ESTIMATION OF METAL IONS BY MACROCYCLIC MEMBRANE ELECTRODES

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By

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **"Estimation of Metal Ions by Macrocyclic Membrane Electrodes"** in partial fulfilment of the requirement for the award of the Degree of **Master of Philosophy** submitted in the **Department of Chemistry** of the University is an authentic record of my own work carried out during a period from January 98 to **July 98** under the supervision of **Dr. A. K. Singh,** Associate Professor, Department of Chemistry, University of Roorkee, Roorkee.

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

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ABSTRACT

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Polystyrene and Poly (vinyl chloride) based membranes of Ph_4(14)tetraene and Me_8(14)ane were prepared and explored for their possible use as Cr^{3+} and Al^{3+} selective electrodes. The solvent mediators dibutyl phthalate (DBP), dibutyl(butyl) phosphonate (DBBP), tris (2-ethylhexyl) triphosphate (TEP) and tributyl phosphate (TBP) were tried to improve the response characteristics of the electrodes as well as sodium tetraphenyl borate (STB) was also used as anion excluder to minimise the interferences by anions. Membranes having macrocycle, STB and Polystyrene in the ratio (w/w) 4:1:1 showed a linear potential response in the concentration range $3.16 \times 10^{-6} - 1.00 \times 10^{-1}$ M with a Nernstian slope of 17.3 mV/decade between pH range 3.0 to 6.5 for Cr^{3+}, while the membranes having Me_8(14)ane, STB, DBP and PVC in the ratio (w/w) 2:1:7:10 show linearity over a concentration range $1.77 \times 10^{-6} - 1.00 \times 10^{-1}$ M with a Nernstian slope of 20 mV/decade between pH range 3.0 to 6.5 for Cr^{3+} and concentration range $1.00 \times 10^{-6} - 1.00 \times 10^{-1}$ M with a Nernstian slope of 20 mV/decade between pH range 2.5 to 7.0 for Al^{3+}.

All the electrodes exhibit a fast response time of 15, 15 and 10s, respectively. Their performance is also satisfactory in partially non-aqueous medium. Potentiometric selectivity coefficient values indicate reasonably good selectivity for Cr^{3+} and Al^{3+} over a number of cations.

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1

INTRODUCTION

1.1 INTRODUCTION

The increasing use of industrial products viz., drugs and pharmaceuticals, alloys and steel, cement and paints, textiles and applications of new, fast analytical techniques and procedures for the analysis of air and soil, water and effluents, blood and biological fluids and dairy products etc. have definitely added to the quality of life for better. This realisation of importance of analytical chemistry in modern day life has led chemists and instrumentalists to develop new instruments, analytical techniques and procedures so as to make large scale analysis convenient, reliable, fast and selective.

Quantitative analysis normally involves the measurement of some property which is related directly or indirectly to the amount of desired constituent in the sample. The analytical techniques are broadly of five types: (i) volumetric (ii) gravimetric (iii) separation (iv) electrical and (v) optical. The first two are usual conventional chemical methods whereas the remaining three involve instrumental methods. A number of instruments such as UV-visible spectrophotometer, atomic absorption spectrophotometer, gas chromatograph, high performance liquid chromatograph, nuclear magnetic resonance spectroscope etc. are now available for analysis. Different techniques and procedures have distinct advantages and disadvantages. While gravimetric procedures are tedious and time consuming, the accuracy and sensitivity are affected by the quality of equivalence point detection system and the presence of competing ions in volumetric procedures. On the other hand, through the analysis by high cost instruments is more sensitive, reproducible and fast, but may be selective or non-selective depending on the component being analyzed and the type of instrumental technique involved. All these analytical techniques require chemical manipulation of sample before measurements [1]. Thus, a technique which involve minimum or no chemical manipulation of sample, is the ideal choice for analytical chemists and such a condition is met to a large extent by ION-SELECTIVE ELECTRODES (ISEs) for the ions for which they are available.

The last few decades have received widespread attention for the development of high performance chemical sensors and this has lead to a search for suitable materials which could be used for the preparation of sensitive and selective ion-sensors or ion-selective electrodes. The use of macrocycles as electroactive components in membrane electrodes has generated widespread interest in developing new ISEs especially for alkali and alkaline earth metals.

Ever since the accidental discovery of 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaazacyclooctadecane (dibenzo-18-crown-6) by Perderson during the preparation of bis (*o*-hydroxy phenoxy) ethyl ether, a large number of similar compounds have been synthesized. Besides crown ethers, hundreds of other macrocycles have been synthesized which provide different donor atoms, ring size and ligand geometries [2]. However, all macrocycles are not useful for preparing membrane electrodes. The membrane of a macrocycle is likely to function as a good ISE. The macrocycle shows (i) high complexation or extraction selectivity for a particular metal cation (ii) enough conformational flexibility for rapid ion-exchange (iii) high lipophilicity to remain in the membrane and (iv) moderate molecular weight to allow high mobility.

Macrocycles based membranes have mostly been explored for the determination of alkali or alkaline earth metal ions [3-5] and only few investigations have appeared detailing their use as sensor for other metal ions [6]. Recently, "armed macrocycles" have been used as new type of metal selective reagents which are characterized by parent macrocyclic ligand and a cation-ligating side arm [7,8]. The armed macrocycles topologically lie between crown ethers and cryptands and exhibit both the kinetically fast complexation properties of crown ethers and three dimensional binding characteristics of cryptands which have most widely and successfully been used in ISE studies. The metal binding features are similar to those of naturally occurring ionophores which effectively and selectively transport several metal cations across a biomembrane [9]. A variety of membrane assemblies have been fabricated using crown ethers [10], cyclodextrin [11], calixarenes [12] and surfactants [13]. In addition to crown ethers, other kinds of macrocyclic ligands such as macrocyclic polyamines, polysulfides, cyclic peptides and cyclophones are also the potential membrane materials. Attempts have been made to attach the ligating side arm groups to various macrocyclic ligands [14]. Their target guest species include alkali, alkaline earth and transition metal cations as well as organic substrates [15]. Literature survey reveals that the first Ni-ISE was developed by Pungor and coworkers [16] using Ni-dimethyl glyoxime complex. Later on, heterogeneous membranes of nickel phosphate [17] in paraffin and silicone rubber, bis-2-(ethylhexyl) phosphate [18] in PVC and nickel complex of 1, 4, 8, 11-tetraazacyclotetradecane [19] in araldite were used for preparing electrodes.

It has also been reported that the macrocycle 5, 7, 7, 12, 14, 14-hexamethyl-1, 4, 8, 11-tetraazacyclotetradeca-4, 11-diene diperchlorate from strong complexes with heavy metals [20, 21]. Many workers have been successful in developing electrodes mainly for Ag^+, Pb^{2+} and Zn^{2+} ions. The PVC-based membranes of 1,4-dithia-15-crown-5, 1,4-dithia-12-crown-4 [22], dodecyl-16-crown-5 [23] and dibenzo-15-crown-4 [24] function as efficient electrodes for Ag^+ ions over the concentration range 10^{-6} - 10^{-1} M. These electrodes show high selectivity for Ag^+ over a number of other metals. Lindner and coworkers [25] used PVC based membranes of benzylimino bis-, acetylimino bis- and toluene-*p*-sulphonyl bis-(N-cyclohexyl-N-ethyl acetamide) and phenyliminobis-(N,N-dicyclohexyl acetamide) for developing Zn^{2+} selective electrodes. The electrodes perform as good potentiometric and optical sensors. Other zinc selective electrodes have been reported by Rocheleaw and Purdy [26] who used zinc orthophosphate and zinc mercuric thiocyanate as electroactive materials on a carbon support. The electrodes work well in the concentration range 10^{-5} - 10^{-2} M for Zn^+ but have limitations that Cu^{2+}, Cd^{2+} and Pb^{2+} cause serious interference. A Zn^{2+} selective electrode was used by Obmetko and coworkers [27] for the determination of zinc in Zn-alloys. In this study, the armed macrocycle 5, 7, 7, 12, 14, 14-hexamethyl-1, 4, 8, 11-tetraazacyclotetradeca-4, 11-diene diperchlorate abbreviated as Me_6 (14) diene $\cdot 2HClO_4$ have been explored for polystyrene based Ag^+ and Zn^{2+}-selective electrodes. Further, a new macrocycle 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,7,11,14-tetraene abbreviated as Me_4(14) tetraene has been explored as PVC based Ni^{2+}-selective electrodes. The results of all the investigations are presented in this chapter.

1.2 MEMBRANE MATERIALS

To act as an electrode, the membrane material should be such that only cations or anions are transported. Ideally, even among the cations or anions only one or few should be able to pass through and others not, which will generate selectivity for the particular cation or anion. Various materials such as inorganic and organic ion-exchangers, solid electrolytes, salts of multivalent metals, metal chelates of various ligands, crown ethers, cryptands, calixarenes and other macrocycles have been used as materials for the preparation of membranes to be used in ISE systems. These active components of the membranes are often called electroactive phase or electroactive materials.

1.3 CLASSIFICATION OF ION-SELECTIVE ELECTRODES (ISES)

ISEs have been classified into two broad categories:

Primary electrodes and *Sensitized ISEs*

1.3.1 Primary electrodes

Primary electrodes have further been divided into two classes:

1.3.1.1 Liquid membrane electrodes

The membrane of these electrodes consists of an organic liquid immiscible with water in which an electroactive material, capable of exchange with ions for which the electrode is selective, has been dissolved. The electroactive materials are usually ion-pairs with the cation or anion having a long hydrocarbon chain. The solvent chosen must be insoluble in water, have low vapour pressure, high viscosity and considerable association of the ions in the membranes. Liquid membrane electrodes are better than solid state electrodes in that they exhibit Nernstian response and show better selectivity. However, they are less durable and the exchanger has to be changed from time to time.

1.3.1.2 Solid-state electrodes

The electrodes in which the physical state of the membrane is solid are usually called solid-state electrodes. Depending on the composition of the membrane, these are further subdivided into the following three categories:

(i) Glass electrodes

These electrodes have membranes made of glass of various compositions. Several hundred papers have been published on glass electrodes ever since the discovery that some glass membranes can be used to determine the pH [28-30]. In the early development stage of the glass electrode for pH determination, the interference of strongly alkaline solutions was experienced which is known as alkaline error and was due to electrode's response to alkaline metal ions. It was thus realised that glass electrodes for cations, mainly for alkali and alkaline earth metal ions, can also be prepared. This has been achieved to a great extent by changing the composition of glass.

(ii) Homogeneous solid-state electrodes

These membranes consist of only one or a mixture of two or more electroactive compounds. Such membranes are either the crystals of the electroactive compounds or the powder of electroactive compound pressed in the form of a pellet or disc under high pressure. These membranes are normally not mechanically very stable.

(iii) Heterogeneous solid-state electrodes

The homogeneous solid-state membranes of most of the electroactive materials are normally fragile and tend to crack on continued usage and quite often on storage. As such while preparing the membranes, an inert binder is added to the electroactive compound. The binder and the electroactive compound are thoroughly mixed and a membrane from the mixture is cast. These membranes have been found to be comparatively more stable and have long life. It is important to mention that the amount of inert binder used should be minimum so that contact between the particles of electroactive material is maintained throughout the body of the membrane. The binder which provides matrix support must be chemically inert, hydrophobic, tough, flexible, crack-resistant and should not swell in sample solution. It should also provide an adhesion to the particles of electroactive material [31]. The inert binders which have been used are silicone rubber, poly (vinyl chloride), polyethane, ceramics, polystyrene and epoxy resins.

1.3.2 Sensitized ISEs

The sensitized ISEs are usually modified form of primary electrodes and are used to determine the concentration of gases and organic molecules rather than ions. They are of two types :

1.3.2.1 Gas-sensing electrodes

These are the sensors composed of an indicator and a reference electrode in contact with a thin film of an inner electrolyte separated from the bulk of the sample solutions by a gas permeable membrane or an air gap. The diffusion of specific gas through the membrane or an air gap alters an equilibrium with in the inner electrolyte in which a way so as to produce a change in the constituent (e.g. the H^+ activity) of the inner electrolyte being measured. This change is then sensed by an ISE and is related to the partial pressure of the gaseous species in the sample.

1.3.2.2 Enzyme electrodes

These are the sensors in which an ISE is covered with a coating containing an enzyme which causes the reaction of an organic or inorganic substance (substrate) to produce species to which the electrode responds. Alternatively, the sensor could be covered with a layer of substrate which reacts with the enzyme.

1.4 LITERATURE SURVEY

A number of ISEs using various electroactive materials and binders have been developed in the above categories for a number of cations and anions. Initial investigations and subsequent work done in this field is summarized in review articles published from time to time. Some specialized reviews by Fricke [32], Freiser [33] and Moody [34] provide an extensive and detailed information on this subject. Periodic reviews in "Analytical Chemistry" [35] cover all the recent publications in this field including theory, methodology and applications of ISEs. Significant papers which highlight various aspects of development in this field are presented in subsequent pages under different heads.

1.4.1 Glass Electrodes

The first glass membrane pH electrode had the composition 22% Na_2O, 6% CaO and 72% SiO_2. In the early development stage of glass electrode for pH determination, the interference of strongly alkaline solutions was experienced. This is known as alkaline error and was due to electrode's response to alkali metal ions. It was thus realized that glass electrodes for cations, mainly for alkali metal ions, can also be prepared. This has been achieved to a great extent by changing the composition of glass. The membranes of modified glass composition are found to respond selectively to cations other than hydrogen ions. For example, the membrane of the glass composition 11% Na_2O, 18% Al_2O_3, 71% SiO_2 and 10.6% Na_2O, 10% Al_2O_3, 79.4% SiO_2 respond selectively to sodium ions as compared to other ions [36]. Similarly, the membranes of glass having composition 25% Li_2O, 15% Al_2O_3, 60% SiO_2 perform satisfactorily as Li^+ - selective electrode.

1.4.2 Homogeneous Solid-state Electrodes

The electrodes prepared in this category are mainly made of silver halide, silver sulphide and lanthanum fluoride membranes and are used for the determination of halide, sulphide and silver ions. One of the most successful and important ISE available belongs to this category and is lanthanum fluoride based F^--selective electrode developed by Frant and Ross [37] in 1966. This electrode exhibits Nernstian response for F^- in the concentration range $10^{-6} - 10^{-1}$ M. As the selectivity of this electrode is excellent with only OH^- interference, the electrode has been used for fluoride determination in various samples such as fertilizers, drinking and waste water, minerals, soil, urine, pharmaceuticals, beverages, toothpastes etc. Another important electrode of this class is silver sulphide based membrane electrode that responds to silver and sulphide ions. The electrode is highly selective to Ag^+ , and Hg^{2+} is the only cationic interferent while in S^{2-} determination only CN^- interferes and that too when present in large concentration. Due to poor mechanical stability, later on, homogeneous membranes of silver halide were replaced by heterogeneous membranes.

1.4.3 Heterogeneous Solid-state Electrodes

The electrodes belonging to this category are the most investigated and have been developed for a large number of cations viz., alkali, alkaline earth and few heavy metals.

1.4.3.1 Electrodes for alkali metal ions

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 the early development of ISEs for these metal ions, inorganic ion-exchangers were used as the electroactive materials for preparing the membranes [38], but the electrodes so developed did not show good selectivity. In eighties and nineties, the materials for preparing the membranes of ISEs for alkali metal ions are generally neutral carriers of different types. Most of the Na^+-selective electrodes developed are based on neutral carriers. The electrodes prepared by Wu et al. [39] based on triglycollic bisdiamides and PVC binder showed good selectivity over other alkali and alkaline earth metals and could be used for the determination of sodium in water with high magnesium content. The electrodes based on the membranes of other neutral carriers such as *p*-tert-butylcalix (4) arylacetate [40], bis (12-crown-4) [41], bis [(12-crown-4)-2-ylmethyl]-2-dodecyl-2-methyl malonate [42] and bis (*o*-methoxy) stilbenzo-24-crown-8 [43] were also found to be Na^+-selective and used for its determination in serum. Recently, Lukyanenko et al. [44] have prepared Na^+-selective electrodes using the membranes of the derivatives of 12-crown-3, 13-crown-4 and 16-crown-5 in PVC. These electrodes showed linear response down to 10 μm of Na^+, high selectivity over K^+, Li^+, Ca^+ and Mg^{2+} were used for its determination in biological fluids.

The important Li^+ - selective electrodes were developed using the neutral carriers, N N N′ N′ -tetraisobutylcyclohexane *cis*-1, 2-dicarboxamide [45] and 12-crown-4 [46] with PVC as binder. These electrodes showed a working concentration range of 10^{-5}- 10^{-1} M and were selective over alkali and alkaline earth metals. Later on, the heterogeneous membranes of barium adduct of polyoxypropaneglycol [47], tris-(2-ethyl hexyl) phosphate [48], 2,9-dibutyl-1,10-phenanthroline [49], ionomycin methylester [50], trioctylphosphine oxide [51] and derivatives of 12-crown-4 [52] were investigated for Li^+-selective electrodes. Gadzekpo and coworkers [53] have written a review which summarizes different types of Li^+-selective electrodes, gives their applications and highlights the problems encountered in the determination of lithium in serum.

A number of ISEs have been developed for K^+ in view of the importance of its determination in biological fluids. The first successful commercially available electrode were developed using PVC based membrane of valinomycin, a neutral carrier [54]. The response characteristics of a K^+-selective electrode based on photo-cured polymer membrane containing valinomycin has been used in flow-injection analysis [55]. A number of K^+-selective electrodes based on crown ethers, 4,4'-di-tert-butyldibenzo-30-crown [56], **15,15'** - octamethylene bis (benzo-15-crown-5) [57], 18-crown-6-tungstophosphoric acid precipitate [58] and bis [(benzo-15-crown-5)-15-ylmethyl] pimelate [42] have been prepared. All these electrodes show high selectivity over alkali and alkaline earth metals and have been used for determining potassium in serum and biological fluids.

The development of ISEs for Cs^+ and Rb^+ is much lesser compared to that for Li^+, Na^+ and K^+. This is apparently because of their absence in biological fluids. PVC based membranes of *cis*-bis (crown ethers) and 15-crown-5-phosphotungstic acid precipitates were found to be sufficiently Cs^+-selective [59, 60]. The electrode showed good selectivity for Cs^+ over alkali, alkaline earth and some transition metals. Chen and Feng [61] used cesium tetraphenylborate incorporated in PVC for preparing Cs^+-selective electrode which shows linear response down to 30 μm but suffers from serious interference from K^+ and Rb^+. Jain and coworkers [62] have used epoxyresin based membranes of rubidium tungstoarsenate to prepare sensors for Rb^+ ions. Recently, a membrane sensor based on indanopyrazolo [1, 5-a] pyrimidines showing good selectivity for Rb^+ over alkali and alkaline earth metals has been reported [63].

1.4.3.2 Electrodes for alkaline earth metals

There has been widespread interest in developing ISEs for determining alkaline earth metals as they exist in diverse samples. Little work has been done on the development of ISEs for two alkaline earth metal ions, Mg^{2+} and Sr^{2+}. Only few such electrodes are reported which show interference to other alkaline earth metal ions. Recently, an electrode prepared using a membrane of phenylene bis (ditolylphosphineoxide) in PVC was reported as Mg^{2+}-sensor [64]. The electrode shows good selectivity towards Mg^{2+} over Ca^{2+} and works well in the concentration range $6.0 \times 10^{-5} - 1.0 \times 10^{-1}$ M. Another electrode for Mg^{2+} has been developed by O'Donnell and coworkers [65] using various octamethylene bis (malonic acid diamides) and tris (malonic acid diamides) in PVC with 2-nitrophenyloctyl ether as solvent mediator. The first useful Sr^{2+}-selective electrode was developed by Baumann [66] using strontium complex of polyethylene glycol as electroactive material. The electrode was selective towards Sr^{2+} over Ca^{2+} and other bivalent cations with the exception of Ba^{2+} and Hg^{2+}. Srivastava and coworkers [67] have reported a heterogeneous membrane using hydrous thorium oxide embedded in polystyrene while Jain and coworkers [68] have used strontium tungstoarsenate in araldite for Sr^{2+}-selective electrodes. The membrane electrode [68] has been used as an end point indicator in the potentiometric titration involving Sr^{2+} ions against diammonium hydrogen phosphate.

Ba^{2+}-selective polymeric membrane electrodes have been constructed from lipophilic electrically neutral carriers [69] and neutral carboxylic polyether antibiotic [70, 71] and have been found suitable for the titration of Ba^{2+} in non-aqueous media and for the determination of SO_4^{2-} in the combustion products. The membranes of benzo-15-crown-5 and its Ba-complex prepared by using an epoxy-resin binder, were also found suitable as Ba^{2+}-sensor [72]. These electrodes show good selectivity for Ba^{2+} and the one based on Ba-complex was used for the titration of Ba^{2+} against SO_4^{2-}. Thomas and coworkers [73] have prepared two ISEs for Ba^{2+} which make use of the membranes of nonionic, Antarox CO-880 and its Ba-complex in PVC matrix. The electrodes were assessed for measuring SO_4^{2-} by analate subtraction. Recently, Bouklouze and coworkers [74] have used ethylene / vinyl acetate based membranes of binaphthyl polyether as Ba^{2+} sensors. The sensors work in the concentration range

$3.0 \times 10^{-6} - 1.0 \times 10^{-1}$ M Ba^{2+} and have been used as indicator electrodes for determining the end point in the potentiometric titration of SO_4^{2-} in mineral water.

Amongst the alkaline earth metals, most investigated and developed ISEs are Ca^{2+}-selective electrodes. The first Ca^{2+}-selective electrode was a liquid membrane electrode developed by Ross [75]. It was prepared by using a liquid membrane of didecyl phosphate in di-n-octyl phosphonate. The useful Ca^{2+}-selective electrodes were developed by Thomas, Moody and coworkers [76, 77] by incorporating Ca-bis-[2, 6-dinitro - 4 - (1, 1, 3, 3-tetramethyl butyl)] phenoxide and Ca-bis-[di-{4-(1, 1, 3, 3-tetra methyl butyl) phenyl}] phosphate in PVC. These electrodes have fast response time, show good selectivity for Ca^{2+} over a large number of cations and have a working concentration range of 10^{-6}-10^{-1} M. Neutral carriers, N N N′ N′-tetracyclohexyl-3- oxapentanediamide [78], $\alpha\alpha'$-bis (di- *p*-tolyl-phosphoryl)-*o*-xylene [79] and neutral carboxylic such as ionomycin, lasalacid, monensin, nigericin and salinomycin [70] in PVC show good selectivity for calcium over alkali and alkaline earth metals.

1.4.3.3 Electrodes for some heavy metal ions

The determination of heavy metal ions in water, soil, effluents and other samples is important in view of their toxic nature above certain concentration level. As such, efforts have been made by many researchers in the field of ISEs to develop sufficiently selective sensor for heavy metal ions which may permit quick and reliable estimation. A large number of electrodes have been reported for the estimation of Ag^+, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Mn^{2+}, Pb^{2+}, Au^{3+}, Cr^{3+} and Bi^{3+} etc.

Linder and coworkers [80] have used the membranes of macrocycle, benzyl iminobis-, acetyliminobis- and toluene-*p*-sulphonyl bis-(N-cyclohexyl N-ethylacetamide) and phenyliminobis-(N, N-dicyclohexyl acetamide) in PVC as Zn^{2+} selective electrodes for potentiometric and optical sensors. Other Zn^{2+} - selective electrodes have reported by Rocheleaw and Purdy [81] who used zinc orthophosphate and zinc mercuric thiocyanate as electroactive material on a carbon support. The electrodes work well in the concentration range 10^{-5} - 10^{-2} M for Zn^{2+} but have limitations that Cu^{2+}, Cd^{2+} and Pb^{2+} cause serious interference.

Au^{3+}-selective electrodes were developed mainly for the determination of gold in alloys and minerals. Au^{3+}-selective electrode based on the membrane of tetraphenylarsonium tetrachloroaurate immobilized in PVC was employed for the determination of gold in minerals [82]. The estimation of gold in Ag-Pd-Au alloys could be successfully achieved by Ortuno and coworkers [83] using Au^{3+}-selective electrode based on a mixture of 1,2,4,6-tetraphenylpyridinium tetra chloroaurate, dibutylphthalate and PVC.

Another coated graphite-epoxy ion-selective electrode for Bi^{3+} based on the ion-pair between the [Bi (EDTA)]-anion and tricaprylmethyl ammonium cation (Aliquat 336S) incorporated onto a poly(vinylchloride) (PVC) matrix [84] has been developed by Orlando Fatibello-Filho and Coworkers.

1.5 THE PROBLEM

The literature survey reveals that a number of electrodes have been developed for alkali, alkaline earth and heavy metal ions. For some metal ions the number of electrodes investigated are as much as 25-30. The development of large number of electrodes for a particular metal ion has been due to the efforts made by the researchers to improve various properties such as the working concentration range, selectivity, reproducibility, life time and response time.

Among trivalent ions, a very little work have been done [82, 83, 84]. These electrodes in general, have wide working concentration range, moderate selectivity and high response time. As the determination of Cr^{3+} and Al^{3+} is important because of its widespread occurrence in diverse sample, different food products (Chocolates, Bournvita, Horlicks, Boost). The efforts were to develop Cr^{3+} and Al^{3+} selective electrodes using Ph_4(14)tetraene and Me_8(14)ane as electroactive materials.

So keeping all these things in mind, we have chosen to analyse some trivalent ions, i.e., Cr^{3+} and Al^{3+} by developing ion sensors.

2

THEORY OF MEMBRANE POTENTIALS

2.1 POTENTIAL OF AN ION-EXCHANGE MEMBRANE

A semipermeable ion-exchange membrane is one which allows the counter ion A to permeate through and restricts the Co-ion,Y . A membrane potential (E_m) is developed when it separates two solutions 1 and 2 containing the counter ion A, due to the diffusion of counter ions from higher to lower concentration and given by the following 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, A = counter ion, Y = Co-ion, Z = charge on ions, t_y = transference number of Co-ion, $a_\pm$ = mean ionic activity of the electrolyte, and $(a_A)_1$ and $(a_A)_2$ represent activities of the counter ions in solutions 1 and 2.

In the above expression, the right hand side consists of two terms. The first term gives the thermodynamic limiting value of the concentration potential and the second term denotes the diffusion potential due to Co-ion flux in the membrane. If the membrane is ideally permselective membrane ($t_y = 0$), then the equation (1) reduces to

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

The equation (2) is similar to so - called Nernst equation and represents Donnan potential for an ideally permselective membrane. Equation (2) takes +ve sign for cations and -ve sign for anions.

The membrane potential measurement is carried out by setting up a cell of the following type:

Solution 2 **Solution 1**

External saturated calomol electrode (SCE)	Test solution or external solution	Membrane	Internal solution	Internal saturated calomel electrode (SCE)

$E_{L(2)}$ $E_{L(1)}$

As a general practice, the concentration of one of the solutions (say 1) is maintained constant (usually 0.1 M) and this solution is referred to as internal solution. Saturated calomel electrode dipped in this internal solution is called internal reference electrode. The membrane together with internal solution and internal reference electrode is one compact unit which as a whole, is called membrane electrode. This membrane electrode is then immersed in solution 2, usually referred to as external solution or test solution, having a SCE as an external reference electrode. The emf of this potentiometric cell is given by the following expression:

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

where, E_{cal} , E_L and E_m refer to calomel electrode, junction and membrane potentials, respectively. Combining equations (2) and (3), the equation (3) takes the form

$$E_{cell} = E_{cal} - E_{cal} + E_{L(1)} + E_{L(2)} \pm \frac{RT}{Z_A F} l_n \frac{(a_A)_2}{(a_A)_1} \qquad (4)$$

For cation exchange membrane,

$$E_{cell} = \left[E_{L(1)} + E_{L(2)} - \frac{RT}{Z_A F} l_n (a_A)_1 \right] + \frac{RT}{Z_A F} l_n (a_A)_2 \qquad (5)$$

As the activity of the internal solution is kept constant and the values of $E_{L(1)}$ and $E_{L(2)}$ remain constant, the term in the parenthesis may be taken equal to a constant E^o. The equation (5) now reduces to

$$E_{cell} = E^o + \frac{RT}{Z_A F} l_n (a_A)_2 \qquad (6)$$

It is evident from equation (6) that the cell potential is directly proportional to the concentration (or activity) of the cation in the external or test solution. At 25°C, the value of $2.303\ RT/Z_A F$ is $0.59/Z_A$ volts. The membrane is said to give 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 called Nernst plots and the slope as Nernstian slope.

The degree of selectivity of the electrode for primary ion A, with respect to an interfering ion B, is expressed by the potentiometric selectivity coefficient $K^{pot}_{A,B}$ and is defined by the following Nikolskii equation

$$E = E^{o} + \frac{2.303RT}{Z_A F} \log\left[a_A + K^{pot}_{A,B} (a_B)^{Z_A/Z_B}\right] \quad (7)$$

where Z_A, Z_B and a_A, a_B are the charges and activity of ions A and B, respectively.

Several methods have been described for the experimental determination of selectivity coefficients [85]. These methods fall into two categories:

2.1.1 Separate Solution Method (SSM)

In this method, the membrane potentials of the electrode E_A and E_B, are measured separately in solutions containing A only of activity a_A (no B present) and B only of activity a_B (no A present), respectively. E_A and E_B are given by the following equations :

$$E_A = E^{o} + \frac{RT}{Z_A F} l_n\, a_A \quad (8)$$

$$E_B = E^{o} + \frac{RT}{Z_A F} l_n\, K^{pot}_{A,B} (a_B)^{Z_A/Z_B} \quad (9)$$

From equations (8) and (9)

$$\log K^{pot}_{A,B} = \frac{E_B - E_A}{2.303RT / Z_A F} + \log \frac{a_A}{(a_B)^{Z_A/Z_B}} \quad (10)$$

The term 2.303 RT/Z_AF is the slope of the Nernst plot. As most of the solid membranes exhibit deviation from Nernstian behaviour, the experimental slope (S), usually differs from the theoretical slope i.e. 2.303 RT/Z_AF. Thus, it is a practice to use `S' instead of Nernstian slope for the calculation of $K^{pot}_{A,B}$. As such equation (10) takes the form

$$\log K^{pot}_{A,B} = \frac{E_B - E_A}{S} + \log \frac{a_A}{(a_B)^{Z_A/Z_B}} \quad (11)$$

Thus, using equation (11) selectivity coefficients $K^{pot}_{A,B}$ can be calculated.

2.1.2 Mixed Solution Method

This method involves the measurement of the electrode potential in a range of solutions containing both A and B of different activities. There are two procedures for determining selectivity coefficients using MSM.

Procedure I

In this procedure, the potentials of the electrode E_A and E_{AB} are measured in solutions of primary ion A only and a mixture of primary and interfering ion B, respectively. E_{AB} would correspond to equation (7) and E_A to equation (8). From equations (7) and (8), the following equation (12) is obtained

$$K_{A,B}^{pot} = \frac{a_A}{(a_B)^{Z_A/Z_B}}\left[\left(10^{\frac{E_{AB}-E_A}{2.303RT/Z_AF}}\right)-1\right] \qquad (12)$$

which gives the value of selectivity coefficient.

Procedure II

When electrode potential measured in a number of solutions of varying a_A and constant a_B is plotted against the activity a_A a curve of the type shown in Fig. A is obtained. This plot generally has three distinct regions.

In the first region PQ, the response of the electrode is linear which indicates that the electrode is responding only to primary ion A with no interference caused by B in this concentration range. In the second region QR, derivation from linearity is caused because now the electrode also responds to the activity of B as the concentration of A decreases. So, in this region (QR), the response of the electrode is mixed and is due to both the ions A and B. The third region indicates that the electrode 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 electrode 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 following equation is obtained from equation (10)

$$K_{A,B}^{pot} = \frac{a_A}{(a_B)^{Z_A/Z_B}} \qquad (13)$$

Equation (13) is used to calculate selectivity coefficients. 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.

2.2 DETERMINATION OF FUNCTIONAL PROPERTIES OF MEMBRANES

The prerequisite for understanding the performance of an ion-exchange membrane is its complete physico-chemical characterisation which involves the determination of all such parameters which affects its electrochemical properties. These parameters are porosity, electrolyte absorption, water content, swelling and electrical conductance. Standard methods used for the determination of functional properties are as follows :

2.2.1 Porosity

The stability, response time and selectivity of an electrode is influenced by the diameter and the multiplicity of the membrane pores. Mizutani and Nishimura [86] gave the method for the estimation of porosity of membrane which is calculated from water content data by using the following formula :

$$\Sigma = \frac{\text{water content}}{A \, . \, L \, . \, \rho_w}$$

where,

A = Area of the membrane, L = Thickness and ρ_w = Density of water.

2.2.2 Electrolyte Absorption

The membrane after attaining equilibrium in 1.0 M NaCl solution was wiped free of adhering electrolyte and then dipped in 20 ml distilled water. It was shaken intermittantly and left as such for few hours. The soution was then transferred to a 100 ml measuring flask. The whole process was repeated three to four times and the entire solution was collected in a measuring flask. It was finally made upto the mark by distilled water and the strength was measured conductometrically.

2.2.3 Water Content

Membrane was kept immersed in a solution of 1.0 M concentration of electrolyte. It was then washed several times with distilled water and the adhering liquid was wiped off with blotting paper. Then the membrane was weighed and dried to a constant weight in a vacuum dessiccator. The difference in the two weighings, divided by the weight of the wet membrane was taken as the water content.

2.2.4 Swelling

After measuring the thickness of the dry membrane, it was immersed into 1.0M solution of NaCl for 24 h and again the thickness was measured after wiping with blotting paper. Difference between the thickness of dry and swollen membrane was taken as a measurement of swelling.

2.2.5 Electrical Conductance

Lakshminarayanaih and Subrahmanyam [87] adopted a method in which mercury pool was used on both sides of the membrane to minimize polarisation at the membrane interface.

The membrane was cemented in between the two half cells with Araldite and kept in contact with electrolyte solution of desired concentration. The solution was then replaced by mercury previously equilibrated with the electrolyte solution of the same concentration. The conductance was determined by connecting the platinum electrode to the conductivity bridge.

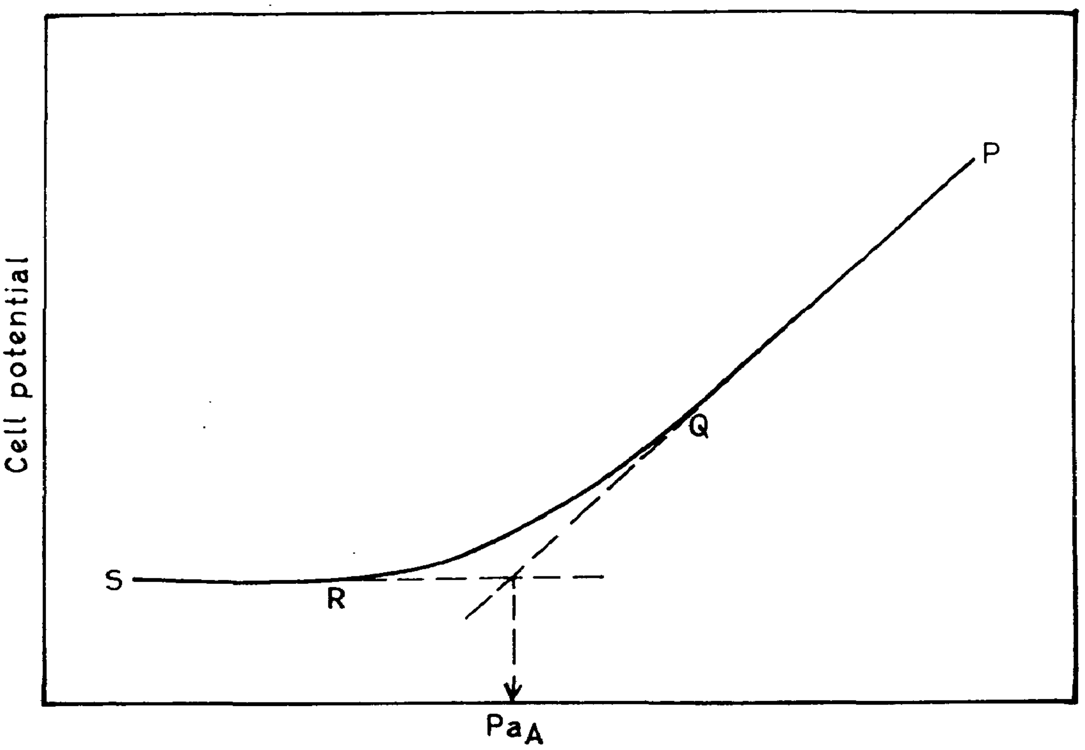

Fig. A : Calibration curve illustrating determination of selectivity coefficient by fixed interference method.

3

EXPERIMENTAL

3.1 REAGENTS

All chemicals used in these studies were analytical grade reagents. Following chemicals were used without purification :

Dibutyl (butyl) phosphate (DBBP), dibutyl phthalate (DBP) (CDH, India), tributyl phosphate (TBP) (BDH, England), tris (2-ethylhexyl) phosphate (TEP), sodium tetraphenyl borate (STB), molecular weight poly (vinyl chloride) (PVC) (BDH, Englnd), Polystyrene (finely grinded) and tetrahydrofuran (THF) (s.d. Fine Chem., India). Sensor materials Ph_4 (14)tetraene and Me_8(14)ane were prepared from literature method. All solution were prepared in double distilled water.

3.2 INSTRUMENTATION

All potential and pH measurements were made on a Electronic Corporation of India Ltd. (ECIL), digital pH meter (model pH 5652).

3.3 SYNTHESIS OF MACROCYCLES

3.3.1 Synthesis of 2,4,9,11-tetraphenyl-1,5,8,12-tetraazacyclotetradeca-1,4,8,11-tetraene [Ph_4(14)tetraene]

6.68 ml (0.1 mol) of ethylenediamine was dissolved in a minimum quantity of methanol and cooled in an ice bath to about 5°C. To this 22.42 g (0.1 mol) of 1,3-diphenyl-1,3-propanedione, diluted with 10 cm^3 of methanol was added. The solution was slowly heated to reflux for 4 h. The solution was then cooled and few drops of perchloric acid was added. Fine crystals of ligand was obtained and washed with a small quantity of ether and then recrystallised with methanol.

3.3.2 Synthesis of 3,10-C-meso-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetrazacyclo tetradecane [Me_8(14)ane]

The ligand 3,10C-meso-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclo tetradeca-4,11-diene dihydroperchlorate [88] abbreviated as 3,10C-meso-Me_8(14)diene·$2HClO_4$ was prepared by the method followed by Busch [89]. The reduction of $Me_8(14)$diene to yield the $Me_8(14)$ane has been carried by the reduction process adopted by Kolinski [90].

3.4 PREPARATION OF POLY (VINYL CHLORIDE) BASED MEMBRANES

Poly (vinyl chloride) (PVC) has been most widely used binder for preparing heterogeneous solid-state membranes as it satisfies most of the requirements for a successful binder. Its small amount is enough to provide adequate mechanical strength which increases the electrodes life to a substantial extent. With PVC matrix support, different membranes showing varying performance can be prepared by using various plasticizers. Thomas and Moody [34] are the pioneers in developing PVC based electrodes and have recommended PVC as the most significant polymer matrix. An important requirement for making PVC membranes of exchangers is that both exchanger and PVC should be soluble in some fast evaporating solvent, usually THF.

A known amount of sensor material was first dissolved in required amount of THF. High molecular weight PVC powder was then added to this solution. After thorough mixing, the resulting solution was poured into a glass casting ring (diameter 10 mm) resting on a glass plate. The solution should be poured gently so that bubbles are not formed. This solution was left for THF to evaporate off. After the evaporation of THF, the solid PVC membrane sticking to the glass plate was removed and glued to one end of a "pyrex" glass tube with araldite. The thickness of the membranes so prepared was ~ 0.5 mm.

3.5 PREPARATION OF POLYSTYRENE BASED MEMBRANES

Polystyrene based membranes were prepared by taking different compositions of the ionophore and polystyrene and the mixture was heated to 80°C under pressure (6000 to 6500 psi) in a die kept in a metallurgical specimen mount press. Membranes were fabricated under optimum conditions of temperature and pressure which were fixed up after a great deal of preliminary investigations. Membranes prepared in this way were quite stable and did not show any dispersion in water or in other electrolyte solutions.

The membranes were also subjected to microscopic and electrochemical examination for cracks and homogeneity of the surface and only those which has smooth surface and generated reproducible potentials were chosen for subsequent investigations. Membrane to membrane (and batch to batch) reproducibility was assured by carefully controlling the conditions of fabrications.

4

RESULTS & DISCUSSION

4.1 MEMBRANES OF Ph_4 (14)tetraene AS Cr (III) - SELECTIVE ELECTRODE

4.1.1 Composition of membranes

Heterogeneous membranes of Ph_4(14)tetraene and polystyrene of different compositions (w/w) were prepared at a temperature of 75-80°C and under a pressure of 6000-6500 psi. The membranes with macrocycles, STB and polystyrene in the ratio 10:1:1 show the large response time with less Nernstian potential response whereas membranes having macrocycle, STB and polystyrene in the ratio 2:1:1 and 8:1:1 (w/w) showed a fast response time (20s) and near Nernstian slopes (22.2 and 19.5 mV/ decade), respectively. The membrane with macrocycle, STB and polystyrene in the ratio 4:1:1 and 6:1:1 (w/w) showed near Nernstian slopes (17.3 and 19 mV/decade) with a response time of 15 and 20s, respectively. Thus, from the above investigations it was found that the membrane no. 2 (table 2) having macrocycle : STB : polystyrene in the ratio 4:1:1 is the best and therefore, studied in detail as Cr^{3+}-selective electrode.

4.1.2 Working concentration range and slope

The membrane to be used in ISEs should generate noiseless and reproducible potentials. These characteristics depend on the perfect equilibrium of the membranes. Imperfect equilibrium give rise to erratic potentials and large response time. The membranes were equilibrated with 1.0 M $CrCl_3$ solution before starting any potential studies. It was found that the equilibration time of 5 days was optimum as the equilibrated membrane gave reproducible potentials and no drift in potential was observed. The potentials of the cell were measured with a fixed concentration (0.1M) of Cr^{3+} as internal solution and varying the Cr^{3+} concentration in test solutions in the range 1.0×10^{-7} - 1.0×10^{-1} M. The potentials observed are plotted against Cr^{3+} concentration in Fig. 1. It is seen from Fig. 1 that the membrane (no. 2) shows linear response in the concentration range 3.16×10^{-6} - 1.00×10^{-1} M with a slope of 17.3 mV per decade of concentration.

4.1.3 Response and life time

The time taken by the electrode assembly to attain a stable potential is taken as the static response time. It was determined for all the membranes and mention in the Table 2. It is seen from the table that the static response time of the membrane sensor is found to be < 15s at all dilutions. Besides this, the potential generated across the membrane were reproducible and the membrane could be successfully used over a period of 4 months without any appreciable drift in potential. The membranes were stored in 0.1 M Cr^{3+} solution when not in use.

4.1.4 pH and solvent effect

The effect of pH on the potential response of these Cr^{3+} - selective electrodes was studied by changing the pH of test solution with HNO_3 and NaOH. This effect was studied at 1.0 x 10^{-2} M of Cr^{3+} ions. The results are shown in Fig. 2 and it is seen that potential is not affected by pH in the range 3.0-6.5. Thus, the electrode to be used in this pH range. The sharp change in potentials at lower pH values (< 3) appears to be due to interference caused by H^+ - ions while at higher pH values (> 6.5) it may be attributed due to the hydrolysis of Cr^{3+}. The performance of this electrode was also investigated partially non-aqueous medium using methanol-water and ethanol-water mixture (Table 4). Potential vs concentration plots in 15%, 25% and 35% (v/v) methanolic and ethanolic solution are shown in Fig. 3 and Fig. 4, respectively. The electrode assembly works satisfactorily upto a 25% (v/v) methanolic and ethanolic content. In these mixtures, the working concentration range and slope remain unchanged.

4.1.5 Selectivity

The selectivity of the electrode was determined by IUPAC recommended Fixed Interference Method (FIM) at 1.0 x 10^{-2} M concentration of interfering ion. A persual of selectivity coefficient data presented in Table 5 shows that the electrode is moderately selective over a number of mono, bi and trivalent cations listed in. Thus, these ions would not cause any significant interference in the determination of Cr^{3+}.

4.1.6 Conclusion

The results of these investigations review that the electrode are having macrocycle, STB and polystyrene in the ratio 4:1:1 as membrane gradient is the best. The electrode works satisfactorily in the concentration range 3.16×10^{-6} - 1.00×10^{-1} M with near Nernstian slope of 17.3 mV per decade of concentration between pH 3.0-6.5.

4.2 MEMBRANES OF Me_8(14)ane AS Cr (III) - SELECTIVE ELECTRODE

4.2.1 Composition of membranes

Heterogeneous membranes of Me_8(14)ane were prepared by dissolving the macrocycle and PVC in diluent THF. The ratio of macrocycle to PVC was varied in order to obtain a composition which gives the membrane showing best performance with regard to working concentration range, slope and response time and it was found that the membrane having 20 mg macrocycle and 160 mg PVC and 20 mg STB exhibited the best results (Fig. 5, Table 6). Further, the effect of plasticizers (solvent mediators) which are used frequently to improve the electrochemical properties of PVC membranes was also studied. For this purpose solvent mediators viz., DBBP, DBP, TBP and TEP were tried.

4.2.2 Working concentration range and slope

The membrane to be used as a sensor, should be capable of generating reversible, noiseless and reproducible potential. These characteristics to a large extent, depend on satisfactory equilibration of membranes. Eratic potentials and large response time arises due to imperfect equilibration. So it is quite essential to optimize the concentration of the contacting solution and the time of equilibrium. The membranes were equilibrated with 1.0M $CrCl_3$ solution before starting any potential studies. It was found that the equilibration time of 4 days was optimum as the equilibrated membranes gave reproducible potentials and no drift in potentials was observed. The potentials of the cell were measured with a fixed concentration (0.1 M) of Cr^{3+} as internal solution and varying the Cr^{3+} concentration in test solutions in the range 1.0×10^{-7} - 1.0×10^{-1} M. The potentials observed are plotted against Cr^{3+} concentration in Fig. 5. It is seen from

Fig. 5 that the membrane (no. 1) having composition 20 mg macrocycle and 160 mg PVC and 20 mg STB shows linear potential response in the concentration range 2.1 x 10^{-6} - 1.0 x 10^{-1} M with a slope of 21.7 mV per decade of concentration. Further, the addition of plasticizer DBP, DBBP, TEP and TBP to membranes was tried and it was observed that the addition of DBBP, TBP and TEP did not contribute significant improvement in working concentration range while the solvent mediator DBP enhanced the working concentration range 1.77 x 10^{-6} - 1.00 x 10^{-1} M with a slope of 20 mV per decade. As observed from Fig. 5 the best performance with regard to concentration range and slope is given by membrane no. 3 containing DBP as the plasticizer.

4.2.3 Response and life time

The time taken by the electrode assembly to attain a stable potential is taken as the static response time. It was determined for all the membranes and mention in the Table 6. It is seen from the table that for the membrane no. 1, which has membrane without plasticizers, the response time is sufficiently high. This high response time makes the membranes less useful. However, with the addition of plasticizers DBBP, DBP, TBP and TEP to the membrane (nos. 2,3,4 and 5) response time is sufficiently reduced to about 15s. Thus in terms of response time the membrane with plasticizers are better than the electrodes having membranes without plasticizers. The potential generated across the membrane were reproducible and the membrane could be successfully used over a period of 4 months without any appreciable drift in potential. The membrane were stored in 1.0 M Cr^{3+} solution, when not in use.

4.2.4 pH and solvent effect

The effect of pH on the potential response of these Cr^{3+} - selective electrodes was studied by changing the pH of test solution with HNO_3 and NaOH. This effect was studied at concentration 1.0 x 10^{-2} M of Cr^{3+} ion. The results are shown in Fig. 6 and it is seen that the potential is not effected by pH in the range 3.0 - 6.5. Thus, the electrode can to be used in this pH range. The sharp change in potential at lower pH values (< 3.0) appears to be due to interference caused by H^+ ions, while at higher pH values (> 6.5) it may be attributed due to the hydrolysis of Cr^{3+}. The performance of this electrode was also investigated in partially non-aqueous medium using methanol-water and ethanol-water mixtures (Table 8).

Potential vs concentration plots in 15%, 25% and 35% (v/v) methanolic and ethanolic solutions are shown in Fig. 7 and Fig. 8 respectively. The electrodes assembly works satisfactorily upto 25% (v/v) methanolic and ethanolic content as in this mixture the working concentration range and slope remain unchanged.

4.2.5 Selectivity

In order to assess the selectivity of the electrode 3, the effect of a number of interfering ions at 1.0×10^{-2} M concentration level on the membrane potential was determined by Fixed Interference Method. The values of potentiometric selectivity coefficients calculated are given in table 9.

4.2.6 Conclusion

The results of these investigations reveal that the electrode having 20 mg $Me_8(14)$ane, 100 mg PVC, 10 mg STB and 70 mg solvent mediator DBP as membrane gradients is the best. The electrode works satisfactorily in the concentration range $1.77 \times 10^{-6} - 1.00 \times 10^{-1}$ M with near Nernstian slope of 20 mV per decade of concentration between pH range 3.0-6.5.

4.3 MEMBRANES OF $Me_8(14)$ane AS Al(III) - SELECTIVE ELECTRODE

4.3.1 Composition of membranes

In order to have a comparative assessment of species, PVC based membrane of $Me_8(14)$ane can be proposed as a sensor, its performance is also assessed for Al(III) ions. Fig. 9 (Table 10) shows that the same electrode for Al(III) ions exhibited the best results.

4.3.2 Working concentration range and slope

The membrane were equilibrated with 1.0 M $AlCl_3$ solution before starting any potential studies. It was found that the equilibration time of 4 days was optimum.

The equilibrated membrane was interposed between the test ($[Al]^{3+} = 1.0 \times 10^{-7}$ to 1.0×10^{-1} M) and internal reference solution ($[Al]^{3+} = 1.0 \times 10^{-1}$ M) and potentials are depicted in Fig. 9. It is seen from Fig. 9 that the membrane no. 1 having composition 20 mg macrocycle, 160 mg PVC and 20 mg STB shows linear potential response in the concentration range $1.58 \times 10^{-6} - 1.00 \times 10^{-1}$ M with a slope of 21.8 mV per decade of concentration. Further the addition of plasticizer DBP, DBBP, TEP and TBP to membranes was tried and it was observed that the addition of DBBP, TBP and TEP did not contribute significant improvement in working concentration range while the solvent mediator DBP enhanced the working concentration range $1.00 \times 10^{-6} - 1.00 \times 10^{-1}$ M with a slope of 20 mV per decade. As observed from Fig. 9, the best performance with regard to concentration range and slope is given by membrane no. 2 containing DBP as plasticizer.

4.3.3 Response and life time

The static response time of the membrane sensor having DBP over the entire linear concentration range of Al^{3+} ions is 10 seconds, while the response time is sufficiently high for the membrane without plasticizer (Table 10). This high response time makes the membranes less useful. The potential generated across the membrane were reproducible and the membrane could be successfully used over a period of 4 months without any appreciable drift in potential.

4.3.4 pH and solvent effect

The pH dependence of the membrane sensor has been tested at the concentration 1.0×10^{-2} M of Al^{3+} ions. The pH of the solutions was adjusted by the addition of HNO_3 and NaOH. The results are shown in Fig. 10 and it is seen that the potential is not affected by pH in the range 2.5-7.0. Thus, the electrode can to be used in this pH range. The sharp change in potentials beyond this range (< 2.5 and > 7.0) may be due to competitive influence of H^+ and OH^- ions. The performance of the proposed electrode system was also investigated in partially non-aqueous media using methanol-water and ethanol-water mixture.

Potential vs concentration plots in 15%, 25% and 35% (v/v) methanolic and ethanolic solutions are shown in Fig. 11 and Fig. 12, respectively. The electrodes assembly works satisfactorily upto 25% (v/v) methanolic and ethanolic content as in this mixture the working concentration range and slope remain unchanged (Table 12).

4.3.5 Selectivity

In order to assess the selectivity of the electrode, the effect of a number of interfering ions at 1.0 x 10^{-2} M concentration level on the membrane potential was determined by Fixed Interference Method. The values of potentiometric selectivity coefficients calculated are given in Table 13.

4.3.6 Conclusion

The results of these investigations reveal that the electrode having 20 mg macrocycle, 100 mg PVC, 10 mg STB and 70 mg DBP as solvent mediator shows best working concentration range 1.00 x 10^{-6} – 1.00 x 10^{-1} M with near Nernstian slope 20 mV per decade of concentration between pH range 2.5-7.0.

5

TABLES

Table 1 : Functional properties of polystyrene based membrane of macrocycle Ph_4(14)tetraene

Membrane	*Water content per gm. of wet membrane $g(H_2O)/g$ (w. mem.)*	*Porosity*	*Swelling per gram (mm)*	*Amount of electrolyte absorbed per gram of wet membrane (moles)*
Ph_4 (14)tetraene	0.0284	0.0305	0.213	$4{\cdot}7 \times 10^{-2}$

Table 2 : Composition of polystyrene based membranes of Ph_4(14)tetraene and performance characteristics of Cr^{3+} - selective electrodes based on them.

Membrane No.	*Composition in ratio (w/w)*			*Working concentration range (M)*	*Slope (mV/decade) $[Cr^{3+}]$*	*Response time (S)*
	Ionophore [(Ph_4(14)tetraene]	*Binder (Polystyrene)*	*STB*			
1	2	1	1	$9.44 \times 10^{-6} - 1.00 \times 10^{-1}$	22.2	20
2	4	1	1	$3.16 \times 10^{-6} - 1.00 \times 10^{-1}$	17.3	15
3	6	1	1	$7.06 \times 10^{-6} - 1.00 \times 10^{-1}$	19.0	20
4	8	1	1	$1.58 \times 10^{-5} - 1.00 \times 10^{-1}$	19.5	20
5	10	1	1	$1.12 \times 10^{-5} - 1.00 \times 10^{-1}$	17.3	30

Table 3 : **Variation in membrane potential of Ph_4(14)tetraene based membrane electrode systems in Cr^{3+} solution of different concentration with an internal reference solution of concentration = 1.0 × 10^{-1} M.**

Test solution M	*Potential observed (- mV) Membrane nos.*				
	1	*2*	*3*	*4*	*5*
1.0 × 10^{-7}	87	85	81	79	74
5.0 × 10^{-7}	87	85	81	79	74
1.0 × 10^{-6}	87	85	81	79	74
5.0 × 10^{-6}	86	81	81	79	73
1.0 × 10^{-5}	83	76	78	78	73
5.0 × 10^{-5}	71	63	65	68	61
1.0 × 10^{-4}	65	57	59	62	55
5.0 × 10^{-4}	50	44	45	47	42
1.0 × 10^{-3}	43	38	40	42	37
5.0 × 10^{-3}	28	25	26	27	25
1.0 × 10^{-2}	23	19	20	21	19
5.0 × 10^{-2}	7	6	6	7	6
1.0 × 10^{-1}	0	0	0	0	0

Table 4 : **Performance of Ph_4 (14)tetraene based membrane no. 2 for Cr^{3+} in 15, 25 and 35% (v/v) non-aqueous medium.**

Percentage (v/v)	*Slope (mV/decade of concentration)*	*Working concentration range (M)*
Nil	17.3	3.16×10^{-6}
Methanol		
15	17.7	3.16×10^{-6}
25	19.0	3.16×10^{-6}
35	21.0	3.98×10^{-5}
Ethanol		
15	17.0	3.16×10^{-6}
25	17.5	3.16×10^{-6}
35	18.6	4.46×10^{-5}

Table 5 : Selectivity coefficient values ($K^{pot}_{Cr^{3+}}$, B) for Cr^{3+}- selective Ph_4 (14) tetraene based solid membrane electrode for chromium ions.

Interfering ions (B)	*Selectivity coefficients by fixed interference method (at 1.0 × 10^{-2} M concentration of interfering ions)*
NH_4^+	1.50 × 10^{-1}
Na^+	1.30 × 10^{-1}
K^+	1.50 × 10^{-1}
Li^+	1.80 × 10^{-1}
Mg^{2+}	1.49 × 10^{-2}
Ca^{2+}	1.12 × 10^{-2}
Sr^{2+}	1.12 × 10^{-2}
Ba^{2+}	1.49 × 10^{-2}
Co^{2+}	1.12 × 10^{-2}
Cd^{2+}	1.12 × 10^{-2}
Pb^{2+}	9.44 × 10^{-3}
Hg^{2+}	1.33 × 10^{-2}
Zn^{2+}	1.12 × 10^{-2}
Ni^{2+}	1.49 × 10^{-2}
Cu^{2+}	1.12 × 10^{-2}
Fe^{3+}	1.33 × 10^{-3}
Al^{3+}	1.19 × 10^{-3}

Table 6 : Composition of PVC membranes of Me_8(14)ane and performance characteristics of Cr^{3+}-selective electrodes based on them

Membrane number or Electrode number	*Composition of membrane*							*Working concentration range (M)*	*Slope (mV/ decade of concentration)*	*Response time (s)*
	Me_8(14)ane	*PVC*	*DBP*	*DBBP*	*TEP*	*TBP*	*STB*			
1	20	160	-	-	-	-	20	$2.10\times10^{-6} - 1.00\times10^{-1}$	21.7	40
2	20	100	-	70	-	-	10	$5.30\times10^{-6} - 1.00\times10^{-1}$	22.5	25
3	20	100	70	-	-	-	10	$1.77\times10^{-6} - 1.00\times10^{-1}$	20.0	15
4	20	90	-	-	-	70	20	$5.02\times10^{-6} - 1.00\times10^{-1}$	18.4	20
5	20	90	-	-	70	-	20	$5.02\times10^{-6} - 1.00\times10^{-1}$	20.0	25

Table 7 : **Variation in membrane potential of $Me_8(14)$ane membrane electrode systems in Cr^{3+} solution of different concentration with an internal reference solution of concentration = 1.0×10^{-1} M.**

Test solution (M)	*Potential observed (- mV) Membrane nos.*				
	1	*2*	*3*	*4*	*5*
1.0×10^{-7}	98	86	92	80	83
5.0×10^{-7}	98	86	92	80	83
1.0×10^{-6}	98	86	92	80	83
5.0×10^{-6}	91	85	83	79	81
1.0×10^{-5}	84	80	78	74	77
5.0×10^{-5}	69	67	64	62	64
1.0×10^{-4}	63	61	58	56	58
5.0×10^{-4}	48	47	45	43	45
1.0×10^{-3}	42	40	39	37	39
5.0×10^{-3}	27	26	25	24	25
1.0×10^{-2}	21	20	19	19	19
5.0×10^{-2}	7	6	6	6	6
1.0×10^{-1}	0	0	0	0	0

Table 8 : Performance of $Me_8(14)$ane based membrane no. 3 for Cr^{3+} in 15, 25 and 35% (v/v) non-aqueous medium.

Percentage (v/v)	*Slope (mV/decade of concentration)*	*Working concentration range (M)*
Nil	20.0	1.77×10^{-6}
Methanol		
15	20.0	1.77×10^{-6}
25	20.0	1.77×10^{-6}
35	22.0	2.20×10^{-5}
Ethanol		
15	20.0	1.77×10^{-6}
25	20.0	1.77×10^{-6}
35	23.3	4.20×10^{-5}

Table 9 : Selectivity coefficient values ($K^{pot}_{Cr^{3+},B}$) for Cr^{3+}-selective Me_8(14)ane based solid membrane electrode for chromium ions.

Interfering ions (B)	*Selectivity coefficients by fixed interference method (at 1.0 × 10^{-2} M concentration of interfering ions)*
NH_4^+	2.1×10^{-1}
Li^+	1.9×10^{-1}
Na^+	1.0×10^{-1}
K^+	1.0×10^{-1}
Rb^+	1.21×10^{-2}
Cs^+	7.94×10^{-3}
Co^{2+}	1.77×10^{-2}
Hg^{2+}	1.77×10^{-2}
Ca^{2+}	1.34×10^{-2}
Zn^{2+}	1.34×10^{-2}
Pb^{2+}	1.12×10^{-2}
Cd^{2+}	9.62×10^{-3}
Cu^{2+}	8.91×10^{-3}
Ni^{2+}	8.91×10^{-3}
Ba^{2+}	7.94×10^{-3}
Sr^{2+}	3.98×10^{-3}
Mg^{2+}	7.94×10^{-3}
Fe^{3+}	6.60×10^{-4}
Al^{3+}	6.31×10^{-4}

Table 10 : Composition of PVC membranes of $Me_8(14)$ane and performance characteristics of Al^{3+}-selective electrodes based on them

Membrane number or Electrode number	*Composition of membrane*							*Working concentration range (M)*	*Slope (mV/ decade of concentration)*	*Response time (s)*
	$Me_8(14)$ane	*PVC*	*DBP*	*DBBP*	*TEP*	*TBP*	*STB*			
1	20	160	-	-	-	-	20	$1.58\times10^{-6} - 1.00\times10^{-1}$	21.8	35
2	20	100	70	-	-	-	10	$1.00\times10^{-6} - 1.00\times10^{-1}$	20.0	10
3	20	100	-	70	-	-	10	$2.82\times10^{-6} - 1.00\times10^{-1}$	22.2	25
4	20	90	-	-	-	70	20	$3.98\times10^{-6} - 1.00\times10^{-1}$	22.0	25
5	20	90	-	-	70	-	20	$3.16\times10^{-6} - 1.00\times10^{-1}$	20.0	20

Table 11 : **Variation in membrane potential of $Me_8(14)$ane based membrane electrode systems in Al^{3+} solution of different concentration with an internal reference solution of concentration = 1.0×10^{-1} M.**

Test solution (M)	*Potential observed (– mV)* *Membrane nos.*				
	1	*2*	*3*	*4*	*5*
1.0×10^{-7}	109	104	100	95	90
5.0×10^{-7}	109	104	100	95	90
1.0×10^{-6}	109	102	100	95	90
5.0×10^{-6}	98	90	95	92	85
1.0×10^{-5}	91	83	88	87	80
5.0×10^{-5}	75	68	73	71	66
1.0×10^{-4}	68	63	66	65	60
5.0×10^{-4}	52	49	51	50	46
1.0×10^{-3}	46	42	44	43	40
5.0×10^{-3}	30	27	30	28	26
1.0×10^{-2}	23	21	23	21	20
5.0×10^{-2}	7	6	7	6	6
1.0×10^{-1}	0	0	0	0	0

Table 12 : Performance of $Me_8(14)$ane based membrane no. 2 for Al^{3+} in 15, 25 and 35% (v/v) non-aqueous medium.

Percentage (v/v)	*Slope (mV/decade of concentration)*	*Working concentration range (M)*
Nil	20.0	1.00×10^{-6}
Methanol		
15	20.0	1.00×10^{-6}
25	21.0	1.00×10^{-6}
35	22.5	1.00×10^{-5}
Ethanol		
15	19.5	1.00×10^{-6}
25	20.0	1.00×10^{-6}
35	22.2	1.10×10^{-5}

Table 13 : Selectivity coefficient values ($K^{pot}_{Al^{3+}}$, B) for Al^{3+}-selective $Me_8(14)$ane based solid membrane electrode for Aluminium ions.

Interfering ions (B)	*Selectivity coefficients by fixed interference method (at 1.0×10^{-2} M concentration of interfering ions)*
NH_4^+	2.50×10^{-2}
Na^+	1.20×10^{-1}
K^+	1.20×10^{-1}
Li^+	1.80×10^{-1}
Mg^{2+}	2.23×10^{-3}
Ca^{2+}	2.23×10^{-3}
Zn^{2+}	2.51×10^{-3}
Sr^{2+}	2.51×10^{-3}
Ba^{2+}	2.23×10^{-3}
Co^{2+}	3.16×10^{-3}
Cd^{2+}	2.23×10^{-3}
Pb^{2+}	3.54×10^{-3}
Hg^{2+}	3.54×10^{-3}
Ni^{2+}	1.12×10^{-3}
Cu^{2+}	3.54×10^{-3}
Cr^{3+}	6.30×10^{-4}
Fe^{3+}	4.70×10^{-4}

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GRAPHS

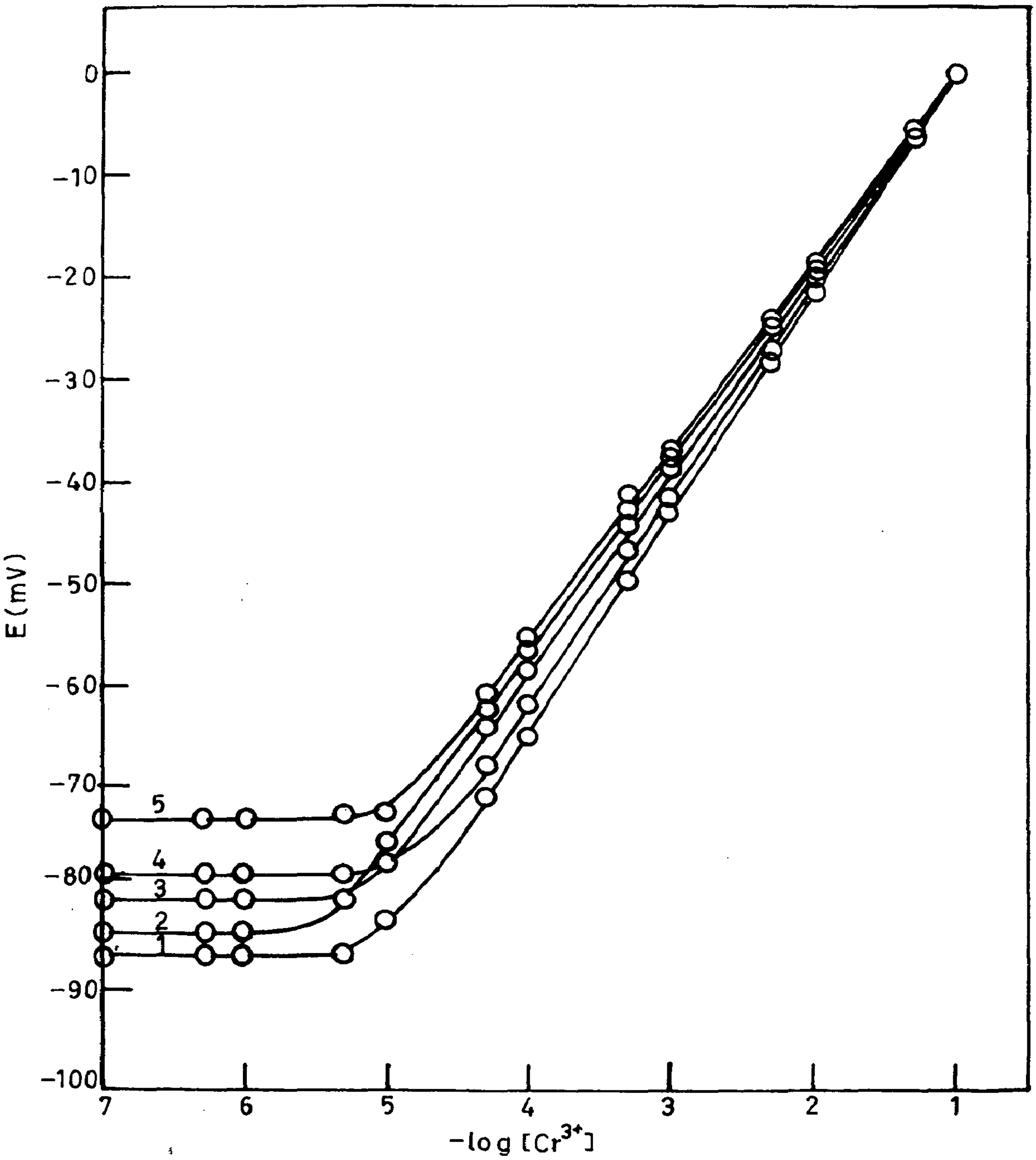

Fig. 1 : Potential vs – log [Cr^{3+}] plots of different compositions.

[Ph_4(14)tetraene]

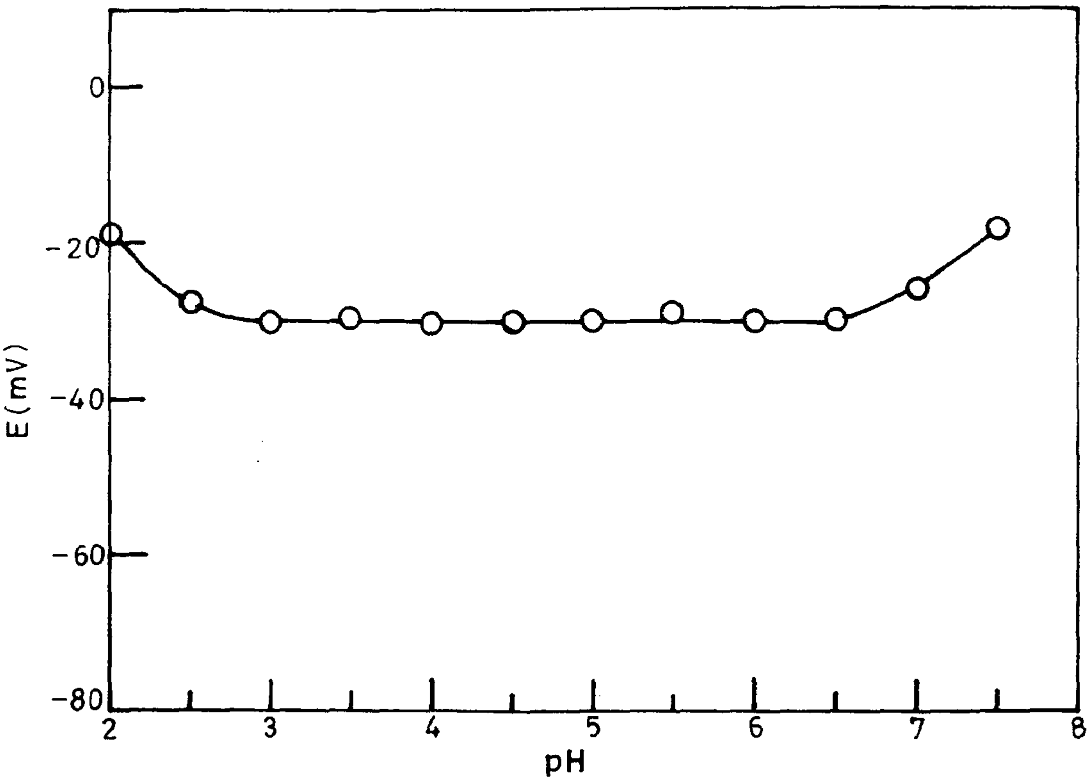

Fig. 2 : Effect of pH on cell potential ; $[Cr^{3+}] = 1.0 \times 10^{-2}$ M

[Ph_4(14)tetraene]

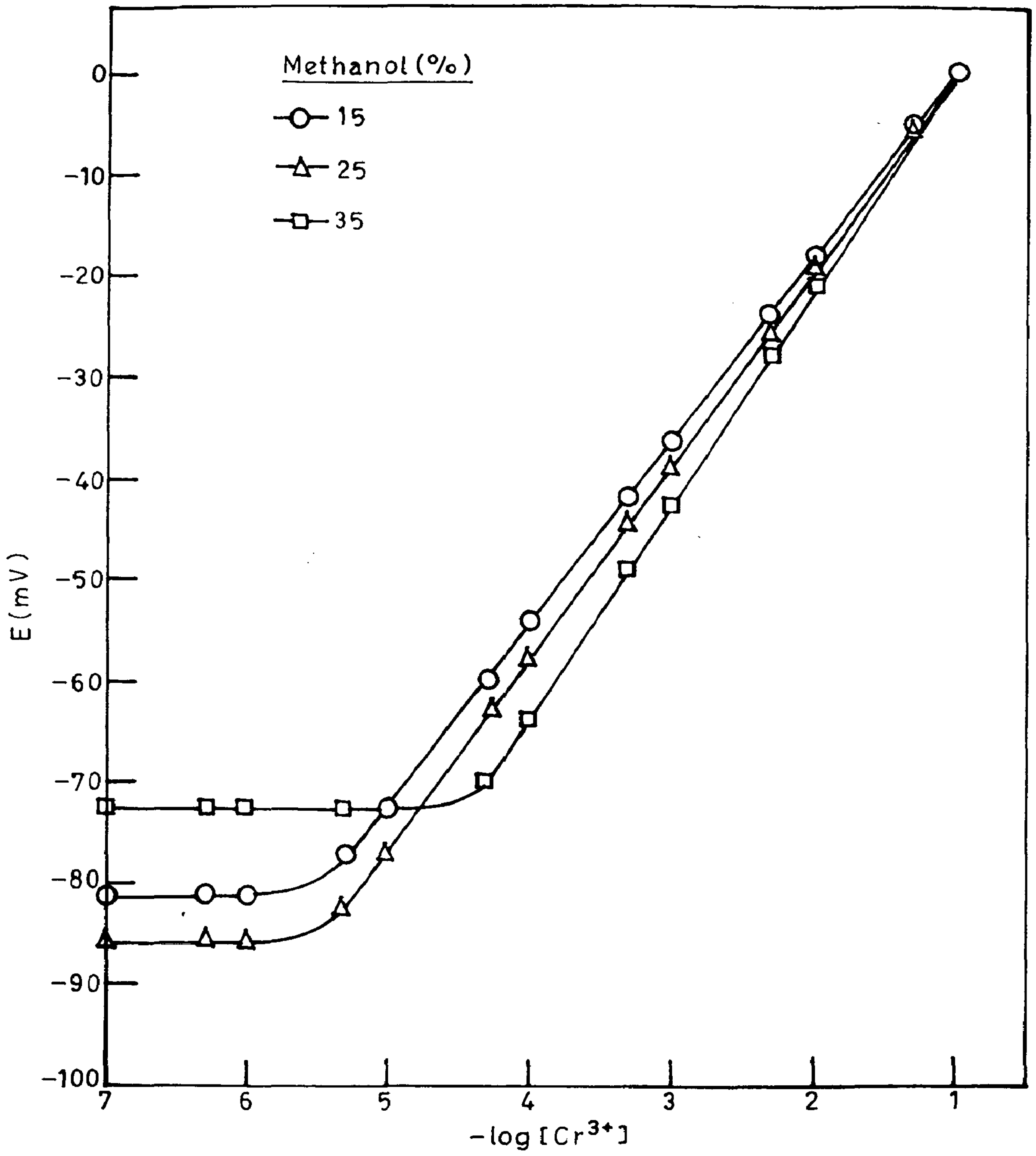

Fig. 3 : Variation of cell potential with Cr^{3+} concentration in methanol-water mixture.

[Ph_4(14)tetraene]

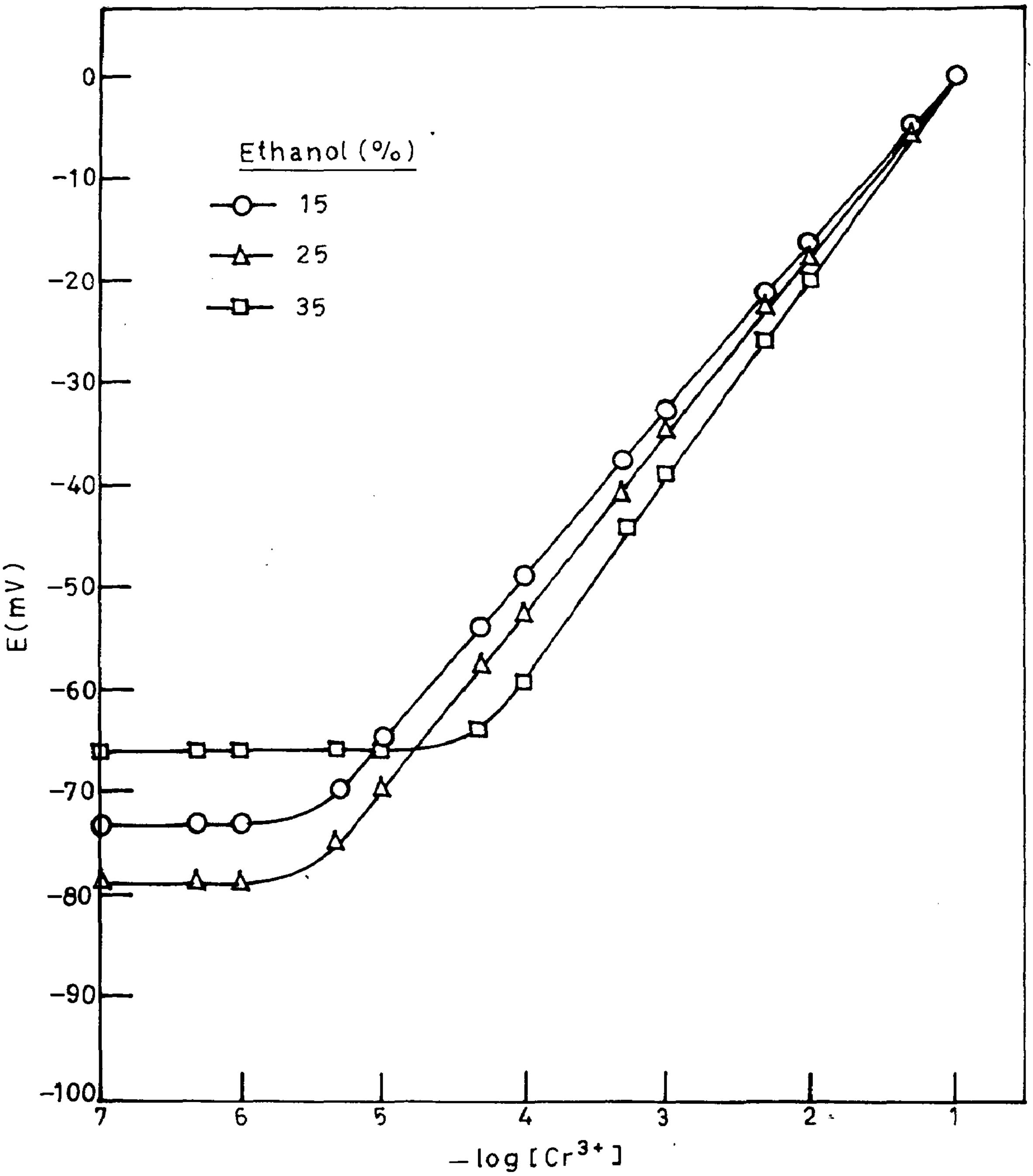

Fig. 4 : Variation of cell potential with Cr^{3+} concentration in ethanol-water mixture.

[Ph_4(14)tetraene]

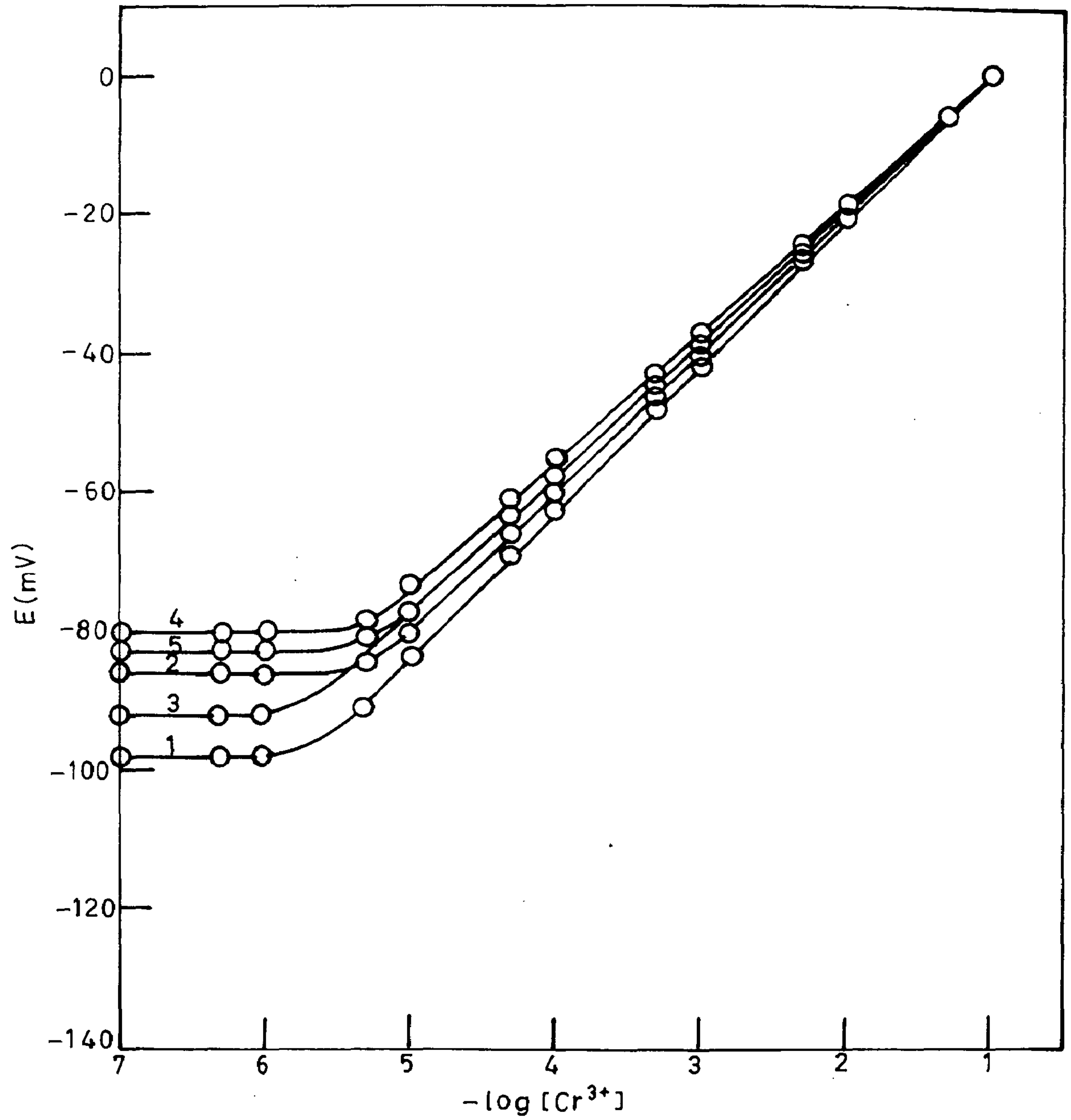

Fig. 5 : Potential vs – log [Cr^{3+}] plots of different compositions.

[Me_8(14)ane]

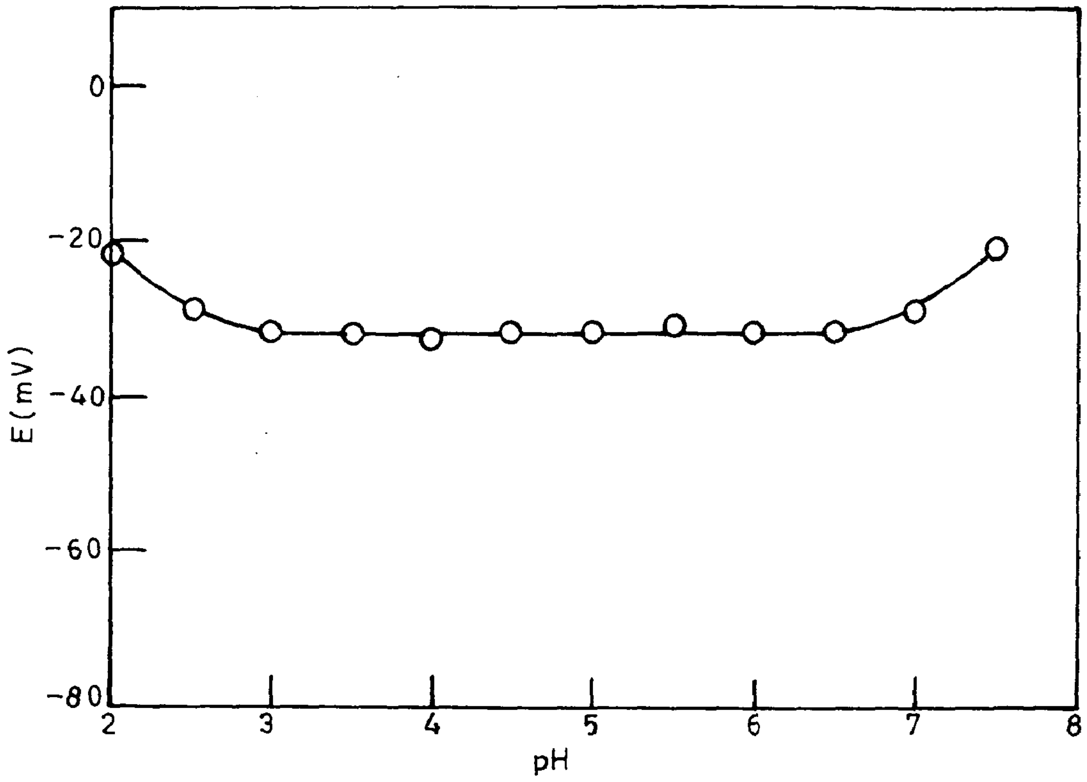

Fig. 6 : Effect of pH on cell potential ; $[Cr^{3+}] = 1.0 \times 10^{-2}$ M

$[Me_8(14)ane]$

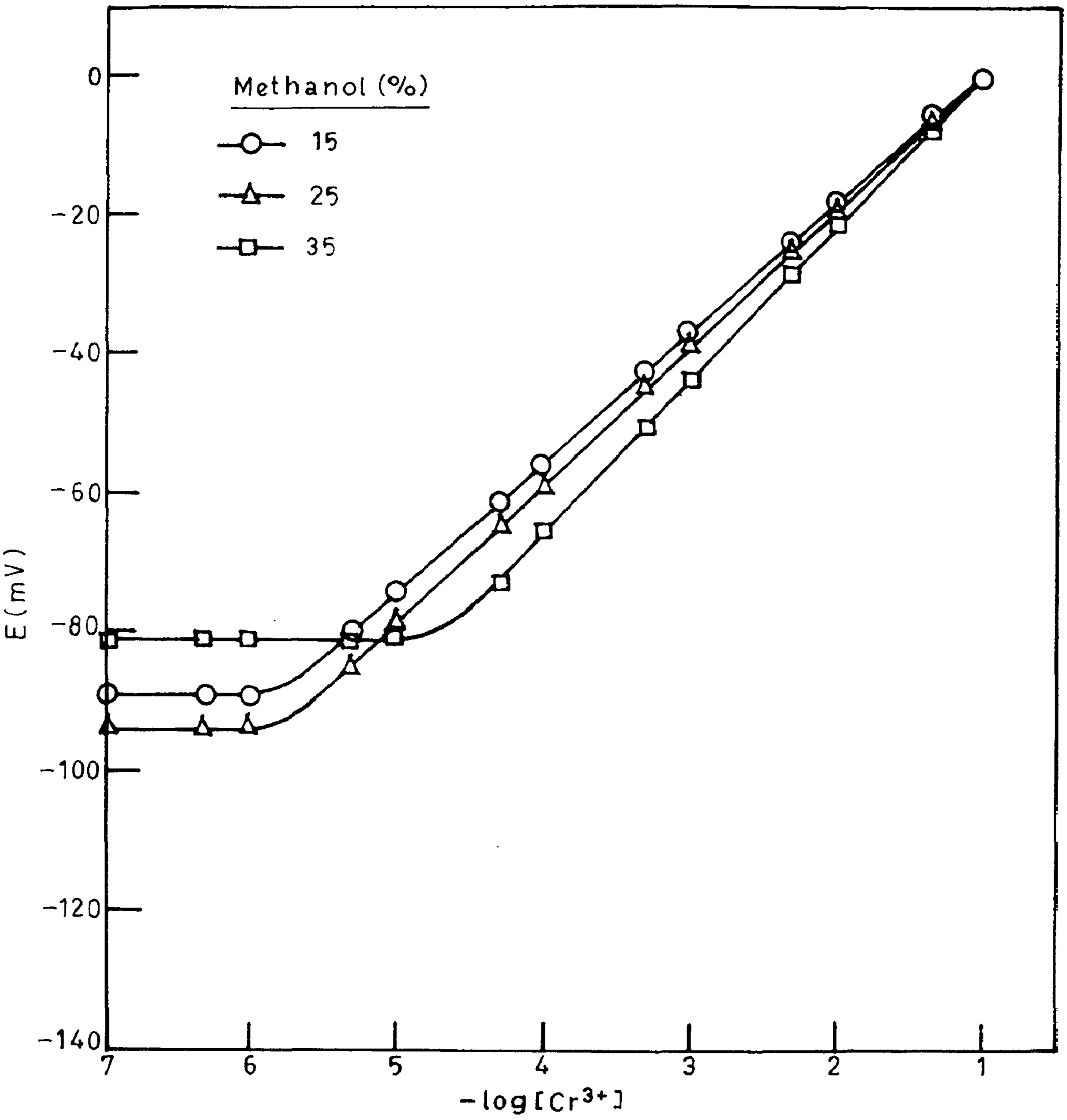

Fig. 7 : Variation of cell potential with Cr^{3+} concentration in methanol-water mixture.

$[Me_8(14)ane]$

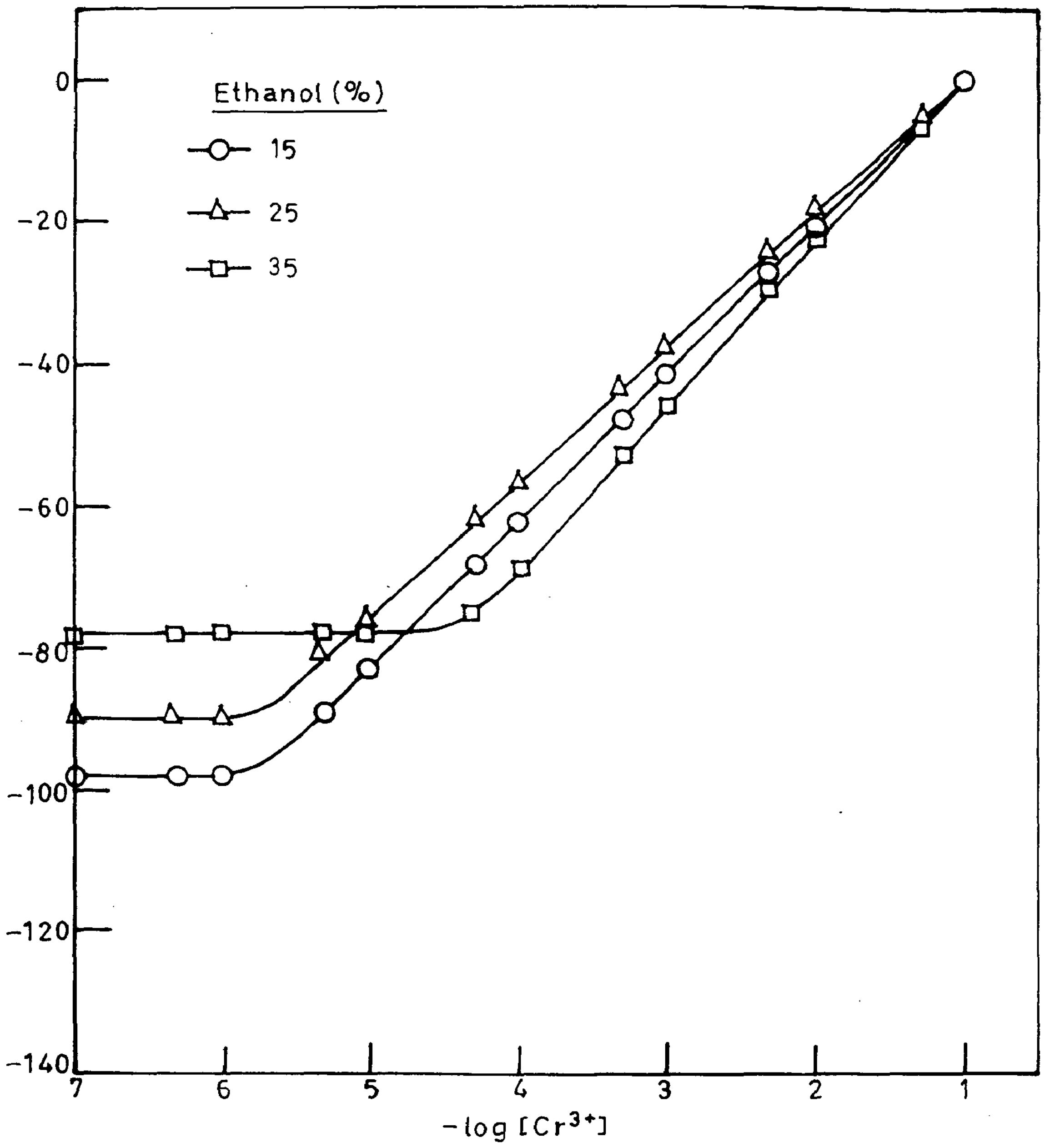

Fig. 8 : Variation of cell potential with Cr^{3+} concentration in ethanol-water mixture.

$[Me_8(14)ane]$

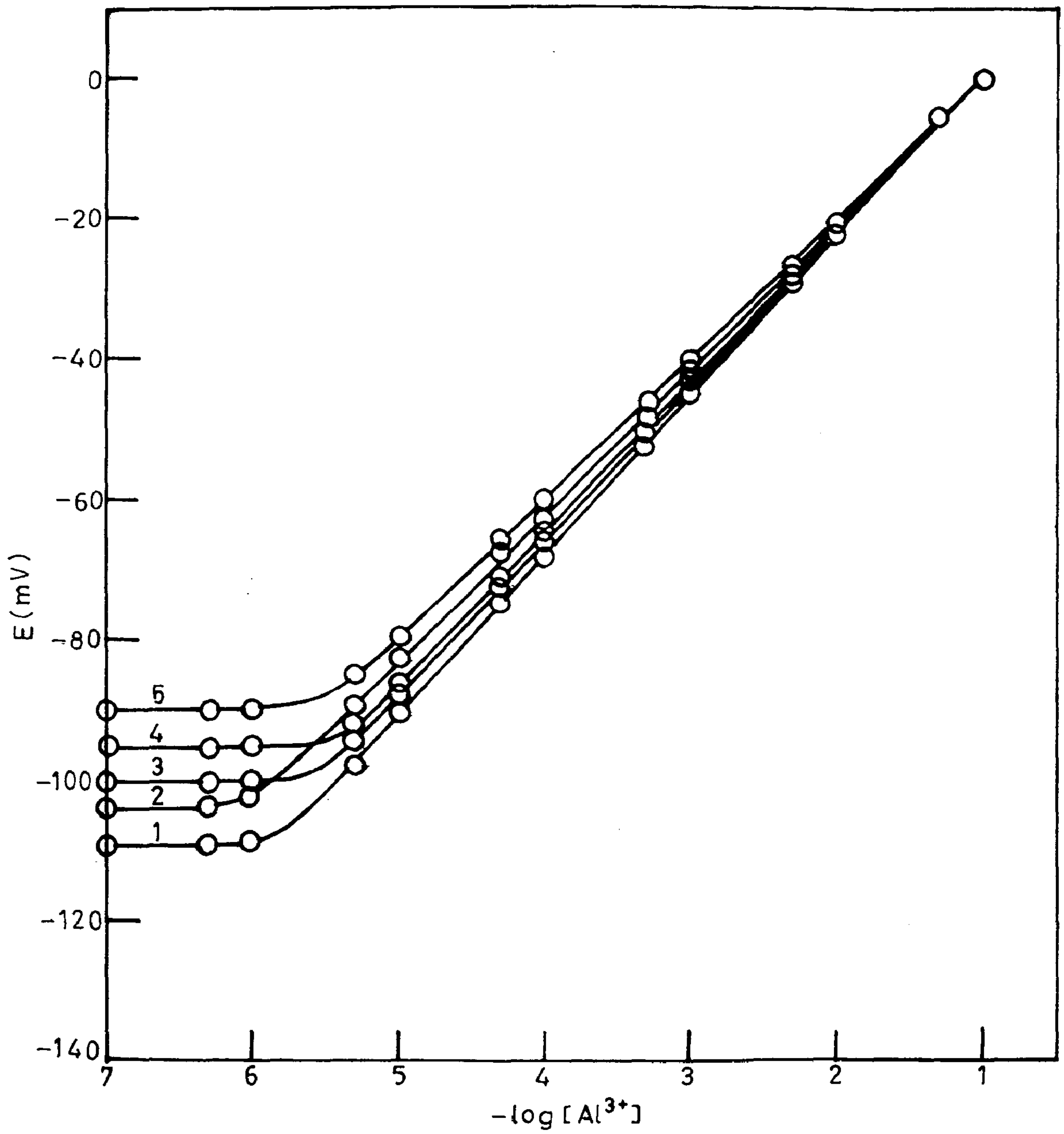

Fig. 9 : Potential vs – log [Al^{3+}] plots of different compositions.

[Me_8(14)ane]

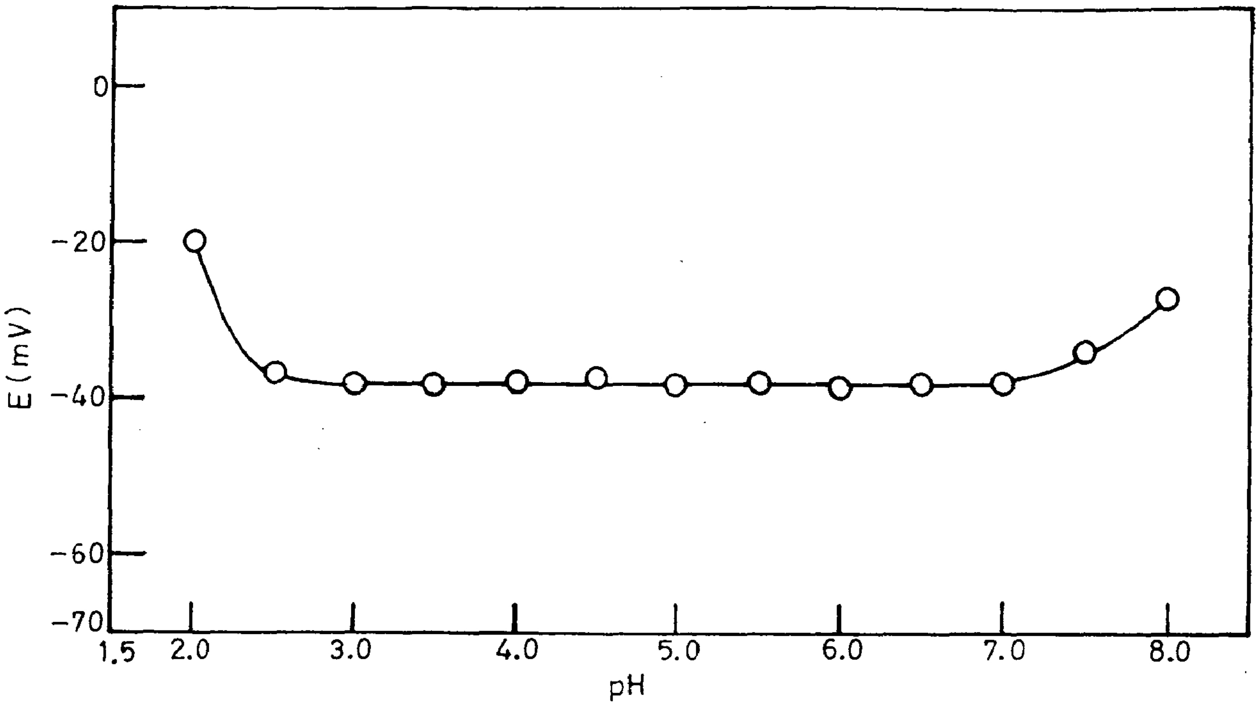

Fig. 10 : Effect of pH on cell potential ; [Al^{3+}] = 1.0 × 10^{-2} M

[Me_8(14)ane]

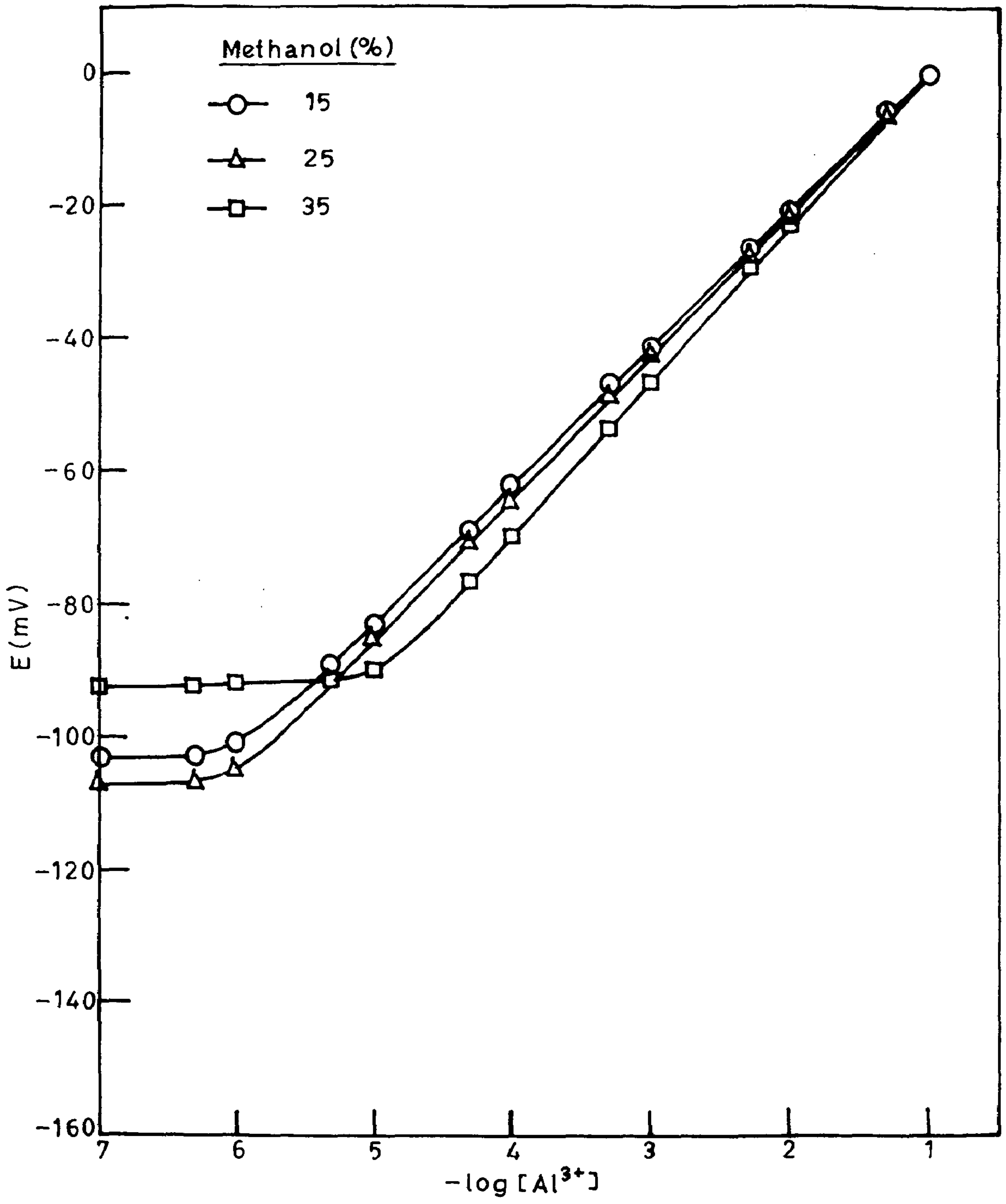

Fig. 11 : Variation of cell potential with Al^{3+} concentration in methanol-water mixture.

[Me_8(14)ane]

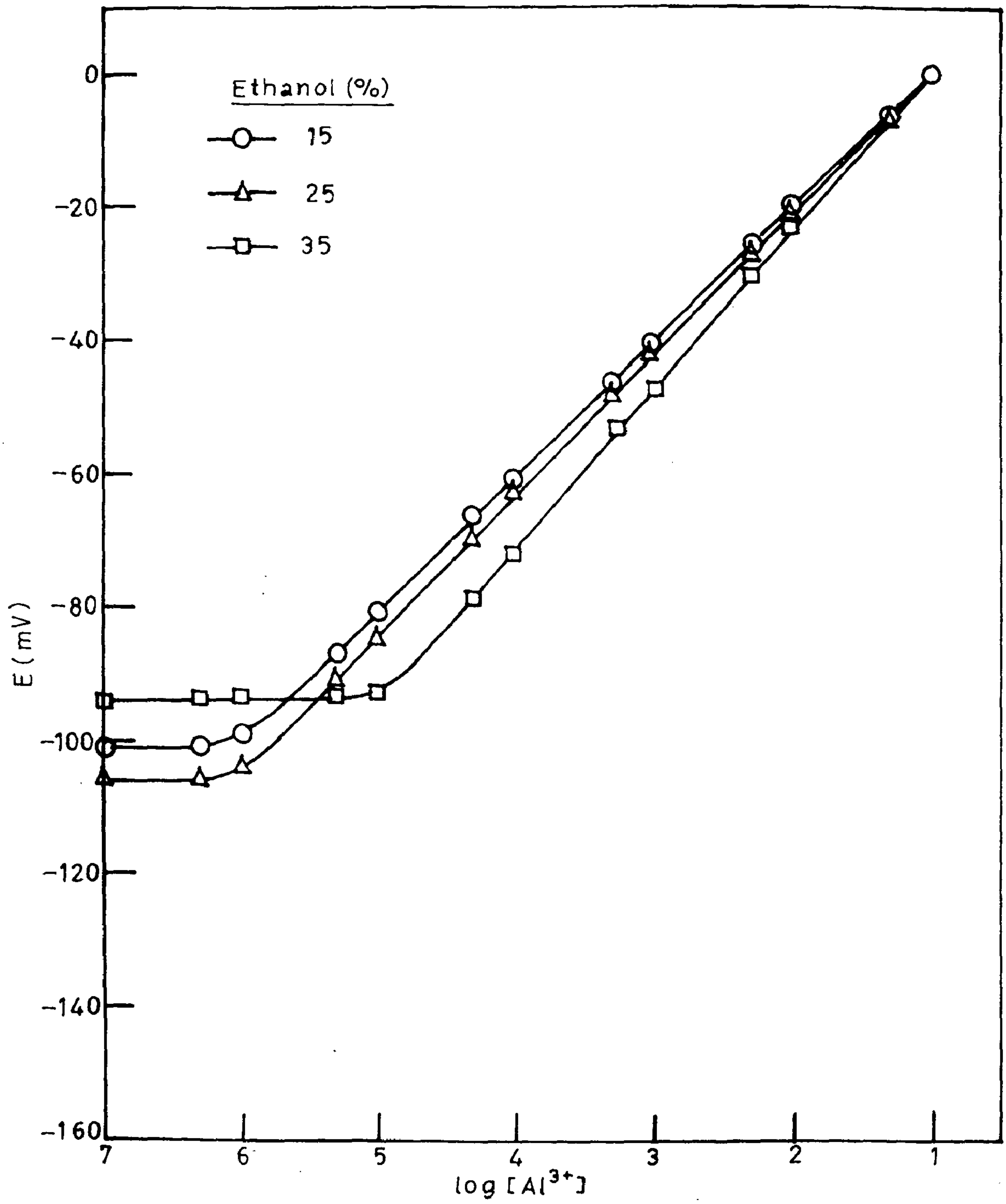

Fig. 12 : Variation of cell potential with Al^{3+} concentration in ethanol-water mixture.

[Me$_8$(14)ane]

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