FABRICATION AND EVALUATION OF MEMBRANES AS SPECIFIC ELECTRODES FOR CALCIUM IONS

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ABSTRACT Membranes fabricated from an inert polyvinyl chloride matrix impregnated with tributyl phosphate and with tributyl phosphate plus thenoyl trifluoroacetone were tested as electrodes specific for calcium ions. Both types of membrane exhibited a high specificity for calcium ions in the presence of sodium, magnesium, and barium ions. In the presence of perturbing ions, the usefulness of membranes is limited by both the transport of current and development of potentials by the interfering ion. An experimental method for evaluating these interfering quantities is presented.

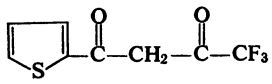
INTRODUCTION

Fabrication of electrodes from membranes with specific permeability towards a single ion has been classified (1) into the following general techniques: (*a*) preparation of porous membranes from materials such as zeolite (2–3); (*b*) incorporation of an insoluble form of the ion being studied into a membrane as a separate phase (4–5); and (*c*) incorporation of specific chelating groups into charged ion exchange membranes (6). So far, membranes fabricated by employing these techniques have not demonstrated satisfactory specificity. A membrane with good specificity towards calcium ions is the multilayer calcium stearate membrane described by Gregor (7). Because of its complicated method of preparation, it has found little use.

In a separate category is the technique of fabricating glass membranes similar to those employed for the measurement of hydrogen ion activity. Considerable success has been achieved with glasses specific for monovalent cations (8) and results have been reported on glasses fabricated into electrodes for the measurement of divalent cations (8–9).

For some time in our laboratory, we have been working on the technique of constructing membranes with the properties of bulk transport for specific metallic ions. Our technique is based on the solvent properties of particular membranes for specific ions with the properties of the membranes determined by the incorporation of selective extractants into the membrane matrix (10).

In this communication, we report on membranes fabricated by incorporating thenoyl trifluoroacetone (TTA)[1]



both as a chelating agent for calcium and as a secondary plasticizer along with tributyl phosphate as the primary plasticizer in a matrix of polyvinyl chloride. The technique has some similarity to that developed by Ross (11) who described the use of liquid ion exchangers as calcium electrodes.

In testing the specificity of the membranes, we have become aware of some of the principal difficulties in characterizing an ion-specific membrane electrode. The purpose of this paper is therefore twofold: to report on the results obtained with our techniques to fabricate an ion-specific membrane for calcium ions; and to discuss the parameters to be measured in characterizing an ion-specific membrane electrode.

EXPERIMENTAL

Preparation of Membranes

The membranes without the chelating agent, TTA, consisting of polyvinyl chloride (PVC) and tributyl phosphate (TBP), were prepared by mixing a 10% (per weight) solution of polyvinyl chloride in cyclohexanone with tributyl phosphate in a ratio PVC TBP of 1:3 (per weight). This mixture was poured in a Petri dish which, in order to ensure homogeneous thickness, was placed in exact horizontal position. After evaporation, an elastic transparent film of good mechanical strength with an uniform thickness of 0.3 mm remained. (The thickness of the film, can, of course, be varied by choice of concentration and amount of mixture used).

To incorporate the chelating agent, the same procedure was followed, using, however, for plasticization of polyvinyl chloride a 25%-solution (per weight) of thenoyl trifluoroacetone (TTA) in tributyl phosphate. The final composition of the membrane after evaporation was therefore PVC:TBP:TTA = 1:3:1.

Measurement of Potentials

The potential developed across the membranes was measured in two different cells. In the first one (see Fig. 1), the membrane was clamped between two halves of a Perspex cell.

The solutions were poured into the two chambers and then calomel electrodes were introduced into the chambers. Radiometer calomel electrodes, K-401, with only a slight leak (10^{-6} mole KCl/hr) were used. The potential between them was less than 1 mv.

In the second cell, the membrane was clamped between two small glass cups (volume of each being about 3 ml), each cup connected to a calomel electrode with the 5-way stopcock of the Cambridge pH meter, Cambridge Instrument Co., Ossining, N. Y. (see Fig. 2).

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[1] Abbreviations used in this communication are: TTA, thenoyl trifluoroacetone; PVC, polyvinyl chloride; and TBP, tributyl phosphate.

This cell allowed a convenient and frequent change of the solutions on both sides of the membrane, and of the liquid junctions between the solutions and the calomel electrodes. There was in this case no contamination of the solutions by KCl, so that this cell gave more accurate and reproducible results, though the first was easier to operate. When the same membrane was measured in both cells, the results obtained were similar within the limit of experimental error of each method.

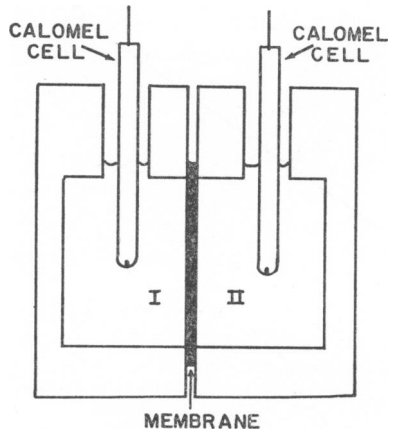

FIGURE 1 Cell for measuring potentials using two low leak calomel electrodes with diffusion stabilized liquid junctions.

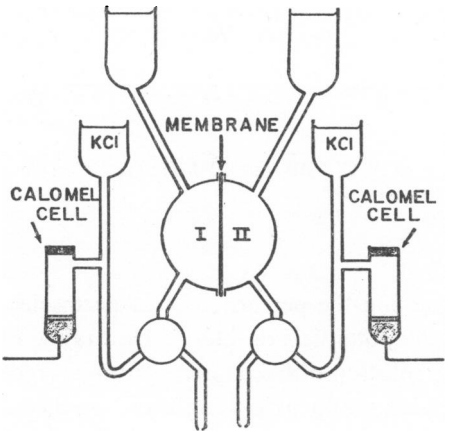

FIGURE 2 Cell for measuring potentials using density stabilized liquid junctions.

For the data presented in Figs. 3–5, the potentials were measured on a Metrohm pH meter, Compensator E388 (Brinkmann Instrument Co., Westbury, N.Y.) which is accurate within ± 0.1 mv. The rest of the data were collected with a Keithly, Model 600A electrometer (Keithly Instrument Co., Cleveland, Ohio) or an equivalent instrument.

As the time to get a reproducible reading varied from a few minutes to a few hours depending on the magnitude of the concentration change (see transients below), a plot was made of the potential versus time. The slope during the 1st minutes was sometimes as high as 10 mv/min. When the slope fell to less than 1 mv/hr, the reading was considered to be sufficiently accurate. The solutions were not stirred during the measurement but solutions were replaced

frequently between measurements. The larger potentials presented in Figs. 3–5 may be considered accurate to within ± 1 mv.

The solutions of $CaCl_2$ were analyzed for Ca^{++} and for Cl^-, and their concentrations were determined to within ± 1%.

All measurements were taken at room temperature, 20.5° ± 0.5°C.

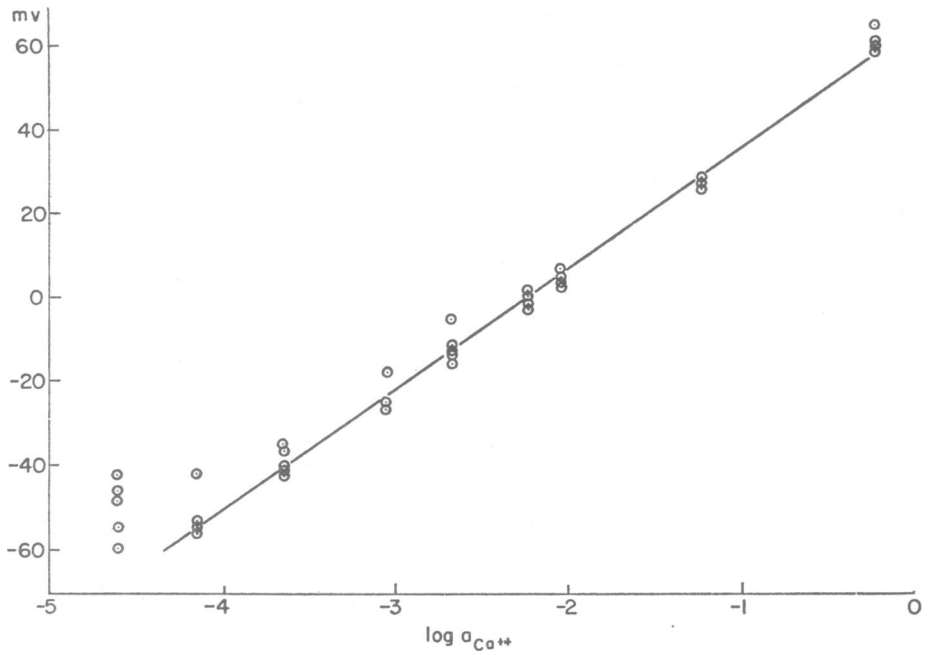

FIGURE 3 emf against log a_{CaCl_2} M of a membrane of PVC, TPB and TTA (1:3:1). Concentration of $CaCl_2$ reference solution: 6.07×10^{-3} M.

RESULTS

Procedure A: The common practice in assaying the performance of permselective membranes involves the measurement of the potentials developed by a range of concentrations of solutions referred to a single solution of fixed concentration. Once this technique yields a voltage response with values approximating those predicted by the Nernst expression, $RT/nf \ln a_2/a_1$, the measurements are repeated with interfering ions added usually only to the solutions which were varied in concentration. Figs. 3–5 illustrate the results of this procedure for calcium ions on two different membranes with interfering solutions containing sodium and magnesium ions. In Figs. 3 and 4, concentrations were converted into activities (12, 13). The plotted line in Fig. 3 represents a slope of 28.9 mv for a tenfold ratio of activities of calcium ion. The slope illustrated in Fig. 4 is 30.0 mv for a tenfold ratio of activities of calcium ion (the theoretical slope is 29.6 mv at 25°C). Fig. 5 illustrates the effect of the perturbing ions, Na^+ and Mg^{++} on the potentials developed by these same mem-

branes. In the experiments illustrated in Fig. 5, the ratio of concentrations of calcium ions was kept constant for each membrane and increasing amounts of the perturbing ion were added to only one side of each membrane until the potential developed was changed significantly. The data of Fig. 5 provide a means of calculating the constants in the empirical equations describing the potentials developed under the

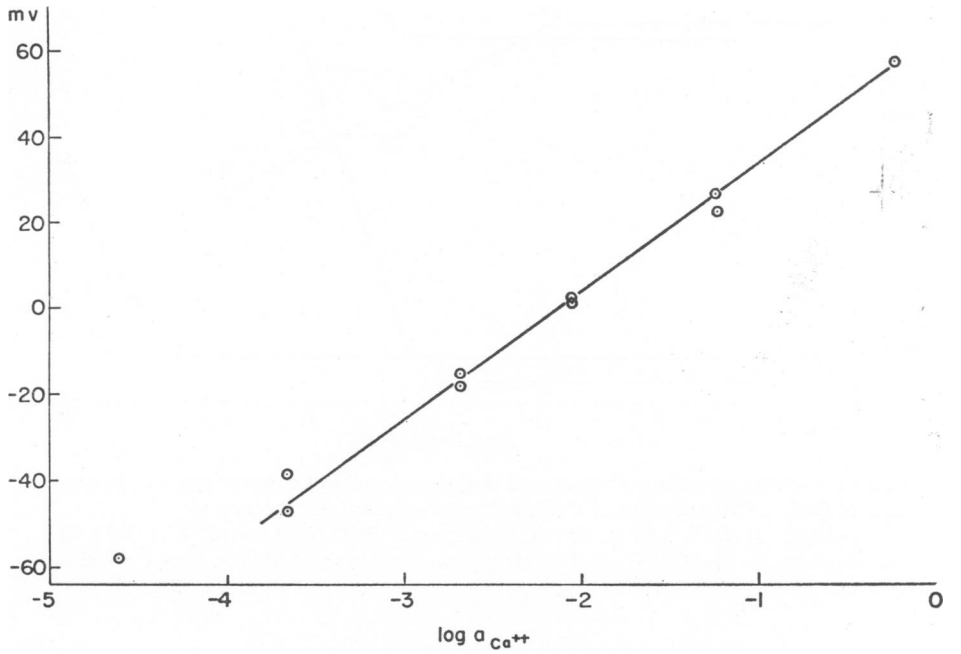

FIGURE 4 emf against log a_{CaCl_2} M of a membrane of PVC and TBP (1:3). Concentration of $CaCl_2$ reference solution: 6.07×10^{-3} M.

conditions for these experiments (9, 14). The equation with Na^+ as the perturbing ion is

$$E = C_{Na} + 29.6 \log (a_{Na}^{2/m} + K_{NaCa}^{1/m} a_{Ca}^{1/m})^m \quad (1)$$

and that for Mg^{++} as the perturbing ion is

$$E = C_{Mg} + 29.6 \log (a_{Mg}^{1/m} + K_{MgCa}^{1/m} a_{Ca}^{1/m})^m \quad (2)$$

where C_{Na}, C_{Mg}, K_{NaCa}, K_{MgCa}, and m are constants, and a_{Ca}, a_{Mg}, and a_{Na} represent the activities of Ca^{++}, Mg^{++}, and Na^+, respectively. The values of the constants K_{NaCa} and K_{MgCa} describe the selectivity of the membrane for calcium ions in the presence of the perturbing ions Na^+ and Mg^{++}, respectively. The larger the

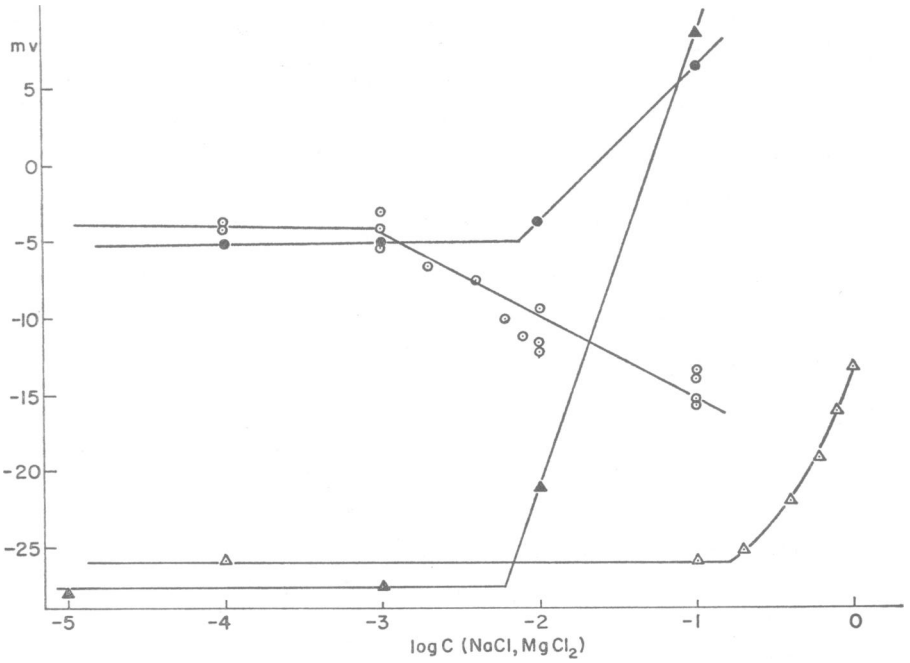

FIGURE 5 Selectivity of membranes: emf against log c of added perturbing salt, in a solution of $CaCl_2$. Concentration of $CaCl_2$ reference solution: 6.07×10^{-3} M.

○—$MgCl_2$ in $CaCl_2$ 3.80×10^{-3} M, membrane of PVC, TBP and TTA (1:3:1); ●—As above, membrane of PVC and TBP (1:3); △—NaCl in $CaCl_2$ 5.33×10^{-4} M, membrane of PVC, TBP and TTA (1:3:1); ▲—As above, membrane of PVC and TBP (1:3).

TABLE I

VALUES FOR CONSTANTS OF EQUATIONS (1) AND (2) WITH Na^+ AND Mg^{++} AS THE PERTURBING ION IN THE MEASUREMENT OF Ca^{++}

Membrane	C_{Na}	C_{Mg}	m		K_{NaCa}	K_{MgCa}
			Na^+	Mg^+		
PVC-TBP (1:3)	66	22	0.36	1.6	2.5	8.7
PVC-TBP-TTA (1:3:1)	1.0	—	1.0	—	180	—

value of the constant, the greater the selectivity for calcium ions. Table I lists the calculated values for the constants describing the data in Fig. 5.

The expected change in potential under the conditions of the experiments illustrated in Fig. 5 derives from the sum of three effects: (*a*) the "bi-ionic" potential where both the transference number and the activity of a perturbing ion determine its contribution to the potential (15), (*b*) the change of the value of the transference

number of the calcium ion in the membrane, and (*c*) the change in activity of the calcium ion in solution on adding the perturbing salt. Of these three effects, the main one is the "bi-ionic" potential resulting in an increase in positive potential (the sign of the potentials are those for the reference solution). The other two effects usually result in a decrease in potential. Thus, there is a tendency for compensating potentials to develop to obscure the effect of perturbing salts before the development of the increase in potential.

The increase in potential occurred for all of the measurements except for those on the effect of Mg^{++} ions. (Similar effects occurred with Na^{+} and Ba^{++}, see below.) With Mg^{++} ions and the PVC, TBP, TTA (1:3:1) membrane, the effect of Mg^{++}

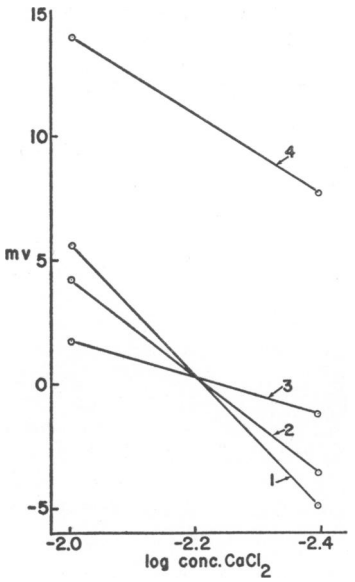

FIGURE 6 Potentials found by measuring a solution, 0.006 M $CaCl_2$, vs two solutions 0.01 and 0.004 M $CaCl_2$ across a PVC + TBP (1:3) membrane. The sign of the potential is that of the 0.006 M $CaCl_2$ solution. *1*, no perturbing ions present; *2*, 0.08 M NaCl added to all three solutions; *3*, 0.4 M NaCl added to all three solutions; *4*, 0.08 M NaCl added only to 0.01 and 0.004 M $CaCl_2$ solutions.

ion was a decrease in the potential (a more negative potential). For a membrane already proved to be highly selective for cations, such a decrease arose from a transient with a long (day or more) half time (see below).

These results lead one to the conclusion that the membranes were performing in a satisfactory manner and may, in fact, be used for the measurement of calcium ion activities in solution with Na^{+} and Mg^{++} ions of concentrations varying from 10–100 times that of the calcium ion solution being measured. With the experimental technique described in Procedure A, both the magnitude of compensating potentials and the quantitative aspects of the transients are left undefined.

Procedure B: An examination of the behavior of a permselective membrane where the experimental design allows for the assay of the value of the transference numbers of the ions involved, as well as transients, is presented in the experiments

illustrated in Figs. 6 and 7 and in the data of Tables II and III. In these experiments, a solution 0.006 M in calcium chloride was measured against two solutions, one 0.01 M, the other 0.004 M in calcium chloride. The effects of the interfering ions were studied by first adding identical concentrations of Na^+, Mg^{++}, and Ba^{++} to all of the three solutions, and then, second, by adding the same concentrations of Na^+, Mg^{++}, and Ba^{++} to only the solutions containing 0.01 and 0.004 M calcium chloride.

The data illustrated in part in Fig. 6 and presented in Table II demonstrate the potential decrease deriving from the decrease in transport number of the measured ion in the membrane, and the increase in potential arising from the potential de-

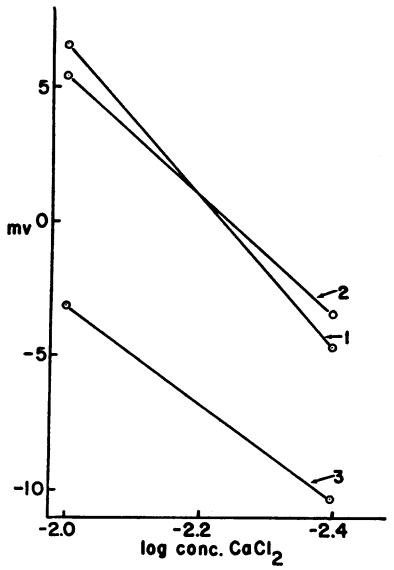

FIGURE 7 Potentials found by measuring a solution, 0.006 M $CaCl_2$, against two solutions, 0.01 and 0.004 M $CaCl_2$, across a PVC + TBP + TTA (1:3:1) membrane. The sign of the potential is that of the 0.006 M $CaCl_2$ solution. *1*, no perturbing ions present; *2*, 0.08 M $MgCl_2$ added to all three solutions; *3*, 0.08 M NaCl added only to 0.01 and 0.004 M $CaCl_2$ solutions

veloped by the interfering cations. When the concentration of the interfering ion is kept the same on both sides of the membrane, the perturbation of the potential developed arises primarily from effects of the interfering ion on the transport of the measured ion across the membrane in the process of developing the equilibrium potential.

The potential developed across a membrane may be expressed as (16, 17)

$$E = -\frac{RT}{F}\sum_i \int_{a_i^I}^{a_i^{II}} \bar{t}_i d \ln a_i \qquad (3)$$

where R, T, and F are the gas constant, temperature, and Faraday, respectively; a_i is the activity of the ith species and $\bar{t}_i$ is the transference number (reduced transport number) of the ith species in the membrane. The transference number of a given

TABLE II

POTENTIALS DEVELOPED BY A 0.0060 M $CaCl_2$ SOLUTION MEASURED AGAINST 0.10 AND 0.004 M $CaCl_2$ SOLUTIONS* ACROSS A POLYVINYL CHLORIDE PLUS TRIBUTYL PHOSPHATE MEMBRANE (1:3) IN THE PRESENCE OF NaCl, $MgCl_2$, AND $BaCl_2$ SOLUTIONS

The sign given is that of the 0.0060 M $CaCl_2$ solution.

Potential of 0.0060–0.010 M pair of solutions	Conc. of perturbing solute in 0.010 M $CaCl_2$	Perturbing solute	Conc. of perturbing solute in 0.0060 M $CaCl_2$	Conc. of perturbing solute in 0.0040 M $CaCl_2$	Potential of 0.0060–0.0040 M pair of solutions
mv	M		M	M	*mv*
+5.6	0.00	—	0.00	0.00	−4.9
+4.2	0.08	NaCl	0.08	0.08	−3.5
+1.8	0.40	NaCl	0.40	0.40	−1.1
+14.0	0.08	NaCl	0.00	0.08	+7.7
+33.0	0.40	NaCl	0.00	0.40	+29.2
+1.8	0.08	$MgCl_2$	0.08	0.08	−1.4
+18.8	0.08	$MgCl_2$	0.00	0.08	+9.2
+3.1	0.08	$BaCl_2$	0.08	0.08	−2.5
+7.2	0.08	$BaCl_2$	0.00	0.08	+3.1

* With these small ratios of concentration, the difference between a concentration and activity ratio is only 4–6% of the value.

TABLE III

POTENTIALS DEVELOPED BY A 0.0060 M $CaCl_2$ SOLUTION MEASURED AGAINST 0.010 M AND 0.0040 M $CaCl_2$ SOLUTIONS ACROSS A MEMBRANE FABRICATED FROM POLYVINYL CHLORIDE, TRIBUTYL PHOSPHATE, AND THENOYL TRIFLUOROACETONE (1:3:1) IN THE PRESENCE OF NaCl, $MgCl_2$, AND $BaCl_2$ SOLUTIONS

The sign given is that of the 0.0060 M $CaCl_2$ solution.

Potential of 0.0060–0.010 M pair of solutions	Conc. of perturbing solute in 0.010 M $CaCl_2$	Perturbing solute	Conc. of perturbing solute in 0.0060 M $CaCl_2$	Conc. of perturbing solute in 0.0040 M $CaCl_2$	Potential of 0.0060–0.0040 M pair of solutions
mv	M		M	M	*mv*
+6.6	0.00	—	0.00	0.00	−4.7
+6.7	0.08	NaCl	0.08	0.08	−4.5
+6.8	0.40	NaCl	0.40	0.40	−5.1
+6.4	1.0	NaCl	1.0	1.0	−4.0
−3.1	0.08	NaCl	0.00	0.08	−10.3
+0.1	0.4	NaCl	0.00	0.4	−10.0
+5.4	0.08	$MgCl_2$	0.08	0.08	−3.5
−12.1	0.08	$MgCl_2$	0.00	0.08	−18.5
−8.0	0.08	$MgCl_2$*	0.00	0.08	−14.8
+6.3	0.08	$BaCl_2$	0.08	0.08	−4.3
−7.0	0.08	$BaCl_2$	0.00	0.08	−8.6

* Measurements made 24 hr after previous experiment.

species is the number of moles of that species transferred across the membrane on the passage of one Faraday of current.

For 1 Faraday of current passed

$$\sum_i \bar{t}_i Z_i = 1 \tag{4}$$

where Z_i is the charge of the species with the transference number $\bar{t}_i$.

For any membrane separating two calcium chloride solutions, the potential becomes

$$\Delta E' = -\frac{RT}{F}\left[\bar{t}'_{Ca} \ln \frac{(a_{Ca})^{II}}{(a_{Ca})^{I}} - \bar{t}_x' \ln \frac{(a_x)^{II}}{(a_x)^{I}} + \bar{t}_w' \ln \frac{(a_w)^{II}}{(a_w)^{I}}\right] \tag{5}$$

where the primed values of the transference numbers refer to average values within the membrane and the subscripts Ca, x, and w refer to the calcium ion, chloride ion, and water, respectively. It is assumed that the large organic anions are equivalent to fixed negative charges within the matrix of the membrane. For a membrane with fixed negative charges, the transference number of the mobile anions, $\bar{t}_x$, is negative and the transference number of the water, $\bar{t}_w$, will be positive. Since the ratio of activities of the water will be the inverse of that of the salt, the sign of the net effect of any water flux will be the same as that for an anionic flux. Thus the result of a water flux will be a decrease in the observed potential developed by the cation.

The data on the two membranes illustrated in Figs. 3, 4, 6, and 7 indicate that the anionic and water fluxes in the membrane lower the potential by only a small (although significant) amount. A small error is thus introduced in the analysis of the effects of the perturbing cations, Na^+, Mg^{++}, and Ba^{++} when the apparent potential, $\Delta E'$, in the absence of these cations is written as

$$\Delta E' = -\frac{RT}{F}\bar{t}'_{Ca} \ln \frac{(a_{Ca})^{II}}{(a_{Ca})^{I}} \tag{6}$$

and the apparent potential in the presence of sodium as a perturbing cation is written

$$\Delta E' = -\frac{RT}{F}\bar{t}'_{Ca} \ln \frac{(a_{Ca})^{II}}{(a_{Ca})^{I}} - \frac{RT}{F}\bar{t}'_{Na} \ln \frac{(a_{Na})^{II}}{(a_{Na})^{I}} \tag{7}$$

The presence of identical concentrations of sodium ion in all three solutions results in the value of zero for $\ln (a_{Na})^{II}/(a_{Na})^{I}$ and introduces only minor perturbations in the values of $\ln (ai)^{II}/(ai)^{I}$ of the other species. The main perturbation resulting from the addition of sodium ion will be that affecting the transport number of the calcium ion as given in equation (2). In the presence of sodium ion (assuming $\bar{t}'_{Cl^-} = 0$)

$$2\,\bar{t}'_{Ca} + \bar{t}'_{Na} = 1.$$

Thus, the depression of the potential observed in the data presented in Figs. 6 and 7 due to the presence of sodium and other perturbing ions may be attributed to the decreases in the values of $\bar{t}'_{Ca}$ because of a significant value of the transference number of the perturbing ion in the membrane. Table IV summarizes the approximate average values of $\bar{t}'_{Ca}$ calculated from the data of Tables I and II, and equations (7) and (8) with the assumptions already specified. Identical activities of perturbing ions on both sides of the membrane will depress the calcium ion potential when there is a significant transport of the perturbing ion in the membrane, but unequa

TABLE IV

APPROXIMATE AVERAGE TRANSPORT NUMBERS ($z_{Ca}\bar{t}'_{Ca}$) FOR CALCIUM IONS IN TWO POLYVINYL CHLORIDE MEMBRANES IN THE PRESENCE OF Na^+, Mg^{++}, AND Ba^{++} IONS

Concentration of calcium solutions: 0.0040–0.010 M in $CaCl_2$.

Membrane	Concentration perturbing ion M	$z_{Ca}\bar{t}'_{Ca}$
PVC + TBP (1:3)	0.00	1.0 (assumed)
	0.08 Na^+	0.73
	0.40 Na^+	0.28
	0.08 Mg^{++}	0.31
	0.08 Ba^{++}	0.53
PVC + TBP + TTA (1:3:1)	0.00	1.0 (assumed)
	0.08 Na^+	0.99
	0.40 Na^+	1.05
	1.00 Na^+	0.92
	0.08 Mg^{++}	0.79
	0.08 Ba^{++}	0.94

activities of the perturbing ion could generate a potential to compensate for that lost from the calcium ions. The data of Figs. 5 and 6 and Tables I and II demonstrate this effect with the perturbing ions added to the 0.004 and 0.01 M $CaCl_2$ solutions but not added to the 0.006 M (reference) solution.

Transients: The response of the two membranes varied considerably with respect to the time for equilibration. The PVC-TBP (1:3) membrane equilibrated relatively rapidly with periods from 3–15 min for all solutions used in the measurements. The PVC-TBP-TTA (1:3:1) membrane equilibrated rapidly with the calcium chloride solutions alone and with equal concentrations of perturbing ions in all solutions, but equilibrated slowly (more than a 24 hr half-time) when the perturbing solutions were placed only on one side of the membrane (see Table II) to give an apparent equilibrium. The potentials found, in addition, were negative (the sign of

the potential was that of the 0.006 M $CaCl_2$ solution) rather than more positive than those without the perturbing solute. Inspection of the potentials over a period of several days revealed a gradual shift to more positive values with minor changes in slope. The effect of Mg^{++} on the measured Ca^{++} potential is demonstrated in Fig. 7. This illustrates the fact that while the magnitude of the potentials changed, the slope, or potential for a given concentration ratio, was reduced by 40%. A membrane which performs in this manner would tend to give useful analytical results under ordinary limited testing procedures.

DISCUSSION

When calcium or any other single ion activity is to be measured with a permselective membrane in a manner similar to the conventional one used for the hydrogen ion, careful measurement is necessary to detect quantitatively the perturbations introduced by other cations. If an assay of the change in potential as a function of concentration yields the Nernst value, additional measurements are required for full characterization of the membrane. Data are presented in this communication emphasizing the following interrelated points: (*a*) sign and value of the potential measured, (*b*) transport number of the cations in the membrane, and (*c*) contribution of the interfering ion toward the measured potential.

Both the absolute value (corrected for the contribution of the measuring electrodes) and sign of the measured potential across a membrane are of particular importance. Examination of only the potential per concentration difference across the membrane may easily lead to erroneous conclusions. If the sign of a measured potential is taken as that of a reference solution (solution *I*) containing calcium chloride on one side of a membrane with a solution (solution *II*) of higher concentration on the other side then the expected sign is a positive one. A positive increase alone on increasing the concentration of solution *II* is not sufficient in characterizing the membrane. If no transients are present, the addition of an interfering cation will tend to both decrease the absolute value of the potential arising from the calcium ion and increase the positive potential across the membrane. These two effects can be separated by keeping the activity ratio of the interfering ion at unity. Under these experimental conditions, the perturbing effect of the interfering ion on the calcium ion potential is one decreasing the value of the transport number of the calcium ion, thereby reducing the magnitude of the membrane potential whether negative or positive. Once the effect of a perturbing ion on the transport number of the calcium is evaluated, the potential contributed by the perturbing ion can be determined. With a reference solution of only $CaCl_2$, perturbing cations will introduce a positive potential increment in the measurement. With assumptions regarding mainly the transport numbers of anions and water, the effects of perturbing ions can be evaluated provided transient potentials are of short duration.

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