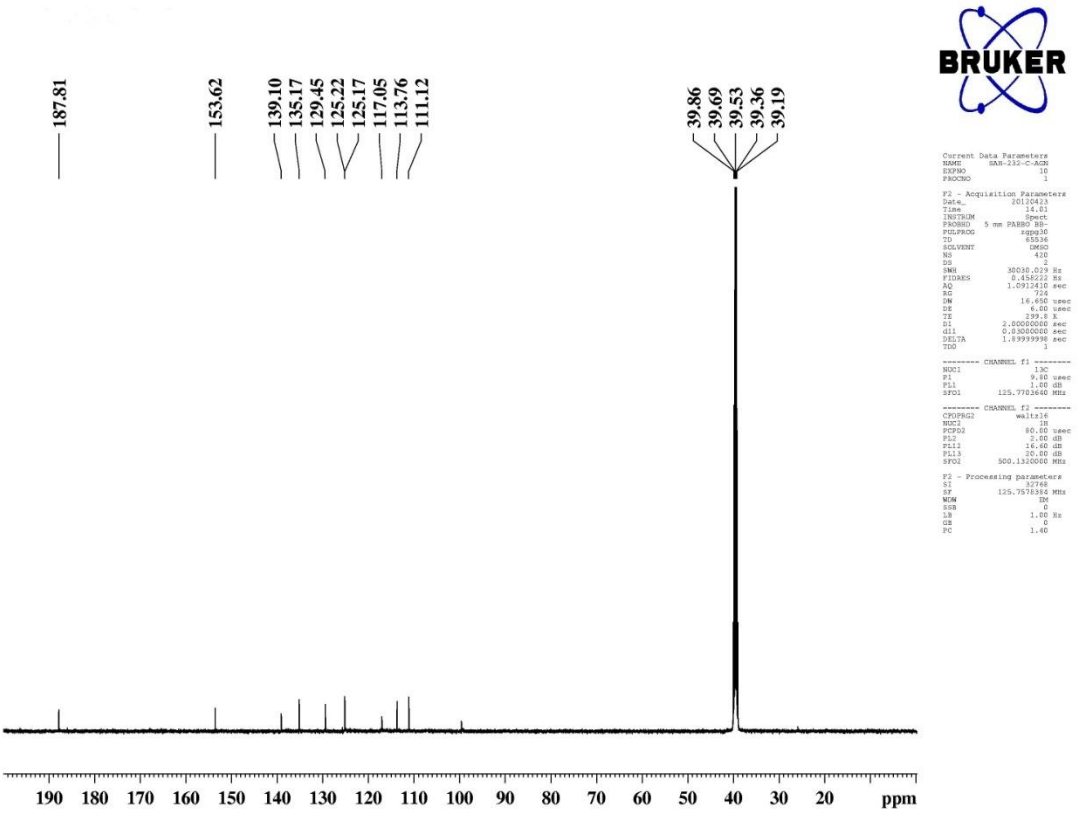
```
Current Data Parameters
NAME       SAH-232-P-AGN
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120423
Time               13.46
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1720407 sec
RG                  90.5
DW                48.400 usec
DE                  6.00 usec
TE                 299.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.90 usec
PL1                 2.00 dB
SFO1         500.1320885 MHz

F2 - Processing parameters
SI                 32768
SF           500.1300064 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{13}C NMR Spectra of L$_5$



```
Current Data Parameters
NAME       SAH-232-C-AGN
EXPNO                 10
PROCNO                 1

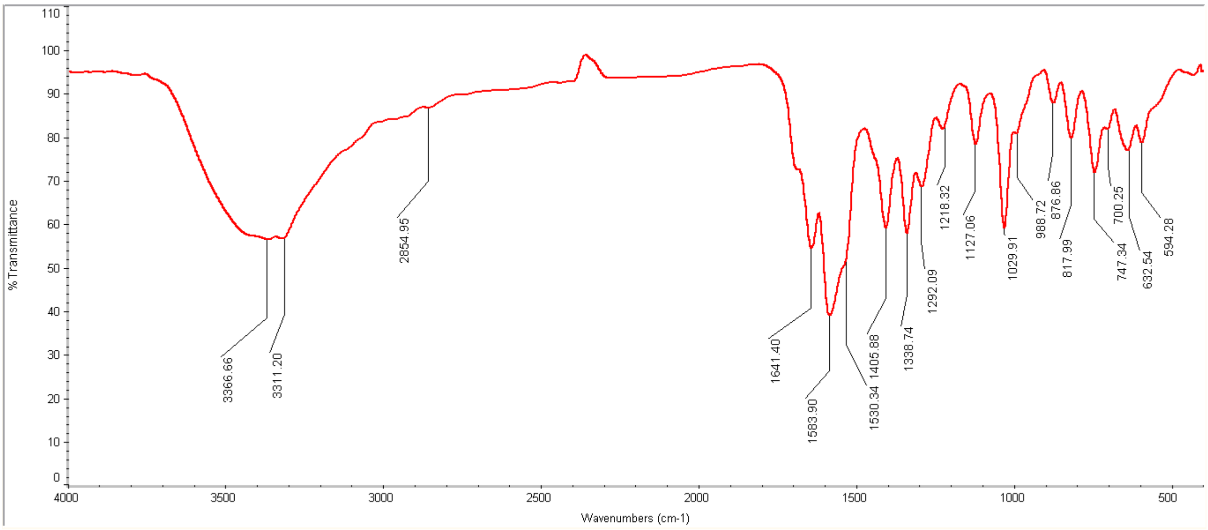
F2 - Acquisition Parameters
Date_           20120423
Time               14.01
INSTRUM            Spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT             DMSO
NS                   420
DS                     2
SWH            30030.029 Hz
FIDRES          0.458222 Hz
AQ             1.0912410 sec
RG                   724
DW                16.650 usec
DE                  6.00 usec
TE                 299.8 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.80 usec
PL1                 1.00 dB
SFO1         125.7703640 MHz

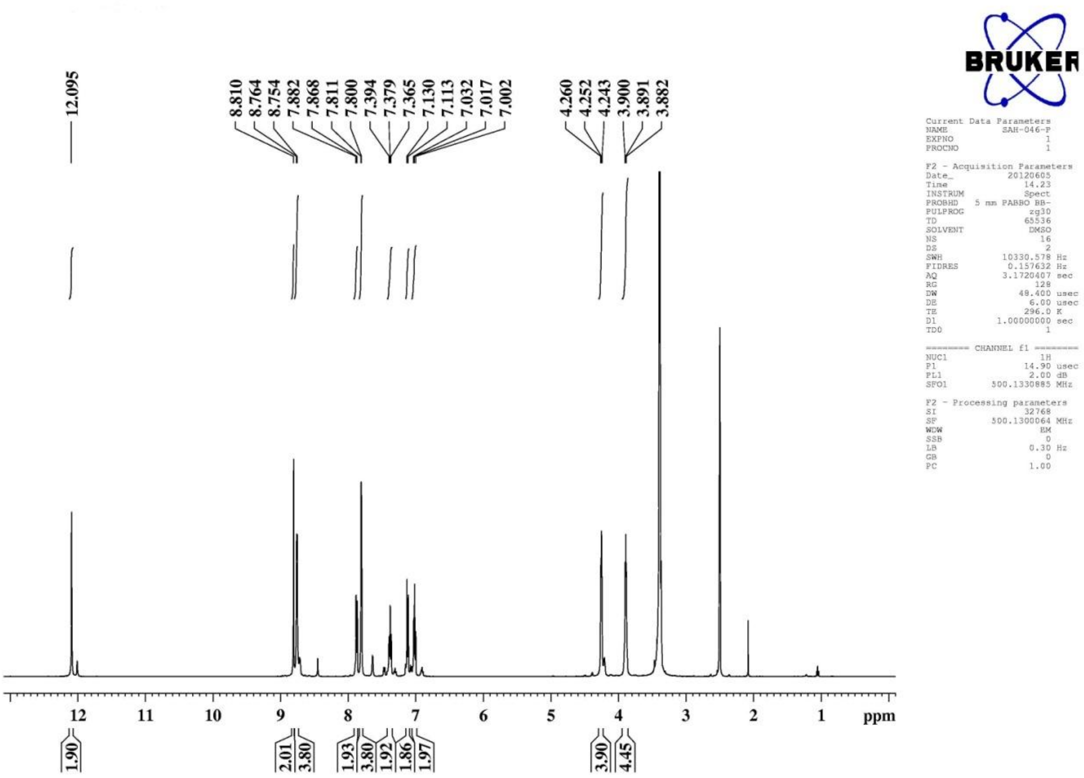
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 2.00 dB
PL12               16.60 dB
PL13               20.00 dB
SFO2         500.1320000 MHz

F2 - Processing parameters
SI                 32768
SF           125.7578384 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

FTIR Spectra of L$_5$



^{1}H NMR Spectra of L_6



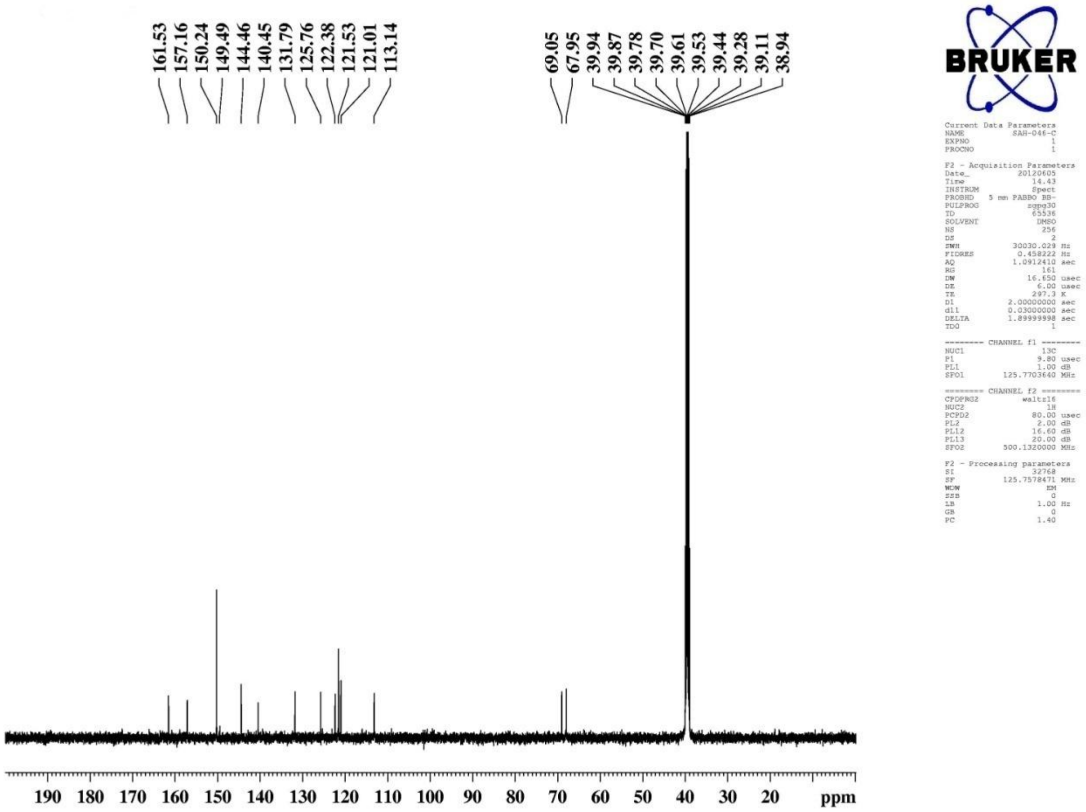
```
Current Data Parameters
NAME          SAH-046-P
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120605
Time              14.23
INSTRUM           Spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT            DMSO
NS                   16
DS                    2
SWH          10330.578 Hz
FIDRES        0.157632 Hz
AQ           3.1720407 sec
RG                  128
DW              48.400 usec
DE                6.00 usec
TE               296.0 K
D1          1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.90 usec
PL1                2.00 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                32768
SF          500.1300064 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

^{13}C NMR Spectra of L$_6$



```
Current Data Parameters
NAME           SAH-046-C
EXPNO                  1
PROCNO                 1

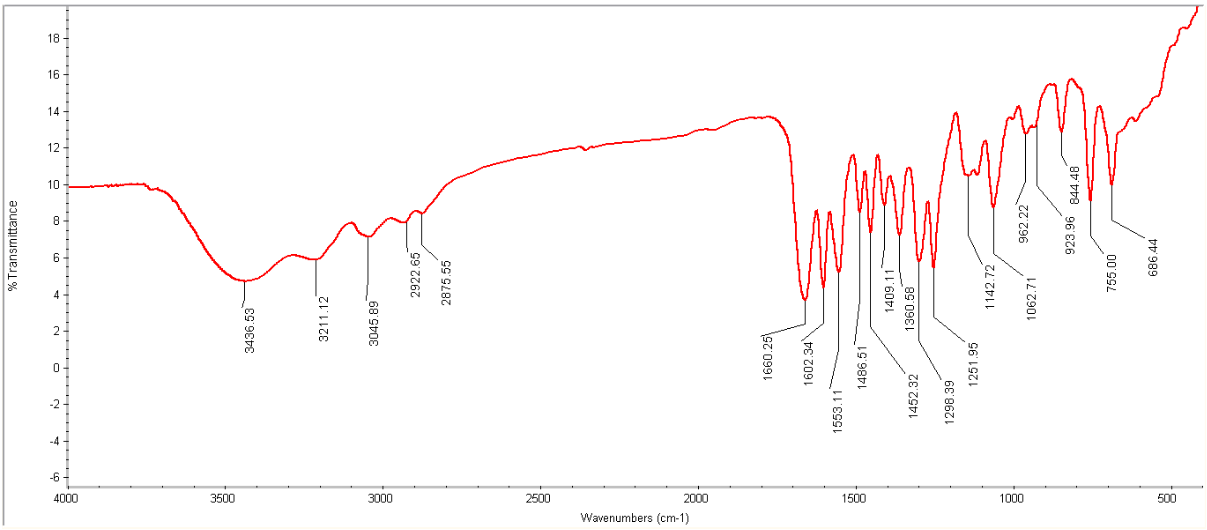
F2 - Acquisition Parameters
Date_           20120605
Time               14.43
INSTRUM            Spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT             DMSO
NS                   256
DS                     2
SWH            30030.029 Hz
FIDRES          0.458222 Hz
AQ             1.0912410 sec
RG                   161
DW                16.650 usec
DE                  6.00 usec
TE                 297.3 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.80 usec
PL1                 1.00 dB
SFO1         125.7703640 MHz

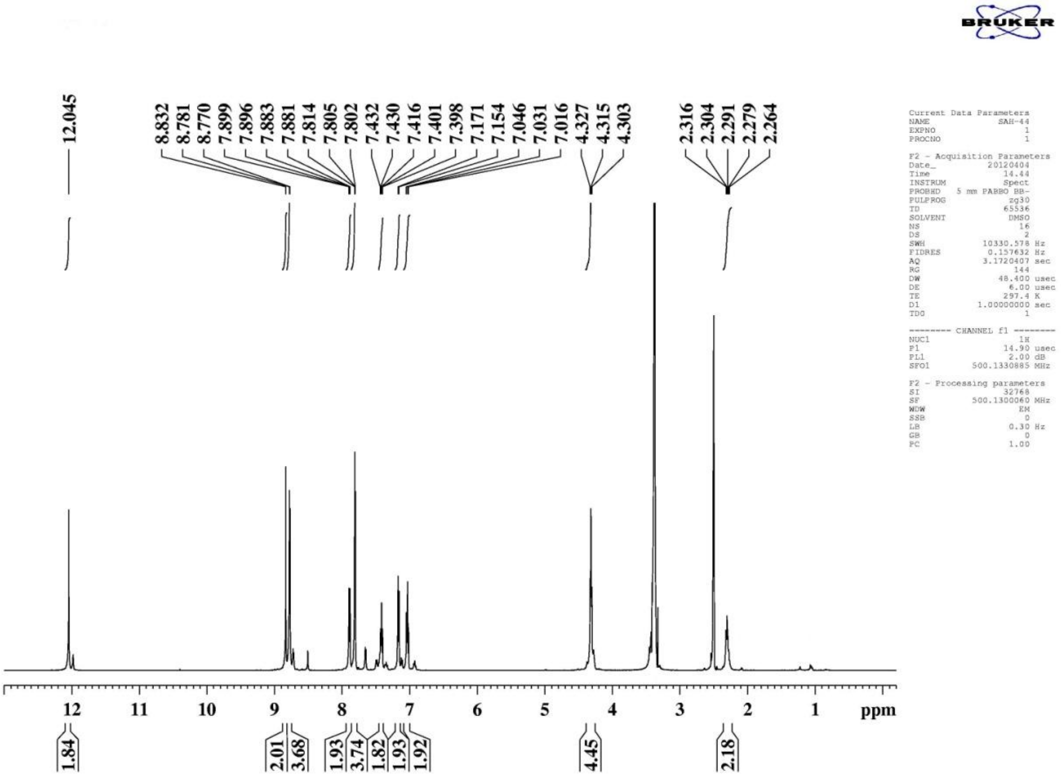
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 2.00 dB
PL12               16.60 dB
PL13               20.00 dB
SFO2         500.1320000 MHz

F2 - Processing parameters
SI                 32768
SF           125.7578471 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

FTIR Spectra of L_6



^{1}H NMR Spectra of L_7



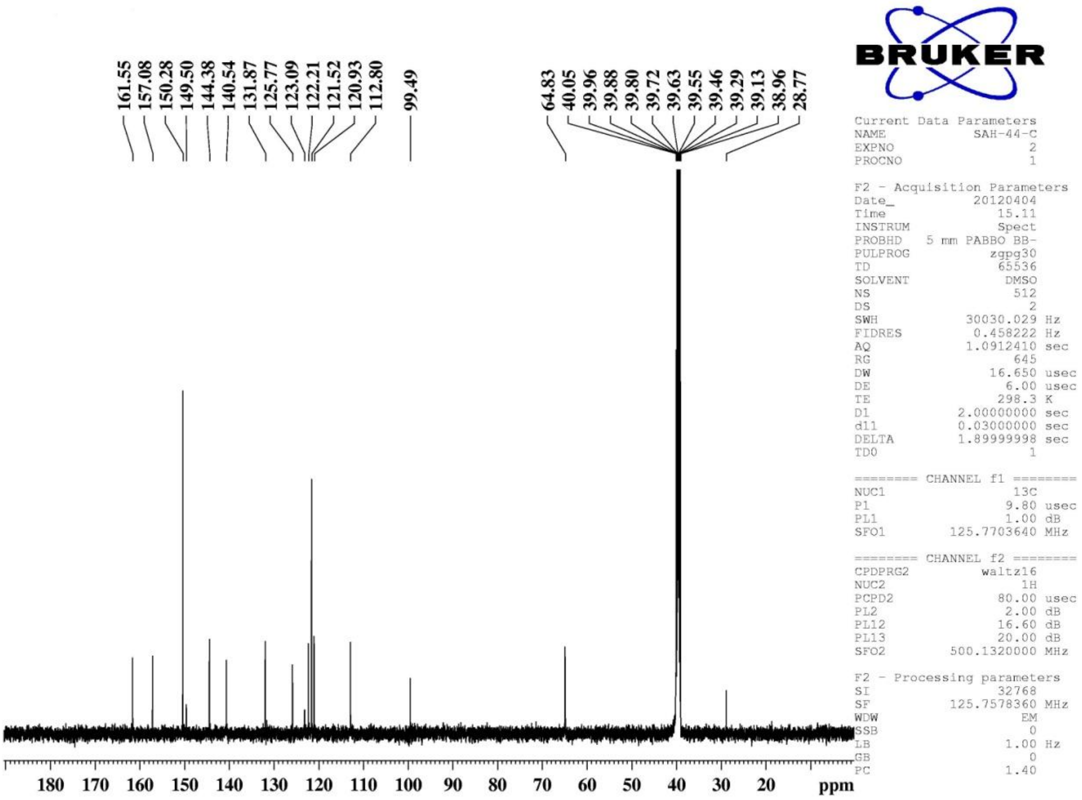
```
Current Data Parameters
NAME              SAH-44
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120404
Time               14.44
INSTRUM            Spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1720407 sec
RG                   144
DW               48.400 usec
DE                 6.00 usec
TE                297.4 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.90 usec
PL1                 2.00 dB
SFO1         500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF           500.1300060 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{13}C NMR Spectra of L_7



```
Current Data Parameters
NAME             SAH-44-C
EXPNO                   2
PROCNO                  1

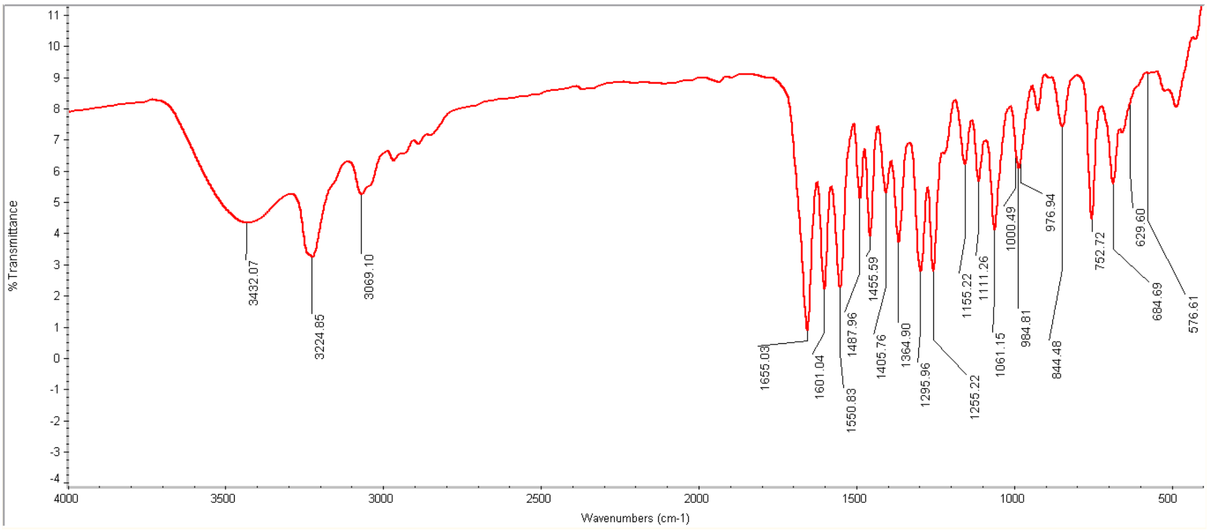
F2 - Acquisition Parameters
Date_            20120404
Time                15.11
INSTRUM             Spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT              DMSO
NS                    512
DS                      2
SWH             30030.029 Hz
FIDRES           0.458222 Hz
AQ              1.0912410 sec
RG                    645
DW                 16.650 usec
DE                   6.00 usec
TE                  298.3 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.80 usec
PL1                  1.00 dB
SFO1       125.7703640 MHz

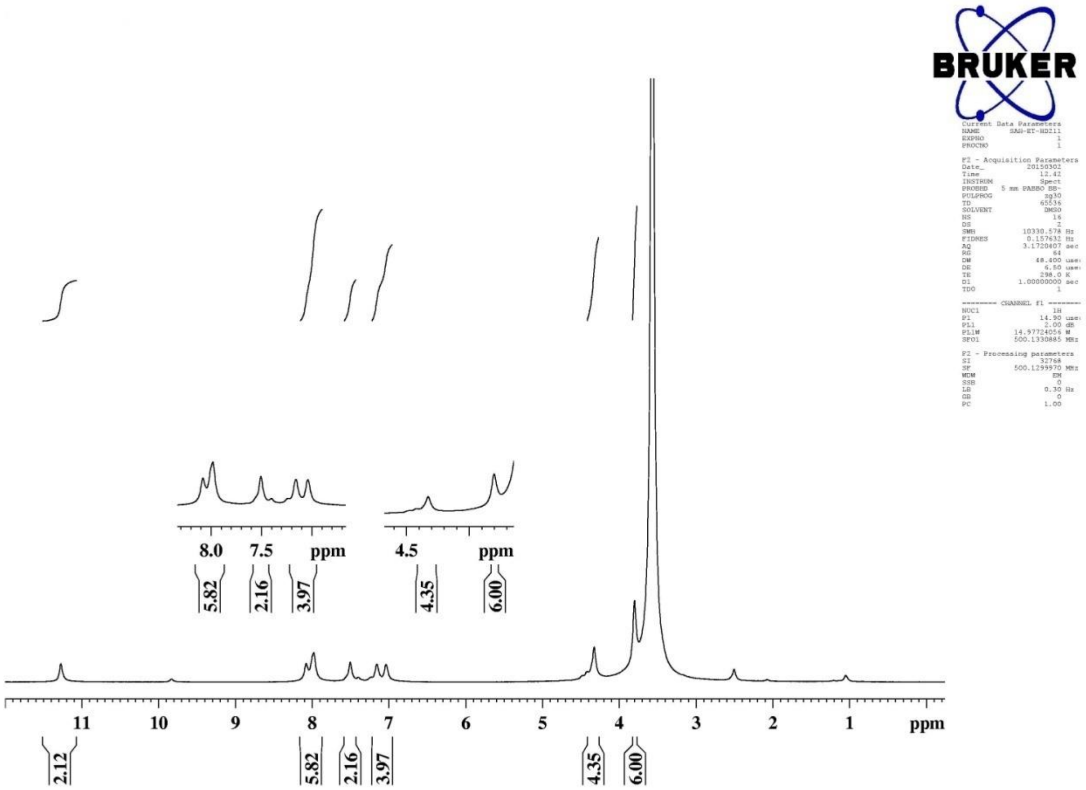
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  2.00 dB
PL12                16.60 dB
PL13                20.00 dB
SFO2       500.1320000 MHz

F2 - Processing parameters
SI                  32768
SF         125.7578360 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

FTIR Spectra of L_7



^{1}H NMR Spectra of L_8



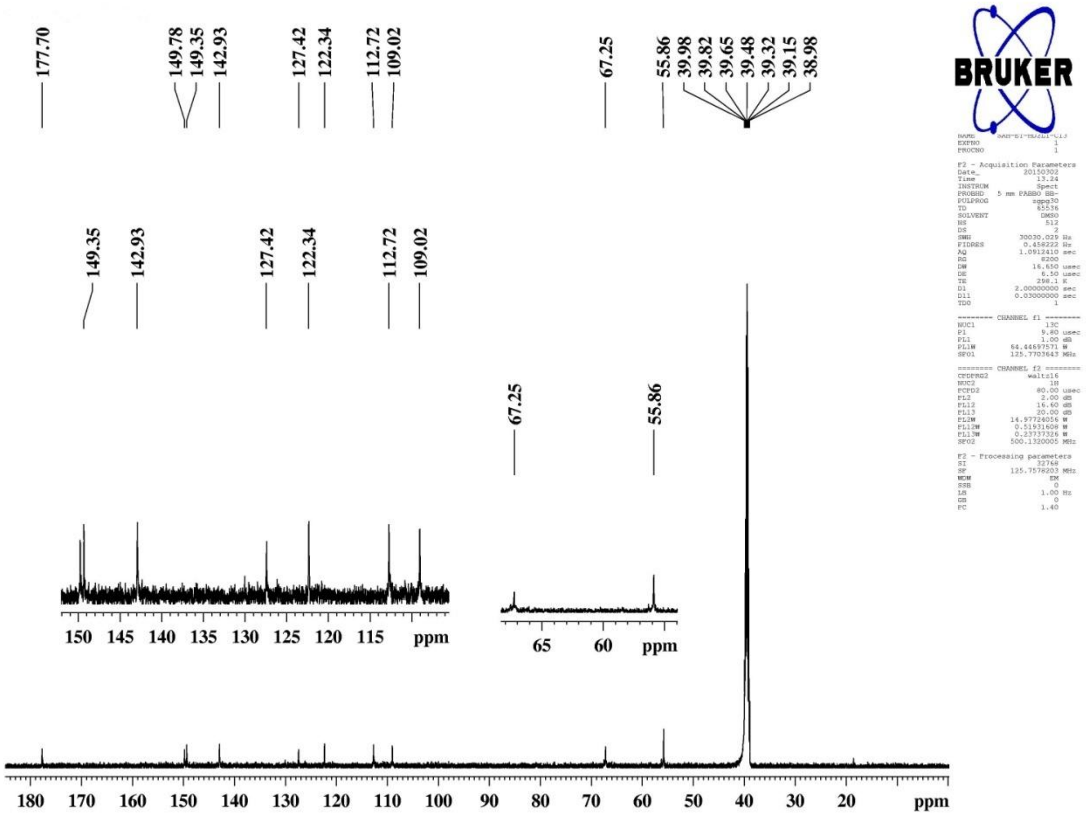
```
Current Data Parameters
NAME          SAH-ET-HD211
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150302
Time                 12.42
INSTRUM              Spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                      16
DS                       2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1720407 sec
RG                      64
DW                  48.400 use
DE                    6.50 use
TE                   298.0 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.90 use
PL1                   2.00 dB
PL1W           14.97724056 W
SFO1           500.1330885 MHz

F2 - Processing parameters
SI                   32768
SF             500.1299970 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

^{13}C NMR Spectra of L$_8$



```
NAME      [illegible]
EXPNO                1
PROCNO               1

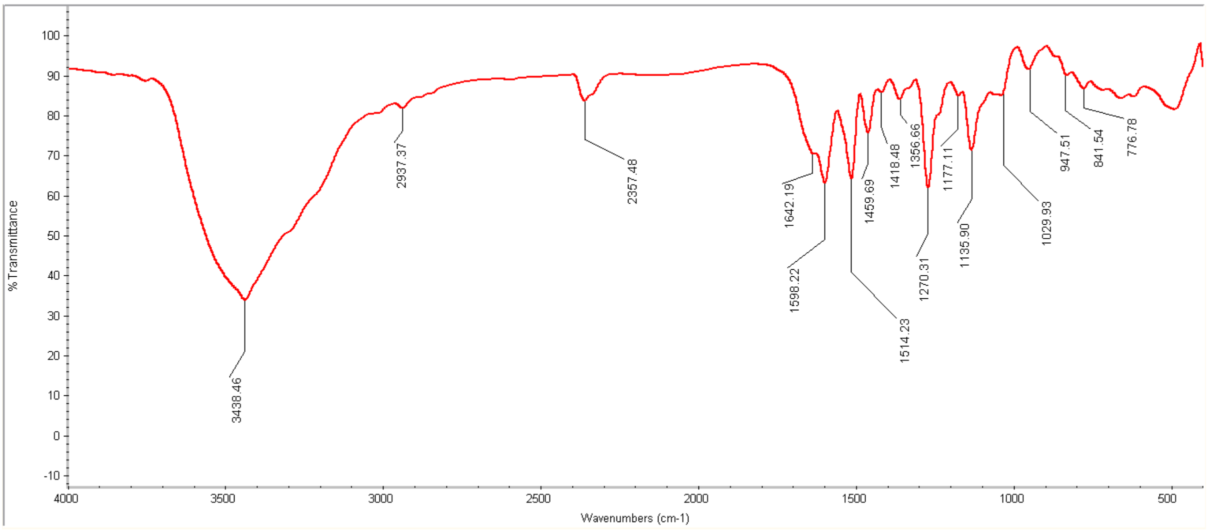
F2 - Acquisition Parameters
Date_         20150302
Time             13.24
INSTRUM          Spect
PROBHD   5 mm PABBO BB-
PULPROG        zgpg30
TD              65536
SOLVENT          DMSO
NS                512
DS                  2
SWH         30030.029 Hz
FIDRES       0.458222 Hz
AQ          1.0912410 sec
RG               8200
DW             16.650 usec
DE               6.50 usec
TE              298.1 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1              13C
P1               9.80 usec
PL1              1.00 dB
PL1W      64.44697571 W
SFO1      125.7703643 MHz

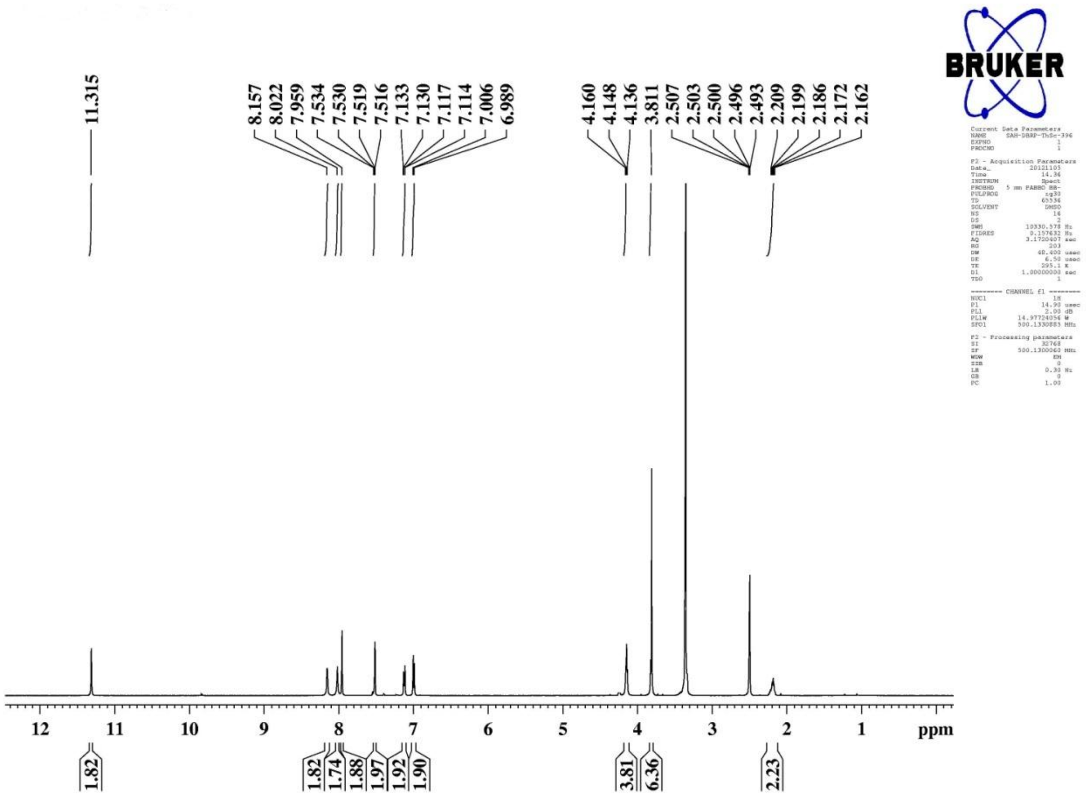
======== CHANNEL f2 ========
CPDPRG2       waltz16
NUC2               1H
PCPD2           80.00 usec
PL2              2.00 dB
PL12            16.60 dB
PL13            20.00 dB
PL2W      14.97724056 W
PL12W      0.51931608 W
PL13W      0.23737326 W
SFO2      500.1320005 MHz

F2 - Processing parameters
SI              32768
SF        125.7578203 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

FTIR Spectra of L_8



^{1}H NMR Spectra of L_9



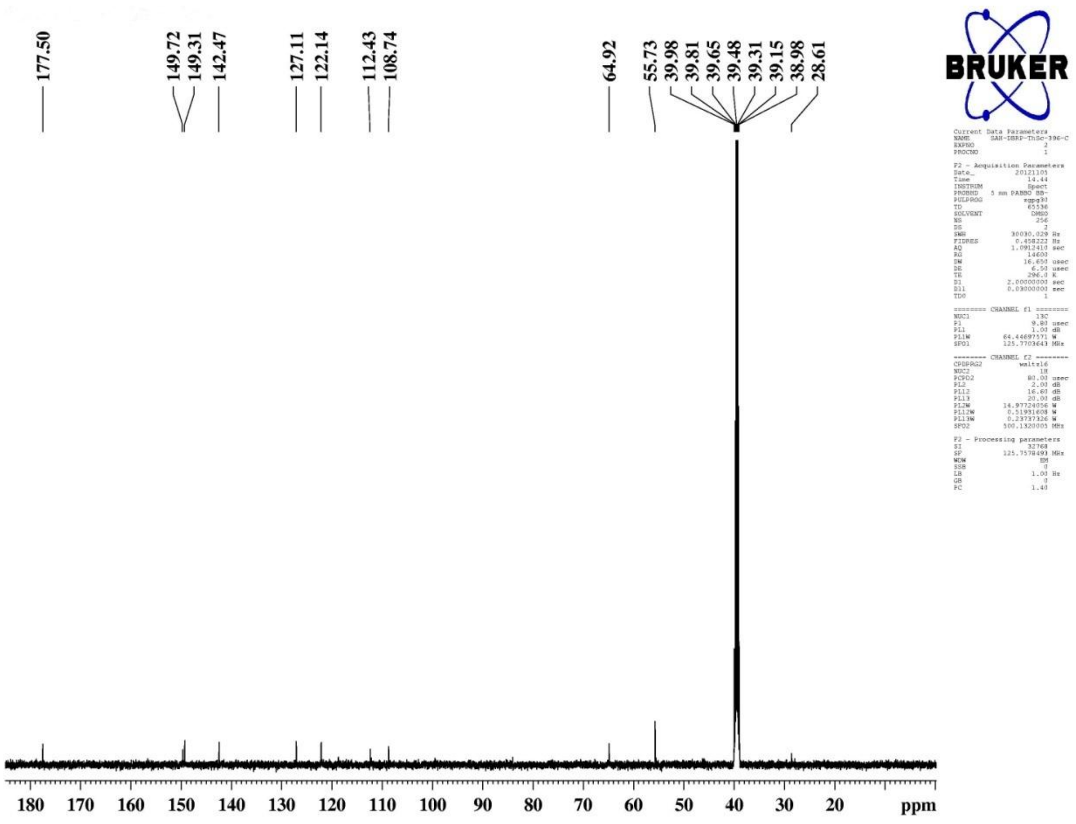
```
Current Data Parameters
NAME      SAH-DBRP-ThSc-396
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20121105
Time                  14.36
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH             10330.578 Hz
FIDRES           0.157632 Hz
AQ              3.1720407 sec
RG                      203
DW                   48.400 usec
DE                     6.50 usec
TE                    295.1 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    14.90 usec
PL1                    2.00 dB
PL1W            14.97724056 W
SFO1           500.1330883 MHz

F2 - Processing parameters
SI                    32768
SF              500.1300060 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

^{13}C NMR Spectra of L$_9$



```
Current Data Parameters
NAME     SAH-DBRP-ThSc-396-C
EXPNO                   2
PROCNO                  1

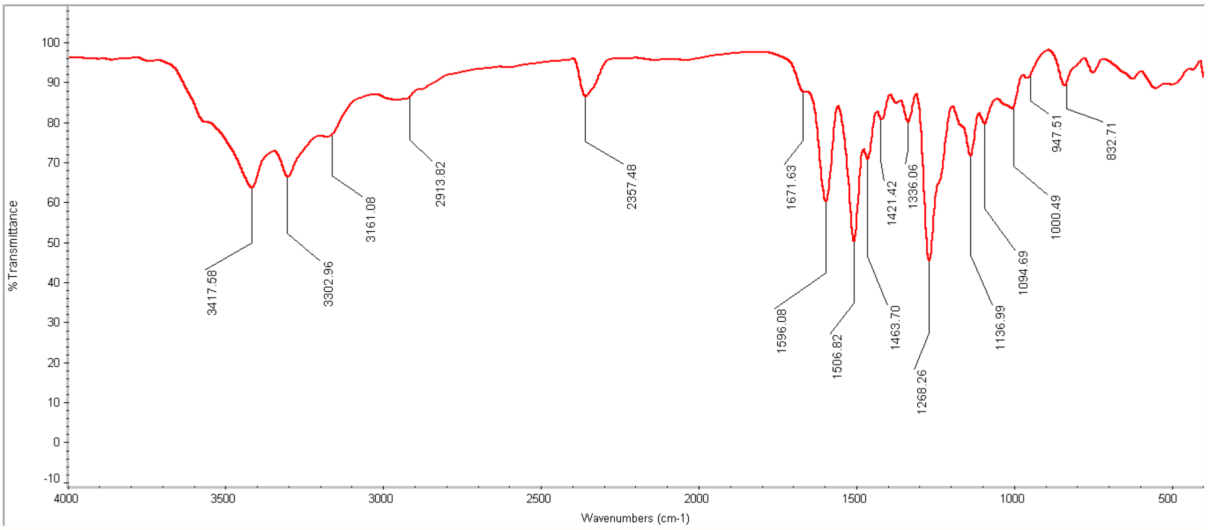
F2 - Acquisition Parameters
Date_            20121105
Time                14.44
INSTRUM             Spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT             DMSO
NS                   256
DS                     2
SWH            30030.029 Hz
FIDRES          0.458222 Hz
AQ             1.0912410 sec
RG                 14600
DW                16.650 usec
DE                  6.50 usec
TE                 296.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.80 usec
PL1                 1.00 dB
PL1W         64.44697571 W
SFO1         125.7703643 MHz

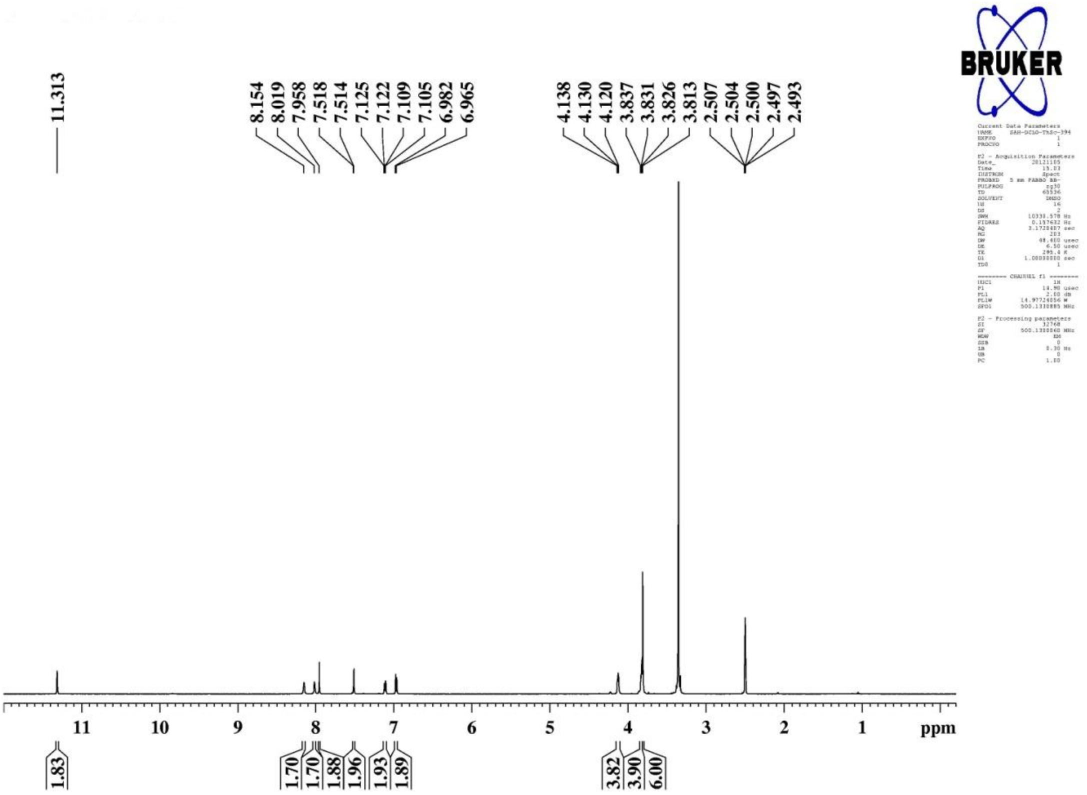
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 2.00 dB
PL12               16.60 dB
PL13               20.00 dB
PL2W         14.97724056 W
PL12W         0.51931608 W
PL13W         0.23737326 W
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7578493 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

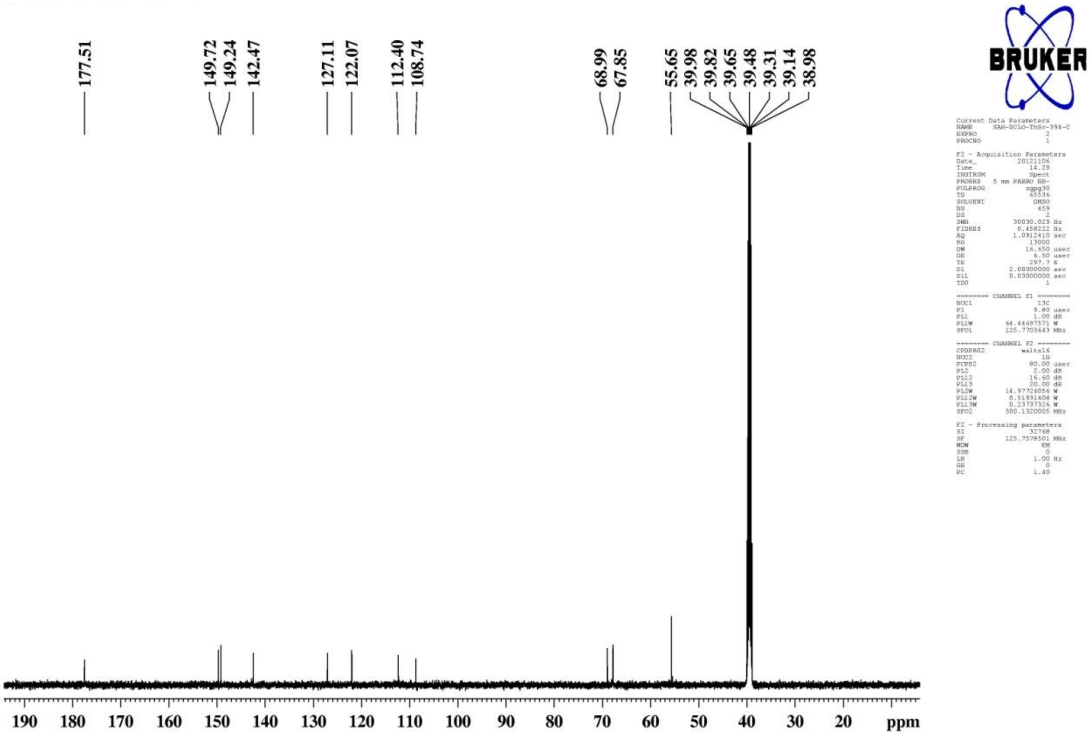
FTIR Spectra of L_9



^{1}H NMR Spectra of L_{10}



^{13}C NMR Spectra of L_{10}



```
Current Data Parameters
NAME     SAH-DC10-ThSc-394-C
EXPNO                      2
PROCNO                     1

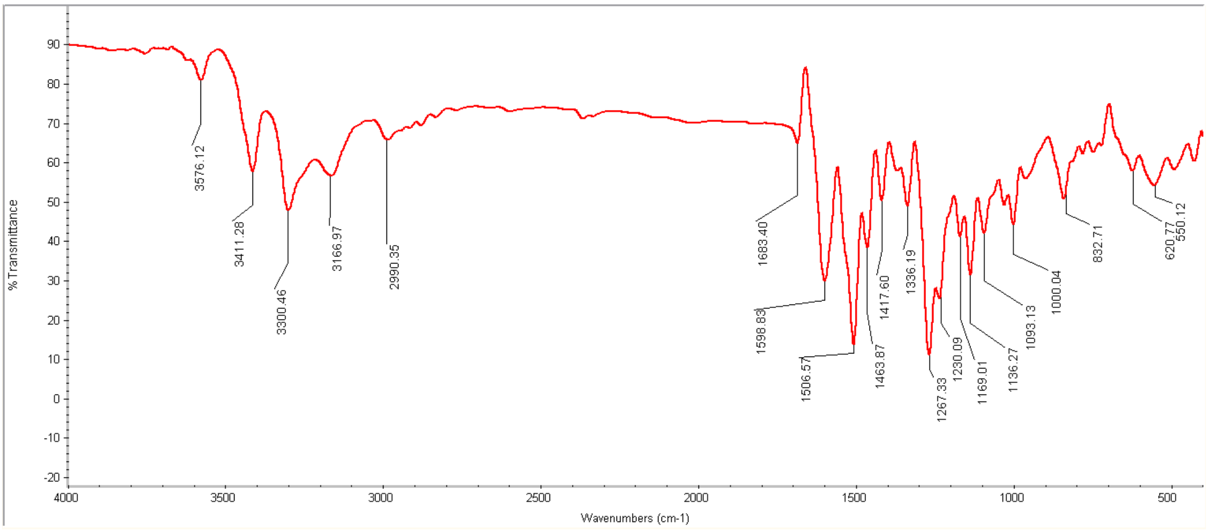
F2 - Acquisition Parameters
Date_             20121106
Time                 14.29
INSTRUM              Spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT              DMSO
NS                    459
DS                      2
SWH             30030.029 Hz
FIDRES           0.458222 Hz
AQ              1.0912410 sec
RG                  13000
DW                 16.650 usec
DE                   6.50 usec
TE                  297.7 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.80 usec
PL1                  1.00 dB
PL1W          64.44697571 W
SFO1          125.7703643 MHz

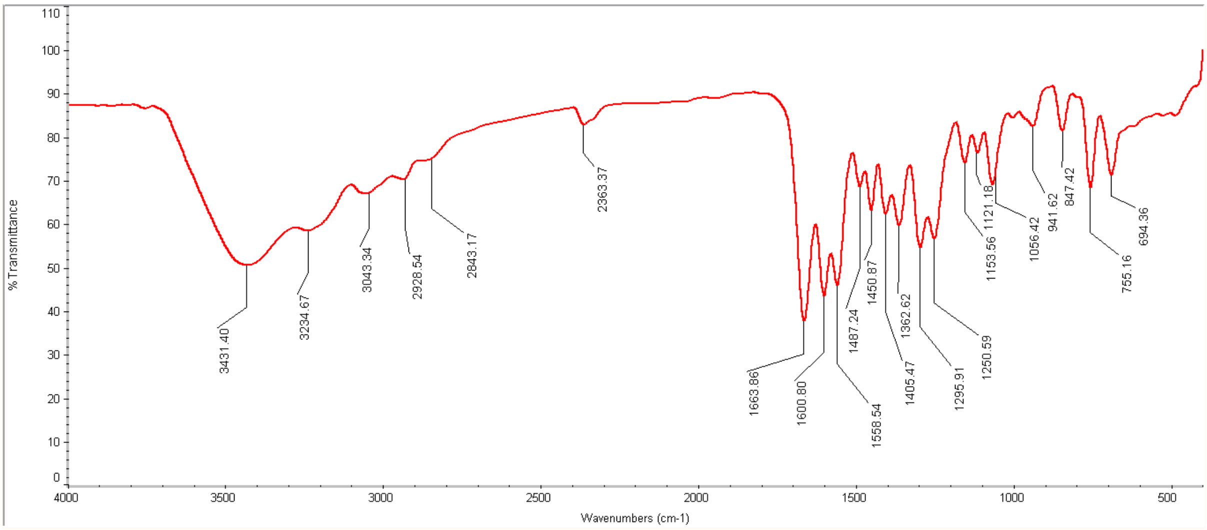
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  2.00 dB
PL12                16.60 dB
PL13                20.00 dB
PL2W          14.97724056 W
PL12W          0.51931608 W
PL13W          0.23737326 W
SFO2          500.1320005 MHz

F2 - Processing parameters
SI                  32768
SF            125.7578501 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

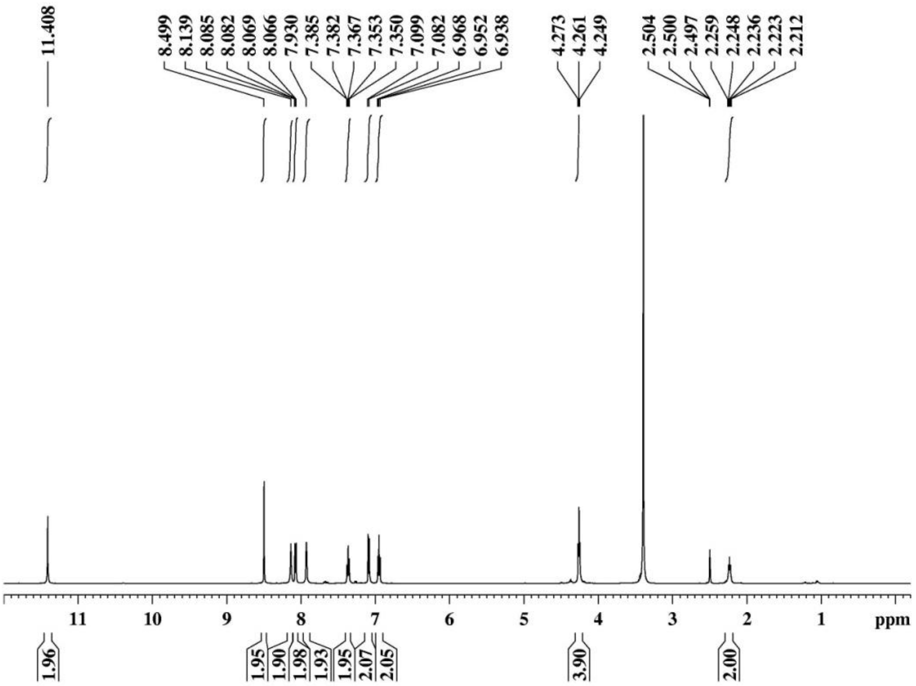
FTIR Spectra of L_{10}



FTIR Spectra of L_{11}



^{1}H NMR Spectra of L$_{12}$



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Current Data Parameters
NAME      SAH-DCL-ThSc-02
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120828
Time                14.32
INSTRUM             Spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                     16
DS                      2
SWH             10330.578 Hz
FIDRES           0.157632 Hz
AQ              3.1720407 sec
RG                    101
DW                 48.400 usec
DE                   6.50 usec
TE                  295.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.90 usec
PL1                  2.00 dB
PL1W          14.97724056 W
SFO1          500.1330885 MHz

F2 - Processing parameters
SI                  32768
SF            500.1300063 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```
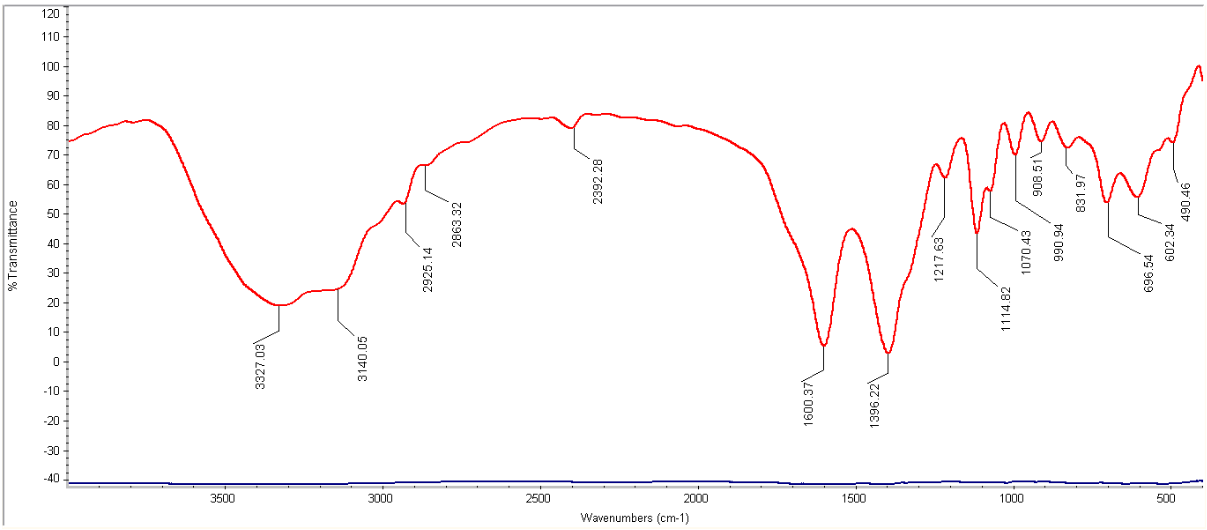
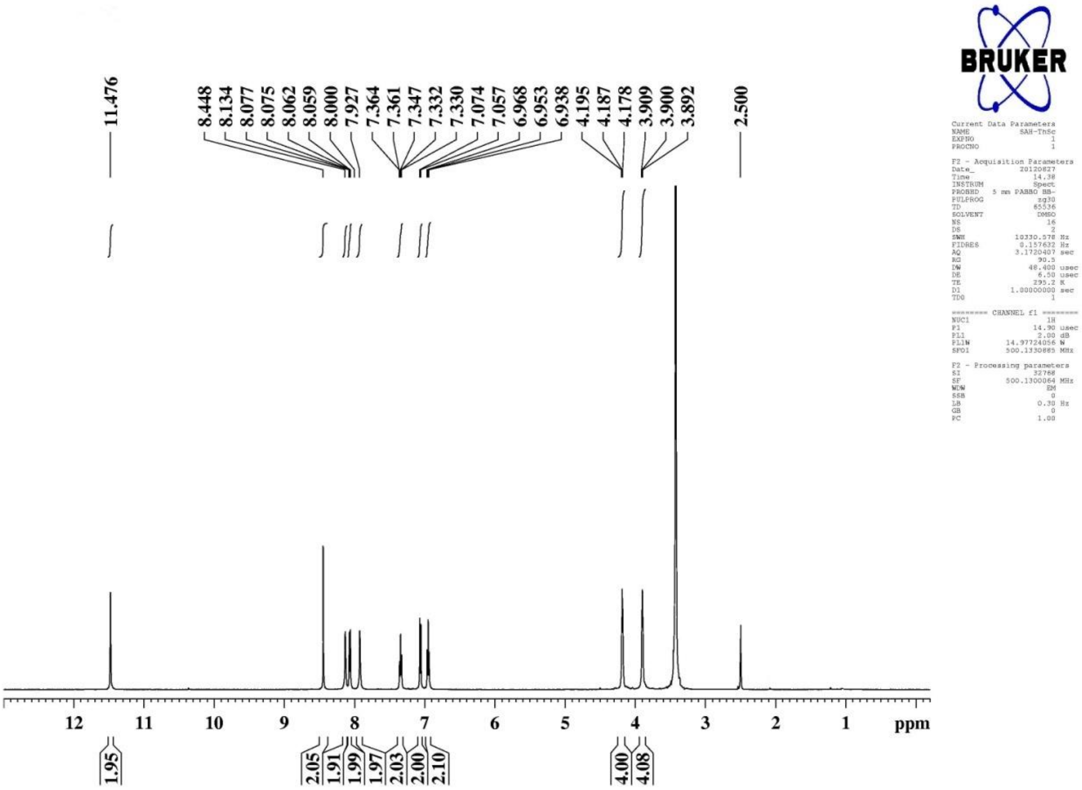

FTIR Spectra of L_{12}

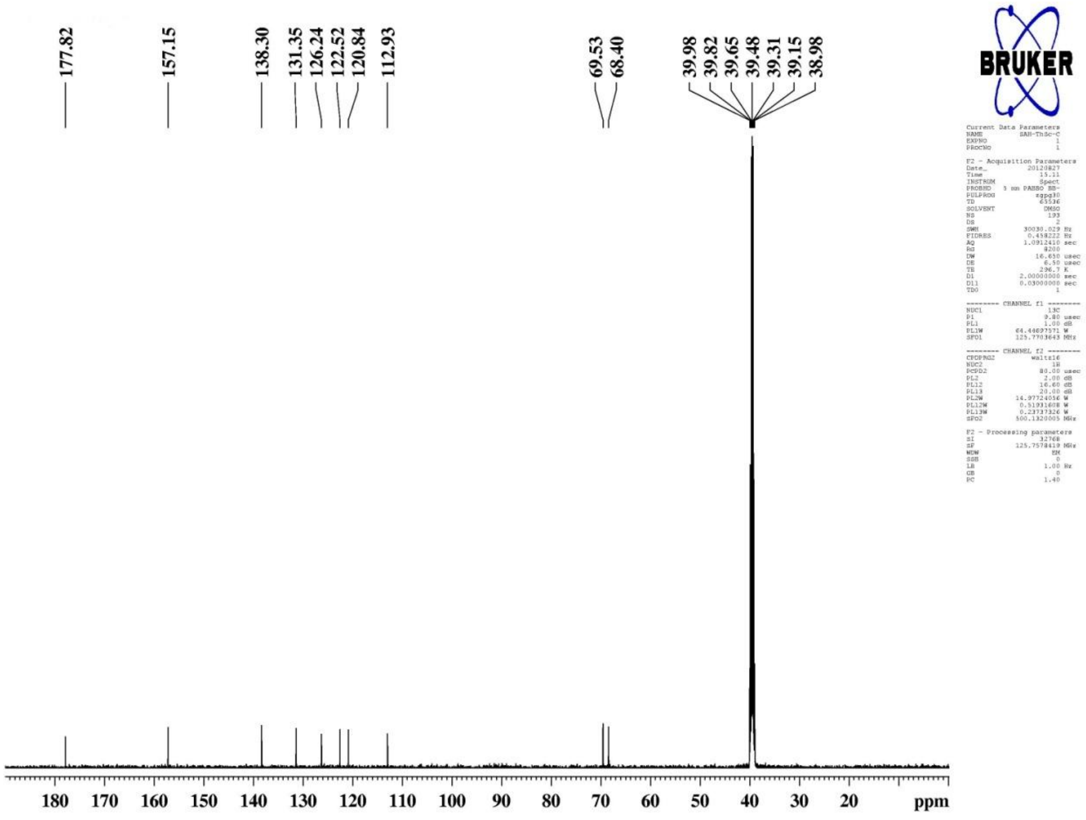


^{1}H NMR Spectra of L_{13}



```
Current Data Parameters
NAME              SAH-ThSc
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20120827
Time                 14.38
INSTRUM              Spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                      16
DS                       2
SWH             10330.578 Hz
FIDRES           0.157632 Hz
AQ              3.1720407 sec
RG                    90.5
DW                  48.400 usec
DE                    6.50 usec
TE                   295.2 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.90 usec
PL1                   2.00 dB
PL1W           14.97724056 W
SFO1           500.1330885 MHz

F2 - Processing parameters
SI                   32768
SF             500.1300064 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

^{13}C NMR Spectra of L$_{13}$



```
Current Data Parameters
NAME          SAH-ThSc-C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120827
Time               15.11
INSTRUM            Spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT             DMSO
NS                   193
DS                     2
SWH            30030.029 Hz
FIDRES          0.458222 Hz
AQ             1.0912410 sec
RG                  8200
DW                16.650 usec
DE                  6.50 usec
TE                 296.7 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.80 usec
PL1                 1.00 dB
PL1W         64.44697571 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 2.00 dB
PL12               16.60 dB
PL13               20.00 dB
PL2W         14.97724056 W
PL12W         0.51931608 W
PL13W         0.23737326 W
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7578419 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```