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Tetraalkylammonium Ion-selective Electrodes with Supporting Electrolytes. An Experimental Test of the Theory of Liquid Ion-exchange Membrane Ion-selective Electrodes Based on the Concept of the Mixed Ion-transfer Potential

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Selectivity characteristics of liquid-membrane ion-selective electrodes for tetraethylammonium and triethylmethylammonium ion-selective electrodes in the presence of homologous tetraalkylammonium ions as interfering ions were studied with supporting electrolytes both in the liquid membrane and in the sample solution. The emf *vs.* logarithm of the concentration of the primary ion curves in the presence of interfering ion were well described by the theory of liquid-membrane ion-selective electrodes which is based on the concept of the mixed ion-transfer potential at the liquid-membrane/sample solution interface. The dependence of the selectivity coefficients on the concentrations of the primary ion in the liquid membrane and of the interfering ion in the sample solution agreed well with the theoretical prediction.

This paper reports a systematic study of the response of tetraethylammonium and triethylmethylammonium ion-selective liquid-membrane electrodes to the primary ion in the presence of interfering ions (a series of homologous tetraalkylammonium ions) in the sample solution and of the primary ion in the liquid membrane; the liquid membrane and the sample solution contained tetrapentylammonium tetraphenylborate (TPnATPB) and lithium sulfate, respectively, as the supporting electrolyte. In a previous paper,1) we derived the theoretical equations for the response of ion-selective electrodes of liquid ion-exchange membrane type and presented the theory of the selectivity coefficient based on the concept of the mixed ion-transfer potential at the liquid-membrane/sample solution interface. The theory expresses the potential and the selectivity coefficient of the electrodes as functions of three factors: difference in the standard ion-transfer potential between the primary and interfering ions, the concentration ratios of the primary and interfering ions, and the mass-transfer coefficient ratios of these ions. The aim of this study is to verify experimentally these theoretical predictions by using the ion-selective electrodes which meet with the assumptions underlying the theory. The theory has assumed the presence of sufficient amounts of supporting electrolytes in both the liquid membrane and sample solution to ensure the absence of the migration of the relevant ions. This assumption is to simplify the treatment and to sculpture the fundamental characteristics of the ion-selective electrodes which are primarily determined by the ion-transfer processes at the liquid-membrane/sample solution interface. Such ion-transfer processes should also be essential in the liquid membrane ion-selective electrodes without having supporting electrolytes, like most of the ion-selective electrodes with liquid ion-exchangers hitherto studied.

Experimental

The electrochemical cells used in the present study are generally represented by:

$$\begin{array}{c|c|l|l|}
\multicolumn{1}{c}{\mathrm{I}} & \multicolumn{1}{c}{\mathrm{II}} & \multicolumn{1}{c}{\mathrm{III}} & \multicolumn{1}{c}{\mathrm{IV}} \\
\mathrm{Ag} & \mathrm{AgCl} & 2\ \mathrm{mmol\ dm^{-3}} & a\ \mathrm{mmol\ dm^{-3}\ R_1TPB} \\
 & & \mathrm{R_1Cl} & 0.1\ \mathrm{mol\ dm^{-3}\ TPnATPB} \\
\multicolumn{1}{c}{} & \multicolumn{1}{c}{} & \multicolumn{1}{c}{(\mathrm{water})} & \multicolumn{1}{c}{(\mathrm{nitrobenzene})}
\end{array}$$

$$\begin{array}{l|c|c|l}
\multicolumn{1}{c}{\mathrm{V}} & \multicolumn{1}{c}{\mathrm{VI}} & \multicolumn{1}{c}{\mathrm{VII}} & \multicolumn{1}{c}{\mathrm{VIII}} \\
b\ \mathrm{mmol\ dm^{-3}\ R_2Cl} & & & \\
x\ \mathrm{mmol\ dm^{-3}\ R_1Cl} & \mathrm{satd.} & \mathrm{AgCl} & \mathrm{Ag} \\
0.1\ \mathrm{mol\ dm^{-3}\ Li_2SO_4} & \mathrm{KCl} & & \\
\multicolumn{1}{c}{(\mathrm{water})} & \multicolumn{1}{c}{} & \multicolumn{1}{c}{} & \multicolumn{1}{c}{}
\end{array} \qquad (\mathrm{I})$$

where phase III is the internal reference solution, phase IV is the liquid membrane, and phase V is the sample solution. R_1^+ and R_2^+ are the primary and the interfering ions, respectively, and TPB^- is tetraphenylborate ion. We used tetraethylammonium ion (TEA^+) for R_1^+ and trimethylethylammonium ion (Me_3EtN^+), trimethylpropylammonium ion (Me_3PrN^+), trimethylbutylammonium ion (Me_3BuN^+), and triethylmethylammonium ion (Et_3MeN^+) for R_2^+ in a series of experiments, and also Et_3MeN^+ for R_1^+ with TEA^+ for R_2^+ in the other series of experiments. Nitrobenzene was used as a solvent of the liquid membrane. In nitrobenzene, the tetraphenylborate salts of these alkylammonium ions are virtually completely dissociated as judged from the conductivity measurements.2) The values of the standard ion-transfer potentials $\Delta_{NB}^{W}\varphi^0$ for the nitrobenzene–water system and of the diffusion coefficients of the relevant ions are given in Table 1, which shows that both $\Delta_{NB}^{W}\varphi_{R_1^+}^0$ and $\Delta_{NB}^{W}\varphi_{R_2^+}^0$ are much more negative than either of $\Delta_{NB}^{W}\varphi_{Li^+}^0$ and $\Delta_{NB}^{W}\varphi_{TPB^-}^0$ and, simultaneously, much more positive than either of $\Delta_{NB}^{W}\varphi_{TPnA^+}^0$ and $\Delta_{NB}^{W}\varphi_{SO_4^{--}}^0$. Thus, the participation of the supporting electrolytes (TPnATPB in the liquid membrane and Li_2SO_4 in the sample solution) in the ion-transfer processes across the liquid-membrane/sample solution interface is very small3) in the concentration ranges of R_1^+ and R_2^+ studied. The interference caused by supporting electrolytes becomes appreciable only when the ratio of the concentration of R_1^+ in the liquid membrane to that in the sample solution is very small.1) In the following, the emf *vs.* logarithm of the concentration curves are analyzed in the lower concentration range of the primary ion in sample solution, where

Table 1. Standard potentials of ion transfer from water to nitrobenzene and diffusion coefficients of the ions in water

ion	$\Delta^{W}_{NB}\phi^{\circ}/V$	$D/\mathrm{cm^2\,s^{-1}}$[5]
Li^+	0.395[1]	—
Me_3EtN^+	0.040[2]	11.0×10^{-6}
Me_3PrN^+	0.006[2]	9.9×10^{-6}
Et_3MeN^+	−0.007[2]	8.2×10^{-6}
Me_3BuN^+	−0.025[2]	8.8×10^{-6}
TEA^+	−0.028[2]	8.3×10^{-6}
$TPnA^+$	−0.343[3]	—
Cl^-	−0.324[1]	—
SO_4^{2-}	$\leqslant -0.4$[4]	—
TPB^-	0.372[1]	—

1) Ref. 3. 2) Calculated from the data in Ref. 4. 3) Extrapolated from the data in Ref. 3. 4) Ref. 5. 5) Ref. 6.

the interference of the supporting electrolyte becomes negligible. $\Delta^{W}_{NB}\varphi^{0}_{Cl^-}$ is also much more negative than either of $\Delta^{W}_{NB}\varphi^{0}_{R_1^+}$ and $\Delta^{W}_{NB}\varphi^{0}_{R_2^+}$. Accordingly, R_1^+ and R_2^+ are practically the only ionic species which pertain to the ion-transfer processes across the interface in the concentration ranges we are concerned with. The potential difference between phases III and IV is solely determined by the distribution potential of a R_1^+ ion for the ions used in this study.[3] It is also unaffected by the composition of phase V, because the liquid membrane is sufficiently thick.[1] The change of the liquid junction potential between phases V and VI with the change of the electrolyte concentration in phase V is negligibly small because of the presence of supporting electrolytes. Therefore, the change of the electromotive force of the cell with the electrolyte concentration in phase V can be ascribed to the change of the potential difference between phases IV and V.

The electrochemical cell(I) was formed in a U-shaped poly(tetrafluoroethylene) tube 9 mm in inner diameter and 10 cm tall. About 8 ml of a nitrobenzene solution was first poured in the cell and then a reference solution and a sample solution were added to the nitrobenzene solution, one in each leg of the cell. A saturated potassium chloride solution saturated with silver chloride made contact with a sample solution *via* a glass frit. The cell was immersed into a water bath kept at 25.0±0.2 °C. The electromotive force (emf) of cell(I) was measured with a Keithley 616 electrometer. The emf was usually stable within 5 min after the formation of the liquid-membrane/sample solution contact, except at the lowest concentration of R_1^+, 0.1 mmol dm^{-3}, at which the emf values were less reproducible, probably due to impurities in the nitrobenzene solution.

Iodide salts of Me_3EtN^+, Me_3PrN^+, Me_3BuN^+, and Et_3MeN^+ were synthesized from trialkylamines and alkyl iodides[7] and then converted to the chloride salts.[8] These alkylammonium chloride and TEACl(Wako Pure Chem. Ind., Japan) were dried over P_2O_5 and used to prepare the stock solutions using thrice distilled water. The stock solutions were treated with silver chloride powder to remove trace iodide ions. TEATPB, Et_3MeTPB, and TPnATPB were prepared by precipitation from aqueous solution (for TEA^+ and Et_3MeN^+) or ethanol solution (for $TPnA^+$) of the iodide salts by adding an equimolar quantity of aqueous or ethanol solution of sodium tetraphenylborate (Dojin Lab., Japan) and were twice recrystallized from acetone. Reagent grade nitrobenzene was treated with active alumina and then equilibrated with thrice-distilled water. All other chemicals were of reagent grade.

Results

Tetraethylammonium Ion-selective Electrode. The electromotive force of the cell(I) was measured at a fixed concentration of TEATPB(R_1TPB) in the liquid membrane and of R_2Cl in the sample solution by varying the concentration of TEACl(R_1Cl) between 0.1 mmol dm^{-3} and 0.5 mol dm^{-3} in the sample solution. The interfering ions R_2^+ studied were Me_3EtN^+, Me_3PrN^+, Me_3BuN^+, and Et_3MeN^+, whose $\Delta^{W}_{NB}\varphi^{0}$'s are all more positive than that of TEA^+ ion. The measured sets of a and b values in the cell(I) are summarized in Table 2. The results for a=2 mmol dm^{-3} are shown in Figs. 1—4. In the absence of R_2^+ ion the emf showed a linear Nernstian response over the concentration range of TEACl studied, except at the highest concentrations (a=0.2 and 0.5 mol dm^{-3}) where interference by the supporting electrolyte occurs. The solid lines in these figures are the theoretical ones calculated from Eqs. 16—21 in Ref. 1 using the values in Table 1 for

Table 2. Concentrations of the electrolytes in cell (I) for the emf measurements of TEA^+ ion-selective electrodes

a/mmol dm^{-3}	b/mmol dm^{-3}	x/mmol dm^{-3}
0.5	1, 10, 50	0.1—500
1	0.2, 1, 2, 5, 10, 50	0.1—500
2	0.2, 1, 2, 5, 10, 50	0.1—500
5	1, 10, 50	0.1—500

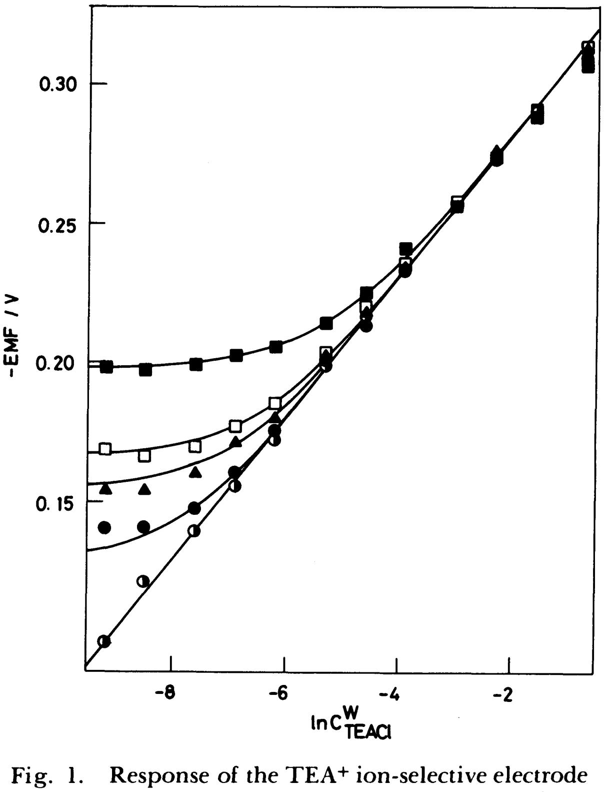

Fig. 1. Response of the TEA^+ ion-selective electrode in the presence of Me_3EtN^+ ion at a=2 mmol dm^{-3} and b=0(◑), 1(●), 5(▲), 10(□), and 50(■) mmol dm^{-3}.

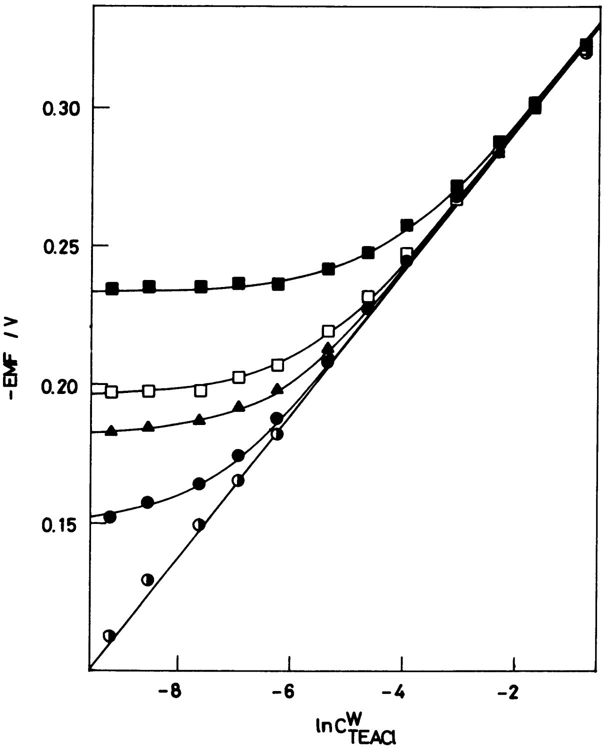

Fig. 2. Response of the TEA^+ ion-selective electrode in the presence of Me_3PrN^+ ion at a=2 mmol dm^{-3} and b=0(◑), 1(●), 5(▲), 10(□), and 50(■) mmol dm^{-3}.

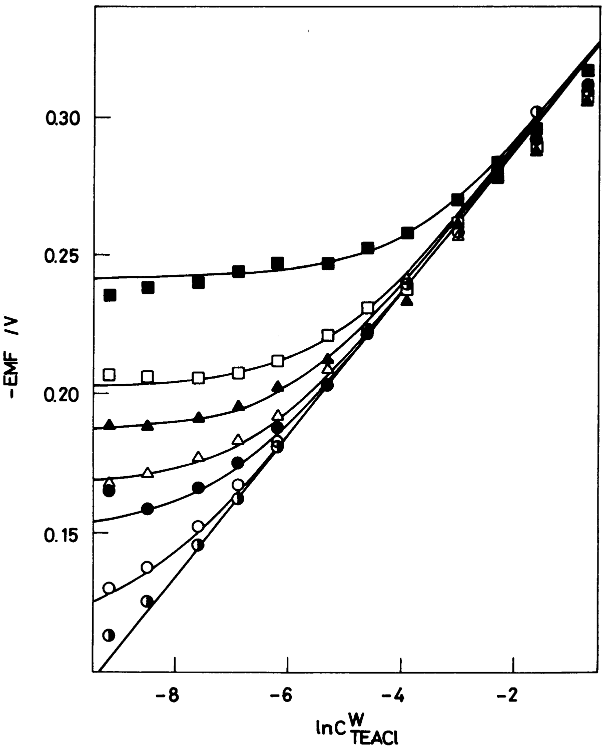

Fig. 3. Response of the TEA^+ ion-selective electrode in the presence of Et_3MeN^+ ion at a=2 mmol dm^{-3} and b=0(◑), 0.2(○), 1(●), 2(△), 5(▲), 10(□), and 50(■) mmol dm^{-3}.

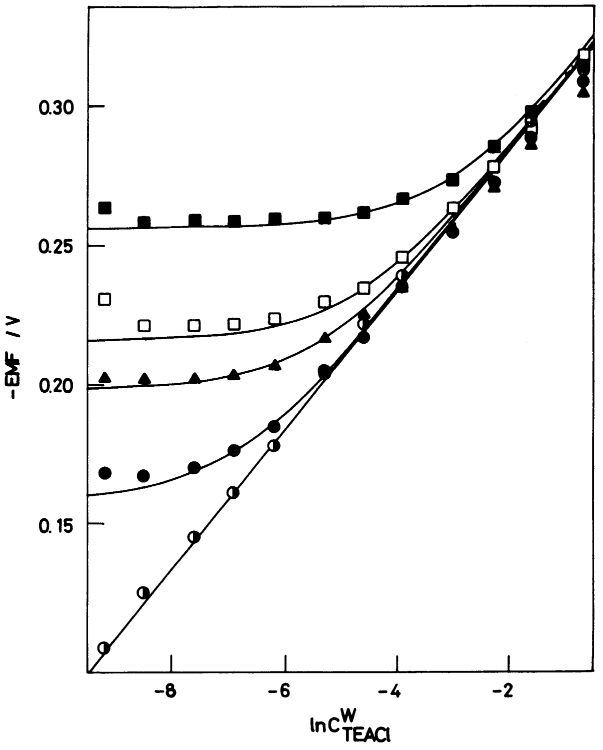

Fig. 4. Response of the TEA^+ ion-selective electrode in the presence of Me_3BuN^+ ion at a=2 mmol dm^{-3} and b=0(◑), 1(●), 5(▲), 10(□), and 50(■) mmol dm^{-3}.

the standard ion-transfer potentials and diffusion coefficients of these ions. The values for the diffusion coefficients in the liquid-membrane were taken as halves of those in the aqueous solution.[9] The ratios of the mass-transfer coefficients of the two ions were equated with the square root of the ratio of their diffusion coefficients; the mass-transfer was considered to occur primarily through diffusion in the present system.

Triethylmethylammonium Ion-selective Electrode. When the standard ion-transfer potential of an interfering ion is negative than that of the primary ion, the theory predicts that the degree of interference becomes more significant and the selectivity coefficient decreases with the decrease of the interfering ion concentration, in contrast to the cases where the standard ion transfer potential of an interfering ion is more positive than that of the primary ion. As an example of such a case, we studied the response of the Et_3MeN^+ ion-selective electrode in the presence of TEA^+ ion at a=2 mmol dm^{-3} and b=0.2, 1, 2, 5, 10, and 50 mmol dm^{-3}. The results are shown in Fig. 5. The solid lines are the theoretical curves calculated as described above.

Discussion

Figures 1—5 clearly show that for all the combinations of the primary and interfering ions studied the calculated curves agree well with the experimental points over wide ranges of the concentrations of the primary and interfering ions. This confirms that the theory of liquid ion-exchange membrane ion-selective electrodes previously derived by Kakiuchi and

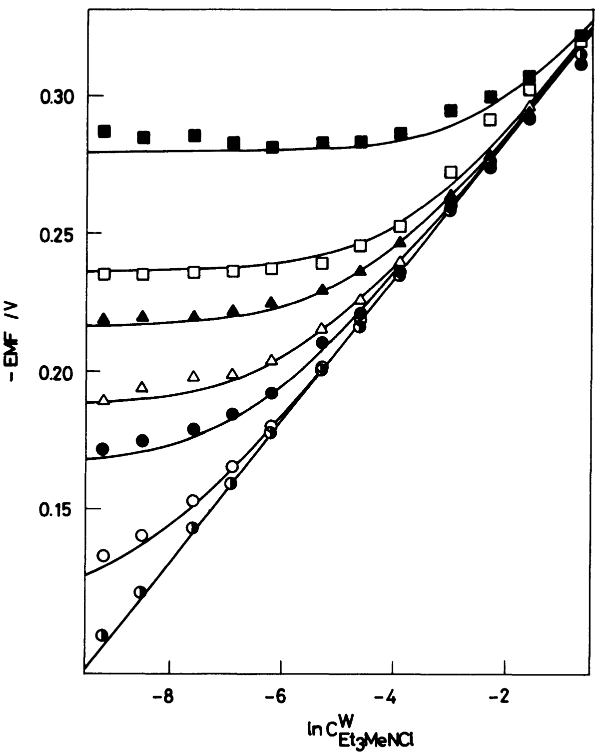

Fig. 5. Response of the Et_3MeN^+ ion-selective electrode in the presence of TEA^+ ion at $a=2$ mmol dm^{-3} and $b=0$(◑), 0.2(○), 1(●), 2(△), 5(▲), 10(□), and 50(■) mmol dm^{-3}.

Senda[1)] satisfactorily describes the emf response of the ion-selective electrodes of the type represented by cell(I).

The selectivity characteristics of ion selective electrodes are usually evaluated by using the selectivity coefficient, $k^{pot}_{i,j}$, defined by the Nicolsky equation.[10)] Although $k^{pot}_{i,j}$ is not a physical constant intrinsic to a given electrode system but depends on experimental conditions such as the concentrations of the relevant ions,[11)] it has been widely used as a convenient measure of the selectivity of ion-selective electrodes.[12)] Moreover, the manner of change of $k^{pot}_{i,j}$ with the concentration of primary ion has been sometimes used as a criterion for the validity of a theory of ion-selective electrodes.[13)] We evaluated the selectivity coefficient of the ion-selective electrode(I) defined by a Nicolsky-type equation:[1)]

$$E = E^{0}_{R_1} - \frac{RT}{F} \ln \frac{c^{W}_{R_1} + k^{pot}_{i,j} c^{W}_{R_2}}{c^{0}_{R_1}} \tag{1}$$

where E is the emf, $E^{0}_{R_1}$ is $\Delta^{W}_{NB}\varphi^{0}_{R_1} + \Delta E_{ref}$, being the potential difference associated with the reference electrodes in the cell(I), and $c^{W}_{R_1}$, $c^{W}_{R_2}$, and $c^{0}_{R_1}$ are the concentrations of R_1^+ and R_2^+ ions in the sample solution and of R_1^+ ion in the liquid membrane, respectively. We used two methods to determine the $k^{pot}_{i,j}$values: Method I using the intersection point of the two linear portions of the emf *vs.* $\log c^{W}_{R_1}$ curve and Method II using the concentration of a primary ion at which the emf *vs.* $\log c^{W}_{R_1}$ curve in the presence of an interfering ion deviates by $(RT/F)\ln 2 = 18$ mV from the curve without interfering ion. The former method gives the $k^{pot}_{i,j}$ value at the infinitely small $c^{W}_{R_1}$,[1)] whereas the latter gives the one at the $c^{W}_{R_1}$ at which the curve deviates by 18 mV from the linear Nernstian response. Method I seems less sensitive to the scattering of the experimental emf values than Method II, since Method I necessarily averages out the scattering by using several points to draw a horizontal line at the lower values of $c^{W}_{R_1}$. However, Method I is not applicable to cases where such a horizontal part of the emf *vs.* $c^{W}_{R_1}$ curve is not attainable experimentally. The results are given in Tables 3—5 together with the theoretical values based on Eq. 24 in Ref. 1. For both methods, the calculated values of $k^{pot}_{i,j}$ agree well with the observed ones. Taking account of the fact that the observed $k^{pot}_{i,j}$ value is very sensitive to small scattering of emf values, this general agreement seems enough evidence of the validity of the theory for predicting the response of the ion-selective electrode of the type represented by the cell(I).

Table 3 shows that the $k^{pot}_{i,j}$ values decrease with the increase of the concentration of the interfering ions. This is what is theoretically expected for the case when the standard ion-transfer potential of the primary ion (TEA^+) is more negative than that of the interfering ion (Me_3EtN^+, Me_3PrN^+, Me_3BuN^+, and Et_3MeN^+). In the case of TEA^+ ion interference with respect to Et_3MeN^+ ion, the standard ion-transfer potential of the primary ion (Et_3MeN^+) is more positive than that of the interfering ion(TEA^+). The theory predicts in this case that the $k^{pot}_{i,j}$ value increases with increasing concentration of the interfering ion, which was confirmed experimentally as shown in Table 4. Such an inversion in the concentration dependence of $k^{pot}_{i,j}$ has been found also for a nitrate ion-selective electrode of liquid ion-exchange membrane type without supporting electrolytes.[15)]

According to the theory, $k^{pot}_{i,j}$ depends not only on the concentration of the ions in sample solution but also on the concentration of the primary ion in liquid membrane. The $k^{pot}_{i,j}$ values for the TEA^+ ion-selective electrode at $a=0.5$, 1, 2, and 5 mmol dm^{-3} in the presence of Et_3MeN^+ in the sample solution at $b=10$ mmol dm^{-3} in cell(I) are given in Table 5. The $k^{pot}_{i,j}$ values determined by Method I clearly show the increasing tendency of $k^{pot}_{i,j}$ with the increase of the concentration of TEA^+ ion in the liquid membrane. Such a change of $k^{pot}_{i,j}$ was less conspicuous for the $k^{pot}_{i,j}$ estimated by Method II, probably because of the larger error inherent to this method.

The selectivity coefficients for a series of interfering ions for a given primary ion are usually discussed in terms of the difference in single ion partition coefficient defined by $K_i = c^{W}_{i}/c^{0}_{i}$ for i ion. By definition the difference in the single ion partition coefficient between two ions, i and j, is related to the difference in the standard ion-transfer potential between the two ions by

TABLE 3. SELECTIVITY COEFFICIENTS OF TEA^+ ION-SELECTIVE ELECTRODE[1)]

Interfering	$c^W(R_2Cl)$	Method I		Method II	
ion	mmol dm^{-3}	k^{pot}_{exptl}	k^{pot}_{calcd}	k^{pot}_{exptl}	k^{pot}_{calcd}
Me_3EtN^+	1	—	0.33	0.28	0.26
	5	—	0.19	0.15	0.15
	10	0.14	0.15	0.11	0.13
	50	0.10	0.10	0.09	0.09
Me_3PrN^+	1	—	0.60	0.43	0.51
	5	—	0.41	0.35	0.37
	10	0.36	0.37	0.30	0.33
	50	0.32	0.31	0.37	0.30
Et_3MeN^+	0.2	—	0.88	0.88	0.81
	1	—	0.70	0.64	0.63
	2	—	0.63	0.62	0.56
	5	0.55	0.55	0.50	0.50
	10	0.54	0.50	0.45	0.48
	50	0.41	0.46	0.41	0.45
Me_3BuN^+	1	—	0.70	0.64	0.63
	5	0.55	0.55	0.50	0.50
	10	0.54	0.50	0.45	0.48
	50	0.41	0.46	0.41	0.45

1) The concentration of TEATPB in the liquid membrane was 2 mmol dm^{-3}.

TABLE 4. SELECTIVITY COEFFICIENTS OF Et_3MeN^+ ION-SELECTIVE ELECTRODE IN THE PRESENCE OF TEA^+ ION[1)]

c^W(TEACl)	Method I		Method II	
mmol dm^{-3}	k^{pot}_{exptl}	k^{pot}_{calcd}	k^{pot}_{exptl}	k^{pot}_{calcd}
0.2	—	1.08	1.37	1.16
1	—	1.38	1.70	1.64
2	1.78	1.64	1.94	1.89
5	—	1.95	2.03	2.10
10	2.02	2.10	1.87	2.18
50	2.79	2.23	2.63	2.25

1) The concentration of Et_3MeN^+ ion in the liquid membrane was 2 mmol dm^{-3}.

TABLE 5. CHANGE OF THE SELECTIVITY COEFFICIENT OF THE TEA^+ ION-SELECTIVE ELECTRODE WITH THE CHANGE OF THE CONCENTRATION OF TEA^+ ION IN THE LIQUID MEMBRANE[1)]

c^{NB}(TEATPB)	Method I		Method II	
mmol dm^{-3}	k^{pot}_{exptl}	k^{pot}_{calcd}	k^{pot}_{exptl}	k^{pot}_{calcd}
0.5	0.45	0.46	0.60	0.45
1	0.51	0.48	0.46	0.46
2	0.54	0.50	0.45	0.48
5	0.64	0.56	0.50	0.52

1) The concentration of Et_3MeN^+ ion in the sample solution was 10 mmol dm^{-3}.

$$\ln(K_i/K_j) = \frac{F}{RT}(z_j\Delta_o^w\varphi_j^0 - z_i\Delta_o^w\varphi_i^0) \tag{2}$$

where K_i and K_j are the single ion partition coefficients for the ions i and j, and z_k is the electric charge of the ion $k(k=i$ or $j)$. When the liquid-membrane contains lipophilic ligands, X, (usually belonging to the family of ionophores) which form complexes MX_n $(n=1, 2, \cdots)$ with the ion M (M=i or j) transferred across the liquid-membrane/sample solution interface, the standard ion-transfer potential $\Delta_O^W\varphi_M^0$ (M=i or j) in Eq. 2 should be replaced by the apparent standard ion-transfer potential $\Delta_O^W\varphi^0_{M,app}$[16)] defined by

$$\Delta_o^w\varphi^0_{M,app} = \Delta_o^w\varphi^0_M - \frac{RT}{z_M F}\ln(\sum_n \beta_n c_X^n) \tag{3}$$

where β_n is the over-all stability constant ($\beta_0=1$) of the complexes MX_n ($n=0, 1, 2, \cdots$), and c_X is the bulk concentration of X in the liquid membrane.

The experimental linear correlation between the logarithm of the selectivity coefficient and the logarithm of the single ion-partition coefficient have long been recognized for the liquid ion-exchange membrane ion-selective electrodes.[17)] The linear correlation is one of the important conclusions of Sandblom *et al.*'s theory[18)] for membrane electrode potential and hence the experimental linear correlation has been considered as demonstrating the essential validity of their theory. In our previous paper we have shown that the dependence of the logarithm of selectivity coefficient on the difference in the standard ion-transfer potential between the primary and interfering ions is approximately linear under certain conditions, but can be remarkably nonlinear, depending on the mass-transfer coefficients of the ions. (See Fig. 4 in Ref. 1). Figure 6 shows a plot of the logarithm of the k_{ij}^{pot} by method I at a=2 mmol dm^{-3} and b=10 mmol dm^{-3} against the difference between the standard ion-transfer potentials of the primary and interfering ions. The upper four circles in Fig. 6 are for the TEA^+ ion-selective electrode with the interfering ions Me_3EtN^+, Me_3PrN^+, Et_3MeN^+, and Me_3BuN^+ and the lowest circle is for the Et_3MeN^+ ion-selective electrode with the interfering ion TEA^+. The selectivity coefficient increased with the increase

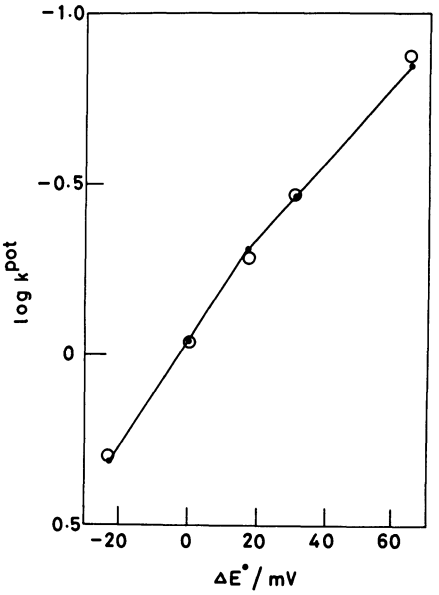

Fig. 6. Change of the logarithm of selectivity coefficient with the change of the difference between the standard ion-transfer potentials of the primary and interfering ions, ΔE. Upper four points are for the TEA^+ ion-selective electrode and the lowest point for the Et_3MeN^+ ion-selective electrode.

of the hydrophobicity of the interfering ions, *i.e.*, with the decrease of the standard ion-transfer potential. The solid line in Fig. 6 connects the theoretical points of $k_{i,j}^{pot}$ indicating a good agreement between the theory and the experimental results. The nonlinearity of the plot in Fig. 6 clearly demonstrates the validity of the theory in which the effect of the mass transfer coefficients of the ions is taken into account.

As demonstrated by this study, the emf response of the liquid ion exchange membrane ion-selective electrodes of the type represented by cell(I) is described well by the theory based on the concept of the mixed ion-transfer potential at the liquid-membrane/sample solution interface. This indicates that the ion-transfer processes at the interface between the liquid membrane and the sample solution has a general importance for the understanding of the basic properties of liquid ion-exchange membrane ion-selective electrodes.

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