December, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (12), 3189—3193 (1977) 3189

A Selectivity Study on Liquid Anion Exchange Membranes*

Nobuo Yoshida** and Nobuhiko Ishibashi

Department of Applied Analytical Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 812

(Received July 7, 1977)

The selectivity of liquid anion exchange membranes consisting of a perchlorate, thiocyanate, or iodide salt of Crystal Violet dissolved in nitrobenzene was studied by measuring membrane potentials. In bi-ionic systems the selectivity coefficient was observed to vary with the concentrations of aqueous solutions and of the ion exchanger in the membrane. This was attributed mainly to the ionic composition at the membrane-solution interface differing from that in the bulk solution. However, when the concentration of the aqueous solutions was sufficiently high in comparison with that of the ion exchanger, a selectivity coefficient intrinsic to a pair of counter ions was obtained. This selectivity coefficient was also applicable to mixed electrolyte systems and was shown to be consistent with the Conti-Eisenman theory on the relation between the selectivity coefficient and ionic parameters.

The potentials measured with liquid membrane electrodes in solutions containing a number of species of univalent ions to which the electrode responds, have been found to obey the following empirical equation:[1,2]

$$E = \text{const} - \frac{RT}{F}\ln\left(a_{\text{i}}+\sum_{\text{j}}K^{\text{pot}}_{\text{i,j}}a_{\text{j}}\right). \qquad (1)$$

Here a_{i} and a_{j} are activities of the primary ion i and any other ion j. $K^{\text{pot}}_{\text{i,j}}$ is the potentiometric selectivity coefficient of ion j over the primary ion. The selectivity coefficient calculated by means of Eq. 1, however, has generally been observed to vary with solution concentration, composition, and ion exchanger concentration in the membrane. Such variations of the selectivity coefficient have been considered to be due to the changes of the ion-exchange selectivity coefficient with solution concentration[2,3] and of the physical properties of the membrane with ion exchanger concentration.[4]

In the present work, the selectivity of liquid anion exchange membranes consisting of a perchlorate, thiocyanate, or iodide salt of Crystal Violet dissolved in nitrobenzene was studied. The variation of the selectivity coefficient is explained in terms of the change of ionic composition at the membrane-solution interface and a selectivity coefficient intrinsic to a pair of counter ions is introduced. This selectivity coefficient is compared with that expected from a theory of a liquid ion exchange membrane.

Experimental

Reagents and Liquid Membranes. All reagents used in this study were of analytical reagent grade. A Crystal Violet salt of anion X (CV–X, where X=ClO_4^-, SCN^-, or I^-) was prepared by dissolving Crystal Violet (obtained as a chloride salt from Kishida Kagaku Co.) in hot water and precipitation with aqueous NaX at the same temperature. The precipitate was washed with demineralized water and dried in vacuum. Liquid membranes were prepared by dissolving a known amount of the Crystal Violet salt in nitrobenzene.

Measurement of Membrane Potentials. Membrane potentials were measured by means of the cell

SCE/KCl-agar bridge/Solution(′)/Liquid membrane/
Solution(″)/KCl-agar bridge/SCE. (2)

Here the symbols (′) and (″) are used to designate the solutions on both sides of the membrane. In cells with solutions containing perchlorate ion, NH_4Cl-agar bridges were used in place of KCl-agar bridges. The experimental cell used was a U-shaped glass tube with 12 cm^3 of the membrane phase at the bottom and 10 cm^3 of each aqueous solution above. The aqueous and the membrane phases were not stirred unless differently indicated. In most experiments, the concentration ranges of the aqueous solutions and of the ion exchanger (the Crystal Violet salt) in the membrane were chosen so as not to cause the elution of the ion exchanger into the adjacent aqueous solutions. All membrane potentials were measured with a Takeda Riken Electrometer TR 8651 at room temperature (23±3 °C), after the cells had been constructed.

Determination of Composition Changes in Aqueous Solutions. Cells of the type: 0.1 M[†] NaI (′)/CV–I in nitrobenzene/0.1 M NaX (″) (where X=NO_3^- or ClO_4^-) were used to examine composition changes in aqueous solutions which may be caused by ion exchange during the measurement of membrane potentials. About 30 min after the construction of the cell, the concentration of iodide ion in solution (″) was determined by using an iodide ion-selective electrode (Toa Denpa Kogyo Co., Model I-125).

Determination of Distribution Coefficients. A nitrobenzene solution of a Fuchsine Basic salt of anion X (X=ClO_4^-, SCN^-, or I^-) was prepared by extraction from a mixture of Fuchsine Basic (obtained as a chloride salt from Kishida Kagaku Co.) and NaX in water. The concentration of the Fuchsine Basic salt in the nitrobenzene solution was of the order of 10^{-4} M. Ten cm^3 of the solution was vigorously agitated with 10 cm^3 of water. The system was maintained overnight in a thermostated water bath (25.0±0.1 °C). After complete separation of the phases the salt concentration in the aqueous phase was determined by measuring the absorbance at 542 nm. Next, the distribution coefficient of the salt was calculated.

Results and Discussion

In order to evaluate the ratios of the activity coefficients (concentration basis) of thiocyanate and perchlorate ions, $y(SCN^-)/y(ClO_4^-)$, at high concentrations (necessary in the following calculation of the selectivity coefficient), concentration potentials were first measured for aqueous NaSCN and $NaClO_4$ solutions. Figure 1 shows the observed potentials as a function of the ion exchanger concentration. In this figure the concentration potentials which are independent of the exchanger concentration (horizontal parts of the curves) may be

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* A preliminary report has been published: N. Yoshida and N. Ishibashi, *Chem. Lett.*, **1974**, 493.

** Present address: Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka 812.

[†] Throughout this paper 1 M=1 mol dm^{-3}.

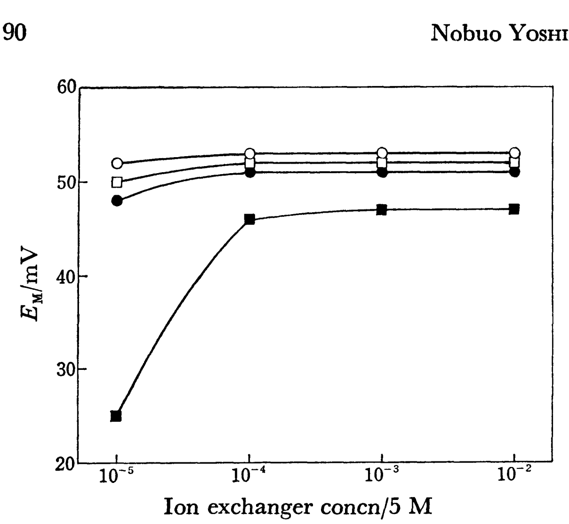

Fig. 1. Concentration potential, E_M, *vs.* concentration of ion exchanger. Systems: ○, 0.01 M NaSCN (′)–0.1 M NaSCN (″); □, 0.01 M NaClO$_4$ (′)–0.1 M NaClO$_4$ (″); ●, 0.1 M NaSCN (′)–1 M NaSCN (″); ■, 0.1 M NaClO$_4$ (′)–1 M NaClO$_4$ (″). Membrane solvent: nitrobenzene. Ion exchangers: ○, ●, CV–SCN; □, ■, CV–ClO$_4$.

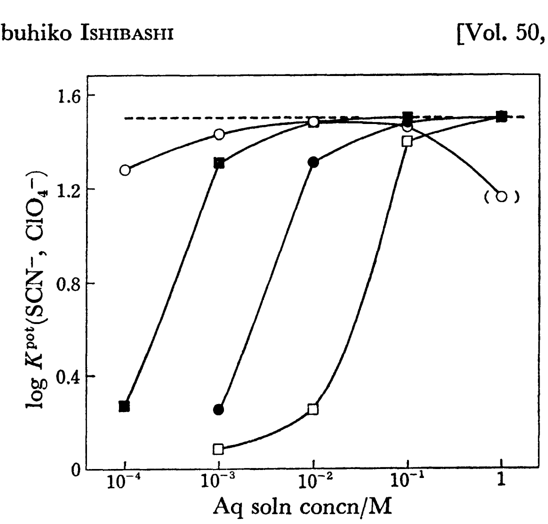

Fig. 2. Variation of the selectivity coefficient with concentrations of aqueous solution and of ion exchanger in the bi-ionic system NaSCN–NaClO$_4$. Membrane solvent: nitrobenzene. Concentrations of ion exchanger (CV–SCN): ○, 5×10^{-5} M; ■, 5×10^{-4} M; ●, 5×10^{-3} M; □, 5×10^{-2} M.

considered to be ideal; the decrement of the potentials at the low exchanger concentrations is presumably due to the incomplete exclusion of the co-ion (sodium ion) from the membrane. By application of the Nernst equation to the former potentials, the values of log{y(SCN$^-$)/y(ClO$_4^-$)} in 0.1- and 1-M solutions were estimated to be 0.02 and 0.09, respectively, where the ratio y(SCN$^-$)/y(ClO$_4^-$) was assumed to be unity below 10^{-2} M. These results were used for the calculation of the selectivity coefficient in the bi-ionic system NaSCN–NaClO$_4$ presented below.[5]

In the case of two univalent counter ions (anions) X and Y, the membrane potential, E_M, in cell (2) may be expressed by

$$E_M = \frac{RT}{F}\ln\frac{a''_X + K^{pot}_{X,Y}a''_Y}{a'_X + K^{pot}_{X,Y}a'_Y}. \tag{3}$$

Here the sign of the potential refers to solution (″). For cells in which solution (′) contains only ion X and solution (″) only ion Y, Eq. 3 reduces to

$$E_M = \frac{RT}{F}\ln\frac{K^{pot}_{X,Y}a''_Y}{a'_X}. \tag{4}$$

Figure 2 shows the selectivity coefficient K^{pot}(SCN$^-$, ClO$_4^-$) for the bi-ionic system NaSCN–NaClO$_4$ in which the membrane (CV–SCN in nitrobenzene) is interposed between solutions of NaSCN (′) and of NaClO$_4$ (″) of the same concentration. The selectivity coefficient was calculated from the measured potential by the use of Eq. 4. (Such a selectivity coefficient is an "apparent" one described below). It is observed that the selectivity coefficient varies with the concentrations of the ion exchanger in the membrane and of the aqueous solutions. However, with membranes having a given concentration of the exchanger, the selectivity coefficient approaches a limiting value (indicated by the dashed line in the figure) with the increasing concentration of the aqueous solutions. With solutions having a given concentration of the electrolytes, the selectivity coefficient also tends toward the same limiting value as the exchanger concentration decreases. As in the case of the concentration potentials described above, the deviation of the parenthesized value from the limiting one is attributed to the incomplete exclusion of the co-ion (sodium ion) from the membrane. Similar results were obtained with the bi-ionic systems NaI–NaClO$_4$ and NaI–NaSCN by the use of nitrobenzene solutions of CV–I as the liquid membranes.[6]

The variation of the selectivity coefficient may be understood from the following argument. In the bi-ionic cell used here, before the aqueous solutions and the liquid membrane are in contact with each other, solution (′) and the membrane contain the same counter ion X, whereas solution (″) contains a different counter ion Y. When the cell is assembled, an exchange of the counter ions occurs between solution (″) and the membrane. Therefore, the ionic composition at the membrane-solution (″) interface is generally different from that in the bulk of solution (″) since a diffusion layer (through which the transport of ions can occur by diffusion only) exists adjacent to the interface. (In experiments of short duration, such a change of ionic composition would be negligible at the membrane-solution (′) interface).

Such a cell is not a true bi-ionic cell and, taking account of the composition change at the interface, we must express the membrane potential of the cell as

$$E_M = \frac{RT}{F}\ln\frac{a^*_X + K^{pot}_{X,Y}a^*_Y}{a'_X} + (\phi''-\phi^*), \tag{5}$$

where the asterisks refer to the interface inside solution (″) and ϕ is the electric potential. As shown in Appendix, since the mobilities of the counter ions used (ClO$_4^-$, SCN$^-$, and I$^-$) are nearly equal in the aqueous solution,[7] the second term in Eq. 5 becomes negligible and $c^*_X + c^*_Y \approx c''_Y \approx c'_X$ (c: concentration). We then obtain (assuming, for simplicity, activities to be equal to concentrations)

$$E_M \approx \frac{RT}{F}\ln\left\{K^{pot}_{X,Y} + (1-K^{pot}_{X,Y})\frac{c^*_X}{c'_X}\right\}, \tag{6}$$

from which an "apparent" selectivity coefficient, $K^{\mathrm{pot}}_{\mathrm{X,Y}}(\mathrm{app})$, (obtained from the straightforward application of Eq. 4 to the cell) is given by

$$K^{\mathrm{pot}}_{\mathrm{X,Y}}(\mathrm{app}) \approx K^{\mathrm{pot}}_{\mathrm{X,Y}} + (1-K^{\mathrm{pot}}_{\mathrm{X,Y}})\frac{c^{*}_{\mathrm{X}}}{c'_{\mathrm{X}}}. \qquad (7)$$

The higher the exchanger concentration compared with the solution concentration, the larger will be the value of $c^{*}_{\mathrm{X}}/c'_{\mathrm{X}}$. Hence $K^{\mathrm{pot}}_{\mathrm{X,Y}}(\mathrm{app})$ becomes correspondingly smaller when $K^{\mathrm{pot}}_{\mathrm{X,Y}}>1$ and larger when $K^{\mathrm{pot}}_{\mathrm{X,Y}}<1$. This indeed the case for the bi-ionic system NaSCN–$\mathrm{NaClO_4}$ presented above, where $K^{\mathrm{pot}}(\mathrm{SCN^-}, \mathrm{ClO_4^-})$ (which is considered to be the limiting value of the selectivity coefficient in this system as described below) is 1.5 on logarithmic scale.

However, in cases where the solution concentration is sufficiently high in comparison with the exchanger concentration, the influence of the composition change at the interface will be negligibly small. The above-mentioned limiting value of the selectivity coefficient (limiting selectivity coefficient) corresponds to such situations of the cell and is considered to be a parameter correctly describing the properties of the membrane.[8)]

Table 1. Changes in composition of aqueous solutions in the cell
0.1 M NaI (′)/CV-I in nitrobenzene/0.1 M NaX (″).

Concn of CV-I / M	X	$c''(\mathrm{I^-})$ / M	$\log K^{\mathrm{pot}}(\mathrm{I^-}, \mathrm{X})$	
			Apparent	Corrected
5×10^{-4}	$\mathrm{NO_3^-}$	4.7×10^{-5}	−1.3	−1.3
5×10^{-3}	$\mathrm{NO_3^-}$	2.6×10^{-4}	−1.2	−1.2
5×10^{-2}	$\mathrm{NO_3^-}$	8.5×10^{-4}	−0.95	−0.98
5×10^{-4}	$\mathrm{ClO_4^-}$	1.1×10^{-4}	1.97	1.97
5×10^{-3}	$\mathrm{ClO_4^-}$	2.9×10^{-4}	1.96	1.96
5×10^{-2}	$\mathrm{ClO_4^-}$	2.0×10^{-3}	1.86	1.86

The variation of the selectivity coefficient may also be attributed partly to the contamination of the bulk solution itself caused by the counter-ion exchange mentioned above. Table 1 shows the composition changes in bulk solutions observed with some bi-ionic cells, together with the apparent selectivity coefficients obtained as before from the measured potentials. In this table $c''(\mathrm{I^-})$ represents the molarity of iodide ions (in solution (″)) which were exchanged for nitrate or perchlorate ions (initially present in solution (″)) during the potential measurement. The selectivity coefficients corrected for the composition change in solution (″) (*i.e.*, calculated by use of Eq. 3 with $a'(\mathrm{NO_3^-})=0$ or $a'(\mathrm{ClO_4^-})=0$) are presented in the last column. As can be seen from the table, however, this correction is small and the selectivity coefficient still shows the variation with the ion exchanger concentration. (Incidentally, the limiting selectivity coefficients $K^{\mathrm{pot}}(\mathrm{I^-}, \mathrm{NO_3^-})$ and $K^{\mathrm{pot}}(\mathrm{I^-}, \mathrm{ClO_4^-})$ were found to be −1.3 and 1.97, respectively, on logarithmic scale). The variation of the selectivity coefficient is thus ascribed mainly to the change of ionic composition at the membrane-solution interface.

The limiting selectivity coefficient is also applied to cells in which the two solutions each contain only one of two species of counter ions but at different concentrations, as long as the composition change at the interface is expected to be small. Figures 3 and 4

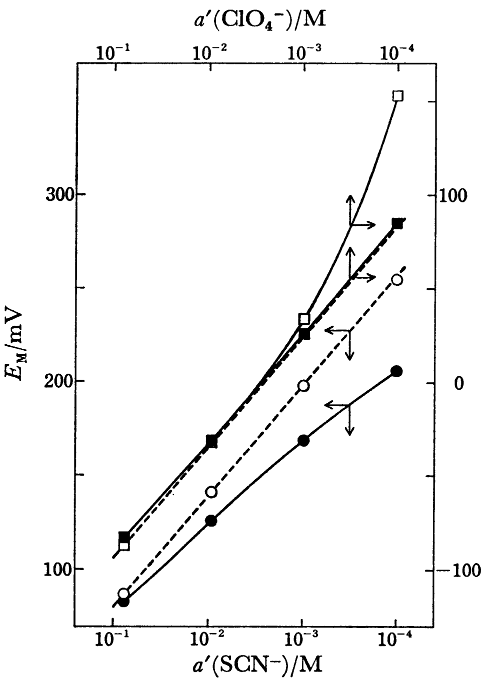

Fig. 3. Membrane potential *vs.* anion activity. Systems: ○, ●, NaSCN with molarity variable (′)–0.1 M $\mathrm{NaClO_4}$ (″); □, ■, $\mathrm{NaClO_4}$ with molarity variable (′)–0.1 M NaSCN (″). Membrane solvent: nitrobenzene. Ion exchangers: ○, □, 5×10^{-4} M CV-SCN; ●, ■, 5×10^{-4} M CV-$\mathrm{ClO_4}$.

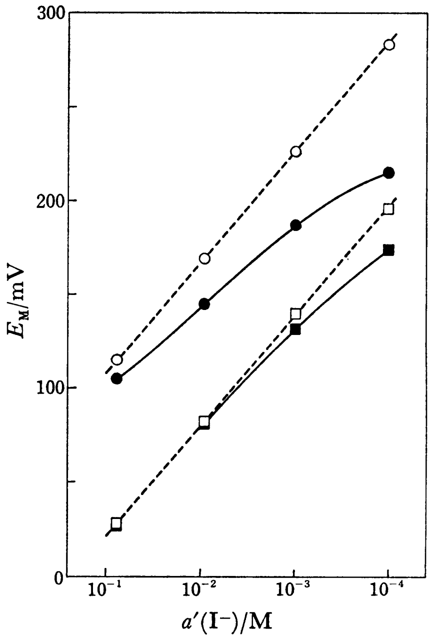

Fig. 4. Membrane potential *vs.* activity of iodide ion. Systems: ○, ●, NaI with molarity variable (′)–0.1 M $\mathrm{NaClO_4}$ (″); □, ■, NaI with molarity variable (′)–0.1 M NaSCN (″). Membrane solvent: nitrobenzene. Ion exchangers: ○, □, 5×10^{-4} M CV-I; ●, 5×10^{-4} M CV-$\mathrm{ClO_4}$; ■, 5×10^{-4} M CV-SCN.

show membrane potentials measured with such cells, where ClO_4^-, SCN^-, and I^- are paired against each other. The observed potentials are indicated by points; the dashed lines represent the values calculated from Eq. 4 with the values of the limiting selectivity coefficient obtained in the corresponding bi-ionic systems (see Table 2). (The solid curves merely connect the experimental points). The experimental points can be seen to agree with the calculated lines in cells of the type: NaX with molarity variable (′)/5×10^{-4} M CV–X in nitrobenzene/0.1 M NaY (″) where $X=SCN^-$, $Y=ClO_4^-$; $X=I^-$, $Y=ClO_4^-$; or $X=I^-$, $Y=SCN^-$. Figures 3 and 4 also illustrate the effect on the membrane potential of varying the counter ion species initially present in the membrane. When in the above cells CV–Y is used, instead of CV–X, as the ion exchanger, the measured potentials become lower than the calculated, which is due to the composition change at the membrane-solution (′) interface. In the cell: $NaClO_4$ with molarity variable (′)/5×10^{-4} M CV–ClO_4 in nitrobenzene/0.1 M NaSCN (″), although solution (′) and the membrane contain the same counter ion, perchlorate ion, the experimental points lie slightly above the corresponding calculated line (dashed). This is probably because the concentration of NaSCN in solution (″) (0.1 M) is not high enough to eliminate completely the effect of the composition change at the membrane-solution (″) interface.

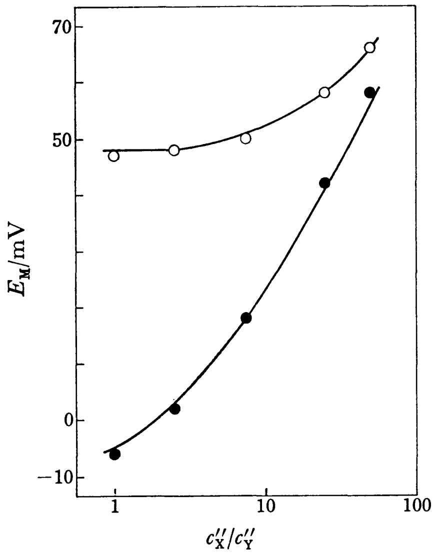

Fig. 5. Comparison of experimental and calculated potentials in the mixed electrolyte system NaX (′)/10^{-4} M CV–X in nitrobenzene/NaX+NaY (″) where $c'_X=10^{-2}$ M, c''_X=variable, and $c''_Y=2\times10^{-3}$ M. ○: $X=SCN^-$, $Y=ClO_4^-$; ●: $X=I^-$, $Y=SCN^-$.

The limiting selectivity coefficient is further applicable to mixed electrolyte systems. Typical data for such systems are shown in Fig. 5. Circles represent the experimentally observed potentials for mixed solutions containing a pair of counter ions, either SCN^-–ClO_4^- or I^-–SCN^-. The curves were drawn according to Eq. 3 with the values of the limiting selectivity coefficient obtained in the corresponding bi-ionic systems. The agreement between the experimental and calculated potentials is seen to be excellent.

As judged from the association constants of ion pairs in nitrobenzene,[9–11] the degree of ion association in the membrane used here is small and virtually negligible at the low exchanger concentrations. For the case of a liquid ion exchange membrane with negligible association, Conti and Eisenman[12] have shown theoretically that the selectivity coefficient between counter ions X and Y is given by

$$K^{\mathrm{pot}}_{\mathrm{X.Y}} = \frac{\bar{u}_Y k_Y}{\bar{u}_X k_X}, \tag{8}$$

where $\bar{u}_X$ and $\bar{u}_Y$ are the mobilities of ions X and Y in the membrane, and k_X and k_Y are the single-ion distribution coefficients between the membrane solvent and water. The selectivity coefficient is therefore expected to be nearly independent of solution concentration, composition, and exchanger concentration, which is consistent with the experimental observations described above.

Table 2. Comparison of limiting selectivity coefficients with calculated values

X	Y	log $K^{\mathrm{pot}}_{\mathrm{X.Y}}$	
		Limiting	Calcd
I^-	ClO_4^-	1.97	1.94
SCN^-	ClO_4^-	1.5	1.39
I^-	SCN^-	0.47	0.546

For a direct comparison of the limiting selectivity coefficient with that expected from Eq. 8, the parameters controlling the selectivity were evaluated. The distribution coefficients of perchlorate, thiocyanate, and iodide salts of Fuchsine Basic between nitrobenzene and water were found to be 68.1, 13.1, and 7.40, respectively. Here the distribution coefficient is given as the ratio of the salt concentration in the organic phase to that in the aqueous phase. The value of k_Y/k_X was calculated from the square of the ratio of these distribution coefficients. The corresponding value of $\bar{u}_Y/\bar{u}_X$ was obtained from the ratio of the limiting ionic conductances.[11,13] The selectivity coefficients calculated by Eq. 8 from these values are compared with limiting selectivity coefficients[14] in Table 2. The limiting selectivity coefficients can be seen to be in good agreement with the calculated values.

Appendix

The ionic fluxes in the diffusion layer (at the solution side of the membrane-solution interface) may be expressed by the following Nernst-Planck equations:

$$J_X = -u_X c_X \frac{\mathrm{d}}{\mathrm{d}x}(RT \ln c_X - F\phi), \tag{A-1}$$

$$J_Y = -u_Y c_Y \frac{\mathrm{d}}{\mathrm{d}x}(RT \ln c_Y - F\phi), \tag{A-2}$$

$$J_{Na} = -u_{Na} c_{Na} \frac{\mathrm{d}}{\mathrm{d}x}(RT \ln c_{Na} + F\phi), \tag{A-3}$$

where J_X, J_Y, and J_{Na} are the fluxes of counter ions (univalent anions) X and Y and sodium ion (co-ion); u_X, u_Y, and u_{Na}, and c_X, c_Y, and c_{Na} are the corresponding mobilities and concentrations (u_X, u_Y, and u_{Na} are assumed to be constants); ϕ is the electric potential; and x is the space coordinate perpendicular to the membrane-solution interface. The conditions of electroneutrality and absence of electric current lead to

$$c_X + c_Y = c_{Na}, \qquad \text{(A-4)}$$

$$J_X + J_Y = J_{Na} = 0, \qquad \text{(A-5)}$$

where it has been assumed that the membrane is impermeable to sodium ion. Inserting Eqs. A-1—A-3 into Eq. A-5 and eliminating $d\phi/dx$, we have

$$\frac{d\{c_{Na}(u_X c_X + u_Y c_Y)\}}{dx} = 0. \qquad \text{(A-6)}$$

For the case where $u_X = u_Y$, Eq. A-6 becomes with the help of Eq. A-4

$$\frac{dc_{Na}}{dx} = \frac{d(c_X + c_Y)}{dx} = 0. \qquad \text{(A-7)}$$

Inserting this result into Eq. A-3 and taking into account Eq. A-5, we obtain

$$\frac{d\phi}{dx} = 0. \qquad \text{(A-8)}$$

Thus the total counter-ion concentration and the electric potential are constant throughout the diffusion layer.

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6) The limiting value of the selectivity coefficient was found to be more easily obtained in cases where the counter ion less extractable into the membrane was initially present in the membrane. In order to determine the limiting value of K^{pot} (SCN^-, ClO_4^-), for example, the membrane containing the less extractable thiocyanate ion was preferable to the membrane containing perchlorate ion.

7) For these ions, the ratio of the limiting ionic conductances does not exceed 1.2 in water. "Landolt-Börnstein Tabellen," Vol. II, Part 7, 6th ed, Springer-Verlag, Berlin, Göttingen, and Heidelberg (1960), pp. 259, 261.

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14) In this case, strictly speaking, the limiting selectivity coefficient must be evaluated under conditions in which a steady state is established across the membrane, since the Conti-Eisenman theory applies only to such experimental conditions. For this purpose membrane potentials were measured by using a cell with a stirred membrane. When the membrane phase is stirred, no concentration gradient of ions exists inside the bulk membrane and a stable concentration gradient will be established in the (unstirred) diffusion layers just internal to each membrane-solution interface. Hence, as far as the membrane potential is concerned, the membrane phase may be regarded as consisting of the two diffusion layers alone where the steady state required by the theory is attained. However, in cells in which the influence of the composition change at the interface (discussed in the text) is negligible, the stirring of the membrane interior had little effect on the membrane potential. Thus the value of the limiting selectivity coefficient was the same with stirred and unstirred membranes.