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The Theory of Liquid Ion-exchange Membrane Ion-selective Electrodes Based on the Concept of the Mixed Ion-transfer Potential**

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The theory of liquid ion-exchange membrane ion-selective electrodes has been developed on the basis of the concept of the zero-current potential, or the mixed potential in the presence of interfering ions, of ion transfer at the interface between a liquid membrane and a sample solution. Under the assumptions of the reversible ion transfer at the interface, the presence of supporting electrolytes in both phases, and the monovalency of all relevant ions, theoretical equations for the mixed potential are derived for two cases; the primary and interfering ions have 1) the same charge sign and 2) the opposite sign. The selectivity coefficients of the ion-selective electrodes can be expressed as a function of the difference between the standard ion-transfer potentials of the primary and interfering ions, the ratios of the mass-transfer coefficients of the ions, and the ratios of the concentrations of the ions. The theoretical prediction has been shown to be applicable to an interpretation of the response of liquid-membrane ion-selective electrodes.

The theory of the ion transport in liquid ion-exchange membrane proposed by Sandblom *et al.*[1] has been widely used for the interpretation of the response of ion-selective electrodes with the liquid ion-exchange membrane. This theory can predict the observed linear relationship between the selectivity coefficient of the ion-selective electrodes and the ion-distribution coefficients. However, the theory seems unsuccessful in explaining the observed fact that the experimental selectivity coefficients vary with the experimental conditions under which the selectivity coefficients are determined.[2—5] Such variation of the selectivity coefficients is one of the puzzles in the field of ion-selective electrodes which have not yet been fully solved.[6] Several attempts have been made to interpret this fact in terms of the concentration polarization of the ions in the solution just outside the membrane.[5,7—12] Most of these treatments presume the validity of the basic assumption implied in the Sandblom *et al.* theory,[1] that of the steady state of the ion transport throughout the liquid-membrane. This assumption, however, is not realistic when the membrane is not thin enough, *e.g.*, in the case of the experiments using a U-shaped cell.[13] Moreover, this theory is obviously not applicable to the ion-selective electrodes with a blocked interface, *e.g.*, coated wire electrodes.[14]

When a relatively thick membrane is brought into contact with a sample solution, the compositions of the inner solution and of the membrane in the vicinity of the membrane-inner solution interface or membrane-electronic conductor interface would remain unchanged unless a sufficiently long time elapses, while the compositions in the vicinity of the membrane-sample solution interface generally change with the time due to the ion-transfer reactions across the interface, resulting in the concentration polarization on both sides of the interface. Therefore, it seems necessary to examine the ion-transfer processes occurring at the membrane-sample solution interface for the understanding of the response of the liquid-membrane ion-selective electrodes.

In the last decade, ion transfer processes between two immiscible electrolyte solutions have been intensively studied using various electrochemical techniques.[15] Since the solvents used for liquid membranes are usually only poorly miscible with aqueous solutions and since the interface between them can be considered as an interface between two immiscible electrolyte solutions, the electrochemistry of the ion transfer at such interfaces has an immediate significance in elucidating the ion-transfer processes occurring at the membrane-solution interface of ion-selective electrodes of the liquid-membrane type. Cammann[16] first suggested the importance of the mixed potential concept[17] at the membrane-solution interface. Koryta[18] has pointed out that the current *vs.* potential curves of the ion transfer at the membrane-solution interface are of fundamental importance in interpreting the response of the ion-selective electrodes and showed that the Nernstian, sub-Nernstian, and super-Nernstian responses can be deduced from the zero current potential of the appropriate "anodic and cathodic waves" of the ion transfers of the relevant ions. Fujinaga and his co-workers[19,20] have advanced this approach and applied it to several types of ion-selective electrodes.

The aim of this study is to present a quantitative theory of the zero-current potential of ion transfer, which we call the mixed potential of ion-transfer in the case of the presence of interfering ions, at the interface between a liquid membrane and a sample solution, and to apply the theory to the interpretation of the response of the ion-selective electrodes with the liquid ion-exchange membrane. The mixed ion-transfer potential can be easily formulated using the current *vs.* potential curves for the transfer of primary and interfering ions when the supporting electrolytes exist in both the liquid membrane and the sample solution. The model system consisting of a liquid membrane and a sample solution, both containing supporting electrolytes, provides us with the characteristics of the ion distribution

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** The main results of the present paper were presented at the 28th Annual Meeting on Polarography, November 11—12, 1982, Sapporo.[31]

processes with mass transfer *per si* at the membrane-solution interface, knowledge which seems essential for understanding the response of the liquid-membrane ion-selective electrodes to various ionic species. The ion-transfer processes at the membrane-sample solution interface should play an essential role in determining the potential response also in the liquid-membrane ion-selective electrode of the type with no such supporting electrolyte, like most of the ion-selective electrodes with liquid ion-exchangers so far studied. The ion-transfer processes are also important in the solid-membrane ion-selective electrodes.

Theoretical

We consider a liquid-membrane ion-selective electrode immersed in a sample solution. The electrochemical cell thus formed may be represented by:

$$\text{Ref. 1}\ \left|\ \begin{matrix}\text{Liquid}\\ \text{Membrane}\end{matrix}\ \right|\ \begin{matrix}\text{Sample}\\ \text{Solution}\end{matrix}\ \left|\ \text{Ref. 2}\right. \tag{I}$$

where Ref. 1 and Ref. 2 are the reference electrodes. Ref. 2 may be a conventional reference electrode, whereas Ref. 1 may consist of an internal solution with a conventional reference electrode, or it may be an electronic conductor in the case of a coated wire electrode. Below, we assume that the potential difference between Ref. 1 and the membrane and that between the sample solution and Ref. 2 are invariant, irrespective of the composition of the membrane and of the sample solution.

When a liquid membrane and a sample solution, both containing electrolytes, are brought into contact to form a membrane-solution interface, ions will generally move across the interface according to the difference in their electrochemical potentials in the two phases. The transfer of ions across the interface is associated with the flow of the current. The net ion-transfer current I across the interface is the sum of the partial ion-transfer currents, I_j, due to the transfer of the j ion across the interface:

$$I = \sum_j I_j \tag{1}$$

The potential of an ion-selective electrode is usually measured under zero-current conditions:

$$I = \sum_j I_j = 0 \tag{2}$$

The inner potential of the sample solution phase, referred to that of the membrane phase, *i.e.*, the liquid junction potential between the two phases, at zero current, $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi(I=0)$, may generally be composed of an interfacial potential and two diffusion potentials:

$$\begin{aligned}\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi(I=0) = \Delta\varphi_{\mathrm{diff}}^{0}(I=0) + \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{interfacial}}(I=0)\\ + \Delta\varphi_{\mathrm{diff}}^{\mathrm{W}}(I=0)\end{aligned} \tag{3}$$

In Eq. 3, $\Delta_{\mathrm{diff}}^{\alpha}\varphi(I=0)$ is the diffusion potential in the α phase($\alpha=0$ or W), where the superscripts O and W denote the membrane and solution phases respectively, and where $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{interfacial}}(I=0)$ is the interfacial potential, which is also called the "phase-boundary potential"[21] or the "Donnan potential".[22] The interfacial potential is determined by the kinetics of ion transfer, which is represented by I_j and which is generally different from the interfacial potential at the distribution equilibrium at which all I_j's are zero and the interfacial potential is identical with the distribution potential.[23] When the partial ion-transfer current is not zero, the diffusion potentials are generally present, even at $I=0$.

The potential of an ion-selective electrode in the cell(I) at zero current, $E(I=0)$, is related to the liquid-junction potential, $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi(I=0)$, by:

$$E(I=0) = E_{\mathrm{mix}} = \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi(I=0) + \Delta E_{\mathrm{ref}} \tag{4}$$

where $E(I=0)$ is the potential of Ref. 2 with respect to Ref. 1 in the cell(I) at $I=0$ and is identical with the mixed ion-transfer potential, E_{mix}, in the presence of interfering ions, and where ΔE_{ref} is the potential difference associated with the reference electrodes in the cell(I), which may include possible liquid-junction potentials at the sample solution-reference electrode and the membrane-reference electrode junctions. We will confine the following treatment to the cases where both the membrane and the sample solution contain a sufficient amount of the supporting electrolytes, so that the migration of the ions becomes negligible. This condition also ensures that the two diffusion potential terms in Eq. 3 are negligibly small;[24] hence:

$$\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi(I=0) \doteqdot \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{interfacial}}(I=0) \tag{5}$$

We assume that the rate of the transfer of ions across the interface is so fast that the Nernst equation:

$$\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{interfacial}} = \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_j^0 + \frac{RT}{z_jF}\ln\frac{\gamma_j^{\mathrm{W},0}}{\gamma_j^{\mathrm{O},0}} + \frac{RT}{z_jF}\ln\frac{c_j^{\mathrm{W},0}}{c_j^{\mathrm{O},0}} \tag{6}$$

holds for every ion passing through the interface, *i.e.*, that the ion-transfer processes are reversible or Nernstain. In Eq. 6, $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_j^0$ is the standard potential of the ion transfer of the ion j from the membrane phase to the sample solution phase;[23] z_j is the electric charge of the ion j; $c_j^{\alpha,0}$(α=O or W) is the surface concentration of the ion j, which is usually considered as the concentration of the ion j just outside the diffuse double layer in the phase α,[25] and $\gamma_j^{\alpha,0}$(α=O or W) is the corresponding activity coefficient of the ion j. R, T, and F have the usual meanings. We also assume that the diffusion coefficients of the ions are independent of the ion concentrations.

When the membrane is so thick that the ion transfer in the membrane phase as well as that in the solution phase meet the condition of semi-infinite mass transfer, the partial current I_j due to the transfer of the ion j through the interface can be written as:

$$\frac{I_j}{z_jFA} = \frac{D_j^{\mathrm{W}}}{\delta_j^{\mathrm{W}}}(c_j^{\mathrm{W}} - c_j^{\mathrm{W},0}) = k_j^{\mathrm{W}}(c_j^{\mathrm{W}} - c_j^{\mathrm{W},0}) \tag{7}$$

$$= -\frac{D_j^{\mathrm{O}}}{\delta_j^{\mathrm{O}}}(c_j^{\mathrm{O}} - c_j^{\mathrm{O},0}) = -k_j^{\mathrm{O}}(c_j^{\mathrm{O}} - c_j^{\mathrm{O},0}) \tag{8}$$

where A is the surface area of the interface; D_j^{α}, δ_j^{α} and k_j^{α} are the diffusion coefficient, the diffusion layer thickness, and the mass-transfer coefficient of the ion j in the phase α(α=O or W) respectively, and c_j^{α} is the concentration of the ion j in the bulkof the phase α(α=O or W) δ_j^{O} and δ_j^{W} have the forms of $1/(\pi D_j^{\mathrm{O}}t)^{1/2}$ and $1/(\pi D_j^{\mathrm{W}}t)^{1/2}$ respectively in the case of a semi-infinite linear diffusion of the ions at a stationary planar interface, where t is the time elapsed from the instant of the contact of the membrane with the sample solution. In Eqs. 7 and 8, the sign of the current is taken as positive(negative) when the positively(negatively) charged ion transfers from the sample solution to the membrane. Equations 7 and 8 hold also in the presence of the convective transport of ions if one chooses appropriate expressions for δ_j^{O} and δ_j^{W}. From Eqs. 6—8 we obtain the equation of a current *vs.* potential curve for the reversible transfer of the ion j through the interface:

$$I_j = \frac{I_{j,\mathrm{lim}}^{\mathrm{O}} + I_{j,\mathrm{lim}}^{\mathrm{W}} \exp(f_j)}{1+\exp(f_j)} \tag{9}$$

where

$$f_j = \frac{z_j F}{RT}(E - E_{1/2,j}^{\mathrm{r}}) \tag{10}$$

and where $I_{j,\mathrm{lim}}^{\alpha}$($\alpha$=W or O) is the limiting current for the transfer of the ion j from the phase α to the other; it is defined by

$$\frac{I_{j,\mathrm{lim}}^{\mathrm{W}}}{z_j FA} = k_j^{\mathrm{W}} c_j^{\mathrm{W}} \tag{11}$$

and

$$\frac{I_{j,\mathrm{lim}}^{\mathrm{O}}}{z_j FA} = -k_j^{\mathrm{O}} c_j^{\mathrm{O}} \tag{12}$$

In Eq. 10, E is the potential of Ref 2 with respect to Ref 1 in the cell(I), while $E_{1/2,j}^{\mathrm{r}}$ is the reversible half-wave potential of the transfer of the ion j and is defined by

$$E_{1/2,j}^{\mathrm{r}} = \Delta_{\mathrm{O}}^{\mathrm{W}} \varphi_j^0 + \frac{RT}{z_j F} \ln \frac{\gamma_j^{\mathrm{W},0} k_j^{\mathrm{W}}}{\gamma_j^{\mathrm{O},0} k_j^{\mathrm{O}}} + \Delta E_{\mathrm{ref}} \tag{13}$$

By substituting Eq. 9 into Eq. 2, we obtain:

$$\sum_j \frac{I_{j,\mathrm{lim}}^{\mathrm{O}} + I_{j,\mathrm{lim}}^{\mathrm{W}} \exp(f_j^0)}{1+\exp(f_j^0)} = 0 \tag{14}$$

where f_j^0 is the f_j at I=0. The potential which satisfies Eq. 14, *i.e.*, $E(I$=0), gives the zero-current ion-transfer potential, or the mixed ion-transfer potential in the case of simultaneous ion transfers of more than two ions.

Below we will consider the mixed ion-transfer potential and the selectivity coefficient for two cases, *i.e.*, the primary and interfering ions have (1) the same charge sign and (2) the opposite charge sign. It is assumed that the electrolytes are completely dissociated in both the membrane and the sample solution, that all the ions are monovalent, and that $\gamma_j^{\mathrm{O},0} = \gamma_j^{\mathrm{W},0} = 1$.

Primary and Interfering Ions with the Same Charge Sign. Consider the case where the membrane that contains three cations, K1, K2, and K4, and an anion, A4, is brought into contact with a sample solution containing two cations, K1 and K3, and an anion, A3. Then, the electrochemical cell can be represented by

$$\begin{array}{c|c|c|c} & \mathrm{K1} & \mathrm{K1,\ K2} & \\ \mathrm{Ref.\ 1} & & & \mathrm{Ref.\ 2} \\ & \mathrm{K3,\ A3} & \mathrm{K4,\ A4} & \\ \multicolumn{1}{c}{} & \multicolumn{1}{c}{\text{Membrane}} & \multicolumn{1}{c}{\text{Sample solution}} & \multicolumn{1}{c}{} \end{array} \tag{II}$$

Suppose also that, among these ions, only K1 and K2 ions can pass through the interface. Such a condition may be fulfilled when the values of the standard ion-transfer potentials for K3 and A4, $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{K3}}^0$ and $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{K4}}^0$, are very negative, while those of K4 and A3, $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{K4}}^0$ and $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{K3}}^0$, are very positive, compared with those of K1 and K2, $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{K1}}^0$ and $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{K2}}^0$. If we regard K1 and K2, as a primary ion and an interfering ion respectively, the electrolytes, K3A3 in the membrane and K4A4 in the sample solution, may be considered to be supporting electrolytes.

The current *vs.* potential curve for the transfer of K1 is schematically represented by Curve 1 in Fig. 1. If $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{K2}}^0 \gg \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{K1}}^0$, the partial ion-transfer current of K2, I_{K2}, is negligibly small around the equilibrium potential of K1, as is shown by Curve 2 in Fig. 1. Then, the potential where the current I becomes zero corresponds to the equilibrium potential for the distribution of K1 between the two phases:

$$E(I{=}0) = \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{K1}}^0 - \frac{RT}{F} \ln (c_{\mathrm{K1}}^{\mathrm{W}}/c_{\mathrm{K1}}^{\mathrm{O}}) + \Delta E_{\mathrm{ref}} \tag{15}$$

When the value of the standard ion-transfer potential of K2 is close to that of K1, as shown by Curve 3 in Fig. 1, the potential at zero current deviates from the equilib-

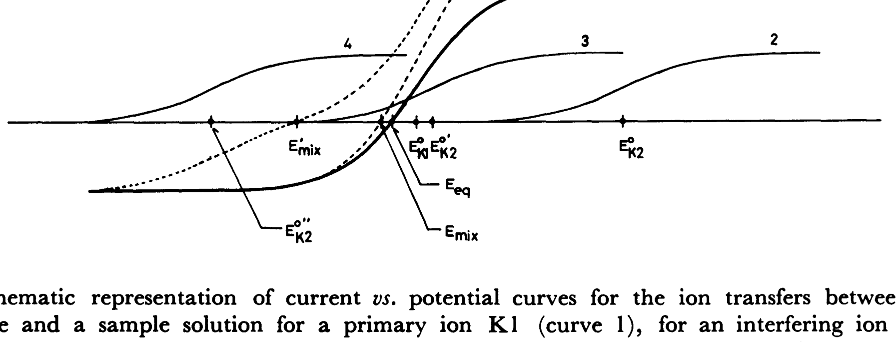

Fig. 1. Schematic representation of current *vs.* potential curves for the ion transfers between a liquid membrane and a sample solution for a primary ion K1 (curve 1), for an interfering ion K2 when $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{K2}}^0 \gg \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{K1}}^0$(2), for K2 when $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{K2}}^0 \fallingdotseq \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{K1}}^0$(3), and for K2 when $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{K2}}^0 \ll \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi_{\mathrm{K1}}^0$(4). Curves 5, 6, and 7 show the total current *vs.* potential curves when the partial currents for K2 are given by (2), (3), and (4), respectively. Standard ion transfer potentials and the mixed ion transfer potentials are indicated on the potential axis.

rium potential of Eq. 15 to the negative direction because of the deformation of the total current *vs.* potential curve (Curve 6 in Fig. 1). Accordingly, the potential at zero current is not the equilibrium potential, but an mixed ion-transfer potential, E_{mix}, in which the ion transfers of both K1 and K2 participate. When $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{K2}} \ll \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{K1}}$, the interference by the K2 ion becomes enormous, as is shown by Curve 7 in Fig. 1.

From Eq. 14, the mixed ion-transfer potential for the cell(II) is given by

$$E_{\mathrm{mix}} = E^0_{\mathrm{K1}} + \frac{RT}{F}\ln J \tag{16}$$

where

$$J = \frac{1}{2}[-(A+B\xi)+\{(A+B\xi)^2+C\xi\}^{1/2}] \tag{17}$$

$$\xi = \exp\left[\frac{F}{RT}\Delta E^0_{\mathrm{K2,K1}}\right] \tag{18}$$

$$A = \left(\frac{k^{\mathrm{W}}_{\mathrm{K2}}}{k^{\mathrm{O}}_{\mathrm{K1}}}\frac{c^{\mathrm{W}}_{\mathrm{K2}}}{c^{\mathrm{W}}_{\mathrm{K1}}} - \frac{c^{\mathrm{O}}_{\mathrm{K1}}}{c^{\mathrm{W}}_{\mathrm{K1}}}\right)\Big/\left(1+\frac{k^{\mathrm{W}}_{\mathrm{K2}}}{k^{\mathrm{W}}_{\mathrm{K1}}}\frac{c^{\mathrm{W}}_{\mathrm{K2}}}{c^{\mathrm{W}}_{\mathrm{K1}}}\right) \tag{19}$$

$$B = \frac{k^{\mathrm{W}}_{\mathrm{K2}}}{k^{\mathrm{O}}_{\mathrm{K2}}}\Big/\left(1+\frac{k^{\mathrm{W}}_{\mathrm{K2}}}{k^{\mathrm{W}}_{\mathrm{K1}}}\frac{c^{\mathrm{W}}_{\mathrm{K2}}}{c^{\mathrm{W}}_{\mathrm{K1}}}\right) \tag{20}$$

$$C = 4\frac{k^{\mathrm{W}}_{\mathrm{K2}}}{k^{\mathrm{O}}_{\mathrm{K2}}}\frac{c^{\mathrm{O}}_{\mathrm{K1}}}{c^{\mathrm{W}}_{\mathrm{K1}}}\Big/\left(1+\frac{k^{\mathrm{W}}_{\mathrm{K2}}}{k^{\mathrm{W}}_{\mathrm{K1}}}\frac{c^{\mathrm{W}}_{\mathrm{K2}}}{c^{\mathrm{W}}_{\mathrm{K1}}}\right) \tag{21}$$

and

$$E^0_{\mathrm{K1}} = \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{K1}} + \Delta E_{\mathrm{rif}}$$

In Eq. 18, $\Delta E^0_{\mathrm{K2,K1}}$ is defined by

$$\Delta E^0_{\mathrm{K2,K1}} = \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{K2}} - \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{K1}} \tag{22}$$

Usually, the selectivity of ion-selective electrodes for the ion *i* over the ion *j* is evaluated through the selectivity coefficient, $k^{\mathrm{pot}}_{i,j}$, defined by the Nicolsky equation,[26] which may be written for the present case as:

$$E = E^0_{\mathrm{K1}} - \frac{RT}{F}\ln\frac{c^{\mathrm{W}}_{\mathrm{K1}}+k^{\mathrm{pot}}_{\mathrm{K1,K2}}c^{\mathrm{W}}_{\mathrm{K2}}}{c^{\mathrm{O}}_{\mathrm{K1}}} \tag{23}$$

We have introduced the $c^{\mathrm{O}}_{\mathrm{K1}}$ term in the denominator of the argument of the logarithm in Eq. 23 in order for the limiting behavior of E at infinitely small $k^{\mathrm{pot}}_{\mathrm{K1,K2}}$ values or at infinitely small $c^{\mathrm{W}}_{\mathrm{K2}}$ values to coincide with that of Eq. 15. By equating E of Eq. 23 with E_{mix} of Eq. 16, one obtains

$$k^{\mathrm{pot}}_{\mathrm{K1,K2}} = (c^{\mathrm{W}}_{\mathrm{K1}}/c^{\mathrm{W}}_{\mathrm{K2}})(c^{\mathrm{O}}_{\mathrm{K1}}/c^{\mathrm{W}}_{\mathrm{K1}}-J)/J \tag{24}$$

Equations 16—24 are applicable to the cases where the primary ion as well as the interfering ion are anions, A1 and A2, in place of K1 and K2 in the cell(II), if one replaces, respectively, the subscripts K1 and K2 with A1 and A2, and if

$$\xi=\exp[(F/RT)\Delta E^0_{\mathrm{K2,K1}}] \text{ and } \Delta E^0_{\mathrm{K2,K1}} = \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{K2}} - \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{K1}}$$

with

$$\xi=\exp[(F/RT)\Delta E^0_{\mathrm{A1,A2}}] \text{ and } \Delta E^0_{\mathrm{A1,A2}} = \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{A1}} - \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{A2}}$$

in these equations.

Primary and Interfering Ions with the Opposite Charge Sign. When the interfering ion has a charge whose sign is opposite to that of the primary ion, the response of the ion-selective electrodes is significantly different from the cases described above. Let us first consider the case in which the primary ion and the interfering ion are a cation K1 and an anion A2 respectively. In this case, the cell may be represented by:

Ref. 1	K1 K3, A3	K1, A2 K4, A4	Ref. 2	(III)
	Membrane	Sample solution		

Figure 2 schematically represents the effect of the interfering anion A2 on the current *vs.* potential curve of the primary ion K1. When $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{A2}} \ll \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{K1}}$ (Curve 2), there is no significant interference. The interference becomes appreciable, however, when $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{A2}}$ is close to $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{K1}}$, as is shown by Curve 5 in Fig. 2. In contrast to

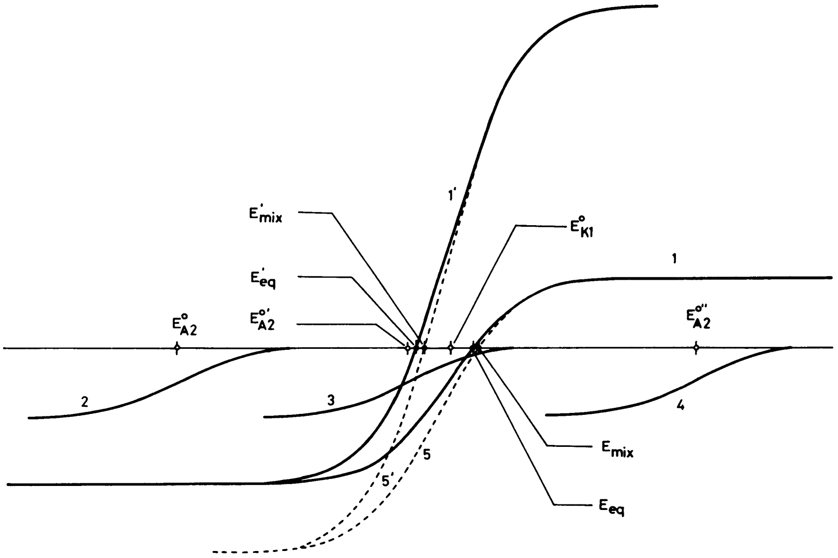

Fig. 2. Schematic representation of current *vs.* potential curves when an interfering ion is an anion A2: the curves for K1 (curves 1 and 1′), for A2 when $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{A2}} \ll \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{K1}}$(2), $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{A2}} \fallingdotseq \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{K1}}$(3), and $\Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{A2}} \gg \Delta_{\mathrm{O}}^{\mathrm{W}}\varphi^0_{\mathrm{K1}}$(4). Curves 1′ represents the current potential curve when $c^{\mathrm{W}}_{\mathrm{K1}}$ is four times larger than that of curve 1. Curves 5 and 5′ are the total current *vs.* potential curves for these two cases.

the interference by a cation K2, the presence of the interfering anion shifts the zero-current ion-transfer potential to the positive direction (Curve 5 in Fig. 2). Another distinctive feature of the anion interference is that the degree of the interference becomes greater with the increase in $c^{\mathrm{W}}_{\mathrm{K1}}$ at a given concentration of A2 in the sample solution, as can be seen from a comparison of Curve 5 with 5′ and of E_{mix} with E'_{mix} in Fig. 2.

Equations 16 and 17 are also valid for the mixed ion-transfer potential for the cell (III), if one defines the terms ξ, A, B, and C in Eqs. 16 and 17 as follows:

$$\xi = \exp\left[\frac{F}{RT}\Delta E^{0}_{\mathrm{A2,K1}}\right] \tag{25}$$

$$A = -\frac{c^{\mathrm{O}}_{\mathrm{K1}}}{c^{\mathrm{W}}_{\mathrm{K1}}} \tag{26}$$

$$B = \frac{k^{\mathrm{O}}_{\mathrm{A2}}}{k^{\mathrm{W}}_{\mathrm{A2}}}\left(1-\frac{k^{\mathrm{W}}_{\mathrm{A2}}}{k^{\mathrm{W}}_{\mathrm{K1}}}\frac{c^{\mathrm{W}}_{\mathrm{A2}}}{c^{\mathrm{W}}_{\mathrm{K1}}}\right) \tag{27}$$

$$C = 4\left(\frac{k^{\mathrm{O}}_{\mathrm{A2}}}{k^{\mathrm{O}}_{\mathrm{K1}}}\frac{c^{\mathrm{W}}_{\mathrm{A2}}}{c^{\mathrm{W}}_{\mathrm{K1}}}+\frac{k^{\mathrm{O}}_{\mathrm{A2}}}{k^{\mathrm{W}}_{\mathrm{A2}}}\frac{c^{\mathrm{O}}_{\mathrm{K1}}}{c^{\mathrm{W}}_{\mathrm{K1}}}\right) \tag{28}$$

where

$$\Delta E^{0}_{\mathrm{A2,K1}} = \Delta^{\mathrm{W}}_{\mathrm{O}}\varphi^{0}_{\mathrm{A2}} - \Delta^{\mathrm{W}}_{\mathrm{O}}\varphi^{0}_{\mathrm{K1}} \tag{29}$$

Equations 16, 17, and 25—29 are applicable to the cases where the primary ion is an anion A1 and the interfering ion is a cation K2, in place of K1 and A2 in the cell (III), if one replaces, respectively, the subscripts K1 and A2 with A1 and K2, and if $\xi=\exp[(F/RT)\Delta E^{0}_{\mathrm{A2,K1}}]$ and $\Delta E^{0}_{\mathrm{A2,K1}}=\Delta^{\mathrm{W}}_{\mathrm{O}}\varphi^{0}_{\mathrm{A2}}-\Delta^{\mathrm{W}}_{\mathrm{O}}\varphi^{0}_{\mathrm{K1}}$ with $\xi=\exp[(F/RT)\Delta E^{0}_{\mathrm{A1,K2}}]$ and $\Delta E^{0}_{\mathrm{A1,K2}}=\Delta^{\mathrm{W}}_{\mathrm{O}}\varphi^{0}_{\mathrm{A1}}-\Delta^{\mathrm{W}}_{\mathrm{O}}\varphi^{0}_{\mathrm{K2}}$ in these equations.

Discussion

Equations 16—22 explicitly relate the mixed ion-transfer potential with the various parameters: the difference between the standard ion-transfer potentials for K1 and K2, $\Delta E^{0}_{\mathrm{K2,K1}}$; the ratios of the mass-transfer coefficients, $k^{\mathrm{O}}_{\mathrm{K1}}/k^{\mathrm{W}}_{\mathrm{K1}}$, $k^{\mathrm{O}}_{\mathrm{K2}}/k^{\mathrm{W}}_{\mathrm{K2}}$, and $k^{\mathrm{W}}_{\mathrm{K2}}/k^{\mathrm{W}}_{\mathrm{K1}}$, and the ratios of the concentrations, $c^{\mathrm{W}}_{\mathrm{K2}}/c^{\mathrm{W}}_{\mathrm{K1}}$ and $c^{\mathrm{O}}_{\mathrm{K1}}/c^{\mathrm{W}}_{\mathrm{K1}}$. E_{mix} is solely determined by the properties of the primary and interfering ions as well as by those of the two solvents and has nothing to do with the nature of the A3 ion, which is usually called the liquid "ion-exchanger" in the membrane. Therefore, for the ion-selective electrode of the type represented by the cell (II) (and also (III)), the term liquid "ion-exchanger" membrane is obviously inadequate.

Figure 3 shows the mixed ion-transfer potentials as a function of $c^{\mathrm{W}}_{\mathrm{K2}}/c^{\mathrm{W}}_{\mathrm{K1}}$ at different values of $\Delta E^{0}_{\mathrm{K2,K1}}$ and at $c^{\mathrm{O}}_{\mathrm{K1}}/c^{\mathrm{W}}_{\mathrm{K1}}=1$, $k^{\mathrm{W}}_{\mathrm{K1}}/k^{\mathrm{O}}_{\mathrm{K1}}=k^{\mathrm{W}}_{\mathrm{K2}}/k^{\mathrm{O}}_{\mathrm{K2}}=\sqrt{2}$, and $k^{\mathrm{W}}_{\mathrm{K2}}/k^{\mathrm{W}}_{\mathrm{K1}}=1$. This figure indicates that E_{mix} shows a Nernstian response to $c^{\mathrm{W}}_{\mathrm{K1}}$ at the higher values of $c^{\mathrm{W}}_{\mathrm{K1}}$ at given values of $c^{\mathrm{W}}_{\mathrm{K2}}$ and $c^{\mathrm{O}}_{\mathrm{K1}}$, but E_{mix} deviates from the Nernstian slope at the lower values of $c^{\mathrm{W}}_{\mathrm{K1}}$. The interference of K2 becomes significant as the difference between the standard ion-transfer potentials for K1 and K2 becomes negative.

Equation 24 expresses $k^{\mathrm{pot}}_{\mathrm{K1,K2}}$ as a function of the difference between the standard ion-transfer potentials of the ions K1 and K2, $\Delta E^{0}_{\mathrm{K2,K1}}$; the concentration ratios, $c^{\mathrm{W}}_{\mathrm{K2}}/c^{\mathrm{W}}_{\mathrm{K1}}$ and $c^{\mathrm{O}}_{\mathrm{K1}}/c^{\mathrm{W}}_{\mathrm{K2}}$, and the ratios of the mass-transfer coefficients, $k^{\mathrm{O}}_{\mathrm{K1}}/k^{\mathrm{W}}_{\mathrm{K1}}$, $k^{\mathrm{O}}_{\mathrm{K2}}/k^{\mathrm{W}}_{\mathrm{K2}}$, and $k^{\mathrm{W}}_{\mathrm{K2}}/k^{\mathrm{W}}_{\mathrm{K1}}$; the selectivity coefficient depends upon these parameters. Among these factors, the difference in the standard ion-transfer potentials $\Delta E^{0}_{\mathrm{K2,K1}}$ is intrinsic for a given set of ions and solvents, whereas the ratios of the maas-transfer coefficients and of the concentrations vary with the experimental conditions. When there is no convective transport of the ions, the ratio of the mass-transfer coefficients is reduced to the square root of the ratio of the diffusion coefficients, for example, $k^{\mathrm{O}}_{\mathrm{K1}}/k^{\mathrm{W}}_{\mathrm{K1}}=(D^{\mathrm{O}}_{\mathrm{K1}}/D^{\mathrm{W}}_{\mathrm{K1}})^{1/2}$; then the ratios of the mass-transfer coefficient are also constants for a given set of ions and solvents.

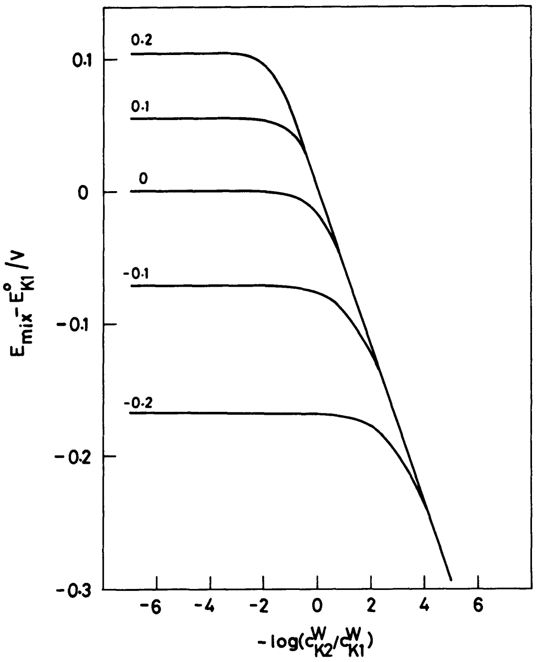

Fig. 3. Dependence of mixed ion transfer potentials on $\log(c^{\mathrm{W}}_{\mathrm{K2}}/c^{\mathrm{W}}_{\mathrm{K1}})$ at $k^{\mathrm{W}}_{\mathrm{K1}}/k^{\mathrm{W}}_{\mathrm{K1}}=k^{\mathrm{O}}_{\mathrm{K2}}/k^{\mathrm{W}}_{\mathrm{K2}}=\sqrt{2}$, $k^{\mathrm{W}}_{\mathrm{K2}}/k^{\mathrm{W}}_{\mathrm{K1}}=1$ and $c^{\mathrm{O}}_{\mathrm{K1}}/c^{\mathrm{W}}_{\mathrm{K1}}=1$ calculated from Eq. 16. Labels indicate the values of $\Delta E^{0}_{\mathrm{K2,K1}}$.

The values of $k^{\mathrm{pot}}_{\mathrm{K1,K2}}$ were calculated from Eq. 24 and are plotted in Fig. 4 as a function of $\Delta E^{0}_{\mathrm{K2,K1}}$ at different values of $k^{\mathrm{W}}_{\mathrm{K2}}/k^{\mathrm{W}}_{\mathrm{K1}}$ when $k^{\mathrm{O}}_{\mathrm{K1}}/k^{\mathrm{W}}_{\mathrm{K1}}=k^{\mathrm{O}}_{\mathrm{K2}}/k^{\mathrm{W}}_{\mathrm{K2}}=\sqrt{2}$ and $c^{\mathrm{O}}_{\mathrm{K1}}/c^{\mathrm{W}}_{\mathrm{K1}}=c^{\mathrm{W}}_{\mathrm{K2}}/c^{\mathrm{W}}_{\mathrm{K1}}=1$. When the value of $k^{\mathrm{W}}_{\mathrm{K2}}/k^{\mathrm{W}}_{\mathrm{K1}}$ is larger than unity, the logarithm of $k^{\mathrm{pot}}_{\mathrm{K1,K2}}$ changes almost linearly with $\Delta E^{0}_{\mathrm{K2,K1}}$. On the other hand, when $k^{\mathrm{W}}_{\mathrm{K2}}/k^{\mathrm{W}}_{\mathrm{K1}}$ is less than unity, the plots deviate from the straight lines at large negative values of $\Delta E^{0}_{\mathrm{K2,K1}}$. The approximate linear relationship between log $k^{\mathrm{pot}}_{\mathrm{K1,K2}}$ and $\Delta E^{0}_{\mathrm{K2,K1}}$ in the positive range of $\Delta E^{0}_{\mathrm{K2,K1}}$ at the lower values of $k^{\mathrm{W}}_{\mathrm{K2}}/k^{\mathrm{W}}_{\mathrm{K1}}$ and in both the positive and negative ranges of $\Delta E^{0}_{\mathrm{K2,K1}}$ at higher values of $k^{\mathrm{W}}_{\mathrm{K2}}/k^{\mathrm{W}}_{\mathrm{K1}}$ is in line with the experimental finding that the logarithm of the selectivity coefficients of the liquid ion-exchange membrane electrodes correlates linearly with the logarithm of the ion-exchange equilibrium constants.[11)]

Figure 4 shows that the selectivity coefficient depends markedly on the value of $k^{\mathrm{W}}_{\mathrm{K2}}/k^{\mathrm{W}}_{\mathrm{K1}}$, especially at the

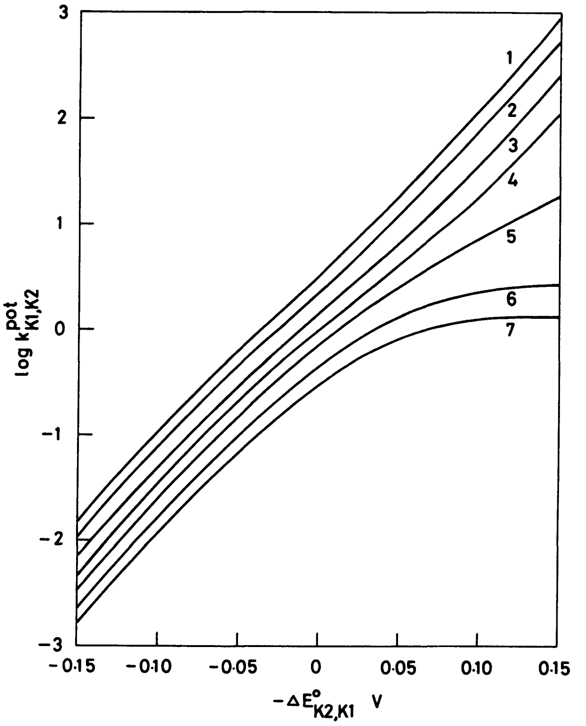

Fig. 4. $\log(k^{\mathrm{pot}}_{\mathrm{K1,K2}})$ *vs.* $\Delta E^{0}_{\mathrm{K2,K1}}$ curves at $k^{\mathrm{W}}_{\mathrm{K2}}/k^{\mathrm{W}}_{\mathrm{K1}}=\sqrt{10}$ (curve 1), $\sqrt{5}$(2), $\sqrt{2}$(3), 1(4), $\sqrt{0.5}$(5), $\sqrt{0.2}$(6), and $\sqrt{0.1}$(7), when $k^{\mathrm{O}}_{\mathrm{K1}}/k^{\mathrm{W}}_{\mathrm{K1}}=k^{\mathrm{O}}_{\mathrm{K2}}/k^{\mathrm{W}}_{\mathrm{K2}}=\sqrt{2}$ and $c^{\mathrm{W}}_{\mathrm{K2}}/c^{\mathrm{W}}_{\mathrm{K1}}=c^{\mathrm{O}}_{\mathrm{K1}}/c^{\mathrm{W}}_{\mathrm{K1}}=1$, calculated from Eq. 24.

negative extreme of $\Delta E^{0}_{\mathrm{K2,K1}}$. This means that, in the absence of convection in both the membrane and the sample solution, the selectivity coefficient depends upon the relative magnitude of the diffusion coefficients of the primary and interfering ions. The dependence of the mixed potential and the selectivity coefficient on the ratio of the mass-transfer coefficients accounts for the effect of the convection on the potential response and the value of the selectivity coefficient of the ion-selective electrodes. The effect of stirring the sample solutions on the potential response of the ion-selective electrodes has been reported.[27] The often observed irreproducible values of the experimental selectivity coefficients may be attributed to such an effect of the mass-transfer coefficients on the selectivity coefficients, since the mass-transfer coefficient is generally not well reproducible under natural convection, which can be caused by the density gradient, accompanied by ion transfers across the membrane-solution interface.

The dependence of $k^{\mathrm{pot}}_{\mathrm{K1,K2}}$ on the concentration ratios, $c^{\mathrm{W}}_{\mathrm{K2}}/c^{\mathrm{W}}_{\mathrm{K1}}$ and $c^{\mathrm{O}}_{\mathrm{K1}}/c^{\mathrm{W}}_{\mathrm{K2}}$, at several values of $c^{\mathrm{O}}_{\mathrm{K1}}/c^{\mathrm{W}}_{\mathrm{K2}}$ was calculated from Eq. 24 for $\Delta E^{0}_{\mathrm{K2,K1}}=0.02$ V (Fig. 5a) and -0.02 V (Fig. 5b). These conditions correspond to those in experiments for the determination of the selectivity coefficients using the procedure in which the concentration of the primary ion in the sample solution is changed while keeping the concentration of the primary ion in the membrane and that of the interfering ion in the sample solution constant.[26] Figures 5a and 5b show that the value of $k^{\mathrm{pot}}_{\mathrm{K1,K2}}$ depends markedly upon both $c^{\mathrm{W}}_{\mathrm{K2}}/c^{\mathrm{W}}_{\mathrm{K1}}$ and $c^{\mathrm{O}}_{\mathrm{K1}}/c^{\mathrm{W}}_{\mathrm{K2}}$, except at the small extreme of $c^{\mathrm{W}}_{\mathrm{K2}}/c^{\mathrm{W}}_{\mathrm{K1}}$. The trend of the change in the $k^{\mathrm{pot}}_{\mathrm{K1,K2}}$ value depends upon the sign of $\Delta E^{0}_{\mathrm{K2,K1}}$. For a positive value of $\Delta E^{0}_{\mathrm{K2,K1}}$, $k^{\mathrm{pot}}_{\mathrm{K1,K2}}$ increases with the increae in $c^{\mathrm{W}}_{\mathrm{K2}}/c^{\mathrm{W}}_{\mathrm{K1}}$, whereas it decreases with the increase in $c^{\mathrm{W}}_{\mathrm{K2}}/c^{\mathrm{W}}_{\mathrm{K1}}$ for a negative value of $\Delta E^{0}_{\mathrm{K2,K1}}$. In both cases, the larger the value of $c^{\mathrm{O}}_{\mathrm{K1}}/c^{\mathrm{W}}_{\mathrm{K2}}$, the greater the change in $k^{\mathrm{pot}}_{\mathrm{K1,K2}}$ with the change in $c^{\mathrm{W}}_{\mathrm{K2}}/c^{\mathrm{W}}_{\mathrm{K2}}$. At the large extreme of $c^{\mathrm{W}}_{\mathrm{K2}}/c^{\mathrm{W}}_{\mathrm{K1}}$, $k^{\mathrm{pot}}_{\mathrm{K1,K2}}$ reaches a constant value whose magnitude depends upon $c^{\mathrm{O}}_{\mathrm{K1}}/c^{\mathrm{W}}_{\mathrm{K2}}$. These figures clearly illustrate that the experimental $k^{\mathrm{pot}}_{\mathrm{K1,K2}}$ values can vary with the experimental conditions.[2–6] For example, the selectivity coefficients are often determined from the intersection of the extrapolation of the two linear portions of a curve similar to those shown in Fig. 3.[28] This $k^{\mathrm{pot}}_{\mathrm{K1,K2}}$ value corresponds to the limiting value of $k^{\mathrm{pot}}_{\mathrm{K1,K2}}$ at the large extreme of $c^{\mathrm{W}}_{\mathrm{K2}}/c^{\mathrm{W}}_{\mathrm{K1}}$ in Figs. 5a and 5b, that is, at the infinitely small concentration of the primary ion. This means that, at a given value of $c^{\mathrm{O}}_{\mathrm{K1}}$, the selectivity coefficient depends on the concentration level of the interfering ion in the sample solution.[6] The theoretical prediction of the dependence of the selectivity coefficient

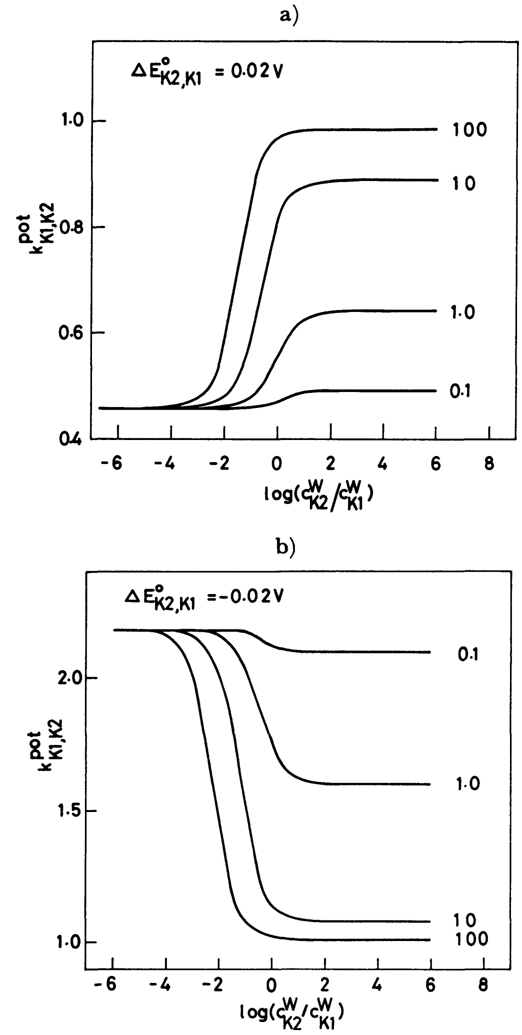

Fig. 5. Change of $k^{\mathrm{pot}}_{\mathrm{K1,K2}}$ with $\log(c^{\mathrm{W}}_{\mathrm{K2}}/c^{\mathrm{W}}_{\mathrm{K1}})$ calculated from Eq. 24 for $\Delta E^{0}_{\mathrm{K2,K1}}=0.02$ V (Fig. 5a) and -0.02 V (Fig. 5b). Labels indicate the values of $c^{\mathrm{O}}_{\mathrm{K1}}/c^{\mathrm{W}}_{\mathrm{K2}}$.

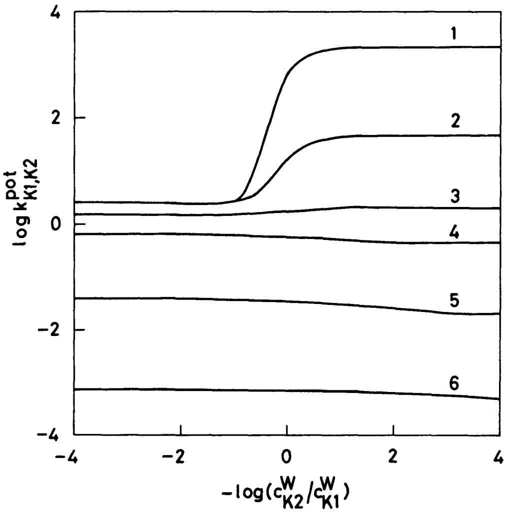

Fig. 6. $\log(k^{\text{pot}}_{\text{K1,K2}})$ *vs.* $\log(c^{\text{W}}_{\text{K2}}/c^{\text{W}}_{\text{K1}})$ curves calculated from Eq. 24 at $\Delta E^{0}_{\text{K2,K1}}=-0.2(1)$, $-0.1(2)$, $-0.02(3)$, $0.02(4)$, $0.1(5)$, and 0.2 V(6), when $k^{\text{W}}_{\text{K1}}/k^{\text{O}}_{\text{K1}}=\sqrt{2}$, $k^{\text{W}}_{\text{K2}}/k^{\text{W}}_{\text{K1}}=1$ and $c^{\text{O}}_{\text{K1}}/c^{\text{W}}_{\text{K1}}=1$.

on the concentrations of the ions, as exemplified in Figs. 5a and 5b, apparently conforms to the trends of the experimental observations found by Srinivasan and Rechnitz[2] for several anion-selective electrodes.

The selectivity coefficient is sometimes determined using the procedure in which the concentration of an interfering ion in a sample solution is changed, while the primary ion concentrations both in the sample solution and in the membrane are kept constant.[3,29] The selectivity coefficients corresponding to such experimental conditions were calculated from Eq. 24 at several different values of $\Delta E^{0}_{\text{K2,K1}}$; they are shown in Fig. 6 as a function of $\log(c^{\text{W}}_{\text{K2}}/c^{\text{W}}_{\text{K1}})$ at $c^{\text{O}}_{\text{K1}}/c^{\text{W}}_{\text{K1}}=1$. For the large positive values of $\Delta E^{0}_{\text{K2,K1}}$, $\log k^{\text{pot}}_{\text{K1,K2}}$ is almost independent of $\log(c^{\text{W}}_{\text{K2}}/c^{\text{W}}_{\text{K1}})$, whereas it varies drastically at the large negative values of $\Delta E^{0}_{\text{K2,K1}}$. In the small values of $c^{\text{W}}_{\text{K2}}/c^{\text{W}}_{\text{K1}}$, $k^{\text{pot}}_{\text{K1,K2}}$ reaches a constant value whose magnitude is dependent on the value of $\Delta E^{0}_{\text{K2,K1}}$. Such behavior of $k^{\text{pot}}_{\text{K1,K2}}$ has also been found experimentally for anion-selective electrodes of the liquid-membrane type.[3,9,11] Senkyr and Petr[9] and Morf[11] have suggested that the selectivity coefficients of anion-selective electrodes with respect to several different interfering ions converge to unity with the decrease in the activity of the interfering ions. However, this is not in conformity with the present theory, as is shown in Fig. 6.

Figure 7 shows the mixed ion-transfer potentials of the cell(III) for several different values of $\Delta E^{0}_{\text{A2,K1}}$ when $c^{\text{W}}_{\text{A2}}/c^{\text{W}}_{\text{K1}}$ is changed, while keeping the $c^{\text{O}}_{\text{K1}}/c^{\text{W}}_{\text{A2}}$ ratio constant. The effect of anion interference is quite different from that of cation interference. When $\Delta E^{0}_{\text{A2,K1}}$ has a large positive value, E_{mix} shows a so-called "super-Nernstian" response in the middle range of $c^{\text{W}}_{\text{A2}}/c^{\text{W}}_{\text{K1}}$. At the large extreme of $c^{\text{W}}_{\text{A2}}/c^{\text{W}}_{\text{K1}}$, E_{mix} *vs.* $\log(c^{\text{W}}_{\text{A2}}/c^{\text{W}}_{\text{K1}})$ curves exhibit the Nernstian response. At the small extreme of $c^{\text{W}}_{\text{A2}}/c^{\text{W}}_{\text{K1}}$, all the curves merge into a single curve with a sub-Nernstian slope.

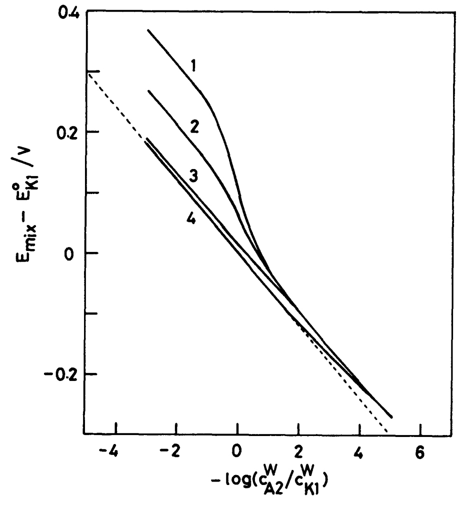

Fig. 7. Variation of E_{mix} with $\log(c^{\text{W}}_{\text{A2}}/c^{\text{W}}_{\text{K1}})$ at $\Delta E^{0}_{\text{A2,K1}}=$ 0.2(1), 0.1(2), 0(3), and -0.1 V(4), when $k^{\text{W}}_{\text{K1}}/k^{\text{O}}_{\text{K1}}=k^{\text{W}}_{\text{A2}}/k^{\text{O}}_{\text{A2}}=\sqrt{2}$, $k^{\text{W}}_{\text{A2}}/k^{\text{W}}_{\text{K1}}=1$ and $c^{\text{O}}_{\text{K1}}/c^{\text{W}}_{\text{A2}}=1$.

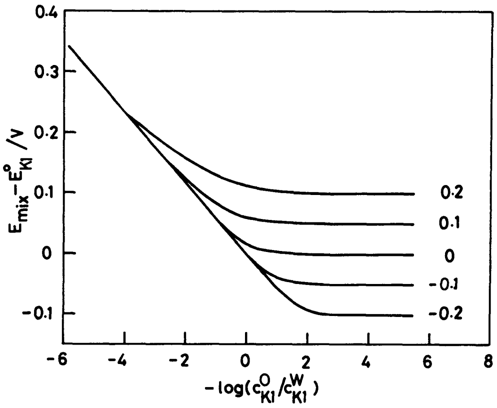

Fig. 8. Variation of E_{mix} with $\log(c^{\text{O}}_{\text{K1}}/c^{\text{W}}_{\text{K1}})$ at $\Delta E^{0}_{\text{A2,K1}}=$ 0.2(1), 0.1(2), 0(3), $-0.1(4)$, and -0.2 V(5), when $k^{\text{W}}_{\text{K1}}/k^{\text{O}}_{\text{K1}}=k^{\text{W}}_{\text{A2}}/k^{\text{O}}_{\text{A2}}=\sqrt{2}$, $k^{\text{W}}_{\text{A2}}/k^{\text{W}}_{\text{K1}}=1$ and $c^{\text{W}}_{\text{A2}}/c^{\text{W}}_{\text{K1}}=1$.

Figure 8 shows the mixed ion-transfer potential of the cell(III) as a function of $\log(c^{\text{O}}_{\text{K1}}/c^{\text{W}}_{\text{K1}})$ at $c^{\text{W}}_{\text{A2}}/c^{\text{W}}_{\text{K1}}=1$ for several different values of $\Delta E^{0}_{\text{A2,K1}}$. Experimentally, such conditions may be met when the concentrations of K1 and A2 in the sample solution are changed by adding a salt K1A2 to the sample solution, *i.e.*, in the case of the so-called co-ion interference.[30] In such cases, the deviation of the potential from the Nernstian behavior becomes significant at the lower values of $c^{\text{O}}_{\text{K1}}/c^{\text{W}}_{\text{K1}}$, *i.e.*, at the larger values of c^{W}_{K1} at a constant c^{O}_{K1} value. A similar change in the potential has been found for a co-ion interference with the nitrate-selective electrodes.[30]

The present theory is limited to the case of the presence of supporting electrolytes in both membrane and solution phases and of the semi-infinite mass-transport of ions. However the above results indicate that the ion transfer across the membrane-sample solution interface plays an essential role in determining the potential of ion-selective electrodes through the interfacial potential and that the concepts of the zero-current potential and the mixed ion-transfer potential are satisfactorily applicable for interpreting the behavior of the ion-selective electrodes with liquid membranes and also with solid membranes.

The present treatment can also be extended to more general cases, *e.g.*, simultaneous ion transfers of more than two ions and arbitrary valencies of the ions, and also to the presence of association between ions and between ions and ligands(ionophores).

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