TETRACHLOROFERRATE(III)-SELECTIVE LIQUID MEMBRANE ELECTRODE BASED ON CRYSTAL VIOLET - STUDIES AND APPLICATIONS

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FUFA AMBACHA

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TO THOSE WHO ASPIRE
AND HAVE THE PATIENCE

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CONTENTS

LIST OF TABLES

ABSTRACT

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FUFA AMBACHA

Research Advisors: Dr. B.S. Chandravnshi and Ato Ghirma Moges

A 7×10^{-4} M Crystal Violet tetrachloroferrate(III) extract in nitrobenzene has been used to construct tetrachloroferrate(III)-selective liquid membrane electrode with a PVC support. The electrode body was made from two concentric Pyrex glass tubes (lengths 120 mm and internal diameters 6 & 12mm) with a 14/23 ground glass joint at a common end and narrower tips at other ends. The experimental conditions have been established to determine 2.5×10^{-5} -5×10^{-2} M iron(III), as tetrachloroferrate(III) and were found to be 4.0-5.5 M in total chloride and 0.75-1.5 M in HCl with slope of 56.0 mV decade^{-1} and a detection limit of 7.9×10^{-6} M iron(III). Selectivity studies with 30 anions and cations have been made to screen the species which may interfere with iron determination. The electrode has been used reliably to measure iron in mineralized and vitaminized syrup, haematite, human blood, and standard samples with direct standard addition, sample addition and standard subtraction potentiometric techniques. EDTA titrations have also shown the feasibility of titration with the proposed electrode down to 1×10^{-4} M iron(III).

1. INTRODUCTION

As an analytical tool, modern potentiometry has its roots in investigations of the behaviour of electrodes and electrolyte solutions extending back in time to the nineteenth century.[1] Potentiometry received strong impetus from the development of pH glass electrode and the definition of practical pH scale. As time went on, electrodes suitable for the accurate measurement of the concentration or activities of ions other than hydrogen were applied to solutions of analytical problems.

The rapid development of ion-selective electrodes over the past two decades, together with the ever-increasing range of their applications, reflect the extent to which these devices meet the need for accurate, cheap and rapid analytical techniques, both in fundamental and applied fields. Despite this explosion of interest, there are still many potential applications to be explored.

1.1 General Considerations

In chemistry, the term "membrane" denotes a thin section of electrically conducting material, which is a separate phase, that regulates the movement of charged species across it, thereby creating conditions for the generation of an electric potential.[2-4] A membrane, separating two electrolytes, which is not equally permeable to all kinds of ions, is known as electrochemical membrane.[2] An electrochemical membrane is, thus, semi-permeable in that it is not equally permeable to all component species.

The term "ion-selective electrode" (ISE) is applied to a range of membrane electrodes which respond selectively towards one (or several) ionic species in the presence of others.[3] Ion-selective electrodes are, in practice, based on electrochemical membranes, i.e. on phases consisting of solid or liquid electrolytes, perfectly separating two electrolyte solutions.[2]

An important property of electrochemical membrane is the electric potential difference that arises between the two separated solutions. This difference is called membrane potential.[2,4]

The so-called membrane potential may be brocken down into a boundary potential, or Donnan potential,[2] which results from complete hindrance to the transfer of one or more kinds of ions across the interface between the two electrolytes and a diffusion potential[2,5] which results from the different mobilities and concentrations of the ions in the electrolytes in contact.

Nernst and Plank were the first to define the concept of diffusion potential. Study of the electrochemistry of membranes was initiated by Ostwald who introduced the concept of semipermable membrane. The electric potential difference on such a membrane is a limitting case of the potential difference on the liquid-liquid interface when the mobility of one kind of ion approaches zero.

Cremer[6] is credited with the discovery of the hydrogen ion-responsive glass electrode (the first ion-selective electrode), but the detailed study was made by Haber and Klemenciewiz.[7] It is remarkable that this is, perhaps, the most well behaved ISE, to date. Nikolsky and Tolmacheva[8] came up with the concept of ion-exchange in their study of glass membranes. The theory and application of glass membrane electrodes have been summarized by Schwabe[9] and Lakshminarayanaiah.[10]

The first attempts to make ion-selective electrodes from materials other than glass were made by Tendeloo[11,12] and Kolthoff and Sanders[13] in the 1930s. The latter prepared halide-selective electrodes from silver halide discs.

Another breakthrough, made by Frant and Ross,[14] is the discovery of the fluoride electrode which is a highly selective electrode to measure fluoride ion activities. Their monocrystal LaF_3 electrode is still the most successful product in this field.

The discovery in 1964 by Moore and Pressman[15] that antibiotic valinomycin exhibits specificity for alkali metal cations led Stefanc and Simon[16] to show that the complexes of such macrocyclic compounds with the alkali metal cations may be used as liquid neutral-carrier membrane in electrodes sensitive to such cations.

The origins of work on liquid ion-exchange materials, culminating in the important calcium,[17] nitrate,[18] and perchlorate[18] responsive electrodes, can be traced to two papers by Sollner and Shean[19], and Bonner and Lunney.[20]

A promising more recent trend is represented by the so-called enzyme electrodes.[21]

The field of ion-selective electrodes have undergone a remarkable development, as shown by the large volume of literature.[22]

Many types of active materials have been used in ISEs to make the membranes, as described in the foregoing discussion.

1.2 Classification of Ion-selective Electrodes

A number of classifications of ion-selective electrodes have been suggested. The International Union of Pure and Applied Chemistry (IUPAC) has suggested the following classification of ISEs.[3,23]

A. Primary electrodes

   1. Crystalline

      i) Homogeneous membrane, a single crystal, e.g., LaF_3 or mixture of salts, e.g., AgI-Ag_2S.

    ii) Heterogeneous membrane, the active substance mixed with an innert matrix, e.g., AgI in silicone rubber

2. Noncrystalline with or without support such as porous glass, Millipore filter, PVC, etc.
    i) Rigid matrix, e.g., Na^+-responsive glass electrodes
    ii) With a mobile carrier which may be positively charged, negatively charged, or neutral, e.g., quaternary ammonium cations, tetraphenylborate anion, and valinomycin.

B. Sensitized electrodes

1. Gas-sensing electrodes with a gas-permeable membrane or an air-gap to separate the sample solution from a thin film of intermediate solution.

2. Enzyme substrate electrodes, with an enzyme coating that causes a reaction with the sample solution producing species to which the sensor responds.

All the electrodes function by making use of their active materials. These materials may thus be broadly classified[3] into the following categories:

A. Glass, e.g., pH sensitive glass.

B. Insoluble inorganic salts, e.g., single crystal LaF_3; mixed salts, $AgI-Ag_2S$; salts in inert matrix, e.g., AgI in silicone rubber.

The common feature of these substances is their ability to bind selectively certain small ions either at charged sites of opposite sign or at neutral sites of organic nature.

The common required property shared by all these electro-active materials, when brought into contact with an electrolyte solution containing suitable ions, is their ability to rapidly set up an exchange equilibrium or ion-exchange process across the phase boundary. A second requisite property is the ability of the active material to conduct electricity. The conduction process may be by ionic, electric, or defect mechanism, or a combination of these, depending on the type of material.

1.3 Organic Ion-exchangers in ISE Potentiometry

Organic ion-exchangers have long been used in ion-exchange separation technique and solvent extraction-spectrophotometric determinations. Similar organic materials are used in the preparation of ISEs. A wide range of ISEs based on organic ion-exchangers has been developed and reported.

The term, "ion-exchange membrane electrode,[11] is taken to mean an electrode having a charged ion-exchanger consisting of large organic molecules as active material.[24] Ion-exchangers are incorporated into the electrode, in a water immiscible organic solvent or in an inert matrix such as PVC, polythene, silicone rubber, etc., or by coating on a metal wire.

The first ion-responsive liquid ion-exchanger electrode was due to Sollner and Shean[19] followed by that of Bonner and Lunney.[20] Their pioneer work resulted in the development of the successful commercial calcium and nitrate ion-responsive liquid ion-exchanger electrodes of Ross.[17,18]

The considerable interest in ISEs that boosted the development of liquid ion-exchanger membrane electrodes soon led to a new range of PVC matrix membrane electrodes.[25]

Latter on Cattrall and Freiser[26] reported the first coated wire electrode (CWE) based on the Ca^{2+}- didecylphosphate/dioctylphenyphosphate system, selective to Ca^{2+} ions.

An organic ion-exchanger based membrane is formed by dissolving its complex or ion-association salt in the organic solvent (for liquid membrane electrodes) or incorporating the active material in inert matrix such as PVC with the aid of volatile solvents (for plastic membrane and CWEs).

The common feature of organic ion-exchangers is their ability to bind selectively certain small ions at charged sites of opposite sign. At the membrane interface, a rapid ion-exchange process takes place between the free ions in the aqueous phases and the same ions bound to the organic site groups. The selectivity of the electrode depends primarily on the selectivity of this ion-exchange process.[34] That is, the organic site should form a more stable complex with ion of interest than with any other ions. Many groups which are interesting from a selectivity standpoint, however, such as most multidentate chelating groups, equilibriate too slowly to give useful electrodes with reasonable response time.[3] For this reason, the ion-association forms have been most frequently used, of which a few examples are cited below.

Potassium tetrakis(p-chlorophenyl) borate in 1,2-dimethylnitrobenzene has been used in liquid ion-exchanger and PVC electrodes for potassium ion determination.[35,36] Electrodes for detergent anions[37] (Crystal Violet alkylbenzene sulphonates in nitrobenzene) and for salicylate[38] (tetra-n-heptyl salicylate in n-decanol) have been reported.

Organic ion-exchange membranes, unlike glass membrane or other membranes, used in the construction of electrodes, have low electrical resistance. This low resistance or high conductance is due to two factors: (1) the porosity of the membrane, and (2) the high density of ionogenic groups. Membranes of low porosity and high charge density are generally well suited for the construction of electrodes.[4]

1.4 Basic Dyes in ISE Potentiometry

Ion-association salts have been widely used in analytical chemistry, especially for the separation of ions by extraction, precipitation, flotation, partition chromatography, and ion-selective electrodes. Of the many suitable cationic or anionic reagents which can react with counterions to form ion-pairs, cationic dyes have most frequently been used in extraction-spectrophotometric determinations of simple anions and metals as anionic complexes.[39]

Accordingly, triphenylmethane cationic dyes have long been used for extraction and spectrophotometric determinations of simple and complex anions such as chloride, bromide, perchlorate, benzene sulphonates[40] and tetrathiocyanatozincate(II).[31,41]

The first report on application of these dyes in ISE potentiometry were those reported by Ishibashi and his associates, in 1973.[42-44]

The electrodes of Ishibashi et al made use of the triphenylmethane dyes, such as Crystal Violet, Methyl Violet, Malachite Green, and Fuchsin Basic, ion-paired with benzene sulphonate as a sulphate - selective electrodes. They used Crystal Violet trifluoroacetate dissolved in nitrobenzene, chloroform, or 1,2-dichloroethane as a liquid trifluoroacetate-selective membrane electrode[42] with a linear response of 10^{-5}-10^{-1} M and a Nernstian slope of 59.0 mV/decade. Another version of their electrodes based on Crystal Violet ligand are the ones selective to monovalent maleate and phthlate anions.[43] These are liquid membrane electrodes consisting of the Crystal Violet salts of the respective organic anions dissolved in nitrobenzene, 1,2-dichloroethane, or chloroform. The response of both the electrodes were linear down to $10^{-4.5}$ M with an ideal Nernstian slope of 58 mV/decade.

Since then a number of workers have dealt with the basic cationic dyes as ligand in ISEs including those of Fogg and co-workers,[45-47] Kataoka etal,[49] Elena and Euqenia,[49] Pon and Lieu,[50] and Pan and Hao.[51]

In 1984, the selectivity coefficients of more than 45 univalent anions were determined for the liquid ion-exchanger membrane electrode selective to NO_3^- based on its Crystal Violet salt in nitrobenzene.[52] Recently, a PVC-type membrane electrode based on Brilliant Green-saccharin ion-pair, selective to saccharin ion, and liquid membrane ISEs based on Crystal Violet and Brilliant Green-perchlorate were developed by Moges and coworkers[32] and by Negash,[53] respectively.

1.5 ISE Potentiometry for Iron Determination

Iron is the second most abundant metal, after aluminium, and the forth most abundant element in the earth's crust.[54] The major ores of iron are haematite, Fe_2O_3, magnetite, Fe_3O_4, limonite, FeO(OH), sederite, $FeCO_3$, and pyrites, FeS_2. Mixed oxides, silicates, and aluminates with a number of metals are also encountered. Natural waters sometimes contain considerable amount of iron. Iron is certainly the most widespread of the heavy or transition metals in living systems.[54] The two main functions of iron-containing materials in the biological systems are: (1) transport of oxygen, and (2) mediation in electron-transfer chains. So much iron is required for these purposes that there is also a chemical system to store and transport iron.

The ferrous alloys, ores, biological materials, and pharmaceuticals are among samples that are often encountered for analysis of iron.

A number of ISE systems have been recommended for the determination of iron. The first Fe^{3+}-selective ISE was due to Trachtenberg and co-workers.[55] Their Fe-dopped $Ge_{28}Sb_{12}Se_{60}$ Vitereous alloys (chalcogenide glass) are sensitive to iron(III) ions.[55,56] There are several points of view on the sensing mechanism of these solid-state ion-selective electrode.[57-60] These electrodes show linear responses in the concentration range 10^{-5}-10^{-1}M Fe^{3+}, with a slope for a monovalent cation

(57-60 mV/decade) despite the ionic charge of Fe(III),(+3), which would have given a slope of 20 mV/decade. The electrodes required frequent reactivation by itching, and the response time of the electrode was excessively long (10-20 minutes) by the standard of other electrodes to reach steady state for 10^{-4} M ferric ions.

Haemin incorporated into silicone rubber was also tried[61] as an electrode selective to Fe^{3+} ions. The electrode gave Nernstian response (about 19 mV per decade) in the concentration range 10^{-4}-10^{-1} M Fe^{3+} ions. This liquid membrane electrode is a chelate forming selective electrode and would consequently equilibrate too slowly.[34] Moreover, because of the rather low slope, the electrode will have relatively reduced sensitivity.

If complexed species of Fe^{3+} with charge lower than three could be employed, it would give greater sensitivity to the analysis because of the larger potential change per log activity. Use is made of this approach by Cattrall and Chin-Poh,[62] who reported the first tetrachloroferrate(III)-selective coated wire electrode(CWE). The electroactive material, tetrachloroferrate(III) salt of tricaprylmethylammonium (Aliquate 336S) with PVC dissolved in tetrahydrofuran or cyclohexanone, was coated on a platinum wire. The electrode responded linearly to $FeCl_4^-$ in the range of 10^{-4}-10^{-1} M Fe^{3+} ions in 6 M(1 M HCl and 5 M LiCl) chloride concentration, with a slope of 55 mV/log concentration. Unfortunately, a stable potential was obtained after 25 minutes for the lower concentrations in the linear range.

Hopirtean and his group also developed tetrachloroferrate(III)-selective liquid membrane electrodes based on triphenyl-pyrylium cation in dichloroethane,[33] in tetrachloroethane,[33] and triphenylthiopyrylium cation in dichloroethane.[63] These electrodes responded with a Nernstian slopes typical of a monovalent anion (58 mV per decade) for 10^{-4}-10^{-1} M $FeCl_4^-$ ions.

Jain and his co-workers[64] showed that an electrode based on the ion-exchanger $K_6Cr_2[Fe(CN)_6]_3.16H_2O$ responds to hexacyanoferrate(II) with linear response range 10^{-4}-10^{-1} M $Fe(CN)_6^{4-}$. The electrode is not very specific for $Fe(CN)_6^{4-}$. In addition, as one can see from the charge of the complex (i.e., -4), the sensitivity must be very low (only about 14.7 mV per decade).

1.6 Objectives of the Present Investigation

As revealed in the foregoing discussion most of the electrodes developed to sense iron(III) have one or more of the following drawbacks: low sensitivity (small slope), narrow linear range, excessively long response time, non-specificity, and easy poisoning. Therfore, from the point of view of these drawbacks and the importance of iron, development of new method was necessitated.

The literature survey showed that no attempt was made to use triphenylmethane dyes such as Crystal Violet to design a liquid membrane electrode selective to tetrachloroterrate(III). Therefore, the objectives of the present investigation are:

1. To design liquid membrane electrode selective to tetrachloroferrate(III) ions based on Crystal Violet-tetrachloroferrate(III) salt.
2. To study the electroanalytical parameters of the electrode, i.e., dynamic (linear) range, slope, effects of pH and chloride concentration, and to determine selectivity coefficients.
3. To study the analytical applications of the liquid membrane ISE

2. THEORETICAL BACKGROUND

2.1 Origin of Membrane Potential

The use of ion-selective electrodes depends on the determination of membrane potentials. These potentials cannot be determined directly, but can be easily derived from the electromotive forces (e.m.f.) for the complete electrochemical cells. These cells comprise the membrane, which is usually in contact, on one side with both a solution(solution 1) containing the ions for which the electrode is selective and a suitable reference electrode and, on the other side, with the test solution (solution 2), in which a second reference electrode is immersed. This cell type is schematically depicted in cell(I)

internal reference electrode ¦ solution 1 ¦¦ membrane ‖ solution2 | external reference electrode (I)

and as schematic assembly in Fig.1.

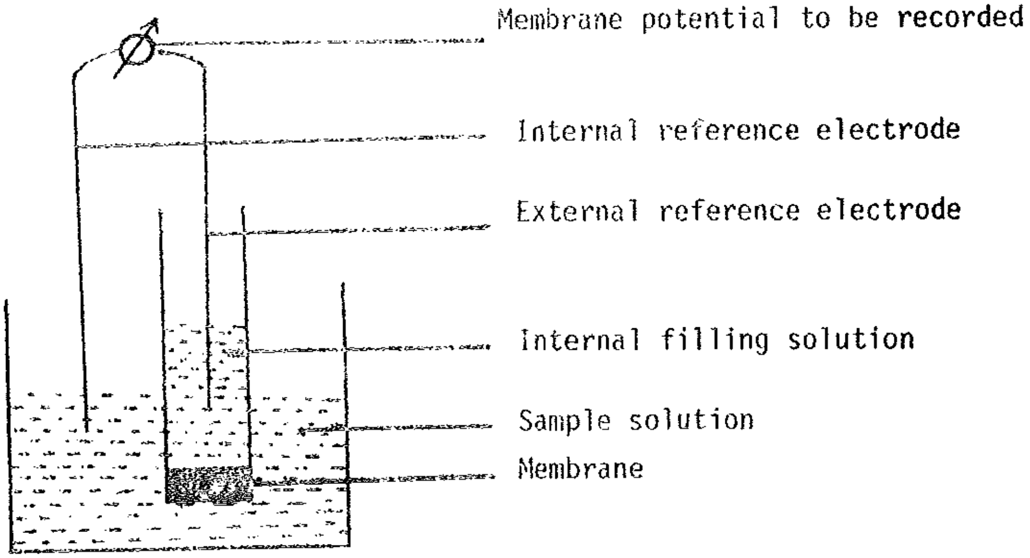

Fig.1. Schematic representation of membrane electrode cell assembly.

The behaviour of the membrane electrode will be determined by the properties of the membrane[4] namely the composition and the velocities at which the components of the phase are able to permeate the membrane.[65] The quantity characterizing the composition of the phase is the partial molar Gibbs free energy of the i^th^ component of the given phase, which is called the electrochemical potential of this component, $\bar{\eta}_i$, taking into account the phase is electrically charged.[2]

The chemical properties of a component of the phase can be characterized by its standard chemical potential, μ_i by its activity, a_i, and the inner or Galvani potential of the phase, ϕ.[2] Thus, the electrochemical potential of the i^th^ component in the membrane phase can be written as[66]

$$\eta_i = \bar{\mu}_i + Z_i F\phi \tag{2.1}$$

where

$$\bar{\mu}_i = \bar{\mu}_i^o + RT \ln a_i \tag{2.2}$$

The electrochemical potential of the same component, i, in aqueous solution will be

$$\eta_i = \mu_i + Z_i F \phi \tag{2.3}$$

where R, T, and F have their usual electrochemical meaning, Z_i is the charge on ion i, the bars indicate the memberane phase, and a_i the activity of component i.

When the solution and the membrane, both containing the i^th^ component, are at equilibrium, it follows that[3,65,66]

$$\bar{\eta}_i = \eta_i$$

that is,

$$\mu_i^o + RT\ln \bar{a}_i + Z_i F \bar{\phi} = \mu_i^o + RT\ln a_i + Z_i F \phi \tag{2.4}$$

$$Z_i F(\phi - \phi) = \mu_i - \bar{\mu} = \mu_i^\circ - \bar{\mu}_i^\circ + RT \ln \left(\frac{a_i}{\bar{a}_i} \right) \qquad (2.5)$$

Equation (2.5) then becomes

$$E = E_0 + \frac{RT}{Z_i F} \ln \left(\frac{a_i}{\bar{a}_i} \right) \text{ -------------------- } \qquad (2.6)$$

where E is the electrode potential and E_0 is the standard electrode potential.

The potentials of the membranes can be explained by taking into consideration both the diffusion and Donnan potentials[65] (two basidphenomena occuring at the interface between two electrolytes[2]).

Difusion Potential. Because of differing diffusion rates of the ions present, an electric potential gradient appears within the liquid junction (the so-called diffusion potential gradient). Between the two solutions, which are assumed to be of uniform composition everywhere outside the liquid junction, an electric potential difference is formed, called the liquid-junction potential, E_L. The liquid-junction potential is given by the relation[2,4,67,68]

$$E_L = - \frac{RT}{F} \int_1^2 \sum_i \frac{t_i}{Z_i} \, d\ln a_i \text{ ----------------------- } \qquad (2.7)$$

where t_i is the transport number of the i^{th} component and is given by

$$t_i = Z_i^2 U_i C_i / \sum_j Z_j^2 U_j C_j \text{ ------------- } \qquad (2.8)$$

U_i in Eqn (2.8) is the particle mobility given by

$$u_i = /Z_i/ \; E \; U_i \text{ ----------------------------- } \qquad (2.9)$$

where u_i is called the electric mobility defined by Eqn (2.9). Z_i, C_i and Z_j, C_j are charge and concentration of components i and j, respectively.

The integration of Eqn (2.7) was based on Plank's[4] assumption and Teorell's[4,69] expression, given elsewhere. Accordingly, the diffusion potential within the membrane expressed as liquid-junction potential(E_L) which is assumed to be that existing in a constrained liquid junction is given by[4]

$$E_L = \bar{U}\,\frac{RT}{F}\quad \ln\ \frac{\bar{U}\bar{X}_1 + (\bar{X}_1^2+4a_{\pm(1)}^2)^{\frac{1}{2}}}{\bar{U}\bar{X}_2 + (\bar{X}_2^2+4a_{\pm(2)}^2)^{\frac{1}{2}}} \qquad (2.10)$$

where $\bar{U} = (\bar{U}_+ - \bar{U}_-)/(\bar{U}_+ + \bar{U}_-)$, $\bar{X}$ is the concentration of ionogenic groups in the membrane, 1,2 indicate the two liquid-junctions, and $a_\pm^2 = \bar{m}_+\bar{f}_+\bar{m}_-\bar{f}_- = a^2$

Donnan Potential. This is a transmembrane difference of electric potential arising when the membrane completely prevents diffusion of at least one type of ion from one solution to the other. When the membrane is placed between two solutions of the same chemical composition, but of different concentrations, a small number of ions pass through the membrane from the solution of higher concentration into that of lower concentration, a transmembrane difference of electric potential is generated and this hinders further passage of the particular ionic species.[2,65] Simultaneously, an electric double layer is formed on both sides of the membrane as illustrated in Fig 2.

When the ionic membrane is bounded by a 1:1 electrolyte of activities a_1 and a_2, the two Donnan potentials, E_1^{Don} and E_2^{Don} at the two interfaces 1 and 2 are given, according to Eqns (2.4) and (2.5) by [2,4]

$$E_1^{Don} = E_1 - \bar{E}_1 = \frac{RT}{ZF} \ln \frac{\bar{a}_{+(1)}}{\bar{a}_{+(1)}} = \frac{RT}{ZF} \ln \frac{a_{-(1)}}{\bar{a}_{-(2)}} \text{ --------- } (2.12)$$

$$E_2^{Don} = E_2 - \bar{E}_2 = \frac{RT}{ZF} \ln \left(\frac{\bar{a}_{+(2)}}{a_{+(2)}}\right) = \frac{RT}{ZF} \ln \left(\frac{a_{-(2)}}{\bar{a}_{-(2)}}\right) \text{ ------- } (2.13)$$

The net Donnan potential therefore is given by

$$E^{Don} = E_1^{Don} - E_2^{Don} = \frac{RT}{ZF} \ln \left(\frac{\bar{a}_{+(1)}}{a_{+(1)}}\right) - \frac{RT}{ZF} \ln \left(\frac{\bar{a}_{+(2)}}{a_{+(2)}}\right)$$

$$= \frac{RT}{ZF} \ln \frac{a_{-(1)}}{\bar{a}_{-(1)}} - \frac{RT}{ZF} \ln \left(\frac{a_{-(2)}}{\bar{a}_{-(2)}}\right) \text{ ------------ } (2.14)$$

The Donnan potential must be measured in such a way that the potential difference between the two solutions is measured.

<u>Potential of Permselective Membrane</u>. Assuming that $\bar{X}$ in Eqn (2.10) is independent of the external electrolyte solution, the total membrane potential is given by the sum of Eqns (2.10) and (2.13) or 2.14). Thus for a highly idealized membrane system ($\bar{f}_+ = \bar{f}_- = 1$) the total membrane potential when agar-KCl salt bridges are used in the measurement is given by

$$E = E_1^{Don} - E_2^{Don} + E_L$$

so

$$E = \frac{RT}{Z_iF} \left[\ln \frac{a_2}{a_1} \frac{(4a_1^2 + \bar{X}^2)^{\frac{1}{2}} + \bar{X}}{(4a_2^2 + \bar{X}^2)^{\frac{1}{2}} + \bar{X}} + \bar{U} \ln \frac{(4a_1^2 + \bar{X}^2)^{\frac{1}{2}} + \bar{U}\bar{X}}{(4a_2^2 + \bar{X}^2)^{\frac{1}{2}} + \bar{U}\bar{X}}\right] \quad (2.15)$$

Donnan term   Diffusion term

When the ion-selective electrode is placed in a solution containing the particular ion (to which the electrode is reversible), diffusion potential is produced and consequently Donnan potential is generated, as pointed out earlier.

An ideal potentiometric measurement, especially in analytical chemistry, would be done in which the reference electrode potential was fixed and only the indicator electrode (the ISE in this case) potential changed with changes in the solution composition. This could be achieved if the liquid-junction potential could be neglected or if the effect is cancelled by having it kept constant.

Membrane Potentials of Liquid Ion-Exchangers. A liquid ion-exchanger membrane is usually formed by dissolving an ion-exchanger in a water-immiscible solvent.

The behaviour of liquid membranes was described by Conti, Eisenman, Sandblom, and Walker.[70-75] Their work was related to the problem of electrical potentials arising across liquid membranes under zero applied potential. The following are based on their works.

The conditions existing in a liquid membrane system are such that the species $\bar{A}^{+}$ and $\bar{X}^{+}$ are in chemical equilibrium with the species $\bar{A}\bar{X}$ in the membrane.

$$\bar{A}^{+} + \bar{X}^{-} \rightleftharpoons \overline{AX} \text{ -- } (2.16)$$

Assuming $\bar{f} = 1$, the law of mass action is valid;

$$K_{AX} = \frac{\bar{C}_{AX}}{\bar{C}_{A}\bar{C}_{X}} \text{ -- } (2.17)$$

If the membrane comes in contact with an aqueous solution of MX (M^{+}+X^{-}), the anionic species will permeate the membrane phase resulting in the exclusion of M^{+} from the membrane phase (Fig.2)

By considering the Nernst-Plank flux equations for ions with the same absolute charge, Conti and Eisenman,[73] and Sandblom, Eisenman and Walker,[74,75] derived expressions for the steady state membrane potential of completely dissociated and strongly associated systems in terms of bathing solution activities and system parameters (single ion extraction coefficients, mobilities, and complex formation constants). According to Sandblom, Eisenman and Walker,[74,75] and Bailescu,[66] the electrode potential of an ion exchanger membrane, solid or liquid, is given by

$$E = E_o + \frac{RT}{Z_i F} \ln \left[\frac{\sum \bar{U}_i k_i a_{i(1)}}{\sum_i \bar{U}_i k_i a_{i(2)}} - \int_1 - \int_2 \right] \qquad (2.18)$$

where Z_i is the valence of the i^{th} counterion species, $a_{i(1)}$ and $a_{i(2)}$ are its activities in the solutions (1) and (2) on each side of the membrane, $\bar{U}_i$ is its mobility within the membrane, and k_i is a constant characteristic of its difference of standard chemical potentials in the membrane vs. Water given by the expression

$$K_i = \exp \left[- \frac{\overset{\circ}{\mu}_i - \bar{\mu}_i^{\circ}}{RT} \right] \qquad (2.19)$$

Eqn (2.18) contains two integral terms, given by Eqns (2.20) and (2.21), whose values depend on the particular characteristics of the liquid ion-exchanger,

$$\int_1 = \int_0^d t \, d \ln \frac{\sum (\bar{U}_{Ai}/K_{Ai}) \, \bar{C}_i}{\sum \bar{U}_i \bar{C}_i} \qquad (2.20)$$

and

$$\int_2 = \int_0^d \frac{\frac{U_A J_A^T}{RT} \, dx}{(\bar{U}_A + \sum \frac{\bar{U}_{Ai}}{\bar{K}_i} \bar{C}_i) \sum \bar{U}_i \bar{C}_i + \bar{U}_A C_A \sum \frac{\bar{U}_{Ai} \bar{C}_i}{K_{Ai}}} \qquad (2.21)$$

in which the subscripts A refer to the dissociated site species, i is one of the n ions present in the system, and the subscripts Ai refer to the undissociated ion pairs. Thus, U_A is the mobility of the undissociated ion pair; and C_{Ai}, C_i, and C_A are the concentrations of undissociated pairs, dissociated counterions, and dissociated sites within the membrane, respectively. 0 and d indicate the two interfaces, d the thickness of the membrane, with the aqueous solutions on both sides. J_A^T, in Eqn (2.21), is the total flux of sites (i.e., free site plus complex fluxs) given by[76]

$$J_A^T = - \bar{U}_A \; [\underbrace{RT \frac{d\bar{C}_A}{dx}}_{\substack{\text{site}\\ \text{diffusion}\\ \text{term}}} + \underbrace{\bar{C}_A FE}_{\substack{\text{site}\\ \text{migra-}\\ \text{tion}\\ \text{term}}} + \underbrace{RT \frac{d\bar{C}_{Ai}}{dx}}_{\substack{\text{complex}\\ \text{diffusion}\\ \text{term}}}] \text{ ------------- } \quad (2.22)$$

while the parameter t in Eqn (2.20) is given by the expression

$$t = \frac{\bar{U}_A \bar{C}_A}{[(\bar{U}_A \, \bar{C}_A / \sum \bar{U}_{Ai} \bar{C}_{Ai}) + 1] \sum \bar{U}_i \, \bar{C}_i + \bar{U}_A \, \bar{C}_A} \quad (2.23)$$

which varies between 0 for complete dissociation and $U_A \; C_A/(C_A U_A + \sum \bar{U}_i \bar{C}_i)$ for strong association.

When the mobility of the site species is negligible compared to that of the counterion (as in solid ion-exchange membrane), J_A^T and t are zero, and Eqn (2.18) reduces to

$$E = E_o + \frac{RT}{Z_i F} \ln \left[\frac{\sum \bar{U}_i k_i a_{i(1)}}{\sum \bar{U}_i k_i a_{i(2)}} \right] \text{ -------- } \quad (2.24)$$

an equation which corresponds to that of a solid ion-exchange membrane. All novel properties of liquid ion-exchange membranes are therefore contained solely in the two integral terms of Eqn (2.18)

In the steady state when $J_A^T = 0$, i.e., $\int_2 = 0$, and when there is strong association, for the case of two counterions X and Y such that $\bar{C}_A = \bar{C}_X + \bar{C}_Y$, it was shown that $\int_1$ can be integrated[66,71,72,74] and Eqn (2.18) becomes

$$E = E_o + \frac{RT}{Z_i F}(1-\tau)\ln\frac{\sum_{i=1}^{2}(\bar{U}_i+\bar{U}_A)k_i a_{i(1)}}{\sum_{i=1}^{2}(\bar{U}_i+\bar{U}_A)k_i a_{i(2)}} + \tau\ln\frac{\sum_{i=1}^{2}\frac{\bar{U}_{Ai}}{K_{Ai}}k_i a_{i(1)}}{\sum_{i=1}^{2}\frac{\bar{U}_{Ai}}{K_{Ai}}k_i a_{i(2)}} \quad (2.25)$$

$$\text{where } \tau = \frac{\bar{U}_A(\bar{U}_{Ay}K_{Ay} - \bar{U}_{Ax}K_{Ax})}{(\bar{U}_x+\bar{U}_A)\,\bar{U}_{Ay}\,K_{Ay} - (\bar{U}_y+\bar{U}_A)\,\bar{U}_{Ax}K_{Ax}} \quad ;\ 0 \le \tau \le 1 \quad \text{-----} \quad (2.26)$$

The relative contributions of the logarithmic terms to the potential are then governed by the parameter τ. The value of τ depends on the properties of the solvent and the ion-exchanger.

One may have a better insight into Eqn (2.18) if the following points are considered.

1. Eqn (2.18) is valid only under the following conditions[66,72,75,77]
   a) the ligands (sites) are situated exclusively within the membrane;
   b) there are no co-ions within the membrane;
   c) there exists an equilibrium between the ion i and the ligand at any point of the membrane;
   d) there are neither ion-association nor ion-aggregates of higher orders;
   e) within the membrane the activities may be considered equal to the concentrations;
   f) no current is flowing through the system.

2. The theoretical advantage offered by liquid over solid ion exchanger lies in the fact that the mobility of the associated species in the liquid ion-exchanger does not depend on the strength of association in contrast to the situation in a solid exchanger.[72] For liquid ion-exchangers there is decrease in potentiometric selectivity with decreasing site and complex mobility; the effect is greatest for high degrees of ion-pairing.[76] Because of the poor mobility, there are few solid ion-exchangers that are selective to divalent ions, for example.[4] Since the sites are mobile in the liquid ion-exchange membranes, there are a number of them that act selectively to divalent ions.[78]

2.2 Potentiometric Selectivity of Membrane Electrodes

For the ion exchange reaction

$$\bar{I}^{z+} + J^{z+} \rightleftharpoons I^{z+} + \bar{J}^{z+} \qquad (2.27)$$

where the overbar denotes ions in the membrane and without bars those in the aqueous phase, application of the law of mass action gives the exchange equilibrium constant A_{ij} as

$$A_{ij} = \frac{a_I \bar{a}_J}{\bar{a}_I a_J} \qquad (2.28)$$

where the a's indicate activities.

Potentiometric selectivity is governed by single ion extraction coefficients, mobilities in the membrane phase, and complex formation constants (exchange equilibrium constants).[73,74,79]

A_{ij} is related to the partition coefficients of ions i and j (K_i and K_j respectively) as

$$A_{ij} = \frac{K_j}{K_i} \qquad (2.29)$$

The sum of the diffusion potential in the membrane, the difference in potential between the membrane and the aqueous phase gives, for ions i and j, the total potential[4]

$$E = (E_1 - E_2) + E_L$$

$$E = \frac{nRT}{F} \ln \frac{\{a_{i(1)}\}^{1/n} + (K_{ij}^{pot}\, a_{j(1)}\}^{1/n}}{(a_{i(2)})^{1/n} + \{K_{ij}^{pot} a_{j(2)}\}^{1/n}} \quad \text{------------------ (2.30)}$$

where K_{ij}^{pot} has been called selectvity coefficient which may include both the chemical (e.g. partition coefficients, solubility products) and the mobility (mobilities in the membrane) factors,[4,79] n is defined by the empirical equation Eqn (2.31)[4,80,81] and depends on the membrane properties only.

$$A_{ij} = \frac{a_j}{a_i} \left(\frac{\bar{X}_i}{\bar{X}_j} \right)^n \quad \text{------------------------------------ (2.31)}$$

in which the $\bar{X}$'s are the mole fractions, and $\bar{X}_i + \bar{X}_j = 1$ is assumed.

If the concentrations on side(2) are held constant, as in a membrane electrode unit, Eqn(2.30) can be written, for n = 1 in the general form of the extended Nikolsky-Eisenman equation:[4,78,79,81,82]

$$E = \text{Constant} \pm \frac{RT}{Z_i F} \ln \quad a_i + \sum_{j \neq i} K_{ij}^{pot} (a_j)^{\ Z_i/Z_j} \quad \text{------- (2.32)}$$

where i is the primary ion of valence z_i to which the membrane electrode is selective, j is the interfering ion of valence Z_j, and K_{ij}^{pot} is the potentiometric selectivity coefficient. The (+) applies for cations and the (-) sign for anions.

For an ion-selective electrode to show Nernstian response towards the primary ion, i, the value of K_{ij}^{pot} must be very small (less than unity).

The sequence of selectivity depends on the standard Gibbs free energy change of reaction (2.27), i.e. on the partial molal free energies of the interactions of the species with water and the membrane site, and is evaluated from hydration energies of the ions and the radii of the sits, counter-and co-ions.[4,71,80,83,84]

Determination of Selectivity Coefficient, K_{ij}^{pot}. No ISE responds exclusively to the ion to which it is designed although it may be more responsive to this primary ion than to others. The degree of selectivity of the electrode for the primary ion, i, with respect to an interfering ion, j, is expressed by the potentiometric selectivity coefficient, K_{ij}^{pot}, defined by Eqn (2.32)

Variations in K_{ij}^{pot} are associated with the mechanism of the electrode response[85] and with the changing environment of the ions in solution. These factors also cause K_{ij}^{pot} to depend on the method used to determine it.[86]

A number of methods[82,83,87] have been described for the experimental determination of selectivity coefficients. These methods fall into two categories: the separate solution method (with the same concentration of i and j or with concentrations of i and j of the same potential); and mixed solution method (suggested by IUPAC[45]).

a) Separate Solution Method. In this method only one ion is used in any test solution.

Method 1. For the primary ion i only in solution (i.e., $a_j = 0$),

$$E_i = E_o + \frac{RT}{Z_iF} \ln a_i \quad \text{------------} \quad (2.33)$$

If the solution is without i (i.e., $a_i = 0$) and contains only ion j, Eqn (2.32) becomes

$$E_j = E_o \pm \frac{RT}{Z_jF} \ \ln K_{ij}^{pot} \ (a_j)^{z_i/z_j} \quad \text{-----------------} \quad (2.34)$$

For the condition $a_i = a_j$, Eqns (2.33) and (2.34) give the relation[80,88,89]

$$\pm\frac{(E_j-E_i)}{S} = \log K_{ij}^{pot} + \left(\frac{Z_i}{Z_j} - 1\right) \ \log a_i \quad \text{----------} \quad (2.35)$$

where $S = 2.03\ RT/Z_iF$ or the experimental slope, E_j and E_i are in millivolts, and (+) applies to cation-and (-) to anion-selective electrodes.

Method 2. If the concentrations of the solution of ion i and of the solution of ion j are chosen such that $E_i = E_j$, then Eqns (2.32) and (2.33) give[66]

$$a_i = K_{ij}^{pot} \ (a_j)^{Z_i/Z_j} \quad \text{------------------------------} \quad (2.36)$$

b) Mixed Solution Method. Both ions i and j are in the same solution in this method. By measuring the potentials of solutions containing a fixed quantity of the interfering ion, j, and varied quantities of the primary ion, i, values of K_{ij}^{pot} can be obtained. Ideally the values of K_{ij}^{pot} can be calculated from Eqn (2.36), a_i and a_j being the activities that are determined from the plot of the measured potential against $P^{a}i$ (Figs. 3).

Method 1. This method depends on finding graphically the point T (Fig.3a) at which the electrode is responding equally to both ions, i.e., $a_i = K_{ij}^{pot} \ (a_j)^{Z_i/Z_j}$. If the line signment DC is straight and parallel to the abscissa, then T is the point of intersection of the extrapolation of AB and DC as shown. Then[24,38]

$$K_{ij}^{pot} = \frac{a_i^{Z_j}(T)}{a_j^{Z_i}} \quad \text{------------------------------} \quad (2.37)$$

Method 2. A more applicable method when DC is not nessessarily parallel to the abscissa is considered here. At a point R where both ions are contributing equally to the electrode response. Eqn (2.36) holds. At this point, Eqn (2.32) together with Eqn (2.36) give

$$E = E_0 \pm \frac{2.303RT}{Z_iF} \log_{10}(2a_{i(R)}) \qquad (2.38)$$

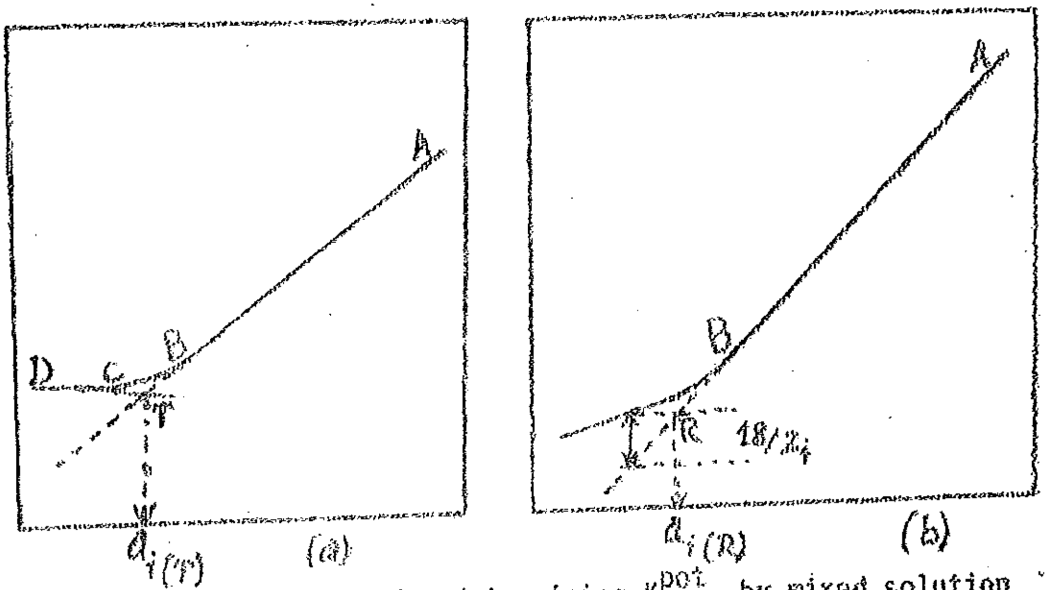

Fig. 3. Typical curves for determining K_{ij}^{pot} by mixed solution method.

The response of the electrode in the absence of j is given by the extrapolation of AB as far as the limit of Nernstian response. The difference between the electrode potential in solution of i with activity $a_{i(R)}$, with and without j at activity $a_{j(R)}$ is therefore given by

$$E = \frac{2.303\ RT}{Z_iF} (\log_{10} 2a_{i(R)}) - \log_{10} a_{i(R)}$$

$$= \frac{2.303\ RT}{Z_iF} \log_{10} 2$$

$$= \frac{18}{Z_i} \text{ mV at } 25°C.$$

$$E = \frac{2.303\ RT}{Z_iF}\ (\log_{10}2a_{i(R)} - \log_{10}a_{i(R)}$$

$$= \frac{2.303\ RT}{Z_iF}\ \log_{10}^{2}$$

$$\doteqdot \frac{18}{Z_i}\ \text{mV at } 25^{\circ}\text{C.}$$

Thus by finding, on the graph, the activity of i at which the experimental line differes from the extrapolation of the Neynstian region by $18/Z_i$ mV (Fig. 3b) the activity $a_{i(R)}$ is determined.

Then[24]

$$K_{ij}^{pot} = \frac{a_{i(R)}^{\;Z_j}}{a_{j(R)}^{\;Z_i}} \quad\text{---}\quad (2.39)$$

Though most of the methods to determine K_{ij}^{pot} use the above procedures, some other methods are also used by different authors.[9,13]

Any two methods seldom yield the same value of K_{ij}^{pot} from a given set of data. For any quoted value to be of use and comparable to other values, full details must be available of both the method of calculation and the experimental procedure used to derive the data (e.g. values of a_j, etc).[28]

2.3 Measurement Techniques (4,24,65,66,90)

The potential behaviour of ISEs in solutions containing ionic species for which the electrodes are selective is described by the Nernst equation. Concentration calculations can be made from ISE potentiometry provided all solutions are treated with high concentration electrolyte whose ions are not sensed by the ISE, since the activity coefficient (f_i) of the ion to be measured is held practically constant,

i.e., $C = f_ia_i$ or $C \propto a_i$.

The use of this equation does not need any knowledge of standard potentials or slope, and the method will compensate for slow drift in both parameters.

Standard Addition Technique. This is a method in which a known volume of a standard solution is added to a known volume of the sample and recording the potential change of the electrode.[97-100] The observed initial potential of the sample solution of unknown concentration (C_x) is given by the Nernst equation

$$E_X = E_o \pm \frac{RT}{ZF} \ln(C_x f_o) + E_L \tag{2.44}$$

On addition of a known volume (V_s) of the standard solution of the test ion of concentration C_s to the initial volume (V_x), the new potential measured (E_t) is given by

$$E_t = E_o \pm \frac{RT}{ZF} \ln \frac{C_x V_x + C_s V_s}{V_x + V_s} f_x + \Delta E_L \tag{2.45}$$

where E_o is a constant, f_x is the activity coefficient, and ΔE_L is the change in the liquid junction potential.

If $f_o = f_x$ and ΔE_L is negligible, the change in potential (ΔE) is found to be

$$\Delta E = \frac{RT}{ZF} \ln \frac{V_x C_x + V_s C_s}{C_x (V_x + V_s)} \tag{2.46}$$

Then

$$C_x = \frac{C_s}{10^{\Delta E/S}(1+ \frac{V_x}{V_s} - \frac{V_x}{V_s}} \tag{2.47}$$

where S is the experimental slope, usually of a lower value than 2.303 RT/ZF, and $\Delta E = E_t - E_x$ for $C_s > C_x$.

Sample Addition to a Standard. Initially the potential (E_s) of a fixed volume (V_s) in ml of a standard solution (C_s) of the test ion is measured. A volume (V_x) of sample solution is then added and the new potential E_t is measured. Reasoning as in the standard addition case, one obtains

$$C_x = C_s\ [10^{\Delta E/S} (1+ \frac{V_s}{V_x}) - \frac{V_s}{V_x}] \text{ ----------- } (2.48)$$

where $\Delta E = E_t - E_s$ for $C_x > C_s$.

Gran's Plot Technique. This is a standard addition method to measure C_x in V_x, involving multiple additions of the standard solution (V_s of C_s) to the sample. In one variation of Gran's plot,[101-103] Eqn (2.45) is re-arranged to give

$$(V_x+V_s)\ 10^{E/S} = 10^{Eo/S}\ (C_xV_x + C_sV_s) \text{ ---------- } (2.49)$$

For the measured potential E. This equation is valid for a solution of high ionic strength and negligible liquid junction potential. A plot of $(V_x+V_s)\ 10^{E/S}$ against V_s gives a straight line which intercepts the abscissa for a value of V_s called V_e, where $C_xV_x = -C_sV_e$. Thus C_x can be calculated as $C_x = -C_sV_e/C_x$.

Standard Subtraction Technique. The standard or known subtraction method[104] is different from the standard addition techinque only in that the standard solution added to the sample is not that of the ion sensed by the electrode but a solution of a species which reacts quantitatively with the analyte. Thus, a decrease in analyte concentration is produced with corresponding change in cell potential. This potential change may be used to calculate the initial analyte concentration in the sample by means of Eqn (2.50) derived in a similar manner to Eqn (2.47)[65]

$$C_x = C_s \left(\frac{V_s}{V_x} \right) \left[\frac{1}{10^{-\Delta E/S} - 1} \right] \quad \text{---------} \quad (2.50)$$

where Δ E is the change in cell potential.

Eqn (2.50) is valid only when the valency of the unknown ion and that of the precipitating or complexing agent added (the standard solution) is the same, and/or their stoichiometric reaction is 1:1. When the valency differs, the stoichiometry differs and the derivations of the equations are more complicated.[24]

Potentiometric Titration Technique.[3,65] The titrant solution is one which will react or complex the ion to be determined. In this method the potential is measured as a function of the volume or amount of titrant added. These methods provide more accurate results at the expense of time.

In potentiometric titrations the end-point can be detected by ion-selective electrode provided the electrode responds to the analyte ion, the titrant species or an indicator ion, so that it reacts with the titrant only when the analyte concentration is near or at the equivalence point.

At the equivalence point, the electrode potential changes rapidly with the titrant volume. There are several ways[105-110] of estimating the end point of potentiometric titrations, of which two are mentioned here.

1. By visual inspection of the graph of potential against volume added; the end point is at the steepest part of the curve.
2. By calculating the rate of change of potential with volume; the end point is the maximum value of this function.

3. EXPERIMENTAL

3.1 Materials and Reagents.

Crystal-Violet (hexamethyl-p- rosaniline hydrogen chloride nonahydrate)(Hopkins and Williams), PVC powder (Fluka), THF (Riedel-de Haen), 1-chloronaphthalene (BDH), nitrobenzene (Riedel-de Haen or BDH), chlorobenzene, 1,2 - dichlorobenzene, 1,2-dichloroethane (all BDH), ferric chloride hexahydrate (BDH), ferric ammonium sulphate (iron alum) (Analar, Hopkins and Williams), lithium chloride (BDH or Riedel-de Haen) and hydrochloric acid (Analar, Reidel-de Haen) were used as received without further purification.

3.2 Preparation of Solutions

3.2.1 Chloride Complexing Solutions I and II. Stock chloride complexing solutions were prepared by dissolving LiCl, to give final concentration of 4 M with respect to LiCl and 1 M with respect to HCl (complexing solution I), or a concentration of $\frac{16}{3}$ M with respect to LiCl and $\frac{4}{3}$ M with respect to HCl (complexing solution II) to dilute the sample solutions.

3.2.2 Standard Iron (III) Solutions. A $1\text{x}10^{-1}$ M iron(III) stock solution was prepared by dissolving iron(III) chloride hexahydrate or iron(III) ammonium sulphate (iron alum) in chloride complexing solution I containing 5 M chloride. Subsequent dilutions were made, using the same complexing solution I, in the range $2.5\text{x}10^{-7}$ $-1\text{x}10^{-1}$ M with respect to iron(III). Fresh dilutions were made for iron(III) concentrations lower than 10^{-5} M. All the serially diluted solutions were stored in polyethylene bottles.

3.2.3 EDTA Solutions. A stock solution of 0.05 M ethylenediaminetetraacetic acid (EDTA) solution was prepared by dissolving the disodium salt in distilled water. The solution was standardised against magnesium chloride (BDH, Analar) using NH_3/NH_4Cl buffer at pH 10 and Eriochrome Black T indicator. A desired concentration of the EDTA solution was prepared by dilution with the complexing solution such that the final chloride solution would be 5 M. The pH adjustment (1.0-1.4) of the solution was made with solid LiOH or saturated NaOH solution perior to final volume.

3.2.4 Foreign Ions Solutions. For the studies of cation and anion inteferences, a stock solution ($4x10^{-2}$ M or $1x10^{-2}$ M) of each of the following salts was prepared: chloride of Hg^{2+}, Sn^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, and Cr^{3+}; nitrates of Cd^{2+} and Ni^{2+}; acetates of Pb^{2+} and Zn^{2+}; sulphates of Cu^{2+}, Fe^{2+}, and Zr^{4+}; sodium salts of VO_3^-, WO_4^{2-}, $C_6H_5COO^-$, $C_2O_4^{2-}$, $S_2O_3^{2-}$, SO_4^{2-}, F^-, Br^-, ClO_4^-, and CH_3COO^- ; ammonium salts of NO_3^- and SCN^-; potassium salts of I^-, IO_4^- , $HC_8H_4O_4^-$; saccharin ion

3.3 Sample Preparation

3.3.1 Iron Ore. The iron ore (haematite), obtained from the Ethiopian Institute of Geological Survey (EIGS), was finely ground and passed through a 200-mm mesh sieve. A 0.1-g portion of the ground sample was mixed with 0.5 g of lithium metaborate and 1 g of lithium tetraborate. The mixture was transfered into a 30-ml platinum crucible and fused in a muffle furnace at 930 °C for 1 h. The melt was cooled, dissoved in 100 ml dilute nitric acid (1:19 v/v) and boiled in a 400-ml beaker. The solution was transfered into a 250-ml volumetric falsk and diluted to volume with 1:19 (v/v) dilute nitric acid. A 5-ml aliquot of this solution was used for analysis after adjusting the chloride concentration to 5 M with 15 ml of complexing solutionII.

3.3.2 Blood Sample. The blood sample from an adult man was decomposed by a reported method.[111,112] That is a 2-ml aliquot of the blood sample was transfered into a 250-ml Kjeldhal flask and decomposed with 10 ml of a mixture of HNO_3, H_2SO_4 and $HClO_4$ (3:1:1 v/v) by heating on a bunsen burner for about 2 h. 10 ml of dilute HCl was then added and the heating was continued until the content was reduced to about 5 ml and then cooled to room temperature. The residue was reboiled with 25 ml distilled water, cooled and transfered quantitatively into a 100-ml volumetric flask and diluted to the mark with distilled water. For total iron determination in blood, 5 ml of this solution was mixed with 15 ml complexing solution II.

3.3.3 Syrup Sample. The syrup sample (Ferlixir®, Nattermann D-5000 Koln 30, FRG) was obtained from a local pharmacy. A 2-ml aliquot of the mineralized and vitamininized syrup was treated with 3 drops (from an eye droper) of a mixture of concentrated nitric and hydrochloric acids (2:1 v/v). The solution was then diluted to 20 ml with complexing solution II for analysis.

3.4 Preparation of Liquid Membrane Electrode

3.4.1 Extraction of Crystal Violet-Tetrachloroferrate(III). 25 ml of 7×10^{-4} M aqueous solution of Crystal Violet was mixed with 25 ml of 5×10^{-2} M iron(III) chloride solution in 4 M LiCl and 1 M HCl. The mixture was transfered into a 100-ml separatory funnel and 25 ml of nitrobenzene was added to it. The mixture was shaken vigorously for two minutes and the two phases allowed to separate for 30 minutes. The organic phase was dried over anhydrous sodium sulphate and used as the liquid membrane.

3.4.2 Construction of Electrode. Concentric Pyrex tubes (about 120 mm long with internal diameter of 6 mm and 12 mm) were joined to a common

14/23 ground glass joint (which fits to Ag/AgCl reference electrode) at one end by glass blowing technique. The other open ends of the concentric tubes were also drawn to respective internal diameters of about 3.3 and 8.8 mm. A 6-mm diameter injection port was made at the outer jacket, below the common joint. This assembly was used as electrode body (Fig.4).

A PVC solution was prepared by dissolving 100 mg of the polymer in 4 ml THF and about 0.25 ml (8 to 10 drops from an eye dropper) of 1-chloronaphthalene was added as plasticizer. The narrow tip of the electrode body was carefully dipped into the PVC every two minutes (to evaporate the THF partially), until the paste attains 2-3 mm thickness with attention not to allow any occlusion of gas bubbles into the PVC paste. The electrode body was then suspended, with the PVC held downwards, in a hood for 24 h. About 2 to 3 ml of Crystal Violet-tetrachloroferrate(III) extract in nitrobenzene was introduced into the outer jacket through the injection port and kept for at least 24 h to saturate the PVC membrane support. The internal filling solution ($1x10^{-3}$ M) iron(III) in the complexing solution I was then introduced into the inner tube to a level at which an internal Ag/AgCl reference electrode would be in contact (Fig. 4). The tip of the electrode was immersed into an aliquot of the $1x10^{-3}$ M iron(III) solution used as internal filling solution, for a 24-h conditioning or when not in use.

3.5 Instrumentation

Potential measurements of test solutions were made at room temperature (22±2 °C) with the liquid membrane electrode against an external calomel reference electrode using Philips P W 9409 digital pH/mV meter of 0.1 mV precision. All measurements were made 20-90 seconds after continuous stirring with a Teflon-coated stirring bar. A complete cell is schematically represented as follows.

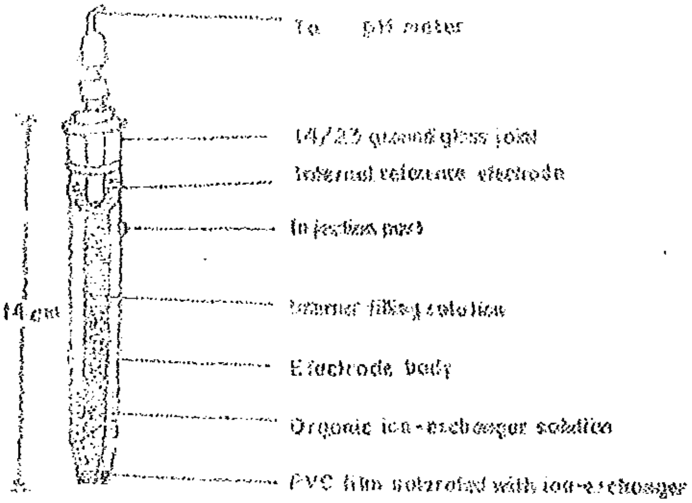

Fig.4 Liquid membrane electrode assembly

$$\mathrm{Ag/AgCl,}\ \begin{array}{c}\text{Internal}\\ \text{Solution}\end{array} \Bigg| \begin{array}{c}\text{Liquid}\\ \text{membrane}\end{array} \Bigg\| \begin{array}{c}\text{Test}\\ \text{solution}\end{array} \Bigg\| \begin{array}{l}\text{Sat.KCl}\\ \mathrm{Hg/HgCl_2}\end{array}$$

pH measurements were made, where necessary, with a Beckman Chem Mate pH-meter.

3.6 General Procedures

3.6.1 Direct Potentiometry. Potentials of $2.5\text{x}10^{-7}$-10^{-1} M solutions of tetrachloroferrate(III) were measured for calibration and other response characteristics of the tetrochloroferrate(III)-selective membrane electrode.

The liquid membrane electrode and the external reference electrode were immersed into a stirred solution (about 20 ml) in a 100-ml beaker. A constant potential was recorded from the pH/mV meter within 20-90 seconds. The potential of an aliquot of a sample in complexing chloride solution I was measured by following the same procedure for the standards. The iron concentration in the sample was determined from the calibration curve, E (mV) vs. log [Fe^{3+}]. Alternately, the iron concentration could be calculated based on a single point calibration method [Eqn (2.42)].

3.6.2 Standard Additon Technique.[113] The potential (E_x) of 10 to 20 ml (V_x) of the sample of concentration C_x of the iron(III) in the complexing solution was first measured. 1 or 2 ml (V_s) of a standard solution (C_s) was added to the sample solution and the new potential (E_t) recorded. The unknown concentration was determined from Eqn (2.47).

3.6.3 Sample Additon Technique.[97,113] The potential (E_s) of 10 to 20 ml (V_s) of a standard iron(III) in the complexing solution was initially measured. A 1 to 2 ml (V_x) aliquot of the sample solution was added and the new potential (E_t) measured. The concentration of iron(III) in the complexing solution was calculated from Eqn (2.48).

3.6.4 Standard Subtraction Method. The pH of the sample solutions, in 5 M chloride, was first adjusted to 1.0-1.4 with solid LiOH or few drops of saturated NaOH solution. The initial potential (E_x) of 15-20 ml (V_x) of the iron(III) sample (C_x) was measured. A 1-2 ml (V_s) aliquot of the EDTA solution (C_s) was then added with subsequent measurement of the new potential. Calculation of the concentration of iron(III) (C_x) in the complexing solution was made according to Eqn (2.50).[65,24]

3.6.5 Potentiometric EDTA Titrations. To test the feasibility of potentiometric EDTA titrations, experiments were run on 10^{-5} to 10^{-2} M of iron(III) in 5 M chloride solutions. About equimolar solutions of EDTA and iron(III) were initially prepared for each titration in the chloride solution. The pH of the iron(III) solutions were then adjusted to 1.0-1.4 with solid LiOH or a few drops of saturated NaOH solution. Titration of the iron(III) solution against EDTA from a 0.05-ml precision burette was performed with the tetrachloroferrate(III)-selective liquid membrane electrode (*vs.* calomel reference electrode). The constant potential after each addition of EDTA was recorded and the inflection point of the titration curve was noted using conventional techniques for the quantitative evaluation of iron(III) in the original solution.

3.7 Study of Conditions.

The influence of the acidity due to HCl was investigated using direct potentiometric procedure (section 3.6.1. herein) maintaining the total chloride concentration at 5 M. The effect of the total chloride concentration was also studied at 1 M HCl.

3.8 Selectivity Coefficient Determination

3.8.1 Separate Solution Method. The potentials of 10^{-2} M solutions of iron(III) (E_i) and the interfering ion (E_j) in 4 M LiCl and 1 M HCl were measured separately. The potentiometric selectivity coefficient (K_{ij}^{pot}) was determined from Eqn (2.35).[80,88,89]

3.8.2 Mixed Solution Method. A 5-ml aliquot of $4x10^{-2}$ M solution of an interfering ion (j) in 5 M chloride were added to 15 ml of $2.5x10^{-7}$ - $1x10^{-1}$ M Fe(III) solutions (see section 3.2.2). The potentials of the resulting solutions were measured and selectivity coefficients were evaluated from the calibration curves (section 2.2) in the presence of each interfering ion[24,38] and Eqn (2.39) of Chapter 2.

4. RESULTS AND DISCUSSION

4.1 Preparation of the Liquid Membrane Electrode.

A liquid membrane electrode was constructed as described in section 3.4.2. The body of the electrode was made from chemically inert and readily available materials, i.e., glass stems.

Defferent materials such as Millipore® filter, glass frit, and porous Teflon sheet were tried to be fixed to the glass stems as membrane support. All failed for mechanical reasons, resulting in leakage.

For these reasons plasticized PVC was reverted to and used as a membrane support. The PVC preparation (section 3.4.2) was proved to be intact with the glass stems, which overcame leakage problem. Similar results have been reported earlier for a PVC membrane electrode.[32] This technique also eliminated the mechanical difficulties resulting from fixing a PVC disc as membrane support, separately prepared by impregnating the ion-exchanger in a polymeric matrix,[114]

Plasticized PVC acts in a microscopic manner-unlike the traditional liquid support matrixes which are macroscopic in nature by forming a molecular network into which the exchangerladen solvents permeate. The PVC swells in the presence of these solvents and releases the solvent to the external sample reluctantly, thus presenting an attractive ISE configuration.[27]

It should be noted that the drying time (section 3.4.2) of, at least, 24 h is essential since failure to do this may cause leakage or very short electrode life time. One should also notice that less than 24 h saturation time of the PVC matrix results in failure to respond indicating slow diffusion rate of the organic solvent in the support.

4.2 Selection of Solvents.

Most of the liquid membranes introduced so far incorporate solvent

The other three widely differ from nitrobenzene in dielectric constant which is one of the most important properties. The Crystal Violet-tetrachloroferrate(III) salt was extracted into each solvent under the same conditions. The extractibility (colour intensity) as visually compared, was in the order: NB > 1,2-DCE > 1,2-DCB > CB. This observation indicates that the ion-association salt is more extractable into a solvent of high dielectric constant.

The extracts were used as liquid membranes. Except the nitrobenzene extract, none of them showed any potential response. This finding may indicate that the electrode behaviour is governed by ion dissociation in the membrane phase.[53]

Based on the above results and the high boiling point (low volatility), low solubility in the aqueous phase, density deffering from that of water for good phase separation, and high viscosity not to pass through the membrane matrix, nitrobenzene was the solvent of choice.

4.3 Influence of Exchanger Concentration in Nitrobenzene.

Three different liquid membrane electrodes with 7×10^{-5}, 1.4×10^{-4} and 7×10^{-4} M Crystal Violet-tetrachloroferrate(III) ($CV^{+}FeCl_4^{-}$) in nitrobenzene were prepared and the response behaviour investigated. The results are shown in Fig. 5. The electrode which incorporated 7×10^{-5} M of the dye showed a linear response only between 2.5×10^{-3} and 2.5×10^{-5} M iron(III) concentration in the test solution with an average slope of -51 mV decade^{-1} concentration change. The case of 1.4×10^{-4} M also showed linearity in the same range but with an increase in slope to -53 mV decade^{-1}. However, the potential readings were not so stable, presumably owing to higher membrane resistance. At 7×10^{-4} M of the dye extract the linear range was widened to 2.5×10^{-5}-5×10^{-2} M iron(III) concentration, with an improved slope of -56 mV per decade of the calibration curve. This concentration in the organic phase resulted in the most stable potential readings. Higher concentration of Crystal Violet could not be tried due to low solubility of the dye. Therefore, the $7x10^{-4}$ M of the dye extract was used as the liquid membrane.

4.4 Response Characteristics of the Electrode.

The electrode was found to respond to $FeCl_4^-$ in a wide range (Fig. 6). The concentration range studied was $2.5x10^{-7}$ to $1x10^{-1}$ M iron(III) ions. The electrode responds to $FeCl_4^-$ with a sub-Nernstian slope (-56 mV/decade) in the concentration range of $2.5x10^{-5}$ to $5x10^{-2}$ M at a temperature of $22^{o}\pm2^{o}$C. This slope is typical of a monovalent anion. Theoretically the slope sould have been 59.2 mV $decade^{-1}$ at 25^{o}C. The deviation to 56 mV is mainly due to the experimental temperature of $22^{o}\pm2^{o}$C. The slope also depends on the behaviour of the electrode. The response time were found to be within 20 seconds for concentrations greater than 10^{-3} M iron(III) and 20-90 seconds for lower concentrations. The slope of the electrode response remained practically constant during the whole life of the electrode. The electrode was found to function properly for over three months. Since liquid membrane ISEs have characteristically larger quantity and mobility of the electroactive materials the electrde surface is inherently renewable. Therefore, the life time of the electrode is determined mainly by mechanical reasons (breakage of membrane support).

The drift in potential measurement using the liquid membrane electrode was evaluated by measuring the potentials of two known and constant concentration of iron(III) ($FeCl_4^-$) was found to be not more than 2 mV/24 h.

The response behaviour of the electrode was studied for other anions. Of these, it was found that the electrode responds to IO_4^-, MnO_4^-, $C_6H_5COO^-$, SCN^-, and ClO_4^- ions, yet, in rather narrow ranges (Table 2).

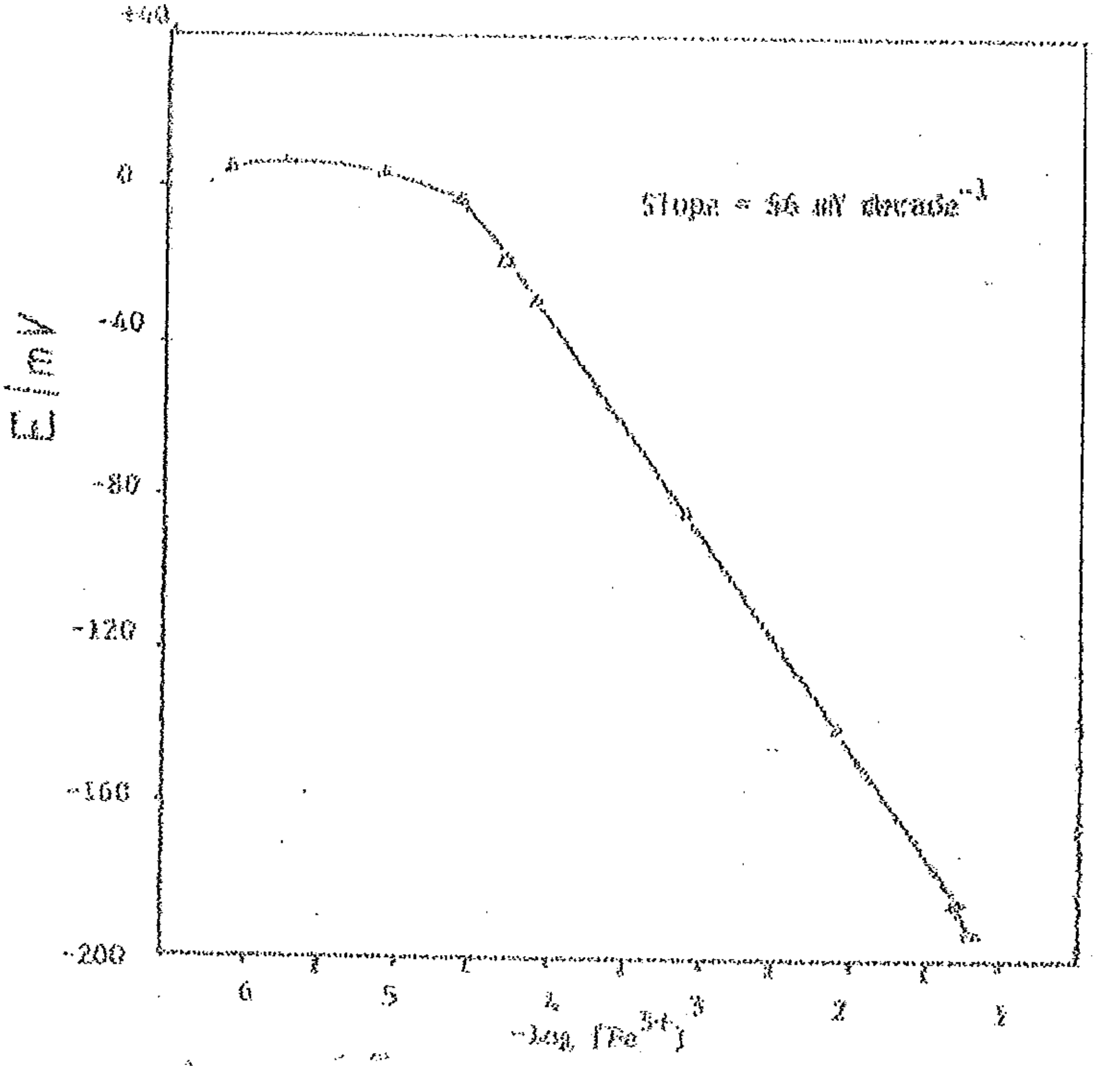

Fig. 6 Calibration curve [[Cl$^-$] = 5.0 M, [H$^+$] = 1.0 M].

Table 2. Response of $CV^+FeCl_4^-$ electrode to other anions

Anion	Slope (mV decade^{-1})	Linear range, M
IO_4^-	-54.8	$2x10^{-2}$ - $2x10^{-4}$
MnO_4^-	-56.6	$4x10^{-2}$ - $4x10^{-4}$
$C_6H_5COO^-$	-45.8	$4x10^{-3}$ - $4x10^{-4}$
SCN^-	-48.0	$4x10^{-2}$ - $4x10^{-3}$
ClO_4^-	-48.7	$4x10^{-2}$ - $4x10^{-4}$

ISEs respond to activities of ions in solutions according to the Nernst equation

$$E = \text{constant} - S \log a_i \qquad (4.1)$$

where S is the experimental slope and a_i is the activity of the ions. At constant high concentration of an "inert" electrolyte, activity can be replaced by concentration due to the constancy of the activity coefficient. Hence

$$E = \text{constant}^* - S \log C_i \qquad (4.2)$$

where constant* is a new constant incorporating the activity coefficient, and C_i is the concentration of the analyte ions. Hence response curves were obtained by ploting the measured potentials (E , mV) Vs - log C_i.

4.5 Effect of Variables on Response.

Since the formation of chlorocomplexes of iron(III) species in aqueous solution are not so favourable even at very high chloride concentration, the actual concentration of the tetrachloroferrate(III) species in any iron(III) solution containing chloride, is lower than the total iron concentration.[62] Therefore it was necessary to use a controlled high concentration of chloride solution which contains hydrochloric acid. Hydrochloric acid suppresses or prevents the hydrolysis of Fe^{3+} in the aqueous phase.

The effect of chloride concentration and hydrochloric acid concentration was studied to get optimum concentrations that would be used in the aqueous solutions.

4.5.1 Effect of Chloride Ion Concentration. In this study, the concentration of HCl was kept constant at 1 M and the total chloride concentration varied using LiCl.

Though the potentials increase with increasing chloride concentration, the difference in potential remained constant for two ion(III) concentration corresponding to a slope of -56 mV perdecade (Figs. 7 and 8 and Table 3), for the total chloride concentration range of 4.0-5.5 M. The shift to more negative potential is pressumably, due to more fraction of complexation of Fe^{3+} to $FeCl_4^-$ with increasing chloride concentration. LiCl was prefered to other salts such as KCl, because of its high solubility.

Table 3. Effect of Chloride ion concentration on electrode response ([HCl] = 1 M)

$[Cl^-]$	Slope[a] mV/decade	Slope[b] mV/decade
2.50	-51.0	-53.1
3.25	-52.8	-53.9
4.00	-55.8	-55.4
4.75	-55.9	-55.8
5.50	-56.1	-56.0

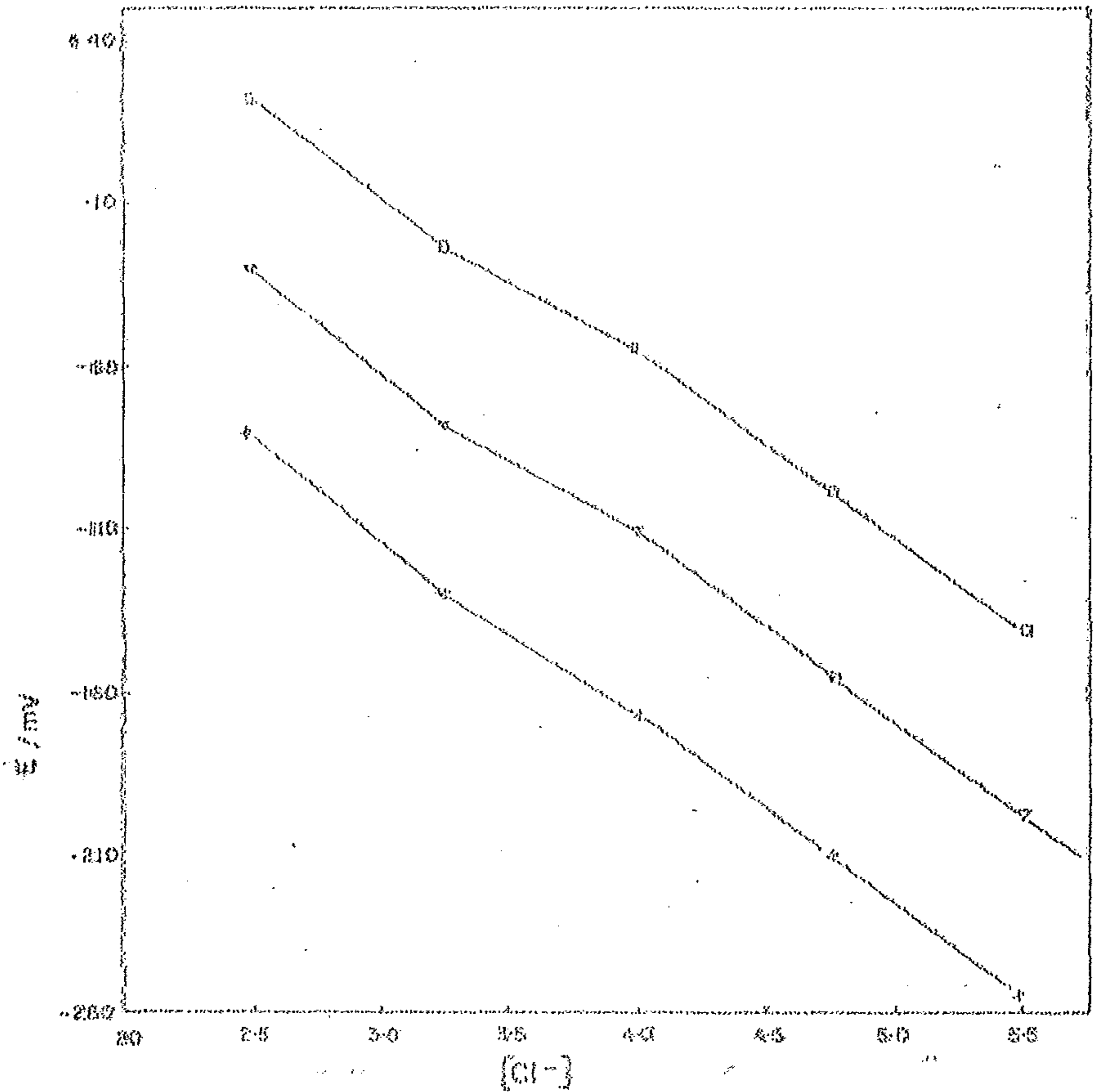

Fig. 7. Effect of chloride ions concentration on potential ([HCl] = 1 M)

(□) 2.5×10^{-2} M Fe^{3+}, (Δ) 2.5×10^{-3} M Fe^{3+}; & ( ) 2.5×10^{-4} M Fe^{3+}

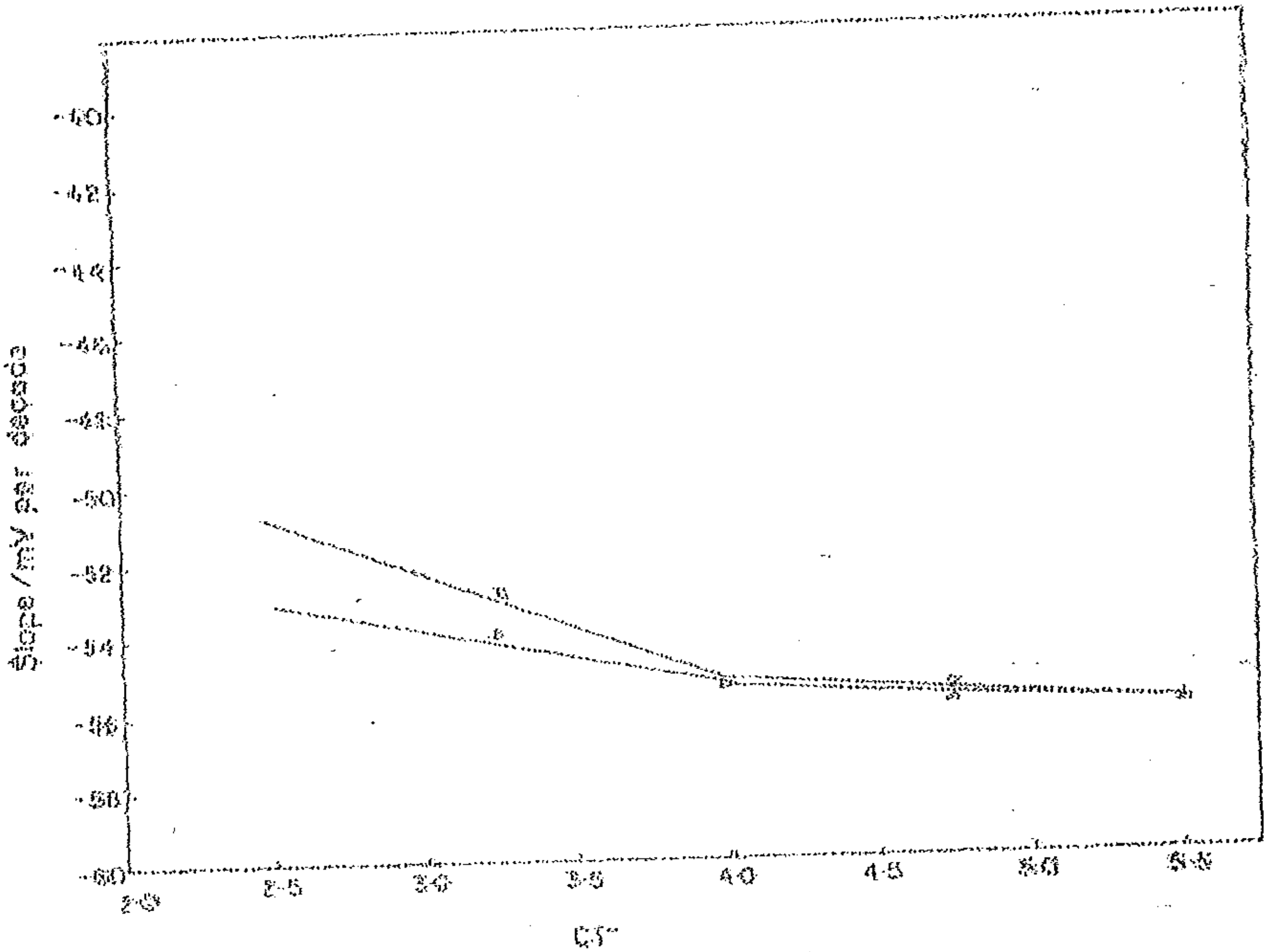

Fig. 8. Effect of chloride concentration on slope ([HCl] = 1M;
(a) slope between $2{\cdot}5 \times 10^{-6}$ M & $2{\cdot}5 \times 10^{-5}$ M Fe^{3+}) &
(b) slope between $2{\cdot}5 \times 10^{-4}$ M & $2{\cdot}5 \times 10^{-3}$ M Fe^{3+}.

[a]Concentration range $2.5x10^{-2}$ $-2.5x10^{-3}$ M Fe^{3+}.

[b]Concentration range $2.5x10^{-4}$ $-2.5x10^{-3}$ M Fe^{3+}.

4.5.2. Effect of HCl Concentration. The behaviour of the electrode towards $FeCl_4^-$ at different HCl concentrations was studied, keeping the total chloride concentration constant at 5 M.

More negative potentials were observed with increasing hydrochloric acid concentration upto 1.0 M HCl and nearly constant potentials within ±1mV, at 1.0-1.5 M. The observed slope of an ionic response was 55-56 mV/decade from 0.75 to 1.5 M HCl (Figs. 9 and 10 and Table 4).

Table 4. Effect of HCl concentration on electrode response towards $FeCl_4^-$ ion ($[Cl^-]$ = 5 M)

HCl,M	Slope[a] mV/decade	Slope[b] mV/decade	Slope[c] mV/decade
0.05	-49.7	-50.3	
0.1	-51.3	-52.0	-52.6
0.5	-52.8	-52.5	-53.0
0.75	-55.3	-55.8	-56.0
1.0	-55.5	-56.0	-56.2
1.25	-55.6	-55.8	
1.5	-56.2	-55.3	-56.4
2.0	-53.6	-53.8	-52.9

[a]Slope between $2.5x10^{-3}$ and $2.5x10^{-2}$ M $FeCl_4^-$.

[b]Slope between $2.5x10^{-4}$ and 2.510^{-3} M $FeCl_4^-$.

[c]Slope between $2.5x10^{-4}$ and $2.5x10^{-5}$ M $FeCl_4^-$.

At concentrations of HCl less than 0.75 M the slopes were found to be between -50 and -53 mV/decade. The behaviour at lower HCl concentrations is expected to be due to hydrolysis of Fe^{3+} ions. At concentrations higher than 1.5 M, decrease in slope was observed and above 2 M HCl the potential readings were not stable. Such observations at higher HCl concentrations (above 1.5 M) could possibly be due to the protonation of the dye which might have resulted in the dissolution of the membrane.

From the above discussions it is clear that one can work in 4-5.5 M total chloride and in the range 0.75-1.5 M HCl concentrations.

Based on these observations, the chloride complexing solution was chosen to be 5 M in total chloride concentration and 1 M in HCl, for other investigations.

4.6 Interference Studies.

The effect of different ions on the electrode response was studied and the selectivity coefficients, K_{ij}^{pot}, were evaluted where appropriate. Both the separate solution and mixed solution methods were employed to calculate the K_{ij}^{pot} values from Eqns 2.35 and 2.39. respectively. Eqn 2.39 together with calibration curves (Fig. 3) explained in section 2.2 was used for the mixed solution method. Calculations were made for various anion and metal ion which form anionic complexes. Table 5 shows the K_{ij}^{pot} values evaluated by the two methods.

There are variations in the K_{ij}^{pot} values obtained by the two methods due to experimental differences. It can be noted that K_{ij}^{pot} values obtained by the two methods are not necessarily the same, as reported for other liquid membrane electrodes.[24]

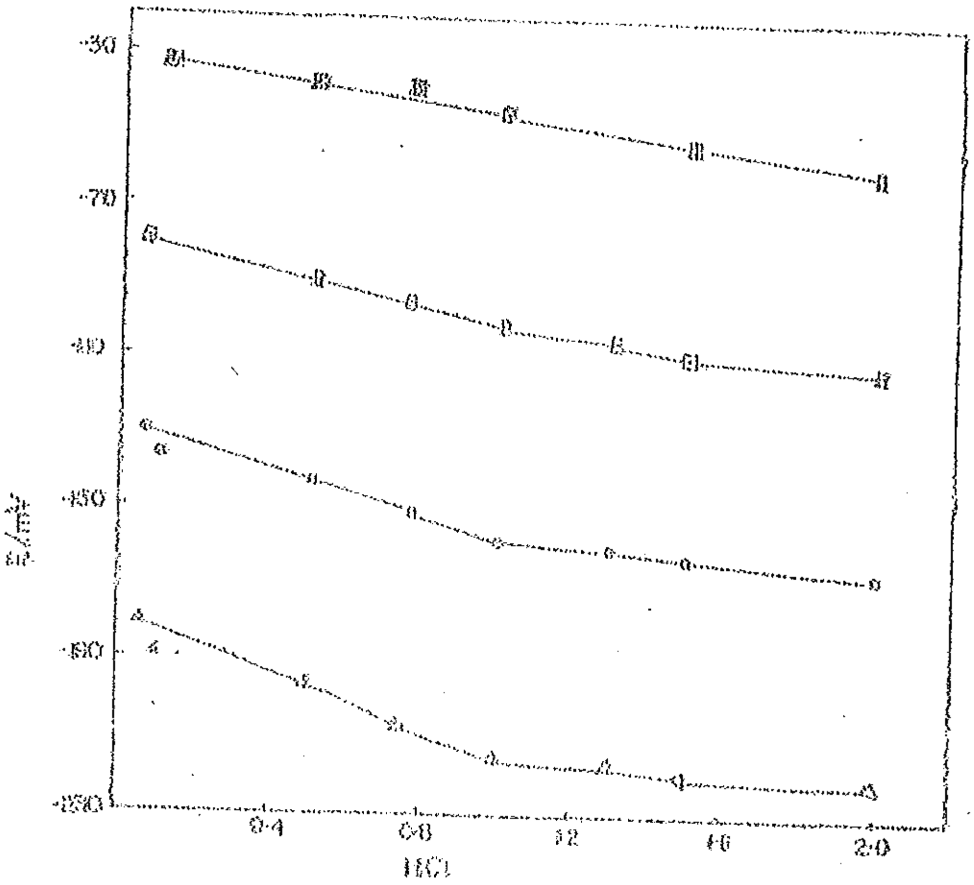

Fig. 9. Effect of HCl concentration on potential response

Concentration of Fe^{3+}

(△) 2.5×10^{-2} M; (o) 2.5×10^{-3} M; (□) 2.5×10^{-4} M; and (⊠) 2.5×10^{-5} M.

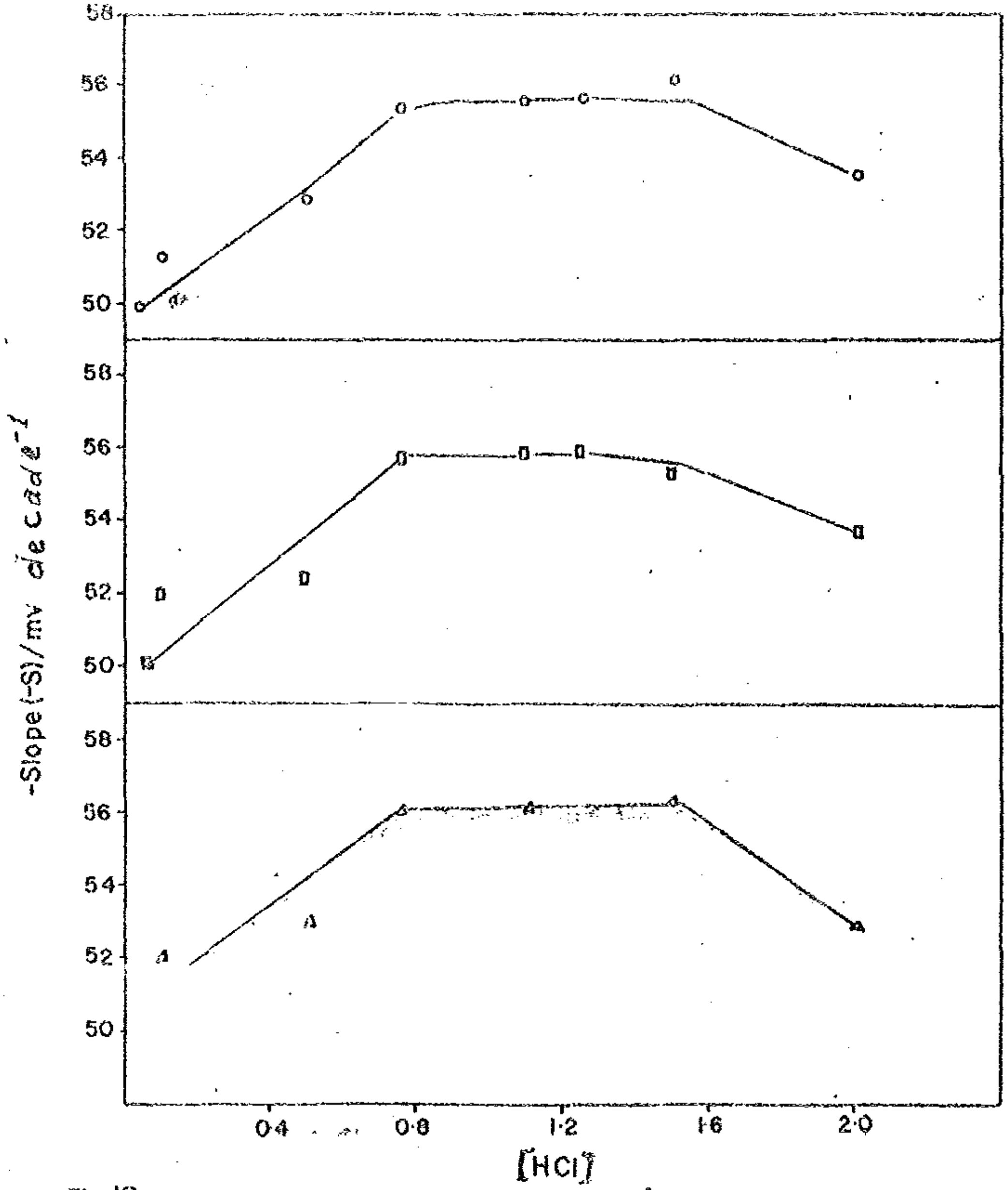

Fig. 10 Effect of HCl concentration on slope

△ slope between $2{\cdot}5\times10^{-2}$ & $2{\cdot}5\times10^{-3}$ MFe^{3+}
□ slope between $2{\cdot}5\times10^{-3}$ & $2{\cdot}5\times10^{-4}$ MFe^{3+}
○ slope between $2{\cdot}5\times10^{-4}$ & $2{\cdot}5\times10^{-5}$ MFe^{3+}

In separate solutions the potentials of the electrode were not stable for Co^{2+}, Cr^{3+}, Pb^{2+}, Fe^{2+}, WO_4^{2-}, IO_4^- saccharin, and ions in the complexing solutions. Moreover MnO_4^-, IO_4^- and WO_4^{2-} ions resulted in unstable potentials in the mixed solution method.

Table 5. Selectivity coefficients, K_{ij}^{pot}, of the Crystal Violet $-FeCl_4^-$ liquid membrane electrode

Interfering ions	K_{ij}^{pot*}	
	Separate solution	Mixed solution
Hg^{2+}	1.03×10^{-1}	1.0×10^{-1}
ClO_4^-	2.4×10^{-1}	-
Cd^{2+}	2.1×10^{-2}	4.0×10^{-2}
$C_6H_5COO^-$	3.2×10^{-3}	2.9×10^{-3}
VO_3^-	2.9×10^{-3}	-
$HC_8H_4O_4^-$	2.9×10^{-3}	8.2×10^{-4}
NO_3^-	1.87×10^{-3}	2.83×10^{-3}
CH_3COO^-	2×10^{-4}	7.4×10^{-4}
SO_4^{2-}	1.5×10^{-4}	2.3×10^{-4}
F^-	1.3×10^{-4}	9.6×10^{-5}
Cu^{2+}	2×10^{-4}	8.9×10^{-5}
Zn^{2+}	2×10^{-4}	7.6×10^{-5}
Mn^{2+}	1.6×10^{-4}	7.9×10^{-5}
$C_2O_4^{2-}$	8.9×10^{-5}	2.8×10^{-5}

* Calculations of K_{ij}^{pot} for Hg^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, and Mn^{2+} were made assuming divalent an ionic chlorocomplexes.

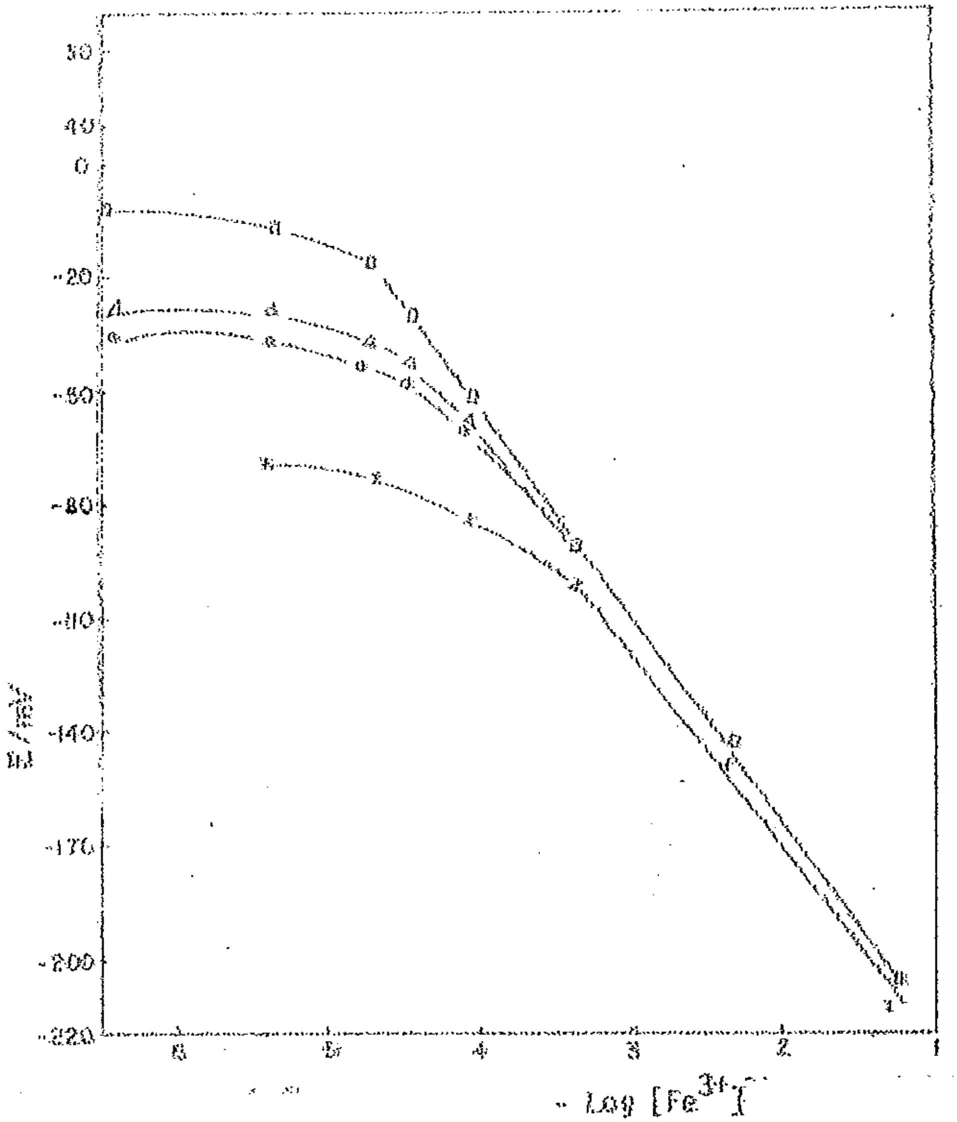

Fig. 11 Curves for evaluating K_{ij}^{pot} of some ions.
(Fe^{3+}; Cr^{3+}; Zr^{4+}; x Br^-)

WO_4^{2-}, Br^-, ClO_4^-, IO_4^- , Zr^{4+} , MnO_4^-, Sn^{2+}, and SCN^- ions caused serious interferences as shown in Table 5 and/or Fig. 11 for some of the ions. Moreover, I^- and $S_2O_3^{2-}$ ions totally poisoned the electrode which no more functioned as $FeCl_4^-$ detector which is very likely due to the reducing effect on $FeCl_4^-$ at the membrane surface. The oxidation of thiosulphate produced light yellow solid with a smell of sulphur.

In the presence of WO_4^{2-} and IO_4^- the potential readings were not stable in both the separate and mixed solutions. Complete interference was observed due to Sn^{2+} as a result of the redox reaction[118]

$$Sn^{2+} + FeCl_4^- = Sn^{4+} + Fe^{2+} + 4Cl^-$$

and the subsequent interference from species such as $SnCl_5^-$[62] although it does not impair electrode function. In the presence of I^- ions, the colour of the iron complex was gradually changed to reddish brown presumably due to formation of molecular iodine. The presence of SCN^- together with the tetrachloroferrate(III) complex in the same solution imparted a red colour to the solution which is due to the formation of iron(III)-thiocyanate complexes. Hence thiocyanate transfer into the membrane phase (see Table 2) and iron(III)-thiocyanate complex formation are believed to be the cause of interference.

In separate solution permanganate (in chloride complexing solution), was found to harden the membrane surface for unknown reasons, without adversely affecting the electrode behaviour. It should be noted that chlorine produced by permanganate could influence the nature of the PVC surface.

4.7 Application of the Liquid Membrane Electrode.

The newly developed tetrachloroferrate(III)-selective liquid membrane electrode was applied to real and standard samples in order to evaluate the reliability of the potentiometric technique for iron determinations.

The samples tested for iron determination were standard iron (iron alum), iron ore (haematite), human blood and a syrup with minerals and vitamins (Firlixir ^{R}). Direct potentiometry was used for all the real samples. Standard addition, standard subtraction (by EDTA) and sample addition techniques were used for all four samples. The equations applied to calculate the iron content in each sample are also indicated in Tables 6-9.

Table 6. Analysis of iron in haematite (Fe found by AAS was 62.16%)

Method	Fe found* percent	Recovery percent	Standard Deviation	Confidence** limit	Eqn no
Direct potentiometry	60.64	97.6	0.06	±0.16	2.42
Sample Addition	62.38	100.3	0.13	±0.34	2.48
Standard addition	63.25	101.7	0.16	±0.42	2.47
Standard subtraction	61.82	99.4	0.02	±0.05	2.50

* Average of triplicate measurements.

** Calculated for n = 3 at t_{98}.

Table 7. Determination of total blood iron (Fe found by Spectrophotometry[110] was 1.3 mg Fe/100ml treated blood)

Method	Fe found* (mg/100ml)	Recovery percent	Standard Deviation	Confidence** limit	Eqn No
Direct potentiometry	1.29	99.6	0.21	±0.55	2.42
Standard addition	1.34	103.4	0.04	±0.10	2.47
Sample addition	1.33	102.7	0.18	±0.47	2.48
Standard subtraction	1.34	103.3	0.23	±0.60	2.50

* Average of triplicate measurements.

** Calculated for n = 3 at t_{98}.

Table 8. Determination of iron concentration in a mineralized and Vitaminized syrup (certified value 1.87 mg Fe/ml)

Method	Fe found* (mg/ml syrup)	Recovery (percent)	Standard deviation	Confidence** limit	Eqn No
Direct polentiometry	1.868	99.88	0.15	±0.39	2.42
Sample addition	1.985	106.16	0.07	±0.18	2.48
Standard addition	1.871	101.00	0.04	±0.10	2.47

* Average of triplicate measurements.

** Calculated for n = 3 at t_{98}.

Table 9. Determination of iron in standard iron (iron alum) solutions.

Method	Iron, mg/100ml		Recovery	Standard	Confidence**	
	Present	Found *	(percent)	deviation	limit	Eqn No
Sample addition	20.94	20.78	99.2	0.02	±0.05	2.48
Standard addition	0.210	0.211	100.5	0.08	±0.21	2.47
Standard subtraction	0.251	0.254	101.2	0.05	±0.13	2.50
EDTA	55.847	55.498	99.4	0.20	±0.52	
Titrations	5.241	5.072	96.88	0.18	±0.47	
	0.530	0.524	101.1	0.25	±0.66	

* Average of triplicate measurements.

** Calculated for n = 3 at t_{98}.

Potentiometric titrations with EDTA were carried out on standard iron(III) solutions to assess the feasibility of the titration with the proposed electrode. Both EDTA and iron(III) solutions contained 5 M chloride, hence, a decrease in the concentration of the tetrachloroferrate(III) species by dilution of the total chloride ion concentration was avoided. The method relies on the concentration decrease of the tetrachloroferrate(III) ion due to complexation of iron(III) by EDTA. The best results were obtained if the total iron(III) concentration was not less than 1×10^{-4} M. Typical titration curves are shown in Fig. 12 for the titration of 1×10^{-2}, 1×10^{-3}, 1×10^{-4} and 1×10^{-5} M total iron(III) solutions. The end point was located from the maximum rate of change of potential per unit volume. The analysis results are also shown in Table 9.

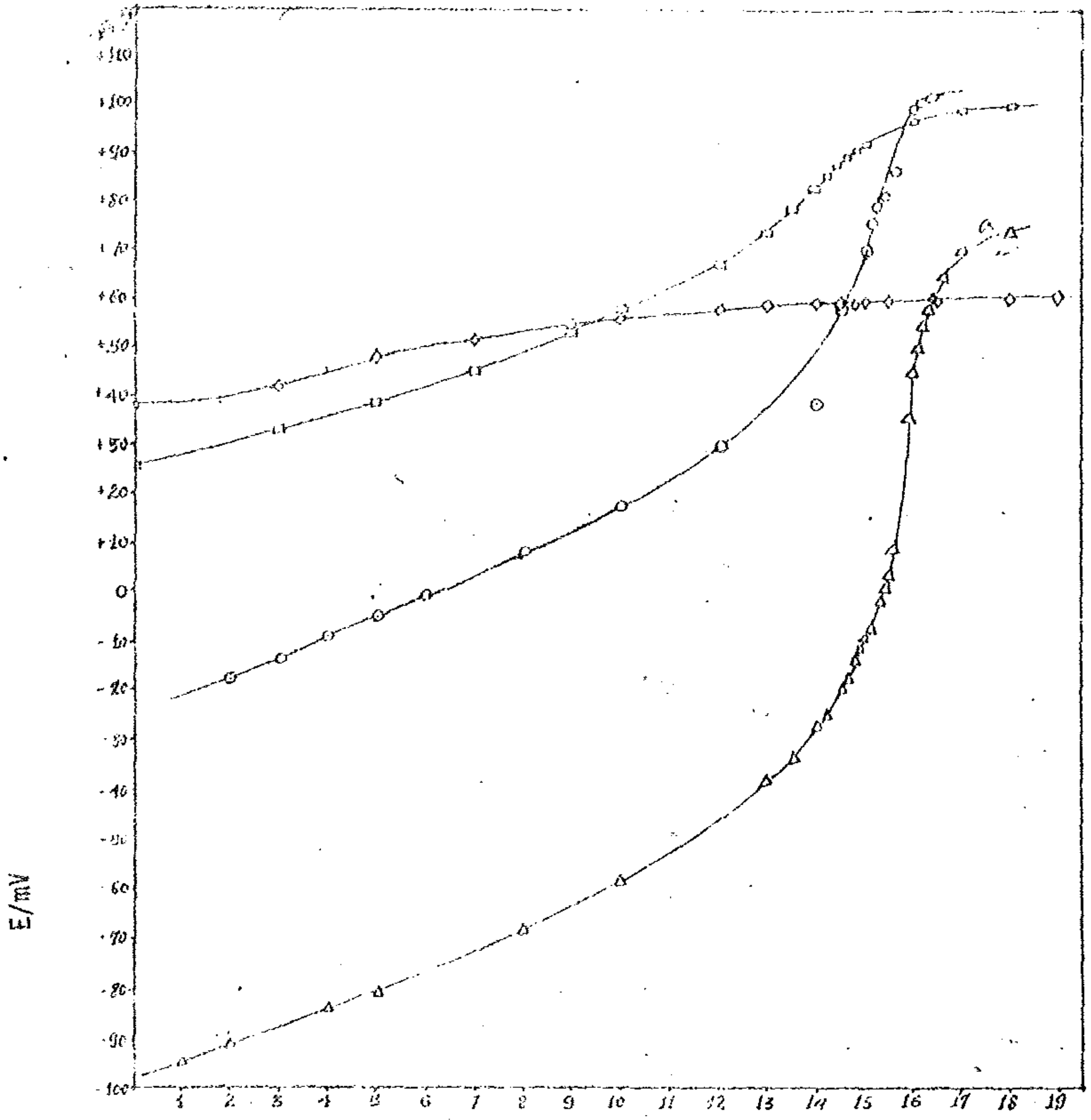

Fig.12 potentiometric titration curves of $FeCl_4^-$ against EDTA

△ 15 ml of $1x10^{-2}$ M Fe^{3+} vs. $9.375x10^{-3}$ M EDTA;

⊙ 15 ml of $9.375x10^{-4}$ M Fe^{3+} vs. $9.023x10^{-4}$ M EDTA;

□ 15 ml of $9.375x10^{-5}$ M Fe^{3+} vs. $1x10^{-4}$ M EDTA; and

◇ 15 ml of $1x10^{-5}$ M Fe^{3+} vs. $1x10^{-5}$ M EDTA.

The experimental values with different techniques for each sample are in good agreement with the accepted or certified values except the sample additon technique for the syrup. The exception may be due to matrix effect or experimental errors. Hence the methods proposed for iron determination with the tetrachloroferrate(III)-selective liquid membrane electrode are fairly precise and reliable.

4.8 Comparison with other Iron-Selective Electrodes.

A comparison of the proposed electrode with other iron-selective electrodes is made with respect to slope, linear range, and response time as summarized in Table 10.

Table 10. Comparison of response characteristics of the tetrachloroferrate(III)-selective electrode with other iron-selective electrodes

Ion-exchanger	Membrane sovent/matrix	Slope (mV/decade	Linear range,M	Response time,min	Ref.
Haemin	nitrobenzene/ silicon rubber	a	$10^{-4}-10^{-1}$	c	61
Chalcogenide glass[b]	Solid	+57.6	$10^{-5}-10^{-1}$	10-20	55
Tricaprylmethyl ammonium chloride	PVC(CWE)	-55.0	$10^{-4}-10^{-1}$	1-25	62
Chromium ferrocyanide	Solid	a	$10^{-4}-10^{-1}$	c	64
Triphenyl pyrylium cation	Di- or tetrachloroethane/ glass frit	-55	$10^{-4}-10^{-1}$	2-3	33
Triphenylthiopyrylium cation	Dichloethane/c	-58.5	$10^{-4}-10^{-1}$	c	63
Crystal Violet	Nitrobenzene/ PVC	-56	$2.5\times10^{-5}-5\times10^{-2}$	0.5-1.5	present work

[a] The slope is reported as "Nernstian" and the exact values are not given.

[b] The slope is typical of a monovalent cation, yet the electrode is responsive to Fe^{3+}

[c] Data not given.

The comparison shows that the proposed electrode has wider linear range and shorter response time than most of the electrodes. The electrode slope is comparable to those electrodes which respond to monovalent ions.

5. CONCLUSION

The present work demonstrates the feasibility of preparing liquid membrane electrodes from commonly available materials in analytical laboratories. The experimental results have also shown that the Crystal Violet-tetrachloroferrate(III) liquid membrane electrode can be used to determine iron in a variety of real samples.

Moreover, the proposed electrode has been found to have a wider linear range and shorter response time than most of the other iron-responsive electrodes.

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