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A study of a divalent cation-selective electrode

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A STUDY OF A
DIVALENT CATION-SELECTIVE
ELECTRODE

BY

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A THESIS
SUBMITTED TO THE GRADUATE FACULTY
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APPROVED:

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DEDICATION

Dedicated to my wife without whom all that follows would be as nothing.

ACKNOWLEDGMENT

With the completion of this work I wish to de express my sincerest thanks to Dr. W. Allan Powell. His personal interest and guidance in this work have been immeasurable.

I wish to thank Mr. James Day, whose expert advice and help contributed much towards the figures presented in this thesis.

Finally, I wish to express my appreciation to Mrs. Gail Clark, who so kindly consented to type this thesis.

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INTRODUCTION

The ion-selective membrane electrode, recently introduced commercially, has shown excellent promise as a tool for determining ionic activities and concentrations in solution. It was the intent of the author to study the Orion divalent cation-selective electrode with two objectives.

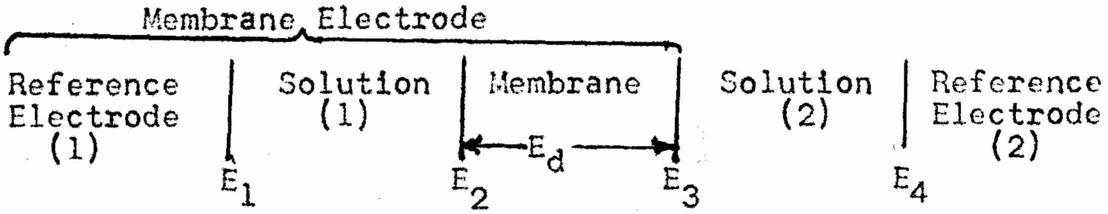
The first objective of this research was to characterize the response of the divalent cation-selective electrode to calcium and magnesium ions in aqueous solutions. The effect of anions, monovalent cations, and pH upon this response was investigated. An examination was made of the response of this electrode to other divalent cations and of the effect of organic solvents on the membrane material.

The second object was to ascertain if this electrode could be used for the quantitative determination of calcium and magnesium in the presence of high levels of sodium by the standard additions technique. A cursory examination of this electrode as an end-point detector in the titration of calcium and magnesium with disodium ethylenediaminetetraacetate and sodium fluoride was also made.

HISTORICAL

The term "membrane electrode" is applied to an electrochemical system in which a reference electrode is separated from the solution upon which a measurement is to be made by a membrane(a) that is permeable to certain ions but not others.

The galvanic cell including the membrane electrode can be represented as follows:



[1]

The emf of this cell is the sum of the phase-boundary potentials E_1, E_2, E_3, and E_4 and a diffusion potential E_d within the membrane:

$$E_{cell} = E_1 + E_2 - E_3 - E_4 + E_d \qquad [2]$$

The sum of the phase-boundary potentials at the membrane-solution interfaces(b), E_2 and E_3, and the diffusion potential, E_d, is the membrane potential, E_m:

$$E_m = E_2 - E_3 + E_d \qquad [3]$$

(a) Such a membrane is termed permselective or semipermeable.

(b) termed Donnan potentials

For an ideally permselective membrane (i.e., permeable for the ion A only) equation [3] reduces to

$$E_m = \frac{RT}{nF} \ln \frac{a_2}{a_1} \qquad [4]$$

where a_1 and a_2 are the activities of the ion A in solutions 1 and 2, respectively. RT/nF is the Nernst factor in which R is the gas constant, T the absolute temperature, F the Faraday constant, and n the charge on the ion A (54).

The emf of the galvanic cell [1] can therefore be expressed as the sum of the electrode potentials, E_1 and E_4, and the membrane potential, E_m:

$$E_{cell} = E_1 - E_4 + E_m \qquad [5]$$

which on substitution of equation [4] , becomes

$$E_{cell} = E_1 - E_4 + \frac{RT}{nF} \ln \frac{a_2}{a_1} \qquad [6]$$

or

$$E_{cell} = E_1 - E_4 - \frac{RT}{nF} \ln a_1 + \frac{RT}{nF} \ln a_2 \qquad [7]$$

There are two methods available for using a galvanic cell incorporating a membrane electrode for the determination of ionic activities. In the first method, the activity of the ion A on one side of the membrane is known, and that on the other side is calculated directly from the measured cell emf and a knowledge of the reference electrode potentials. In the second method, a solution of known constant activity of the ion A is used for solution 1, and a series of standard solutions of known but different activities of A are used for solution 2. A plot of E_{cell} vs - ln a or - log a of the standard solutions can then be used as a working curve to determine unknown activities of A directly from the measured cell emf.

In the second method, reference electrode 1 and solution 1 are inside the membrane electrode and are called the internal reference electrode and the internal reference solution, respectively, while solution 2 and reference electrode 2 are outside the membrane electrode and are called the test solution and the external reference electrode.

The working curve used in the second method is a straight line which follows the equation

$$E_{cell} = E^{o'} + \frac{RT}{nF} \ln a \qquad [8]$$

where a is the activity of the ion in the external solution and $E^{o'}$ is a constant obtained from the calibration curve and not a "standard potential" in the usual sense. Comparison of equations [7] and [8] shows that the term $E^{o'}$ is the sum of the first three terms of equation [7] and is a constant, since with the experimental design of the second method these three terms are constant. However, even with the most ideal permselective membrane, there are two possible additional sources of potential in the cell. One is a liquid junction potential that may arise if a calomel electrode is used as an external reference electrode, and the other is a membrane asymmetry potential that arises because the two surfaces of the membrane are not identical and do not behave exactly alike. These two potentials are included in the $E^{0'}$ term of equation [8] and are small enough that they may be ignored in most analytical work.

The first significant use of a membrane electrode was the development of the proton-sensitive glass electrode and its widespread adoption for the measurement of pH. The development of membrane electrodes made from materials other than glass which will respond, as does the glass electrode, to only one ionic species has been attempted for the past thirty years. Membranes studied for this purpose include reacted collodion, clay and mineral membranes, solid and liquid synthetic ion-exchange resins, precipitated-impregnated membranes, pressed-pellet membranes, and single-crystal membranes.

This report will be concerned primarily with the development and analytical utilization of membrane electrodes responsive to ions other than the proton.

I. Glass Membrane Electrodes

In 1906, Cremer (19) observed that the potential of an electrode made from a glass bulb was dependent upon the acidity of the solutions in contact with the glass. Three years later, Haber and Klemensiewicz (51) obtained acid-base titration curves similar in shape to those obtained with a hydrogen electrode and concluded that the glass electrode responded in a Nernstian manner to hydrogen ion activity.

In 1922, Hughes (62) directly compared the glass electrode with the hydrogen electrode and observed that the glass electrode potential deviated from the Nernst equation in basic solution. Dole (22) soon showed that this alkaline error was due to the glass electrode responding to cations other than H^+. In 1934, Lengyel and Blum (82) reported that the potentials of membrane electrodes made from alumino-silicate or borosilicate glasses were almost as sensitive to alkali ions as to H^+. Tendeloo (181, 191) reported constructing glass electrodes that in $CaCl_2$ or $Ca(NO_3)_2$ solutions acted as a calcium ion-sensitive electrode.

However, in the years from 1934 to 1957, little interest was taken in the possibilities of developing and using glass electrodes for the measurement of ions other than H^+. Instead, efforts were directed toward the development of a pH glass electrode with high H^+ sensitivity and low alkaline error. The studies have been well summarized by Perley (125, 126), Dole (23), and Bates (6).

In 1957, Eisenman, Rudin, and Casby (28) reported a thorough study of the electrode properties of sodium aluminosilicate glasses over a wide range of compositions. They found that all glass electrodes containing Al_2O_3 were highly sensitive to alkali ions.

As shown in Figure 1, the electrode response of 2% Al_2O_3 these Al_2O_3-containing glasses was independent of pH, except in the most acid solutions, and was determined by the alkali-metal ion concentration in neutral and basic solutions. To describe the response of these glass electrodes in a solution containing two monovalent cations, a mixture of either hydrogen ion and alkali-metal ion or two alkali-metal ions at a constant pH, Eisenman et al. (28) presented the following empirical equation

$$E = E^{o'} + \frac{RT}{nF} \ln \left[(A^+)^{1/n_{AB}} + K^{1/n_{AB}} (B^+)^{1/n_{AB}} \right]^{n_{AB}} \qquad [9]$$

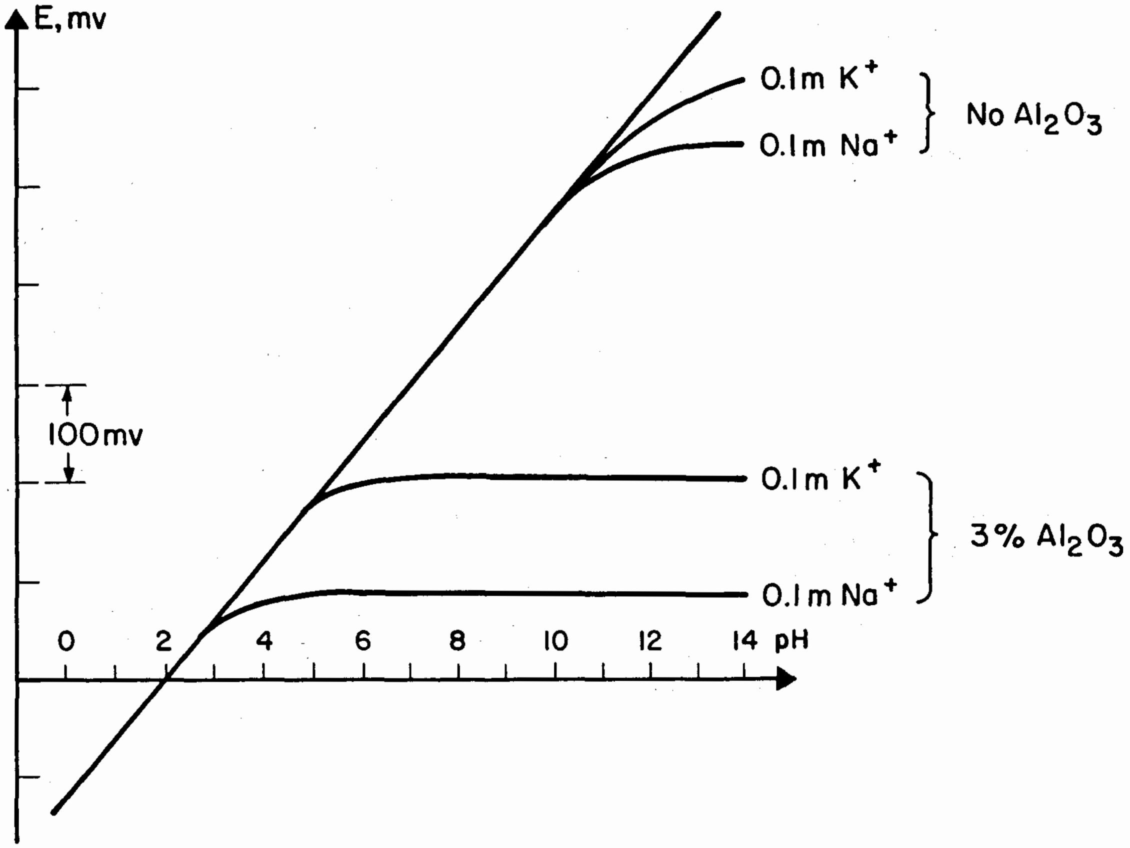


FIGURE 1

Effect of Al_2O_3 on Response of Glass Electrode where K_{AB} and n_{AB} were adjustable parameters which were constant for a given electrode and cation pair, and (A^+) and (B^+) were the activities of the ions A and B, respectively. The constant K_{AB} expressed the selectivity of the electrode for ion A relative to ion B[a]. The constant n_{AB} varied from 1 to 5.

Of equal importance was the discovery of Eisenman et al. (28) that the electrode selectivity for different cations relative to one another varied in a systematic and reproducible manner with glass composition. The discovery led them to recommend general glass compositions which had sufficiently high selectivity for Na^+ or K^+ to be of practical use as electrodes to measure Na^+ or K^+.

Eisenman's historic paper was the starting point for intense developmental studies on glass electrodes selective for particular cations. Glass electrodes useful for the measurement of Tl^+, Li^+ (106), NH_4^+ (107) and Ag^+ (16), and with improved selectivity for Na^+ (105, 130, 178) and K^+ (130), were soon reported. Other workers (35, 194) reported developing glass electrodes sensitive to the divalent alkaline-earth cations. Empirical electrode response equations analogous to that presented by Eisenman (28) for monovalent-monovalent cation systems were

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[a] Thus, if $K_{AB} = 0.01$, the electrode is 100 times more sensitive or selective to A^+ than B^+

presented by these workers for binary mixtures of divalent-divalent cations

$$E = E^{o'} + \frac{RT}{2F} \ln \left[(M^{2+})^{1/m} + K_{MN}^{1/m} (N^{2+})^{1/m} \right]^{m} \quad [10]$$

and divalent-monovalent cations

$$E = E^{o} + \frac{RT}{2F} \ln \left[(M^{2+})^{1/m} + K_{MA}^{1/m} (A^{+})^{2/m} \right]^{m} \quad [11]$$

where the parentheses indicate ionic activity, K_{MN} and K_{MA} were selectivity constants, and m was an adjustable parameter which was constant for a given electrode and cation pair.

In the early 1960's, several companies introduced commercially available monovalent cation-selective glass electrodes. These commercial glass electrodes fall into two main categories (142):

(i) sodium-selective electrodes which are generally 1000 times more sensitive to sodium than to potassium, and

(ii) cation-selective electrodes which respond to a range of monovalent cations and are generally about 30 times more sensitive to potassium than to sodium ion.

Monovalent cation-selective electrodes have found widespread use for the direct potentiometric determination of alkali ions in solution. Several workers (53, 200) determined the sodium content of high-purity boiler-feed waters in the concentration range 1 to 50 ug/liter

(4×10^{-8} to 2×10^{-6} Molar). Comparison of the electrode method with a flame photometric technique showed the latter to be faster, less precise, and more dependent on operator technique. Jacobson (68) described an AutoAnalyzer system incorporating a sodium-sensitive electrode for quality-control use in the pharmaceutical industry. Other analytical measurements reported include the determination of sodium in acidic silica sols (180) and in interstitial waters (167) as well as the determination of several organic cations by direct potentiometry (148).

Direct measurement of the NH_4^+ produced by the reaction between urea and the enzyme urease was utilized by several workers for the determination of urea (72) and urease activity (71). This reaction was ingeniously used by Guilbault and Montalvo as the basis for a urea-specific electrode (47, 48). The urease enzyme was immobilized in a layer of polyacrylamide gel on the surface of a cation-sensitive electrode. The urea diffused through the gel layer of immobilized enzyme and decomposed to ammonium ion, which was sensed by the glass electrode. These authors (110) also found that the glass electrode, when coated with the urease gel, was much more sensitive to ammonium ions than when uncoated.

The range of applications of cation-sensitive glass electrodes to biomedical research and clinical analyses has been even more extensive than to inorganic problems.

Sodium and potassium ion-sensitive electrodes have been used to directly measure ionic activities in biologic media both *in vitro* and *in vivo*. Both applications have utilized the full spectrum of electrode size from the macro to the ultramicro. This extensive body of literature has been excellently reviewed by Moore (111).

A potassium-sensitive electrode was used by Geyer and Frank (39) as an end-point detector for the potentiometric titration of potassium with calcium tetraphenylborate. This titrimetric method was applied to the determination of Cs^+, Rb^+, NH_4^+, and Ag^+ by Rechnitz et al. (143) by use of a cation-sensitive electrode. The solubilities of the alkali-metal tetraphenylborate precipitates are so sufficiently similar that mixtures of the ions were not resolved by a single titration.

Geyer et al. (38) carried out precipitation titrations of Ag^+ with chloride, iodide, and cyanide ions using an ion-sensitive glass electrode. They reported no break in the titration curve with HCl as the titrant; a small break with NaCl, KCl, and KI; and a well-defined break with $MgCl_2$ or CaI_2. When silver was titrated with CN^-, only the first break corresponding to the precipitation of AgCN was observed; a second break representing the formation of $Ag(CN)_2$ was not observed because the concentration of Ag^+ was too low for the electrode to sense. However, Gerchman and Rechnitz (37) reported that the glass electrode did indicate both end points. Mokady (109) titrated Cl^- with Ag^+ using a sodium-sensitive electrode and obtained an L-shaped titration curve.

The response of cationic glass electrodes to monovalent cations in binary mixed solvents containing organic constituents was studied by Rechnitz and co-workers (149, 153). Using ethanol, ethylene glycol, acetone, and dimethylformamide as the organic solvents, they found that the electrode response in solvent mixtures containing a low percentage of water was slightly decreased from that in pure H_2O. McClure and Reddy (92) studied the electrode response in propylene carbonate, acetonitrile, and dimethylformamide and confirmed that the response of the glass electrode was essentially solvent independent for a given concentration and type of solute.

II. Mineral Membranes

The possibility of using insoluble minerals as ion-selective membranes for electrodes was investigated by several workers. Tendeloo (182, 183, 184) reported that electrodes prepared from thin plates of fluorite could be used for the potentiometric determination of calcium concentrations in $Ca(NO_3)_2$ solutions, with and without gelatin, and in milk; but the electrode response, while linear over the concentration range 1.0 to 1×10^{-4} M, was much lower than the theoretical value. Anderson (1) claimed that Tendeloo did not prove the electrode to be calcium specific.

Marshallet al. (93, 94, 95, 96, 97, 98, 99, 100. 101, 102, 103, 104) investigated the use of zeolite and zeolite-like minerals as membranes. They found that by proper heat treatment of the membrane it was possible to prepare electrodes sensitive only to monovalent cations, others sensitive to divalent cations, and still others sensitive to both. These electrodes were valence selective in that they responded to all ions of a given valence rather than being ion selective and responding only to one ion.

III. Reacted Collodion Membranes

Sollner and Gregor (44, 45, 172, 173, 174, 175, 176) investigated electrodes incorporating a reacted collodion membrane. These membranes were prepared by casting two successive films of collodion cotton using a test-tube as a former. After most of the solvent had evaporated, the film was coagulated in water. The film was then either immersed in N NaOH to produce cation sensitivity or soaked in a basic protamine sulfate solution to produce anion sensitivity. The chemically treated collodion membrane was then dried and mounted.

In pure solutions, these membranes had theoretical electrode response to monovalent ions. However, the electrodes were valence selective rather than ion selective and were very susceptible to deterioration.

IV. Synthetic Ion-Exchange Resin Membranes

The years following 1950 saw the increasing use of synthetic ion-exchange resins as membranes for electrodes. This type of membrane can be prepared in two ways:

(i) as a homogeneous sheet consisting of only the ion-exchange resin; or

(ii) as a heterogeneous membrane in which particles or beads of the ion-exchange resin are incorporated into an inert binder which provides the required cohesion and mechanical strength.

Wyllie and Patnode (205) studied electrodes that had a theoretical response to sodium ion in pure solutions. Kressman (78) reported that the response of a potassium ion-sensitive electrode was dependent upon the associated anion although Nernstian slope was observed in all solutions. Other workers have reported electrodes sensitive to divalent cations (169) and inorganic anions (4). However, these membranes were selective to an ion valence type only and not to individual ions.

Parsons (121) studied titrations of sulfate ion with barium using both cation- and anion-sensitive membranes. Basu (5) reported obtaining L-shaped curves when he used an anion-sensitive membrane electrode for titrations of the halides with silver ions. Ijsseling and Van Dalen (63, 64, 65, 66, 67) very critically studied the theoretical and experimental aspects of the use of ion-exchange resin membrane electrodes in potentiometric titrations.

V. Multilayer Membranes

Gregor and co-workers (3, 42, 43, 163) developed the multilayer membrane electrodes. The membrane consisted of parallel monomolecular layers of alkaline-earth salts of high molecular weight organic acids. The organic acids used were stearic, hexadecyl- and octadecylsulfuric, and hexadecylorthophosphoric. The membrane was mounted between the electrolyte solutions such that the direction of ionic transport was normal to the axis of orientation of the long chain acids in the monolayers.

These electrodes were alkaline-earth cation selective only when the membrane was pressurized. In an unpressurized cell assembly, the electrodes were selective in pure solutions of alkaline-earth salts but not in mixed solutions containing appreciable amounts of alkali-metal ions.

VI. Precipitate Impregnated Membrane Electrodes

Electrode selectivity has been sought by incorporating into the membranes some insoluble salt of the ion of interest. Tendeloo and Krips (185, 186, 187, 188, 189) studied paraffin membranes incorporating calcium oxalate, a non-ionic detergent, and a gauze which supported the membrane. The electrode response to $CaCl_2$ in the concentration range 1.0 to 1×10^{-3} M was linear but less than theoretical. They reported that KCl or $MgCl_2$ interfered only at levels greater than 0.01M. Tendeloo and van der Voort (190) investigated a similar membrane incorporating calcium stearate. They found this electrode to have a stronger Ca^{2+} response and less K^+ interference than the oxalate electrode.

However, Cloos and Fripiat (18) found the calcium oxalate-paraffin electrode to be porous and non-specific. Shatkay (166) reported that a pure paraffin membrane gave the same response as the calcium oxalate-paraffin membrane, and neither worked without the gauze being present.

Fisher and Babcock (29) reported that a barium sulfate-paraffin membrane electrode was not selective to either cations or anions. Even so, the electrode was useful as an indication for titrations of sulfate with barium. Hirsch-Ayalon (56) prepared barium sulfate-cellophane membranes by placing barium hydroxide on one side of the membrane and sulfuric acid on the other. In a similar fashion, Liteanu and Mioscu (88, 89, 90) prepared membranes of barium sulfate impregnated parchment paper.

Pungor and Hollos-Rokosinyi (134) described a silver iodide-paraffin membrane electrode that had Nernstian response to Ag^+ and I^- even in the presence of high concentrations of KCl and Na_2SO_4. In subsequent work, Pungor et al. (52, 133, 139) described electrodes sensitive to Cl^-, Br^-, I^-, $SO_4{}^{2-}$, and $PO_4{}^{3-}$ made from silicone rubber membranes incorporating the insoluble salts of the ions: AgCl, AgBr, AgI, $BaSO_4$, and $BiPO_4$, respectively. The silicone rubber was used to give the membranes improved mechanical properties.

The silver halide membrane electrodes are commercially available and have been independently appraised. Rechnitz et al. (146) reported that the iodide-sensitive electrode showed a linear response to iodide ions over the concentration range 1.0 to 5 x 10^{-7} M with a slope of 56 mv/pI. The electrode response to iodide was not influenced by the nature and charge type of cation present. The electrode had good selectivity for iodide over bromide, chloride, phosphate, perchlorate, and sulfate. Titration of iodide with silver ion produced a well defined S-shaped curve. Rechnitz and Kresz (147) studied the bromide- and chloride-sensitive electrodes. They reported the AgCl membrane electrode showed Nernstian response to chloride concentrations from 1.0 to 5 x 10^{-4} M, and the AgBr electrode to bromide concentrations from 1.0 to 7 x 10^{-5} M. The response of the silver bromide membrane electrode was interfered with by iodide ion, while the response of the silver chloride membrane electrode was affected by both iodide and bromide ions. Other anions such as nitrate, perchlorate, and sulfate had negligible effect on the response of both electrodes.

Potentiometric titrations of Cl^- or Br^- with Ag^+, using the appropriate indicator electrode, yielded excellent S-shaped curves. Several workers (50, 136) reported all three silver halide membrane electrodes responded to cyanide ion. The chloride-sensitive electrode has been used to determine chloride in aqueous cheese homogenates (58) and in the chloride salts of some drugs (120).

Rechnitz et al. (152) reported a preliminary evaluation of prototype sulfate- and phosphate-sensitive electrodes. They found the sulfate electrode had an approximately theoretical response (31 mv/pSO_4) at concentrations of K_2SO_4 greater than 1×10^{-4} M. The halide ions interfered in concentration above 10^{-3} M. Although the phosphate-sensitive electrode showed poor stability with a drift of 1 mv/10 min., the titration of H_3PO_4 with NaOH yielded a two end-point titration curve with stoichiometry correctly corresponding to the neutralization of the first and second hydrogen, respectively.

In an attempt to construct a very selective phosphate electrode, Guilbault and Brignac (46) studied the electrode properties of a number of inorganic phosphates embedded in silicone rubber. The salts tried were: $AlPO_4$, $CrPO_4$, $FePO_4$, $Co_3(PO_4)_2$, $LaPO_4$, $Co(HPO_4)$, $Co(en)_3PO_4$, and $Mg_2P_2O_7$. Although the electrodes prepared were reproducible and linearly responsive to phosphate ion, they lacked selectivity and responded to all of the anions studied. This was confirmed by Buchanan and Seago (15) and Pelletier-Morazzani and Baffier (124) who found that electrodes prepared from the phosphates of cobalt, nickel, copper, and manganese impregnated in either paraffin, collodion, or silicone rubber were non-specific, responding to the total ion content.

The behavior of a sulfide electrode which consisted of silver sulfide-impregnated silicone rubber has been described by Pungor et al. (132, 135). A cyanide-sensitive electrode has also been described (137, 138).

MacDonald and Toth (91) studied the electrode properties of several insoluble fluorides embedded in silicone rubber in an attempt to develop a fluoride-selective membrane electrode. Thorium fluoride electrodes were unreproducible while both lanthanum fluoride and calcium fluoride electrodes gave fluoride-selective responses that were close to theoretical over the 10^{-2} to 10^{-4} M concentration range. The method of preparing the precipitate was important, for only those membranes incorporating a salt precipitated from solutions containing an excess of metal ion had a fluoride-selective response.

VII. Liquid Membrane Electrodes

In these electrodes, the ion-sensitive membrane is formed from a water-immiscible liquid. There are at present two types of liquid membranes: one type is based on liquid ion-exchangers; the other on macrocyclic antibiotic molecules. The liquid is held mechanically rigid by a thin porous disc of inert material.

Liquid ion-exchangers are solutions, in water-immiscible organic solvents, of compounds consisting of an ionogenic group attached to an organic molecule of sufficiently high molecular weight to make these compounds and their salt forms very sparingly soluble in aqueous electrolyte solutions (54). If the ionogenic group upon ionization produces a negatively charged salt, the membrane is cation-sensitive; if a positively charged salt, anion-sensitive.

A. Cation-Sensitive Electrodes

1. Calcium Electrode

A liquid membrane electrode sensitive to Ca^{2+} was introduced in 1966. The ion-sensitive membrane consisted of a liquid ion-exchanger formed by dissolving the calcium salt of didecylphosphate in dioctylphenylphosphonate (40, 154, 157, 204).

Ross (156) reported this electrode had a theoretical response to calcium-ion activity over the concentration range 1.0 to 1×10^{-4} M. The effect of foreign cations on the electrode potential for all ions investigated was described by the following empirical equation

$$E = E^{o'} + \frac{RT}{2F} \ln \left[A_{Ca^{2+}} + K_i A_i^{2/Z_i} \right] \qquad [12]$$

where A_i and Z_i referred to the activity and charge of the interfering ion i. Only hydrogen ion represented a serious interference. Rechnitz and Lin (151) essentially confirmed the findings of Ross, but they reported values of K_i for monovalent and divalent cations four to ten times larger. Whitfield and Leyendekkers (203) reported the electrode selectivity varied with concentration and was a function of solution composition as well as ionic strength.

Houston and Butler (59) investigated the behavior of the calcium electrode in concentrated solutions. They found that the most accurate measurement of calcium was obtained when the internal reference solution was similar in concentration to the test solution. The internal reference solution was varied from 0.10 to 2.89 M with no effect on the electrode activity slope. The authors obtained theoretical response in 5 and 6 M solutions of $CaCl_2$.

Mukherji et al. (76, 112) described the titration of calcium with di-sodium EDTA at a pH of 10. Beyond the end-point the potential rose slightly due to the response of the electrode to the sodium ions added with the EDTA. Precision and accuracy were improved by the presence of alkali cations. Divalent cations, which reacted with the EDTA, and anions, which reacted with the calcium, interfered with the titration. Glauser et al. (41) reported evidence of a Ca_2 EDTA complex in a similar titration. Successful automated titrations of calcium with EDTA were reported by Tackett (179).

Ruzicka and Tjell (161) described an AutoAnalyzer system incorporating this electrode for use in clinical analyses of serum. Other workers reported successful calcium determinations by direct potentiometry in milk and dairy products (77), beer (115), and sea water (193).

2. Divalent Cation Electrode

The divalent cation-selective electrode was primarily designed for the measurement of water hardness and the determination of calcium and magnesium.

Thompson (192) used this electrode for the direct potentiometric measurement of magnesium ion in sea water. The electrode was calibrated with synthetic sea water solutions that contained the competing ions present and varied only the concentration of magnesium ion. Garvin (36) used the same method to determine Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} in cell suspensions. Fleet and Rechnitz (30) used this electrode in flowing systems to monitor the magnesium- and beryllium-ion activities.

3. Cupric and Lead Electrodes

Liquid membrane electrodes sensitive to Cu^{2+} and Pb^{2+} were commercially introduced in 1967. The ion-sensitive membrane consisted of a liquid ion-exchanger formed by dissolving the metal salt of a high molecular weight S-alkylthioglycolic acid in a 50:50 mixture of n-decanol and dichlorobenzene (158).

Rechnitz and Lin (150) reported the cupric ion-selective electrode had a Nernstian response to cupric-ion activity over the 10^{-2} to 10^{-5} molar range in aqueous solutions of pH 3.5 to 6.5. The anions, Cl^-, Br^-, ClO_4^-, and $C_2O_4^{2-}$, were found to interfere with the operation of the electrode. The authors postulated that the interference was due to the formation of copper compounds which were soluble in the liquid ion-exchanger.

The lead ion-sensitive electrode was claimed to have a linear response to lead-ion concentration over the 2×10^{-2} to 1×10^{-5} molar range (117).

The manufacturer stopped selling these two electrodes in 1968.

4. Potassium Electrodes

Attempting to develop a highly selective potassium electrode, Pioda et al. (127, 128) studied the electrode properties of liquid membranes formed by dissolving macrocyclic antibiotics in hydrophobic organic solvents. The antibiotics used were monactin, nonactin, and valinomycin. These three were chosen because they formed complexes with alkali-metal ions having formation constants which were considerably larger for potassium than for sodium ions. They found that a membrane consisting of an 0.009 M solution of valinomycin in diphenyl ether was highly potassium selective. The membrane electrode had a linear response to potassium ion activity over the range 1 x 10^{-1} to 1 x 10^{-6} M, with a selectivity for K^+ over Na^+ and H^+ of 4000:1 and 20,000:1, respectively.

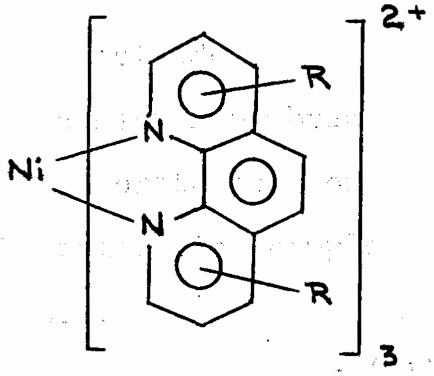
Frant and Ross (34) studied potassium selective electrodes with valinomycin-organic solvent membranes. They reported that their electrodes had an approximately theoretical response to potassium-ion activity over the concentration range 1 x 10^{-1} to 1 x 10^{-6} M. The selectivities for K^+ over NH_4^+, H^+, Na^+, and Ca^{2+} were 50:1, 100:1, 13,000:1, and greater than 5000:1.

The potassium ion-selective electrode of Frant and Ross is commercially available and has been independently appraised. Lal and Christian (80) reported a linear response to potassium-ion activity over the range 1 x 10^{-1} to 1 x 10^{-4} M. In pure potassium salt solutions, the shape was less than theoretical and was dependent upon the anion present. The selectivity for K^+ over Na^+ varied ten thousand fold as a function of sodium ion concentration. The tetraphenylborate ion affected the electrode response, thus limiting its use in potentiometric titrations of potassium with sodium tetraphenylboron.

B. Anion-Sensitive Electrodes

1. Nitrate Electrode

The membrane of this electrode consisted of a liquid ion-exchanger formed by dissolving the nitrate salt of the cationic nickel complex of a high molecular weight orthophenanthroline ligand



R = alkyl or aryl

in a nitrated aromatic liquid such as p-nitrocymene (155).

Potterton and Shults (131) reported the electrode responded in an approximately Nernstian manner to nitrate-ion activity over the concentration range 10^{-1} to $10^{-4.5}$ M at a pH between 4 and 9. The anions NO_2^-, Cl^-, EDTA, and F^- interfered with the electrode response to NO_3^-.

Paul and Carlson (122) used the electrode for the direct determination of nitrate in aqueous extracts of dried plant tissues. Aluminum resin added during extraction eliminated bicarbonate interference and reduced organic anion interference. Chloride, if present in high levels, was removed by adding silver resin. Other workers reported similar direct nitrate measurements in water (74), soil slurries (14), and soil extracts (114).

The direct titration of nitrate with diphenylthallium (III) sulfate was described by DiGregorio and Morris (21). The response of the electrode to the sulfate ion from the titrant distorted the titration curves.

2. Perchlorate Electrode

The liquid-ion exchanger membrane of this electrode consisted of the perchlorate salt of a positively charged iron (II) orthophenanthroline complex dissolved in an aromatic solvent (155).

In a study by Hseu and Rechnitz (61), this electrode was shown to have a Nernstian reponse to perchlorate-ion activity over the 10^{-1} to $10^{-3.5}$ molar range in aqueous solutions of pH 4 to 11. The electrode had good selectivity for perchlorate ion over common univalent anions such as nitrate, acetate, bicarbonate, and the halides. Baczuk and DuBois (2) reported finding that the electrode responded linearly to permanganate, periodate, and dichromate ions over approximately the same concentration range as perchlorate. A similar response to perrhenate and thiocyanate ions and a very high sensitivity to anionic mercury (II) halide complexes were observed by Hirsch and Portock (55).

Baczuk and DuBois (2) used the electrode as an end-point detector for the potentiometric precipitation titration of perchlorate with tetraphenylarsonium chloride. Extremely large amounts of several univalent anions distorted the titration curve by decreasing both the magnitude and the slope of the end-point break. Smith and Manahan (171) improved the titration method by working at 2°C. The lower temperature decreased the solubility of the precipitate and sharpened the titration curves, thus resulting in greater accuracy and lower limits of detection.

3. Tetrafluoroborate Electrode

Carlson and Paul (17) converted a nitrate ion-selective electrode to one selective for tetrafluoroborate. They extracted the liquid ion-exchanger with a solution of boric and hydrofluoric acids, thereby converting the nitrate salt to the tetrafluoroborate form. The electrode responded linearly to BF_4^- ion over three decades of concentration in the pH range 3 to 11. The interference from several anions was estimated, with nitrate and iodide being the greatest.

A potentiometric method for the determination of boron in waters, soil, and ashed plant tissues was developed by Carlson and Paul (17). Boron was removed from the aqueous extraction solution by passage through a boron-specific ion-exchange resin column. The boron absorbed on the resin reacted with hydrofluoric acid to form tetrafluoroborate which was then eluted with NaOH. The tetrafluoroborate content of the eluate was directly measured by the ion-selective electrode.

Smith and Manahan (171) used the electrode to monitor the titration of tetrafluoroborate with tetraphenylarsonium chloride. Comparing titrations at 25°C and 2°C, they found that the decreased solubility of the precipitate at the lower temperatures improved the accuracy of the titration.

4. Chloride Electrode

Lee (81) described a method for the continuous measurement of hydrogen chloride levels in gas and aerosol samples. The gaseous sample was drawn through a scrubbing tower where the HCl was absorbed in a stream of water. The resulting solution then flowed to a detector cell when the chloride-ion concentration was measured by the electrode.

VIII. Solid-State Membrane Electrodes

These electrodes utilize insoluble inorganic salts in either single-crystal or pressed-pellet form as the ion-sensing membrane.

A. Anion-Sensitive Electrode

1. Fluoride Electrode

In 1966, Frant and Ross (32) announced a fluoride ion-selective electrode. The membrane was a single crystal of europium (II)-doped lanthanum (III) fluoride. The electrode had Nernstian response to fluoride-ion activity over the 10^{-1} to 10^{-6} molar range in solutions of pH 4 to 9. The common anions Cl^-, NO_3^-, and SO_4^{2-} did not interfere with the electrode response to fluoride activity.

The unusual selectivity of this electrode has been studied and confirmed by a number of workers. Mesmer (108) and Warner (198) examined in detail the interference of chloride ion. Electrode response to fluoride down to 2×10^{-7} M was Nernstian in the presence of 1 M sodium chloride. Srinivasan and Rechnitz (177) studied the behavior of the electrode in acidic solutions of pH 1 to 3. They reported theoretical response to free fluoride ion and no response to any protonated fluoride species (i.e. HF_2^-). Similar results were observed by Baumann (8), who reported that the electrode response to sodium fluoride was the same in 1, 5 and 10 M phosphoric acid as in water alone. Bock and Strecker (12) reported small, negligible potential shifts resulted from the addition of large concentrations of the non-ionic compounds, glucose, urea, and hydrogen peroxide, to 10^{-3} sodium fluoride solutions. Thus, extensive studies have proved the lanthanum fluoride membrane electrode truly specific in its response to fluoride ion.

Lingane (86, 87) studied the electrode for end-point detection in titrations of fluoride with thorium (IV), lanthanum (III), and calcium. In neutral, unbuffered solutions, lanthanum was found to be the best of the three titrants. Although titrations with thorium produced the greatest overall change in cell emf, the slope of the titration curve in the vicinity of the equivalence point was less than with lanthanum, while calcium showed no inflection at all. In addition, the equivalence point potential was independent of the amount of fluoride when titrated with lanthanum but varied considerably in the thorium titration. Use of an acetate buffer for pH control resulted in increased fluoride ion concentrations after the equivalence point. Lingane further reported that titrations in 60 to 70 volume percent ethanol solutions produced a considerable improvement in the titration curves. The solubility product of all three metal fluoride precipitates was decreased to such an extent that the titrations were quite successful; however, the lanthanum titrations were still the best.

Other workers have used the electrode to monitor titrations with fluoride as the titrant. Baumann (7) utilized the insolubility of lithium fluoride in ethanol as the basis for a very accurate and precise titration of lithium. A similar nonaqueous titration of aluminum with fluoride has also been reported (9). Jaselskis and Bandemer (69) determined aluminum by titration with fluoride to a fixed cell emf. The unknown concentration of Al^{3+} was directly read from a linear plot of the millimoles of fluoride used to reach the same emf vs. millimoles of aluminum. Fluoride has been determined in a wide variety of samples by either direct or titrimetric methods. The high selectivity of the electrode for fluoride ion has eliminated the separations by either distillation or anion exchange that were so difficult in the earlier methods.

Frant and Ross (33) described a method for the determination of fluoride in public water supplies. This technique was based on a 1:1 dilution of both standards and samples with a high ionic strength buffered complexing solution. This total ionic strength buffer (TISAB) solution, which contained glacial acetic acid, sodium chloride, and sodium citrate with its pH adjusted to 5 by sodium hydroxide, performed three functions:

(i) the total ionic strength was fixed by the high level of ions in the TISAB;

(ii) the solutions were buffered in a pH range which avoided interference from hydroxide ion; and

(iii) Fe^{3+} and Al^{3+} were complexed by citrate, thus displacing any bound fluoride.

This method eliminated virtually all of the effects due to the background variation of water supplies and made possible the use of a single calibration curve for a wide range of water samples. The TISAB method has been extended to fluoride determinations in sea water (199) and urine (195).

Baumann (8) determined trace amounts of fluoride in highly acid solutions by a standard additions method. Liberti and Mascini (83) determined fluoride in synthetic samples by the use of Gran's Plots. The technique was essentially a series of known additions but did not work well in the presence of large excesses of complexing agents. Durst (25) described a technique for the measurement of fluoride by analate addition. The inverse of the standard additions method, analate additions, calculated the unknown concentration from the measured change in potential produced by addition of an aliquot of the analate to a standard solution of known concentration.

Analytical methods that employed drastic pretreatments such as fusion or decomposition of the sample have been described for the determination of fluoride in metal alloys (140, 141), metal oxides (129), mineral and rocks (27, 49, 197, 201), and in bone (168). Fluoride has been determined in organic compounds after a hot flask combustion of the material (31, 84, 123, 165).

Durst and Taylor (26) described modification of the fluoride electrode to permit measurements in volumes as small as 50 microliters. In a subsequent paper (24), Durst described a fluoride microelectrode that could be used in a 2 microliters sample volume.

2. Sulfide Electrode

The ion-sensitive membrane of this electrode consisted of a pressed pellet of silver sulfide. Several workers (60, 85) have evaluated this electrode. They reported

Nernstian response to silver ion over the range from 10^{-1} to 10^{-4} M and to sulfide ion from 10^{-2} to 10^{-7} M. The effect of a number of ions was found to be negligible: the anions Cl^-, Br^-, I^-, SCN^-, CrO_4^{2-}, NO_3^-, $C_2O_4^{2-}$, and SO_4^{2-} did not affect the response to sulfide, and Hg^{2+} was the only cationic interference.

Hseu and Rechnitz (60) reported the electrode worked well as an indicator electrode in potentiometric titrations of either sulfide or silver. Light and Swartz (85) compared the silver sulfide membrane electrode with a classical $Ag\text{-}Ag_2S$ electrode of the second kind and found the former to be superior. Several workers (70, 79) have used the electrode to monitor argentometric titrations of halide ions.

Muller et al. (113) used the electrode to determine silver in the range of 50 parts per billion (5×10^{-7} M) by the standard additions method.

3. Halide Electrodes

Electrodes sensitive to chloride, bromide, and iodide ions used a mixture of silver sulfide and the respective silver halide in pressed pellet form as the ion-sensing membrane (116).

Katz and Mukherji (70) reported that potentiometric titrations of single halide solutions with silver using the appropriate indicator electrode were accurate when the halide concentration was greater than 10^{-3} M. Each of the electrodes was used to monitor the argentometric titration of teriary halide mixtures. Only the iodide electrode showed three distinct end-points with the order of precipitation: iodide, bromide, chloride.

Van Loon (196) described a method for the determination of chloride in minerals. Bromide and iodide interference was eliminated by reaction with chromic acid.

B. Cation-Sensitive Electrodes

Commercially available electrodes sensitive to cupric, lead, and cadmium ions used a mixture of silver sulfide and the respective divalent-metal sulfide in pressed-pellet form as the ion-sensing membrane.

1. Cupric Electrode

The solid-state membrane cupric-ion electrode was evaluated by Rechnitz and Kenny (144). They reported the electrode response to cupric ion was Nernstian over the concentration range from 10^{-1} to 10^{-6} M in water and from 10^{-1} to 10^{-4} M in binary aqueous-nonaqueous solutions of methanol, acetone, and acetonitrile. The electrode was effectively used for the complexometric titration of cupric ion with several ligands in methanol, acetone, and acetonitrile.

Several workers (10, 160) reported that the solid-state copper electrode could be used for the complexometric titration of non-electrode metal ions. In these titrations, copper (II)-ligand complex was added prior to titration to serve as an indicator and the copper electrode was the end-point detector. Using this technique, metal ions such as zirconium (IV), iron (III), thorium (IV), samarium (III), and lanthanum (III) were potentiometrically titrated. Indicator titrations of calcium were superior to titrations that used the liquid membrane calcium-selective electrodes as end-point detectors. The former titration went to lower calcium levels, and there was no sodium interference.

2. Lead Electrode

Rechnitz and Kenny (145) reported the response of this solid-state membrane electrode to lead ion was approximately Nernstian over the concentration range 10^{-1} to 10^{-5} M in water and binary aqueous-organic solutions of methanol, dimethylsulfoxide, 1, 4-dioxane, and acetonitrile. The electrode had excellent selectivity for Pb^{2+} over divalent cations such as nickel, manganese, zinc, and magnesium; the selectivities varied with concentration and solvent system. The electrode effectively monitored the complexometric titrations of lead ion with several ligands in aqueous, 50% acetonitrile, and 50% dimethylsulfoxide solutions.

Ross and Frant (159) used this electrode for the direct potentiometric titration of sulfate with lead perchlorate. The titrations were performed in a 50 volume percent dioxane solution in order to decrease the solubility of the $PbSO_4$ precipitate and increase the potential change at the end-point.

In this solvent system, the minimum titratable sulfate concentration was 5 x 10^{-5} M. Chloride, nitrate, and bicarbonate in greater than ten-fold excess interfered by forming mixed precipitates such as $Pb_2(NO_3)_2SO_4$ and, in addition, tended to decrease the end-point potential break because of complex formation with Pb^{2+}. Selig (164) adapted this titrimetric method to the micro- and semimicro-analysis of sulfur in organic compounds after oxygen-flask combustion..

3. Cadmium Electrode

Brand et al. (13) reported this electrode had approximately Nernstian response to cadmium ion in the concentration range 10^{-1} to below 10^{-6} M in pure and mixed solutions of water and dimethylsulfoxide. The electrode had very good selectivity for cadmium over cations such as zinc, cobalt, nickel, magnesium, calcium, and the alkali metals; however, Mn^{2+}, Pb^{2+}, Tl^{+}, and Fe^{2+} did interfere with electrode response in an unexplained manner. The authors found the electrode had a linear response to aluminum-ion activity over the concentration range 10^{-2} to 10^{-5} M. Surprisingly, the reported Nernst factor of 28.4 mv was much more nearly equal to that corresponding to n = 2 (29.2 mv) rather than n = 3 (19.7 mv). The electrode proved satisfactory for detecting the end-point in titrations of cadmium with EDTA and oxine in aqueous and nonaqueous solutions.

EXPERIMENTAL

I. Reagents

All chemicals used were of reagent or equivalent grade.

All water used was first passed through a Barnstead Bantam Demineralizer, then distilled from an alkaline potassium permanganate solution.

II. Apparatus

Research pH meter, Model 101900; Beckman Instruments, Incorporated.

This instrument is essentially a line-operated electronic null-balance potentiometer. It incorporates a solid-state amplifier with a range of -1400 to + 1400 millivolts. The readout is graduated in increments of 0.2 mv and can be easily read to the nearest 0.1 mv. Incorporated into the input circuit is a standard cell which is used as a secondary input to calibrate the readout. This gives a relative accuracy of ± 0.3 mv over the entire millivolt range (11).

Ionalyzer® Divalent-Cation Electrode, Model 92-32; Orion Research, Incorporated.

This electrode is supplied in a kit which contains the electrode body, a box of porous membranes, one vial each of liquid ion-exchanger and internal reference solution, as well as the equipment required for electrode assembly (118).

Ionalyzer® Single Junction Reference Electrode, Model 90-01; Orion Research, Incorporated.

This electrode, when filled with the Orion 90-00-01 filling solution, is claimed to exhibit potential characteristics similar to those of a saturated calomel electrode (119).

Electrode Holder, Model 92-00-01; Orion Research, Incorporated. This holder will hold an Orion liquid membrane electrode and two other electrodes at an angle of 20° with respect to the vertical. The ion-sensitive electrode was mounted at this angle to prevent air bubbles from being trapped under its slightly concave bottom surface (118).

Sargent Thermonitor® Controlled Constant Temperature Bath, Catalogue Number S-84810; E. H. Sargent and Company. The temperature of this bath is regulated by a controller whose actuation is determined by a glass bead thermistor immersed in the bath liquid and connected as one arm of an A.C. Wheatstone bridge in the controller. Heat input to the bath is continuously adjusted in accordance with the direction and magnitude of the deviations of bath temperature. Once properly set, a given temperature will be maintained at ± 0.01°C (162). In the present work, the bath was filled with Fisher Inhibited Bath-oil, Catalogue No. 0-5, and the temperature was set at 30.00°C.

The remainder of the equipment used was common laboratory equipment.

III. Assembly of the Divalent-Cation Electrode

An exploded view and cross-section are shown in Figures 2 and 3, respectively.

Prior to filling, the electrode body, bottom cap, and membrane spacer assembly are rinsed with petroleum ether and allowed to air dry completely. Using the plastic tweezers provided, a porous membrane, shiny side up, is placed exactly in the center of the membrane spacer assembly. Taking care not to alter the membrane alignment by jarring the electrode, the bottom cap is replaced and screwed on until finger tight. Using the glass syringe provided, liquid ion-exchanger is introduced into the appropriate filling hole. As the membrane absorbs the liquid ion-exchanger, it becomes translucent. The internal reference solution is introduced into the center filling hole with the syringe provided. It is essential that no air bubbles be entrapped in the internal reference solution chamber. The top cap is replaced and screwed on finger tight (118). Once assembled, the electrode was allowed to stand a minimum of one hour, usually overnight, before any measurements were made.

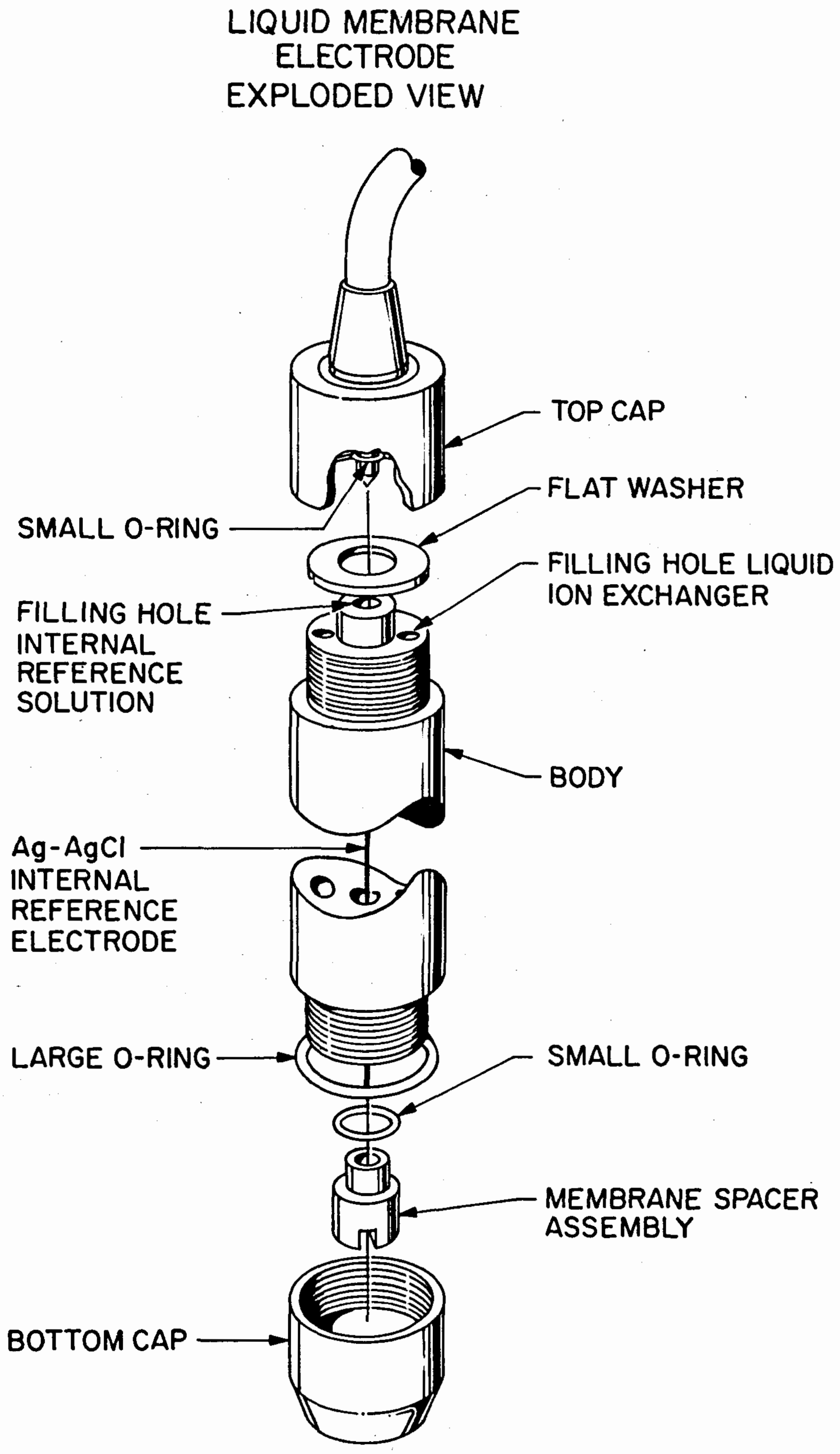

LIQUID MEMBRANE ELECTRODE EXPLODED VIEW
TOP CAP
FLAT WASHER
SMALL O-RING
FILLING HOLE LIQUID ION EXCHANGER
FILLING HOLE INTERNAL REFERENCE SOLUTION
BODY
Ag-AgCl INTERNAL REFERENCE ELECTRODE
LARGE O-RING
SMALL O-RING
MEMBRANE SPACER ASSEMBLY
BOTTOM CAP

FIGURE 2

LIQUID MEMBRANE ELECTRODE CROSS SECTION

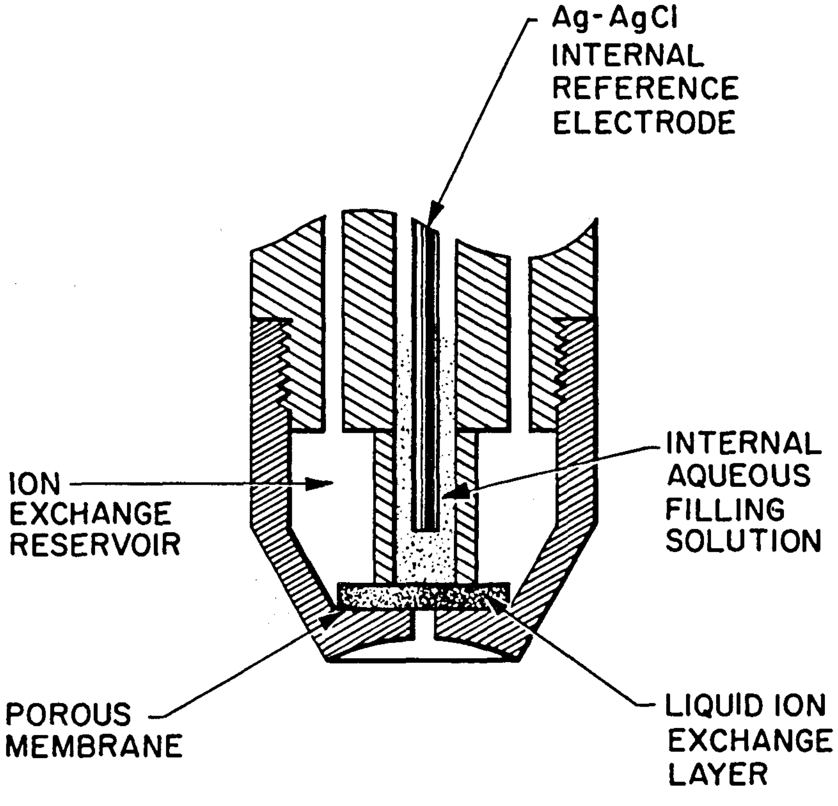


FIGURE 3

IV. The Electrochemical Cell

The electrochemical cell consisted of the Orion divalent cation-selective electrode and the Orion reference electrode. All potentiometric measurements were made with the Beckman research model pH meter. A constant test solution temperature of 30.00°C was maintained by immersion of the cell in the Sargent thermonitor controlled constant temperature bath. The test solutions were stirred constantly by means of a Teflon-coated magnetic stirring bar. The pH of the test solutions was measured with a conventional pH glass electrode.

V. Characterization of the Electrode

The initial efforts of this research were centered on evaluation of the response and selectivity characteristics of the divalent cation-selective electrode as a function of solution composition.

A. Response to Calcium and Magnesium

1. In Pure Solutions Containing Calcium and Magnesium

Stock solutions of the acetate, chloride and nitrate salts of calcium and magnesium were prepared as follows:

$Ca(C_2H_3O_2)_2$ - A 0.6 M solution was made by dissolving 105 grams of the monohydrate in distilled, deionized water and diluting to one liter.

$CaCl_2$ - A 1.5 M solution was made by dissolving 220 grams of the dihydrated salt in distilled, deionized water and diluting to one liter. The solution was filtered through glass wool to remove any undissolved solids.

$Ca(NO_3)_2$ - A 1.5 M solution was made by dissolving 360 grams of the hexahydrate in distilled, deionized water and diluting to one liter.

$Mg(C_2H_3O_2)_2$ - A 1.5 M solution was made by dissolving 320 grams of the tetrahydrate in distilled, deionized water and diluting to one liter.

$MgCl_2$ - A 1.5 M solution was made by dissolving 310 grams of the hexahydrate in distilled, deionized water and diluting to one liter.

$Mg(NO_3)_2$ - A 1.5 M solution was made by dissolving 380 grams of the hexahydrate in distilled, deionized water and diluting to one liter.

The calcium solutions were analyzed by complexometric titration with standardized disodium ethylenediaminetetraacetate (Na_2H_2EDTA) using calcein as the indicator (20). The magnesium solutions were similarly titrated using Eriochrome Black T as the indicator (202). These stock solutions were stored in polyethylene reagent bottles to minimize contamination and concentration changes.

The calcium and magnesium response of the divalent cation-selective electrode was determined by measurement of the emf of the cell

$$\text{Divalent Cation Electrode} \; \Big| \; \text{Test Solution} \; \Big| \; \text{Reference Electrode} \qquad [13]$$

in a series of standard solutions. The standard solutions were prepared by dilution of the appropriate stock solutions and covered the concentration range 1×10^{-6} to 1.0 M. The pH of the standard solutions was adjusted to 7.0 by the addition of small increments of dilute HCl or NaOH.

The response of this electrode as a function of calcium-ion or magnesium-ion concentration is shown in Figures 4 and 5. The electrode concentration response curves were not linear over the entire range of concentrations studied; curvature was observed at high and low concentrations. However, between these two extremes, the concentration response was linear. By regression analysis, the data in this linear region was fitted to the Nernst-like equation

$$E = E_c^o + S_c \log \left[M^{2+}\right] \qquad [14]$$

where E = measured cell emf

E_c^o = concentration-response constant

FIGURE 4

Electrode Response as a Function
of Calcium Ion Concentration

⊙——⊙ Calcium Chloride
⊡----⊡ Calcium Nitrate
△—·—△ Calcium Acetate

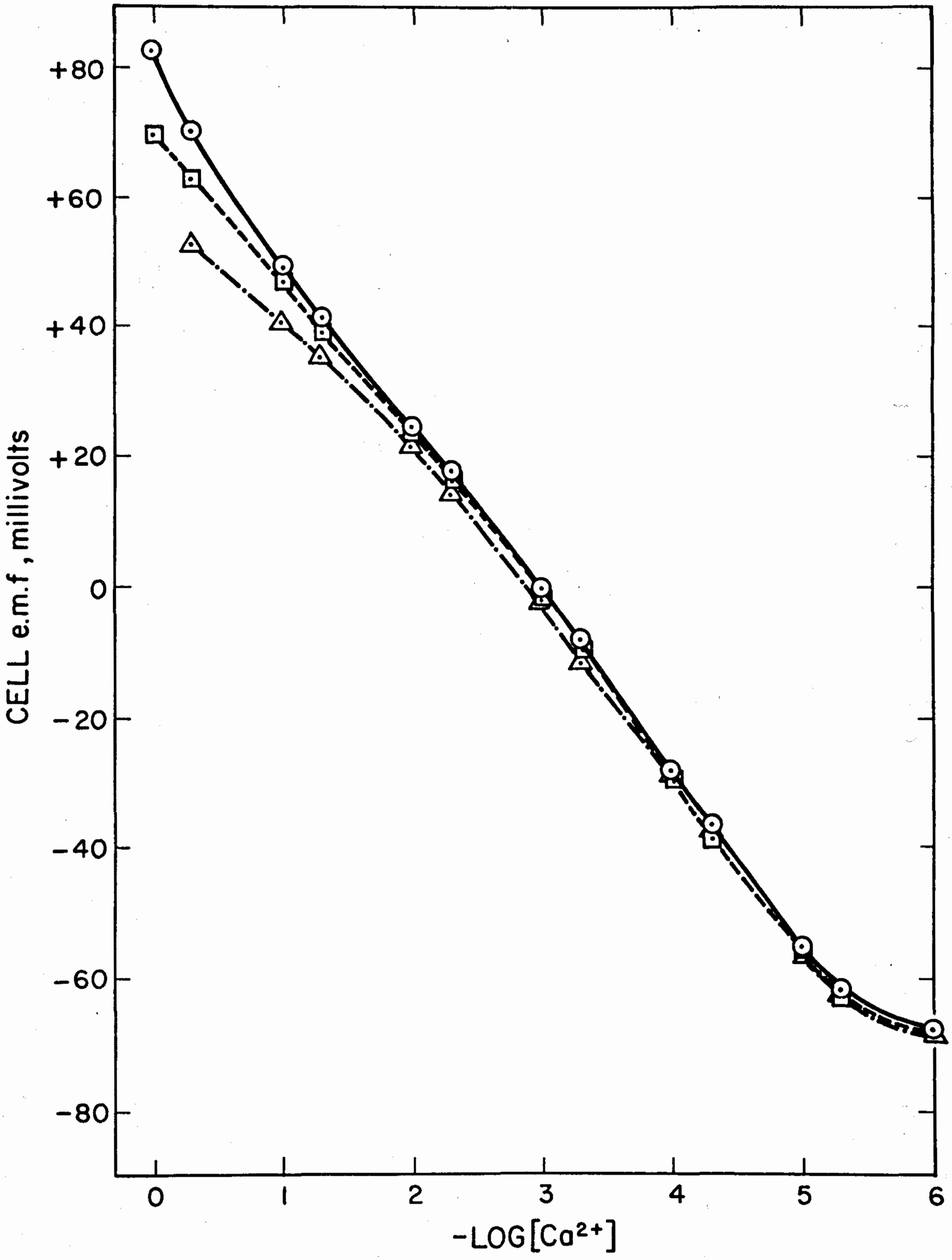
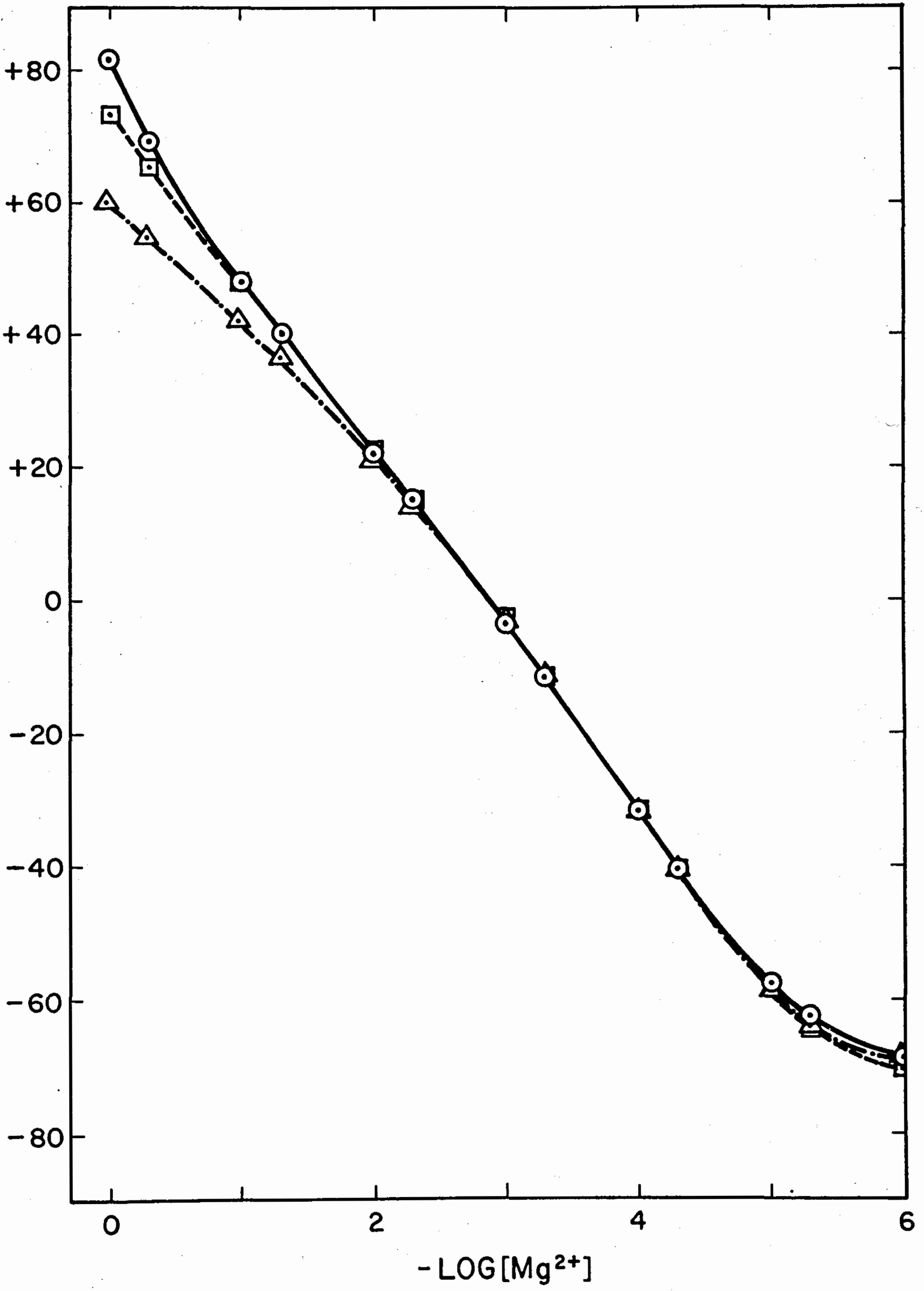

+80
+60
+40
+20
0
-20
-40
-60
-80
CELL e.m.f , millivolts
0
1
2
3
4
5
6
-LOG[Ca2+]

FIGURE 5

Electrode Response as a Function
of Magnesium Ion Concentration

⊙——⊙ Magnesium Chloride
⊡----⊡ Magnesium Nitrate
△—·—△ Magnesium Acetate


+80
+60
+40
+20
0
-20
-40
-60
-80
0
2
4
6
- LOG [Mg2+]

S_c = concentration-response slope

$[M^{2+}]$ = concentration of divalent cation

The results are summarized in Table I.

Table 1

Electrode Response to Calcium and Magnesium

Results of Regression Analysis

Salt Solution	Concentration Range of Linear Electrode Response	E_c^o mV	S_c mv/pM
$CaCl_2$	$5 \times 10^{-1} - 5 \times 10^{-6}$ M	77.1	26.3
$Ca(NO_3)_2$	$1 \times 10^{-1} - 5 \times 10^{-6}$ M	75.0	26.0
$Ca(Ac)_2$	$1 \times 10^{-2} - 5 \times 10^{-6}$ M	71.7	25.4
$MgCl_2$	$5 \times 10^{-1} - 5 \times 10^{-6}$ M	76.3	26.8
$Mg(NO_3)_2$	$5 \times 10^{-1} - 5 \times 10^{-6}$ M	74.6	26.3
$Mg(Ac)_2$	$1 \times 10^{-2} - 5 \times 10^{-6}$ M	75.6	26.6

As expected, the concentration range of the linear response and the terms E_c^o and S_c were dependent upon the anion associated with the alkaline-earth cation. The anion effect was especially pronounced with the acetate ion at higher concentrations. This effect was probably due to increased ionic interaction between the alkaline-earth cation and the acetate anion.

Plots of cell emf versus calcium-ion or magnesium-ion activity are shown in Figures 6 and 7, respectively. For the solutions of $CaCl_2$, $Ca(NO_3)_2$, $Ca(C_2H_3O_2)_2$ and $MgCl_2$, ionic concentrations in the range 10^{-1} to 10^{-3} M were converted to activities using activity coefficients from the literature (118). In solutions less concentrated than 1×10^{-3} M, values of cell emf measured in the alkaline-earth chloride solution and activities calculated by the values of Kielland (75) were used. The divalent cation-selective electrode had linear response to calcium-ion and magnesium-ion activity in the concentration range 1×10^{-1} to 1×10^{-5} M. A regression analysis to fit the data in this region to the Nernst equation

$$E = E_a^o + S_a \log \quad a_2 \qquad [15]$$

where E_a^o = activity-response constant
S_a = activity-response slope
a_2 = activity of divalent cation

gave

$$E = 93.1 + 30.0 \log (a_{Ca^{2+}}) \qquad [16]$$

for the calcium-ion activity response curve (correlation coefficient r = 0.9993) and

$$E = 90.6 + 30.1 \log (a_{Mg^{2+}}) \qquad [17]$$

for the magnesium-ion activity response curve (correlation

FIGURE 6

Electrode Response as a Function of Calcium Ion Activity

⊙ $CaCl_2$	Activity Coefficients Taken From Literature
⊡ $Ca(NO_3)_2$	
△ $Ca(Ac)_2$	
◉ $CaCl_2$	Activity Coefficients Calculated From Theory

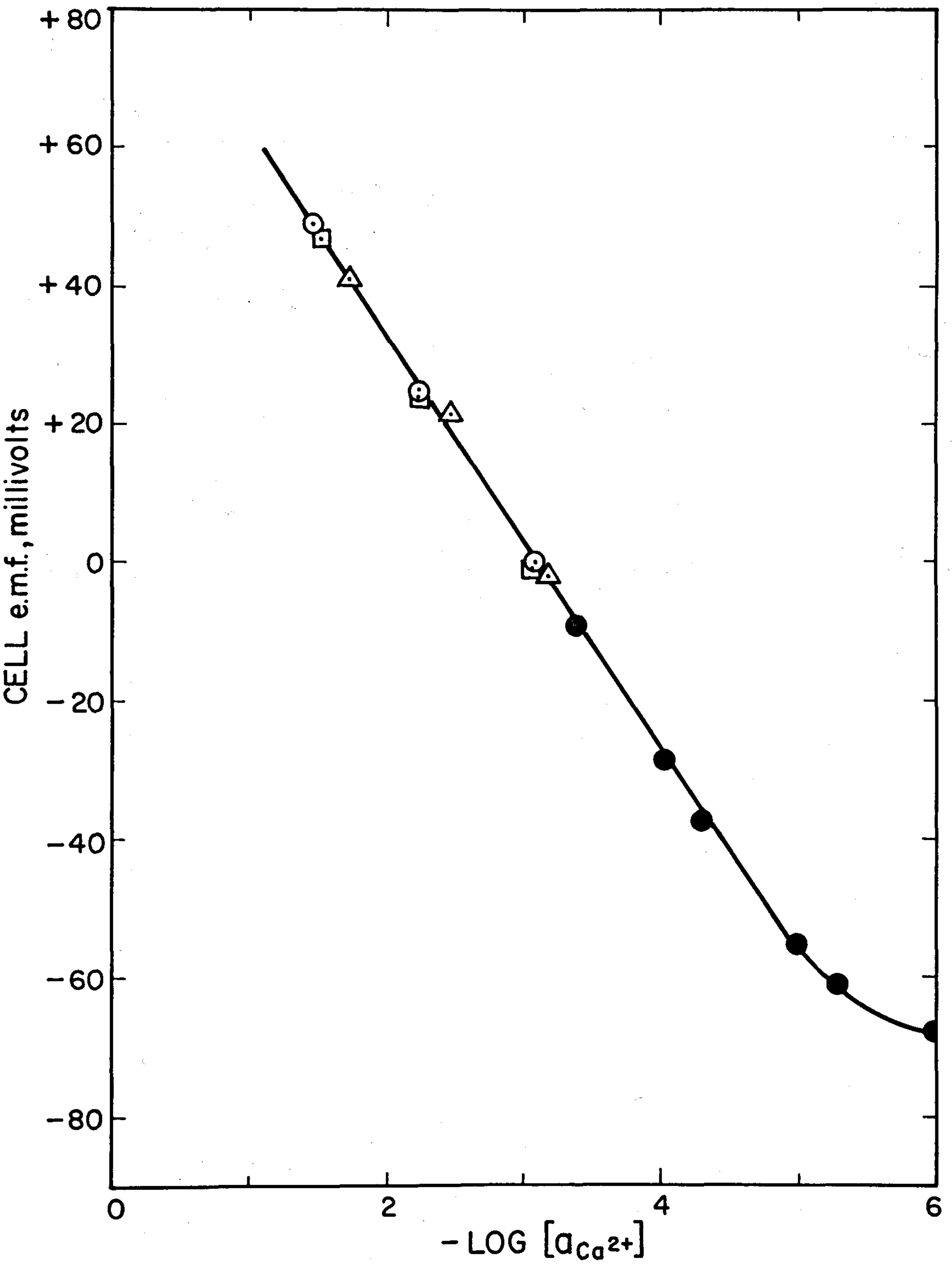
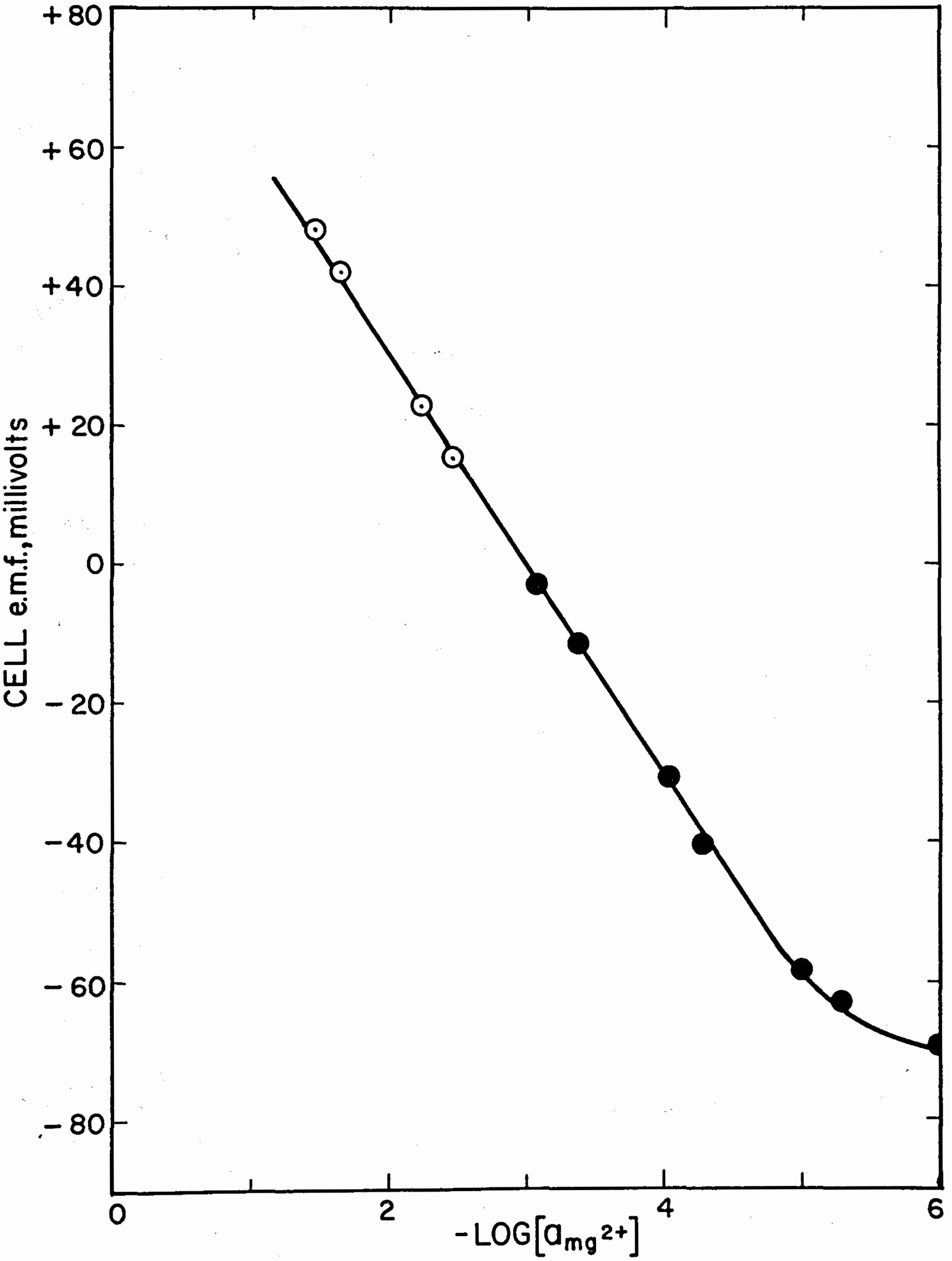

+80
+60
+40
+20
0
-20
-40
-60
-80
CELL e.m.f., millivolts
0
2
4
6
$-\mathrm{LOG}\ [a_{Ca^{2+}}]$

FIGURE 7

Electrode Response as a Function
of Magnesium Ion
Activity

⊙ $MgCl_2$ - Activity Coefficients Taken From Literature

● $MgCl$ - Activity Coefficients Calculated From Theory


+80
+60
+40
+20
0
-20
-40
-60
-80
CELL e.m.f., millivolts
0
2
4
6
$-\mathrm{LOG}[a_{mg^{2+}}]$

coefficient r = 0.9998). The experimentally obtained slopes of 30.0 mv/p_aCa^{2+} and 30.1 mv/p_aMg^{2+} were in good agreement with the theoretical slope of 30.1 mv/p_aM^{2+} predicted by the Nernst equation. No anion effect on the activity response of the electrode was observed. Once ionic concentrations have been converted to activities, a straight line plot is obtained regardless of the anion associated with the metal cation.

In the concentration range 10^{-5} to 10^{-6} M, the response plots were curved with sub-Nernstian response. Below 1 x 10^{-6} M, the plots formed a plateau, and the electrode did not respond to changes in sample cation activity. This behavior was probably caused by the very small but finite solubility of the calcium-organophosphate ester salt in the aqueous phase (118). In very dilute sample solutions, the liquid ion-exchange resin saturated the solution in the immediate vicinity of the ion-sensing membrane and by dissociation raised the concentration of calcium ion to a fixed level.

The emf of the experimental cell drifted with time. Over a twenty-four hour period, random (bidirectional) drifts varying from 0.2 to 2.5 mv were observed; however, over an extended period of thirty days of use, the cell emf drifted 20-30 mv to more negative values. These variations in cell emf were caused by drift in the potential of the ion-selective electrode, for the Orion reference electrode showed no change in potential when measured against a saturated calomel electrode. The small daily random drifts may possibly be due to changes in the membrane asymmetry potential. The long-term monotonic drift may possibly be due to changes in the concentration of the internal reference solution. The decrease in the level of the internal reference solution suggested that water had evaporated and the solution had become more concentrated. Operational compensation for drift was achieved by assigning a zero cell emf to a 1×10^{-3} *M* calcium chloride solution at pH 7 and making all other emf measurements relative to this standard emf. With hourly standardization, the measured cell emf's were reproducible to ± 0.5 mv in solutions more concentrated than 1×10^{-5} *M*; in more dilute solutions, they were reproducible to ± 1.7 mv.

2. Effect of Monovalent Cations

It has been found that the response of most ion-selective electrodes to the ion of primary interest is affected by foreign ions. This effect can be either indirect, with the electrode responding to an altered primary ion activity, or direct, with the electrode responding to the foreign ion itself.

In this section, the effect of the monovalent cations Na^+, K^+, and NH_4^+ upon the response of the divalent cation-selective electrode to Ca^{2+} and Mg^{2+} was investigated. These three monovalent ions were selected because of the widespread use of their salts in analytical chemistry.

For this study the metal ions were added as their chloride salts. The preparation of stock solutions of $MgCl_2$ and $CaCl_2$ have been previously described. Stock solutions of the monovalent cation chlorides were prepared as follows:

NaCl - A 1.000 Msolution was made by dissolving 58.448 grams of the oven-dried salt in distilled, deionized water and diluting to one liter.

KCl - A 1.000 M solution was made by dissolving 74.557 grams of the oven-dried salt in distilled, deionized water and diluting to one liter.

NH_4Cl - A 1.5 M solution was made by dissolving 80 grams of the salt in distilled, deionized water and diluting to one liter. The solution was analyzed by Kjeldahl distillation of the ammonia into a 4% boric acid solution. The ammonium borate formed was titrated with standard 0.1N HCl using bromcresol-green indicator (170).

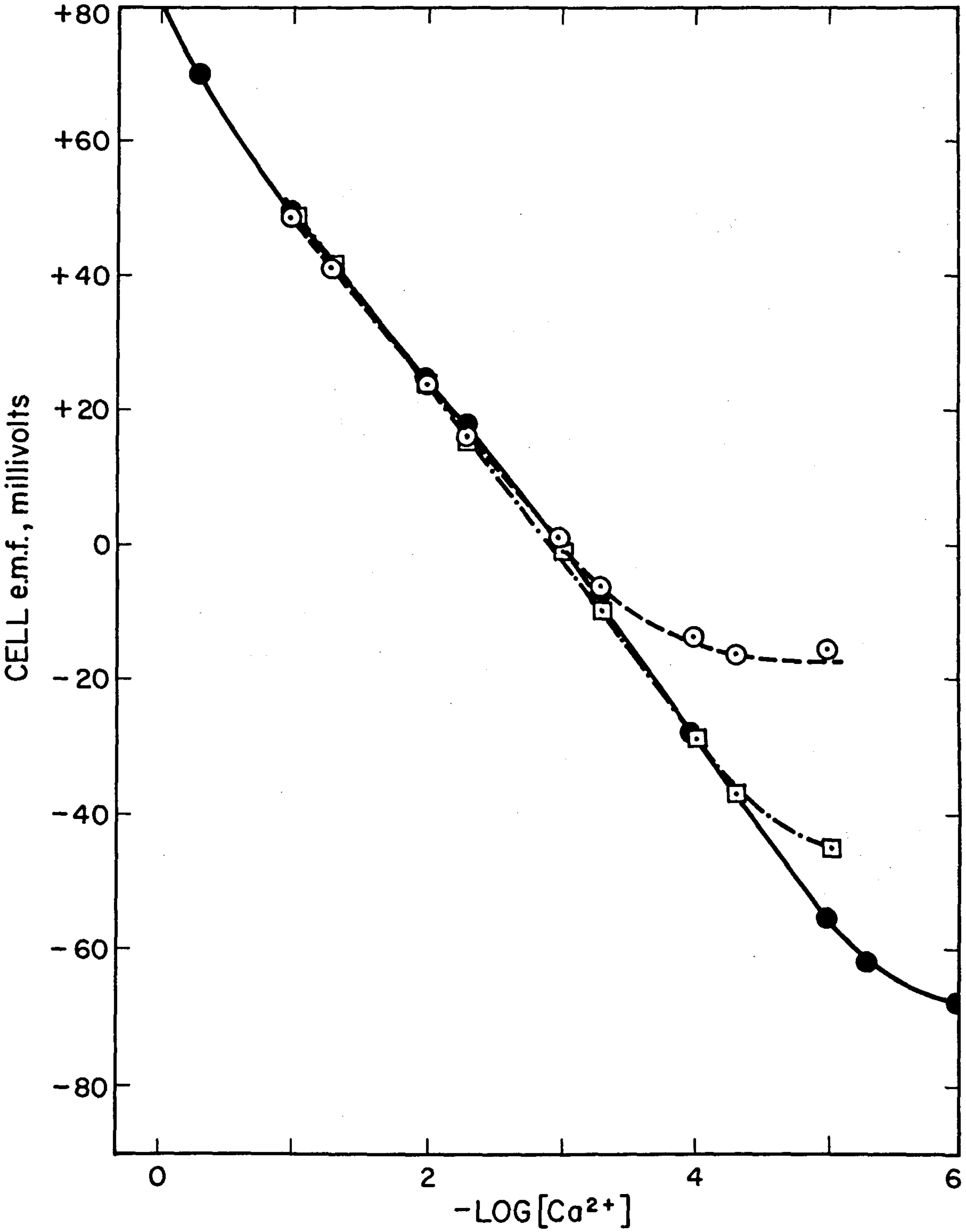
Each of the stock solutions was then diluted to the concentrations required for this study.

Measurements of cell emf were made in binary mixed solutions in which the concentration of the monovalent cation

FIGURE 8

Effect of Na^+ on Electrode
Response to Ca^{2+}

●——● Pure $CaCl_2$
⊙----⊙ $CaCl_2 + 10^{-1}$ M NaCl
⊡—·—⊡ $CaCl_2 + 10^{-2}$ M NaCl



CELL e.m.f., millivolts
+80
+60
+40
+20
0
-20
-40
-60
-80
0
2
4
6
$-\mathrm{LOG}[Ca^{2+}]$

FIGURE 9

Effect of K^+ on Electrode
Response to Ca^{2+}

●——● Pure $CaCl_2$
⊙----⊙ $CaCl_2$ + 10^{-1} M KCl
⊡—·—⊡ $CaCl_2$ + 10^{-2} M KCl

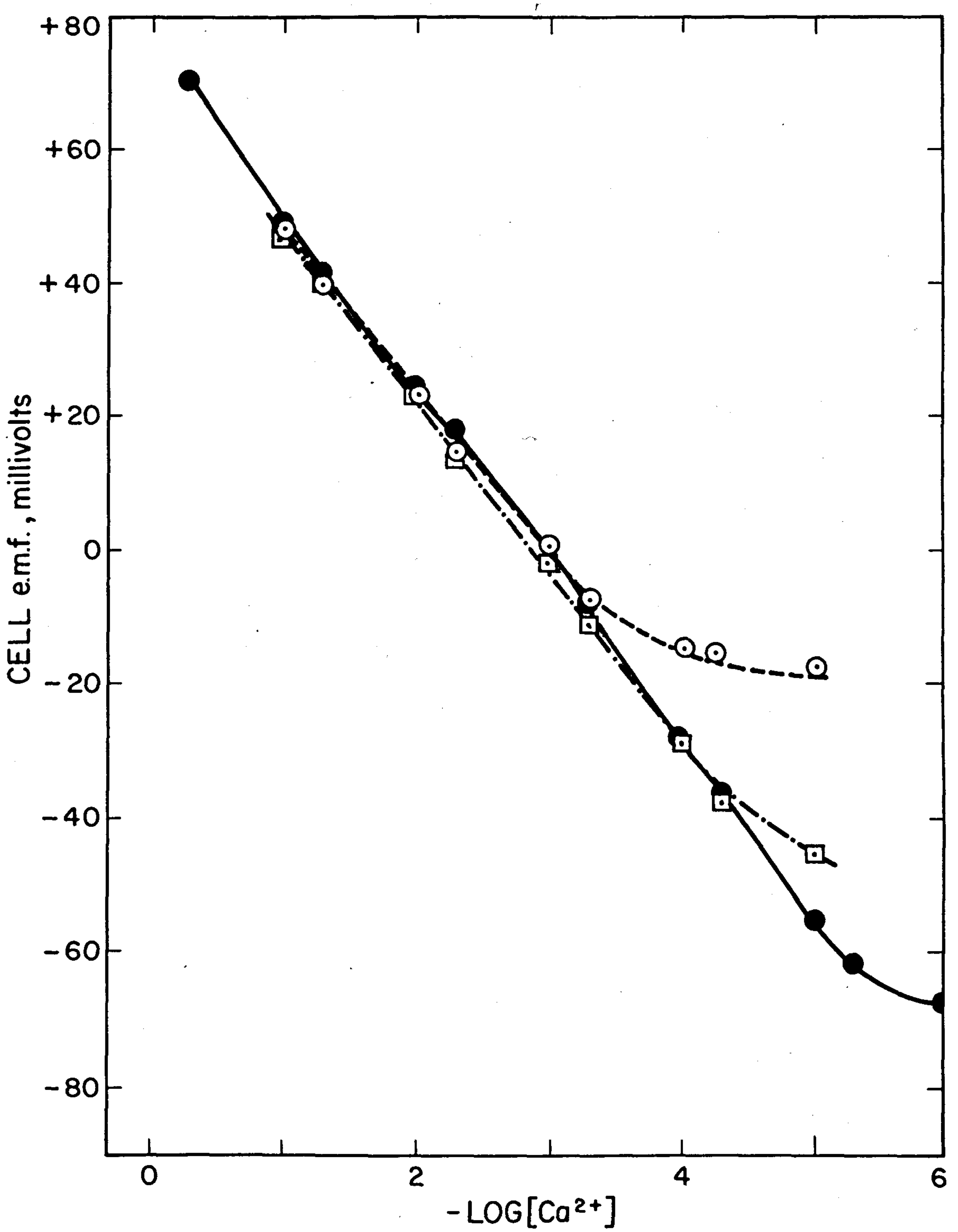

+80
+60
+40
+20
0
-20
-40
-60
-80
CELL e.m.f., millivolts
0
2
4
6
-LOG[Ca2+]

FIGURE 10

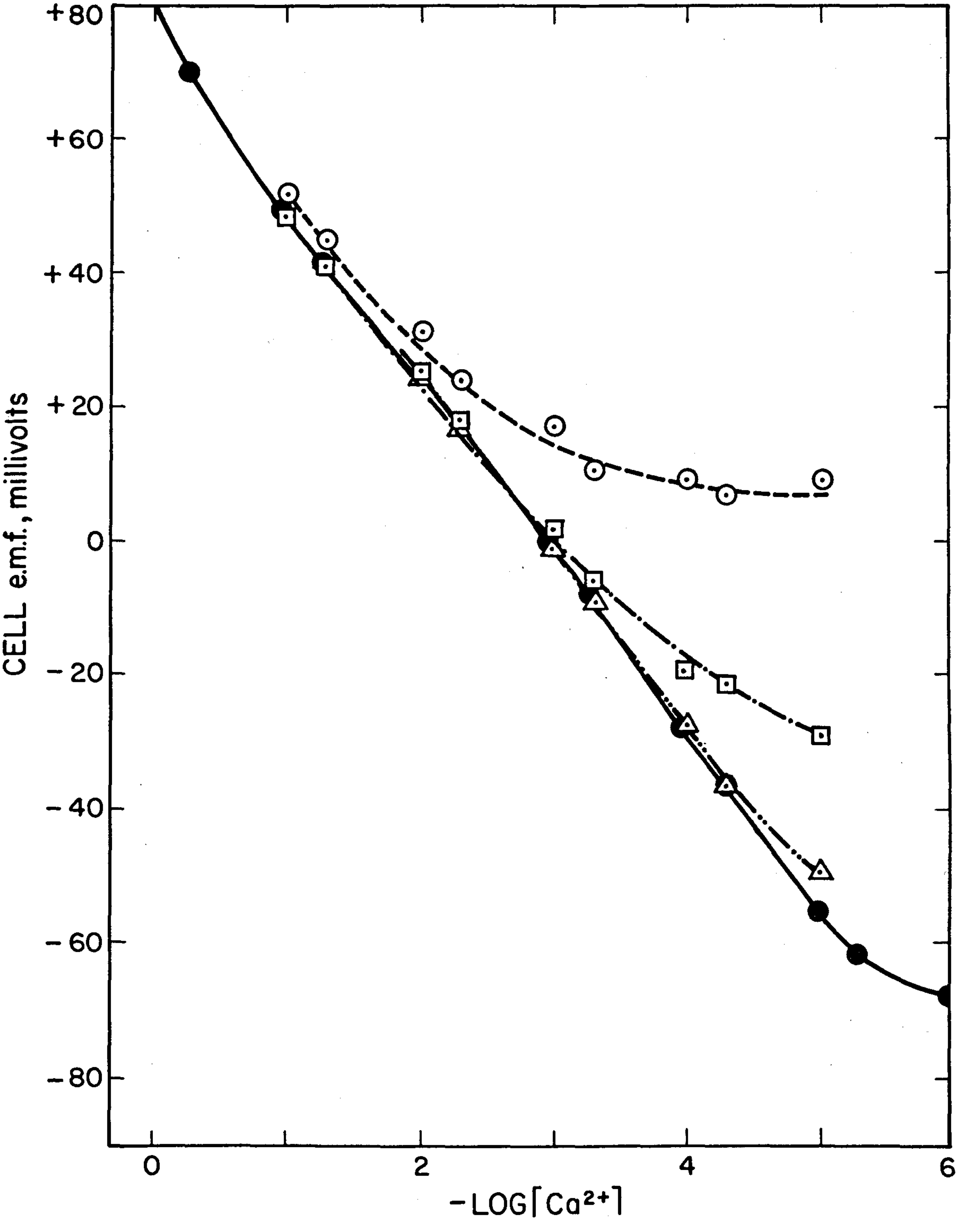
Effect of NH_4^+ on Electrode
Response to Ca^{2+}

●——● Pure $CaCl_2$

⊙----⊙ $CaCl_2$ + 10^{-1} M NH_4Cl

⊡—·—⊡ $CaCl_2$ + 10^{-2} M NH_4Cl

△—··—△ $CaCl_2$ + 10^{-3} M NH_4Cl



+80
+60
+40
+20
0
-20
-40
-60
-80
CELL e.m.f., millivolts
0
2
4
6
-LOG[Ca²⁺]

FIGURE 11

Effect of Na^+ on Electrode
Response to Mg^{2+}

●——● Pure $MgCl_2$
⊙----⊙ $MgCl_2$ + 10^{-1} M NaCl
▣—·—▣ $MgCl_2$ + 10^{-2} M NaCl

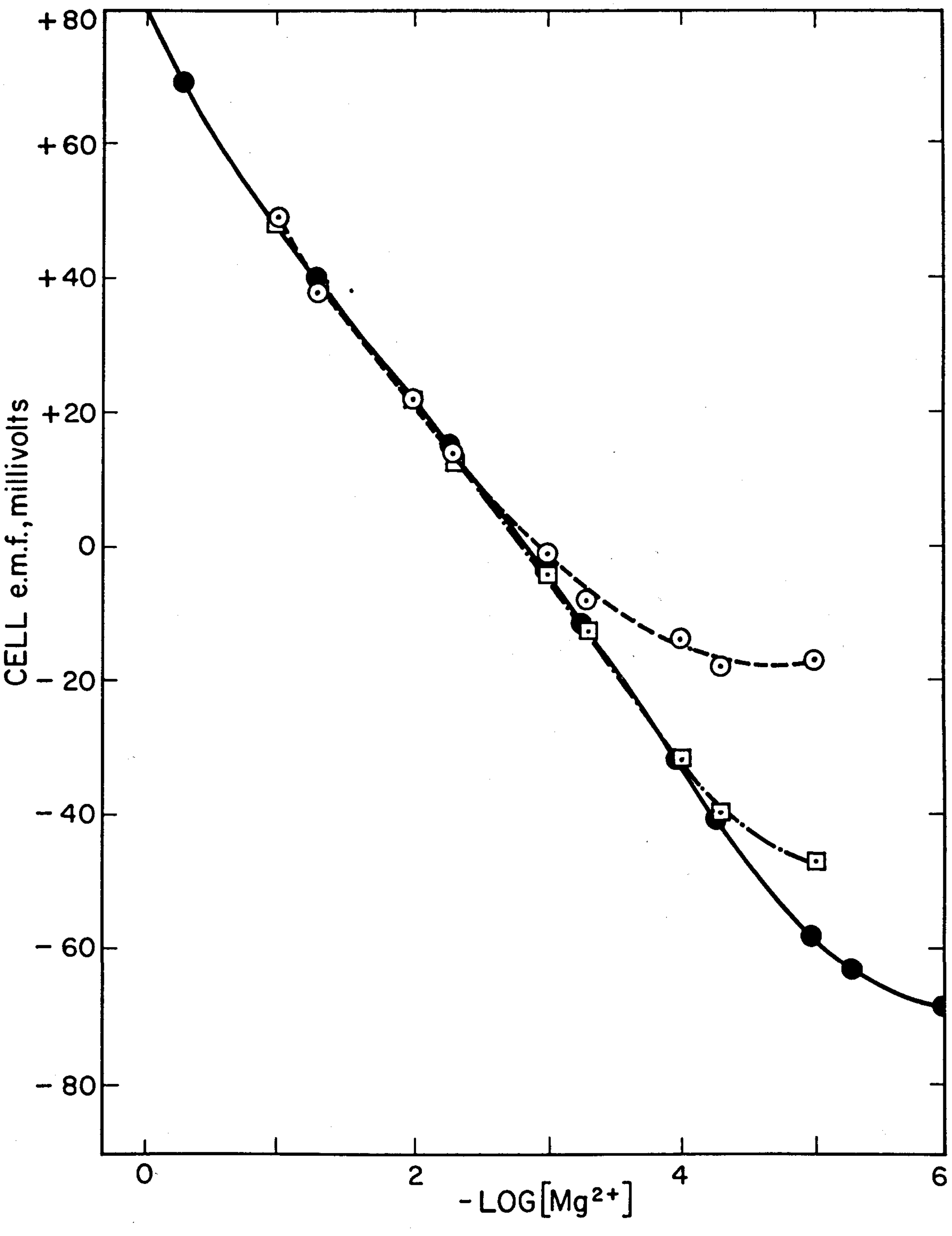
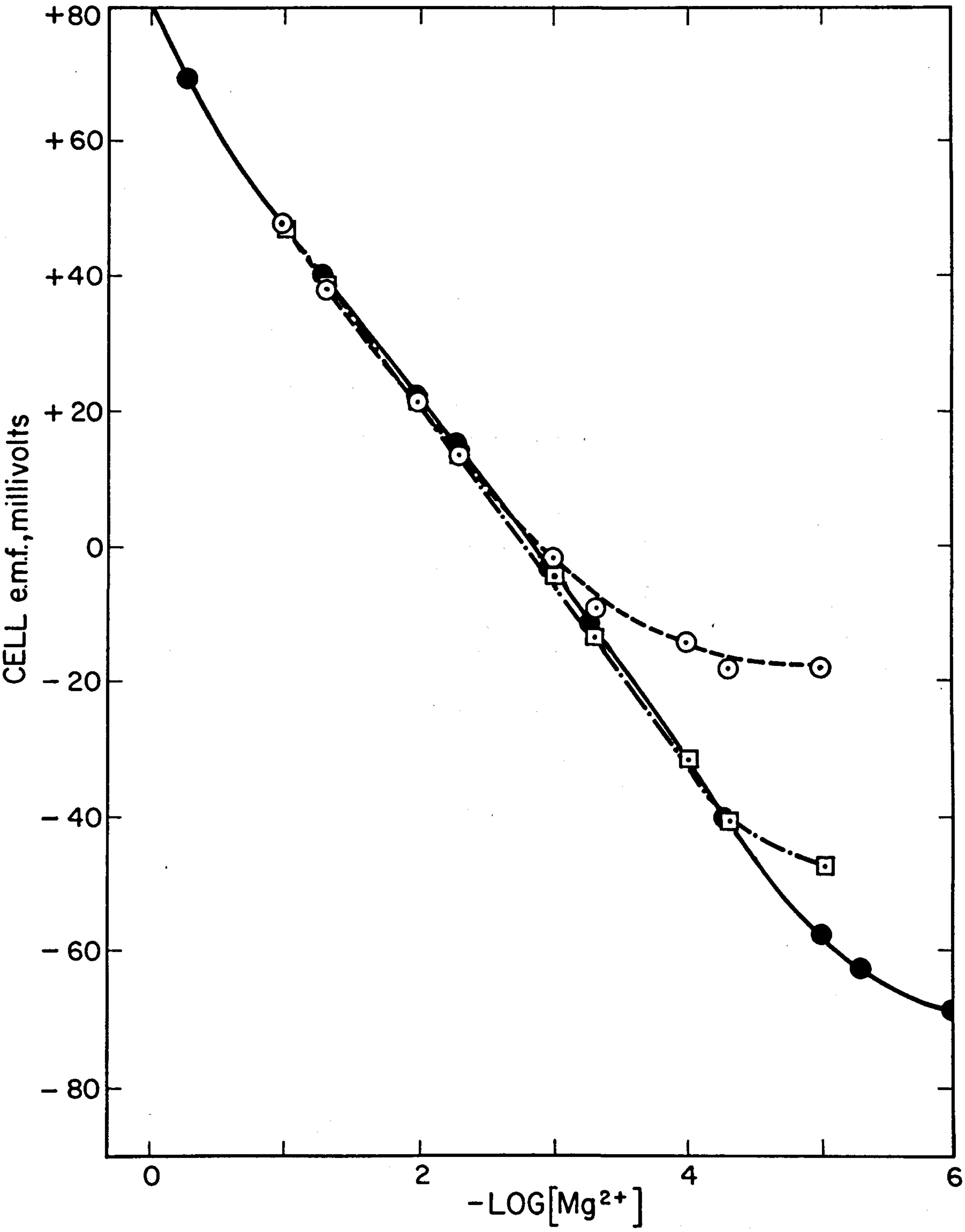

CELL e.m.f., millivolts
+80
+60
+40
+20
0
−20
−40
−60
−80
0
2
4
6
−LOG[Mg²⁺]

FIGURE 12

Effect of K^+ on Electrode
Response to Mg^{2+}

●——● Pure $MgCl_2$
⊙- - - -⊙ $MgCl_2$ + 10^{-1} M KCl
⊡—·—⊡ $MgCl_2$ + 10^{-2} M KCl

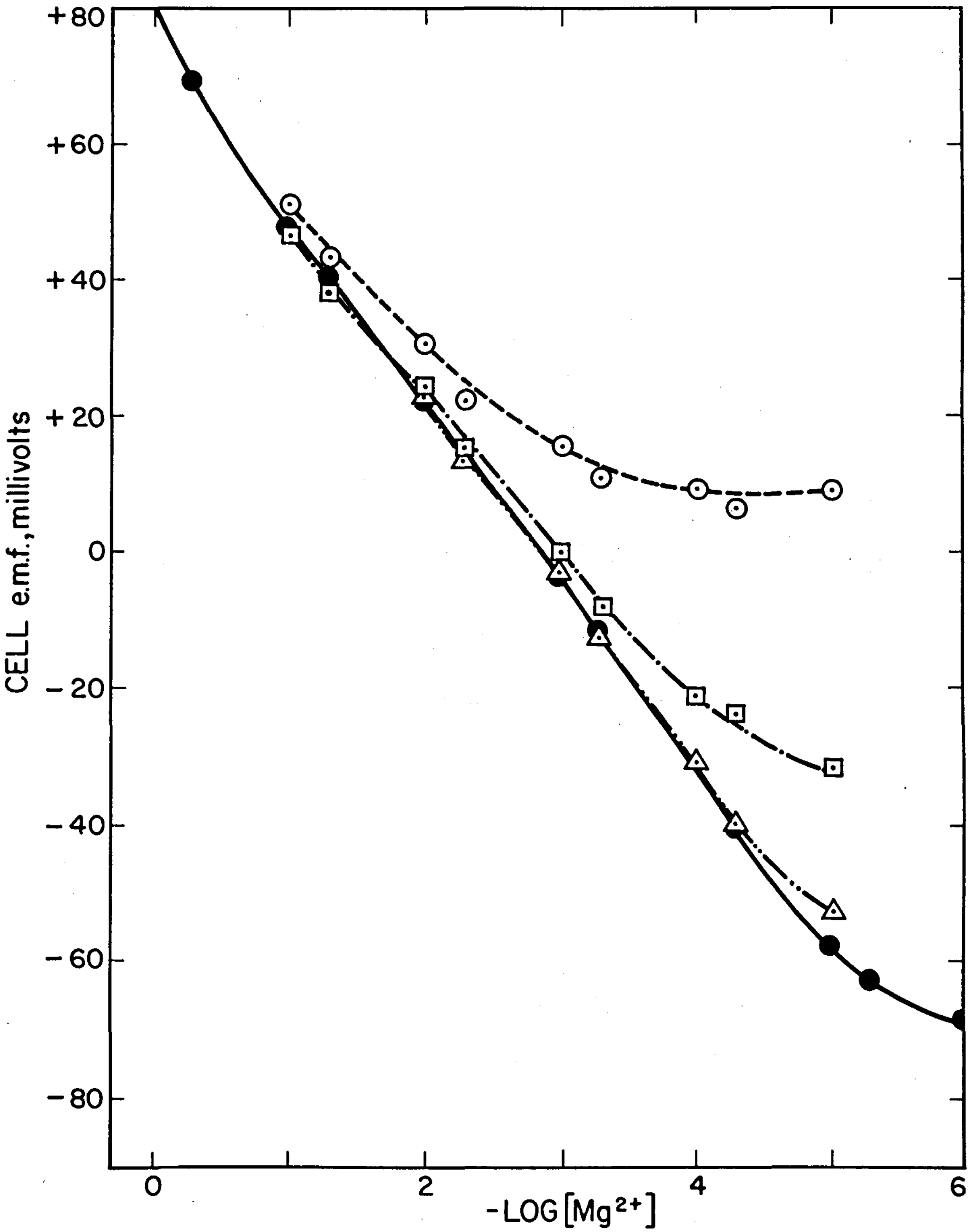


+80
+60
+40
+20
0
-20
-40
-60
-80
CELL e.m.f., millivolts
0
2
4
6
-LOG[Mg²⁺]

FIGURE 13

Effect of NH_4^+ on Electrode Response to Mg^{2+}

●——●	Pure $MgCl_2$
⊙- - - -⊙	$MgCl_2$ + 10^{-1} M NH_4Cl
⊡—·—⊡	$MgCl_2$ + 10^{-2} M NH_4Cl
△··—△	$MgCl_2$ + 10^{-3} M NH_4Cl


+80
+60
+40
+20
0
-20
-40
-60
-80
CELL e.m.f., millivolts
0
2
4
6
-LOG [Mg2+]

cation was held constant at either 1×10^{-1}, 1×10^{-2}, or 1×10^{-3} M while the concentration of the divalent cation was varied from 1×10^{-1} to 1×10^{-5} M. The pH of the solutions was adjusted to 7.0 ± 0.1 by the addition of small increments of either HCl or NaOH.

The effect of Na^+, K^+, or NH_4^+ on the concentration response of the electrode to Ca^{2+} and Mg^{2+} is shown in Figures 8 through 13, respectively. The membrane electrode responded to the monovalent cation when the cell emf in the binary solution was more positive than in the corresponding pure solutions.

Evaluative studies of ion-selective electrodes have reported the effect of foreign ions on the electrode response to the primary ion in terms of a selectivity ratio, K_{21}, calculated from the empirical equation

$$E = E_a^o + \frac{RT}{Z_2F} \ln \left[a_2 + K_{21} a_1^{(Z_2/Z_1)} \right] \qquad [18]$$

where a_2 = activity of primary ion of charge Z_2

a_1 = activity of foreign ion of charge Z_1

Accordingly, the selectivity of the divalent cation electrode can be expressed as the ratios K_{CaNa}, K_{MgNH_4}, ..., etc, calculated from the equation

$$E = E_a^o + \frac{RT}{2F} \ln \left[a_2 + K_{21} a_1^2 \right] \qquad [19]$$

Two methods for the determination of K_{21} were used.

Method I: Equation [19] is combined with the equation for the membrane electrode in a solution containing only the primary divalent cation

$$E' = E_a^o + \frac{RT}{2F} \ln a_2' \qquad [20]$$

to yield

$$E - E' = \frac{RT}{2F} \ln \left[\frac{a_2 + K_{21} a_1^2}{a_2'} \right] \qquad [21]$$

which can be rearranged to give an explicit expression for K_{21}.

$$K_{21} = \frac{\left[e^{\left(\frac{E-E'}{RT/2F} \right)} \right] a_2' - a_2}{a_1^2} \qquad [22]$$

Light and Swartz (85) have employed this method to evaluate selectivity ratios for the sulfide ion-selective electrode by measuring E' and E in solutions containing 10^{-2} M Na_2S and 10^{-2} M Na_2S + 10^{-2} M NaCN, respectively, both solutions being 1 molar in sodium hydroxide.

Method 2: An alternative treatment is to express the cell emf E measured in the binary mixed solution in terms of an effective divalent cation activity $(a_2)_e$

$$E = E_a^o + \frac{RT}{2F} \ln (a_2)_e \qquad [23]$$

Combining equations [19] and [23] and simplifying, one obtains

$$(a_2)_e = a_2 + K_{21}a_1^2 \qquad [24]$$

which can be rearranged to yield

$$K_{21} = \frac{(a_2)_e - a_2}{a_1^2} \qquad [25]$$

The selectivity ratios were calculated only for those solutions in which definite electrode response to the monovalent cations was observed. Concentrations were converted to activities by the Kielland values (75). The results are summarized in Tables 2 through 4.

Table 2

Selectivity Ratio of Sodium for Divalent Cation-Selective Electrode

Concentration		K_{CaNa}		K_{MgNa}	
M^{2+}	Na^+	Method 1	Method 2	Method 1	Method 2
1×10^{-3}	1×10^{-1}	0.079	0.077	0.093	0.083
5×10^{-4}	1×10^{-1}	0.045	0.051	0.054	0.051
1×10^{-4}	1×10^{-1}	0.041	0.041	0.053	0.050
5×10^{-5}	1×10^{-1}	0.035	0.035	0.040	0.038
1×10^{-5}	1×10^{-1}	0.035	0.041	0.039	0.047
1×10^{-5}	1×10^{-2}	0.184	0.234	0.197	0.265

Table 3

Selectivity Ratio of Potassium for Divalent Cation-Selective Electrode

Concentration		K_{CaK}		K_{MgK}	
M^{2+}	K^+	Method 1	Method 2	Method 1	Method 2
1×10^{-3}	1×10^{-1}	0.078	0.077	0.086	0.076
5×10^{-4}	1×10^{-1}	0.040	0.047	0.050	0.048
1×10^{-4}	1×10^{-1}	0.039	0.039	0.054	0.051
5×10^{-5}	1×10^{-1}	0.038	0.041	0.041	0.043
1×10^{-5}	1×10^{-1}	0.031	0.037	0.036	0.044
1×10^{-5}	1×10^{-2}	0.165	0.215	0.173	0.243

Table 4

Selectivity Ratio of Ammonium for Divalent Cation-Selective Electrode

Concentration		K_{CaNH_4}		K_{MgNH_4}	
M^{2+}	NH_4^+	Method 1	Method 2	Method 1	Method 2
1×10^{-1}	1×10^{-1}	2.386	4.293	3.317	5.013
5×10^{-2}	1×10^{-1}	1.309	2.148	1.879	1.894
1×10^{-2}	1×10^{-1}	1.041	1.008	1.279	1.158
5×10^{-3}	1×10^{-1}	0.582	0.590	0.619	0.588
1×10^{-3}	1×10^{-1}	0.466	0.462	0.556	0.520
5×10^{-4}	1×10^{-1}	0.263	0.284	0.379	0.366
1×10^{-4}	1×10^{-1}	0.296	0.294	0.383	0.362
5×10^{-5}	1×10^{-1}	0.229	0.236	0.301	0.282
1×10^{-5}	1×10^{-1}	0.242	0.288	0.298	0.362
1×10^{-3}	1×10^{-2}	3.330	3.879	4.795	4.051
5×10^{-4}	1×10^{-2}	1.720	2.172	2.581	2.374
1×10^{-4}	1×10^{-2}	1.363	1.323	1.792	1.635
5×10^{-3}	1×10^{-2}	1.432	1.457	1.617	1.506
1×10^{-5}	1×10^{-2}	0.839	1.001	1.088	1.001
1×10^{-5}	1×10^{-3}	6.304	9.365	8.218	10.226

The values of the selectivity ratios appear to be dependent upon the concentration of both primary and foreign ions. The question arises whether this dependence may not be an artifact of the changes in solution concentration, affecting the results through changes in either ionic strength or liquid junction potential at the external reference electrode. The ionic strength effect, however, has been taken into account by converting the ionic concentrations into activities. Changes in the liquid junction potential of the external reference electrode can be ruled out because the potential is unaffected by wide differences in ionic concentrations as indicated by the Nernstian slope obtained in pure solutions of the divalent cations in the concentration range 1×10^{-1} to 1×10^{-5} M.

Similar variations in selectivity ratios have been reported by other workers. Rechnitz and Kenny (145) reported the selectivity of the solid-state lead electrode for Pb^{2+} over other divalent cations decreased ten-fold when the lead concentration changed from 10^{-2} M to 10^{-3} M in the presence of 0.1 M interfering cation. Lal and Christian (80) reported the selectivity for K^+ over Na^+ varied by a factor of ten thousand with the liquid membrane potassium-ion electrode. Houston and Butler (59) found the selectivity ratio K_{CaNa} for the liquid ion-exchange calcium-selective electrode varied greatly in $NaCl-CaCl_2$

solutions of constant ionic strength. To explain this phenomenon, they postulated that species such as CaClR (where R was the decylphosphate group in the ion exchanger) instead of CaR_2 were present in the organic phase at high chloride ion concentrations. This condition would have made the liquid ion exchange membrane permeable to chloride ions. This alteration of the composition of the liquid membrane would have changed the selectivity ratio. However, Houston and Butler did point out that this explanation was speculative and that other phenomena also might have been responsible for the observed deviations from ideal selectivity.

From the data presented in the present work and in the literature, the selectivity ratio is shown to be concentration dependent. This variation is so extreme that it raises the question of whether equation [19] is valid. The data show that the electrode response to calcium and magnesium is altered more by ammonium ions than by sodium or potassium ions.

3. Effect of pH

The dependence of the cell emf on the pH at various $CaCl_2$ and $MgCl_2$ concentrations is shown in Figures 14 and 15. The concentrations of divalent cation chloride used were 1×10^{-1}, 1×10^{-2}, 1×10^{-3}, 1×10^{-4}, and 1×10^{-5} M.

FIGURE 14

Effect of pH on Electrode
Response to Ca^{2+}

⊙—·—⊙ 10^{-1} M $CaCl_2$
■----■ 10^{-2} M $CaCl_2$
△——△ 10^{-3} M $CaCl_2$
●----● 10^{-4} M $CaCl_2$
⊡—·—⊡ 10^{-5} M $CaCl_2$

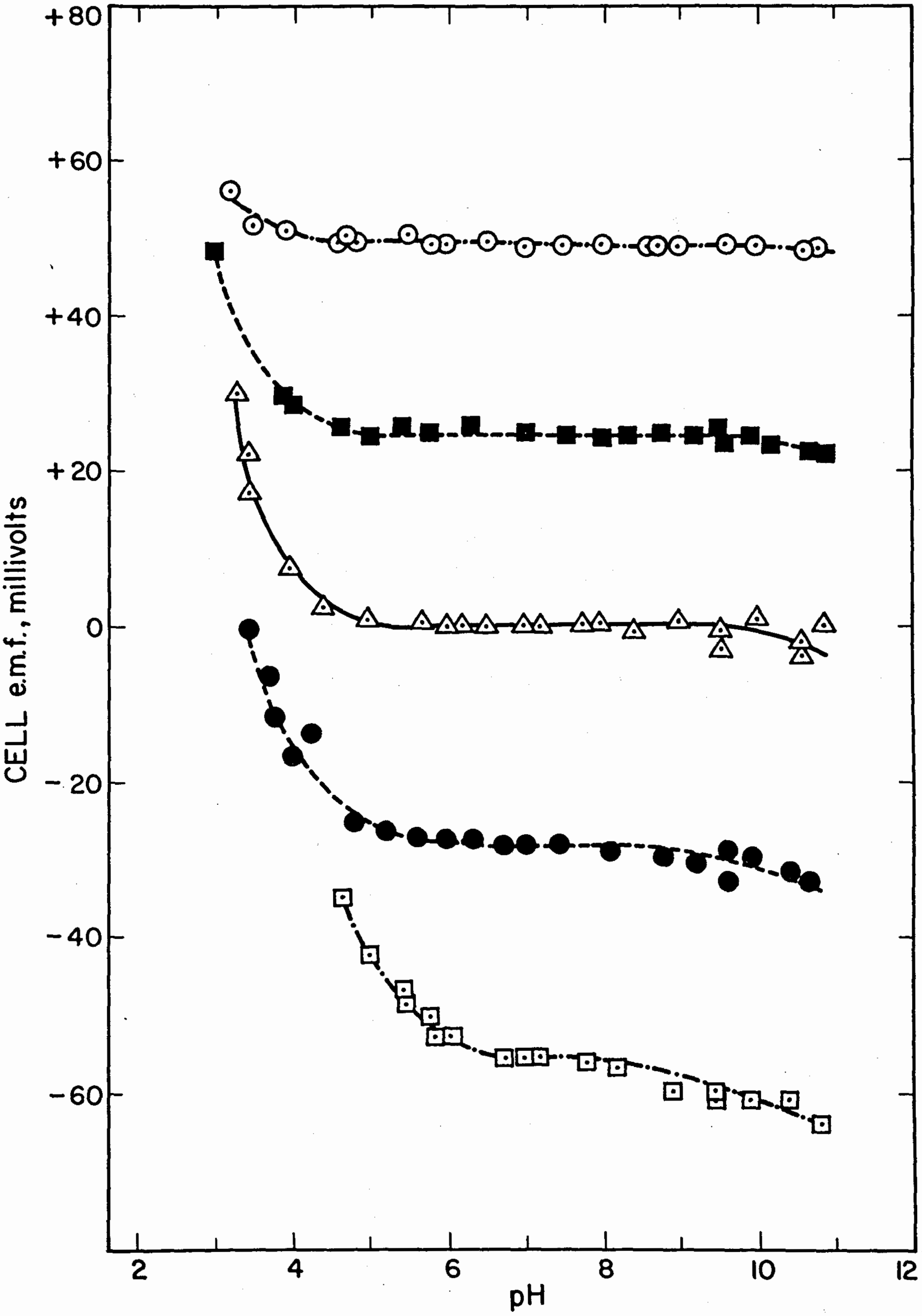
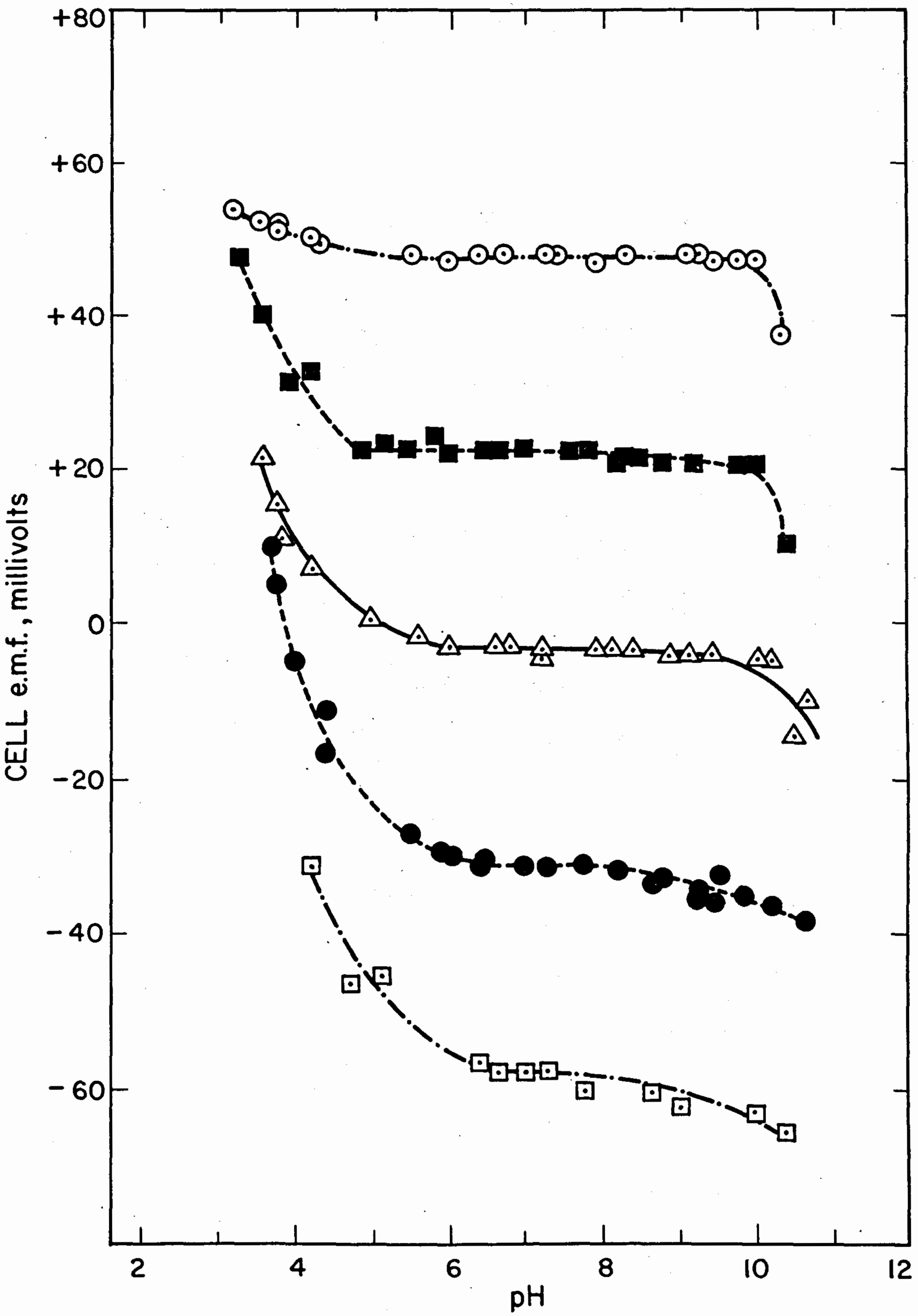

+80
+60
+40
+20
0
-20
-40
-60
CELL e.m.f., millivolts
2
4
6
8
10
12
pH

FIGURE 15

Effect of pH on Electrode Response to Mg^{2+}

⊙—·—⊙ 10^{-1} M $MgCl_2$
■----■ 10^{-2} M $MgCl_2$
△——△ 10^{-3} M $MgCl_2$
●----● 10^{-4} M $MgCl_2$
⊡—·—⊡ 10^{-5} M $MgCl_2$


+80
+60
+40
+20
0
-20
-40
-60
CELL e.m.f., millivolts
2
4
6
8
10
12
pH

The pH values were varied from 3.0 to 10.7 by the addition of small increments of HCl and NaOH.

The pH range in which the cell emf was independent of solution pH became smaller as the divalent cation concentration decreased. Deviations in the cell emf were positive if the solution was too acidic and negative if the solution was too basic. Optimum electrode response to calcium and magnesium was achieved when the pH of the test solution was in the range 6.5 to 7.5.

The increasing positive deviations in cell emf with decreasing pH indicated the electrode was responding to hydrogen ions. The negative shifts in cell emf at high pH's indicated the electrode was sensing decreased divalent cation activity. The activity was reduced by chemical reactions. One such reaction would be the complexation of calcium or magnesium by hydroxide ion as shown

$$Ca^{2+} + OH^- = CaOH^+$$

$$Mg^{2+} + OH^- = MgOH^+$$

With increasing pH, the hydroxide ion concentration would increase, the chemical equilibria would be shifted further to the right, and the amount of free divalent cation would decrease. Another possibility would be the reaction of the calcium or magnesium ion with the carbonate ion to produce the insoluble salt. Carbonate would be present to some extent in all the sample solutions as a result of absorption of CO_2 from the air -- the higher the pH, the greater the CO_2 absorption.

B. Response to Other Divalent Cations

Since the manufacturer claimed that this liquid-membrane electrode was divalent cation selective, the electrode response was determined in pure solutions of barium (II), cobalt (II), copper (II), iron (II), manganese (II), nickel (II), strontium (II), and zinc (II). Accordingly, 0.5 M stock solutions of either the chloride or nitrate salts of these cations were prepared as follows:

$Ba(NO_3)_2$ - 33 grams of the salts were dissolved in 250 ml distilled, deionized water. The solution was analyzed by titration with standardized Na_2H_2EDTA using Eriochrome Black T as the indicator (202).

$Co(NO_3)_2$ - 38 grams of the hexahydrate were dissolved in 250 ml distilled, deionized water. The solution was standardized by titration with Na_2H_2EDTA with murexide as the indicator (202).

$Cu(NO_3)_2$ - 30 grams of $Cu(NO_3)_2 \cdot 3H_2O$ were dissolved in 250 ml distilled, deionized water. The solution was standardized by EDTA titration with murexide as the indicator (202).

$FeCl_2$ - 25 grams of $FeCl_2 \cdot 4H_2O$ were dissolved in 250 ml of distilled, deionized water. The solution was analyzed by titration with standarized potassium permanganate reagent (170).

$MnCl_2$ - 25 grams of $MnCl_2 \cdot 4H_2O$ were dissolved in 250 ml of distilled, deionized water. Solution was standardized by EDTA titration with Eriochrome Black T as indicator (202).

$Ni(NO_3)_2$ - 45 grams of the hexahydrated salt were dissolved in 250 ml of distilled, deionized water. The solution was analyzed by titration with standardized Na_2H_2EDTA using murexide as the indicator (202).

$SrCl_2$ - 33 grams of the hexahydrate were dissolved in 250 ml of water (distilled, deionized). The solution was standardized by EDTA titration with phthaleincomplexone indicator (202).

$Zn(NO_3)_2$ - 47 grams of $Zn(NO_3)_2 \cdot 6H_2O$ were dissolved in 250 ml of distilled, deionized water. The solution was standardized by titration with EDTA using Eriochrome Black T as the indicator (202).

Measurements of cell emf were made in standard solutions which varied in concentration from 1×10^{-1} M to 1×10^{-5} M. The electrode concentration-and activity-response curves were similar in contour to those obtained with calcium and magnesium. The data were fitted by regression analysis to obtain values of E and S as before. The results are summarized in Table 5.

Table 5

Electrode Response to Divalent Cations

Divalent Cation	Concentration Response E^o_c mv	S_c mv/pM	Activity Response E^o_a mv	S_a mv/p_aM
Ba^{2+}	69.2	25.6	9.7	29.8
Sr^{2+}	65.7	25.1	89.4	29.6
Co^{2+}	78.6	26.1	96.5	30.1
Cu^{2+}	93.9	27.0	107.9	30.4
Fe^{2+}	95.4	27.0	109.4	30.4
Mn^{2+}	84.7	27.2	96.2	30.4
Ni^{2+}	80.1	26.7	93.9	30.1
Zn^{2+}	91.2	26.6	106.1	30.0
Ca^{2+}	77.1	26.3	93.1	30.0
Mg^{2+}	76.3	26.8	90.6	30.1

The selectivity of the liquid membrane electrode for other divalent cations relative to calcium or magnesium can be expressed as the selectivity ratios K_{CaZn}, K_{MgFe}, ..., etc., calculated from the equation

$$E = E_a^o + \frac{RT}{2F} \ln \left[a_2 + K_{21} a_1 \right] \qquad [26]$$

If the test solution does not contain the primary cation (i.e. calcium or magnesium) but any other divalent cation with a selectivity ratio K_{21}, the electrode potential, E, in such a solution can be expressed by equation [27], obtained by substituting $a_2 = 0$ in equation [26] :

$$E = E_a^o + \frac{RT}{2F} \ln K_{21} + \frac{RT}{2F} \ln a_1 \qquad [27]$$

Combining equation [20]

$$E' = E_a^o + \frac{RT}{2F} \ln a_2' \qquad [20]$$

with equation [27] yields

$$E - E' = \frac{RT}{2F} \ln K_{21} + \frac{RT}{2F} \ln a_1 - \frac{RT}{2F} \ln a_2' \qquad [28]$$

If $a_1 = a_2$, the equation simplifies to

$$\ln K_{21} = \frac{E-E'}{RT/2F} \qquad [29]$$

The selectivity ratio K_{21} can then be calculated from values of E and E' measured in pure solutions of the divalent cation and calcium or magnesium at equal activities. The results so obtained are summarized in Table 6.

Table 6

Selectivity Ratios of Foreign Divalent Cations

Cation	Equation [29]		Equation [30]	
	K_{CaM}	K_{MgM}	K_{CaM}	K_{MgM}
Ba^{2+}	0.65	0.84	0.54	0.65
Sr^{2+}	0.52	0.67	0.42	0.53
Co^{2+}	1.21	1.55	1.03	1.34
Cu^{2+}	3.09	3.99	2.86	3.55
Fe^{2+}	3.47	4.48	3.14	3.92
Mn^{2+}	1.48	1.91	1.35	1.88
Ni^{2+}	1.15	1.49	1.09	1.31
Zn^{2+}	2.72	3.52	2.72	3.32

It seemed to the author that the values of K_{21} as calculated by the preceding method would not accurately describe the effect of other divalent cations on the electrode response to calcium and magnesium. Therefore, it was decided to determine the selectivity ratios from measurements in mixed solutions. Accordingly, the cell emf was measured in binary mixed solutions in which the concentration of the foreign divalent cation was held constant at 1 x 10^{-2} M while the concentration of calcium or magnesium was varied from 1×10^{-1} to 1×10^{-5} M. The selectivity ratio was calculated by equation [30] :

$$K_{21} = \frac{\left[e^{\left(\frac{E - E'}{RT/2F}\right)}\right] a'_2 - a_2}{a_1} \qquad [30]$$

This equation was derived from equation [26] in the same manner as equation [22] was derived from equation [19]. As shown in Table 7, the selectivity ratios calculated by this method are not concentration dependent.

Table 7

Selectivity Ratio of Zinc for Divalent Cation Selective Electrode

Concentration Ca^{2+}	Zn^{2+}	K_{CaZn}
5×10^{-2}	1×10^{-2}	2.84
1×10^{-2}	1×10^{-2}	2.78
5×10^{-3}	1×10^{-2}	2.77
1×10^{-3}	1×10^{-2}	2.86
5×10^{-4}	1×10^{-2}	2.64
1×10^{-4}	1×10^{-2}	2.81
5×10^{-5}	1×10^{-2}	2.73
1×10^{-5}	1×10^{-2}	2.35

The selectivity ratios calculated by equation [30] are listed in Table 6 for comparative purposes.

It is an interesting but unexplained observation that equation [18]

$$E = E_a^o + \frac{RT}{Z_2F} \ln \left[a_2 + K_{21}a_1^{(Z_2/Z_1)} \right] \quad [18]$$

accurately describes the response of the divalent cation-selective electrode in divalent-divalent cation mixtures but not in monovalent-divalent cation mixtures.

C. Behavior of Liquid-Ion Exchange Resin in Organic Solvents

Several workers have used the solid-state membrane electrodes in non-aqueous media (86, 87, 144, 145, 159). Similar utilization of a liquid membrane electrode would be governed by the effect of the organic solvent on the membrane material. If the liquid ion-exchanger were soluble in the organic solvent or reacted with it, then the electrode could not be used in solutions of that organic solvent.

The behavior of the liquid ion exchange resin in organic solvents was determined by the addition of 3.0 ml of the organic in 0.5 ml increments to 0.2 ml of the resin. The results are summarized as follows:

1. A homogeneous brownish-red solution was obtained. This behavior indicated the resin was completely soluble.

Methanol
Ethanol
n-Propanol
iso-Propanol
n-Butanol
sec-Butanol
tert-Butanol
Propylene glycol
Benzene
Toluene
Hexane
Cyclohexane
Chloroform
Carbon Tetrachloride
Methylene Chloride
Carbon Disulfide
Ethyl Ether
p-Dioxane
Tetrahydrofuran
Pyridine

2. A heterogeneous mixture which consisted of a white precipitate and a brownish-red supernatant liquid was obtained. This behavior indicated one component of the liquid ion-exchanger was soluble in the organic solvent while the other was either insoluble or reacted with it.

Methyl Ethyl Ketone
Acetone
Ethylacetate
Dimethylsulfoxide
Acetonitrile
N,N-Dimethylformamide

3. A heterogeneous mixture which consisted of two liquid phases was obtained. The top layer was the liquid exchanger; the bottom layer was the organic solvent. This behavior indicated the resin was probably insoluble in the organic liquid.

Ethylene Glycol

These solubility studies indicate that the liquid membrane electrode should be used only in aqueous solutions. Also, several good solvents for cleaning the electrode were found.

VI. Applications of the Electrode

As shown in the historical, the analytical applications of ion-selective electrodes are many and varied. In general, the analytical techniques fall into one of two classes: direct potentiometric measurements based on the Nernst equation, or potentiometric titrations.

This phase of the research was centered on evaluation of the divalent cation-selective electrode as an analytical sensor. Each of the two classes of techniques is illustrated: the first by the standard additions method, and the second by the titration of calcium and magnesium with EDTA and NaF.

A. Standard Additions Method

There are three methods commonly used to relate the potential of an ion-selective electrode to the concentration of the primary ion.

The first method is generally used with complex systems where the concentration of foreign ion in the sample solution is high. An empirical calibration curve is constructed using a series of standard solutions with backgrounds closely approximating that of the test solution and varying only in the concentration of the primary ion. Using the divalent cation-selective electrode, Thompson (192) measured Mg^{2+} in sea water, and Garvin (36) measured Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} in cell suspensions by this method.

For less complex systems, a second method exists in which an excess of an inert electrolyte is added to the test solution to swamp out interferences and variations in the sample solution background. An empirical calibration curve is constructed from a series of standard solutions treated in an identical manner. The best example of this method is the procedure described by Frant and Ross (33) for the determination of fluoride in public water supplies using a fluoride ion-selective electrode and a total ionic strength adjustment buffer (TISAB).

A third method, which is very convenient for the determination of the total concentration of a species in very complex systems, is the standard additions technique. This method can be used in solutions with backgrounds containing high concentrations of foreign ions or complexing agents. The only preliminary requirement is a precise knowledge of the electrode response to the primary ion. The method consists of measuring the change in electrode potential developed when a small volume of solution of known primary ion concentration is added to a known volume of sample solution. The original sample concentration is calculated from the measured change in cell emf. No calibration curve is required.

The standard additions method has been used for the determination of total calcium in beer using the calcium ion-selective electrode (115). In the beer samples, any proteins and other calcium-complexing agents were present in a 50 to 100 fold excess over the calcium present. It was not necessary to know the nature of the complexing agents or the total ionic strength of the solution.

Experimentally, the method described was very simple. The slope of the calibration curve was determined from cell emf measurements in pure $CaCl_2$ solutions. The potential of the calcium ion-selective electrode was measured in 100 ml of unknown solution of pH 6.0. Then

1.0 ml of a standard 0.1 M $CaCl_2$ solution was added and the electrode potential measured again. The total calcium concentration in the beer sample was then calculated from the equation

$$C = \frac{C_{\Delta}}{(\text{Antilog } \Delta E/S)-1} \qquad [31]$$

where C is the original concentration of calcium in the sample, C_{Δ} the change in concentration of the standard solution due to addition, ΔE the change in electrode potential, and S the slope of the electrode concentration-response curve.

This method looked highly promising, for it seemed to offer a technique whereby ionic concentrations could be determined rapidly and easily in complex systems having high backgrounds without prior knowledge of the sample matrix. For this reason, it was decided to investigate the standard additions method to ascertain if it could be used to determine total calcium or magnesium concentrations.

However, equation [31] was derived by assuming the volume of the added standard solution to be negligible in comparison to the original sample solution volume. In the present work, this assumption may not be valid; therefore, a more general form of the standard additions equation was derived.

The cell emf E measured in the sample solution of concentration C of primary ion and known volume V is given by the Nernst equation

$$E = E_c^o + S_c \log C \qquad [32]$$

where E_c^o is the concentration-response constant and S_c is the concentration response slope. After addition of a known volume V_s of a standard solution of known concentration C_s of primary ion, the cell emf E_f measured in the test solution of concentration C_f and volume V_f is given by

$$E_f = E_c^o + S_c \log C_f \qquad [33]$$

However,

$$C_f V_f = CV + C_s V_s \qquad [34]$$

and

$$V_f = V + V_s \qquad [35]$$

Substituting equation [35] into equation [34] and solving for C_f yields

$$C_f = \frac{CV + C_s V_s}{V + V_s}$$

which is then substituted into equation [33] to produce

$$E_f = E_c^o + S_c \log \left[\frac{CV + C_s V_s}{V + V_s}\right] \qquad [37]$$

The difference in the cell emf due to the standard addition is the difference between equations [32] and [37]

$$\Delta E = E_f - E = S \log \left[\frac{(CV + C_s V_s)}{C\ (V+V_s)}\right] \qquad [38]$$

or

$$\frac{\Delta E}{S} = \log \left[\frac{(CV + C_s V_s)}{C\ (V+V_s)}\right] \qquad [39]$$

Taking antilogarithms and solving for the concentration of the original sample solution

$$C = \frac{C_s}{\left(\frac{V + V_s}{V_s}\right) 10^{\Delta E/S} - \frac{V}{V_s}} \qquad [40]$$

The above equation takes into consideration the changes in concentration and volume of both the standard and sample solutions.

Equation [31] is a simplified approximate form of equation [40] and can be easily derived from it. When the assumption $V_s \ll V$ made in the derivation of equation [31] is applied to equation [40], the term $(V+V_s)/V_s$ is approximately equal to V/V_s, and the equation reduces to

$$C = \frac{C_s V_s}{V(10^{\Delta E/S} - 1)} \qquad [41]$$

Since C_Δ in equation [31] is the change in concentration of the standard solution due to the addition and is equal to $C_s V_s/V$, equations [31] and [41] are equivalent.

All results in this section were calculated using equation [40].

This phase of the research was centered on the determination of calcium and magnesium in the range of concentrations from 1×10^{-3} to 1×10^{-5} M. The determinations were made in pure solutions containing only a divalent cation and in mixed solutions containing both a divalent cation and sodium ion. All metal ion solutions used were prepared from the chloride salts. All test solution volumes were 100.0 ml.

It can be seen from equation [40] that the accuracy and precision to which C was determined depended directly on the reliability to which C_s, V, V_s, S, and ΔE were known. The concentration of the standard solution, C_s, and the volumes of the sample solution, V, and the added standard solution, V_s, were measured as accurately as normal volumetric techniques permitted. The slope, S, had been determined previously with a high degree of reliability and was taken to be 26.3 mv/pCa for calcium and 26.6 mv/pMg for magnesium. The measured change in cell emf, ΔE, was therefore the most critical measurement. To insure maximum accuracy and precision in ΔE, all potentiometric measurements were made after the cell emf had become constant to within ± 0.1 mv.

The relative uncertainty in the ΔE measurement can be reduced, and optimum results obtained by varying the concentration and volume of the standard solution added to the sample. To determine the effect of these two parameters, standard solutions of $MgCl_2$ were added incrementally to sample solutions of $MgCl_2$ of 1×10^{-5} M concentration. As shown in Table 8, the best results were obtained when sufficient reagent of 0.1 M concentration was added to produce a change in the cell emf of from 50 to 80 mv.

The following procedure was used for the analysis of unknown sample solutions. The 0.1 M standard solution was added drop-wise to the constantly stirred sample solution.

Table 8

Effect of Volume and Concentration of Standard Solution on Recovery

Increment Volume-ml	ΔE mv	Recovery %
1×10^{-1} M $MgCl_2$ Standard Solution		
0.5	46.1	93.7
1.0	53.9	94.1
2.0	60.9	101.2
3.0	65.1	104.3
4.0	68.7	100.8
5.0	71.8	95.4
6.0	73.9	94.5
8.0	76.8	96.2
10.0	79.1	96.7
1×10^{-2} M $MgCl_2$ Standard Solution		
0.5	21.0	96.4
1.0	28.5	91.7
2.0	36.0	90.9
3.0	40.4	90.9
4.0	43.4	91.9
5.0	45.8	92.0
6.0	47.8	91.7
8.0	50.6	93.7
10.0	52.6	96.7
1×10^{-3} M $MgCl_2$ Standard Solution		
0.5	5.0	91.0
1.0	8.4	91.8
2.0	13.3	89.9
4.0	18.9	92.1
6.0	23.0	88.7
8.0	25.6	89.8
10.0	27.8	89.3

The addition of standard solution was stopped when either the cell emf had changed 60 to 70 mv or the volume of added reagent reached 10.0 ml.

Sample solutions of $CaCl_2$ and $MgCl_2$ which covered the concentration range from 1×10^{-5} M to 1×10^{-3} M were prepared. With the sample volume used, these concentrations represented a weight range of 0.04→4.0 mg of calcium and 0.02→2.4 mg of magnesium. As shown in Tables 9 and 10, the recoveries ranged from 86% to 109% with an average recovery of 94%.

The method was then applied to sample solutions containing sodium chloride. Sodium was present at concentrations ranging from 1×10^{-3} M to 5×10^{-2} M which is equivalent to a weight range of 2.3 to 115 mg. The method gave correct results only when the concentration of sodium ion was less than 100 times the divalent cation concentration. When the concentration of sodium was above this limit, high recoveries of calcium and magnesium were reported. When the sodium ion concentration was below this limit, the method worked well. As shown in Tables 11 and 12, the recoveries ranged from 89% to 122% with an average of 99%.

Table 9

Recovery of Calcium In Pure Solutions

Mg Calcium		Average %		Relative
Present	Found	Recovery	n	Precision(a)
4.01	3.95	98.5	14	± 6.8%
2.00	1.85	92.5	6	± 7.4%
0.401	0.368	91.8	11	± 8.4%
0.200	0.188	94.0	6	± 12.1%
0.0401	0.0375	93.5	9	± 14.0%

Table 10

Recovery of Magnesium In Pure Solutions

Mg Magnesium		Average %		Relative
Present	Found	Recovery	n	Precision(a)
2.43	2.34	96.3	9	± 6.7%
1.22	1.14	93.4	6	± 8.3%
0.243	0.228	93.8	9	± 4.9%
0.122	0.112	91.0	6	± 11.8%
0.0243	0.0230	94.6	9	± 11.9%

(a) at the two sigma level

Table 11

Recovery of Calcium in Solutions Containing Sodium

Mg Sodium Present	Mg Calcium		Average % Recovery	n	Relative Precision(a)
	Present	Found			
115	4.01	4.28	106.7	6	± 6.2%
23.0	4.01	3.92	97.8	9	± 8.0%
23.0	0.401	0.410	102.2	9	± 8.2%
11.5	0.401	0.403	100.5	9	± 9.3%
2.3	0.401	0.370	92.3	4	——
2.3	0.0401	0.380	94.8	6	± 11.2%

Table 12

Recovery of Magnesium in Solutions Containing Sodium

Mg Sodium Present	Mg Magnesium		Average % Recovery	n	Relative Precision(a)
	Present	Found			
115	2.43	2.55	105.0	9	± 6.9%
23.0	2.43	2.33	95.9	6	± 7.2%
23.0	0.243	0.253	104.1	9	± 8.5%
11.5	0.243	0.246	101.2	9	± 10.0%
2.3	0.243	0.230	94.7	3	——
2.3	0.0243	0.0222	91.4	6	± 12.9%

(a) at the two sigma level

It appears that the standard additions method cannot be used for the determination of total calcium and magnesium concentrations in complex systems containing foreign ions at concentration levels high enough to alter the response of the divalent cation-selective electrode to the primary ions. It is necessary to have some knowledge of the sample matrix before this method can be used.

B. Potentiometric Titrations

In contrast to the direct potentiometric methods based on the Nernst equation, potentiometric titrations are generally more accurate and precise. For this reason, a cursory examination was made of the ability of the divalent cation-selective electrode to monitor titrations of calcium and magnesium with EDTA and NaF.

1. EDTA Titrations

According to the comprehensive work of Welcher (202), the complexometric titration of calcium and magnesium with EDTA is generally carried out at a pH of 10 or higher. Usually, the pH is adjusted by the addition of an ammonium chloride-ammonium hydroxide buffer. Unfortunately, the ammonium ion significantly alters the response of the divalent cation-selective electrode to calcium and magnesium.

A 0.2 M solution of Na_2H_2 EDTA was prepared by dissolving 74 grams of the dihydrated salt in one liter distilled, deionized water. The solution was standardized by titration against $CaCO_3$ using calcein as the indicator (20). This stock solution was diluted with distilled, deionized water and 2M NaOH to produce a titrant that was 0.0938 M in Na_2H_2 EDTA and 0.2 M in NaOH. The use of this highly alkaline EDTA solution as the titrant eliminated the need for a high pH buffer.

For the complexometric titrations, the sample solution consisted of 10.0 ml of either a 0.0998 M $CaCl_2$ solution or a 0.0957 M $MgCl_2$ solution added to 90 mls distilled, deionized water. The pH of the sample solutions was adjusted to 10.0 by the addition of 2 M NaOH. In the course of the titrations, the solution pH rose to 11.9. The titrations were carried out in the usual manner with care being taken that the cell emf had stabilized before the next increment of titrant was added. In the immediate vicinity of the equivalence point, the electrode showed considerable potential drift and required waiting periods of 4 to 6 minutes to obtain a steady value. Outside of this region, the electrode response was more rapid with a steady cell emf being obtained in one minute or less.

The resulting titration curves are shown in Figure 16. The total potential change from the start to the conclusion was 55 mv for the calcium titration and 60 mv for the magnesium titration. No sharp drop in cell emf, which would have indicated an end point, was readily observed in either titration. Therefore, it was necessary to use two other methods to locate the end-point. The first method evaluated the end-point from the first derivative curve of the titration data, the end-point having been taken where the slope, $\Delta E/\Delta V$, was a maximum. The second method placed the end-point at that point in the titration curve where the cell emf abruptly began to plateau prior to increasing. The end-points obtained by these two methods are compared with those obtained by visual titrations using metallochromic indicators in Table 13.

FIGURE 16

Titration of Calcium and Magnesium

With EDTA

⊙——⊙ Calcium

⊡——⊡ Magnesium

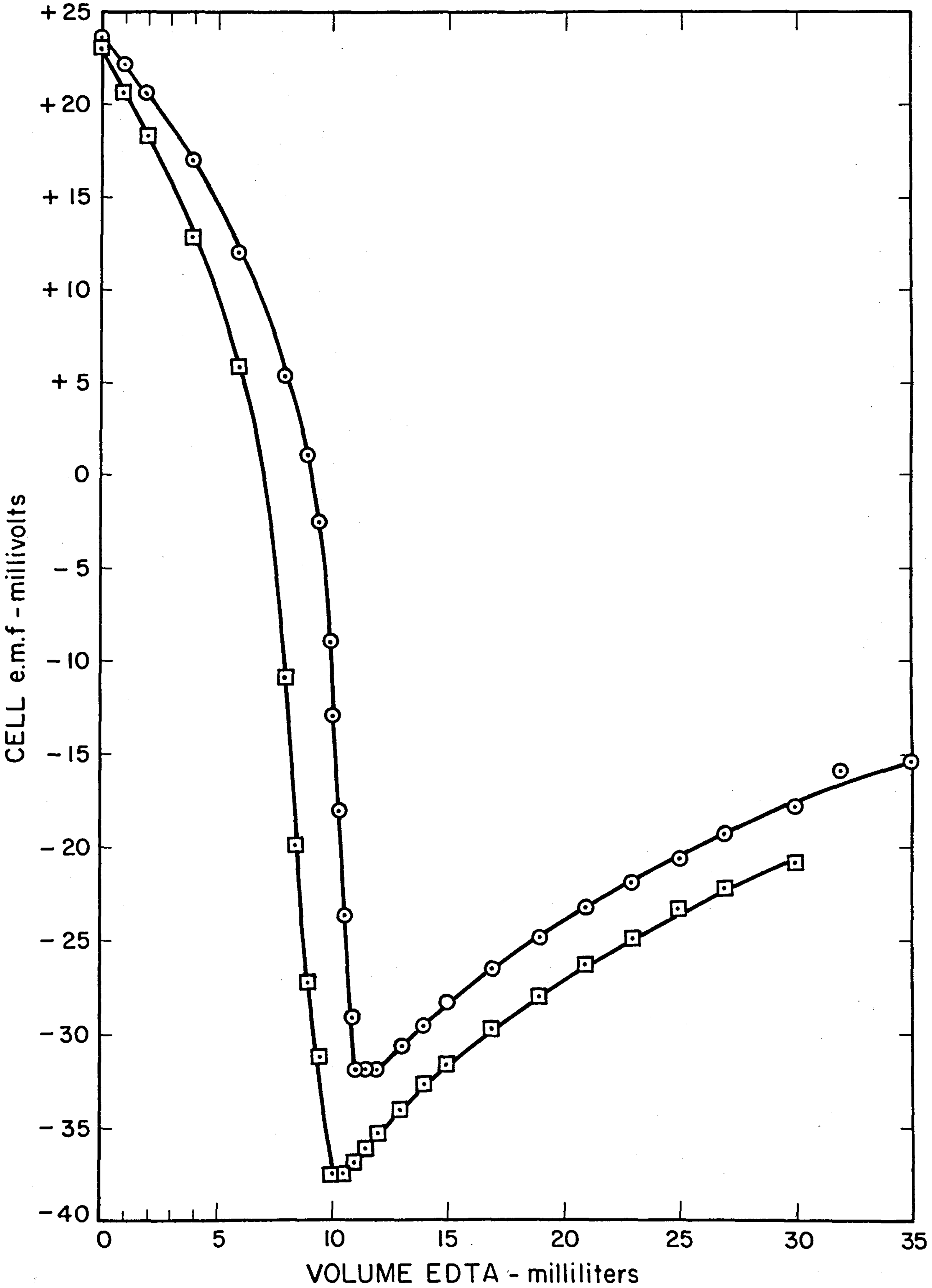

+25
+20
+15
+10
+5
0
-5
-10
-15
-20
-25
-30
-35
-40
CELL e.m.f - millivolts
0
5
10
15
20
25
30
35
VOLUME EDTA - milliliters

Table 13

Comparison of Methods for End-Point Detection

Ion Titrated	Visual Titration Volume ml	Electrode Titration First Method Volume ml	First Method Error	Second Method Volume ml	Second Method Error
Ca^{2+}	10.63	10.8	1.9%	11.0	3.8%
Mg^{2+}	10.20	10.0	2.0%	10.0	2.0%

Each titration was performed three times. The variation in cell emf between different runs did not exceed a maximum of 1.1 mv. As a result, the variation in end-point volume was only ± 0.1 ml for a precision of 0.9% in the calcium titration and 1.0% in the magnesium titration.

Comparable titrations of calcium with EDTA using the calcium ion-selective liquid-membrane electrode have been reported by several authors. Mukherji and co-workers (76, 112) reported titrating 2→10 mg of calcium with an average error of 2%. Tackett (179) reported an automatic titration with an error of 0.12% and a relative precision of ± 0.05%.

As shown in Figure 16, the emf rose after the end-point. This positive deviation was probably due to the presence of sodium ions and was in direct contrast to the behavior reported for the calcium ion-selective electrode. With the Ca^{2+} electrode, different workers (76, 112, 151, 179) reported observing either a constant potential or a slight positive increase after the end-point. This comparison emphasizes the improved calcium-sodium selectivity of the calcium-ion-selective electrode.

2. Fluoride Titrations

Lingane (86) used the fluoride ion-selective solid-state membrane electrode to monitor titrations of fluoride with calcium. An identical titration, with the divalent cation-selective electrode as the potentiometric monitor, was carried out.

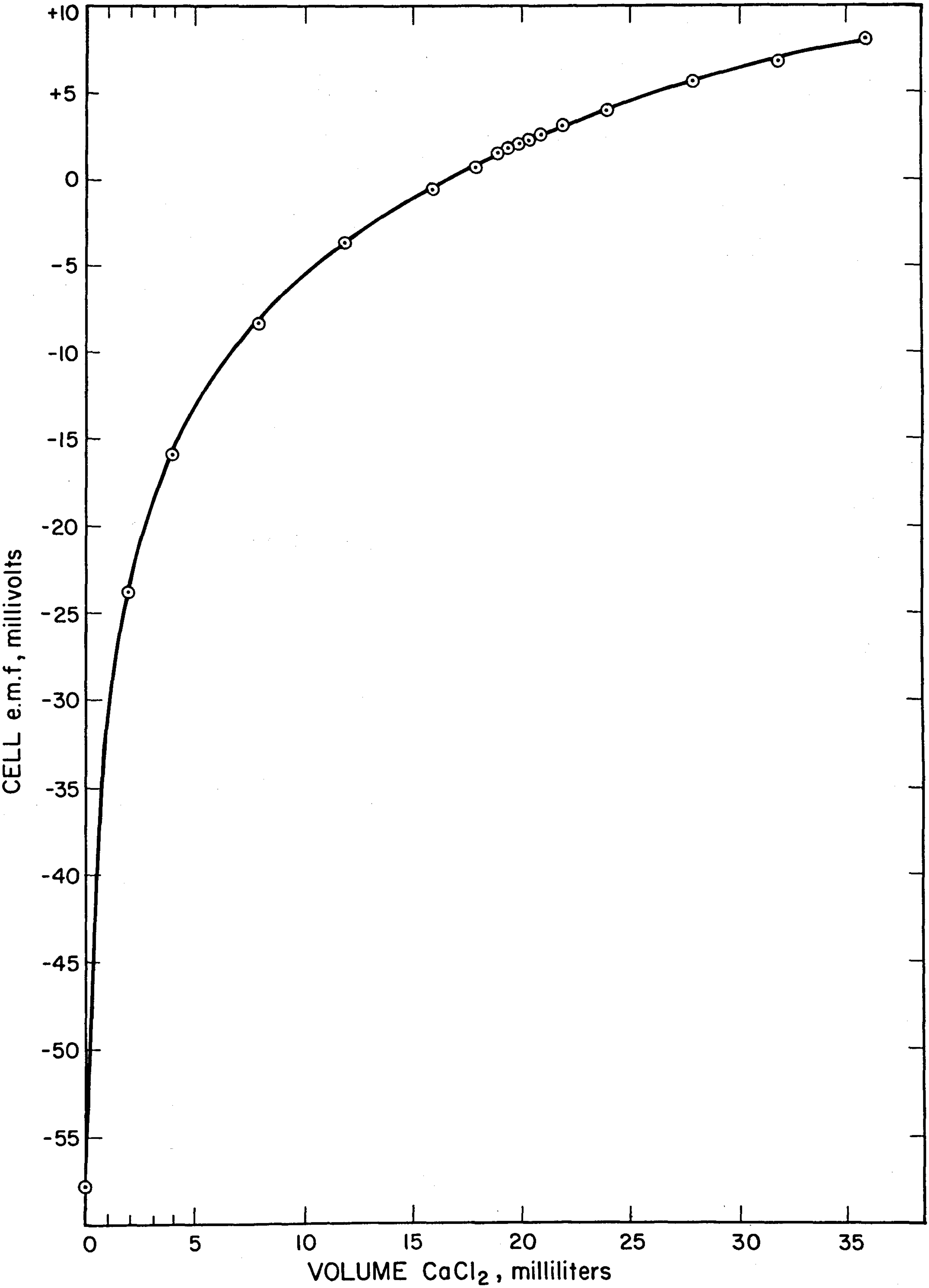
A 0.1000 M solution of NaF was prepared by dissolving 4.2000 grams of the oven-dried (110°C) salt in distilled, deionized water and diluting to one liter. The sample solution was prepared by diluting 4.0 ml of the stock solution to 100 ml with distilled, deionized water. The pH of the sample solutions was adjusted to 7.00 by the addition of 2 M NaOH. The solutions were titrated with 0.0100 M $CaCl_2$ with care being taken that the cell emf had stabilized before the next increment of titrant was added. After each addition, a stable electrode response was obtained within one minute. In the course of the titrations, the pH of the sample solutions dropped to 6.60.

The resulting titration curve is shown in Figure 17. The plot was completely devoid of detail; it was essentially a smooth curve with no break to indicate the end-point. Lingane (86) obtained a straight line with no inflection at the equivalence point. The solubility of calcium fluoride in water was too large to permit the titration of fluoride ion with calcium in purely aqueous media. Lingane was able to carry out successful titrations only by going to a 75% ethanol solution. Use of this media sufficiently decreased the solubility product of calcium fluoride that an end-point was obtained. Such an alternative was not available with the divalent cation-selective electrode because of the incompatibility of the ethanol with the liquid ion-exchange resin, as shown previously.

For the purpose of comparison, the inverse titrations—i.e. the titration of calcium and magnesium with sodium fluoride—were carried out. For these titrations, the sample solution consisted of 10.0 ml of either a 0.0980 *M* $CaCl_2$ solution or a 0.0977 *M* $MgCl_2$ solution added to 90 ml distilled, deionized water. The pH of the test solutions was initially adjusted to 7.0 with 2 *M* NaOH and dropped to a final value of 6.7. The titrant was the 0.1000 *M* solution of sodium fluoride described earlier and, the titrations were carried out in the manner described previously. Waiting periods of 8 to 10 minutes were

FIGURE 17

Titration of Fluoride With Calcium Chloride


+10
+5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
CELL e.m.f, millivolts
0
5
10
15
20
25
30
35
VOLUME $CaCl_2$, milliliters

required to obtain a steady cell emf in the vicinity of the equivalence point. Outside of this region the electrode response was more rapid, with a steady cell emf being obtained in one minute or less.

The resulting titration curves are shown in Figure 18. Comparison of the curves show that the calcium titration was far superior to the magnesium titration. The total potential change from the start of the titration to its conclusion was 57 mv for the calcium samples but only 10 mv for the magnesium solutions. The plot for the magnesium titration was a smooth curve with no break to indicate an end-point. The calcium titration curve appeared to be very good since it had a very large break. However, the potential break did not indicate an end-point close to the theoretical equivalence point. In both cases the solubility of the metal fluoride in water was too large to permit a successful titration.

The theoretical volume of NaF required at the equivalence point in the calcium titration was 19.60 ml and 19.54 ml in the magnesium titration. The potential at the theoretical equivalence point in the calcium titration was -5.8 mv, which corresponded to a calcium ion concentration of 7.4×10^{-4} M[a].

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[a] The concentration of Na^+ at the equivalence point was 1.6×10^{-2} M. The concentration of Ca^{2+} and Mg^{2+} were taken from the electrode response curves in the presence of 1×10^{-2} M NaCl.

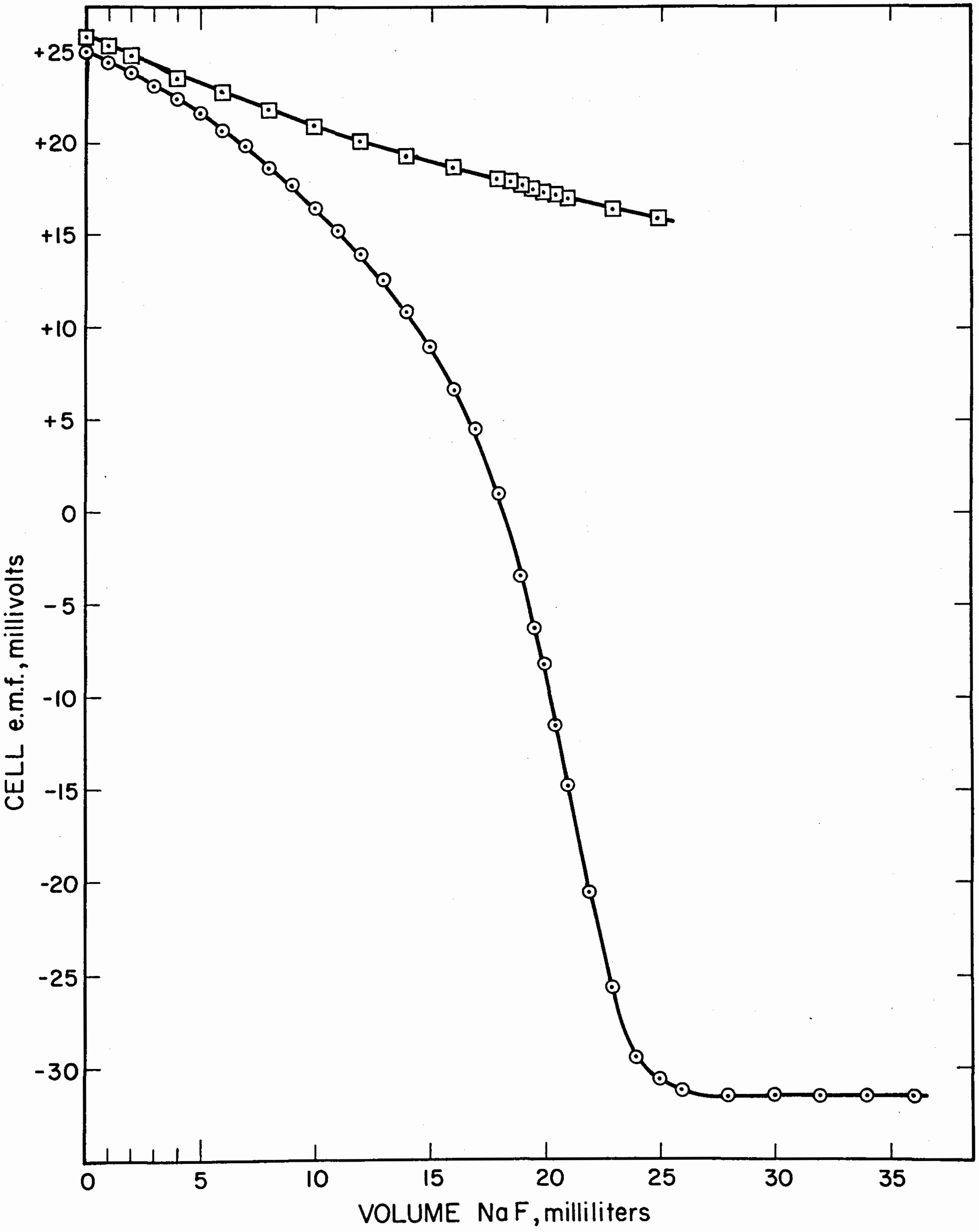
FIGURE 18

Titration of Calcium and Magnesium

With NaF

⊙——⊙ Calcium

⊡——⊡ Magnesium


+25
+20
+15
+10
+5
0
-5
-10
-15
-20
-25
-30
CELL e.m.f., millivolts
0
5
10
15
20
25
30
35
VOLUME NaF, milliliters

Since the concentration of fluoride ion was twice this value, the solubility product was $(7.4 \times 10^{-4})(1.5 \times 10^{-3})^2$, or 1.7×10^{-9}. A similar calculation from the data of the magnesium titration with an equivalence point potential of +17.8 mv gave 2.0×10^{-6} as the solubility product of magnesium fluoride.

The solubility product of 1.7×10^{-9} for CaF_2 agreed well with the value of 5.3×10^{-9} reported by Lingane (86) but differed considerably from the handbook (57) value of 3.95×10^{-11}. The calculated solubility product of 2.0×10^{-6} for MgF_2 also did not agree well with the handbook value of 6.4×10^{-9}. The discrepancy between the experimental and handbook values for the solubility product may be due to the small particle size of the freshly precipitated metal fluorides, for the smaller precipitate particles are more soluble than larger ones.

SUMMARY

The performance of a liquid-membrane electrode selective for divalent cations has been evaluated.

The response of the electrode to calcium and magnesium ions was determined over the range of concentrations from 1 x 10^{-6} to 1.0 M. Plots of cell emf versus the logarithm of the ionic concentration were not linear over the entire concentration range; curvature was observed at high and low concentrations. The concentration range of linear electrode response was dependent upon the anion associated with the alkaline-earth cation. Plots of cell emf versus the logarithm of the ionic activity were linear over the range of concentrations from 1 x 10^{-5} to 1 x 10^{-1} M. The slopes of the activity response curves were in good agreement with the theoretical value predicted by the Nernst equation.

The effect of the monovalent cations Na^+, K^+, and NH_4^+ on the electrode response to Ca^{2+} and Mg^{2+} was determined. Selectivity ratios calculated using the

modified Ross equation were dependent on the concentrations of both monovalent and divalent cations.

The electrode response to calcium and magnesium ions was determined at different pH values. The pH range in which the cell emf was independent of solution pH decreased as the alkaline-earth cation concentration decreased. Deviations in the cell emf were positive in highly acidic solutions and negative in highly basic solutions. Electrode response to calcium and magnesium was at an optimum when the solution pH was between 6.5 and 7.5.

The response of the electrode to other divalent cations was also determined. Plots of cell emf versus ionic concentrations and activities were linear over the range of concentrations from 1×10^{-5} to 1×10^{-1} M. The slopes of the activity-response curves were in good agreement with the theoretical value predicted by the Nernst equation. The selectivity of the electrode for other divalent cations relative to calcium or magnesium was determined by calculating selectivity ratios using the Ross equation. Values of the selectivity ratio calculated from cell emf measured in separate pure solutions and in mixed solutions were in agreement and were not concentration dependent.

The behavior of the liquid ion-exchange resin was determined in a number of organic solvents. Only ethylene glycol appeared to be compatable with the resin. The other organic solvents dissolved either one or both of the components of the liquid ion-exchanger.

The electrode was used for the determination of small amounts of calcium and magnesium by the standard additions method.. Calcium in the range 0.040 to 4.0 mg and magnesium in the 0.024 to 2.4 mg range were quantitatively determined in the presence of a 50 to 100-fold excess of sodium.

A cursory examination of this electrode as a monitor of potentiometric titrations involving calcium and magnesium was performed. EDTA titrations of calcium and magnesium compared favorably with similar titrations using metallochromic indicators. The titration of fluoride with calcium chloride was unsuccessful; the titration curve having no break to indicate the end-point. The titrations of calcium and magnesium with sodium fluoride were slightly better but still not good enough for analytical applications. From the calculated values of K_{sp} for CaF_2 and MgF_2, it appeared that the solubility of the metal fluorides in water was too large to permit successful titrations in purely aqueous solutions.

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