

Selectivity Studies on Liquid Membrane, Ion-Selective Electrodes

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A series of anion-selective electrodes of the liquid membrane type has been rigorously examined with respect to selectivity characteristics using three different experimental methods. This evaluation gives, for the first time, an understanding of how selectivity ratios depend on concentration levels and other variables and yields a recommended procedure for the consistent numerical determination of selectivity ratios. The resulting selectivity data are examined in terms of a theory of liquid membrane electrodes.

SINCE THE INTRODUCTION of the liquid membrane electrode selective for calcium in 1967 (1), many new electrodes of this type with selective response to both cations and anions have become available. Evaluative studies (2-6) of these electrodes have demonstrated the Nernstian response and dynamic range of these electrodes, but have also revealed their gradual loss of selectivity and general deterioration with time under extended use.

Generally speaking, the selectivities of liquid membrane electrodes for the ion of primary interest with respect to common interfering ions are only moderate (7-8). Nevertheless, the electrodes have been successfully employed analytically for direct potentiometry or potentiometric titrations (3, 5, 6, 9-13) under suitable conditions where interfering ions are absent or present in low concentrations.

If the full usefulness of ion-selective electrodes of the liquid membrane type is to be realized, reliable methods of establishing their selectivity characteristics and accurate numerical data on selectivities must be made available. Unfortunately, there is little agreement in the literature regarding optimal methods of determining selectivities or, even, on the selectivity ratios of a specified electrode. In part, this difficulty arises from a lack of systematic study and from the tendency to report selectivities under a single, and often arbitrary, set of conditions.

In this paper we, therefore, set out to evaluate the selectivities of a series of anion-selective, liquid membrane electrodes

systematically under a wide range of solution variables and by a number of different experimental methods under carefully controlled conditions. Meaningful and consistent data can be obtained and these data can be understood in terms of a theoretical treatment (14) of liquid ion-exchange electrodes.

THEORETICAL

The potentials measured with liquid membrane electrodes in solutions containing the primary ion and any other ion to which the electrode responds, have been found to fit the empirical equation

$$E = E_o - 2.303 \frac{RT}{F} \log (a_1 + Ka_2) \quad (1)$$

where a_1 = activity of the primary univalent anion 1

a_2 = activity of any other univalent anion 2, to which the electrode responds

and K = selectivity ratio of anion 2 for the given electrode.

The selectivity ratio can be evaluated, using this equation, by carrying out potentiometric measurements in solutions containing mixtures of the ions of interest or by utilizing a series of solutions each containing only a single salt. Three major evaluative methods may be used.

Method I. The potential of an ion-selective electrode in a solution containing only the primary univalent anion is given by

$$E_1 = E_o - 2.303 \frac{RT}{F} \log a_1 \quad (2)$$

If the solution does not contain the primary anion but any other univalent anion with a selectivity ratio K , the potential of the electrode in such a solution can be expressed by Equation 3, obtained by substituting $a_1 = 0$ in Equation 1:

$$E_2 = E_o - 2.303 \frac{RT}{F} \log K - 2.303 \frac{RT}{F} \log a_2 \quad (3)$$

If $a_1 = a_2$,

$$\log K = \frac{E_1 - E_2}{2.303 RT/F} \quad (4)$$

It has been usual, following Eisenman, to calculate K from values of E_1 and E_2 measured at a concentration of 0.1M (15, 16). However, K can be obtained from measurements at any other concentration, as long as the two ions are at the same activity in their respective solutions.

Method II. If Equations 2 and 3 are combined with $E_1 = E_2$, we get

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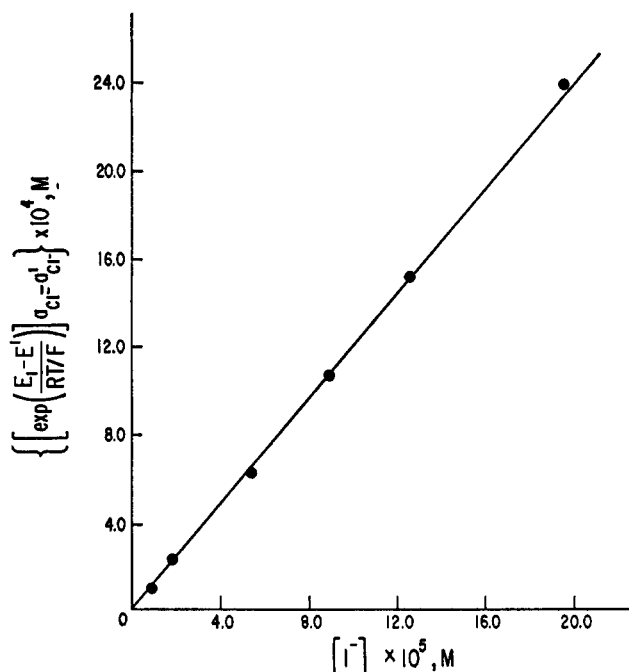


Figure 1. Selectivity plot for iodide with chloride ion-selective electrode (Test of Equation 9)

$$K = \frac{a_1}{a_2} \quad (5)$$

where a_1 and a_2 are the activities of the two ions which produce the same potential when present separately. There is no indication in the literature regarding the use of Equation 5 for evaluating K , although Rechnitz and co-workers (16) have given a definition of selectivity ratio on the basis of this equation.

Method III. Methods I and II involve measurements in solutions containing only one of the ions in any test solution. In method III, the potential of the electrode in a solution containing both the ions is utilized in the calculation. Combining Equations 1 and 2, one obtains

$$E_1 - E = 2.303 \frac{RT}{F} \log \left(\frac{a_1 + Ka_2}{a_1} \right) \quad (6)$$

which can be rearranged to give an explicit expression for K ,

$$K = \frac{\left(\exp \left\{ \frac{E_1 - E}{RT/F} \right\} \right) a_1 - a_1}{a_2} \quad (7)$$

Light and Swartz (15) have employed method III to evaluate selectivity ratios for the sulfide ion-selective electrode, by measuring E_1 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 III (Graphical). Instead of using Equation 7 to calculate the selectivity ratio from only two potential measurements, one in a pure solution of anion 1 and the other in a mixture of anion 1 and anion 2, a graphical procedure involving a series of measurements can be adopted. Experimentally, the potential E_1 is first measured in a known volume of the solution containing anion 1 at an activity a_1 and known volumes of a stock solution containing anion 2 are added successively, the potential E' being measured after each addition. Thus a series of values of E' is obtained, each

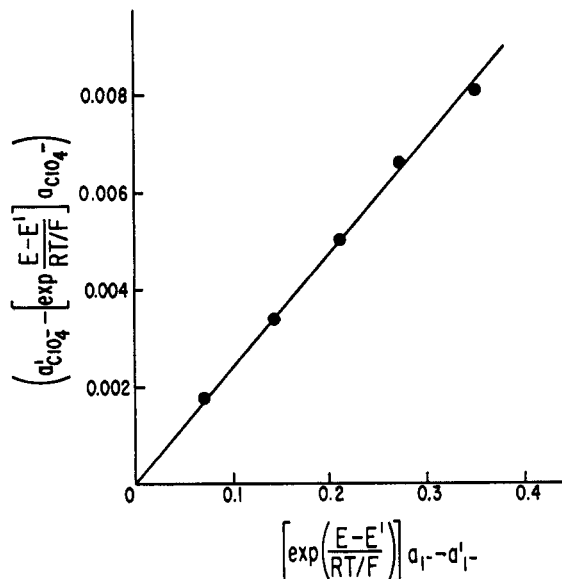


Figure 2. Selectivity plot for iodide with perchlorate ion-selective electrode (Test of Equation 10)

value corresponding to a set of values for the activities of anion 1 and anion 2 in the same solution. Alternatively, E' may be measured in a series of separately prepared solutions containing varying activities of the two ions.

If E' is the potential measured in any one of the series of solutions, it is given by

$$E' = E_o - 2.303 \frac{RT}{F} \log (a'_1 + Ka'_2) \quad (8)$$

Combining Equations 2 and 8, one obtains

$$\left[\exp \left\{ \frac{E_1 - E'}{RT/F} \right\} \right] a_1 - a'_1 = Ka'_2 \quad (9)$$

If the left hand side of Equation 9 is plotted against a'_2 , the graph should be a straight line passing through the origin and its slope should give the value of the selectivity ratio K .

However, a different procedure is called for when evaluating low values of K . In such cases, the potential will not be sensitive to small increments of concentration of the anion 2. A series of values of E' will, therefore, have to be measured varying the concentration of the primary anion, while keeping the concentration of the other anion at a fairly high value.

Combining Equations 1 and 8 and rearranging,

$$a'_1 - \left[\exp \left\{ \frac{E - E'}{RT/F} \right\} \right] a_1 = K \left[\left(\exp \left\{ \frac{E - E'}{RT/F} \right\} \right) a_2 - a'_2 \right] \quad (10)$$

A plot of the left hand side of Equation 10 against the function within the brackets on the right hand side should be a straight line passing through the origin and its slope should give the value of the selectivity ratio, K .

EXPERIMENTAL

The liquid membrane electrodes utilized in this study are the nitrate ion-selective electrode (model 92-07), the chloride ion-selective electrode (model 92-17), and the perchlorate ion-selective electrode (model 92-81), all obtained from Orion Research, Inc. EMF measurements are made using a Beckman Expandomatic pH meter with a saturated calomel electrode (Leeds & Northrup) as the reference electrode.

Table I. Selectivity Ratio of Chlorate for Nitrate Ion-Selective Electrode

[NO ₃ ⁻], (<i>M</i>)	Method I			Method II			Method III (Graphical)		
	<i>a</i> _{NO₃⁻} , (<i>M</i>)	Inst.	Steady	<i>a</i> _{NO₃⁻} , (<i>M</i>)	<i>a</i> _{ClO₃⁻} , (<i>M</i>)	<i>K</i>	Level of <i>a</i> _{NO₃⁻}	Range of <i>a</i> _{ClO₃⁻}	<i>K</i>
0.100	0.0755	1.71	1.41	0.0755	0.0521	1.45
0.010	0.00899	1.66	1.29	0.00899	0.00713	1.26	0.0090	0.0033– 0.0090	1.21
0.0010	0.000964	1.55	1.37	0.000964	0.000714	1.35	0.00096	0.00035– 0.0010	1.23
0.00010	0.000099	1.00	1.23	0.000099	0.0000812	1.22	0.000099	0.000036– 0.0001	1.14

Table II. Selectivity Ratio of Bromide for Nitrate Ion-Selective Electrode

[NO ₃ ⁻], (<i>M</i>)	Method I			Method II			Method III (Graphical)		
	<i>a</i> _{NO₃⁻} , (<i>M</i>)	<i>K</i>		<i>a</i> _{NO₃⁻} , (<i>M</i>)	<i>a</i> _{Br⁻} , (<i>M</i>)	<i>K</i>	Level of <i>a</i> _{NO₃⁻}	Range of <i>a</i> _{Br⁻}	<i>K</i>
		Inst.	Steady						
0.100	0.0755	0.15	0.16	0.00985	0.0755	0.13
0.010	0.00899	0.17	0.15	0.00116	0.00899	0.13	0.03	0.013– 0.024	0.09
0.0010	0.000964	0.27	0.20	0.000177	0.000964	0.18	0.003	0.0015– 0.0028	0.11
0.00010	0.000099	0.28	0.24	0.0005	0.0014– 0.0024	0.13

Table III. Selectivity Ratio of Iodide for Nitrate Ion-Selective Electrode

[NO ₃ ⁻], (<i>M</i>)	Method I			Method II			Method III (Graphical)		
	<i>a</i> _{NO₃⁻} , (<i>M</i>)	<i>K</i>		<i>a</i> _{NO₃⁻} , (<i>M</i>)	<i>a</i> _{I⁻} , (<i>M</i>)	<i>K</i>	Level of <i>a</i> _{NO₃⁻}	Range of <i>a</i> _{I⁻}	<i>K</i>
		Inst.	Steady						
0.100	0.0755	16.2	21.5	0.0755	0.00463	16.3	0.075	0.0026– 0.012	15.7
0.010	0.00899	15.1	22.2	0.00899	0.000746	12.0	0.009	0.0003– 0.0015	12.5
0.0010	0.000964	13.6	16.9	0.000964	0.000157	6.1	0.00096	0.00003– 0.00016	8.9
0.00010	0.000099	5.1	8.9	0.000099	0.0000362	2.7	0.000099	0.000003– 0.000016	3.2

Table IV. Selectivity Ratio of Bromide for Chloride Ion-Selective Electrode

[Cl ⁻], (<i>M</i>)	Method I			Method II			Method III (Graphical)		
	<i>a</i> _{Cl⁻} , (<i>M</i>)	<i>K</i>		<i>a</i> _{Cl⁻} , (<i>M</i>)	<i>a</i> _{Br⁻} , (<i>M</i>)	<i>K</i>	Level of <i>a</i> _{Cl⁻}	Range of <i>a</i> _{Br⁻}	<i>K</i>
0.100	0.0755	Inst. 2.86	Steady 2.79	0.0755	0.0202	3.73	0.0755	0.02–0.04	3.42
0.0100	0.00899	3.00	2.88	0.0296	0.00899	3.29	0.0172	0.004–0.017	3.47
0.0010	0.000964	2.29	2.70	0.00288	0.000964	2.99	0.00186	0.00037–0.0018	2.95
0.00010	0.000099	1.29	1.72	0.000202	0.000099	2.04	0.00019	0.000038–0.00019	2.58

For measurements with the perchlorate and chloride electrodes, the reference electrode is used in conjunction with a Fisher remote reference junction filled with 4*M* sodium chloride solution and 10⁻³*M* sodium fluoride solution, respectively.

Sodium salts are used as sources of the anions studied and all stock solutions are prepared by weight from reagent grade chemicals. EMF measurements are made under constant conditions by taking 50 ml of solution for each measurement in a cell thermostated at 25 ± 0.1 °C, immersing the electrodes to a constant depth in the solution, and stirring at a constant rate by means of a magnetic stirring bar.

RESULTS AND DISCUSSION

Figure 1 shows a typical plot for the evaluation of the selectivity ratio with respect to iodide for the chloride ion-selective electrode using Equation 9. In making this plot and in the entire study, ionic concentrations have been converted to activities using the ion activity coefficients tabulated by Kielland (17). Figure 2 shows a selectivity plot which has

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Table V. Selectivity Ratio of Nitrate for Chloride Ion-Selective Electrode

[Cl ⁻], (M)	Method I			Method II			Method III (Graphical)		
	a_{Cl^-} , (M)	K		a_{Cl^-} , (M)	$a_{\text{NO}_3^-}$, (M)	K	Level of a_{Cl^-}	Range of $a_{\text{NO}_3^-}$	K
0.100	0.0755	4.14	4.09	0.0755	0.01282	5.89	0.0755	0.02–0.04	4.38
0.0100	0.00899	4.12	3.97	0.0438	0.00899	4.90	0.017	0.004–0.015	4.67
0.0010	0.000964	2.58	3.10	0.00361	0.000964	3.77	0.002	0.0004–0.0018	4.15
0.00010	0.000099	1.28	1.68	0.000218	0.000099	2.20	0.0002	0.00004–0.00019	2.62

Table VI. Selectivity Ratio of Iodide for Chloride Ion-Selective Electrode

[Cl ⁻], (M)	Method I			Method II			Method III (Graphical)		
	a_{Cl^-} , (M)	K		a_{Cl^-} , (M)	a_{I^-} , (M)	K	Level of a_{Cl^-}	Range of a_{I^-}	K
0.100	0.0755	23.1	17.1	0.0755	0.00283	26.7	0.0755	0.02–0.04	23.9
0.0100	0.00899	21.2	16.3	0.0166	0.000964	17.6	0.009	0.00036–0.008	20.7
0.0010	0.000964	10.8	13.3	0.00899	0.000512	17.3	0.002	0.00036–0.0018	14.8
...	0.002	0.000009–0.0002	11.9
0.00010	0.000099	1.6	4.4	0.000469	0.000099	4.8	0.0002	0.0000038–0.00004	6.0

Table VII. Selectivity Ratio of Iodide for Perchlorate Ion-Selective Electrode

[I ⁻], (M)	Method I			Method II			Method III (Graphical)		
	a_{I^-} , (M)	K		[ClO ₄ ⁻] ^a	[I ⁻]	K	Level of [I ⁻]	Range of (ClO ₄ ⁻)	K
0.100	0.0755	0.013	0.016	0.00115	0.1	0.012	0.1	0.002–0.009	0.023
0.010	0.00899	0.020	0.015	0.00015	0.01	0.015	0.05	0.004–0.007	0.020
0.001	0.000964	0.046	0.030	0.00003	0.001	0.030
0.00010	0.000099	0.154	0.071

^a The ionic strength in perchlorate solutions was maintained equal to that in the iodide solution by means of sodium chloride.

been constructed employing Equation 10, for evaluating the selectivity ratio of iodide for the perchlorate ion-selective electrode. The straight line graphs passing through the origin, obtained as in Figures 1 and 2, when experimental data are plotted according to Equations 9 and 10, are in accord with theoretical expectations showing that the graphical procedure can be employed with confidence for the evaluation of selectivity ratios.

Nitrate Ion-Selective Electrode. The values of the selectivity ratios of chlorate, bromide, and iodide ions for the nitrate ion-selective electrode evaluated at different concentration levels by the three different methods are given in Tables I, II, and III, respectively. Two sets of values are given under method I, one set calculated on the basis of potentials measured immediately after the introduction of the electrodes into the solution and the second set calculated on the basis of the steady values of the potentials, the times required for the attainment of the steady value ranging from 5 to 30 minutes.

In the case of chlorate and bromide, for which the selectivity ratios are low, the three methods give values which agree reasonably well. However, methods I and II, which depend on measurements in pure solutions, yield slightly higher values than method III, in which measurements are made in solutions containing both anions. The high selectivity case of iodide is quite different. Here method I gives values which are different from those given by methods II and III, which show reasonably good agreement among themselves. This observation can be correlated with the iodide concentration employed at each level of nitrate concentration in the three methods. In the first method, the iodide concentration is equal to the nitrate concentration while in the other two methods the iodide concentrations are low compared to nitrate. It is interesting that the instantaneous values obtained in the first method agree with the values of methods II and III at comparable iodide activities. It can be concluded that the selectivity ratio for iodide is concentration-dependent below 0.01M, decreasing with further dilution.

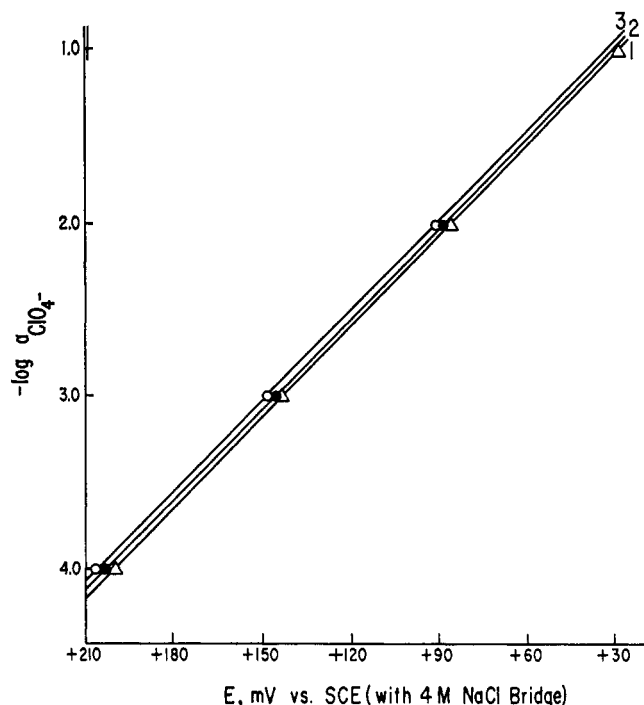


Figure 3. Response of perchlorate ion-selective electrode to perchlorate ion in (1) 0.1M NaCl, (2) 0.1M HCl, and (3) 0.1M NaOH

Chloride Ion-Selective Electrode. Tables IV, V, and VI contain the selectivity ratio values of bromide, nitrate, and iodide, respectively, for the chloride ion-selective electrode. Here again, the same general features are noticed. The fall in the value of the selectivity ratio at low concentrations, which is very evident in the case of iodide, is also noticeable in the case of bromide and nitrate.

Perchlorate Ion-Selective Electrode. The perchlorate ion-selective electrode has been known to show poor response to ions other than hydroxide and iodide, for which the manufacturer's instruction manual (8) gives a selectivity ratio of 1.0 and 1.2×10^{-2} , respectively. Table VII gives the values of the selectivity ratio for iodide obtained in this study. They compare well with the manufacturer's value. The increase noticed at the lowest concentration using method I could be attributed to the introduction of some perchlorate into the iodide solution by the dissolution of the membrane resin itself.

In the case of the hydroxide ion, however, preliminary experiments gave results inconsistent with the reported selectivity ratio of 1.0 for this ion. The potentials of the perchlorate ion-selective electrode in sodium iodide and sodium hydroxide solutions at different concentrations are given in Table VIII. While in the case of iodide the potential becomes less positive with increase in concentration as required theoretically for an ion to which the electrode responds, in the case of hydroxide the potential is found to be more positive at the higher concentrations. Also, according to the plot of potential *vs.* pH at constant perchlorate concentration and at constant ionic strength given by Hseu and Rechnitz in their evaluation of the perchlorate ion-selective electrode (5), the potential becomes more positive at high pH values. In view of these observations, there seems to be an indication of a shift in the E_0 value of the electrode at different hydroxide concentration levels rather than a response for the hydroxide ion equal to that of the perchlorate ion. Indeed, calibration curves for perchlorate having a Nernstian slope can be obtained even in the presence of 0.1M NaOH. Figure

Table VIII. Potentials of Perchlorate Ion-Selective Electrode in Solutions of Sodium Iodide and Sodium Hydroxide

Concn, (M)	Potential (mV <i>vs.</i> SCE with 4M NaCl bridge)	
	I ⁻	OH ⁻
0.1	+138	+297
0.01	+173	+268
0.001	+205	+260
0.0001	+235	+270

3 shows potential *vs.* concentration plots obtained with the perchlorate ion-selective electrode in solutions of sodium perchlorate in presence of 0.1M NaOH, 0.1M HCl, and 0.1M NaCl. The three plots are closely spaced straight lines having almost the same slope. Thus, it should be possible to use the perchlorate ion-selective electrode at both low and high pH values, if calibration and sample measurements are made at the same concentration of acid or base.

The selectivity studies with the nitrate, chloride, and perchlorate ion-selective electrodes show that the graphical procedure for the evaluation of selectivity ratios yields consistent values. This procedure, involving measurements in solutions containing both the ions, is preferable to the other two methods in that it produces less change in the nature and composition of the membrane phase and also corresponds more closely to practical analytical situations where the primary ion has to be estimated in the presence of the interfering ion.

Our finding that the selectivity ratios of ions with high values of K show a definite decrease at low concentrations requires theoretical explanation. The question arises whether this cannot be an artifact of the changes in solution concentration, affecting the result *via* ionic strength and liquid junction changes on the reference side. The ionic strength effect has, however, been taken into account by converting the concentrations to activities employing the available ion activity coefficients. Changes in liquid junction potential on the reference side can be ruled out because only potential values resulting from small step changes in the concentration of one of the ions are used in the evaluation of K by the graphical method. Each value of K is, therefore, evaluated from potential differences measured in solutions having essentially the same liquid junction. Moreover, the calibration graphs obtained from measurements in pure solutions of the ions in the concentration range of $10^{-4}M$ to $10^{-1}M$ give a Nernstian slope, indicating that even wide differences in concentrations do not sufficiently change the liquid junction potential to invalidate the basic relationship. The observed decrease in selectivity ratio at low concentration should, therefore, be considered in the light of presently available theories of liquid ion-exchange membrane electrodes.

Sandblom, Eisenman, and Walker (14) have deduced an expression for the potential of a liquid ion-exchange membrane for the special case of two counter ions and strong association between ion and site in the membrane phase; we conclude that this case corresponds most nearly to these commercially available liquid membrane ion-selective electrodes. The following expression can be written for this potential when the electrode is anion-selective:

$$E = \text{constant} - (1 - \tau) \frac{RT}{F} \ln \left(a_1 + \frac{u_2 + u_s}{u_1 + u_s} \frac{k_2}{k_1} a_2 \right) - \tau \frac{RT}{F} \ln \left(a_1 + \frac{u_2}{u_{1s}} \frac{k_2}{k_1} \frac{K_1}{K_2} a_2 \right) \quad (11)$$

Here u_1 , u_2 , u_s , u_{1s} , and u_{2s} are the mobilities in the membrane phase of anion 1, anion 2, the dissociated resin cation, the undissociated ion pair of the resin cation and anion 1, and the undissociated ion pair of the resin cation and anion 2, respectively. k_1 and k_2 are constants related to the standard chemical potentials of anion 1 and anion 2, respectively. In the external solution and membrane phase, K_1 and K_2 are dissociation constants of ion pairs of the exchanger cation with anion 1 and anion 2, respectively, and

$$\tau = \frac{u_s(K_1 u_{2s} - K_2 u_{1s})}{(u_1 + u_s)u_{2s}K_1 - (u_2 + u_s)u_{1s}K_2} \quad (12)$$

Equation 11 differs from the empirical Equation 1 in that the former consists of two logarithmic terms, each having the same form as the single term in Equation 1. However, if τ is very nearly unity or zero, one of the two terms in Equation 11 becomes negligible and Equation 11 reduces to the same form as Equation 1. Alternatively, as has been suggested by Sandblom, Eisenman, and Walker (14), Equation 11 can be replaced with good approximation by an equation consisting of a single logarithmic term, by introducing "average ionic selectivities." Hence, the selectivity ratio appearing in Equation 1 may be regarded only as an average value and, therefore, may show the kind of variation we found experimentally. Further, the selectivity ratio in the second logarithmic term of Equation 11 has been equated to the ion-exchange equilibrium constant since it is reasonable to assume that $u_{1s} = u_{2s}$ (14). However, in the derivation of Equation 11, the dissociation constants K_1 and K_2 have been defined only in terms of concentrations of the various species in the membrane phase and not in terms of their activities. Con-

sequently, the quantity $\frac{k_2}{k_1} \frac{K_1}{K_2}$ is only the ion-exchange selectivity coefficient and not the ion-exchange equilibrium constant. It is interesting to note that the ion-exchange selectivity coefficients of certain anions in the case of solid anion-exchangers show a decrease at low concentrations of the ion of interest in the external solution (18, 19). Thus, the decrease in selectivity ratios at low concentrations, observed in this study, might be related to a similar decrease in the ion-exchange selectivity coefficient, itself.

While the specific origin of this special effect can only be surmised at this point, it is nevertheless clear that the selectivities of the liquid membrane electrodes we studied are largely consistent with current theories of "mobile-site" type membrane electrodes. Furthermore, the adoption of our graphical procedure permits the evaluation of selectivity ratio values which are both internally consistent and applicable to a range of solution conditions. This finding is highly encouraging because it demonstrates that meaningful comparisons can be made between individual electrodes, as well as classes of electrodes, used under different experimental conditions and in different laboratories.

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Difference between the Inflection Point and the Equivalence Point in Coulometric Titrations of Weak Acids

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Mannitoboric acids of varying pK_a were successfully used to test independently the validity of the Roller equation for evaluation of the error due to noncoincidence of the inflection point and the equivalence point of acid base titration. The use of mannitoboric acid in media of different mannitol concentrations has provided the first test of the Roller equation under conditions where both parameters, c and K_a are varied for a single acid of known stoichiometry. Moreover, the applicability of the Roller equation to complex systems such as boric acid-mannitol has not been established prior to this investigation.

IT HAS BEEN KNOWN for many years that as the acids become progressively weaker and the hydrolysis of their salts more pronounced, the inflection point of a potentiometric acid-base titration curve occurs prior to the stoichiometric equivalence point. The subject has been treated theoretically in great detail in the early part of this century (1-11).

According to Roller (4) the difference between pH at the equivalence point (ep) and the pH at the inflection point (ip) can be represented by the following equation:

$$(pH)_{ep} - (pH)_{ip} = 0.65 \sqrt{K_w/cK_a}$$

where K_w is the ion-product constant for water ($K_w = 10^{-14}$ at 25 °C), c is the concentration of the salt of the weak acid at the equivalence point (moles/liter), and K_a is the dissociation constant of the weak acid. It is apparent from this equation that $(pH)_{ep} - (pH)_{ip}$ in an unsymmetrical titration of weak acid with strong base becomes larger as the concentration of salt at the equivalence point is decreased and as the acid becomes weaker.

Converting the above equation to reflect the error in the titer as a function of cK_a , Roller arrived at essentially the following relationship:

(1) E. D. Eastman, *J. Amer. Chem. Soc.*, **47**, 332 (1925).

(2) E. D. Eastman, *ibid.*, **50**, 418 (1928).

(3) E. D. Eastman, *ibid.*, **56**, 2646 (1934).

(4) P. S. Roller, *ibid.*, **50**, 1 (1928).

(5) P. S. Roller, *ibid.*, **54**, 3485 (1932).

(6) P. S. Roller, *ibid.*, **57**, 98 (1935).

(7) S. Kilpi, *Z. Phys. Chem.*, Leipzig, **173**, 223 (1935).

(8) *Ibid.*, p 427.

(9) *Ibid.*, p 435.

(10) *Ibid.*, p 239.

(11) D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, pp 307-312.