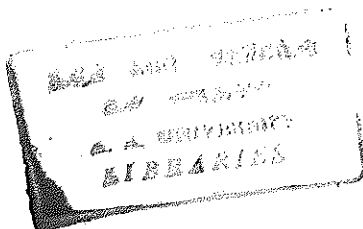


STUDIES
ON
PERCHLORATE AND HYDROGEN PHTHALATE LIQUID MEMBRANE
ELECTRODES BASED ON CRYSTAL VIOLET AND
BRILLIANT GREEN



A Thesis
Presented to
The School of Graduate Studies
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In Partial Fulfillment of the
Requirement for the Degree of
Master of Science in Chemistry

By
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TO MY FATHER, MOTHER,
SISTERS AND BROTHERS

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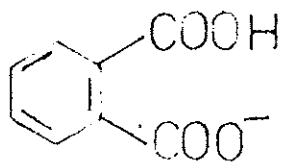
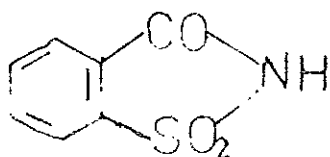
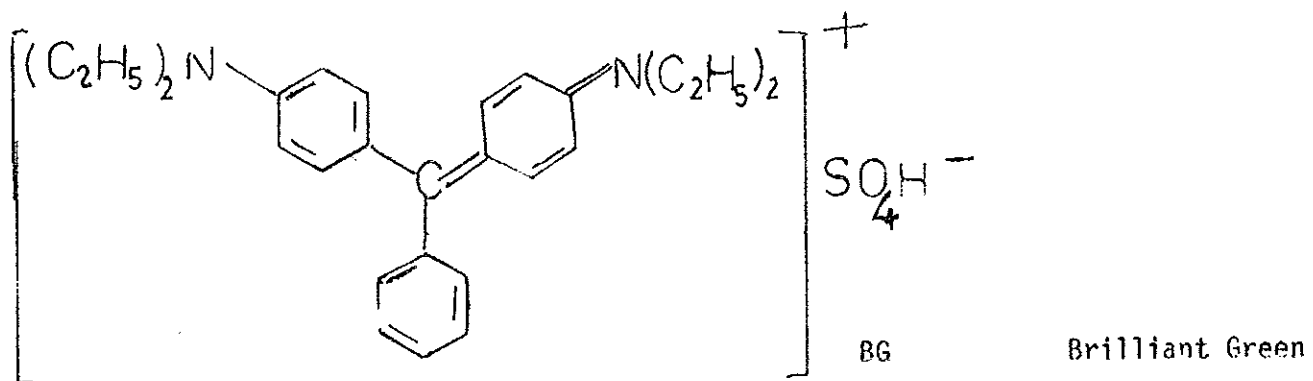
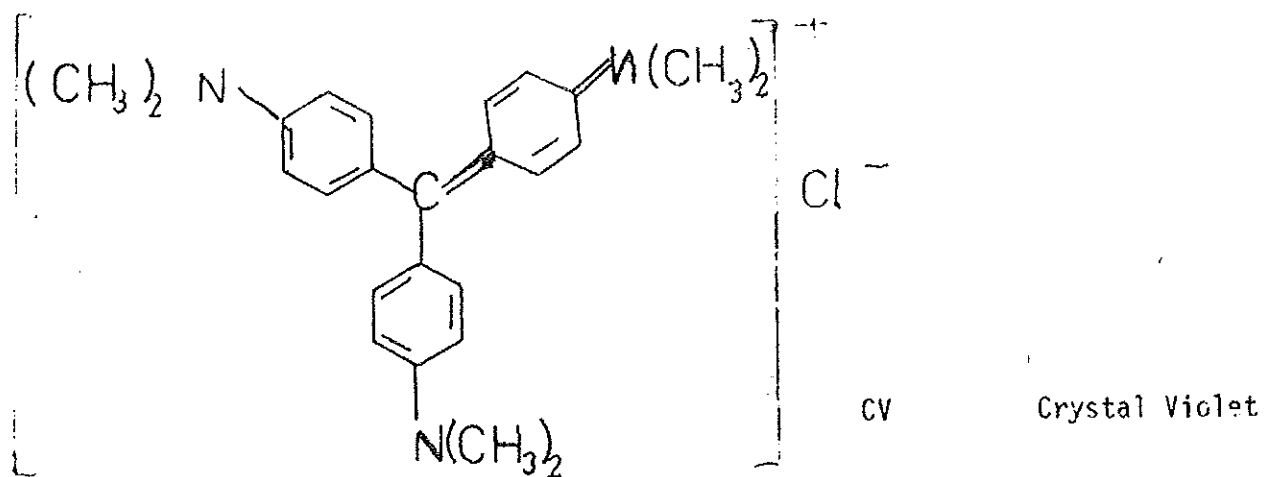
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ABSTRACT

STUDIES ON PERCHLORATE AND HYDROGEN PHTHALATE LIQUID
MEMBRANE ELECTRODES BASED ON CRYSTAL VIOLET AND
BRILLIANT GREEN

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Liquid membrane holders were designed from concentric pyrex tubes by glass blowing and employed to design perchlorate and hydrogen phthalate electrodes based on Crystal Violet perchlorate and Brilliant Green hydrogen phthalate salts. Polyvinyl chloride discs, with 1-chloronaphthalene as plasticizer, were used to support the liquid membranes which consisted of nitrobenzene, 1,2-dichloroethane or 1,2-dichlorobenzene in the case of Crystal Violet perchlorate and nitrobenzene in the case of the other. Several electroanalytical parameters have been evaluated and both perchlorate and hydrogen phthalate electrodes respond to perchlorate, periodate, iodide, saccharin, and hydrogen phthalate, with selectivity in that order. The electrodes were found to respond to these anions within 60 seconds, in wide concentration ranges (slopes 52-60 mv/decade) with detection limit of 6.7×10^{-7} to 4.7×10^{-5} M. The perchlorate electrode was employed to determine perchlorate in artificial samples with three potentiometric methods and results were found to have reasonable accuracy and precision.

1. INTRODUCTION

Ion-selective electrodes have been the subject of rapidly increasing interest over the past twenty years and their development has opened up a new field of potentiometry. The speed at which this field developed is a measure of the degree to which the electrodes meet the requirements of an analyst for rapid, accurate and low cost analysis.

Any phase that separates two other phases to prevent mass movement between them but allows passage with various degrees of restriction of one or several species of the external phases may be defined as a membrane which when used as an electrode in an electrochemical cell constitutes a membrane electrode. At the membrane solution interface, rapid exchange takes place between the free ions in the aqueous phase and the same or different ion bound to large groups in the membrane phase.

The behaviour of a membrane electrode will be determined by the properties of the membrane electroactive material which is a solid or a liquid containing ionized or ionizable groups. Generally such groups, used for membrane preparation, have the ability of binding certain ions selectively either at a charged site of opposite sign or at a neutral site of organic nature.

Most of the membranes used as electrodes possess some capacity of undergoing ion exchange. Consequently, they are ion-selective in that a cation exchanger is selective to cations and an anion exchanger is selective to anions. The selectivity of membrane electrodes depends on the selectivity of the ion-exchange process and on the mobility of the dissociated or associated species in the membrane phase.

1.1 Historical Development of Ion-Selective Electrodes (1-4)

The study of the electrochemistry of the membrane was initiated by Ostwald (5) who introduced the concept of semipermeable membranes as membranes impermeable to certain ionic species but permeable to others. The electric potential difference on such a membrane is a limiting case of the potential difference on the membrane-solution interface when the mobility of one kind of ion approaches zero. A small number of permeating ions penetrates through the interface and forms an electrical double layer there which is the source of the electrical potential difference.

The history of the discovery of membrane electrode starts with the observation by Cremer (6) in 1906 and the more detailed investigation by Haber (7), which showed that a hydrogen ion-sensing glass electrode responds to the activity of hydrogen ion according to the Nernst equation. It is remarkable that this is, perhaps, still one of the best such electrodes at present. In the twenties and thirties Michelis (8) and Sollner (9) were particularly notable for their work in the field of porous membranes. The theory of porous membranes, which are easily permeable for some kinds of ions with the opposite charge, has since been developed by Teorell (10) and by Meyer and Sievers (11). Moreover, Nikolskii and Tolmacheva (12) introduced the concept of ion-exchange in their study of glass membranes around the end of 1930's.

After numerous attempts to design a membrane electrode based on various crystalline materials, Pungor and Hallos-Rokosly (13) eventually succeeded in preparing the first workable ion-selective electrode with a precipitate-based heterogeneous membrane. However, real success in this area stems from the development of the first fluoride ion-selective membrane

electrode composed of a single crystal of lanthanum fluoride by Frant and Ross (14). Their fluoride electrode to date is the most successful product employed for fluoride determination.

Liquid membrane ion-selective electrodes containing dissolved organic ion-exchangers were first used by Sollner and Shean (15,16), but these sensors showed only perm-selectivity, that is, selectivity toward the sign of the ionic charge rather than the kind of ion. Since then, liquid membrane ion-selective electrodes containing an ion-exchanger of anionic type, selective to divalent cation (17), containing electrically neutral antibiotics (18,19) and macro-cyclic compounds (20-23), selective to alkali metals cations have been developed. Membrane electrodes employing ion-association and chelation systems, incorporating organic solvents have been explored and applied for the analysis of anions and cations (24-30). Also sensors have been developed for the analysis of aminoacids (31-33).

A promising trend in the development of ion-selective electrodes is represented by the so-called enzyme electrodes, in which the sensor is covered with a polymeric matrix containing a suitable enzyme (34). The idea was first introduced into electro-analytical chemistry by Clark and Lyons (35) who designed a glucose electrode by immobilizing glucose oxidase between cuprophane membranes and determined amperometrically the hydrogen peroxide formed.

Subsequently, Guilbault and co-workers (34,36) devised enzyme electrodes for the potentiometric determination of various substances of biological importance, which are converted into species monitored by ion-selective electrodes. The substance to be determined reacts in the enzyme layer and yields a product which is capable of giving a suitable sensor signal.

Beside these, conventional glass (37,38), homogenous solid state (39), liquid ion-exchanger (49) and neutral carrier complex (41) electrodes are some of the ion-selective electrodes used in enzymology.

In addition to accounts of the construction, assessment and application of ion-selective electrodes for individual ions or groups of ions, there are many specialized reviews, with many references, on the theory of, and recent progress with, such electrodes (42-46).

1.2 Classification of Ion-Selective Electrodes (3,4)

Ion-selective electrodes are classified in different ways, of which the most important are based on the physical state of the substances that form the electrode membrane and based on the type of active material used to make the membrane. In the former case, they are classified as ion-selective electrodes (i) with solid membranes and (ii) with liquid membranes. This classification is probably useful, especially from the theoretical point of view.

The most logical classification, from both practical and theoretical points of view, is based on the type of active material used to make the membrane. If this classification is used the majority of ion-selective electrodes fall easily into three main classes. These classes of electrodes are as follows.

i) Glass Electrodes. The most familiar glass membrane electrodes is the pH type. Its potentiometric behavior can be described and it is the most thoroughly investigated and highly developed of all ion-selective electrodes; because of the extreme properties of hydrogen ions, in particular their very high mobility, this electrode is extraordinarily well-behaved

having very high selectivity and a long response range (pH 0 to 14). Subsequently, glass electrodes for the measurements of Na^+ , K^+ , NH_4^+ and some other cations activities have been developed.

The electrode potential is made up of a number of constant and variable terms (3). The constant terms include a time dependent diffusion potential, due to the flux of monovalent cations from the dry glass; the potential across the hydrated layer due to the charge separation produced by the opposing fluxes of the sensed ion and ions from the glass; diffusion and phase boundary potentials on the inner surface of the glass. The variable term which contributes to the potential of the glass membrane electrode is the activity of the ion giving rise to Nernstian response.

ii) Electrodes based on inorganic salts. Electrodes based on inorganic salts were the first of the new generation of ion-selective electrodes which succeeded the glass electrodes. They are constructed in various forms. Such membranes are usually termed as either homogeneous or heterogeneous depending on the composition of the membrane matrix.

Into this class fall the electrodes based on the silver halides, silver sulfides, lanthanum fluoride, and heavy metal sulfides, and ions measured by this class of electrodes includes, F^- , Cl^- , Br^- , I^- , CN^- , S^{2-} , Ag^+ , Cu^{2+} and Pb^{2+} .

iii) Electrodes based on organic ion-exchangers. Organic ion-exchangers are used to make electrodes with liquid or polymer membranes which are selective to anions or cations. Generally ion-exchanger membranes contain ionogenic groups fixed to the resin or glass frits or polymer matrix with negative groups such as $-\text{SO}_3^-$, $-\text{COO}^-$, etc., in the case of cation exchange membranes, and with positive groups such as $-\text{NH}_3^+$, $-\text{NH}_2^+$, $-\text{NH}^+$ etc., in the case of anion exchange membranes. Organic ion-exchange membranes,

unlike glass membranes or other membranes used in the construction of electrodes, have low electrical resistance. This low resistance or high conductance is due to two factors; (i) the porosity of the membrane and (ii) the charge density of ionogenic groups. Membranes of low porosity and high charge density are well suited for the construction of electrodes.

In the case of neutral carrier-based electrodes the active materials usually employed are macrotetralides (tetralactone of nonactinc acid and its derivatives), polyethers, depsipeptides (α -aminoacids and α -hydroxyalephaticacids alternately bound in a ring), and other substances. These molecules all have closely knit structures with a central cavity and tends to favor complexation with ions which are similar in size to the cavity. Thus, by correct choice of carrier and solvent, electrodes have been made with high selectivity for cations including K^+ , NH_4^+ , Ca^{++} , Na^+ , Ba^{++} , etc. The best example of this group is valinomycin, an antibiotic, which is highly selective to potassium ion (20).

Apart from these classes two other types of sensors have been described. These are enzyme electrode, and ion-sensitive field effect transistors (ISEFT's) whose funcitons are based on the above mentioned membrane electrodes.

1.3 Membrane Electrodes Based on Triphenylmethane Dyes (Literature Survey).

Of the many suitable cationic or anionic reagents which can react with counterions to form ion-pairs, cationic dyes have been most frequently used in extraction-spectrophotometric determination of organic and inorganic anions (47) and since 1973, in liquid and polymer membrane ion-selective electrode preparations.

The application of triphenylmethane dyes based on anion selective liquid membrane electrodes have been employed for the first time by Ishibashi and his associates (26,48,49). Their electrodes made use of the triphenylmethane dyes, such as Crystal Violet, Methyl Violet, Malachite Green and Fuchsine Basic, ion-paired with benzene sulphonate and α -naphthalene sulphonate as a sulphonate selective electrode and Crystal Violet ion-paired with phthalic acid and maleic acid as the respective acid selective electrodes in organic solvents.

Subsequently, Fogg and co-workers used a solution of Brilliant Green ion-paired with tetrafluoroborate (50), perchlorate (51) in chlorobenzene and perrhenate (52) in 1,2-dichlorobenzene by saturating a natural rubber as a membrane electrode which is selective to the respective anions. These electrodes exhibit a Nernstian response in the range of 10^{-3} - 10^{-1} M for the first two and 10^{-5} - 10^{-2} M for perrhenate. The ion-association salts of Methylene Blue-perchlorate (53) was also extracted into nitrobenzene to be used as perchlorate sensing liquid membrane electrode. The selectivity coefficient (the relative effects of various anions on the electrode potential), were evaluated and reported in the decreasing order of $\text{IO}_4^- > \text{I}^- > \text{SCN}^- \gg \text{SO}_4^{2-}, \text{NO}_3^-, \text{Cl}^-, \text{Br}^-$.

Besides, liquid membrane electrodes selective to ClO_4^- , SCN^- , BF_4^- and NO_3^- based on the triphenylmethane dyes: Malachite Green, Fuchsine, Crystal Violet, Methyl Violet, Gentian Violet and Alkali Blue have been used as electroactive materials, in nitrobenzene or tetrachloroethane (54).

At the beginning of 1980's Pan and his associates reported a PVC membrane ion-selective electrode based on ion-pair of triphenylmethane dye perchlorate, as an electroactive material (55). They derived an empirical

formula relating the measured selectivity coefficient to the ratio of charge to the thermochemical radius of anions. They also reported a PVC membrane incorporating an Ethyl Violet periodate complex which is selective to periodate (56).

The response of a perchlorate ion-selective electrode to a wide range of periodate concentration has been reported (57) and detailed studies of the performance characteristic of the perchlorate electrode as a periodate sensor and its applications to the determination of α -diols (58,59) and carbohydrates (60) have been described. Also the response of the Orion Perchlorate liquid membrane electrode to a series of substituted benzoate and phenylacetate ions (61) and the response of $\text{Fe}(\text{phen})_3^{2+}$ (phen = phenanthroline) based perchlorate electrode to permanganate and dichromate have been noted (57).

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 crystal Violet in nitrobenzene (62).

Recently a PVC membrane electrode selective to saccharine, iodide, perchlorate and hydrogen phthalate based on the Brilliant Green-Saccharin ion-pair has been designed by Moges and co-workers and employed to assay saccharin tablets at a rate of 15-30 samples per hour with various potentiometric methods (63).

1.4 Aim and Scope of Present Investigation

The foregoing literature survey reveals that:

- a) although the response behaviour of perchlorate ion-selective electrode based on triphenylmethane dyes including Brilliant Green and Crystal Violet for different ions having relatively high selectivity has been investigated, the response behaviour for ions having lower selectivity have not been studied;

- b) most of the anion-selective electrodes based on triphenylmethane dyes designed have high selectivity for perchlorate ion, however, these electrodes have not been employed as perchlorate sensors;
- c) even though the selectivity coefficient is a function of distribution ratio, association constant and mobility of dissociated or associated ions in the membrane, no attempt has been made to determine such analytical parameters for the liquid membrane ion-selective electrodes of triphenylmethane dyes.

Hence the aims of present investigation were:

- i) to study the response behavior of perchlorate electrode based on Crystal Violet and Brilliant Green dyes in organic solvent towards iodide, saccharin, periodate, and hydrogen phthalate;
- ii) to study the response behavior of the Brilliant Green hydrogen phthalate liquid membrane ion-selective electrode to perchlorate, iodide, saccharin, and hydrogen phthalate;
- iii) to evaluate the analytical parameters such as selectivity coefficient, ionic strength and pH-effects.
- iv) to determine the distribution ratio and association constant for different ion-pairs and correlate these with selectivity coefficient;
- v) to see the relation between selectivity coefficient and standard free energy of hydration for different anions.

2. THEORY

2.1 Membrane Electrode Potential (3,64)

Electrical potentials arising across membranes when they separate two electrolyte solutions may be referred to as membrane potential. The potential may arise as a diffusion potential across the membrane due to differences in the mobilities of the ions. There are also other ways in which a potential might arise across the membrane. The simplest way is to have it arise as an ohmic potential drop by passing electric current from an external source of emf through the system. Another way would be to have it arise as a static potential by adding to one of the compartments some charged species that cannot pass through the membrane.

The use of ion-selective electrodes depends on the determination of this potential (membrane potential) and relating it to the activity of the ion of interest according to the Nernst equation. These potentials cannot be determined directly, but can easily be derived from the emf values for the complete electrochemical cells, which comprise a membrane separating two solutions (') and (") and two reference electrodes (internal and external reference electrodes). If the membrane has the same overall composition, the membrane potential depends on the activities of the ions in the solutions on the two sides of the membrane. Any other process within the membrane has no effect on the membrane potential.

On the other hand, at the interface between two phases containing electrically charged particles (electrons, ions and even dipoles), electrical potential differences normally occur. The membrane potential of such

$$E'_{Don} = E' - \bar{E}' = \frac{RT}{F} \ln \frac{\bar{a}'_+}{a'_+} = \frac{RT}{F} \ln \frac{a'_-}{\bar{a}'_-} \quad [2.1]$$

$$E''_{Don} = E'' - \bar{E}'' = \frac{RT}{F} \ln \frac{\bar{a}''_+}{a''_+} = \frac{RT}{F} \ln \frac{a''_-}{\bar{a}''_-} \quad [2.2]$$

The net Donnan Potential therefore given by:

$$E'_{Don} - E''_{Don} = \frac{RT}{F} \ln \frac{\bar{a}'_+}{a'_+} - \frac{RT}{F} \ln \frac{\bar{a}''_+}{a''_+} \quad [2.3a]$$

$$= \frac{RT}{F} \ln \frac{a'_-}{\bar{a}'_-} - \frac{RT}{F} \ln \frac{a''_-}{\bar{a}''_-} \quad [2.3b]$$

where E' , \bar{E}' , E'' , and \bar{E}'' are the electrical potentials generated by the passage of ions from higher concentration to lower concentration and the terms with overbars refer, to the membrane phase. The Donnan potential results from the complete hindrance to the transfer of one or more kind of ion across the interface between the two electrolytes.

The diffusion potential $\psi = \bar{E}'' - \bar{E}'$ within the membrane is assumed to be that existing in a constrained liquid junction. The expression for ψ is given as (64).

$$\psi = \bar{U} \frac{RT}{F} \ln \frac{\bar{U} \bar{X}' + (\bar{X}'^2 + 4a_{\pm}'^2)^{\frac{1}{2}}}{\bar{U} \bar{X}'' + (\bar{X}''^2 + 4a_{\pm}''^2)^{\frac{1}{2}}} \quad [2.4]$$

where $\bar{U} = \frac{\bar{u}_+ - \bar{u}_-}{\bar{u}_+ + \bar{u}_-}$, \bar{X} is the concentration of ionogenic groups in the membrane \bar{u} is the mobility, the diffusion potential results from the different mobilities and concentrations of the ions in the electrolytes in contact. Thus, for a highly idealized membrane system the activity coefficients of membrane ions are equal to one ($\bar{\gamma}_+ = \bar{\gamma}_- = 1$), the total membrane potential, E , when agar -KCl salt bridges are used in the measurement is given by

$$E = E'_{Don} - E''_{Don} + \psi \quad [2.5]$$

So, by inserting the appropriate values of the potential from equations 2.2 to 2.4 in equation 2.5:

$$E = \frac{RT}{F} \left[\ln \frac{a''}{a'} \frac{(4a'^2 + \bar{X}^2)^{\frac{1}{2}} + \bar{X}}{(4a''^2 + \bar{X}^2)^{\frac{1}{2}} + \bar{X}} + \bar{U} \ln \frac{(4a'^2 + \bar{X}^2)^{\frac{1}{2}} + \bar{U} \bar{X}}{(4a''^2 + \bar{X}^2)^{\frac{1}{2}} + \bar{U} \bar{X}} \right] \quad [2.6]$$

Three important cases of equation (2.6) are of interest:

i) When $a \ll \frac{\bar{X}}{2}$, equation 2.6 reduces to the Nernst equation

$$E = \frac{RT}{F} \ln \frac{a''}{a'} \quad [2.6a]$$

ii) When $a \gg \frac{\bar{X}}{2}$, equation 2.6 reduces to an equation which gives the value for the diffusion potential between two solutions of activities a' and a'' . The mobility values would correspond to those prevailing in the aqueous solution although diffusion would be occurring across the membrane.

iii) When $a \approx \frac{\bar{X}}{2}$, the ionogenic groups are able to distinguish between counterions and coions to some extent so that the mobility values correspond to the membrane phase. Thus, equation 2.6 reduces to

$$E = \frac{RT}{F} \frac{\bar{u}_+ - \bar{u}_-}{\bar{u}_+ + \bar{u}_-} \ln \frac{a'}{a''} \quad [2.6b]$$

or

$$E = \frac{RT}{F} (\bar{t}_+ - \bar{t}_-) \ln \frac{a'}{a''}$$

where \bar{t}_+ and \bar{t}_- are the transport numbers of counterions and coions for negatively charged membrane phase.

2.2 Electrode Potential of Liquid Ion-Exchanger (2,64-67)

When a membrane matrix contains an ionizing species which is preferentially soluble in a water-immiscible organic solvent, it will operate as a liquid ion-exchanger. These are formed by dissolving a liquid ion-exchangers (such as ion-association salt, chelate complex) in water immiscible solvent. Unlike solid ion-exchangers, which have their ionogenic groups fixed to the membrane matrix, the ionogenic groups (sites) of liquid ion-exchangers are mobile. Depending on the solvent used to form the ion-exchange membrane, the sites would be completely dissociated if the dielectric constant of the solvent is high or highly associated if the dielectric constant of the solvent is low.

The electrode potential of an ion-exchanger membrane (whether the membrane is solid or liquid) $\Delta E(t)$ at any time, t , has been shown by Sandblom, Eiesenman and Walker (66) as

$$\Delta E(t) = \frac{RT}{Z_i F} \ln \frac{\sum_i \bar{u}_i k_i a_i^I}{\sum_i \bar{u}_i k_i a_i^{II}} \quad [2.7]$$

Where Z_i is the valence of the i^{th} counterion species, a_i^I and a_i^{II} are its activities in the solutions (I) and (II) on each side of the membrane, \bar{u}_i is its mobility within the membrane and k_i is a constant, characteristic of the difference of standard chemical potentials in the membrane vs water, given by the expression;

$$k_i = \exp\left(-\frac{(\mu_i^\circ - \bar{\mu}_i^\circ)}{RT}\right) \quad [2.7a]$$

where μ_i° and $\bar{\mu}_i^\circ$ are the standard chemical potentials of ion, i , in the aqueous solution and in the membrane phase respectively.

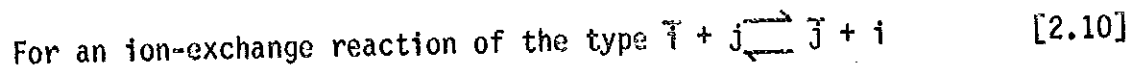
both instantaneously and in the steady state, with

$$\tau = \frac{\frac{\bar{u}_{2s}}{K_2} - \frac{\bar{u}_{1s}}{K_1}}{(\bar{u}_1 + \bar{u}_s) \frac{\bar{u}_{2s}}{K_2} - (\bar{u}_2 + \bar{u}_s) \frac{\bar{u}_{1s}}{K_1}} ; 0 \leq \tau \leq 1 \quad [2.9b]$$

Thus the expression for the electrode potential of a membrane electrode consisting of an ion-exchanger with strong association contains two logarithmic terms, whose relative contributions depend on the parameter τ .

2.3 Selectivity Coefficient (2,64,68,69)

The selectivity of an electrode is represented by its ability to distinguish between different ion species present in the contact solution. An electrode is ideally selective, i.e., specific, when its potential is not affected by ionic species present in the sample solution other than the ion for which the electrode is selective. If another, interfering, ion is present at a concentration which is large with respect to the primary ion, the electrode response will have contributions from both the primary and the interfering ions.



the diffusion potential is derived by integrating the Nernst Planck flux equation (69) which gives:

$$\psi = \frac{nRT}{F} \ln \left[\frac{(a_i^I)^{1/n} + (\bar{u}_j/\bar{u}_i) K^{1/n} a_j^I{}^{1/n}}{(a_i^I)^{1/n} + K (a_j^I)^{1/n}} \right] - \frac{nRT}{F} \ln \left[\frac{(a_i^{II})^{1/n} + (\bar{u}_j/\bar{u}_i) K^{1/n} a_j^{II}{}^{1/n}}{(a_i^{II})^{1/n} + K^{1/n} (a_j^{II})^{1/n}} \right] \quad [2.11]$$

$$K_{ij}^{pot} = \frac{\bar{u}_j k_j}{\bar{u}_i k_i}; \quad [2.16]$$

for dissociated ions. For associated ions, there are two cases:

a) for poorly mobile site, ($\tau = 0$), the expression for K_{ij}^{pot}

$$K_{ij}^{pot} = \frac{(\bar{u}_j + \bar{u}_s) K_j}{(\bar{u}_i + \bar{u}_s) K_i} \quad [2.17]$$

since $\bar{u}_x \ll \bar{u}_i, \bar{u}_j$;

$$K_{ij}^{pot} = \frac{\bar{u}_j K_j}{\bar{u}_i K_i} \quad [2.17a]$$

b) for highly mobile site,

$$K_{ij}^{pot} = \frac{\bar{u}_{is} k_i K_{js}}{u_{is} k_i K_{is}} = \frac{\bar{u}_{js} K_{ij}}{\bar{u}_{is}} \quad [2.18]$$

where k_i and k_j are partition coefficients; K_{is} and K_{js} are association constants and K_{ij} is the equilibrium constant given by

$$K_{ij} = \frac{K_j K_{js}}{K_i K_{is}} \quad [2.18a]$$

The mobility ratio of the counter ion species \bar{u}_j/\bar{u}_i in equation 2.16 is simply the ratio of the limiting single-ion conductance $\lambda_j^\circ/\lambda_i^\circ$; that is

$$\bar{u}_j/\bar{u}_i = \frac{\lambda_j^\circ}{\lambda_i^\circ} \quad [2.16a]$$

where as the mobility ratio $\frac{\bar{u}_j + \bar{u}_s}{\bar{u}_i + \bar{u}_s}$ in equation 2.17 is the ratio of the limiting equivalent conductance of the j and i forms of the ion-exchanger.

$$\left(\frac{\bar{u}_j + \bar{u}_s}{\bar{u}_i + \bar{u}_s}\right) = \frac{\lambda_{js}^{\circ}}{\lambda_{is}^{\circ}} = \frac{\lambda_j^{\circ} + \lambda_s^{\circ}}{\lambda_i^{\circ} + \lambda_s^{\circ}} \quad [2.17b]$$

For a given pair of counter ions each of these terms should be a constant, related to the properties of the solvent and the ion-exchanger.

In equation 2.14, if the concentration on one side ("") is held constant, as in a practical membrane electrode unit, it reduces to:

$$E = \text{constant} + \frac{nRT}{F} \ln [a_i^{1/n} + (K_{ij}^{po+} a_j)^{1/n}] \quad [2.14a]$$

Equation 2.14a is valid for a monovalent ion in the presence of another monovalent ion. Garrels and his associates (70) have given equations applicable to divalent ions in the presence of monovalent ions, namely

$$E = \text{Constant} + \frac{nRT}{F} \ln \left\{ (a_i^{2+})^{1/n} + [K_{ij}^{po+} (a_j^+)^2]^{1/n} \right\} \quad [2.14b]$$

and divalent ions in the presence of other divalent ions namely

$$E = \text{Constant} + \frac{nRT}{2F} \ln \left\{ (a_i^{2+})^{1/n} + (K_{ij}^{po+} a_j^{2+})^{1/n} \right\} \quad [2.14c]$$

These equations for $n = 1$ may be written in the general form of the extended Nicolsky equation (71)

$$E = \text{Constant} \pm \frac{RT}{z_i F} \ln \left[a_i + \sum_{j \neq i} K_{ij}^{po+} (a_j)^{z_i/z_j} \right] \quad [2.14d]$$

Where i is the primary ion of valence Z_i to which the membrane electrode is selective and j is the interfering ion of valence Z_j ; the (+) sign applies for cations and (-) sign for anions.

There are a number of methods that can be used for the determination of selectivity coefficients, however, there is little agreement in the literature regarding optimal methods for determining the selectivity coefficients of ion-selective electrodes.

Most of the methods for the determination of selectivity coefficient K_{ij}^{pot} , are based on emf measurement either in separate or in mixed solutions. The potential measured with liquid ion-selective electrode in solutions containing the primary ion and any other ions to which the electrode responds, has been found to fit the empirical equation 2.14 d.

The selectivity coefficient can be evaluated using equation 2.14d carrying out potentiometric measurements in solutions containing mixtures of the ions of interest (mixed solution method) or by utilizing a series of solutions each containing an ion of interest (separate solution method). Based on these measured potentials, three major evaluative techniques can be devised.

- i) The potential of an ion-selective electrode in a solution containing only the primary ion i , (i.e., $a_j = 0$, j being the interfering ion) is given by

$$E_1 = E_0 \pm \frac{RT}{Z_i F} \ln a_i \quad [2.19a]$$

If the solution is without ion i (i.e., $a_i = 0$) and contains only ion j equation 2.17 becomes

$$E_2 = E_0 \pm \frac{RT}{Z_i F} \ln K_{ij}^{pot} a_j^{Z_i/Z_j} \quad [2.19b]$$

For conditions, $a_i = a_j$, equations 2.19a and 2.19b give the relation:

$$\pm \left(\frac{E_2 - E_1}{S} \right) = \log K_{ij}^{\text{pot}} + \left(\frac{Z_i}{Z_j} - 1 \right) \log a_i \quad [2.20]$$

$$\text{where } S = \frac{2.303RT}{Z_i F}$$

ii) If the concentrations of the solution of ion i and of the solution of ion j are chosen such that $E_1 = E_2$, then equations 2.18 and 2.19 reduce to:

$$K_{ij}^{\text{pot}} = \frac{a_i}{(a_j)^{Z_i/Z_j}} \quad [2.21]$$

This method usually involves, measuring the emf in solutions containing a fixed quantity of the interfering ion and a varying activity of the primary ion for which the electrode is selective or vice-versa, where a_i and a_j are as defined by (73). That is from the plots of the potential of the mixtures $v_s - \log a_i$ the activity a_i can be determined where a_i at which $E_1 = E_2$ is the activity at which the electrode potential deviates by $18/Z_i$ from the extrapolation of the linear portion of the calibration graph.

iii) In methods (i) and (ii) only one ion is used in any test solutions. In this method both ions are utilized. Strivanson and Rechnitz (68) combined equations 2.14d and 2.19a to obtain:

$$E_1 - E = \pm S \log \left(\frac{a_i + K_{ij}^{\text{pot}} a_j^{Z_i/Z_j}}{a_i} \right) \quad [2.22]$$

which can be rearranged to give an explicit expression for K_{ij}^{pot} as

$$K_{ij}^{pot} = \frac{\exp \pm \frac{Z_i F (E_1 - E)}{RT} a_i - a_j}{(a_j)^{Z_i/Z_j}} \quad [2.23]$$

This equation makes it possible to calculate K_{ij}^{pot} directly or graphically. This is done by adding increasing quantities of ion j to a solution containing ion i. After each addition of ion j, the potential E^* is measured. E^* can also be measured for different solutions containing ions i and j in different proportions. Thus, E^* according to equation 2.14d can be calculated as follows if it is measured in any one of the series of solutions.

$$E^* = E_0 \pm \frac{RT}{Z_i F} \ln(a_i^* + K_{ij}^{pot} a_j^{*Z_i/Z_j}) \quad [2.24]$$

combining this equation with equation 2.18 gives

$$K_{ij}^{pot} a_j^{*Z_i/Z_j} = \exp \pm \left[\frac{Z_i F (E^* - E_1)}{RT} \right] a_i - a_i^* \quad [2.25]$$

If the right-hand side of equation 2.25 is plotted against $a_j^{*Z_i/Z_j}$, the graph should be a straight line passing through the origin and its slope should give the value of the selectivity coefficient, K_{ij}^{pot} .

2.4 Response Time (2,75)

One of the critically limiting factors in the use of ion-selective membrane electrodes, especially in routine analysis, is their so-called response time. A theoretical treatment of the dynamic characteristics that can be applied to ion-selective electrodes based on solid (precipitate, single crystal, or/and glasses) and liquid membranes, has been presented by Markovic and Osburn (74) and Morf, Lindner and Simon (75).

Ideally, the response of a membrane which allows transport of a specific ion, i.e., which is permselective for the ion to be determined is given by the Nernst equation,

$$\Delta E = E_i^{\circ} + \Delta E' \pm \frac{RT}{Z_i F} \ln a_i \quad [2.26]$$

where E_i° is the standard potential of the membrane electrode assembly, dependent on the composition of the internal solution and on the system of reference electrodes, but independent of the sample solution; $\Delta E'$ is the potential contribution produced by diffusion layers within the aqueous system on the sample side (liquid junction potential). For practical cases, it is convenient to choose $\Delta E' \approx 0$.

It must be pointed out that Nernst equation is clearly based on the assumption of thermodynamic equilibrium at the phase boundaries between the membrane and outside solution. If this equilibrium state holds throughout the sample solution, then one may apply the usual relation

$$E = E_i^{\circ} \pm \frac{RT}{Z_i F} \ln a_i \quad [2.27]$$

Obviously, deviations from this practical form of Nernst equation may arise because of generally time-dependent deviations between the measured activity, a_i^{\dagger} and the intrinsic sample activity, a_i . Such activity gradients are related to diffusion processes within the boundary layers of the sample solution (unstirred layer) which are produced as well by the equilibration between the bulk of the sample and the interface, such as by the diffusion in the adjoining bound layer of the membrane. Therefore, these processes determine the response time of a sensor, at the same time, they impose a lower limit on the linear response range (lower detection limit).

The expanded theoretical treatment of the dynamic characteristics gives the following equation;

$$a_i^t/a_i = 10 \frac{E(t) - E(\infty)}{S} = 1 - (1 - a_i^o/a_i) e^{-t/\tau'} \quad [2.28a]$$

where a_i^t is the activity in the boundary-face of sample solution at time $t \geq 0$; a_i and a_i^o are the activity in the bulk of sample solution at the time $t \geq 0$ and $t < 0$, respectively. S is the slope of the linear response function; $E(t)$ is the potential at time t . $E(\infty)$ is the final potential after attainment of steady state or equilibrium state. The time constant τ' or the "relaxation time" of the ion-selective electrode which may be identified with its response time, is given by

$$\tau' = \frac{4\delta^2}{\pi^2 D'} \quad [2.28b]$$

where δ being the thickness of the boundary layer (diffusion layer) and D' is the diffusion coefficient of the ions within the aqueous boundary layer.

According to equation 2.28b one of the parameters affecting the dynamic response characteristics of ion-exchange membrane electrodes is the thickness of the aqueous diffusion layer. This can be drastically reduced by stirring; it also depends on the shape and conditions of the electrode surface on the composition of the sample solution. A drastic increase of the response time has to be endured when using sample solutions which induce extensive diffusion processes through the membrane surface. Delays in the electrode response of serious proportions have been observed in two cases: first, in the presence of interfering ions that encroach upon the membrane composition and second, in the region of the lower detection limit where dissolution reaction proceeds.

2.5 Measurement Techniques (2,3,4,64,76)

i) Calibration Method: A standard solution is made up containing the analyte ion in a known concentration. The pH and ionic strength of the standard solution should be as close as possible to the corresponding values as the sample. By placing the ion-selective electrode, together with an appropriate reference electrode, into the unknown sample solution and the standard solution two potentials can be recorded as E_{sample} and E_{standard} , respectively. It follows from the Nernst equation that

$$E_{\text{sample}} - E_{\text{standard}} = S \log \frac{a_{\text{sample}}}{a_{\text{standard}}} \quad [2.29]$$

from which the sample activity can be calculated. The value of the slope can be determined experimentally, using two standard solutions of known different concentrations. This approach requires no knowledge of the standard potential of the electrode pair, it does assume that the value of slope is constant and that there is a linear relationship between potential and $\log(\text{activity})$.

The next most complex method involves the use of two standard solutions in which the analyte activities are a_{S_1} and a_{S_2} . If the analyte activity in the sample is a_x , then applying the Nernst equation to all three solutions,

$$\frac{(E_x - E_{S_1})}{(E_{S_1} - E_{S_2})} \log \left(\frac{a_{S_1}}{a_{S_2}} \right) = \log \left(\frac{a_x}{a_{S_1}} \right) \quad [2.30]$$

from which a_x may be calculated. No knowledge of standard potential or slope is needed, and this method will compensate for slow drift in both parameters. Again, a linear response over the range of interest is assumed.

ii) Standard addition technique: The achievement of optimum accuracy in the potentiometric determination of ion concentrations with ISE's requires that the measurement of a potentials in a standard solution having exactly the same medium, at a concentration very close to that of the sought-for ion, and under identical conditions at about the same time. Such conditions are approximated by a method variously known as standard addition, known increment or spiking. Basically the method consists of measuring the potential of the electrode system in a relatively large, accurately measured volume of the sample solution, adding a known small volume of a relatively concentrated solution of the sought-for ion and recording the potential after the addition of standard. The initial concentration may be calculated from the potential shift.

The observed initial potential of the sample solution of unknown concentration, C_x , is given by the Nernst equation. Thus

$$E_1 = E_0 + \frac{RT}{Z_i F} \ln (C_x \gamma_x) + E_L \quad [2.31]$$

E_L , being the liquid junction potential.

An addition of a known amount of test ion (V_s ml of known concentration C_s to initial volume V_x), the new potential measured is given by

$$E_2 = E_0 + \frac{RT}{Z_i F} \ln \left(\frac{C_x V_x + C_s V_s}{V_x + V_s} \right) \gamma_x + E_L \quad [2.32]$$

Assuming the constancy of E_L and that $\gamma_x = \frac{1}{x}$, subtracting eqn. 2.31 from eqn. 2.32 gives

$$\Delta E = E_2 - E_1 = \frac{RT}{Z_i F} \ln \left(\frac{C_x V_x + C_s V_s}{(V_x + V_s) C_x} \right); \quad [2.33]$$

On rearrangement equation 2.33 gives

$$\frac{\Delta E}{S} = \log \frac{C_x V_x + C_s V_s}{(V_x + V_s) C_x} \quad [2.34]$$

where S is the Nernst slope ($= 2.303RT/z_1 F$) experimentally determined by using a series of known standard solutions. Equation 2.34 may be rearranged to give

$$C_x = \frac{C_s V_s}{V_x + V_s} (10^{\Delta E/S} - \frac{V_x}{V_x + V_s})^{-1} \quad [2.35]$$

Thus C_s can be evaluated.

If V_s is assumed to be much smaller than V_x , the shift in potential of equation 2.34 can be related to the original concentration, C_x , by the following equation,

$$\Delta E = S \log \left(1 + \frac{C_s V_s}{C_x V_x} \right) \quad [2.36]$$

or

$$(10^{\Delta E/S} - 1) = \left(\frac{C_s}{C_x} \frac{V_s}{V_x} \right) V_s \quad [2.37]$$

Equation 2.37 indicates that C_x may be calculated from a single addition or preferably determined from the slope of a plot of $(10^{\Delta E/S} - 1)$ vs V_s , where several additions of standard are made.

The same technique can be used the other way round, also called "analate addition". In this technique the electrodes are placed in a known volume of V_s of a standard solution, and the potential E_1 measured (77,78). (To this is added a volume V_x of the unknown sample and the new potential E_2 is measured. The concentration of the unknown solution, C_x , can then be calculated from the equation.

$$C_x = \frac{10^{\Delta E/S} (V_s + V_x) C_s - C_s V_s}{V_x} \quad [2.38]$$

This equation is simply derived using C_s in place of C_x in equation 2.31 subtracting it from equation 2.32 and rearranging.

iii) Gran's plots: Gran's plots were devised by Gran (79) in 1952 as a way or linearizing the data obtained in potentiometric titrations and thus easily and precisely locating the equivalence points of titrations. Equation 2.32 can be rearranged to give

$$(V_x + V_s) 10^{\frac{E_2 F}{2.03RT}} = 10^{\frac{(E_0 + E_2) F}{2.303RT}} \gamma'_x (C_x V_x + C_s V_s)$$

A plot of $(V_x + V_s) 10^{\frac{E_2 F}{2.303RT}}$ against V_s gives a straight line which intercepts the abscissa for a value of V_s called V_e where $C_x V_x = -C_s V_e$ (80,81). Thus, C_x can be evaluated since V_e, V_x and C_s are known.

iv) Standard Subtraction: The standard or known subtraction method (82) is different only in that the standard solution added to the sample is not a determinant solution but a solution of a species which reacts quantitatively with the determinant. Thus, a decrease in determinant concentration is produced with corresponding change in cell potential; this potential change may be used to calculate the initial determinant concentration in the sample by means of the following equation.

$$C_x = \frac{C_x V_x}{V_x - (V_x + V_x) 10^{\Delta E/S}} \quad [2.39]$$

2.6 Electrical Conductance (83-85)

Electrolytes conduct current by transport of ions in contrast to electronic conductors or n-type semiconductors in which electrons are the charge carriers, or p-type semiconductors in which positive holes predominantly carry the current. Electrolytic conduction often is accompanied by transfer of mass as well as charge across the electrode-electrolyte interface with the formation or discharge of ions at (usually metallic) electrodes. Massive ions rather than delocalized electrons, drift through the bulk medium under the influence of an electric field generally at velocities five orders of magnitude lower than electron velocities. These distinctions dictate differences in the methods of measurement.

The conductivity (or specific conductance), k , of a material (an electrolyte) may be thought of as the conductance (reciprocal of resistance) of a cube of 1 cm edge, assuming the current to be perpendicular to opposite faces of the cube. Since it depends partly on the number of charge carriers, a more useful indication of the nature of interactions of the constituents with the medium is the conductance per unit concentration of charge carrying constituent or equivalent conductance $\lambda = k/C$, C is the concentration in equivalents per cm^3 (normality times 1000).

Electrical conductance measurements, particularly, in non aqueous solvents, provide several important parameters. The basic quantity of interest is the equivalent or molar conductance of the electrolyte at infinite dilution, λ_0 . The parameter λ_0 coupled with the transference numbers (the fraction of the current carried by various constituents) provides information on single ion conductance mobilities, λ_0^+ and λ_0^- , for cations and anions, respectively. The mobilities of ions are a basic, for example in estimating

the degree of ionic solvation and ion size, in the understanding and development of electrolysis, and in high energy organic electrolyte batteries.

A second area which has received considerable attention is the study of ion-association using electrical conductance as a probe. Determination of the equivalent conductance λ as a function of concentration of the electrolyte, followed by analysis using an appropriate equation gives rise to a value for K_A , the association constant.

The determination of experimental conductometric data is relatively simple. However, the clear interpretation of the measured data is more difficult. The concentration dependent association and dissociation reactions occurring in solution give rise to changes in the ionic strength and hence in the activity coefficients, and this shows up as apparent ion concentration or mobility changes in the conductivity data. These changes cannot be eliminated by adjustment of the system to constant ionic strength, since the salts added for this purpose contribute to the conductivity. Conductivity examination must therefore be carried out in solutions containing only the components under investigation. Even, in such systems, where generally only ion-pair formation takes place, exact results can be obtained only by fairly complex theoretical calculations.

Several equations are available for the analysis of conductance data. Apparently all the equations give essentially identical values for λ_0 and in cases where the ion-pairing is considerable, a fairly close agreement exists in the values obtained for the association constants, K_A . Of the equations used for the analysis of conductance data, the Arrhenius-Ostwald and the Shedlovsky equations can be used without the need for any rigorous computer analysis.

The Arrhenius-Ostwald Equation. Using the assumption that the degree of idssociation of an electrolyte, α , was equal to λ/λ_0 and the law of mass action, Arrhenius and Ostwald deduced the relationship.

$$\frac{1}{\lambda} = \frac{1}{\lambda_0} + \frac{C\lambda K_A}{\lambda_0^2} \quad [2.40]$$

where K_A is the association constant, λ_0 is the equivalent conductance at infinite dilution, and C is the concentration of the electrolyte in equivalents per liter of solution. A plot of $\frac{1}{\lambda}$ vs. $C\lambda$ is very useful in obtaining an approximate values for both λ_0 and K_A . In using many of the more recent conductance equations, the Arrhenius-Ostwald approach is used as a starting point to obtain approximate values of λ_0 and K_A , both of which are required as the starting values in the computer programs. The plot of $\frac{1}{\lambda} \sqrt{S} C\lambda$ is also essential to eliminate points that are obviously inaccurate.

The Shedlovsky Equation: A modification of the Arrhenius-Ostwald function was generated by Shedlovsky. The equation is

$$\frac{1}{\lambda S(Z)} = \frac{K_A C \gamma_{\pm}^2 S(Z)}{\lambda_0^2} + \frac{1}{\lambda_0} \quad [2.41]$$

$S(Z)$ is the Shedlovsky function, $[\frac{Z}{2} + (1 + (\frac{Z}{2})^2)^{\frac{1}{2}}]^2$,

where $Z = S(\lambda_0)^{-3/2} (C\lambda)^{\frac{1}{2}}$. S is the Onsager coefficient, $\alpha\lambda_0 + \beta$, where

$$\alpha = \frac{(0.8204 \times 10^6)}{(\epsilon T)^{3/2}} \quad \text{and} \quad \beta = \frac{(82.501)}{(\epsilon T)^{\frac{1}{2}}}$$

C is the molar concentration, γ_{\pm} is the mean ionic activity coefficient on the molar scale, ϵ and η are the dielectric constant and the viscosity of the solvent, respectively, and T is absolute temperature.

The Shedlovsky equation has the advantage that it can be applied in almost every case and is not dependent on data of high precision as are required in the frequently used Fuoss-Onsager (86,87) and other equation (83).

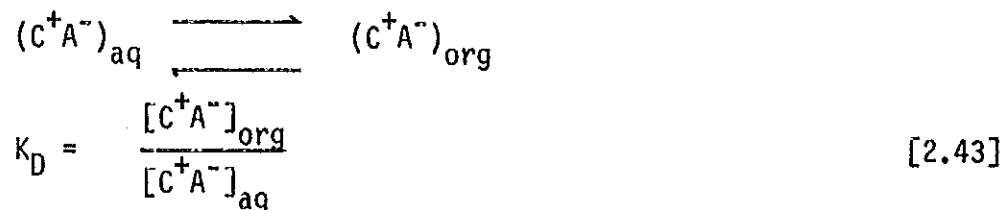
2.7 Extraction of Ion-Pairs (88,89)

An extraction system in which a monovalent cation (C^+) reacts with a monovalent anion (A^-) to form only one kind of ion-pair (C^+A^-) in the aqueous phase and in which the extracted ion-pair does not dissociate or aggregate, involves the following equilibria.

The ion-association constant in aqueous solution, K_A , refers to the reaction

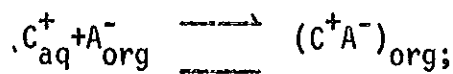


The distribution coefficient of the ion-pair (C^+A^-) between the aqueous and organic phases, K_D , refers to the equilibrium



where the subscript org and aq refers to the organic and the aqueous phases, respectively.

The extraction constant K_{ex} refers to the equilibrium



$$K_A = \frac{[C^+A^-]_{org}}{[C^+]_{aq}[A^-]_{aq}} = \frac{[C^+A^-]_{org}}{[C^+]_{aq}^2} = \frac{[C^+A^-]_{org}}{[A^-]_{aq}^2} \quad [2.44]$$

Since $[C^+]_{aq} = [A^-]_{aq}$ by electroneutrality.

or

$$K_{ex} = K_D \cdot K_A \quad [2.45]$$

The distribution ratios of C^+ or A^- between the aqueous and organic phases D_{C^+} or D_{A^-} , are described by

$$D_{C^+} = \frac{[C^+A^-]_{org}}{[C^+]_{aq} + [C^+A^-]_{aq}} \quad [2.46]$$

$$D_{A^-} = \frac{[C^+A^-]_{org}}{[A^-]_{aq} + [C^+A^-]_{aq}} \quad [2.47]$$

From equations 2.42-2.47 the following equation can be derived

$$D_{C^+}^{-1} = K_D^{-1} + (K_{ex}[A^-]_{aq})^{-1} \quad [2.48]$$

and

$$D_{A^-}^{-1} = K_D^{-1} + (K_{ex}[C^+]_{aq})^{-1} \quad [2.49]$$

The plots of $D_{C^+}^{-1}$ against $[A^-]_{aq}$ or $D_{A^-}^{-1}$ against $[C^+]_{aq}$ must be linear; from the intercept of the y-axis and the slope, K_D and K_{ex} can be calculated.

3. EXPERIMENTAL

3.1 Reagents

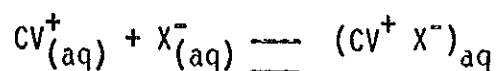
Stock Solution: $1.0 \times 10^{-1}M$ solutions of sodium perchlorate monohydrate, potassium iodide, potassium hydrogen phthalate (all BDH) and saccharin sodium dihydrate (pharmaceutical grade) were prepared and diluted to desired concentrations with distilled water. A $1.0 \times 10^{-2}M$ solution of potassium periodate was also prepared. For pH adjustments, 0.1 M sodium hydroxide and 0.25 M acetic acid were used. Interference studies were made using aqueous solutions of $1 \times 10^{-2}M$ potassium and ammonium salts of the anions investigated.

Aqueous solutions of $1.0 \times 10^{-3}M$ Crystal Violet and Brilliant Green (both Hopkins and Williams) were used to prepare ion-association salts of perchlorate, iodide, hydrogen phthalate and saccharin.

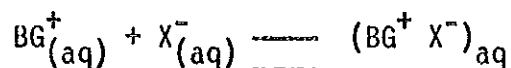
Nitrobenzene (Riedel-de Haem), 1,2-dichloroethane, 1,2-dichlorobenzene (both BDH) and other solvents were used without further purification.

3.2 Preparation of Ion-Association Salts of Basic Dyes

The Crystal Violet or Brilliant Green salt of each of the anions (perchlorate, iodide, hydrogen phthalate and saccharin) was prepared by shaking 20 ml of $10^{-2}M$ aqueous solution of the anion with 100 ml of $10^{-3}M$ aqueous solution of the basic dye. The resulting mixture was saturated with sodium chloride to promote precipitation of the ion-association salt and allowed to stand over night. The hydrogen phthalate and saccharin salts were found to be viscous and sticky while the perchlorate and iodide salts were dense enough to settle at the bottom of the vessel. The reaction of the ion-association salt formation follows



or



where X^- was ClO_4^- , I^- , Sacc^- , or HP^- and CV^+ and BG^+ stands for Crystal Violet and Brilliant Green cations respectively. Each product was separated by centrifugation, washed twice with distilled water and dried at 50-60°C for 5-6 hours. A stock solution of 10^{-3}M each of the salts was then prepared in nitrobenzene or 1,2-dichloroethane or 1,2-dichlorobenzene for the desired investigation.

3.3 Design of Liquid Membrane Electrodes

Membrane Holder: Concentric Pyrex tubes (a length of 138 mm and a width of 6.7 mm outer tube and a length of 115 mm and width of 3.8 mm of inner tube) with a common 14/23 ground glass joint at one end were glass-blown to narrower tips (of about 3 mm width) at the other end of the tubes (Fig. 1) and the assembly was used as the electrode body.

Membrane Preparation: A polyvinyl chloride (PVC) solution was prepared by dissolving 100 mg of the polymer powder in a mixture containing 3 ml of tetrahydrofuran (THF) and 0.25 ml of 1-chloronaphthalene (plasticizer). The narrower ends of the membrane holder were dipped into the PVC solution every two minutes until the tube ends were covered with a thin film (about 1-2 mm thick) of the viscous solution. Care was taken not to allow any gas bubble in the film. The membrane holder was then kept up right in a hood to evaporate the THF. About 3 ml of 2×10^{-4} - $6 \times 10^{-4}\text{M}$ nitrobenzene, 1,2-dichlorobenzene or 1,2-dichloroethane solution of the basic dye (Crystal Violet or Brilliant Green) perchlorate or hydrogen phthalate salts was introduced into the outer tube of the membrane holder using the injection port (Fig. 1) and allowed to saturate the PVC membrane with the basic dye

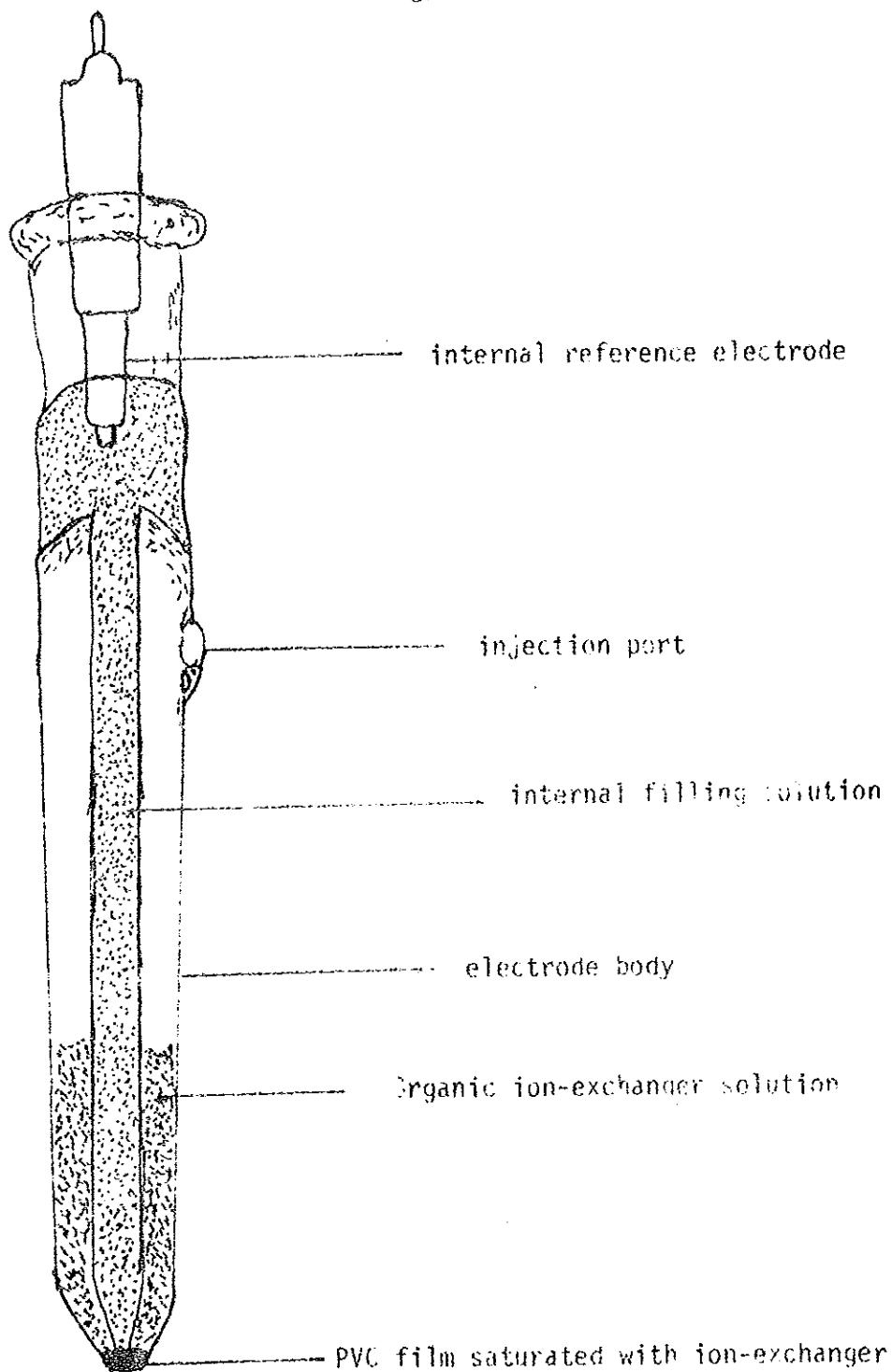
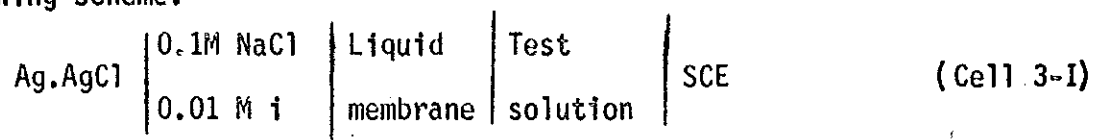


Fig. 3.1 Liquid membrane electrode

solution for 24 hours. The internal filling solution was of $10^{-2}M$ sodium perchlorate monohydrate or potassium hydrogen phthalate in 0.1 M sodium chloride for the perchlorate or hydrogen phthalate electrodes, respectively. The inner tube was filled with the appropriate internal filling solution to a level at which an internal Ag/AgCl reference electrode would be in contact. The electrode was always kept in a $10^{-2}M$ aqueous solution of the anion for which the electrode was designed.

3.4 Instrumentation

Potential measurements of solutions were made with the liquid membrane electrode against a saturated calomel reference electrode (SCE) using a Philips P W 9409 digital pH/mv meter of 0.1 mv precision. Equilibrium potentials of the solutions were measured 1-2 minutes after continuous stirring with a Teflon coated stirring bar. The complete cell is represented by the following scheme.



where i is perchlorate or hydrogen phthalate.

pH measurements of solutions were made with a Beckman Chem Mate pH meter equipped with a hydrogen-sensitive glass electrode.

For the determination of the distribution ratios of the ion-association salts between water and a water-immiscible organic solvent, the absorbance of the dye in the organic solvent was measured with a Beckman Model 24-uv-vis spectrophotometer equipped with 1-cm matched quartz cells.

Conductometric measurements of the basic dye salts in nitrobenzene (or 1,2-dichloroethane or 1,2-dichlorobenzene) were made with a Wheatstone conductivity bridge of Toshinawa Industries LTD Model 890 (at a constant frequency of 50 Hz) equipped with a conductivity cell (Industrial Instruments CO.).

3.5 General Experimental Procedures

Potential Measurements: Potentials of 10^{-8} - 10^{-1} M solutions of the anion, to which the electrode responds, were made to evaluate the response behavior of the liquid membrane electrode. All potential measurements were carried out at ambient temperature, i.e., at $25 \pm 1^\circ\text{C}$.

Selectivity Coefficient Determination. Both separate solution and mixed solution methods were applied to evaluate the selectivity of the perchlorate and hydrogen phthalate electrodes. In the separate solution method, the potentials of 10^{-2} M solutions of the primary ion i and the interfering ion \bar{j} were measured separately and evaluated according to equation 2.20. In the mixed solution method the potentials of 10^{-6} - 10^{-1} M solutions of i containing a constant concentration of ion \bar{j} (10^{-2} M), which was 10 ml in both cases, were measured and the selectivity coefficients, when $E_j = E_i$, were evaluated based on equation 2.21. The activity a_i at which $E_j = E_i$ was the activity at which the electrode potential of the mixture deviates by $18/z_i$ from the extrapolation of the linear portion of the calibration graph of potential vs. $-\log a_i$.

Determination of Extraction Constant. The distribution ratios of each of the basic dye salts of perchlorate, iodide, hydrogen phthalate, and saccharin between aqueous and nitrobenzene (or 1,2-dichloroethane) phases were determined spectrophotometrically. Samples of 10 ml of 10^{-5} M solutions of the salts in nitrobenzene or 1,2-dichloroethane were shaken with 10 ml of distilled water for five minutes. The organic phases were separated, dried over anhydrous sodium sulphate (which was white after washing) and used for spectrophotometric determination. The absorbance of standard solutions of each of the salts and the remaining dye in the organic phase after partition were measured at 585 nm for Crystal Violet and 624 nm for Brilliant Green.

The concentration of each salt in the organic phase was determined from calibration plots of absorbance vs concentration of standard ion-association salt solution. The difference between the initial concentration of the salt and the concentration after partition gave the salt concentration in the aqueous phase. The concentrations of the ion-association salt in organic and the aqueous phase were used to evaluate the extraction constant according to equation 2.44.

Determination of association Constant. Association constants were calculated from the conductivity measurements. The stock solution of ion-association salt was serially diluted from $10^{-3}M$ down to $10^{-5}M$. The resistance of each solutions was measured. The conductance of the salts were calculated after subtracting the conductance of the solvent from the conductance of the solution. From the plots of λ (molar conductance of the salts) vs $C^{\frac{1}{2}}$, approximate λ_0 were evaluated and used in Shedlovsky equation.

4. RESULTS AND DISCUSSION

4.1 Preparation of Liquid Membrane Electrodes

The materials tried as a membrane matrix were glass frit, Porous Teflon and millipore filters. Attempts were made to fix them to glass with epoxy resins. Difficulties observed with such types of membrane matrix were mainly mechanical. One was the gradual loss of the ion-exchanger by dissolution into the test solution; the dissolved ion-exchanger was constantly supplied from the organic phase of the liquid membrane in contact with the matrix. Another difficulty was that it was not possible to achieve perfect filling of the membrane matrix pores with the liquid ion-exchangers.

These complications were overcome by dipping the tip of the electrode body into PVC solutions in THF with chloronaphthalene as a plasticizer (63). The thickness of the PVC disc after evaporation of THF was found to be in the range of about 1-2 mm. This method of fixing the membrane matrix to the holder overcame the leakage problem associated with the use of adhesives. It also avoided the mechanical difficulties resulting from fixing a disc of membrane; separately prepared by impregnating the ion-exchanger in a polymeric matrix (90).

4.2 Selection of Membrane Solvents and Ion-Exchanger Concentrations

The selectivity of a membrane electrode is governed by both the mobility of the ions in the membrane and the equilibrium that exists at the membrane-solution interfaces (extraction and ion-exchange equilibrium constants) (64). In the case of liquid membrane electrodes, in which there is association of dissociation of the electroactive salts, these selectivity parameters are dependent on the nature of the solvents. The choice of a membrane solvent to achieve selectivity is based on its dielectric constant.

Other requirements of solvent properties in liquid membrane electrode preparations include (i) immiscibility with the aqueous phase (ii) low solubility of the matrix in the membrane solution and (iii) high viscosity so that it do not pass through the membrane matrix. Moreover, solvents have been chosen by considering their ability to dissolve the ion-exchangers.

Nitrobenzene, chlorobenzene, 1,2-dichlorobenzene, 1,2-dichloroethane, and chloroform were tested as membrane solvents in view of these factors. Since chloroform and chlorobenzene have low dielectric constants (4.80 and 5.621), respectively, and they were not used as membrane solvents. Moreover, the salts were found to be of low solubility so the resulting exchanger solution had high resistance. The solvents having higher dielectric constant such as nitrobenzene and 1,2-dichloroethane (34.82 and 10.36 at 25°C) were selected as a membrane solvents for the basic dye salts under study. Only the perchlorate salts of the two basic dyes were appreciably soluble in 1,2-dichlorobenzene (9.93) and Crystal Violet perchlorate was studied as membrane material in this solvent. In these three solvents linear potential response of the perchlorate liquid membrane electrodes have been observed.

Various concentrations (10^{-5} - 10^{-3} M) of Crystal Violet perchlorate in nitrobenzene were tried as a liquid ion-exchangers, to saturate the PVC membrane matrix. For concentrations below 3×10^{-4} M, the electrode potentials were unstable, owing to the high resistance of the membrane, while at those greater than 6×10^{-3} M, the potential of the electrode decreased, probably due to elution of membrane solute into the adjacent aqueous solutions. Hence, the available concentration range in the organic solvent was 3×10^{-4} - 6×10^{-4} M. The same concentration ranges of the salts were used for the other liquid membrane electrodes in the other solvents.

The times to saturate the PVC matrix with the solution of the electroactive salts in nitrobenzene, 1,2-dichloroethane or 1,2-dichlorobenzene were found to be about 24, 48 and 36 hours, respectively. The difference in saturation time is believed to be due to differences in the diffusion rates of the solvents into the PVC matrix.

4.3 Response Characteristics of Electrodes

The Crystal Violet and Brilliant Green perchlorate and Brilliant Green hydrogen phthalate electrodes were found to respond to perchlorate, periodate, iodide, saccharin, and hydrogen phthalate ions in wide concentration ranges as shown on Tables 4.1-4.4. These linear responses are typical of ion-selective electrodes. One of the potential use of such electrodes, which have only modest selectivities and respond to a number of ions, is in electrochemical detection of mixtures of such ions after chromatographic separation (91).

The cell assembly used to measure potentials was indicated in the experimental section (section 3.4) Cell (3.1). The response potentials (E) of these electrodes to the mentioned anions, i , follows the Nernst equation.

$$E = \text{Constant} - S \log a_i \quad [4.1]$$

where S is the experimental slope and a_i is the activity of the anion. The potential measured in aqueous solutions of the ions results mainly from an ion-exchange equilibrium between the membrane (memb.) and aqueous (aq.) phases,



The measured potential responses as a function of pa_1 ($pa_1 = -\log a_1$) of perchlorate, periodate, iodide, saccharin and hydrogen phthalate ions are shown in Fig. 4.1 - 4.3 for the Crystal Violet perchlorate electrode in nitrobenzene and 1,2-dichlorobenzene and for the Brilliant Green perchlorate in nitrobenzene as a membrane solvent. The responses of perchlorate based on the two dyes have no significant difference in their slopes (which are near Nernstian), linear response ranges, or detection limits in nitrobenzene (Tables 4.1 and 4.2). However, in 1,2-dichlorobenzene the slopes of the perchlorate electrode in response to iodide, saccharin and hydrogen phthalate were found to be slightly lower than that in nitrobenzene (Table 4.3).

The responses of the Brilliant Green hydrogen phthalate electrode to perchlorate, iodide, saccharin and hydrogen phthalate are also shown on Fig. 4.4 and the data are summarized in Table 4.4.

Table 4.1
Response Characteristics of the Crystal Violet Perchlorate
Electrode in Nitrobenzene

Anions	Slope, mv/ pa_1	Concentration Range of Nernstian Response (M)	Limit of Detection (M)	pH Range
ClO_4^-	59.0	$3.5 \times 10^{-6} - 1 \times 10^{-1}$	9.6×10^{-7}	3-11
IO_4^-	57.5	$5 \times 10^{-6} - 1 \times 10^{-2}$	1.4×10^{-6}	5*
I^-	57.0	$1 \times 10^{-4} - 1 \times 10^{-1}$	7.5×10^{-6}	3.5-7.0
$Sacc^-$	58.7	$5 \times 10^{-4} - 1 \times 10^{-1}$	1.3×10^{-5}	3-10
Hp^-	56.6	$5 \times 10^{-5} - 1 \times 10^{-1}$	1.0×10^{-5}	3-4

Hp^- : hydrogen phthalate, $Sacc^-$ = saccharine

* aqueous potassium periodate

Table 4.2

Response Characteristics of Brilliant Green-perchlorate
Electrode in Nitrobenzene

Anion	Slope, mv/ p_{a_1}	Concentration Range of Nernstian response (M)	Limit of detection (M)	pH Range
ClO_4^-	56.5	3.8×10^{-6} - 1×10^{-1}	1.7×10^{-6}	3.5-9.0
IO_4^-	57.0	1×10^{-6} - 1×10^{-2}	6.7×10^{-7}	5*
I^-	53.0	5×10^{-4} - 1×10^{-1}	2.4×10^{-5}	3.5-7.0
Sacc^-	60.5	5×10^{-5} - 1×10^{-1}	8.4×10^{-6}	3.5-9.0
HP^-	56.4	1×10^{-5} - 1.5×10^{-2}	5×10^{-6}	3-4.0

* Aqueous Potassium Periodate.

Table 4.3

Response characteristics of Crystal Violet Perchlorate
Electrode in 1,2-dichlorobenzene

Anions	Slope mv/ p_{a_1}	Concentration range of Nernstian Slope (M)	Limit of Detection (M)
ClO_4^-	56	7.6×10^{-6} - 1×10^{-1}	2×10^{-6}
IO_4^-	57.8	1×10^{-5} - 1×10^{-2}	2.2×10^{-6}
I^-	51.6	5×10^{-4} - 1×10^{-1}	4.7×10^{-5}
Sacc^-	53.6	2.5×10^{-4} - 1×10^{-1}	8.9×10^{-6}
HP^-	53.6	5×10^{-4} - 1×10^{-1}	3.2×10^{-6}

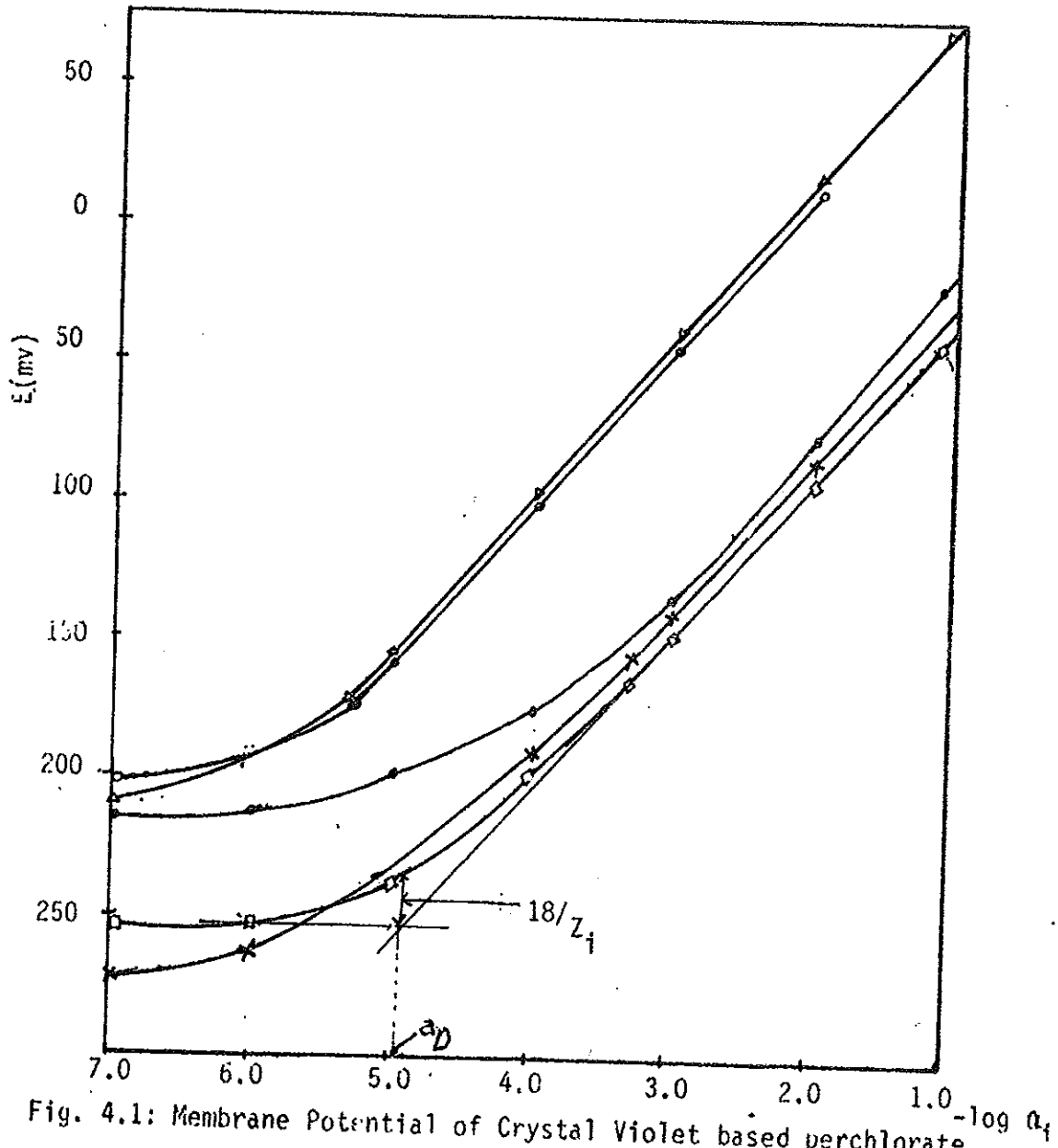


Fig. 4.1: Membrane Potential of Crystal Violet based perchlorate electrode responding to ClO_4^- (Δ), IO_4^- (\circ), I^- (\times), Sacc^- (\cdot) and Hpht^- (\square): Membrane solvent is nitrobenzene

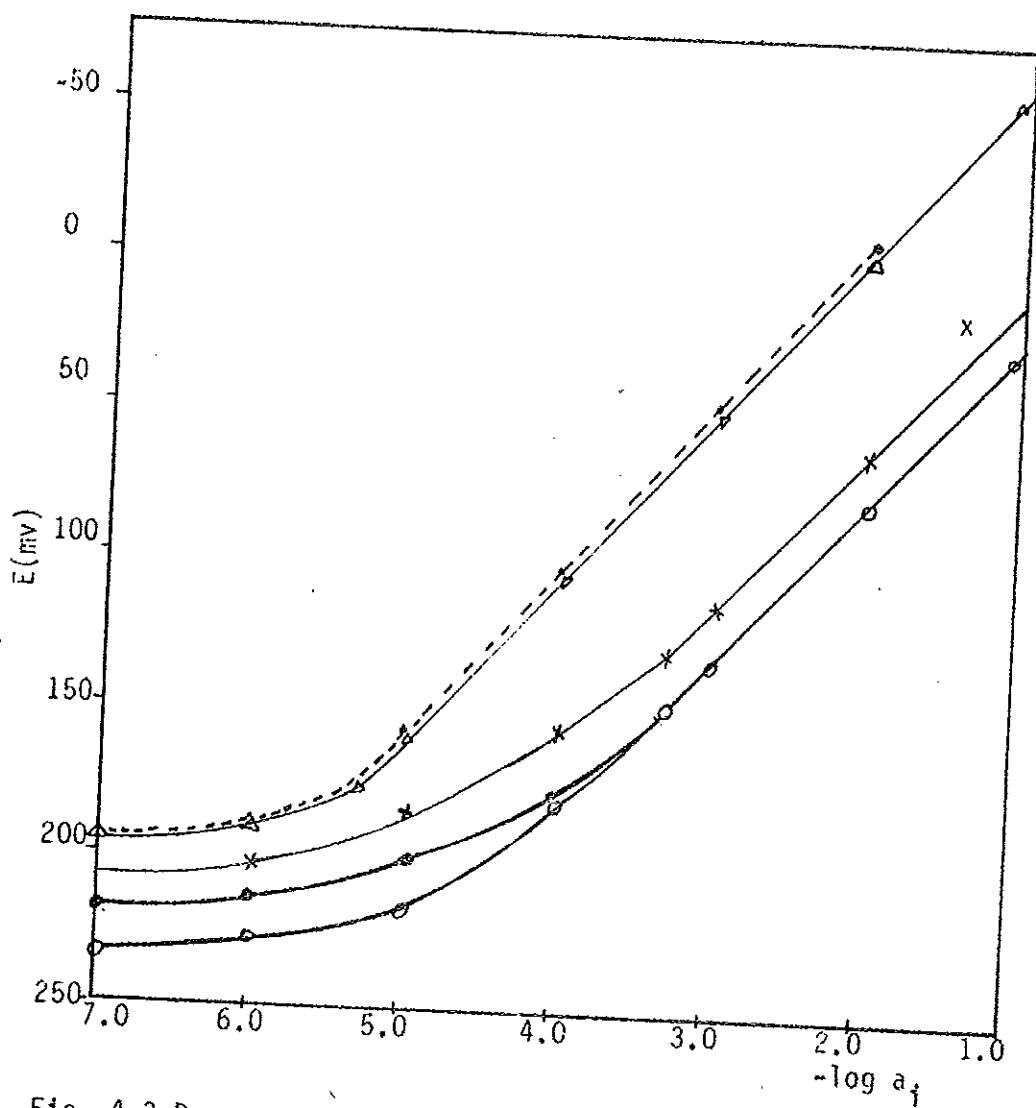


Fig. 4.3 Response of Crystal Violet perchlorate electrode to anions IO_4^- (---); ClO_4^- (Δ), I^- (\times); Sacc^- (\bullet), and HP^- (\circ). Membrane solvent 1,2-dichlorobenzene

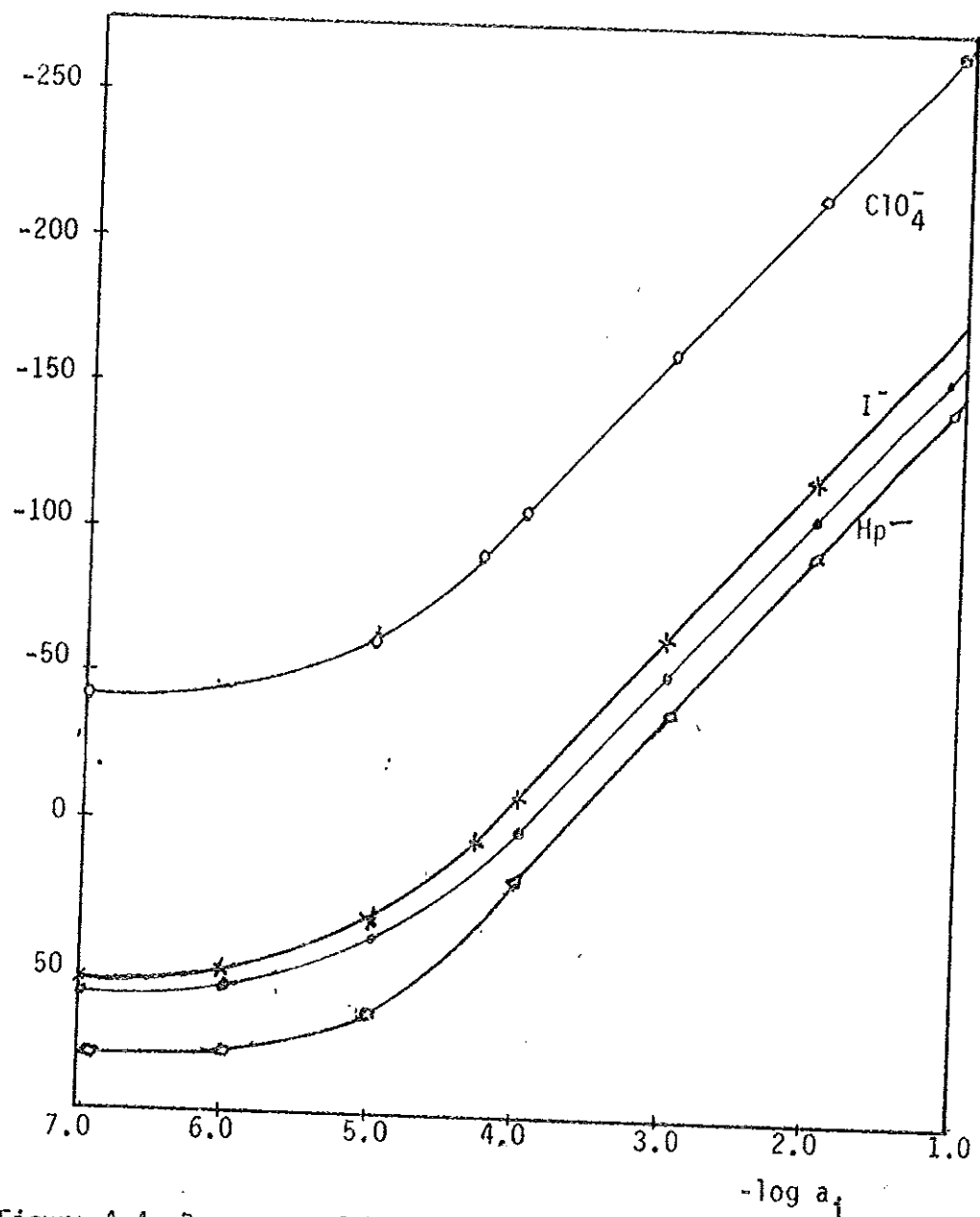


Figure 4.4 Response of Brilliant Green based hydrogen phthalate electrode to anions ClO_4^- (O); I^- (x); Sacc^- (•) and HP^- (Δ). (Membrane solvent nitrobenzene).

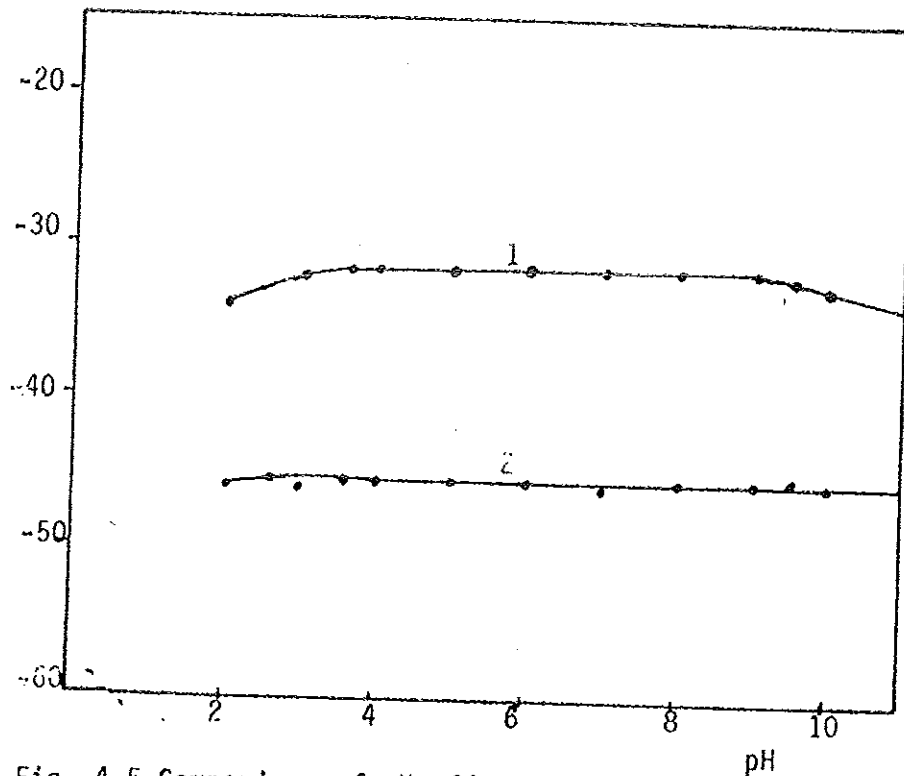


Fig. 4.5 Comparison of pH effect on Brilliant Green (1) and Crystal Violet (2) perchlorate electrode responding to $10^{-2}M ClO_4^-$ (Membrane solvent nitrobenzene).

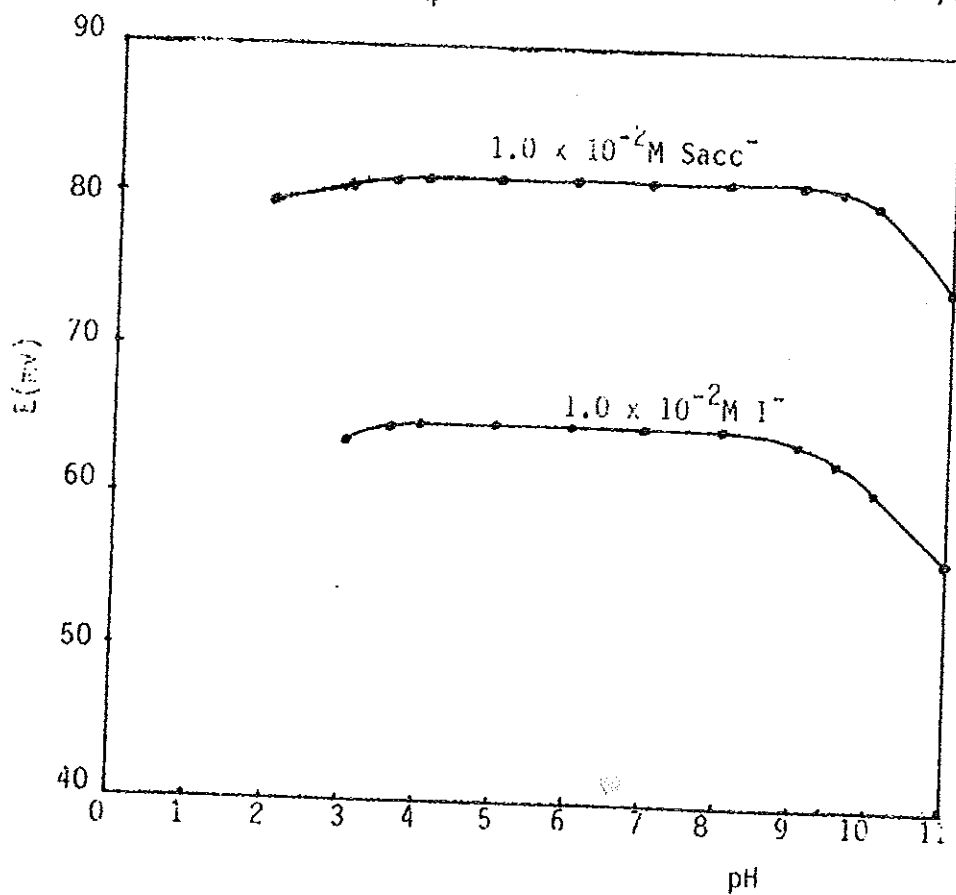


Fig. 4.6 Effect of pH on Brilliant Green based perchlorate electrode responding to saccharin and iodide.

The response of Crystal Violet perchlorate electrode to hydrogen phthalate had very narrow pH-independent range (pH 3.0-4.0). As the pH increases the response potential became more and more positive showing a decrease in the concentration of the monovalent anion in the aqueous phase. After adding an equivalent amount of sodium hydroxide (pH 7.2), however the potential sharply changed to more negative values which may be due to the response of the electrode to divalent phthalate ion.

The same trend was also observed in the case of Brilliant Green perchlorate electrode in the pH study (Fig. 4.6) except that the potential which is independent of pH was within a narrow pH range (Table 4.2). This narrow pH range relative to the Crystal Violet perchlorate electrode may be attributed to the easier protonation and formation of a carbinol of Brilliant Green (51).

The effect of pH on the potentials of periodate solutions was not evaluated because periodate ion was not of our primary interest in the study.

4.6 Extraction Constant

The extraction data of ion-association salt provides useful information for the selection of proper membrane solvents and electroactive ion-pairs in the design of liquid membrane electrodes. Liquid ion-exchangers were developed initially as liquid extraction systems, and it is interesting to note the parallel pattern between the ratio of the extraction constants for ion pair formation and the selectivity coefficient.

The extraction constants of the salts for the partition equilibria between water and nitrobenzene and 1,2-dichloroethane were determined spectrophotometrically (47,88) and calculated using equation 2.44, as mentioned on the experimental part. As shown in Table 4.5, the extraction

constant of the ion-pairs of Brilliant Green and Crystal Violet are comparable in nitrobenzene, while the ion-pairs of Crystal Violet salts in 1,2-dichloroethane are less than that of in nitrobenzene. This may be accounted for by the fact that, the ion-pairs are preferentially solvated by the molecules of dipolar aprotic solvents, such as nitrobenzene, by a combination of dispersion and ion-dipole interaction (83). Even so, the larger K_{ex} values in both solvents show that both nitrobenzene and 1,2-dichloroethane can be used as membrane solvents for ion-pairs of perchlorate, saccharine, iodide, and hydrogen phthalate with Brilliant Green and Crystal Violet.

Table 4.5
Extraction Constants of Crystal Violet and Brilliant Green
ion-association salts

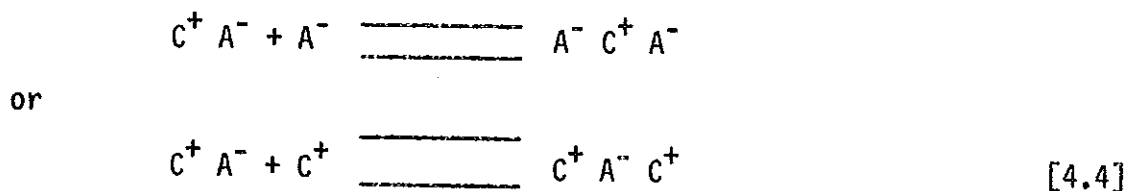
Anions associated	$\log K_{ex}$		
	Crystal Violet nitrobenzene	1,2-dichloroethane	Brilliant Green nitrobenzen
ClO_4^-	8.389	7.778	7.580
I^-	6.954	6.643	7.158
Sacc $^-$	7.580	6.710	6.379
HP $^-$	7.415	5.725	7.815

4.7 Association Constant

The electrical conductivity and the association constants of the ion-association salts have been determined in order to select the proper solvent and to explain the selectivity behavior of the liquid membrane electrodes.

Figure 4.7, 4.8 and 4.11 show plots of λ vs $C^{\frac{1}{2}}$ from which approximate λ_0 values were obtained to evaluate values of λ_0 and association constants, K_A , by the Shedlovsky equation (equation 2.41). The plots of $\frac{1}{\lambda S(z)}$ as a function of $C\lambda\gamma_{\pm}^2 S(z)$, for the nitrobenzene and 1,2-dichloroethane solutions of the Crystal Violet salts are illustrated in Figures 4.9, 4.10, and 4.12. They have been seen to be linear with an intercept at $\frac{1}{\lambda_0}$ and a slope of K_A/λ_0^2 . The limiting ionic conductance (λ_0) and the association constants for the ion-association salts of Crystal Violet with perchlorate, iodide, saccharine, and hydrogen phthalate in the two solvents are summarized in Table 4.6.

As shown on λ vs. $C^{\frac{1}{2}}$ plots (Fig. 4.7-4.9), the curves fall very rapidly with increasing concentration indicating extensive ion-association. Moreover, the salts of Crystal Violet have higher conductance in nitrobenzene than in 1,2-dichloroethane, showing that the ion pairs are more easily dissociated in nitrobenzene than in 1,2-dichloroethane. The association constants in 1,2-dichloroethane ($\epsilon = 10.36$), however, were found to be lower than in nitrobenzene ($\epsilon = 34.82$). This is in contrast to the effect of dielectric constant of solvents on dissociation of ion-association salts. This is probably due to the formation of ion-triplets which are formed as a result of large electrostatic interactions. In such solvents of lower permittivity, beside the ion-pairs, there exists an interaction between the free ions and the ion-pairs to form ion-triplets as indicated by Fuoss and his associates (94).



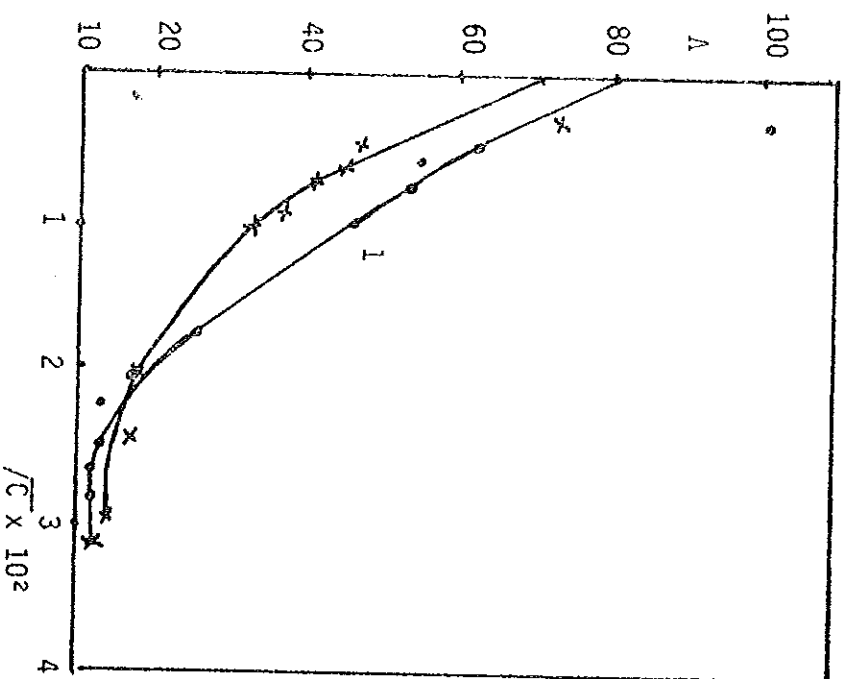


Fig. 4.7 Molar conductance ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) of Crystal Violet ion-pairs in nitrobenzene plotted as a function of square root of molar concentration (1) $\text{CV}^+\text{ClO}_4^-$, (2) CV^+I^-

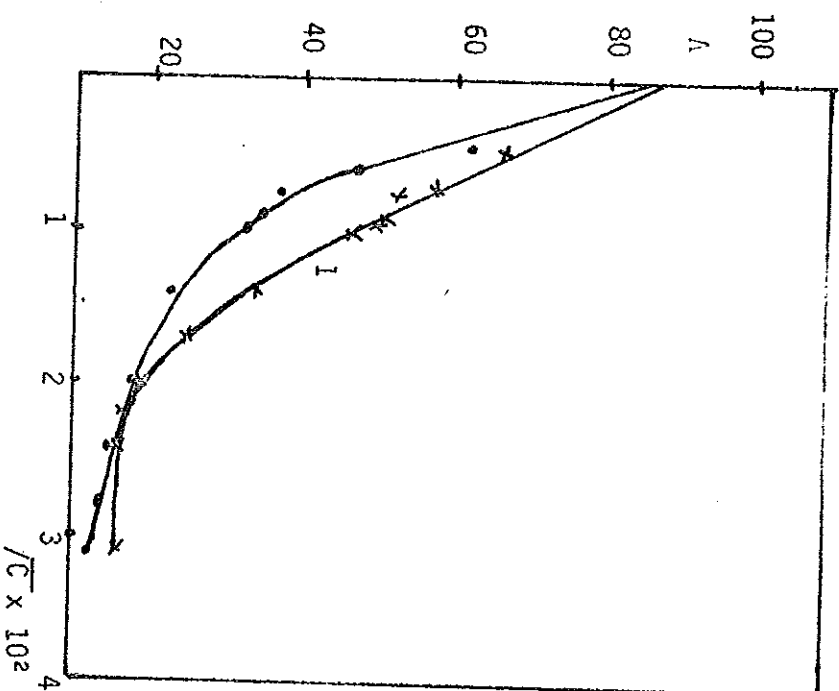


Fig. 4.8 Molar conductance ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) of Crystal Violet ion-pairs in nitrobenzene plotted as a function of square root of molar concentration (1) CV^+HP^- , (2) CV^+Sacc^-

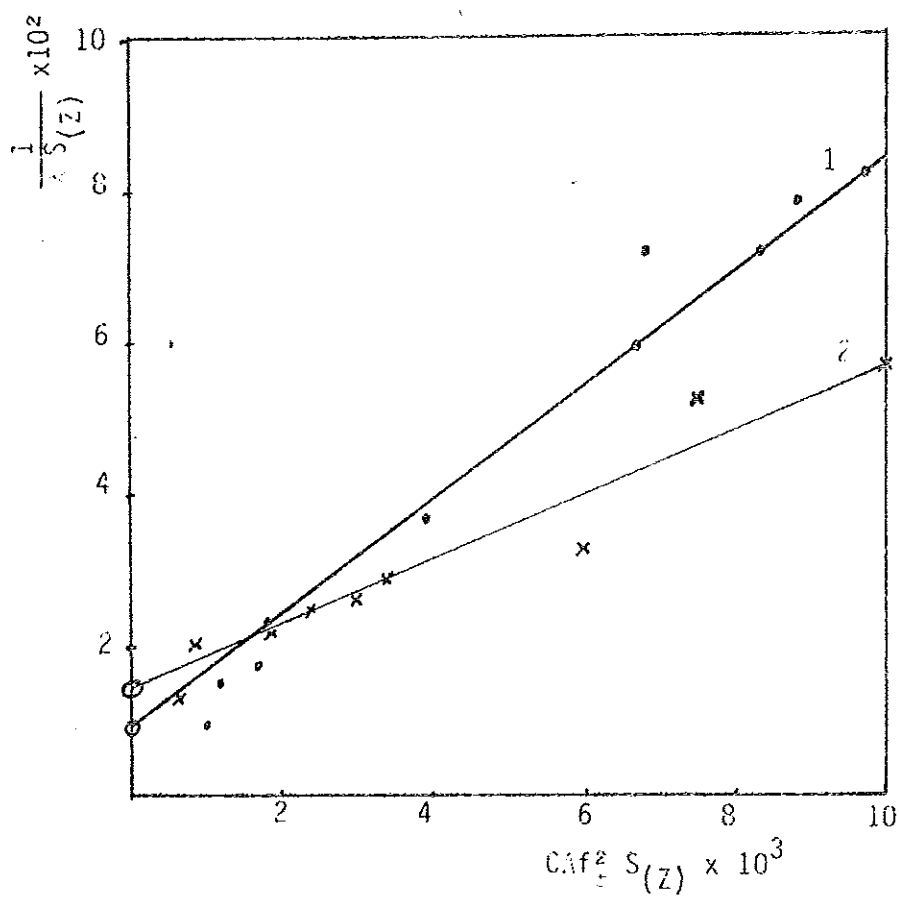


Fig. 4.9 Plots of Shedlovesky function for the determination of association constant and limiting molar conductance in nitrobenzene.

1) $CV^+ClO_4^-$

2) CV^+I^-

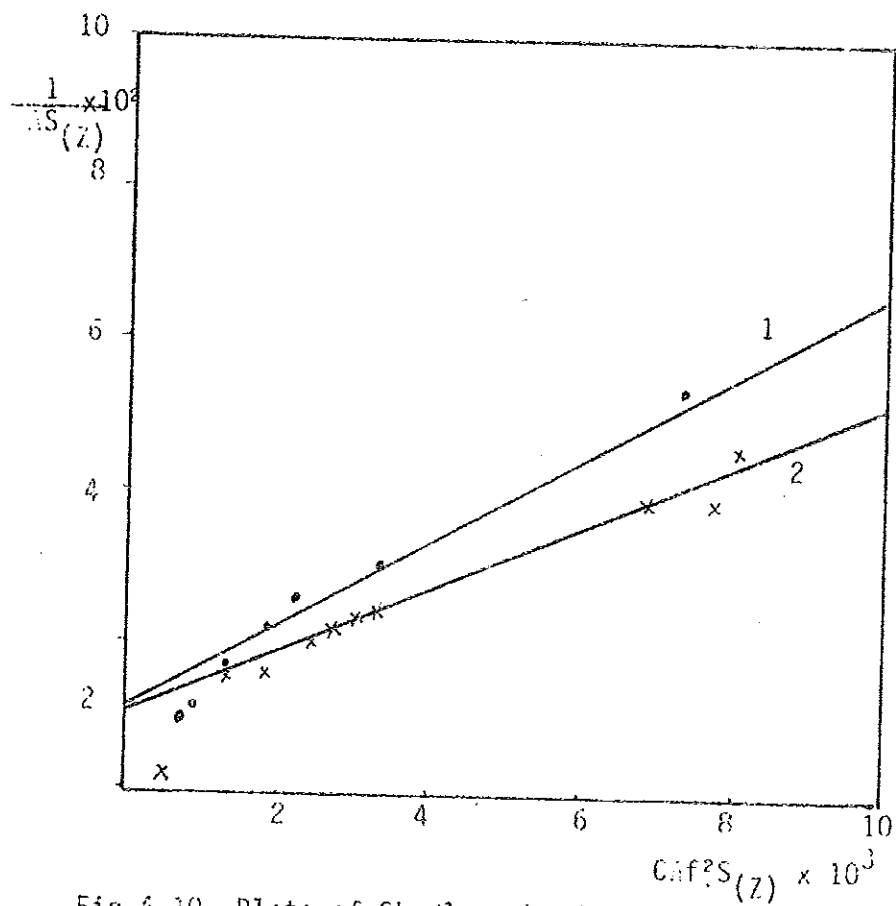


Fig 4.10 Plots of Shedlovesky function f or the determination of association constant and limiting molar conductance in nitrobenzene

- 1) $CV^+ Sacc^-$
- 2) $CV^+ HP^-$

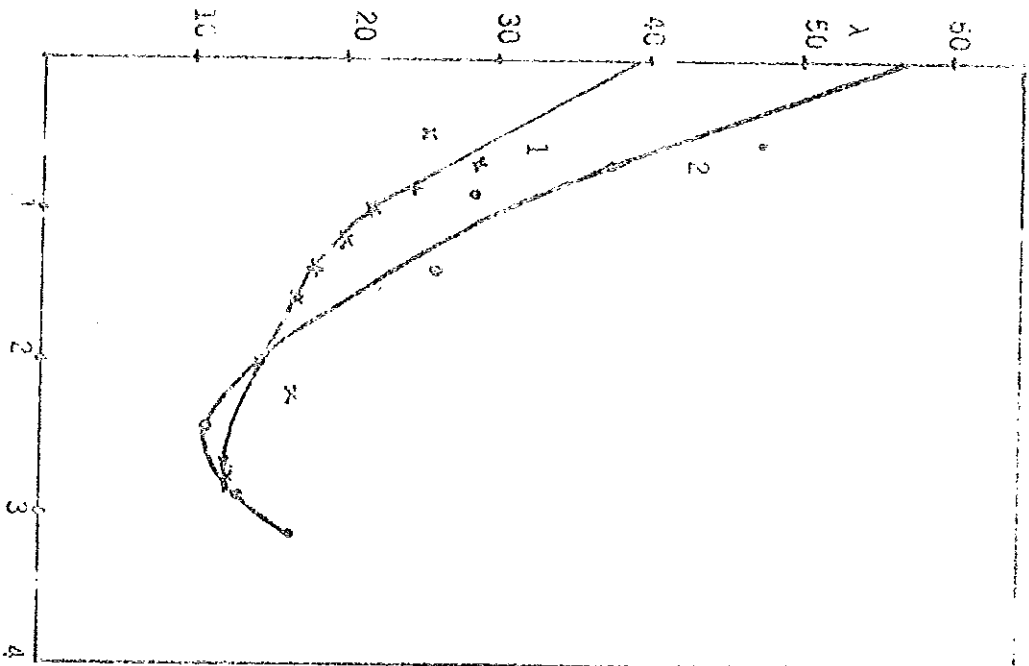


Fig. 4.11 Molar conductance ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$) of Crystal Violet (1) $\text{C}_{10}\text{H}_8\text{N}_2$ and (2) Saccharin. 1,2-dichloroethane plotted as a function of molar concentration

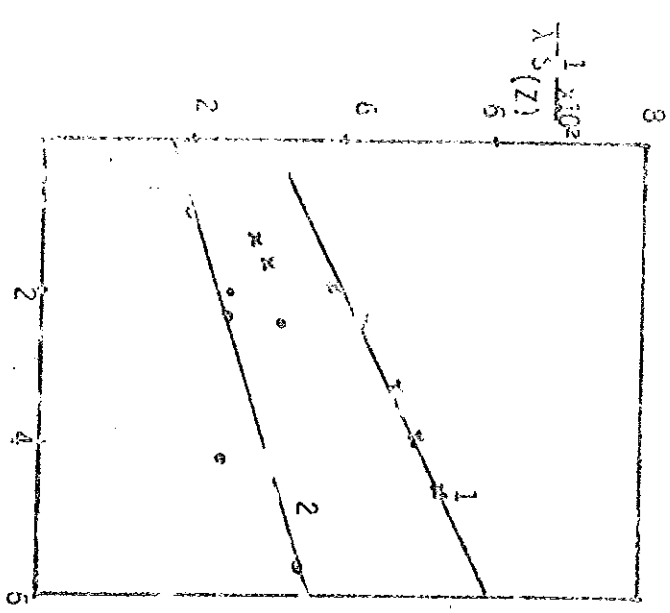


Fig. 4.12 Steadlovsky function for the determination of association constant and limiting molar conductance; (1) Crystal Violet perchlorate and (2) Crystal Violet saccharine

Hence the conductivity of the ionic species in solvents of low dielectric constant (ϵ), such as 1,2-dichloroethane, may not only be from the mobilities and charges of the free ions, but also from the ion-triplets. That is, the observed conductance were the sum of the conductance of the free ions and that of the triple ions. The formation of triple ions is often indicated by a minimum in the plot of λ vs. $C^{\frac{1}{2}}$ or $\log \lambda$ vs. $\log C$ as shown on Fig. 4.11 for the case of the Crystal Violet Saccharin ion-association salt.

Table 4.6
Limiting Conductance (λ_0 in $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$) and
Association Constant K_A , of Crystal Violet Salts
in Nitrobenzene and 1,2-dichloroethane

Crystal Violet ion-paired with	in nitrobenzene		in 1,2-dichloroethane	
	λ_0	K_A	λ_0	K_A
ClO_4^-	108.1	8.9×10^4	32.8	5.7×10^3
I^-	66.9	2.0×10^4	29.8	4.7×10^3
Sacc $^-$	86.9	3.8×10^4	52.6	7.9×10^3
HP $^-$	90.9	3.4×10^4	60.6	1.2×10^4

4.8 Selectivity of Membrane Electrodes

The influence of various foreign ions on the electrode responses were investigated by evaluation of selectivity coefficients, k_{ij}^{po+} . Both the separate and mixed solution methods were employed to calculate the values using equation 2.20 and 2.21, respectively. In equation 2.21, the activity of the interfering ion a_j was taken to be a constant while the

activity, a_i , was calculated as described on the experimental part/p using figures like that of 4.13. Tables 4.7 and 4.8 show the respective K_{ij}^{pot} values for Crystal Violet perchlorate and Brilliant Green hydrogen phthalate electrodes using nitrobenzene as membrane solvent. The variations in K_{ij}^{pot} values by the two methods are believed to be due to the different experimental errors. Despite this, the order of selectivity using the two methods is generally the same for the two electrodes. It should be noted however, that the electrode selectivity coefficient is not necessarily be constant unless the ions i and j are sensed by electrodes with identical slopes.

Table 4.7
Selectivity Coefficients K_{ij}^{pot} of the crystal Violet based perchlorate liquid membrane electrode using nitrobenzene as membrane solvent

Interfering ions (j)	K_{ij}^{pot}	
	Separate Soln. Method	Mixed Soln. method
ClO_4^-	1.00	1.00
IO_4^-	0.78	0.98
I^-	1.62×10^{-2}	1.48×10^{-2}
Sacc ⁻	1.52×10^{-2}	1.32×10^{-2}
HP ⁻	1.22×10^{-2}	9.87×10^{-3}
MnO_4^-	12.13	10.65
SCN^-	6.74×10^{-2}	7.44×10^{-2}
F^-	2.17×10^{-4}	8.84×10^{-3}
Cl^-	5.04×10^{-4}	5.91×10^{-4}
Br^-	3.50×10^{-4}	8.84×10^{-3}
ClO_3^-	1.00×10^{-2}	9.93×10^{-3}
BrO_3^-	4.70×10^{-4}	4.98×10^{-4}
IO_3^-	4.03×10^{-4}	1.48×10^{-4}
NO_3^-	2.21×10^{-3}	1.76×10^{-3}
Acetate	4.03×10^{-3}	9.91×10^{-4}
Benzoate	4.32×10^{-4}	5.27×10^{-4}
Ox^{2-}	9.97×10^{-5}	6.38×10^{-5}
SO_2^{2-}	4.97×10^{-5}	6.28×10^{-5}

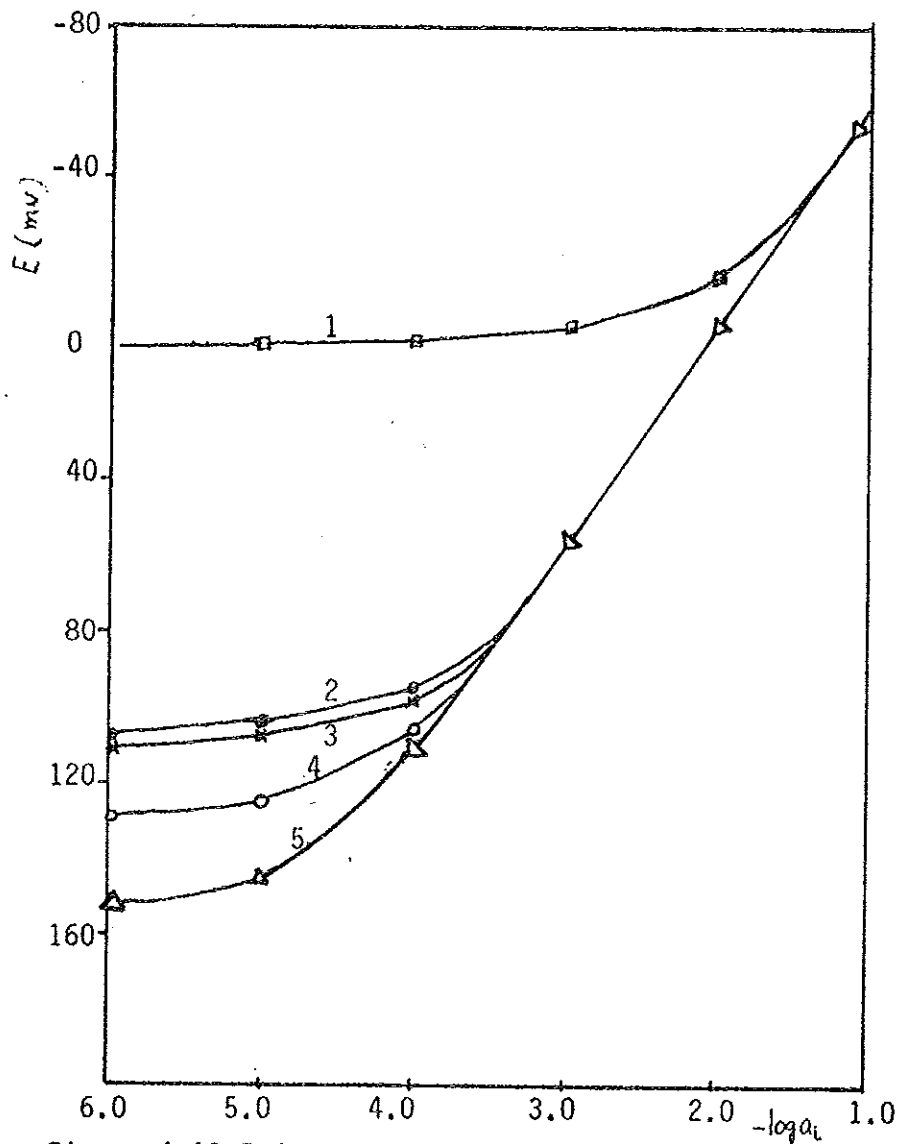


Figure 4.13 Effect of interference on Crystal Violet based perchlorate electrode response, in the presence of $10^{-2}M$ (1) IO_4^- (2) I^- , (3) $Sacc^-$; (r) HP^- 5. Cl^- ; to ClO_4^- ion. Electrode membrane solvent is nitrobenzene.

It can be observed from Table 4.7 and Fig. 4.13 that the perchlorate electrode has higher selectivity towards permanganate and periodate ions. The hydrogen phthalate electrode has highest selectivity to permanganate, perchlorate and periodate, and higher selectivity to thiocyanate, iodide, saccharin, and salicylate. Both electrodes respond to perchlorate hydrogen phthalate, iodide and saccharin (Fig. 4.1-4.4). However, the perchlorate electrode responds to periodate, the response of the hydrogen phthalate electrode to periodate was unstable, which can be due to some oxidation reactions.

Table 4.8
Selectivity Coefficient, K_{ij}^{pot} , of the Brilliant Green based hydrogenphthalate liquid membrane electrode, nitrobenzene as a membrane solvent

Interfering ion (j)	K_{ij}^{pot}	
	Separate soln. method	Mixed soln. method
HP ⁻	1.00	1.00
ClO ₄ ⁻	108.5	105.92
IO ₄ ⁻	105.8	104.31
I ⁻	1.3	1.32
Sacc ⁻	1.23	1.25
MnO ₄ ⁻	1.47 x 10 ³	
SCN ⁻	5.74	5.30
F ⁻	9.56 x 10 ⁻⁴	6.65 x 10 ⁻⁴
Cl ⁻	4.65 x 10 ⁻⁴	2.79 x 10 ⁻³
Br ⁻	2.00 x 10 ⁻²	3.81 x 10 ⁻²
ClO ₃ ⁻	0.758	0.83
BrO ₃ ⁻	1.27 x 10 ⁻²	1.25 x 10 ⁻²
IO ₃ ⁻	3.73 x 10 ⁻³	3.52 x 10 ⁻³
NO ₃ ⁻	8.42 x 10 ⁻³	8.48 x 10 ⁻²
Acetate	6.76 x 10 ⁻³	4.79 x 10 ⁻³
Benzoate	1.04 x 10 ⁻²	2.80 x 10 ⁻²
Salicylate	1.21	1.12
C ₂ O ₄ ²⁻	6.85 x 10 ⁻³	8.82 x 10 ⁻³
SO ₄ ⁼	1.36 x 10 ⁻³	4.62 x 10 ⁻³

Hydration Energy and Membrane Selectivity: Reinsfelder and Shultz (95)

showed the selectivity of nitrate liquid membrane electrodes towards anions generally decreased with increasing hydration energy. The nitrate electrodes studied were based on tris (1,10-phenanthroline) iron (II) -, tris (4,7-diphenyl-1,10-phenanthroline) iron (II) - and tetraheptylammonium nitrate ion-pairs using nitrobenzene and chloroform as membrane solvents. The selectivity order was $\text{PF}_6^- > \text{ClO}_4^- > \text{SCN}^-$, I^- , $\text{BF}_4^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^-$. This decreasing selectivity order was observed irrespective of ion-exchange site or solvent indicating that the aqueous solvation energies play a predominant role in determining selectivities to these ions. The same order of selectivity $\text{ClO}_4^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^-$, acetate, and F^- was also observed by Fogg and co-workers (51) for the Brilliant Green perchlorate liquid membrane electrode although no discussion was made as to relationship between selectivity and hydration energy of anions.

It is interesting to note that the selectivity order of the perchlorate and hydrogen phthalate electrodes towards the monovalent anions studied in this work follow the same pattern. Based on the hydrogen phthalate electrode, the selectivity order was $\text{MnO}_4^- > \text{ClO}_4^- \approx \text{IO}_4^- > \text{SCN}^- > \text{I}^- > \text{Sacc}^- > \text{Salyicylate} > \text{Z hydrogen phthalate} > \text{ClO}_e^- > \text{NO}_3^- > \text{Br}^- > \text{BrO}_e^- > \text{Cl}^- > \text{F}^-$.

Table 4.9 below shows roughly the correlation between increasing standard free energy of hydration of the anions studied and decreasing electrode selectivity.

Table 4.9

Comparison of the standard free energy of hydration of anions (ΔG_h^0) and the K_{ij}^{pot} values of the Brilliant Green hydrogen phthalate electrode (membrane solvent nitrobenzene)

Anion	G_h^0 (KCal/mol ⁻¹)(96)	$\log K_{ij}^{pot}$
ClO_4^-	-47.00	2.02
IO_4^-	-45.55	2.02
SCN^-	-60.91	0.72
I^-	-52.62	0.11
ClO_3^-	-59.62	-0.10
NO_3^-	-60.50(97)	-1.01
Br^-	-61.53	-1.42
Cl^-	-68.43	-2.33

It should also be of interest to note that selectivity is related not only to hydration energy but also to ionic radius. This has been observed by examination of the relationship between K_{ij}^{pot} and ionic radius of the halide ions (which are in the same group of the periodic Table) as shown in Table 4.10 for the Brilliant Green hydrogen phthalate electrode.

Table 4.10

Comparison of ionic radii (r_i), standard enthalpy of hydration (ΔH_h^0) and K_{ij}^{pot} of hydrogen phthalate electrode for halide ions

Anion	I^-	Br^-	Cl^-	F^-
$r_i(A^0)$ (98)	2.20	1.96	1.81	1.33
$H_h^0(KJ mol^{-1})(98)$	-305	-347	-381	-515
K_{ij}^{pot}	1.32	3.81×10^{-2}	2.7×10^{-3}	6.65×10^{-4}

The relation between selectivity coefficient & hydration energy or ionic radii can be explained as follows (99):

For the ion-exchange reaction of equation 4.2, the standard free energy change ($-\Delta G_{ij}^0$) is dependent on the partial molar free energies (μ 's) of the interactions of the species with water and the membrane site (C^+)(99).

$$\Delta G_{ij}^0 = (\mu_i - \mu_j) + (\bar{\mu}_j - \bar{\mu}_i) \quad [4.5]$$

the term $\mu_i - \mu_j$ can be calculated from the known hydration energies of ions. The term $\bar{\mu}_j - \bar{\mu}_i$ was evaluated by Eisenman (99) by using a model in which the sites (C^+), devoid of water molecules, are contained in the membrane at various separation.

The relation between free energy change and potential selectivity coefficient can be derived using the following relations: When $a_i = a_j$ the selectivity coefficient is given by equation 2.20, for monoanions, as

$$\log K_{ij}^{\text{pot}} = \frac{E_j - E_i}{S}$$

where $S = \frac{2.303RT}{F}$ and the change in free energy brought about by passage of n faradays (F) electricity, due to the reacting species in the cell, is given by

$$-\Delta G = nEF \quad [4.6]$$

Thus, E_j and E_i are given by

$$E_j = \frac{-\Delta G_j}{nF}$$

and

$$E_i = \frac{-\Delta G_i}{nF} \quad [4.7]$$

Substituting the values of E_j and E_i from equation 4.7 to equation 2.20 results

$$\log K_{ij}^{\text{pot}} = \frac{\Delta G_i - \Delta G_j}{2.303nRT} = \frac{\Delta G_{ij}}{2.303nRT} \quad [4.8]$$

However, ΔG_{ij} is dependent on hydration energies and electrostatic interaction energies, as indicated by equation 4.5 and Table 4.9. Though the information dealing about the later case was not given, hydration energy is a predominant factor (in equation 4.8) to determine potential selectivity coefficient as shown in table 4.9..

Relation Between K_{ex} , K_A and K_{ij}^{pot} : The relationship between the selectivity coefficient of the membrane electrodes to the various physicochemical parameters as derived in the theoretical equations above are summarized by Wuhrmann and his associates (72), from which it is seen that the selectivity of the membrane electrode is governed by both the mobility of the ions in the membrane and the equilibrium that exists at the membrane-solution interfaces (eg., partition coefficient, ion-exchange equilibrium constants).

Though the relative ionic mobilities, a non equilibrium factor, should be taken into account for more quantitative description, an attempt was made to relate mainly chemical factors, such as, extraction constants and association constants to the selectivity coefficients of the electrodes investigated.

From Table 4.11 and Figure 4.14 it is possible to note the relation between the competitive extraction of the ion-association salts into or their relative association in, nitrobenzene and the selectivity coefficient, though iodide shows anomaly. This correlation indicates that the extraction parameters or/and the association constant quantitatively determines the selectivity characteristics of the liquid membrane electrodes. Thus, as shown in Table 4.11 and Figure 4.14, the perchlorate ion was highly selected,

by both the perchlorate and the hydrogen phthalate electrodes, owing to its higher extractability and association constants relative to the other anions. For the other anions since they have comparative selectivity coefficient it was not possible to discuss the relation between their relative extractability or/and the association constants and their selectivity coefficients. If this work has been extended on measurements of K_A and K_{ex} , for ions having considerable difference of selectivity coefficient, the plots of $\log K_{ij}^{pot}$ vs $\log \frac{K_{ex}, C^+ j^-}{K_{ex}, C^+ i^-}$ or $\log \frac{K_A, C^+ j^-}{K_A, C^+ i^-}$ given on Figure 4.14 would be linear.

Such relations has been shown in an earlier study (32) involving various aminoacids and organic anion responsive electrodes based on tetrahexylammonium salts.

Table 4.11

Logarithmic Values of Ratio's of K_{ex} , K_A , of crystal Violet
 pot
 Salts and K_{ij} for Crystal Violet perchlorate electrodes
 (membrane solvent nitrobenzene)

Crystal Violet Salts	$\log \frac{K_{ex}, C^+ j^-}{K_{ex}, C^+ i^-}$	$\log \frac{K_A, C^+ j^-}{K_A, C^+ i^-}$	$\log K_{ij}^{pot}$
$C^+ ClO_4^-$	0	0	0
$C^+ I^-$	-1.435	-0.646	-1.790
$C^+ Sacc^-$	-0.809	-0.371	-1.818
$C^+ HP^-$	-0.974	-0.424	-1.914

The extraction constant and association constant of Crystal Violet iodide were found to be less than those of saccharin and hydrogen phthalate. The selectivity of the electrode to iodide however was higher than those of the two ions. A complete explanation of this anomaly cannot be given unless the actual values of mobilities of the ions in the liquid membranes are available.

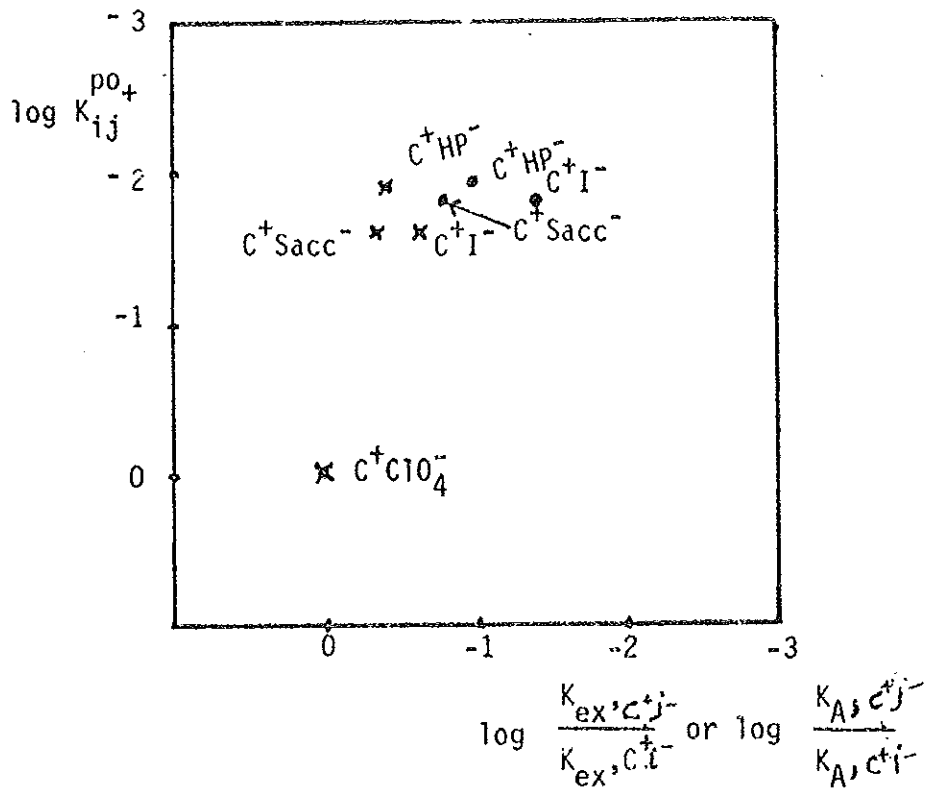


Fig. 4.14 Plots of $\log K_{ij}^{po}$, for Crystal Violet perchlorate electrode, as a function of logarithms of the extraction constant ratios (·) and association constant ratios (x) for Crystal Violet salts in nitrobenzene

4.9 The Application of the Perchlorate Electrode to the Determination of Perchlorate

The perchlorate electrode was applied for the determination of perchlorate in the aqueous samples, using the three potentiometric methods discussed in the experimental section.

In direct potentiometry, the concentration of the unknown perchlorate was determined from a calibration plot of $E(\text{mv})$ vs. $\log[C\text{ClO}_4^-]$ or by a single point calibration method, based on $C_x = C_s 10^{\Delta E/S}$, where C_x is the unknown concentration of perchlorate, C_s is a standard perchlorate solution and ΔE is the potential difference between the unknown perchlorate (E_{sample}) and the standard solutions (E_{standard}) as described by equation 2.29.

In single standard addition technique the unknown perchlorate was evaluated using equation 2.35.

Gran's plot (79) was also applied to evaluate the perchlorate concentration following the method illustrated by Liberti and Mascini (100). A plot of $(v_x + v_s) 10^{-E/S}$ ($= y$) against v_s ($= x$) gave a linear relation of the type $y = a + bx$. The straight line obtained (Fig. 4.15) intercepted the abscissa for an equivalent volume V_e of the standard where $C_x V_x = -C_s V_e$. The final concentration of the excess perchlorate was calculated by C_x $C_x = -(C_s V_e) / V_x$. The quantity V_e was more reliably calculated from $V_e = -a/b$ after evaluating the slope of Gran's plot, b , and the intercept at the y-axis, a . The data obtained from these potentiometric techniques are summarized in Table 4.12. In this table, it can be seen that Gran's plot technique has the highest recovery. Because the results are dependent on several

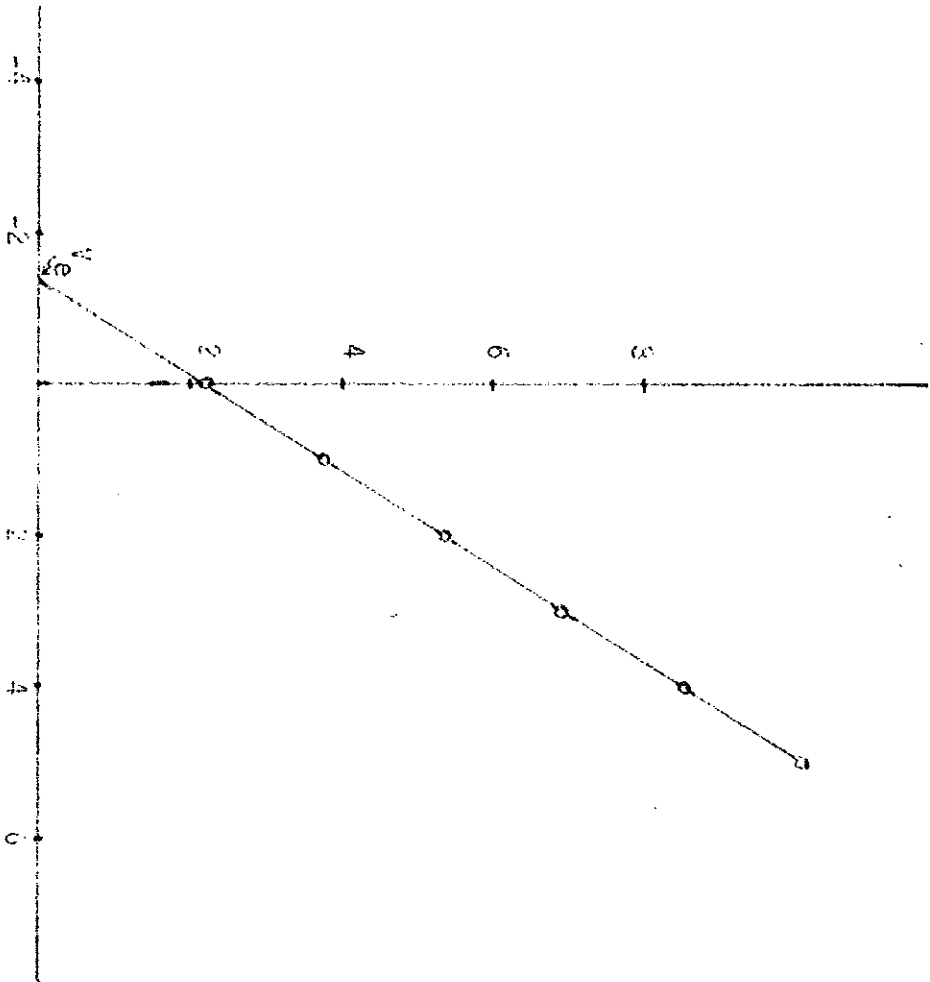


Fig. 4.15 Gran's plot, for the determination of perchlorate by multiple standard addition technique, $1.0 \times 10^{-1} M = 0.6 \times 10^{-2} M$.

readings, the effect of random errors in individual readings on the result is reduced, and the accuracy and the precision may be increased. This technique also minimizes the effects of interference which cannot be eliminated in direct determination.

The results show that the electrode can be used to determine perchlorate in aqueous samples with reasonable precision and accuracy.

Table 4.12

Determination of Perchlorate in artificial samples using the Crystal Violet perchlorate electrode

Perchlorate taken $M(\text{mgml}^{-1})$	Direct Method*			Single Standard addition Method*			Gran's Plot Method*		
	Found ₁ $M(\text{mg ml}^{-1})$	Recovery %	Standard deviation %	Found $M(\text{mgml}^{-1})$	Recovery %	Standard deviation %	Found ₁ $M(\text{mg ml}^{-1})$	Recovery %	Standard deviation %
5.74×10^{-3} (0.806)	5.65×10^{-3} (0.790)	98.4	1.02	5.67×10^{-3} (0.796)	98.9	1.30	5.69×10^{-3} (0.799)	99.1	1.65
6.66×10^{-3} (0.930)	6.42×10^{-3} (0.901)	98.0	2.40	6.45×10^{-3} (0.906)	98.5	2.10	6.50×10^{-3} (0.913)	99.2	2.20
6.62×10^{-3} (0.931)	6.50×10^{-3} (0.912)	98.2	1.70	6.63×10^{-3} (0.941)	100.2	0.90	6.58×10^{-3} (0.924)	99.4	2.10

* Average of three measurements

4 Comparison with other Liquid Membrane Electrodes

A comparative study of the designed electrodes with other electrodes for the response of perchlorate and hydrogen phthalate in reard to slope, pH and range of concentration is summarized in table 4.13.

The slopes of the perchlorate and hydrogen phthalate electrodes have values similar to other which are typical of liquid membrane lectrodes. The Nernstian response ranges are wider than most of the others. The response ranges of the perchlorate electrodes are similar to those of the commercial, Orion, plastic membrane. The pH ranges are also in close agreement.

The designed perchlorate electrodes can also be used to detect iodide, saccharin, and hydrogen phthalate anions. Perchlorate determination is possible in the presence of a ten-fold concentration of these ions as low as perchlorate concentration of $10^{-3}M$. The hydrogen phthalate electrode is also useful for the determination of perchlorate in the absence of these anions.

Table 4.13
Comparison of response of perchlorate and hydrogen phthalate
liquid membrane electrode based on different ion-exchangers

Ion-exchanger	membrane solvent/matrix	Slope, mv decade	Range of Nernstian Response(M)	pH range	Ref.
Orion-perchlorate	plastic membrane	56±2	7×10^{-6} -1		101
*NEBA-perchlorate	1,2-dichloro- benzene	59.0	1×10^{-4} -1.0	1-12	102
Brilliant Green perchlorate	Chlorobenzene	57-57.5	10^{-3} - 10^{-1}	4.7-8.0	51
Berberine- perchlorate	nitrobenzene	57.0	10^{-4} - 1.0	1-13	103
Nitro-perchlo- rate	nitrobenzene	56.0	2×10^{-5} - 10^{-2}	2.5-8.5	104

Table 4.13 Contd.

tris(1,10-phenanthroline) iron (II) perchlorate	nitrobenzene	57.0	$10^{-3.5} - 10^{-1}$	4.11	95
Crystal Violet hydrogen phthalate	nitrobenzene	58.0	$10^{-5} - 10^{-2}$	4.0	48
Brilliant Green perchlorate	nitrobenzene	56.4	$3.8 \times 10^{-6} - 10^{-1}$		This thesis
Crystal Violet perchlorate	nitrobenzene	59.0	$3.5 \times 10^{-6} - 10^{-1}$		"
Brilliant Green hydrogen phthalate	nitrobenzene	56.3	$10^{-5} - 10^{-1}$		"

* NEBA: N-Ethylbenzothiozol-2, 2-azaviolene

5. CONCLUSION

Investigations on Crystal Violet perchlorate and Brilliant Green hydrogen phthalate electrodes have shown that the liquid membrane electrodes made from the ion-association salts can be used to detect various of the anions in aqueous systems. Such electrodes could be of potential use as electrochemical detectors in liquid chromatographic systems to simultaneously characterize and equantitatively determine the ions sensed by the electrodes.

A very high selectivity of these electrodes towards perchlorate, relative to saccharin, hydrogen phthalate, and iodide which have about the same selectivity order, was found to be associated with relatively high extraction and association constants. An investigation of selectivity coefficients of the electrodes towards monovalent ions has also shown that the hydration energies of the anions have a predominant role in determining the selectivity of the electrodes.

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