PERCHLORATE ION SELECTIVE SENSOR BASED ON NEWLY SYNTHESIZED N^1, N^3 - DI (1H-BENZOIMIDAZOLE-2-YL) ISOPHTHALAMIDE RECEPTOR

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CANDIDATE'S DECLERATION

I hereby certify that the work which is being presented in the thesis entitled, **"Perchlorate ion selective sensor based on newly synthesized N^1, N^3-di(1H-benzoimidazole-2-yl)isophthalamide receptor"** in the partial fulfilment of the requirement for the award of the Degree of **Master of Technology** in **Advanced Chemical Analysis** 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 under the supervision of **Prof. A.K. Jain.**

I have not submitted the matter embodied in this report for the award of any other degree of this or any other Institute/University.

Dated: 28/06/06

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

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ABSTRACT

Novel ionophore, N^1,N^3-di(1H-benzoimidazole-2-yl)isophthalamide receptor **(I)** has been synthesized and characterized by UV, IR and CHN analysis. Polyvinyl chloride (PVC) based membranes of **(I)** have been prepared and explored as ClO_4^- selective sensors. Effect of various plasticizers viz., tris(2-ethylhexyl) phosphate (TEHP), dibutyl phosphate (DBP), dioctyl phosphate (DOP), diethyl phosphate (DEP), tricresyl phosphate (TCP) and a cation excluder, tridodecylmethylammonium chloride (TDDMACl) was studied in detail and improved performance was observed at several instances. Optimum performance was observed with the membrane having **(I)**-PVC-TDDMACl-DOP in the ratio 1:120:1:200 (mg). The sensor works satisfactorily in the concentration range 1.8×10^{-5} - 1.0×10^{-1} M with near Nernstian compliance (52.0 mV per decade of activity) between pH 5.0-9.0 with a fast response time of about 12s. The potentiometric selectivity coefficient values as determined by Fixed Interference Method (FIM) indicate selective response for ClO_4^- in presence of interfering ions. The sensor exhibits adequate shelf life (~2 months) with good reproducibility (std. dev. ± 0.4 mV).

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1. INTRODUCTION

Analytical chemistry has contributed greatly to the development of a number of methods for the analysis of industrial products viz. drugs and pharmaceuticals, alloys and steels, cement and paints, textiles and polymers, ceramics and glasses, insecticides and fungicides etc. Analytical chemists working in the industries have to deal with a large number of samples on a day-to-day basis and therefore look forward to deal with a large number of analytical procedures that are fast, selective and require minimum chemical manipulations. Ion selective sensors (ISSs') meet these requirements to a great extent. Moreover, analysis by these sensors could be non-destructive and adaptable to small sample volumes with possible applications in real-time analysis, which is particularly important for the rapid measurement in various samples. The growth of this technique has been fast in relation to other techniques partly because the sensors become commercially available soon after their development and also, quite easy to fabricate in the laboratory. In view of the importance of ISSs', attempts are being regularly made to have newer and better sensors for various chemical species.

Ion selective sensors are based on highly selective ionophores usually embedded in a polymer matrix membrane which are normally backside contacted with an aqueous electrolyte and an internal reference element. Such membranes when placed across two appropriate solutions, allows the transport of a particular cationic or anionic species. As a result of restricted transport of ions, a potential difference across the membrane is developed which is used for the determination of particular ionic species. The ionophore is primarily responsible for the ion selectivity of the sensor by selectively and reversibly binding the ion of interest. Various materials tried or being tried as ionophore include macrocycles, crown ethers, calixarenes, diamide receptors, inorganic and organic ion exchangers etc. as they respond selectively to specific ions. As such a number of sensors have been developed for various ions but only few of them have been found to be sufficiently selective and, thus, made commercially available.

1.1 History

The roots of ion-selective sensors as an analytical technique extend back to the pioneer Luigi Galvani (1737-1798) who observed generation of membrane potential as a result of natural bioelectric phenomenon while dissecting a frog. However, the scientific basis to this phenomenon was given in 1890 when W. Ostwald proposed that the semi-permeability of the membrane was the main cause of potential generation. The first landmark in the history of ISSs' was the discovery of glass sensing pH electrode in 1906 by Cremer. In addition to glass, other materials were also tried to make ISSs'. Efforts in this direction were initiated by Kolthoff and Sanders in 1937 who made first silver halide disk electrodes. The commercial development of ISSs' began when Frant and Ross developed calcium and fluoride selective sensors in the mid 1960s. After glass sensors, the fluoride selective sensors, based on lanthanum fluoride doped with europium fluoride, is the second best sensor developed so far. This discovery generated widespread interest in developing ion-selective sensor and since then numerous probes have been developed for the analysis of samples containing many different ions.

1.2 Membrane

Ion selective sensors consists of a membrane which separates two solutions and forms a sharp boundary between them. For the membrane to act as sensor it should be semi permeable i.e. it allows some ions to pass through and prevents others. When such a semi-permeable membrane separates two solutions, movement of selective ions across it leads to the formation of electrical double layer which is the source of electric potential. The observed potential which may be considered as junction potential, develops at the interface, is basically due to two processes:

1. Different mobilities of ions through the membrane resulting in diffusion potential.
2. Donnan potential which arises due to complete hindrance or non-transport of one or more kind of ions across the interface between the two electrolytes.

The potential developed as a function of concentration of ions on the two sides of the membrane, can therefore be used to determine the concentration of an unknown solution.

1.3 Membrane Materials

The materials that are used to prepare a membrane which allows selective transport of the ions are called electroactive materials. The diffusion of ions through the membranes of electroactive compounds is due to their different properties such as ion exchange reactions, selective complexation, defects in crystals, selective uptake or due to specific cavity size. Thus, different electroactive materials belonging to various categories such as solid electrolytes, organic and inorganic ion exchangers, metal chelates of various ligands, salts of multivalent metals, crown ethers, calixarenes and cryptands have been used for preparing ISSs' membranes. The ideal sensor material is the one which shows high selectivity only to a particular cation or anion and very poor for others.

1.4. Classification of Ion Selective Sensors

ISSs' have been classified into three broad categories as per IUPAC recommendation:

1.4.1 Primary Ion Selective Sensors

1.4.2 Compound or Multiple Membrane Ion Selective Sensors

1.4.3 Metal Contact or All Solid State Ion Selective Sensors

1.4.1 Primary Ion Selective Sensors

Primary Ion Selective Sensors have been further divided into two classes:

1.4.1.1 Liquid Membrane Sensors

These are electrodes with mobile charged sites. Hydrophobic cations, hydrophobic anions or neutral carriers when dissolved in a suitable solvent and held in an inert support (e.g., poly(propylene carbonate) filter), provide membranes which are sensitive to changes in the activities of a particular ions. The solvent must be viscous and should have low vapour pressure.

1.4.1.2 Solid-State Membrane Sensors

The sensors, where the physical state of the membrane is solid, are usually called solid-state membrane sensors. Depending upon the composition of the membrane, these are further subdivided into the following three categories:

(a) Glass Sensors

These sensors have membranes made of glasses of various compositions.

(b) Homogeneous Membrane Sensors

The homogeneous membrane sensors are those which have membrane only of electroactive compound. The compound may be in the form of a crystal or a pressed disc of the powder of a compound. Only few ion selective sensors have been developed using homogeneous membrane system. The reason being that the homogeneous membranes are generally not mechanically stable and tend to break down resulting in short shelf life of the membrane.

(c) Heterogeneous Membrane Sensors

These electrodes are prepared of an active substance, or a mixture of active substances, mixed with an inert matrix (such as silicone rubber, PVC), or placed on hydrophobized graphite or conducting epoxy resin, to form a heterogeneous sensing membrane. Inert matrix is used to impart stability to the membranes.

1.4.2 Compound or Multiple Membrane Ion Selective Sensors

1.4.2.1 Gas-Sensing Sensor

This type of sensor is composed of an ISS (indicator electrode) and a reference electrode in contact with a thin film of solution, which is separated from the bulk of the sample solution by a gas-permeable membrane or an air gap. This intermediate solution interacts with the gaseous species under test (penetrated through the membrane or an air gap), which results in a change of a measured constituent (e.g., the H^+ activity) of the intermediate solution. This change is then sensed by the ion selective sensor and is related to the partial pressure of the gaseous species in the sample.

1.4.2.2 Enzyme Substrate Sensor

In this type of sensors, the membrane is covered with a coating containing an enzyme, which reacts with an organic substance (substrate) resulting in a species to which an ISS responds. Alternatively, the sensor could be covered with a layer of substrate, which reacts with the enzyme, co-factor, or inhibitor to be assayed.

1.4.3 Metal Contacted or All Solid State Ion Selective Sensors

There is no inner electrolyte solution in these electrodes and the inner reference electrode is replaced by an electronic conductor, e.g., a bromide sensor film of AgBr is reversibly contacted with Ag, or an anion sensor based on cation radical salts is contacted with Pt.

1.5 Literature Survey

A number of ISSs' for analytical purpose have been reported in the literature. The reported work has been described in the number of book and reviews. Some of important books are authored by Koryta [1], Bailey [2] and Florida [3]. Periodic reviews in "Analytical Chemistry" [4-8] cover all the recent publications in this field including methodology, theory and applications of ISSs'. In the following pages, only significant papers which highlight various important aspects of the development of ISSs' are presented.

1.5.1 Cation Selective Sensors

The determination of alkali metals, specially Li^+, $K^+$and Na^+ is of importance as they are commonly found in biological fluids. In the early development of ISSs' for these metal ions, inorganic ion exchangers were used as electroactive materials in the membrane phase [9] but the developed sensors exhibited poor selectivity. Later on, different types of crown ethers such as decalino-14-crown-4 [10], 9-crown-3 [11], and benzoyloxymethyl -12-crown-3 [12] were used to prepare Li^+ selective sensor which responded to Li^+ concentration over the range of 1µM - 1.0M with Nernstian slope. Gupta *et al.* developed a Li^+ selective sensor by using triethyleneglycolmonomethyl ether end- grafted carbosiloxane dendrimer (III) which showed working range of 2.5×10^{-5} to 1.0×10^{-1} M with a slope of 52.0 mV per decade of activity. The sensor can be used over a period of 2 month with good reproducibility [13].

The Na^+ selective sensor prepared by Wu *et al.* [14] based on triglycollic bis diamides and PVC binder performed well compared to earlier reported sensors. Calixarenes have been extensively used as carriers for the fabrication of sodium selective sensors. Prominent among these are the sensors developed by symmetrical, unsymmetrical and bridged calix[4]arene derivatives [15], triestermonoacid derivative of p-tert-butylcalix[4]arene [16], and p-tert-butylcalix[4]arylacetate [17]. 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.

The first K^+ selective sensor was developed by using PVC based membrane of valinomycin, as uncharged macrocyclic ether [18]. Yan *et al.* [19] developed a K^+ selective sensor based on calix[6]arene hexaester and applied it to determine K^+ content in human serum. Nickel(II) hexacyanatoferrate based K^+ selective sensor has also been developed by Mortiner *et al.* [20] which was found highly selective for K^+ over other alkali and alkaline earth metals and has been used to determine potassium in biologically important fluids.

The development of ISSs' for Cs^+ and Rb^+ is relatively much less as compared to ISSs' for Li^+, Na^+, K^+ ions. This is probably due to lesser interest in these ions as they are not present in biological fluids. Some of the Cs^+ selective sensors are based on membrane of dibenzo-24-crown-8 [21], doubly crowned calix[4]arene in 1,3 alternative conformations [22]. Kim *et al.* [23] developed Cs^+ selective sensor by using calix[4]arene dibezocrown ether which showed linear response to Cs^+ in the concentration range of 1.0×10^{-6} to 1.0×10^{-1} M with Nernstian slope. Yang *et al.* [24] used decylidene bis (4'-benzo-15-crown -5) ether as a electroactive material for the fabrication of Rb^+ selective sensor which exhibited a near Nernstian slope over the working concentration range of 50 μM to 0.1 mM with a slope of 52 mV/decade of activity with a detection limit down to 20 μM.

The development of ISSs' for alkaline earth metals has been of deep interest due to their occurrence in diverse samples. Amongst alkaline earth metal ion sensors, most investigated and developed are Ca^{2+} selective sensors. The first Ca^{2+} selective sensor was developed by Ross [25]. It was prepared by using a liquid membrane of didecylphosphate in di-n-octylphosphonate. This did not give good results as it showed high response time and poor selectivity. The sensor developed by using 1,7-di[2-(1-phenylazo)napthyl]-1,4,7-trioxaheptane [26] displays a linear response over a working concentration range of 30nM – 0.1M Ca^{2+} with a detection limit down to 10nM Ca^{2+}. It was used for the determination of Ca^{2+} in neutral and mineral water and in urine. Recently, Gao and Song [27] prepared a calcium selective sensor using hydroxyapatite as electroactive material. The sensor exhibited near Nernstian response in the working concentration range of 10μ M - 6.1 M.

Gupta *et al.* [28] prepared Mg^{2+} selective sensor by using neutral carrier benzo-15-crown-5 (I) which worked well over a wide concentration range of 1.0×10^{-5} to 1.0×10^{-1} M Mg^{2+} with a Nernstian slope of 31.0±1.0 mV per decade of activity. The response time of the sensor is 15 s and the membrane can be used over a period of 4 months with good reproducibility. Baniwal *et al.* [29] developed Mg^{2+} selective sensor by using PVC based membranes of macrocycles 4,11-dimethyl-2,4,9,11-tetraethyl -1,5,8,12-tetraazacyclotetradeca-1,8-diene (I) and 4,11-dioxa-2,9-dimethyl- 1,5,8,12- tetraazacyclo tetradeca-1,8-diene (II) as a electroactive materials which works well over a wide concentration range of 1.9×10^{-6} to 1.0×10^{-1} M with a Nernstian slope of 29 mV per decade of activity between pH 2.5 and 6.5.

Determination of barium assumes importance because of its widespread occurrence in drug and mineral water. Initially natural carboxylic polyether antibiotics [30, 31] and lipophilic electrically neutral carriers [32] were used to prepare barium selective sensors. Singh and coworkers [33] developed Ba^{2+} selective sensor by using PVC based membrane of 2,3,4-pyridine-1,3,5,7,12-pentaazacyclopentadeca-3-ene which worked well over a wide concentration range of 1.4×10^{-6} to 1.0×10^{-1} M with a Nernstian slope of 30.0 mV per decade of activity between pH 2.5 and 7.0.

Baumann [34] initiated the work for the developement of Sr^{2+} selective sensors by using strontium complex of polyethylene as ion active material. These sensors showed interference to Ba^{2+} and Hg^{2+}. Jain *et al.* [35] used araldite based membrane of strontium tungstoarsenate to prepare Sr^{2+} selective sensor while Srivastava *et al.* [36] used hydrous thorium oxide as electroactive material embedded in polystyrene. This sensor has been found to be highly selective towards Sr^{2+} over other cations except Pb^{2+} and Na^{+}.

The determination of heavy ions in water, soil and food samples is important in view of their toxic nature above certain concentration level. Zhang *et al.* [37] prepared Ag^{+} selective sensor by using 5,10,15-tris(pentafluorophenyl)corrole as an electroactive material. The sensor exhibited linear potential response over a concentration range of 5.1×10^{-6} to 1.0×10^{-1} M with a near Nernstian slope of 54.8 mV/decade of activity. The useful working pH range for the sensor is 4.0 to 8.0, and it shows a fast response time of <30 s. Kim and coworkers [38] developed Ag^+ selective sensor by using dithiocarbamoyl groups on a 7-deoxycholic amide as electroactive material.

A Hg^{2+} selective sensor based on polyaniline Sn(IV) phosphate was reported by Khan *et al.* [39] which worked in the linear concentration range of 1.0×10^{-6} to 1.0×10^{-1} M with a slope of 30 mV per decade of activity. Gupta *et al.* [40] also developed a Hg(II) selective sensor which showed a linear response to Hg^{2+} ions in a concentration range of 1.2×10^{-5} to 1.0×10^{-1} M with a slope of 25 ± 0.1 mV per decade of activity over the pH range 6.6 – 9.3. Singh and coworkers [41] prepared Hg^{2+} selective sensor using 2,3,4,9,10,11- dipyridine- 3,10- diaza - 1,5,8,12-tetrathiacyclotetradeca-2,9-diene as an ionophore. The sensor showed near Nernstian slope of 30.0 mV per decade of activity and found to be chemically inert and of adequate stability with a response time of 18s.

Cu^{2+}, Co^{2+} and Ni^{2+} selective sensors were developed to determine their concentration in alloys, minerals and various wastewater. Oliveira *et al.* [42] developed copper selective sensor by using macrocycles viz., 4-phenyl-11-(1-oxodecyl)- 1,7-dithia-11-aza-4-phosphacyclotetradecane and 4-phenyl-4-sulfide-11-(1-oxodecyl)- 1,7-dithia-11-aza-4-phosphacyclotetradecane. The sensors exhibits Nernstian response towards Cu^{2+} ions over the concentration range of 3.0×10^{-6} to 1.0×10^{-2} M within the pH range of 3.9–6.4. Ocypa *et al.* [43] developed Cu^{2+} selective sensor by using poly (3, 4-ethylenedioxythiophene) doped with hexacyanoferrate (III) ions as ionophore. This sensor worked up to lower detection limit of 10^{-7} M $CuSO_4$. Hossein and coworkers [44] reported Co^{2+} selective sensor by using (2-mercapto-4-methyl phenyl)- 2-benzamido- 3-phenyl-thiopropenoate as neutral carrier, which showed detection limit of 1.0×10^{-7} M.

Yari and coworkers [45] reported Ni^{2+} selective sensor by using dioxime derivative, (2*E*, 3*E*)-2*H*-1,4-benzothiazine-2,3(4*H*)-dione dioxime as a neutral ionophore. The prepared membrane exhibits a near Nernstian response for Ni^{2+} ions over a wide concentration range 1.0×10^{-6} to 1.0 M. Gupta and coworkers [46] explored 5,7,12,14-tetramethyldibenzotetraazaannulene for the developement of Ni^{2+} selective sensor. The sensor showed good selectivity for Ni^{2+} over a number of interfering ions. A Zn^{2+} selective sensor based on dibenzo-24-crown-8 (I) was reported by Gupta *et al.* [47] which worked in the concentration range of 9.2×10^{-5} to 1.0×10^{-1} M with Nernstian slope of 29.0 ± 0. 5 mV per decade of activity. Gholivand *et al.* [48] developed Zn(II) selective sensor by using bis(2-nitrophenyl)disulfideas an ionophore. The sensor worked over wide concentration range of 2.9×10^{-7} to 3.2×10^{-2} M with a slope of 29.9±0.4 mV per decade and response time of 10s.

Lee *et al.* [49] developed Pb (II) selective sensor by using *meso*- tetrakis (2-hydroxy-1-naphthyl)porphyrin (THNP) and *meso*-tetrakis(2-methoxy-1-naphthyl) porphyrin (TMNP) atropisomers as membrane carriers. The sensor showed good Nernstian response (29.2±0.3 mV per decade of activity) and working concentration range of 3.2×10^{-5} to 1×10^{-1} M with a fast response time <10 s. Bhat and coworkers [50] developed Pb^{2+} selective sensor by using 4-*tert*-butylcalix[6]arene as neutral carrier. The sensor was used for the determination of lead in Eveready battery waste and electroplating waste. Au^{3+} selective sensors were developed mainly to determine its concentration in minerals and alloys. The membranes of tetraphenylarsonium tetrachloroaurate embedded in PVC were employed for the determination of gold in minerals [51].

1.5.2 Anion Selective Sensors

Besides metal ions, efforts have also been made by many workers to develop sensors for the determination of anions. Nakamura *et al.* [52] reported a fluoride selective sensor based on phthalocyanine cobalt(III) as an electroactive material and they used it to estimate fluoride in nonaqueous medium and pharmaceuticals. Fluoride selective sensor was also prepared by pressing CaF_2 or LaF_3 or a mixture of both in form of pellets [53]. The sensor exhibited the working concentration range of 10μM - 10mM F^- with a detection limit as low as 0.6μM. Shamsipur *et al.* [54] developed a bromide selective sensor based on benzoderivative of xanthanium bromide salt. A Iodide selective sensor based on Ni(II) tetra azaunulene macrocyclic complex has been reported by Xing and coworkers [55]. Shamsipur *et al.* [56] reported Iodide-selective sensors by using Schiff base complex of Fe(III) as a suitable carrier. The sensor exhibits Nernstian slope of 71.0±0.3 mV per decade of activity for I^- ion over a wide concentration range of 1.0×10^{-6} - 5.0×10^{-1} M. The proposed sensor was used as an indicator sensor in potentiometric titration of iodide ion. Chloride selective homogeneous membrane having Ag_2S-AgCl mixture as electroactive material have been reported [57, 58]. Attempts have also been made to prepare Cl^- selective membranes by using other electroactive materials. Hiiro and Coworkers [59] reported a tridodecylmethylammonium chloride based membrane sensor for chloride ions and used it to determine chloride content in blood.

A nitrate selective sensor was developed by Exposito *et al.* [60] using tris(2-aminoethyl)amino triamide derivative as an electroactive material which exhibited a

Nernstian response over the concentration range of 1.0×10^{-5} to 1.0×10^{-1} M with a slope of 54.7 mV/decade of activity. Ardakani *et al.* [61] developed nitrate selective sensor by using complex of bis(2-hydroxyacetophenone)ethylenediimine vanadyl (IV) as an electroactive material. The sensor exhibited Nernstian slope of 58.5±1.0 mV per decade of activity and working concentration range of 5.0×10^{-6} to 1.0 M

A phosphate selective sensor developed by Goff *et al.* [62] using heterocylic macrocycles as an electroactive material. The sensor exhibited linear working concentration range of 1.0×10^{-6} to 3.9×10^{-3} M HPO_4^{2-} with Nernstian slope of 29.7±0.9 mV per decade of activity. Ganjali *et al.* [63] developed salicylate selective sensors by using a new tetracoordinate organonickel complex which showed a Nernstian response to salicylate ions over a wide concentration range of 1.0×10^{-5} - 1.0×10^{-1} M. The sensors were successfully used for determination of salicylate in biological samples.

Ganjali *et al.* [64] developed sulfate selective sensor by using 4-(4-bromophenyl)-2,6-diphenylpyrilium perchlorate (BDPP) as an elctroactive material which showed Nernstian slope over the concentration range of 1.0×10^{-6} to 1.0×10^{-2} M. The sensor was used as an indicator electrode in potentiometric titration of sulfate and barium ions. Shamsipur *et al.* [65] reported sulfate selective sensor based on 2, 5-diphenyl-1, 2, 4, 5-tetra aza-bicyclo[2.2.1]heptane as a neutral carrier. The sensor showed a linear response in the working concentration range of 9.0×10^{-6} to 1.0×10^{-1} M with a slope of 28.8±0.2 mV per decade of activity.

Segui *et al.* [66] developed thiocyanate selective sensor by using polyamines viz., octyl-[2-(2-octylamino-ethylamino)-ethyl]-amine and octyl-{2-[2-(2-octylamino-ethyl amino)-ethylamino]-ethyl}-amine as anion ionophores. The sensors worked over narrow concentration range of 1.0×10^{-5} to 1.0×10^{-1} M with near Nerstian slope of 57.2 mV/decade of activity. Erden and coworkers [67] developed thiocyanate selective sensor by using 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetracyanometoxycalix[4]arene as an electroactive material which exhibits a linear response over the concentration range of 3.0×10^{-5} to 1.0×10^{-1} M SCN^- with a slope of 52.0 ± 0.2 mV/decade of activity.

A perchlorate selective sensor was developed by Jain *et al.* [68] using brucine, cinchonidine, emetine and benzyldimethyltetradecylammonium chloride (zephiramine) in nitrobenzene which respond to perchlorate ion over a narrow concentration range of 5.0×10^{-4} to 1.0 M ClO_4^- and showed strong interference to permanganate ion. Hassan *et al.* [69] developed perchlorate selective sensor by using nitron-perchlorate ion-pair complex, in nitrobenzene which worked in the narrow concentration range of 2.0×10^{-5} to 1.0×10^{-2} M perchlorate with a slope of -56.8 ± 0.7 mV/decade of activity and showed high response time of 20–90s. Michael *et al.* [70] developed perchlorate selective sensor by using N-ethyl-benzothiazole-2,2′-azaviolene perchlorate in 1,2-dichlorobenzene and in β,β′-dichlorodiethyl ether as an electroactive material which showed strong interference to iodide and tetrafluoroborate ions. Casabo *et. al.* [71] reported perchlorate selective sensor based on phosphadithiamacrocycle (I) as an electroactive material which showed woking concentration range of 6.0×10^{-7} to 1.0×10^{-2} M and showed interference to SCN^- and BF_4^- ions.

1.6 The Problem

An overview of literature already presented reveals that a number of ion sensors for alkali, alkaline earth, heavy metals and anions have been reported. For every single ion, a number of sensors using different materials are reported. This is due to the fact that researchers have tried to improve working concentration range, selectivity, life time and response time of already reported sensors using 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. Among anions, the sensors developed for perchlorate ion exhibit narrow working concentration range, low pH range, high response time and suffered serious interference from OH^-, $NO3^-$, SCN^-, BF_4^- ions. Therefore, there is need to develop a selective and sensitive sensor for perchlorate.

Recent investigations have shown that neutral hydrogen bonding diamide receptors bind specific anions through hydrogen bonds. Keeping this in view, we have synthesized a newly hydrogen bonding diamide receptor N^1, N^3-di(1H-benzoimidazole-2-yl)isophthalamide and explored as perchlorate selective ionophore. Therefore, PVC based membranes of this diamide receptor have been prepared and studied.

The results presented subsequently show that membranes act as selective sensor for perchlorate and therefore, can be used for its determination.

2. THEORY

The utility of ion selective sensor depends on the membrane potential determination. It is not possible to determine membrane potential directly but can be derived from the emf values of a complete electrochemical cell [72], which consists of the membrane separating two solutions 1 and 2 and two reference electrodes as shown in Fig. 1.

2.1 Potential of an Ion Exchange Membrane

A semipermeable ion-exchange membrane when placed between two solutions of different concentration of an electrolyte AY allows the diffusion of A from higher to lower concentration side as membrane is more permeable to these ions and hinders partially or totally the diffusion of other ion Y. As a result, an electrical double layer is formed across the membrane and electrical potential gradient thereby generated. This potential is called membrane potential (E_m) [73] and is the sum of Donnan and diffusion potential. Since potential developed across a membrane depends upon the activity of a particular charged species, it can be used to determine the activity of that species in any solution. Membrane potential Em is given by the expression:

$$E_m = \frac{2.303RT}{Z_A F}\left[\log\frac{(a_A)_2}{(a_A)_1} - (z_Y - z_A)\int_1^2 t_Y^- d\log a^{\pm}\right] \qquad .....(1)$$

where z_A and z_Y are the charges on the ion A and Y, respectively, t_y^- is the transport number of Y, $a^{\pm}$ is the mean activity of electrolyte and $(a_A)_1$ and $(a_A)_2$ denote the activities of A ions in solutions 1 and 2, respectively.

First term on the right hand side of the equation (1) gives the thermodynamic limiting value of the concentration potential, i.e. Donnan potential while the second term denotes the diffusion potential due to co-ion flux in the membrane. However, if the membrane is considered to be ideally permselective ($t_y^-=0$), then equation (1) takes the form of the Nernst equation.

$$E_m = \pm \frac{2.303RT}{Z_A F} \log \frac{(a_A)_2}{(a_A)_1} \qquad \text{.....(2)}$$

The equation (2) represents Donnan potential for an ideally permselective membrane. The sign will be +ve for cation selective and –ve for anion selective membranes. It can also be said that it gives thermodynamic limiting value of the concentration potential.

The following cell set up is generally used for the measurement of membrane potential using saturated calomel electrodes (SCE) or other reference electrodes.

External reference electrode (SCE)	‖	External or Test solution of AY	Membrane	Internal solution of AY	‖	Internal reference electrode (SCE)
		2		1		
	$E_{L(2)}$				$E_{L(1)}$	

Generally, compartment 1 contains reference or internal solution whose concentration is kept constant. The saturated calomel electrode dipped in this solution is known as internal reference electrode. The membrane together with internal solution and internal reference electrode is known as membrane electrode or membrane sensor. The saturated calomel electrode dipped in external solution, which is usually referred to as test solution or sample, is known as external reference electrode.

The potential of the above cell assembly is given by the expression

$$E_{cell} = E_{cal} + E_{L(2)} + E_m + E_{L(1)} - E_{cal} \quad \text{........(3)}$$

where E_{cal}, E_L and E_m are the saturated calomel electrode potential, junction potential and membrane potential, respectively. From equations (2) and (3):

$$E_{cell} = E_{cal} - E_{cal} + E_{L(1)} + E_{L(2)} \pm \frac{2.303RT}{Z_A F} \log \frac{(a_A)_2}{(a_A)_1}$$

or

$$E_{cell} = \left[E_{L(1)} + E_{L(2)} - \frac{2.303RT}{Z_A F} \log (a_A)_1 \right] + \frac{2.303RT}{Z_A F} \log (a_A)_2 \quad \text{.....(4)}$$

(For cation exchange membrane)

The values of $E_{L(1)}$ and $E_{L(2)}$ are small and generally remain constant. Also the term $\frac{2.303RT}{Z_A F} \log (a_A)_1$ remains constant if the concentration of internal solution is not changed. Therefore, in a given experimental set up, all the terms in parenthesis of equation (4) are constant and can be substituted by a constant E^0. The value of E^0 would change only when experimental conditions are changed. The equation (4) becomes:

$$E_{cell} = E^0 + \frac{2.303RT}{Z_A F} \log (a_A)_2 \quad \text{.....(5)}$$

Attempts are generally not made to determine the membrane potential by subtracting external SCE potential. The whole electrochemical cell as described above is taken as a sensor and the value of E_{cell} gives activity of the ion of interest. If for a developed membrane sensor, the slope of the plot between E_{cell} and $\log (a_A)_2$ comes out to be equal to theoretical slope i.e. $\frac{0.0591}{Z_A}$, then the membrane is said to be ideal as it has responded according to Nernst equation (5) [74-76]. The slope of such a membrane is called Nernstian slope.

2.2 Selectivity

Selectivity is an important characteristic of a sensor that delineates the extent to which the device may be used in the estimation of analyte ion in the presence of other ions. The ion for which the sensor is designed is called primary ion and all other ions are referred to as interfering ions or foreign ions or secondary ions. In fact, no ISS 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 [1]

$$E = E^{\circ} \pm \frac{2.303RT}{z_A F} \log \left[a_A + \sum K_{A,B}^{Pot} \, a_B^{z_A/z_B} \right] \qquad .....(6)$$

where z_A, z_B, a_A and a_B are the charges and activity of ions A and B, respectively. It is apparent from equation (6) 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 sensor responds more to A in comparison to B i.e., the sensor 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 sensor'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 (6), but now it depends on the values of z_A and z_B. For different values of z_A and z_B, $K_{A,B}^{Pot}$ values showing equal response to both A and B have been computed from equation (6) at an activity of 10^{-2} M B and are summarized in Table 1. The $K_{A,B}^{Pot}$ values indicating equal response for both ions A and B not only depends on z_A and z_B but also on the concentration of interfering ions. At an activity of 10^{-3} M of B, selectivity coefficient values change drastically as seen from Table 2. Thus, it is seen from Table 1 and 2 that the discussion of the selectivity of the sensors is rather difficult. At an activity of 10^{-2} M, with $z_A=z_B=1$, $K_{A,B}^{Pot}>1$ indicate interference but with $z_A=2$ and $z_B=1$, $K_{A,B}^{Pot}>1$, does not indicate any serious interference. The interference become serious when $K_{A,B}^{Pot}>100$. As a matter of fact, with $z_A=2$ and $z_B=1$, a value of $K_{A,B}^{Pot}$ upto 100 means that sensor is more selective to A compared to B. Similar problem also exists when $z_A=1$, $z_B=2$ or $z_A=2$, $z_B=3$ etc. 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 have proposed a modification in the Nicolsky equation. They neglected the power term from the equation (6) and reported the data [77]. The selectivity coefficient data reported in this way (i.e. by neglecting the power term, z_A/ z_B) comes out to be on a scale for which $K_{A,B}^{Pot}=1$ indicates equal response for both A and B irrespective of their charges.

It is important to emphasize that selectivity coefficient values signify the selectivity only at the conditions of determination but in actual practice the interference caused depends on the relative concentration of the primary and interfering ions and other experimental conditions. Though the selectivity coefficient values may not reflect exactly the interference level but still they are very important parameters to estimate the likely performance of a sensor. However, it has been seen that the deviation between the expected performance of a sensor on the basis of selectivity coefficient and the experimental performance is not large. Therefore, it is necessary to evaluate the performance of a sensor in the presence of other ions by determining selectivity coefficient. A number of methods have been described to determine selectivity coefficient [78-80] and they are grouped into the following categories.

2.2.1 Separate Solution Method (SSM)

2.2.2 Mixed Solution Method (MSM)

2.2.3 Matched Potential Method (MPM)

2.2.1 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 emf of this cell E_A is related to the primary ion by the equation

$$E_A = E^0 + \frac{2.303RT}{z_A F}\log a_A \qquad \text{.......(7)}$$

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

$$E_B = E^0 + \frac{2.303RT}{z_A F}\log \mathrm{K}_{A,B}^{Pot}(a_B)^{z_A/z_B} \qquad \text{......(8)}$$

From equations (7) and (8)

$$\log \mathrm{K}_{A,B}^{Pot} = \frac{E_B - E_A}{2.303RT/z_A F} + \log \frac{a_A}{(a_B)^{z_A/z_B}} \qquad \text{.......(9)}$$

When $E_A = E_B$

$$\mathrm{K}_{A,B}^{Pot} = \frac{a_A}{(a_B)^{z_A/z_B}} \qquad \text{......(10)}$$

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 [81].

2.2.2 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), this method is preferred over separate solution method. There are two procedures for determining selectivity coefficients using MSM.

Procedure I

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 (7). 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

$$E = E^\circ + \frac{2.303RT}{z_A F} \log \left[a_A + K_{A,B}^{Pot} (a_B)^{z_A/z_B}\right] \qquad \ldots(11)$$

From equations (7) and (11)

$$K_{A,B}^{Pot} = \frac{a_A}{(a_B)^{z_A/z_B}} \left[\left(\frac{E_{A,B} - E_A}{10^{2.303RT/z_A F}}\right) - 1\right] \qquad \ldots\ldots\ldots\ldots(12)$$

Thus, knowing E_A and E_{AB} 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. 2. 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_{AB} can be calculated by the following equation (10) already derived under separate solution method.

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

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 coefficients [82, 83]. The reason being 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.

2.2.3 Matched Potential Method (MPM)

The Matched Potential Method (MPM), which is independent of the Nickolsky-Eisenmann equation, was proposed by Gadzekpo and Christian [84] to overcome the difficulties in obtaining accurate selectivity coefficients when ions of unequal charge are involved. In this method, the selectivity coefficient K_{AB}^{Pot} is given by the expression

$$K_{A,B}^{Pot} = \frac{a'_A - a_A}{a_B} = \frac{\Delta a_A}{a_B} \qquad ......(13)$$

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. This method provides practically realistic values of $K_{A,B}^{Pot}$. The characteristics of Matched Potential Method 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 [85].

It is seen from the above paragraphs that the selectivity of ion selective sensor depends on the experimental conditions, usually the concentration of ions and the method of determination. It is for this reason, $K_{A,B}^{Pot}$ is not called selectivity constant but selectivity coefficient. Further, different methods give different values of selectivity coefficient as the conditions prevailing at the membrane-solution interface are not same [5, 86, 87]. In this thesis, the selectivity coefficient values have been determined using Fixed Interference and Matched Potential methods and the values have been worked out from the experimental data using equations (10) and (13).

3. EXPERIMENTAL

3.1 Reagents

All reagents were of analytical grade and used without further purification. Isophthaloyl dichloride, Aldrich, Germany; 1H-benzoimidazole-2-amine, Acros organics, USA; triethylamine (Et_3N), tridodecylmethylammonium chloride (TDDMACl) and high molecular weight polyvinyl chloride (PVC), Aldrich, USA; tris(2-ethylhexyl) phosphate (TEHP), E. Merck, Germany; dibutyl phosphate (DBP), Reidel, India; dioctyl phosphate (DOP), diethyl phosphate (DEP), Reidel, India; Tricrecyl phosphate (TCP) Aldrich, USA were used as obtained. Analytical reagent-grade tetrahydrofuran (THF) and sulphuric acid were obtained from Ranbaxy, India. Standard solutions were prepared with double distilled water. Working solutions of different concentrations were prepared by diluting 0.1 M stock solutions.

3.2 Synthesis of N^1, N^3-di(1H-benzoimidazole-2-yl)isophthalamide receptor (I)

The solution of isophthaloyl dichloride (1.014 g, 5 mmol) in 5 mL of dry THF was added dropwise to the mixture of Et_3N (1.4 mL), 1H-benzoimidazole-2-amine (1.33 g, 10 mmol) and 200 mL of dry THF over a period of 5 min. After continuous stirring for 24 hours, the mixture was filtered and filtrate evaporated. The solid residue obtained was purified by crystallization from THF to yield **(I)** (80%), yellow solid (Fig. 3). Decompose at 300 °C; λ_{max} = 261 nm (Fig. 4); IR: υ(-C=O, amide)= 1644cm^{-1}, υ (-NH)=3434 cm^{-1} (Fig. 5) ; Anal. Calcd. for $C_{22}H_{16}N_6O_2$: C, 66.6; H, 4.0; N, 21.2%; Found: C, 66.0; H, 3.6; N, 20.1%.

3.3 Preparation of Membranes

The PVC based membranes were prepared by dissolving appropriate amounts of **(I)**, TDDMACl, plasticizers (DOP, TEHP, DBP, DEP and TCP) and PVC in THF (10 mL). After complete dissolution of all the components and thorough mixing, homogeneous mixture was poured into polyacrylate rings placed on a smooth glass plate. THF was allowed to evaporate for about 24 h at room temperature. To obtain membranes with reproducible characteristics, the solvent evaporation was carefully controlled otherwise morphology and thickness of the membranes shows significant variation which ultimately affected the sensor response. The transparent membranes of 0.5 mm thickness were removed carefully from the glass plate. A 5 mm diameter piece was cut out and glued to one end of a "Pyrex" glass tube. The membranes thus prepared were equilibrated for 2 days in 0.5 M ClO_4^- solution.

3.4 Potential measurement and Apparatus

The potential and pH measurements were carried out at 25±0.1°C with a digital potentiometer (Model 5652 A, ECIL, India) and Century Microvoltmeter (Model CVM 301, India) by setting up the following cell assembly, employing saturated calomel electrodes (SCE) as a reference electrodes.

SCE / internal solution (0.1M, ClO_4^-) / membrane / test solutions / SCE

IR spectra were recorded on Perkin-Elmer 1600 series FT-IR spectrophotometer. The melting points were determined on Buchi SMP 20 melting point apparatus. Elemental analysis was performed with Vario EL III instrument.

4. RESULTS AND DISCUSSION

In preliminary investigations, potentiometric response of the sensors having membrane of composition (mg) (I):TDMACl:PVC (1:1:120) was tested for a number of anions. The potential response of various sensors is shown in Fig. 6. Among the anions, the best response was observed for ClO_4^- ion, therefore, the ionophore was selected as suitable sensor material for ClO_4^- selective sensor.

4.1 Working Concentration Range and Slope

The potential of the membranes of **(I)** was investigated as a function of ClO_4^- activity in the range of 1.0×10^{-6} to 1.0×10^{-1} M and the values obtained are shown in Table 3 and Fig.7. The working concentration range and slope have been evaluated from the plots of Fig 7 and compiled in Table 4. A perusal of data presented in Table 4 indicates that the sensor no.1 having membrane without plasticizer exhibits a narrow working concentration range of 4.4×10^{-5} - 1.0×10^{-1} M with a slope 49.0 mV/decade of activity. The sensitivity, linearity, and selectivity obtained for a given ionophore depend significantly on the membrane composition and nature of plasticizer used. Further, it has been shown that the presence of appropriate amount of lipophilic cationic additives in the anion selective membrane sensors is necessary to introduce perm selectivity. Thus, several membranes of varying plasticizers (DOP, TEHP, DEP, DBP and TCP) / cation excluder (TDDMACl) / PVC/ carrier (I) ratios were tested. The optimum membrane ingredient showing the most sensitive, reproducible, and stable results was obtained with a plasticizer/ PVC ratio of ~ 1.6 together with 1% ionophore and 1% cation excluder (Table 4). Of the five plasticizers added, the best performance characteristics are obtained with the membrane having DOP plasticizer (sensor no. 2). This sensor exhibits widest working concentration range 1.8×10^{-5} - 1.0×10^{-1} M with the slope of 52 mV $decade^{-1}$ of activity.

4.2 Response and Life Time

The response time has been measured as the time taken by the sensor to attain a stable potential. It has been determined for all the six sensors and mentioned in Table 4. It is seen from the table that response time of the sensor having membrane (no. 1) without plasticizer is sufficiently high (45s). However, with the addition of plasticizers to the membranes (nos. 2-6), response time is sufficiently reduced. It could be due to change in properties of the membranes caused by the addition of the plasticizers which brings about transition temperature of the polymer matrix near to ambient temperature [62]. Among all the sensors prepared with different plasticizers, the sensor no. 2 with DOP plasticizer improved the response time to maximum extent. This sensor generates stable and reproducible potential within 12s. The sensors could be used over a period of two months. However, the membranes were stored in 0.5 M ClO_4^- solution when not in use.

4.3 pH and Solvent Effect

In order to investigate the pH effect on the potential response of the sensor, the potential was measured at fixed concentration of ClO_4^- solution i.e. 1.0×10^{-3} M having different pH values. The pH of solution was varied from 1.0 – 12.0 by the addition of HNO_3 or ammonia. The potential variation as a function of pH is plotted in Fig. 8. It is seen that useful pH range for this sensor is 5.0 – 9.0 because in this range potential remains constant. The performance of the sensor system was also investigated in partially non-aqueous medium using methanol-water, ethanol-water and acetone-water mixture. Thus, the potential response of the sensor as a function of ClO_4^- ion activity was determined in 10%, 20% and 30% (v/v) methanol-water, ethanol-water and acetone mixtures and from the response obtained, working concentration range and slope were evaluated which are compiled in Table 5. It is seen from the table that the sensor worked satisfactorily up to 20% (v/v) non aqueous content as in these mixtures the working concentration range and slope remain almost same. However, above a 20% non-aqueous content, the slope and working concentration range are appreciably decreased.

4.4 Selectivity

When measuring real samples by ion sensors, the response of the sensor to the primary ion can be affected by the presence of other ions. Potentiometric selectivity coefficients, defined with reference to the Nikolsky–Eisenman equation, are commonly used as the quantitative expression of the ability of the sensor to respond primarily to the analyte ion in the presence of interfering ions. In this study, potentiometric selectivity coefficients of the proposed sensor were determined by the FIM. In FIM, the potential was measured for solutions containing varying concentration of ClO_4^- and fixed interfering ion concentration (1.0×10^{-2} M). The selectivity coefficients were determined from the plots (Figs. 9-13) and complied in Table 6. It is seen, the sensor exhibits selective response toward ClO_4^- ion and follows selectivity pattern for several anions in the order of $ClO_4^- > SCN^- > I^- > C_6H_5COO^- > CrO_4^{2-} > CH_3COO^- > CO_3^{2-} > Cr_2O_7^{2-} > NO_3^- > H_2PO_4^- > HCO_3^- > HPO_4^{2-} > SO_4^{2-} > F^-$. It is further seen from the Table 6 that selectivity coefficients are considerably smaller than unity which indicate that the sensor under consideration is sufficiently selective towards ClO_4^- over a number of interfering ions and hence can be used for ClO_4^- determination in the presence of these ions by direct potentiometry.

5. CONCLUSION

The results indicate that the membranes of N^1, N^3-di(1H-benzoimidazole-2-yl)isophthalamide receptor **(I)** are sufficiently selective for ClO_4^- ion over a number of other ions. The addition of plasticizers to the membranes improved the performance of the sensors as the working concentration range is increased, the slope becomes equal or nearer to Nernstian value and response time is drastically reduced from 45 to 12s. Of all the sensors investigated, the sensor no. 2 having membrane with composition of 1:1:120:200 mg (**I**:TDDMACl:PVC:DOP) is the best. The performance of this sensor is comparable to the reported ClO_4^- sensors [68-71] in terms of working concentration range, slope, pH effect and reproducibility. However, the sensor is superior to existing ones in terms of fast response time (12s) and selectivity as reported sensors exhibit significant interference to SCN^- and I^- ions whereas these ions do not cause any interference in its performance. Thus, the sensor can be used for the determination of ClO_4^- in the presence of various interfering ions by direct potentiometry and is an improvement over the reported sensors.

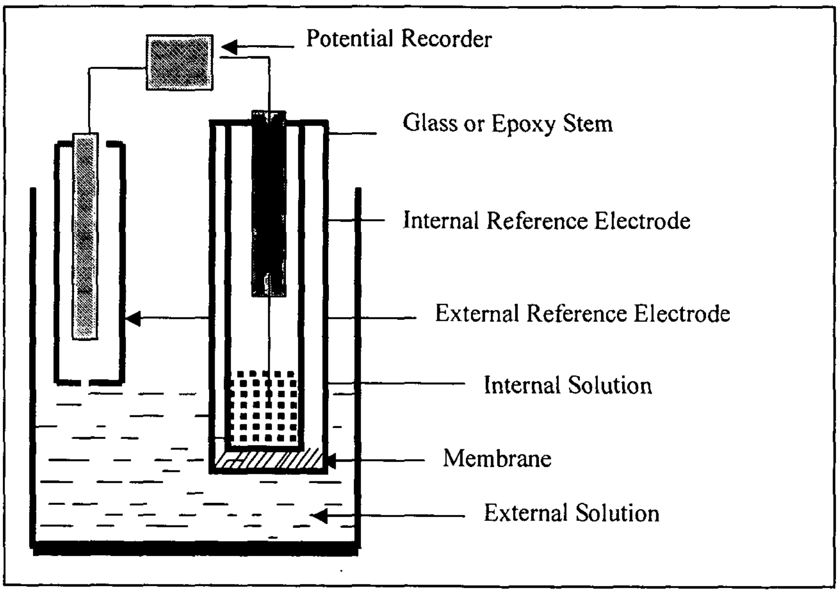

Fig. 1. Schematic cell diagram employing ISE

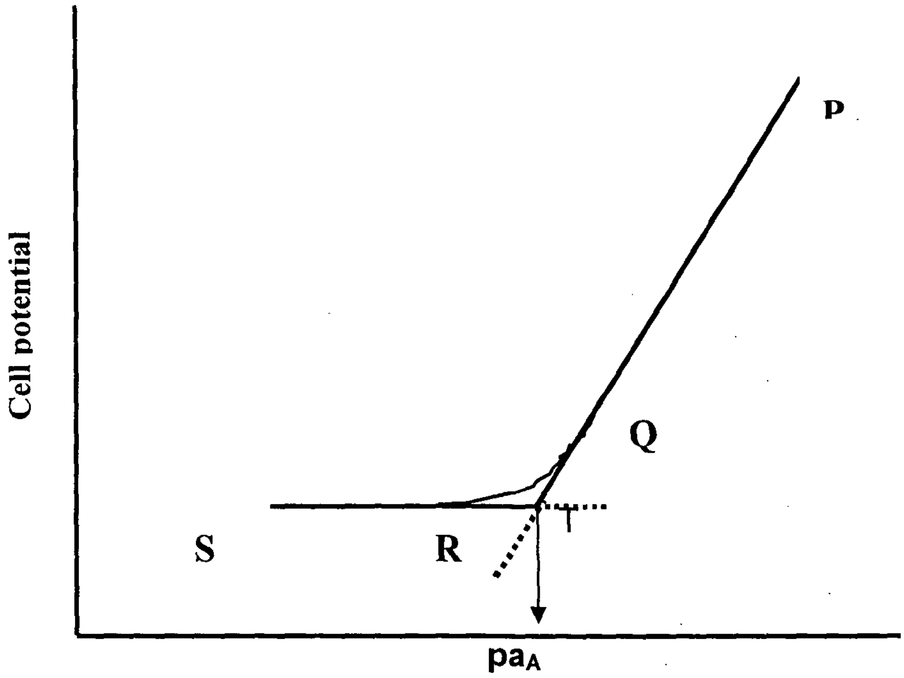

Fig. 2. Calibration curve illustrating the determination of selectivity coefficient by Fixed Interference Method

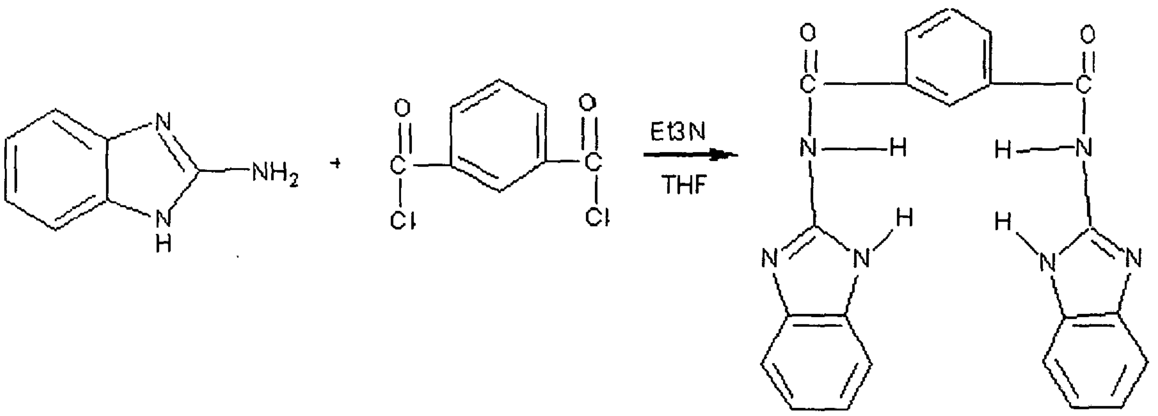

Fig. 3. Synthesis of N^1,N^3-di(1H-benzoimidazole-2-yl)isophthalamide receptor (I)

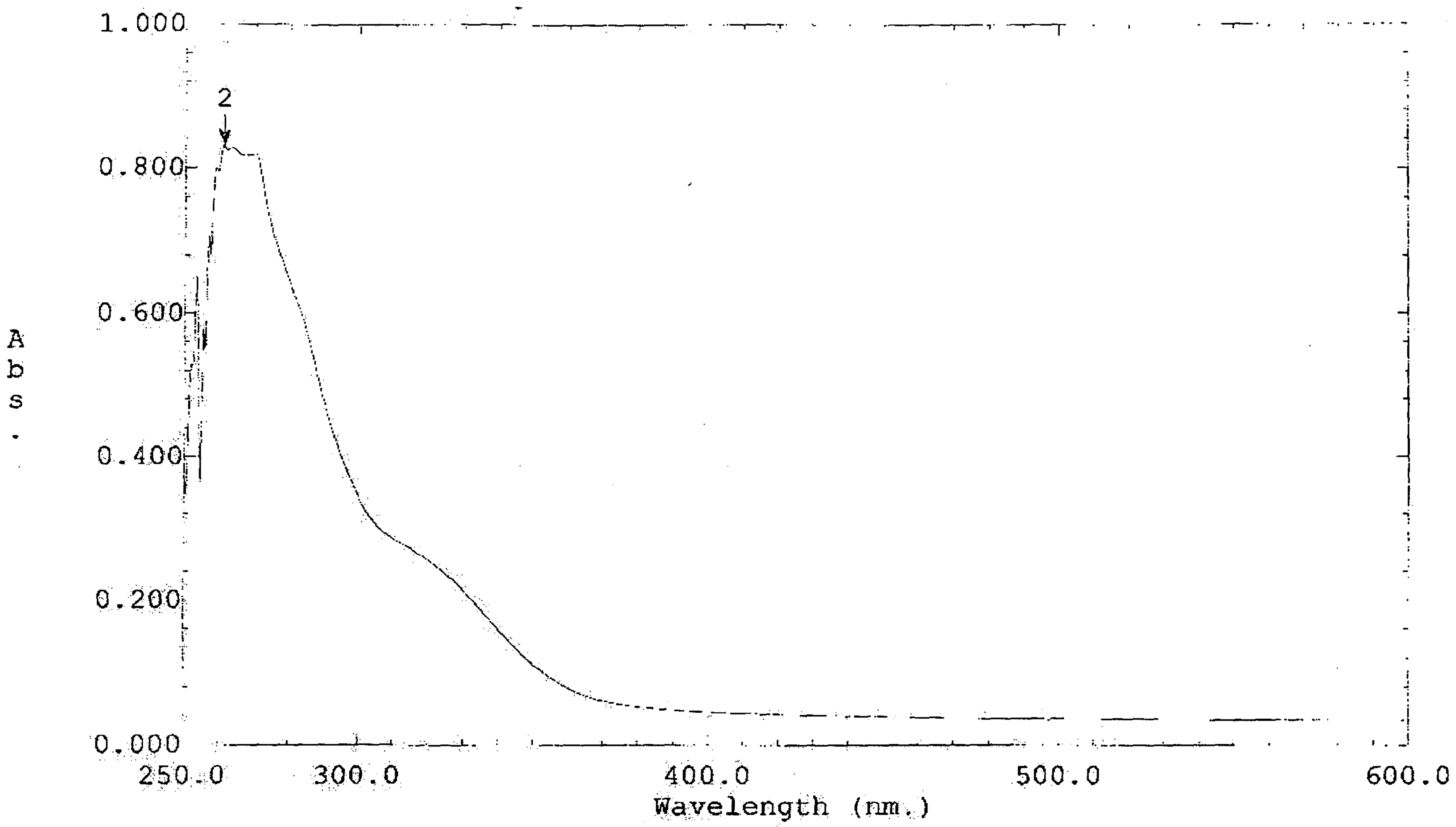

Fig. 4. UV Spectra of N^1, N^3-di(1H-benzoimidazole-2-yl)isophthalamide receptor

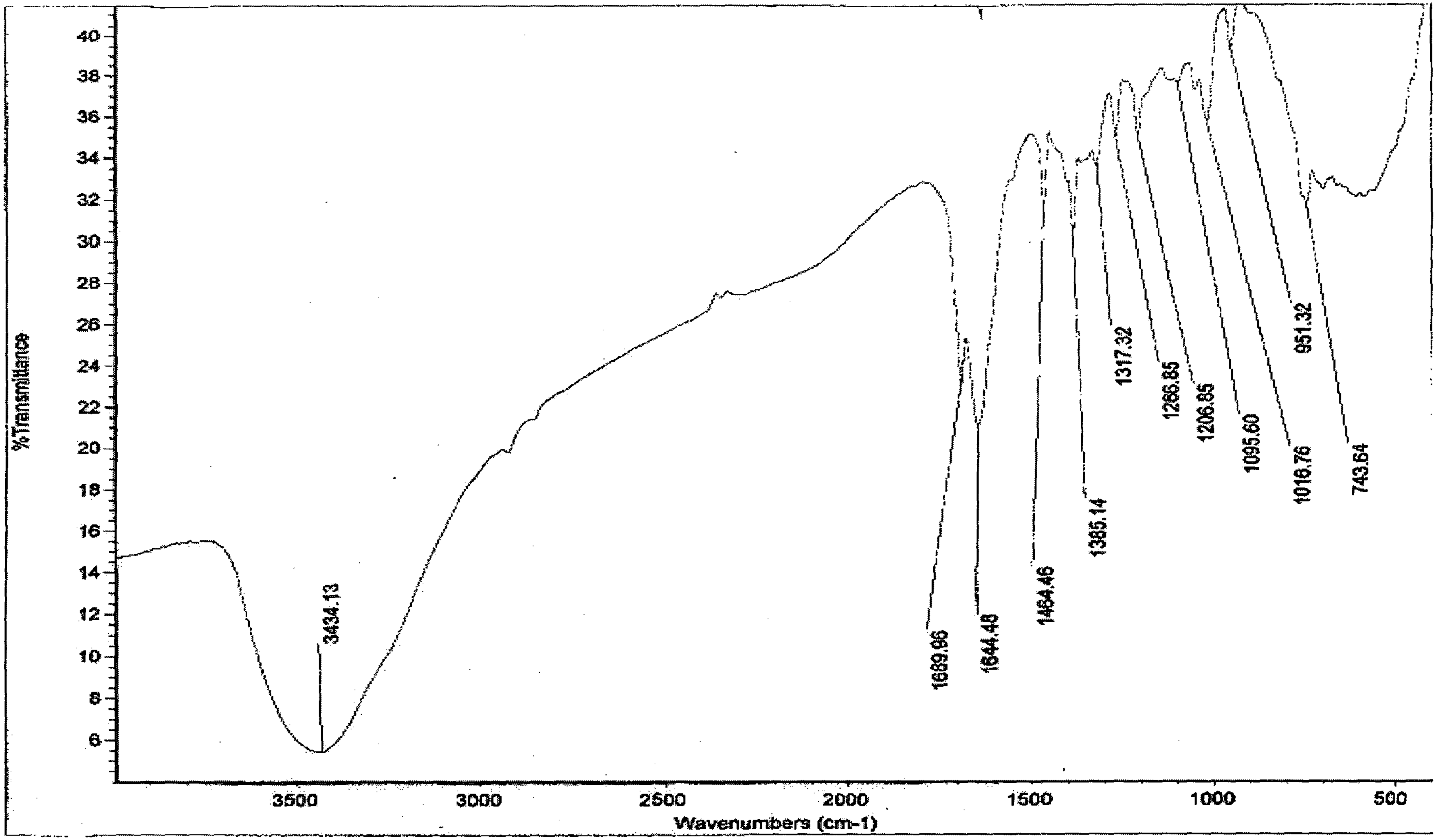

Fig. 5. IR Spectra of N^1, N^3-di(1H-benzoimidazole-2-yl)isophthalamide receptor

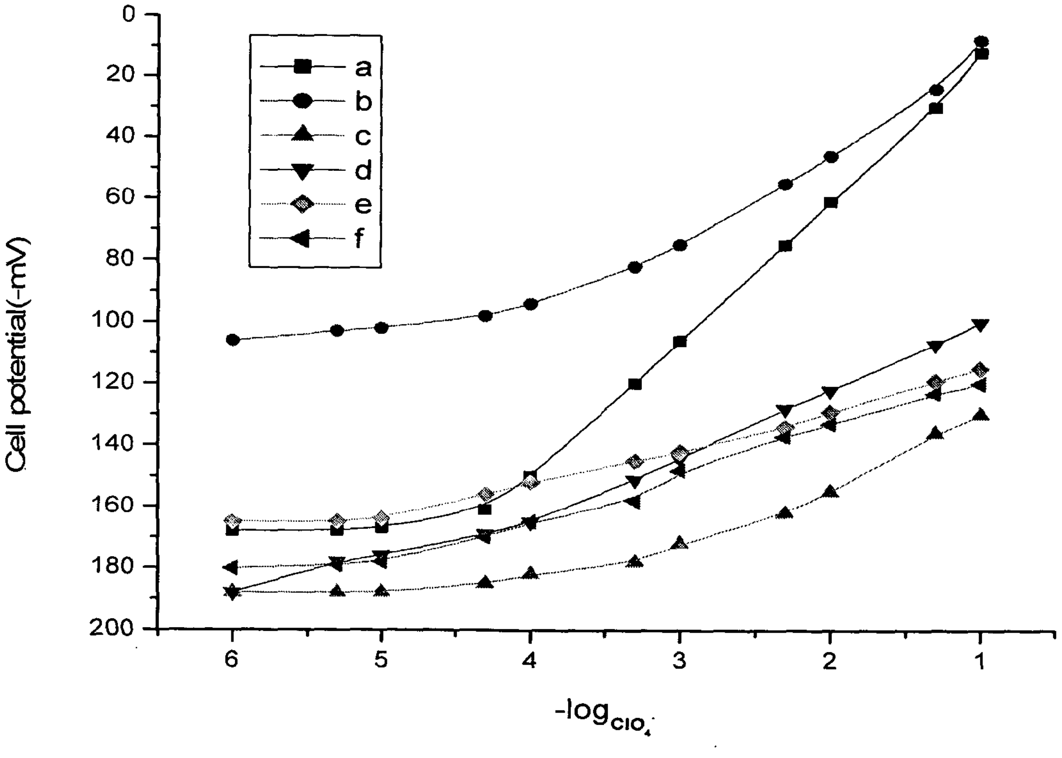

Fig. 6. Response of the N^1, N^3-di(1H-benzoimidazole-2-yl)isophthalamide receptor based membranes (without plasticizer) to (a) perchlorate (b) dichromate (c) sulphate (d) bicarbonate (e) nitrate (f) thiocyanate

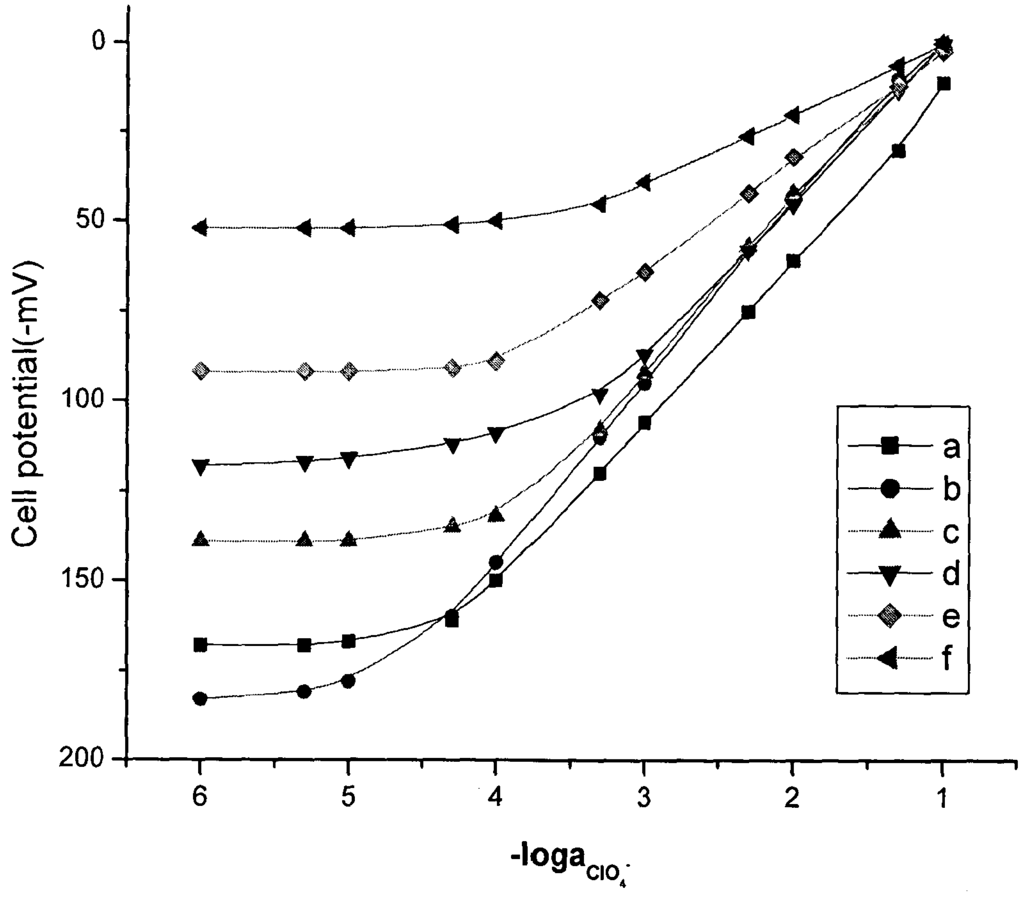

Fig. 7. Variation of membrane potential with activity of ClO_4^- ions of PVC based membranes of (I) (a) without plasticizer and with plasticizer (b) DOP (c) TEHP (d) TCP (e) DBP (f) DEP

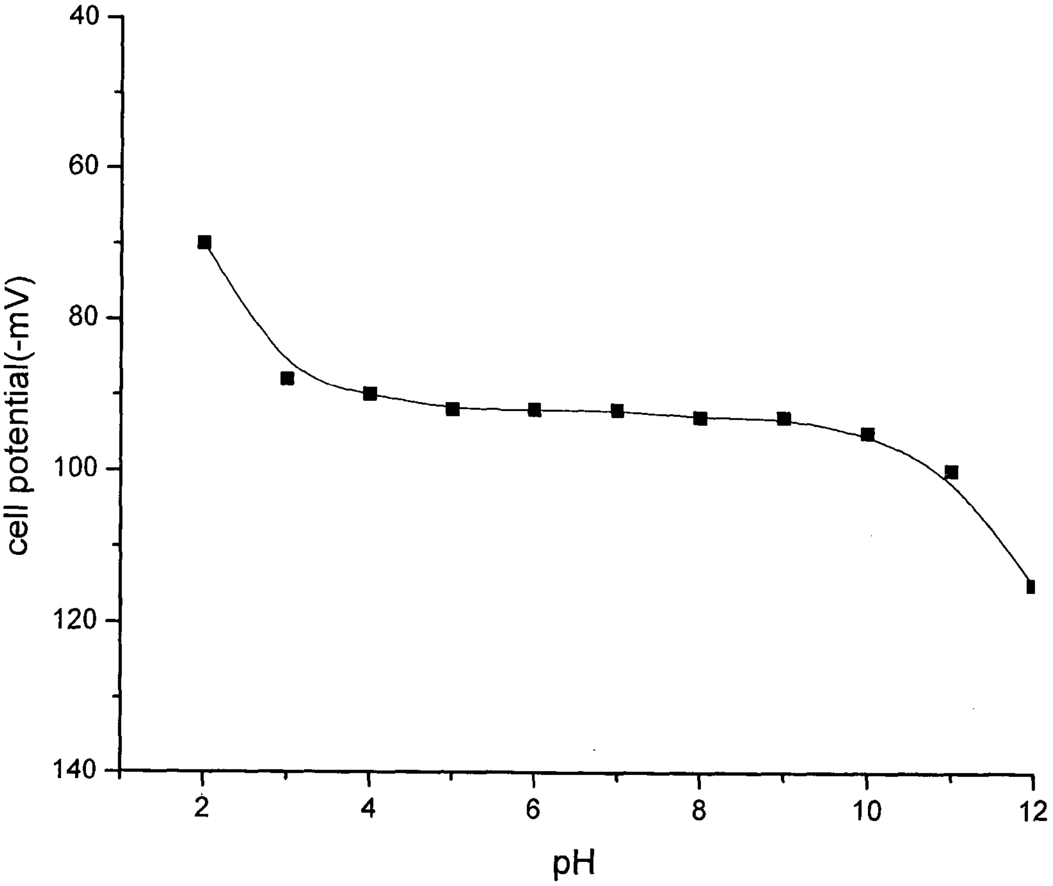

Fig. 8. Variation of membrane potential with pH

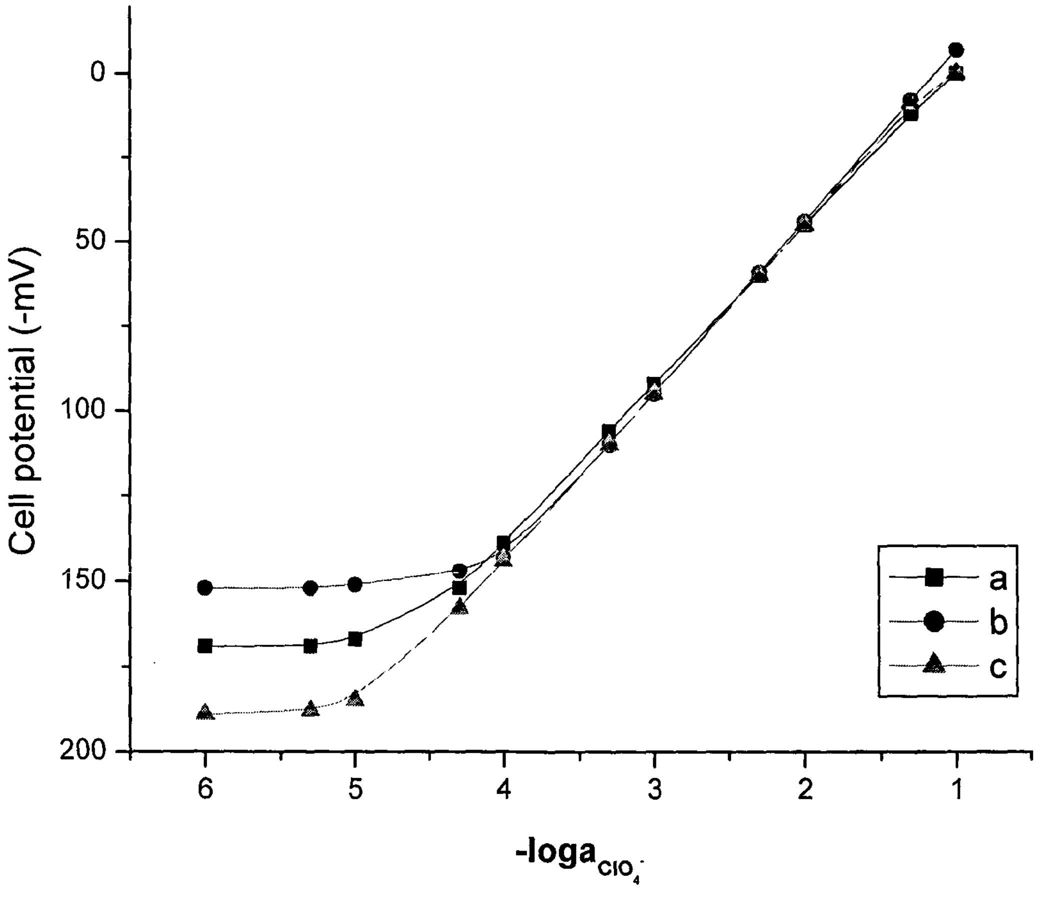

Fig. 9. Variation of membrane potential with activity of ClO_4^- ions in presence of interfering ions (a) HCO_3^- (b) I^- (c) F^-

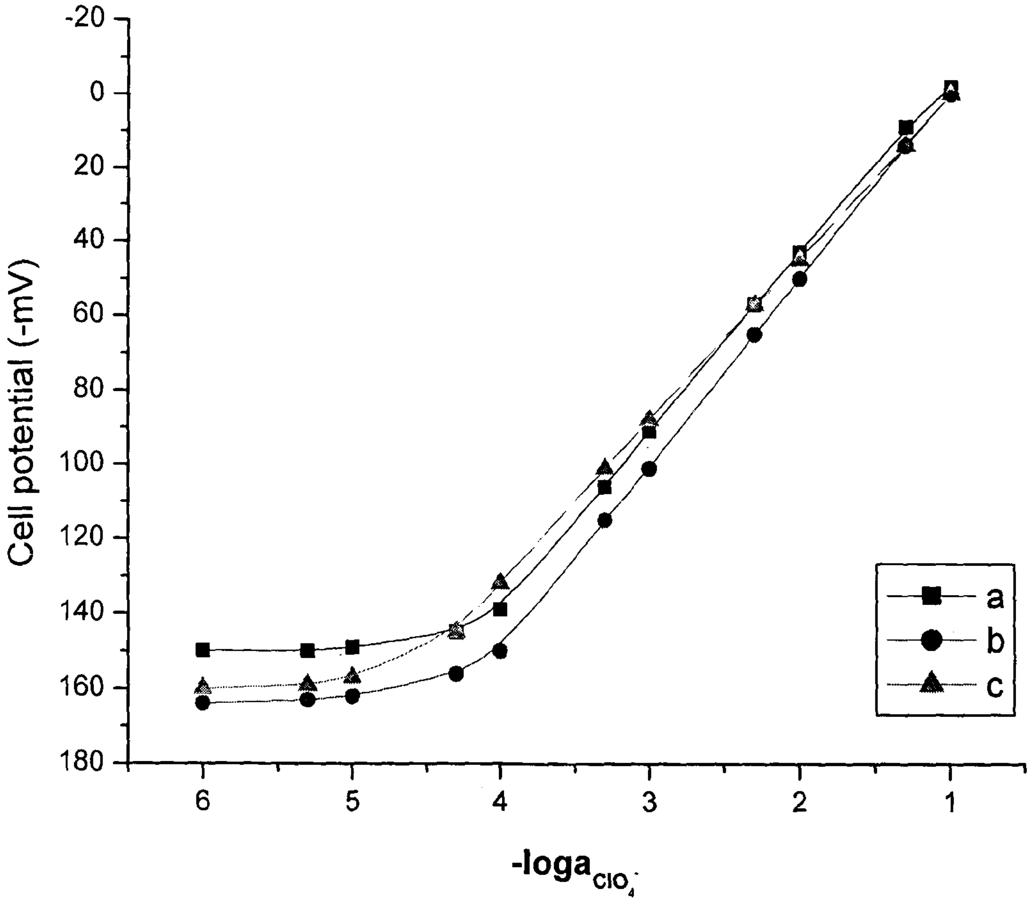

Fig. 10. Variation of membrane potential with activity of ClO_4^- ions in presence of interfering ions (a) $C_6H_5COO^-$ (b) CH_3COO^- (c) $H_2PO_4^-$

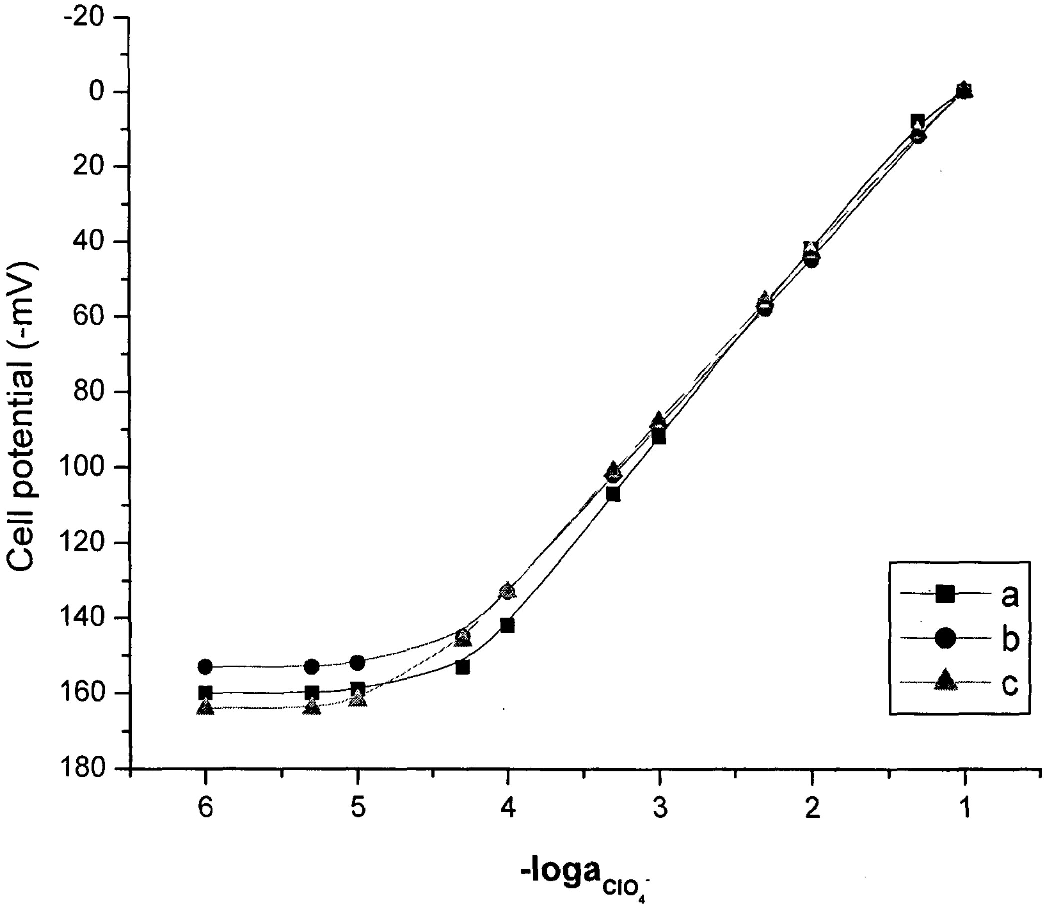

Fig. 11. Variation of membrane potential with activity of ClO_4^- ions in presence of interfering ions (a) CrO_4^{2-}(b) NO_3^- (c) SO_4^{2-}

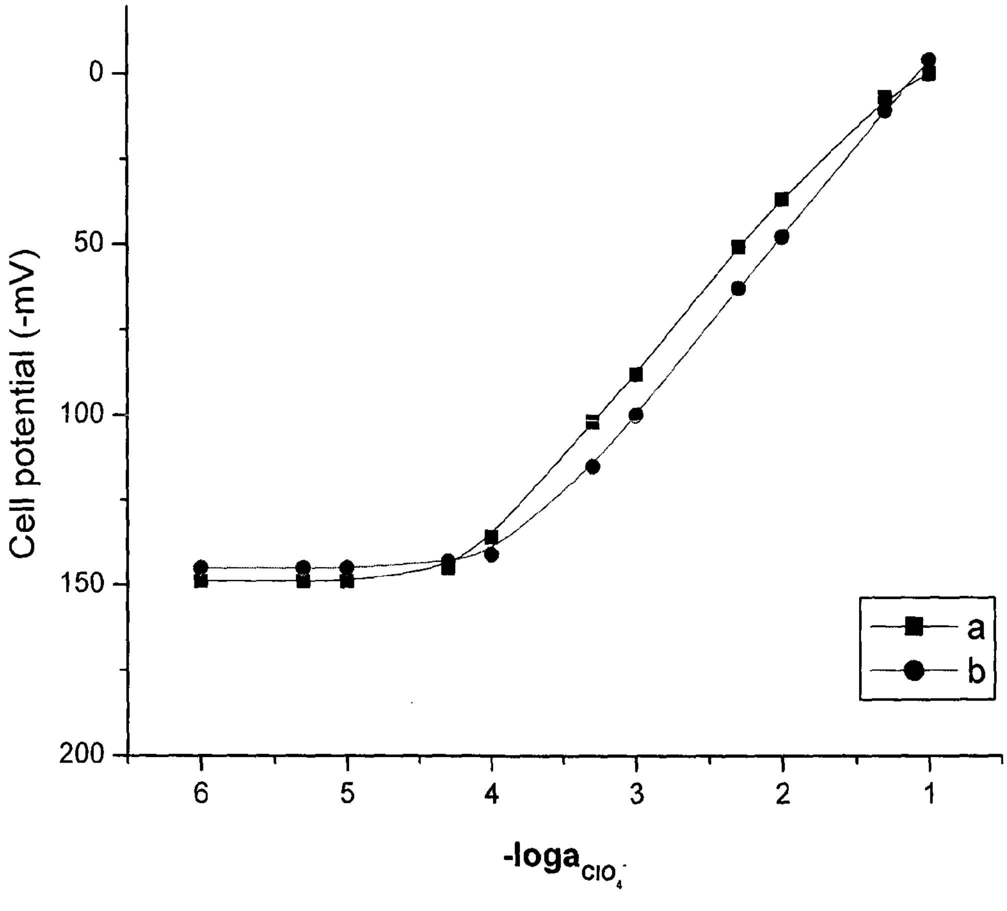

Fig. 12. Variation of membrane potential with activity of ClO_4^- ions in presence of interfering ions (a) CO_3^{2-} (b) SCN^-

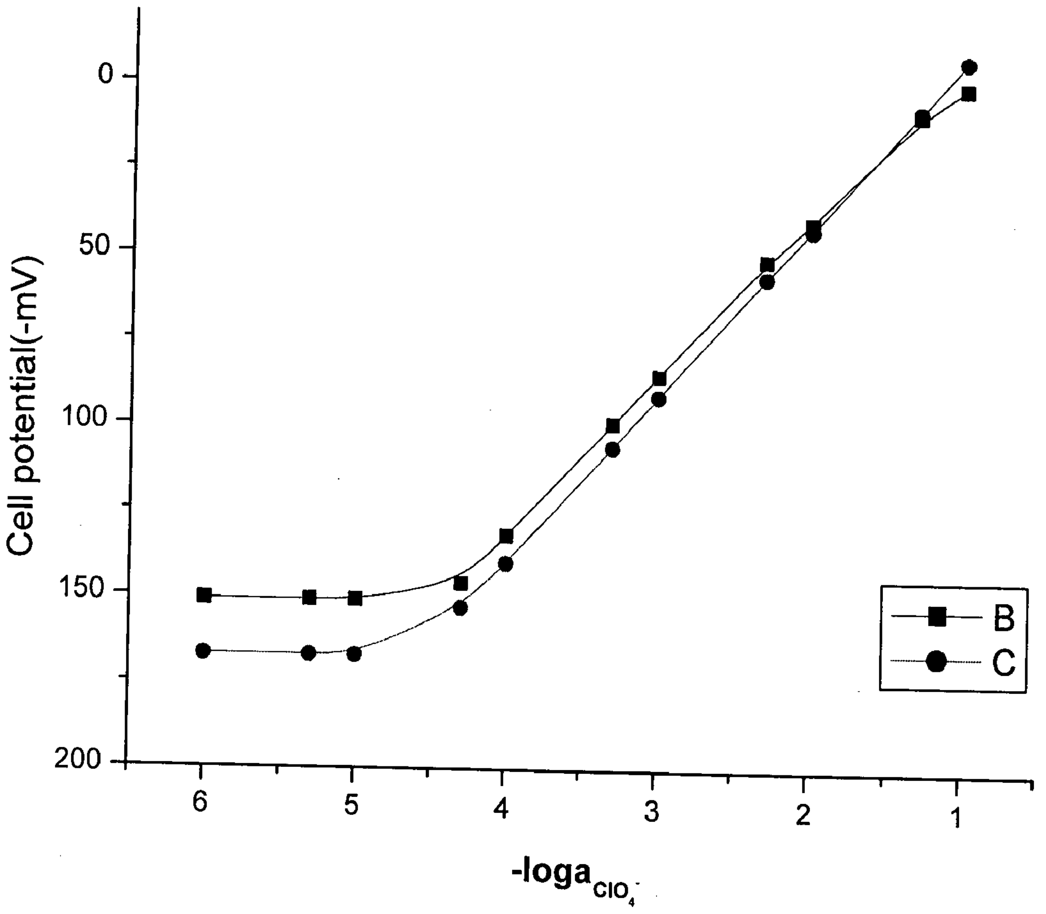

Fig. 13. Variation of membrane potential with activity of ClO_4^- ions in presence of interfering ions (a) $Cr_2O_7^{2-}$ (b) HPO_4^{2-}

Table 1. Selectivity coefficient values ($K_{A,B}^{Pot}$) indicating equal response of the sensor to both primary (A) and interfering ion (B) at an activity of 1.0 × 10^{-2} M of B.

Charge on primary ion (A), z_A	Charge on interfering ion (B), z_B	$K_{A,B}^{Pot}$ Values
1	1	1.00
1	2	0.10
1	3	0.05
2	1	100
2	2	1.00
2	3	0.20
3	1	10^4
3	2	10.00
3	3	1.00

Table 2. Selectivity coefficient values showing equal response for primary (A) and interfering ion (B) at an activity of 1.0 × 10^{-3} M of B.

Charge on primary ion (A), z_A	Charge on interfering ion (B), z_B	$K_{A,B}^{Pot}$ Values
1	1	1.00
1	2	0.03
1	3	0.01
2	1	1000.0
2	2	1.00
2	3	0.10

Table 3. Cell potential of membrane electrode with and without plasticizer

Concentration (M)	Potential of Membranes(-mV)					
	without plasticizer	DOP	DEP	DBP	TEHP	TCP
1.0 x 10^{-6}	168	183	52	92	139	118
5.0 x 10^{-6}	168	181	52	92	139	117
1.0 x 10^{-5}	167	178	52	92	139	116
5.0 x 10^{-5}	161	160	51	91	135	112
1.0 x 10^{-4}	150	145	50	89	132	109
5.0 x 10^{-4}	120	110	45	72	108	98
1.0 x 10^{-3}	106	95	39	64	92	87
5.0 x 10^{-3}	75	58	26	42	57	58
1.0 x 10^{-2}	61	44	20	32	42	45
5.0 x 10^{-2}	30	10	6	12	7	13
1.0 x 10^{-1}	12	0	0	2	0	0

Table 4. **Composition of PVC based membranes of N^1,N^3-di(1H-benzoimidazole-2-yl)isophthalamide receptor (I) and performance characteristics of ClO_4^- selective sensors based on them.**

Sensor No.	Composition of membranes (amount (mg) of different components added)								Working concentration range, (M)	Slope (-mV/ decade of activity)	Response time (s)
	(I)	PVC	TDDMACl	DOP	TEHP	DEP	DBP	TCP			
1	1	120	1						4.4×10^{-5} - 1.0×10^{-1}	49.0	45
2	1	120	1	200					1.8×10^{-5} - 1.0×10^{-1}	52.0	12
3	1	120	1		200				1.6×10^{-4} – 1.0×10^{-1}	50.0	16
4	1	120	1			200			2.5×10^{-4} – 1.0×10^{-1}	19.0	20
5	1	120	1				200		3.1×10^{-4} – 1.0×10^{-1}	31.0	15
6	1	120	1					200	1.7×10^{-4} – 1.0×10^{-1}	42.0	15

Table 5. Performance of ClO_4^- selective sensor no. 2 in non-aqueous media

Non-aqueous content (% v/v)	Slope, (-mV/decade) of activity	Working concentration range, M
0	52.0	$1.8 \times 10^{-5} - 1.0 \times 10^{-1}$
Methanol		
10	52.0	1.8×10^{-5}-1.0×10^{-1}
20	52.0	2.0×10^{-5}-1.0×10^{-1}
30	45.7	6.0×10^{-5}-1.0×10^{-1}
Ethanol		
10	52.0	1.8×10^{-5}-1.0×10^{-1}
20	52.0	2.0×10^{-5}-1.0×10^{-1}
30	45.6	6.3×10^{-5}-1.0×10^{-1}
Acetone		
10	52.0	1.8×10^{-5}-1.0×10^{-1}
20	52.0	1.8×10^{-5}-1.0×10^{-1}
30	44.8	6.8×10^{-5}-1.0×10^{-1}

Table 6. **Selectivity coefficients of sensor no. 2 as determined by the Fixed Interference Method (FIM).**

Interfering ion (M)	**Selectivity coefficient ($K^{pot}_{ClO_4^-,B}$)**
SCN^-	1.4×10^{-2}
HCO_3^-	2.2×10^{-3}
SO_4^{2-}	1.9×10^{-3}
CH_3COO^-	3.9×10^{-3}
I^-	7.9×10^{-3}
CO_3^-	3.9×10^{-3}
CrO_4^{2-}	4.4×10^{-3}
$C_6H_5COO^-$	5.6×10^{-4}
NO_3^-	3.1×10^{-3}
F^-	1.1×10^{-3}
HPO_4^{2-}	2.5×10^{-3}
$H_2PO_4^-$	2.2×10^{-3}
$Cr_2O_7^{2-}$	3.5×10^{-3}

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