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The Influence of a Co-ion on the Potential of a Liquid Ion-exchnger Membrane Electrode

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The potential of a liquid ion-exchanger membrane electrode was affected by a co-ion, *i.e.*, an ionic species with the same charge sign as the ion-exchange site in the liquid membrane, when the co-ion in the sample was lipophilic. An aspect of the influence or interference of the co-ion on the response of the electrode is clarified theoretically, based on the three-region concept of the membrane potential. Theoretical predictions of the co-ion interference are illustrated by the measurement of potentials of a nitrate-sensitive nitrobenzene membrane electrode for sample solutions containing sodium nitrate, tetramethylammonium nitrate and the like. The co-ion interference became more important for increased extractability of the co-ion in the nitrobenzene–water system, specifically the order is $Rb^+ < Cs^+ < (CH_3)_4N^+$, and for a decrease in the concentration of the ion-exchanger in the membrane. Co-ion interference appeared for high concentration levels of the ion to be determined and produced a negative error in the activity measurement. The results are in good agreement with the theoretical predictions.

Recently, it has been pointed out both theoretically and experimentally that the interference of an ionic species with the charge sign opposite to that of the ion to be determined, the so-called co-ion, causes problems in the activity measurement of the ion using a liquid membrane electrode of the neutral carrier type.[1–4] According to the Teorell-Meyer-Sievers theory of membrane potentials,[5] the interference of a co-ion is anticipated in the response of a usual liquid ion-exchanger membrane electrode. Nevertheless, studies on the influence of a foreign ion on the response of such an electrode has been heretofore restricted to the interference of an ionic species with the same charge sign as the ion to be determined, the so-called counter ion. Little, therefore, is known about the effects of co-ion interference on the response of a liquid ion-exchanger membrane electrode.

In this report, the membrane potential of a liquid ion-exchanger membrane electrode is discussed theoretically in the case in which the co-ion in the sample solution is not completely rejected by the membrane, and the theoretical predictions are compared with experimental results.

Theoretical

We will analyze the membrane potential of the following membrane system with the help of a three-region concept of the membrane potential, *i.e.*, the regions of the two interfacial potential differences and of the diffusion potential in the membrane. The membrane system consists of a liquid ion-exchanger and two aqueous solutions. The membrane contains an electrolyte S-i, and is denoted by an asterisk. One aqueous solution marked by a prime contains an electrolyte A-i, and corresponds to the inner reference solution of an i ion-sensitive liquid ion-exchanger membrane electrode. The other solution designated by a double prime contains an electrolyte B-i and corresponds to the sample solution. We take the space coordinate x to be in the direction of the membrane thickness. The origin of the x-axis is placed at the membrane-reference solution interface. The x value of the other interface is denoted by d. The following assumptions are made:

(i) All the electrolytes dissociate completely in all phases.

(ii) The ion-exchange site S is confined to the membrane, and the concentration of ion-exchange sites in the membrane $C_s{}^*$ is constant throughout.

(iii) While co-ion A in the reference solution is completely rejected by the membrane, co-ion B in the sample solution is not completely rejected by the membrane, and dissolves into the membrane with the ion i.

(iv) The concentrations are equal to the activities and vary linearly with x within the membrane.

(v) Electroneutrality holds.

First, the equation which expresses the diffusion potential in the membrane is derived. According to the Nernst-Planck equation, we can write this as:

$$\phi_n^* = -U_n^* C_n^* (\partial \tilde{\mu}_n^* / \partial x), \quad (\mathrm{n}: \mathrm{A, B, i, S}). \tag{1}$$

Assumptions (ii) and (iii) allow us to write the relation:

$$\phi_A^* = \phi_S^* = 0 \tag{2}$$

When no current flows,

$$I^*/F = \sum_n z_n \phi_n^* = 0 \quad (\mathrm{n}: \mathrm{B, i}). \tag{3}$$

From Eqs. 1, 2, and 3, the following relation can be obtained:

$$\partial \Psi^* / \partial x = -(RT/F)(\sum_n z_n U_n^* C_n^* \partial \ln C_n^* / \partial x)/(\sum_n z_n^2 U_n^* C_n^*) \quad (\mathrm{n}: \mathrm{B, i}). \tag{4}$$

Integrating Eq. 4 from $x=0$ to d under the foregoing assumptions, one obtains the relation in the case of $|z_n|=1$:

$$\Psi^*(0) - \Psi^*(\mathrm{d}) = ((RT/z_i F)(U_i^* - U_B^*)/(U_i^* + U_B^*)) \times \ln(((U_i^* + U_B^*) C_i{}^*(\mathrm{d}) - U_B^* C_s^*)/U_i^* C_s^*). \tag{5}$$

Next, we consider the interfacial potential differences. From the electrochemical equilibria at the respective boundaries, $x=0$ and $x=\mathrm{d}$, we have the relations:

$$\begin{aligned} \Psi' - \Psi^*(0) &= -(\mu^\circ - \mu^{\circ *})/z_i F + (RT/z_i F) \ln (C_i^*(0)/a_i') \\ \Psi^*(\mathrm{d}) - \Psi'' &= (\mu^\circ - \mu^{\circ *})/z_i F + (RT/z_i F) \ln (a_i''/C_i^*(\mathrm{d})) \end{aligned} \tag{6}$$

From assumption (v) and the electrochemical equilibrium at the membrane-sample solution interface, x=d, we obtain the relation:

$$C_i^*(\mathrm{d}) = (C_s^* + (C_s^{*2} + 4k_ik_B(a_i'')^2)^{1/2})/2. \quad (7)$$

Adding together Eqs. 5 and 6, and inserting Eq. 7, we obtain the desired equation which expresses the influence of the co-ion on the potential E_M of the liquid ion-exchanger membrane electrode:

$$\begin{aligned} E_M = \Psi' - \Psi'' &= (RT/z_iF)\ln(a_i''/a_i') \\ &- (RT/z_iF)\ln((C_s^* + (C_s^{*2} + 4k_ik_B(a_i'')^2)^{1/2})/2C_s^*) \\ &+ ((RT/z_iF)(U_i^* - U_B^*)/(U_i^* + U_B^*))\ln(((U_i^* + U_B^*) \\ &\times ((C_s^* + (C_s^{*2} + 4k_ik_B(a_i'')^2)^{1/2})/2) - U_B^*C_s^*)/U_i^*C_s^*). \end{aligned} \quad (8)$$

Experimental

The influence of the co-ion on the potential E_M of the i ion-sensitive electrode was examined by EMF measurement of the following electrochemical cells:

+SCE/Reference Solution (A-i)/Liquid Membrane/
Sample Solution (B-i)/SCE− (9)

and

+SCE/Reference Solution (A-i)/Liquid Membrane/
Sample Solution (A-i, B-j)/SCE−, (10)

where j is a foreign ion with the same charge sign as the i ion. The j ion selected scarcely interferes with the activity measurement of the i ion. The interference effects of co-ions were examined for the response of nitrate-sensitive and methylephedrine-sensitive electrodes using cells (9) and (10), respectively. The liquid membrane in cell (9) was a nitrobenzene solution of the nitrate salt of crystal violet, and that in cell (10) was a nitrobenzene solution of the tetraphenylborate (TPB) salt of methylephedrine (MEP). The reference solutions in cells (9) and (10) were 1.00×10^{-2} M(M=mol dm^{-3}) solutions of sodium nitrate and methylephedrine hydrogenchloride, respectively. Electrolytes B-i used in cell (9) were sodium nitrate, rubidium nitrate, cesium nitrate and tetramethylammonium nitrate. Sodium nitrate, sodium iodide and sodium thiocyanate were used as the electrolyte B-j in cell (10). The procedures for the preparation of the membrane solutions and the EMF measurement have been described in detail elsewhere.[6-8]

Results and Discussion

Equation 8 can be reduced to a Nernstian equation, when $4k_ik_B(a_i'')^2$ is sufficiently smaller than the square of the concentration of the ion-exchanger in the membrane, C_s^{*2}. On the other hand, the second and third terms of Eq. 8 may contribute to E_M when $4k_ik_B(a_i'')^2$ is not much smaller than C_s^{*2} and co-ion B thus interferes with the activity measurement of the i ion using the i ion-sensitive electrode with the liquid ion-exchanger membrane. In most liquid ion-exchanger membrane electrodes, the mobilities of ions in the membrane are not so different for the ions of interest, whereas the partition coefficients of the ions differ greatly for these ions.[9-13] Accordingly, the effect of co-ion interference can be discussed in a first approximation, neglecting the contribution of the third term of Eq. 8 to E_M. Since the value of $(C_s^* + (C_s^{*2} + 4k_ik_B(a_i'')^2)^{1/2})/2C_s^*$ is always larger than unity when the co-ion enters the membrane, the observed potential E_M gives a lower activity of the i ion than true value. The co-ion interference thus leads to a negative error in the activity measurement of the i ion, whereas a positive error is measured in the usual interference of a foreign counter-ion species. From Eq. 8 the effect of co-ion interference can be summarized as follows:

(i) Co-ion interference becomes more important with decreasing concentration of the ion-exchanger in the membrane; conversely, the co-ion interference can be reduced by increasing the concentration of the ion-exchanger in the membrane.

(ii) Co-ion interference occurs at high activity levels of the objective ion i, whereas the interference of a foreign counter ion occurs at low activity levels of the i ion.

(iii) Co-ion interference increases with increasing extractability of the co-ion.

To illustrate the theoretical predictions, the nitrate-sensitive membrane electrode system (9) was selected because it is likely to fulfill most of the foregoing assumptions.[9-13]

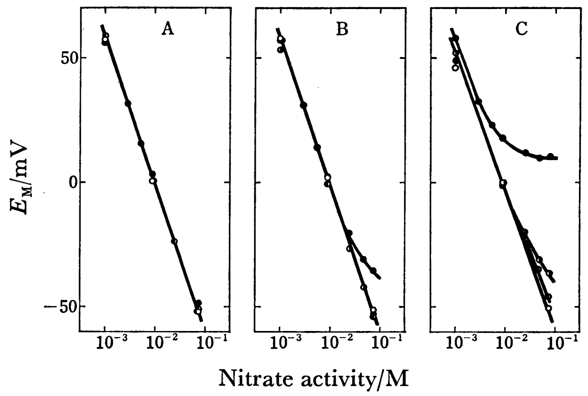

Fig. 1. The interference of a co-ion or cation in the response of the nitrate-sensitive electrode with the nitrobenzene membrane containing the nitrate salt of Crystal Violet as an ion-exchanger.
Concentration of the ion-exchanger in the membrane: (A) 1.0×10^{-3} M, (B) 1.0×10^{-4} M, (C) 1.0×10^{-5} M; Nitrate salt in the sample solution: $NaNO_3$ (○), $RbNO_3$ (◑), $CsNO_3$ (◐), $(CH_3)_4N\,NO_3$ (●); Temp: 24±1 °C.

In Fig. 1, the potentials of the nitrate-sensitive electrode are shown. The potential was stable in the concentration range above 10^{-3} M of the sample salt. Below 10^{-3} M, however, the potential was somewhat unstable in the initial stage of the measurement. In such cases, the stationary values observed after a delay of 15—20 min are used.

A membrane with a 10^{-3} M ion-exchanger showed a Nernstian response to all of nitrate salts up to 10^{-1} M. In the case of a membrane with a 10^{-4} M ion-exchanger, the response for tetramethylammonium nitrate differed from the ideal Nernstian response in the activity level above 10^{-2} M. A negative error was observed in accordance with theoretical predictions. A large deviation from Nernstian response was observed for the response of a membrane with a 10^{-5} M ion-exchanger. Except

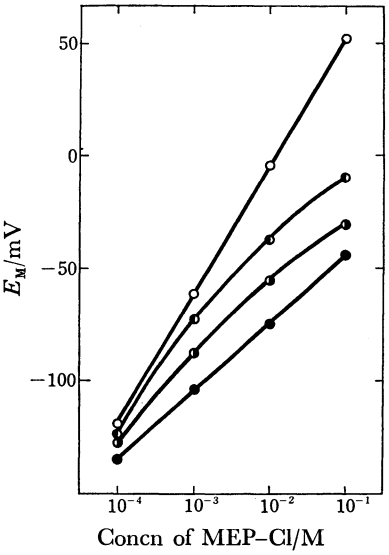

Fig. 2. The response of the methylephedrine-sensitive electrode for sample solutions containing methylephedrine hydrogenchloride (MEP–Cl) and sodium salts of inorganic anions.

Liquid membrane of the electrode: 1.0×10^{-4} M nitrobenzene solution of MEP–TPB; Sample solution: MEP–Cl only (○), MEP–Cl+0.5 M $NaNO_3$ (◐, MEP–Cl+0.1 M NaI (◑), MEP–Cl+0.1 M NaSCN (●); Temp: 20°C.

for the case of sodium nitrate, the responses were no longer Nernstian in the relatively high activity levels of the sample salt. In this case, the extent of the interference is distinguishable for the co-ion species. The order of increasing interference is $Rb^+ < Cs^+ < (CH_3)_4N^+$. This order is in agreement with the increasing extractability of the ions in the nitrobenzene–water system.[10] The results are thus in good agreement with the theoretical expectations. An example of co-ion interference for electrode response is shown for a sample solution containing mixed electrolytes A-i and B-j (cell (10)) in Fig. 2. The methylephedrine-sensitive electrode showed a nearly Nernstian response for a sample solution containing only methylephedrine hydrogenchloride (MEP-Cl).[8] In the presence of the sodium salt of nitrate, iodide or thiocyanate, the electrode response was no longer Nernstian. A negative error was observed. The order of increasing interference is also in agreement with the increasing extractability of the ions in the nitrobenzene–water system, *i.e.*, $NO_3^- < I^- < SCN^-$.[11]

Usually, it is considered that co-ions do not affect the response potential of a liquid ion-exchanger membrane electrode. As shown by this work, however, co-ions do, in some cases, interfere strongly with the activity measurement of the objective ion of the electrode, especially when a lipophilic ion is contained in the sample as a co-ion. In this connection, the recent study of Llenado on the calcium electrode response in the presence of ionic surfactants is interesting because it is anticipated that ionic surfactants may show this type of interference.[14] In conclusion, *the presented results suggest that co-ion interference should be considered in the analytical use of a liquid ion-exchanger membrane electrode, in addition to the consideration of the usual interference of foreign counter ions.*

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Symbols

a	:	activity
C	:	concentration
I	:	electric currnt
U	:	mobility of ion
k	:	partition coefficient of ion
Ψ	:	inner potential
ϕ	:	flux of ion
$\tilde{\mu}$	:	electrochemical potential
μ°	:	standard chemical potential in water
$\mu^{\circ *}$	:	standard chemical potential in organic phase
i	:	objective ion of the electrode
A	:	co-ion A
B	:	co-ion B
S	:	ion-exchange site
x	:	distance variable

* denotes a quantity in the membrane
′ denotes a quantity in the reference solution
″ denotes a quantity in the sample solution

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