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Effect of Diffusion Layers on Bi-ionic Potentials across Liquid Ion-exchange Membranes

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In a bi-ionic system in which a liquid membrane is interposed between aqueous solutions containing different counterions, the solution composition is often not maintained uniform right up to the membrane–solution interface owing to the presence of diffusion layers adjacent to the interface. Taking the effect of the diffusion layers into account, an expression is derived for the bi-ionic potential across a membrane having completely dissociated ion-exchange sites and counterions. The expression contains as an empirical parameter the ratio between the thicknesses of the diffusion layers at the solution and membrane sides of the interface. The expression is found to agree with experimental data, with the parameter given a single value.

The electric potential difference, V, between two aqueous solutions (′) and (″) separated by a liquid ion-exchange membrane is usually given in the form of the following empirical equation:[1–3)]

$$V=\frac{RT}{F}\ln\frac{a_i{}'+\sum\limits_j K_{i,j}^{pot}a_j{}'}{a_i{}''+\sum\limits_j K_{i,j}^{pot}a_j{}''},\tag{1}$$

where a_i and a_j are the activities of univalent counterions i and j, respectively, in solutions (′) and (″), and $K_{i,j}^{pot}$ is the potentiometric selectivity coefficient of ion j over ion i. In particular, when ion-exchange sites and counterions are completely dissociated in the membrane, Eq. 1 was also derived theoretically by Conti and Eisenman,[4)] who showed that the selectivity coefficient is given by

$$K_{i,j}^{pot}=\frac{\bar{u}_j k_j}{\bar{u}_i k_i},\tag{2}$$

where $\bar{u}_i$ and $\bar{u}_j$ are the mobilities of ions i and j, respectively, in the membrane, and k_i and k_j are the single-ion distribution coefficients between the membrane solvent and water. However, Eq. 1 is sometimes observed to be only approximate, since the selectivity coefficient changes with the solution concentration and composition. In a previous study,[5)] electric potentials were measured for liquid membranes having dissociated sites and counterions, and the results were compared with those predicted by the Conti-Eisenman theory. The theory was found to be applicable only when the concentrations of aqueous solutions were sufficiently high in comparison with that of an ion exchanger in the membrane. Deviation from the theory occurring in other cases was attributed to the ionic composition at the membrane–solution interface differing from that in the bulk solution owing to the presence of diffusion layers adjacent to the interface. The effect of diffusion layers on the membrane potential has been discussed quantitatively for solid ion-exchange membranes,[6–8)] but not for their liquid counterpart.

In the present paper, the Conti-Eisenman theory is extended so as to incorporate the effect of the diffusion layers, and an expression is derived for the membrane potential in a bi-ionic system. The validity of this expression is examined by a comparison with experimental results.[5)]

Theoretical

The system considered is a bi-ionic cell in which a liquid membrane with an ion exchanger RY is interposed between two aqueous solutions (′) and (″) containing different counterions X and Y of equal valence z, respectively, but with a common co-ion M of valence z_M:

$$\begin{array}{c|c|c} \text{Solution (}'\text{)} & \text{Liquid membrane} & \text{Solution (}''\text{)} \\ \text{MX} & \text{RY} & \text{MY}\ . \end{array}\tag{3}$$

(The treatment given below can be readily extended to more general systems in which the solutions and membrane contain both counterions.) It is assumed that the ion-exchange sites (R) and counterions are completely dissociated in the membrane and that the aqueous and membrane phases are impermeable to R and M, respectively. In cell (3), a continuous exchange of the counterions occurs across the membrane–solution (′) interface. As a result, the concentrations of the counterions at the interface generally differ from those in the bulk phases, since two diffusion layers (through which the transport of the ions can take place by diffusion only) are present adjacent to the interface. The situation is schematically shown in Fig. 1, where C is the concentration of the counterions; a and b refer to the membrane–solution (′) and membrane–solution (″) interfaces, respectively; a superscript bar refers to the membrane phase; and δ and $\bar{\delta}$ are the thicknesses of the diffusion layers at the solution and membrane sides of interface a, respectively. Contamination of the bulk phases by the counterion exchange, however, is assumed to be negligible in the present treatment.

In order to obtain an expression for the total membrane potential in cell (3), the two phase-boundary potentials $(\bar{\phi}^a-\phi^a)$ and $(\phi''-\bar{\phi}^b)$ and the two dif-

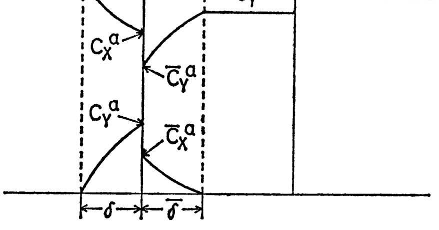

Fig. 1. Concentration profiles of counterions X and Y in the bi-ionic system (schematic).

fusion potentials within the diffusion layers ($\phi^a-\phi'$) and ($\bar{\phi}^b-\bar{\phi}^a$) should be evaluated, where ϕ is the electric potential. If thermodynamic equilibrium is assumed to be established at the membrane–solution interfaces, the electrochemical potentials of the counterions are continuous at the interfaces. Thus we have at interface a,

$$\mu_X{}^\circ + RT\ln y_X{}'C_X{}^a + zF\phi^a = \bar{\mu}_X{}^\circ + RT\ln\bar{y}_X\bar{C}_X{}^a + zF\bar{\phi}^a, \tag{4}$$

$$\mu_Y{}^\circ + RT\ln y_Y{}'C_Y{}^a + zF\phi^a = \bar{\mu}_Y{}^\circ + RT\ln\bar{y}_Y\bar{C}_Y{}^a + zF\bar{\phi}^a, \tag{5}$$

where μ° is the standard chemical potential and y the activity coefficient, for which the superscript a is not used since it is assumed to be constant throughout the diffusion layers. Rearrangement of Eq. 4 yields

$$\bar{\phi}^a - \phi^a = \frac{RT}{zF}\ln\frac{k_X y_X{}'C_X{}^a}{\bar{y}_X\bar{C}_X{}^a}, \tag{6}$$

where k is the single-ion distribution coefficient defined by

$$k = \exp\left(\frac{\mu^\circ-\bar{\mu}^\circ}{RT}\right). \tag{7}$$

Subtraction of Eq. 4 from Eq. 5 gives

$$\frac{C_Y{}^a\bar{C}_X{}^a}{C_X{}^a\bar{C}_Y{}^a} = K, \tag{8}$$

where K is the equilibrium selectivity coefficient given by

$$K = \frac{k_X y_X{}'\bar{y}_Y}{k_Y y_Y{}'\bar{y}_X}. \tag{9}$$

At interface b, we get an equation corresponding to Eq. 6:

$$\phi'' - \bar{\phi}^b = \frac{RT}{zF}\ln\frac{\bar{y}_Y\bar{C}_Y{}^b}{k_Y a_Y{}''}, \tag{10}$$

where $a_Y{}''$ is the activity of counterion Y in solution ($''$).

The diffusion potentials can be evaluated by considering the steady transport of the ions inside the diffusion layers. Expressing the ionic fluxes by the Nernst-Planck equations, we have, for the diffusion layer at the solution side of interface a,

$$J_X = -u_X C_X\frac{d}{dx}(RT\ln C_X+zF\phi) = \text{const}, \tag{11}$$

$$J_Y = -u_Y C_Y\frac{d}{dx}(RT\ln C_Y+zF\phi) = \text{const}, \tag{12}$$

$$J_M = -u_M C_M\frac{d}{dx}(RT\ln C_M+z_M F\phi) = 0, \tag{13}$$

where J is the ionic flux, u the mobility (assumed to be constant throughout the diffusion layer), and x the space coordinate perpendicular to the membrane–solution interfaces. Since no electric current flows through the present system,

$$J_X + J_Y = 0. \tag{14}$$

Substitution of Eqs. 11 and 12 into Eq. 14 yields

$$\frac{d\phi}{dx} = -\frac{RT}{zF}\frac{d\ln(u_X C_X+u_Y C_Y)}{dx}. \tag{15}$$

Integration of Eq. 15 across the diffusion layer leads to

$$\phi^a - \phi' = \frac{RT}{zF}\ln\frac{u_X C_X{}'}{u_X C_X{}^a+u_Y C_Y{}^a}. \tag{16}$$

Alternatively, the electric potential gradient $d\phi/dx$ can be expressed from Eq. 13 as

$$\frac{d\phi}{dx} = -\frac{RT}{z_M F}\frac{d\ln C_M}{dx}, \tag{17}$$

so that

$$\phi^a - \phi' = \frac{RT}{z_M F}\ln\frac{C_M{}'}{C_M{}^a}. \tag{18}$$

The diffusion layer at the membrane side of interface a can be treated by regarding the co-ions as the sites in the above calculation. Thus, we get an equation corresponding to Eq. 16:

$$\bar{\phi}^b - \bar{\phi}^a = \frac{RT}{zF}\ln\frac{\bar{u}_X\bar{C}_X{}^a+\bar{u}_Y\bar{C}_Y{}^a}{\bar{u}_Y\bar{C}_Y{}^b}. \tag{19}$$

Combining Eqs. 6, 10, 18, and 19 and using Eqs. 8 and 9, we have the total membrane potential V:

$$V = \phi'' - \phi' = \frac{RT}{F}\left\{\frac{1}{z}\ln\frac{y_Y{}'(K\bar{r}C_X{}^a+C_Y{}^a)}{a_Y{}''}+\frac{1}{z_M}\ln\frac{C_M{}'}{C_M{}^a}\right\}, \tag{20}$$

where

$$\bar{r} = \bar{u}_X/\bar{u}_Y. \tag{21}$$

With the use of the electroneutrality condition

$$zC_X + zC_Y + z_M C_M = 0, \tag{22}$$

Eq. 20 is written as

$$V = \frac{RT}{zF}\ln\left[\frac{y_Y{}'C_X{}'}{a_Y{}''}\left\{(K\bar{r}-1)\frac{C_X{}^a}{C_X{}'}+\frac{C_M{}^a}{C_M{}'}\right\}\left(\frac{C_M{}^a}{C_M{}'}\right)^{-z/z_M}\right]. \tag{23}$$

For the calculation of V the concentrations $C_X{}^a$ and $C_M{}^a$ at interface a are required. They can be determined in the following way. It follows from Eqs. 15 and 17 that within the diffusion layer at the solution side,

$$C_M{}^{-z/z_M}(u_X C_X+u_Y C_Y) = \text{const}. \tag{24}$$

Applying Eq. 24 to both ends of the diffusion layer and taking Eq. 22 into account, we get

$$C_X{}^a = \frac{z_M}{z}\frac{1-r(C_M{}^a/C_M{}')^{z/z_M-1}}{r-1}C_M{}^a \tag{25}$$

or

$$\frac{C_X{}^a}{C_X{}'} = \frac{r(C_M{}^a/C_M{}')^{z/z_M-1}-1}{r-1}\frac{C_M{}^a}{C_M{}'}, \tag{26}$$

where

$$r = u_X/u_Y. \tag{27}$$

Likewise, the following relation holds inside the diffusion layer at the membrane side:

$$\bar{C}_R{}^{-z/z_R}(\bar{u}_X\bar{C}_X+\bar{u}_Y\bar{C}_Y) = \text{const}, \tag{28}$$

so that

$$\bar{C}_X{}^a = \frac{z_R}{z}\frac{1-(\bar{C}_R{}^a/\bar{C}_R{}^b)^{z/z_R-1}}{\bar{r}-1}\bar{C}_R{}^a, \tag{29}$$

where the electroneutrality condition in the membrane

$$z\bar{C}_X + z\bar{C}_Y + z_R\bar{C}_R = 0 \tag{30}$$

has been used. Introducing Eqs. 25 and 29 into Eq. 8, taking Eqs. 22 and 30 into account, we obtain

$$\left(\frac{\bar{C}_R{}^a}{\bar{C}_R{}^b}\right)^{z/z_R-1} = \frac{(K\bar{r}-1)r(C_M{}^a/C_M')^{z/z_M-1}-K\bar{r}+r}{(K-1)r(C_M{}^a/C_M')^{z/z_M-1}-K+r}. \tag{31}$$

It is now necessary to derive another relationship between the unknown quantities $C_M{}^a$ and $\bar{C}_R{}^a$. Combination of Eqs. 11, 12, and 22 gives

$$\frac{J_X}{u_X}+\frac{J_Y}{u_Y}=\frac{z_M}{z}RT\frac{dC_M}{dx}+z_MFC_M\frac{d\phi}{dx}. \tag{32}$$

Using Eqs. 14 and 17 to eliminate J_Y and $d\phi/dx$ and integrating, we have

$$J_X=\left(1-\frac{z_M}{z}\right)RT\frac{u_X}{r-1}\,\frac{C_M{}^a-C_M'}{\delta}. \tag{33}$$

A similar expression is valid for the diffusion layer at the membrane side:

$$\bar{J}_X=\left(1-\frac{z_R}{z}\right)RT\frac{\bar{u}_X}{\bar{r}-1}\,\frac{\bar{C}_R{}^b-\bar{C}_R{}^a}{\bar{\delta}}. \tag{34}$$

In the steady state ($J_X=\bar{J}_X$), it follows from Eqs. 33 and 34 that

$$\frac{(C_M{}^a/C_M')-1}{1-(\bar{C}_R{}^a/\bar{C}_R{}^b)}=\frac{(1-z_R/z)\bar{u}_X(r-1)\delta\bar{C}_R{}^b}{(1-z_M/z)u_X(\bar{r}-1)\bar{\delta}C_M'}. \tag{35}$$

Thus, the membrane potential can be calculated from Eqs. 23, 26, 31, and 35, if the mobilities of the counterions and the quantities K and $\delta/\bar{\delta}$ are known. The effect of the diffusion layers appears through the parameter on the right-hand side of Eq. 35. Two limiting cases are noted. When the parameter is very small, it is seen from Eqs. 35, 31, and 26 that $C_M{}^a/C_M'$ and $C_X{}^a/C_X'$ approach unity, *viz.*, the effect of the diffusion layers becomes negligible. Under such circumstances Eq. 23 is reduced to the form of Eq. 1 with the selectivity coefficient $K^{\text{pot}}_{Y,X}$ given by $\bar{r}(k_X\bar{y}_Y/k_Y\bar{y}_X)$. The latter equation is identical with that of Conti and Eisenman[4] for the system in question, if the ratio of the activity coefficients in the membrane $\bar{y}_Y/\bar{y}_X$ is taken as equal to unity (see Eq. 2). On the other hand, when the above parameter is extremely large, it is found from Eqs. 35, 31, and 26 that $(C_M{}^a/C_M')^{1-z/z_M}\rightarrow r$ and $C_X{}^a/C_X'\rightarrow 0$. In other words, the concentration gradient of counterion X (in the diffusion layer at the solution side) reaches its maximum value, and there are no concentration gradients within the membrane. The situation corresponds to what is known as "film diffusion control" in solid membrane systems.[6] For this case the membrane potential is obtained from Eq. 23 as

$$V=\frac{RT}{zF}\ln\frac{ry_Y'C_X'}{a_Y''}. \tag{36}$$

In particular, when the mobilities of the counterions are the same in both solutions and membrane ($u_X=u_Y=u$ and $\bar{u}_X=\bar{u}_Y=\bar{u}$), Eq. 23 takes a simpler form. Since Eqs. 22 and 24 show that the concentration C_M of the co-ions is constant across the diffusion layer, Eq. 23 becomes

$$V=\frac{RT}{zF}\ln\frac{y_Y'C_X'\{(K-1)(C_X{}^a/C_X')+1\}}{a_Y''}. \tag{37}$$

Here $C_X{}^a/C_X'$ is evaluated as follows. From the constancy of C_M and Eqs. 22, 17, and 11, we get

$$C_Y{}^a=C_X'-C_X{}^a, \tag{38}$$

$$J_X=RTu(C_X'-C_X{}^a)/\delta. \tag{39}$$

Similarly, for the diffusion layer at the membrane side, we have

$$\bar{C}_Y{}^a=\bar{C}_Y{}^b-\bar{C}_X{}^a, \tag{40}$$

$$\bar{J}_X=RT\bar{u}\bar{C}_X{}^a/\bar{\delta}. \tag{41}$$

Equating Eq. 39 with Eq. 41, we get

$$\bar{C}_X{}^a=(u\bar{\delta}/\bar{u}\delta)(C_X'-C_X{}^a). \tag{42}$$

Introducing Eqs. 38, 40, and 42 into Eq. 8 and solving the result with respect to $C_X{}^a/C_X'$, we find that

$$\frac{C_X{}^a}{C_X'}=\left(\left\{K\left(1-\frac{\bar{u}\delta\bar{C}_Y{}^b}{u\bar{\delta}C_X'}\right)-2\right\}+\left[\left\{K\left(1-\frac{\bar{u}\delta\bar{C}_Y{}^b}{u\bar{\delta}C_X'}\right)-2\right\}^2+4(K-1)\right]^{1/2}\right)\Big/2(K-1). \tag{43}$$

In this case, the effect of the diffusion layers is given in terms of the parameter $\bar{u}\delta\bar{C}_Y{}^b/u\bar{\delta}C_X'$. It is negligible when $\bar{u}\delta\bar{C}_Y{}^b/u\bar{\delta}C_X'\rightarrow 0$, and largest when $\bar{u}\delta\bar{C}_Y{}^b/u\bar{\delta}C_X'\rightarrow\infty$.

Comparison with Experimental Results

Experimental data were reported for the bi-ionic potentials across liquid anion membranes [nitrobenzene solutions of a Crystal Violet (CV) salt] separating aqueous solutions containing $NaClO_4$, NaSCN, or NaI.[5] Values of k_X/k_Y were also determined by measuring the distribution coefficients of the counterions between nitrobenzene and water. The results are as follows: $k(ClO_4^-)/k(I^-)=84.7$, $k(ClO_4^-)/k(SCN^-)=27.0$, $k(SCN^-)/k(I^-)=3.13$. The assumptions made in the present treatment seem to be satisfactory for these membrane systems. The counterions have approximately the same mobility in both water and nitrobenzene, the ratio being less than 1.16 and 1.12 at infinite dilution in water[9] and nitrobenzene,[10] respectively. The experimental potentials are therefore compared with those expected from Eqs. 37 and 43. (The small difference between the counterion mobilities is disregarded here and hence Eq. 23 is not employed, in view of the approximate nature of the assumption involved in the theory that the counterion mobilities are constant throughout the diffusion layers.)

In the calculation of membrane potentials, the data on k_X/k_Y given above were used to obtain the selectivity coefficient K. The activity coefficient y in solutions was calculated from the Debye-Hückel equation with Kielland's ion-size parameters.[11] In the membrane the activity coefficient $\bar{y}$ was assumed to be the same for all the counterions. The mobility ratio $\bar{u}/u$ was evaluated from the mobilities of iodide ions estimated from the equivalent conductance data for NaI[12] in water and CV-I[13] in nitrobenzene by assuming that their transport numbers are independent of concentrations and equal to those at infinite dilution. The value of $\delta/\bar{\delta}$ can be determined by means of Eqs. 37 and 43 from one potential measurement with a system of known values of K and $\bar{u}/u$, and can be used to predict all other membrane potentials, as long as cell geometry and stirring conditions in the membrane

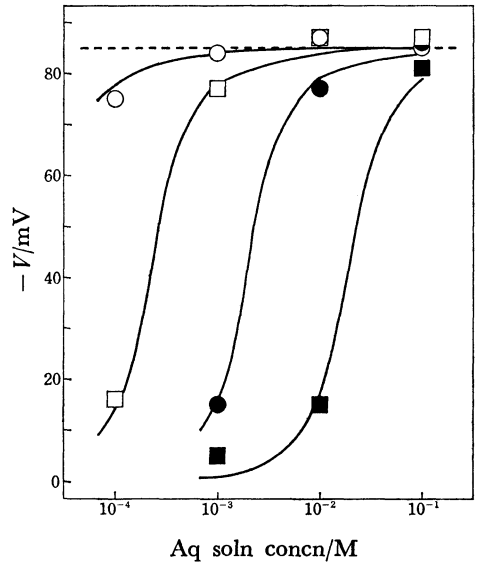

Fig. 2. Comparison of experimental potentials (points) with those calculated from Eqs. 37 and 43 (solid curves) for the bi-ionic system NaClO$_4$(′)/CV–SCN in nitrobenzene/NaSCN (″). The value of the empirical parameter $\delta/\bar{\delta}$ (see Fig. 1) is taken as 1.8. Exchanger (CV–SCN) concentrations: ○, 5×10^{-5} M; □, 5×10^{-4} M; ●, 5×10^{-3} M; ■, 5×10^{-2} M. The broken line indicates the value of the potential expected from the Conti-Eisenman theory, or from Eq. 37 when the effect of diffusion layers is neglected, *i.e.*, $C_X^a/C_X'=1$.

and solutions remain unchanged. In the experimental work mentioned above, neither the membrane nor the solution phases were stirred. The value of $\delta/\bar{\delta}$ was taken here as 1.8.

Figure 2 shows membrane potentials in the bi-ionic system NaClO$_4$–NaSCN in which a membrane (nitrobenzene solution of CV–SCN) is interposed between aqueous solutions of the two counterions (ClO$_4^-$ and SCN$^-$) at the same concentration and at the same activity.* The experimental potentials are indicated by points. When the effect of diffusion layers is absent, the membrane potential for this system is calculated from the Conti-Eisenman theory, or from Eq. 37 with $C_X^a/C_X'=1$. It is independent of the concentrations of the aqueous solutions and of the ion exchanger in the membrane. The calculated value is 85 mV and is given by a broken line. The Conti-Eisenman theory is seen to be valid only when the solution concentration is more than *ca.* 20 times as high as the exchanger concentration. The solid curves, on the other hand, represent values of the potential predicted from Eqs. 37 and 43.[14] They reproduce the experimental values quantitatively.

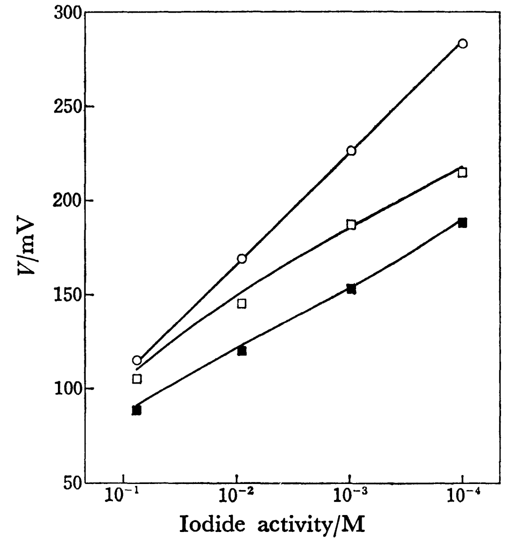

Fig. 3. Comparison of experimental potentials (points) with those calculated from Eqs. 37 and 43 with $\delta/\bar{\delta}=1.8$ (curves) for systems of the types: ○, 0.1 M NaClO$_4$ (′)/5×10^{-4} M CV–I in nitrobenzene/NaI (″); □, NaI (′)/5×10^{-4} M CV–ClO$_4$ in nitrobenzene/0.1 M NaClO$_4$ (″); ■, NaI (′)/10^{-2} M CV–ClO$_4$ in nitrobenzene/0.1 M NaClO$_4$ (″). The potentials are shown as positive.

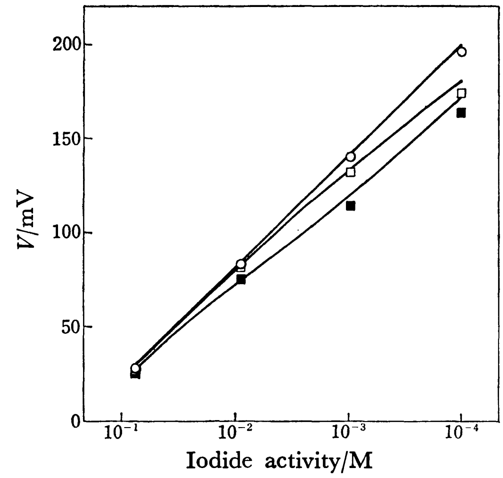

Fig. 4. Comparison of experimental potentials (points) with those calculated from Eqs. 37 and 43 with $\delta/\bar{\delta}=1.8$ (curves) for systems of the types: ○, 0.1 M NaSCN (′)/5×10^{-4} M CV–I in nitrobenzene/NaI (″); □, NaI (′)/5×10^{-4} M CV–SCN in nitrobenzene/0.1 M NaSCN (″); ■, NaI (′)/10^{-2} M CV–SCN in nitrobenzene/0.1 M NaSCN (″). The potentials are shown as positive.

In Figs. 3 and 4, membrane potentials observed with the systems NaClO$_4$–NaI and NaSCN–NaI are plotted as a function of iodide ion activity.[15] The curves represent the values calculated by Eqs. 37 and 43. Agreement between the calculated and experimental potentials is good. The effect of diffusion layers is absent only in systems of the type: 0.1 M NaX (′)/5×10^{-4} M CV–I in nitrobenzene/NaI (″) where X=ClO$_4^-$ or SCN$^-$.

The results indicate that the concept of diffusion layers is useful in the theoretical interpretation of liquid membrane potentials.

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* In this paper 1 M=1 mol dm^{-3}.

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