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The Selectivity Evaluation of an Ion-selective Electrode with a Liquid Membrane by Electrode Response to a Foreign Ion

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The potential responses of liquid-membrane electrodes to foreign ions were examined. The electrode response obeyed the Nikolsky equation when the selectivity for the foreign ion was nearly equal to or higher than that for the objective ion and when the concentration of the foreign ion in the sample solution was sufficiently higher than that of the ion-exchanger in the liquid membrane. The Nikolsky equation, however, did not hold for the response when the selectivity for the foreign ion over the objective ion was extremely low or when the concentration of the sample was not so high. Such a non-ideal response was ascribed to the variation in the ionic composition at the membrane-solution interface caused by the ion-exchange. From the measurement of the electrode potential under conditions when the response obeyed the Nikolsky equation, the selectivity coefficient for the foreign ion over the objective ion could be obtained successfully as an intrinsic value of the electrode membrane. The selectivity value thus obtained was in good agreement with the value estimated from the Sandblom-Eisenman-Walker theory on the electrode selectivity. The additivity of the membrane potential was also described.

In recent years, many liquid membrane electrodes have been developed for the activity measurements of various inorganic and organic ions in aqueous solutions.[1-4] The selectivities of these electrodes have been evaluated by using several methods, such as the mixed-solution method and the separate-solution method.[5-7] It has been observed, however, that the selectivity values thus obtained are not always constant but vary with the method employed and the conditions of measurement.[5,8,9]

In a previous communication, Yoshida and one of the present authors (N.I.) have briefly reported on one way to evaluate an intrinsic selectivity value for a given electrode.[10] This paper will describe the details of this approach and will present the selectivity values of several liquid membrane electrodes obtained through the approach. The relationship between the selectivity values and ionic parameters, such as the mobility and the ion-partition coefficient, will also be mentioned.

Experimental

Reagents and Sensitive Liquid Membranes. All the chemicals used were of a reagent-grade quality. Aqueous solutions of sodium salts of various inorganic and organic anions were used as sample and reference solutions. In the case of cation-selectivity evaluation, aqueous solutions of alkali metal chlorides and quaternary ammonium chlorides were used. A liquid ion-exchanger membrane consisted of an organic solution of an ion-pair of an objective ion with an ion-exchange-site ion, such as the crystal violet, tris(bathophenanthroline)iron(II), methyltricaprylylammonium, and dipicrylaminate ions. Nitrobenzene, nitromethane, 1,2-dichloroethane, chloroform, and 1-decanol were used as solvents of the membranes. The liquid membrane solutions were prepared by the same procedures as in previous papers.[11,12]

Potential Measurement. A glass U-tube cell reported on in a previous paper was used for the set-up of the cell (1) in order to evaluate the selectivity of the i-ion-sensitive membrane to the foreign j-ion:[13]

$$+\text{SCE or Ag-AgCl/Reference Solution (i)/ Liquid Membrane (S-i)/Sample Solution (j)/ SCE or Ag-AgCl}- \quad (1)$$

where S denotes the ion-exchange site in the membrane. The electromotive force of Cell (1) was measured by using a Takeda Riken Electrometer TR-8651. A silver/silver chloride electrode was used as the reference electrode for the study of the cation selectivity. A saturated calomel electrode (SCE) was used in evaluations of the anion selectivities. A sample or reference solution was connected to the reference electrode by means of an agar salt bridge saturated with potassium chloride or ammonium chloride.

Alternatively, the electromotive force of Cell (2) was measured according to Shean's method.[14]

$$+\text{SCE/Solution (i)/Membrane (i)/Membrane (j)/ Solution (j)/SCE}- \quad (2)$$

Results and Discussion

Electrode Responses for Solutions of Foreign Ions. In the determination of the selectivity coefficient of an ion-selective electrode with a liquid membrane, it is usually assumed that the electrode response for a sample solution containing a monovalent objective ion, i, as well as a foreign ion, j, obeys the following Nikolsky equation (3):

$$E_{\mathrm{M}} = \pm 2.303RT/F \log\left(\left(a_{\mathrm{i}}'' + K_{\mathrm{i,j}}^{\mathrm{Pot}} a_{\mathrm{j}}''\right)/a_{\mathrm{i}}'\right) \quad (3)$$

where a_{i} and a_{j} are the activities of the corresponding ions, i and j. Prime and double prime refer to the reference and sample solutions respectively. The $K_{\mathrm{i,j}}^{\mathrm{Pot}}$ symbol represents the potentiometric selectivity coefficient for the j ion over the i ion. The plus and minus signs at the top in Eq. (3) stand for the responses of cation- and anion-selective electrodes respectively. For a sample solution containing the j ion alone, Eq. (3) reduces to:

$$E_{\mathrm{M}} = \pm 2.303RT/F \log\left(K_{\mathrm{i,j}}^{\mathrm{Pot}} a_{\mathrm{j}}''/a_{\mathrm{i}}'\right) \quad (4)$$

From Eq. (4), a plot of E_{M} against $\log a_{\mathrm{j}}''$ may be expected to be on a straight line with a Nernstian slope under a constant activity of a_{i}'.

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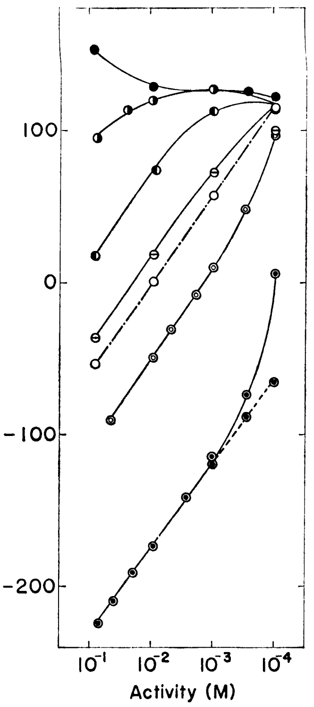

Fig. 1. Potential responses of the hydrogenmaleate ion-selective electrode for the solutions of foreign anions. Membrane: 10^{-4} M nitrobenzene solution of crystal violet salt of hydrogenmaleate.
Temp. 20 °C.
○: hydrogenmaleate (— — —), ●: acetate,
◑: chloride, ◐: anthranilate, ⊖: trifluoroacetate,
◎: hydrogenphthalate, ⊙: perchlorate (Broken line shows the membrane potential of the cell (2)).

Figure 1 shows the observed potentials of the hydrogenmaleate ion-selective electrode for the sample solutions, each solution containing only a single anion species. The conversions of the concentrations of the ions to ionic activities were made by means of the Debye-Hückel equation, using Kielland's ion-size parameters,[15] except for the activities of hydrogenmaleate, hydrogenphthalate, and trifluoroacetate ions, which were calculated by using the values of the parameters assumed in previous papers.[16,17] The parameter for the anthranilate ion was assumed to be equal to that of the chlorobenzoate ion. For the solution of the objective hydrogenmaleate ion, a Nernstian response was obtained over a wide concentration range.[17] The electrode responses for the solutions of foreign ions, however, were not always Nernstian. Foreign ions (acetate, chloride, trifluoroacetate and anthranilate ions) giving higher potentials than hydrogenmaleate ion do not so seriously interfere with the activity measurement of the hydrogenmaleate ion, as may be understood from their low selectivities as estimated by means of Eq. (4). Potential-activity curves on these kinds of ions have lower slopes at low activity levels than does a Nernstian one, as is shown in Fig. 1. In the cases of acetate and chloride ions, the potentials were unstable in the initial stage of measurement and it took several hours to attain stationary values of potentials. The reproducibility was also relatively poor, especially at low activity levels. For trifluoroacetate and anthranilate ions, the electrode shows stable and reproducible potentials which obey Eq. (4) down to 10^{-3} M, although the potential drifts were observed initially and a period of more than 60 min was required to obtain constant values of the potentials at 10^{-4} M. Foreign ions (hydrogenphthalate and perchlorate ions) giving lower potentials than the hydrogenmaleate ion seriously interfere with the activity measurement of the hydrogenmaleate ion, even if trace amounts of these kinds of ions coexist in the sample solutions. In the activity levels higher than $10^{-2.5}$ M, the electrode potentials were stable and reproducible; they obeyed Eq. (4). On the other hand, remarkable potential drifts were observed initially, and it took several hours to attain constant potentials at activity levels lower than 10^{-3} M. The slopes of the activity-potential curves in such a stationary state were higher than a Nernstian slope.

Thus, the slopes of the potential-activity curves for foreign ions at low activity levels are different from a theoretical Nernstian value. The slope of the potential-activity curve for the foreign ion with a selectivity lower than that of the objective ion is lower than a Nernstian slope, while that for the foreign ion with a higher selectivity is higher. Response patterns similar to those of foreign ions were observed on the responses of the chloride, nitrate, hydrogenphthalate, and perchlorate ion-selective electrodes prepared in this laboratory. As may be seen in Fig. 2, the commercial nitrate ion-selective electrode of Orion 92-07 also showed a similar response pattern.

When the i-ion-selective electrode is immersed in a sample solution containing the j ion alone, the following ion-exchange reaction (5) occurs between the membrane and the sample solution, resulting in the forma-

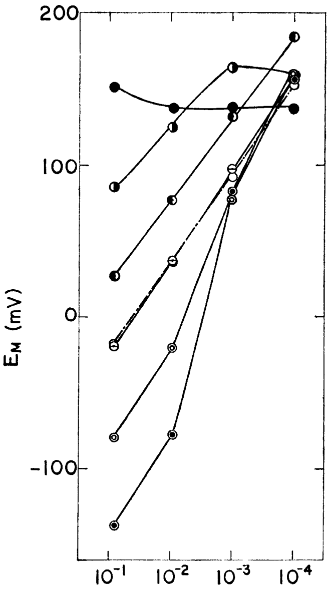

Fig. 2. Potential responses of the nitrate ion-selective electrode (Orion 92-07) for the solutions of foreign anions.
Temp. 20 °C.
○: nitrate (— — —), ●: acetate, ◑: chloride,
◐: bromide, ⊖: chlorate, ⊙: perchlorate, ◎: iodide.

tion of a diffusion layer containing the j ion as well as the i ion:

$$\text{i (Membrane)} + \text{j (Solution)} \rightleftharpoons \text{j (Membrane)} + \text{i (Solution)} \qquad (5)$$

Hence, it is more realistic to describe the electrode potential or membrane potential by means of Eq. (3), with the activities of the i and j ions on the aqueous side of the interface, $a_{\mathrm{i}}''(0)$ and $a_{\mathrm{j}}''(0)$. Since the ion-exchange process (5) proceeds stoichiometrically in most cases, it may reasonably be assumed that $a_{\mathrm{j}}''(0)$ is approximately equal to $a_{\mathrm{j}}''-a_{\mathrm{i}}''(0)$. Accordingly, the electode response to a foreign anion, j, may be expressed as follows:

$$E_{\mathrm{M}} = -2.303RT/F \log\left((a_{\mathrm{i}}''(0)+K_{\mathrm{i,j}}^{\mathrm{pot}}(a_{\mathrm{j}}''-a_{\mathrm{i}}''(0)))/a_{\mathrm{i}}'\right) \quad (6)$$

If the value of $K_{\mathrm{i,j}}^{\mathrm{pot}}$ is smaller than unity, the value of $(a_{\mathrm{i}}''(0)+K_{\mathrm{i,j}}^{\mathrm{pot}}(a_{\mathrm{j}}''-a_{\mathrm{i}}''(0)))$ is greater than the value of $K_{\mathrm{i,j}}^{\mathrm{pot}}\, a_{\mathrm{j}}''$. Therefore, the electrode potential, E_{M}, is lower than that which would be expected from Eq. (4). If the activity of the j ion in the sample solution, a_{j}'', is very high, and if $K_{\mathrm{i,j}}^{\mathrm{pot}}$ is moderately small, the potential will be governed by the $K_{\mathrm{i,j}}^{\mathrm{pot}}\, a_{\mathrm{j}}''$ quantity. Accordingly, the slope of the potential-activity curve is lower at low concentrations of the j ion and tends to approach a Nernstian slope at higher concentrations. In the cases of the acetate and chloride ions, however, $K_{\mathrm{i,j}}^{\mathrm{pot}}$ is much smaller than unity and the observed slope is quite different from the theoretical one. This means that the evaluation of $K_{\mathrm{i,j}}^{\mathrm{pot}}$ by means of Eq. (4) by using the activity of the foreign ion, j, in the bulk of the sample solution and the observed potential is practically difficult. On the other hand, $K_{\mathrm{i,j}}^{\mathrm{pot}}$ is nearly equal to unity in the cases of the anthranilate and trifluoroacetate ions. Hence, the observed potentials obey Eq. (4) at higher concentrations. Thus, the $K_{\mathrm{i,j}}^{\mathrm{pot}}$ can be determined by means of Eq. (4).

If a value of $K_{\mathrm{i,j}}^{\mathrm{pot}}$ is greater than unity, the value of $(a_{\mathrm{i}}''(0)+K_{\mathrm{i,j}}^{\mathrm{pot}}(a_{\mathrm{j}}''-a_{\mathrm{i}}''(0)))$ may be smaller than that of $K_{\mathrm{i,j}}^{\mathrm{pot}}a_{\mathrm{j}}''$. Consequently, the electrode potential, E_{M}, becomes higher than that calculated from Eq. (4). The value of $(a_{\mathrm{i}}''(0)+K_{\mathrm{i,j}}^{\mathrm{pot}}(a_{\mathrm{j}}''-a_{\mathrm{i}}''(0)))$ is approximately equal to the value of $K_{\mathrm{i,j}}^{\mathrm{pot}}\, a_{\mathrm{j}}''$ if the concentration of the j ion in the sample solution is sufficiently higher than that of the ion-exchanger or the objective counter ion in the membrane. At such high activity levels of the j ion, the electrode response, again, would obey Eq. (4); it is also possible to evaluate $K_{\mathrm{i,j}}^{\mathrm{pot}}$ from the observed potential and the a_j'' activity in the bulk of the sample solution. The responses of the hydrogenmaleate electrode to the perchlorate and hydrogenphthalate ions are examples of this kind of response.

Thus, the observed potential does not always correspond to a true activity of the j ion in the bulk of the sample solution, when the value of $K_{\mathrm{i,j}}^{\mathrm{pot}}$ differs too greatly from unity.

Additivity of the Electrode Potential or Membrane Potential. When the $K_{\mathrm{i,j}}^{\mathrm{pot}}$ is nearly equal to or greater than unity, and when the concentration of the foreign ion, j, in the sample solution is sufficiently higher than that of the ion-exchanger in the liquid membrane, the counter ion within the membrane in the neighborhood of the solution-membrane interface is exchanged almost completely by the foreign j ion. That is, Cell (1) is essentially converted into Cell (2). The electrode potential or membrane potential measured under such conditions can be regarded as substantially a kind of bi-ionic potential (B.I.P.) in the liquid ion-exchanger system; it obeys Eq. (4), as was mentioned in the previous section. As is illustrated in Fig. 1, this expectation can be experimentally confirmed by measuring the membrane potential of Cell (2), which consists of two component membranes responsive to hydrogenmaleate and perchlorate respectively. Shean *et al.* have found the additivity of the B.I.P.s arising across the liquid ion-exchanger membranes which consist of a given ion-exchanger in a given solvent of the membrane.[14] An analogous additivity of the potential has been observed on the electrode potential or membrane potential of Cell (1) as follows:

$$E_{\mathrm{M}(1,n)} = E_{\mathrm{M}(1,2)} + E_{\mathrm{M}(2,3)} + \cdots + E_{\mathrm{M}(i,i+1)} + \cdots \cdots + E_{\mathrm{M}(n-1,n)} \qquad (7)$$

where $E_{\mathrm{M}(1,n)}$ and $E_{\mathrm{M}(i,i+1)}$ are the membrane potentials of Cells (8) and (9) respectively.

Reference Solution	Liquid Membrane	Sample Solution	
Counter Ion, 1 (a_1')	(S–1)	Counter Ion, n (a_n'')	(8)

Reference Solution	Liquid Membrane	Sample Solution	
Counter Ion, i (a_{i}')	(S–i)	Counter Ion, $i+1$ (a_{i+1}'')	(9)
	(i: 1, 2, ⋯, $n-1$)		

TABLE 1. ADDITIVITY OF MEMBRANE POTENTIAL (I) AT 20 °C Alkali Metal Ion-selective Electrodes

Counter ion in membrane[a]	Reference solution (1.00×10^{-1}M)	Membrane potential $E_{\mathrm{M}(i,j)}$ in mV								
		Sample solution (1.00×10^{-1}M)								
		NaCl		KCl		RbCl		CsCl		$(\mathrm{Pr})_4\mathrm{NCl}$
Na⁺	NaCl	0		116		156		203		473
			(116)[b]		(40)		(47)		(270)	
K⁺	KCl	−100		0		41		90		355
			(100)		(41)		(49)		(265)	
Rb⁺	RbCl	−122		−38		0		46		315
			(84)		(38)		(46)		(269)	
Cs⁺	CsCl	−155		−82		−45		0		269
			(73)		(37)		(45)		(269)	

a) Membranes are 1.0×10^{-4} M nitrobenzene solutions of alkali metal dipicrylaminates. b) Figures in parentheses denote differences between adjacent potential values.

Table 2. Additivity of membrane potential (II), at 20 °C
Anion-selective Electrodes

Solvent of membrane	Counter ion in membrane	Reference solution (1.00×10^{-2}M)	Membrane potential in mV										
			Sample solution, as sodium salt (1.00×10^{-2}M)										
			Cl^-		HMA^-		Saicylate		HPA^-		ClO_4^-		
Nitrobenzene[a]	Cl^-	NaCl	0	(−155)	−155	(−43)	−198	(−6)	−204	(−125)	−329		
	HMA^- [b]	NaHMA			0	(−43)	−43	(−7)	−50	(−127)	−177		
	HPA^- [c]	NaHPA							0	(−125)	−125		
1,2-Dichloroethane[a]	Cl^-	NaCl	0	(−138)	−138	(−34)	−172	(−8)	−180	(−120)	−300		
	HMA^-	NaHMA			0	(−34)	−34	(−9)	−43	(−117)	−160		
	HPA^-	NaHPA							0	(−116)	−116		
Chloroform[a]	Cl^-	NaCl	0	(−129)	−129	(−10)	−139	(−26)	−165	(−33)	−198		
	HMA^-	NaHMA			0	(−10)	−10	(−25)	−35	(−35)	−70		
	HPA^-	NaHPA							0	(−33)	−33		
		(1.00×10^{-1}M)	(1.00×10^{-1}M)										
			Cl^-		Br^-		NO_3^-		I^-		ClO_4^-		SCN^-
1-Decanol[d]	Cl^-	NaCl	0	(−25)	−25	(−6)	−31	(−36)	−67	(−8)	−75	(−19)	−94
	NO_3^-	$NaNO_3$	31	(−25)	6	(−6)	0	(−36)	−36	(−9)	−45	(−19)	−64

a) Crystal violet was used as the ion-exchange site in the membrane (1.00×10^{-4} M). b) HMA^- denotes hydrogenmaleate ion. c) HPA^- denotes hydrogenphthalate ion. d) Methyltricaprylylammonium ion was used as the ion-exchange site in the membrane (1.00×10^{-3} M).

Here, 1, 2, —, n-1, and n are monovalent counter ions with the same sign of charge. In order for Eq. (7) to be valid, the following requirements (10) should be satisfied in addition to the conditions of the concentrations of the sample solution and liquid membrane solution mentioned at the beginning of this section:

$$\left.\begin{array}{l} a_i' = a_{i+1}' \quad (i\colon 1, 2, \cdots, n-2) \\ a_i'' = a_{i+1}'' \quad (i\colon 2, 3, \cdots, n-1) \\ K_{\mathrm{I,J}}^{\mathrm{Pot}} \gtrsim \text{unity} \quad (i\colon 1, 2, \cdots, n-1) \end{array}\right\} \qquad (10)$$

In Table 1, the membrane potentials of alkali metal ion-selective electrode membranes, which consist of 10^{-4} M nitrobenzene solutions of dipicrylaminates of alkali metals, are summarized. The membrane containing sodium dipicrylaminate gives a potential difference of 473 mV between the solutions of sodium chloride and tetrapropylammonium chloride $(Pr)_4NCl$. This is almost entirely consistent with the algebraic sum of $E_{\mathrm{M(Na,K)}}$, $E_{\mathrm{M(K,Rb)}}$, $E_{\mathrm{M(Rb,Cs)}}$, and $E_{\mathrm{M(Cs,(Pr),N)}}$, which is 472 mV. On the other hand, the membrane containing cesium dipicrylaminate yields a potential difference of −155 mV between the solutions of cesium chloride and sodium chloride. This is not equal to the sum of $E_{\mathrm{M(Cs,Rb)}}$, $E_{\mathrm{M(Rb,K)}}$, and $E_{\mathrm{M(K,Na)}}$, which is −183 mV. Thus, the additivity of the potential does not hold when the $K_{\mathrm{I,J}}^{\mathrm{pot}}$ is considerably smaller than unity. The additivity relation was also observed on the potentials of the liquid membranes responsive to monovalent anions, as is illustrated in Table 2.

When the $K_{\mathrm{I,J}}^{\mathrm{pot}}$ is sufficiently less than unity or when the concentration of the foreign ion in the sample solution is not sufficiently higher than that of the ion-exchanger in the liquid membrane, Cell (1) is not converted into Cell (2), but into the two ionic cells on the foreign ion and the objective ion. Therefore, the additivity of the potential does not hold under such conditions.

Inter-ionic Selectivity of the Liquid Membrane. From the additivity of the membrane potential, one can obtain the following Eq. (11):

$$K_{i,n}^{\mathrm{Pot}} = K_{1,2}^{\mathrm{Pot}} K_{2,3}^{\mathrm{Pot}} \cdots K_{i,i+1}^{\mathrm{Pot}} \cdots K_{n-1,n}^{\mathrm{Pot}} \qquad (11)$$

where $K_{i,i+1}^{\mathrm{pot}}$ is the selectivity coefficient of the i-ion selective electrode for the $i+1$ ion over the i ion. Judging from the conditions on the additivity of the membrane potential, the selectivity for the 1, 2, —, n ions should increase in the sequence of the numbers. Equation (11) implies that the inter-ionic selectivity of a liquid membrane consisting of a given ion-exchange site and a given solvent of the membrane can be evaluated from the potential measurements of the 1-ion selective electrode for the solutions of foreigh ions, 2, 3, —, n. The 1 ion as a reference on selectivity evaluation should have such a degree of extractability

TABLE 3. MEMBRANE POTENTIALS ($E_{M(Cl,j)}$ or B.I.P.$_{Cl,j}$) AND SELECTIVITY COEFFICIENTS (log $K_{Cl,j}^{pot}$), Temp. 20 °C

Ion (j)	Solvent of membrane							
	Nitrobenzene[a)]		1,2-Dichloroethane[a)]		Chloroform[a)]		1-Decanol[b)]	
	$E_{M(Cl,j)}$[c)] (mV)	log $K_{Cl,j}^{pot}$	$E_{M(Cl,j)}$[c)] (mV)	log $K_{Cl,j}^{pot}$	$E_{M(Cl,j)}$[c)] (mV)	log $K_{Cl,j}^{pot}$	$E_{M(Cl,j)}$[c)] (mV)	log $K_{Cl,j}^{pot}$
Cl^-	0	0.00	0	0.00	0	0.00	0	0.00
Br^-	−88	1.51	−78	1.34	−79	1.36	−25	0.43
NO_3^-	−145	2.49	−124	2.13	−81	1.39	−31	0.53
ClO_3^-	−160	2.75	−142	2.44	−96	1.65	−29	0.50
I^-	−224	3.85	−204	3.51	−178	3.06	−67	1.15
SCN^-	−242	4.16	−223	3.83	−168	2.89	−94	1.61
BF_4^- [e)]	−270	4.64	−241	4.14	−126	2.17	−24	0.41
ClO_4^-	−329	5.66	−300	5.16	−198	3.40	−75	1.29
Benzoate	−57	0.97	−46	0.79	−17	0.28	−75	1.26
p-Aminosalicylate[e)]	−101	1.74	—	—	−22	0.38	—	—
Trifluoroacetate[e)]	−130	2.24	—	—	−67	1.15	—	—
Benzenesulfonate[c)]	−135	2.32	−87	1.50	—	—	−58	1.00
Hydrogenmaleate[e)]	−155	2.67	−138	2.37	−129	2.22	−56	0.96
Salicylate[e)]	−198	3.40	−172	2.96	−139	2.39	−122	2.10
Hydrogenphthalate[e)]	−204	3.51	−180	3.09	−165	2.84	−91	1.56
Benzylate[e)]	−214	3.68	−197	3.39	−162	2.79	—	—
1-Naphthalenesulfonate[e)]	−215	3.70	−205	3.51	—	—	−99	1.70

a) Membranes consisted of an organic solution of chloride salt of crystal violet (1.0×10^{-4}M). b) The membrane consisted of 1-decanol solution of methyltricaprylylammonium chloride (1.0×10^{-3}M). c) Concentrations of reference and sample solutions were 1.00×10^{-2}M. d) Concentrations of reference and sample solutions were 1.00×10^{-1} M. e) Selectivity coefficients were calculated by using concentrations instead of activities.

TABLE 4. MEMBRANE POTENTIALS ($E_{M(Na,j)}$ OR B.I.P.$_{Na,j}$) AND SELECTIVITY COEFFICIENTS (log $K_{Na,j}^{pot}$), AT 20 °C

Ion (j)	Solvent of membrane			
	Nitrobenzene[a)]		Nitromethane[a)]	
	$E_{M(Na,j)}$[b)] (mV)	log $K_{Na,j}^{pot}$	$E_{M(Na,j)}$[b)] (mV)	log $K_{Na,j}^{pot}$
Na^+	0	0.00	0	0.00
K^+	116	2.00	79	1.37
Rb^+	156	2.70	112	1.94
Cs^+	203	3.50	144	2.49
Tetramethyl-ammonium	297	5.12	—	—
Tetraethyl-ammonium	380	6.52	—	—
Tetrapropyl-ammonium	473	8.11	—	—

a) Membranes consisted of an organic solution of sodium dipicrylaminate (1.0×10^{-4}M). b) Concentrations of reference and sample solutions were 1.00×10^{-1}M.

that the ion is sufficiently confined to the membrane for us to obtain the stable potential. Therefore, chloride and sodium ions were selected as our references. In Table 3, the membrane potentials of the chloride ion-selective electrodes for solutions of various anions are listed. The selectivity coefficients in the table are values relative to the reference chloride ion. The selectivity values for monovalent cations are summarized in Table 4, along with the membrane potentials of the sodium ion-selective electrodes. With respect to anion selectivity, nitrobenzene and 1,2-dichloroethane give membranes with a higher inter-ionic selectivity than chloroform. The 1-decanol membrane has a low inter-ionic selectivity. For cations, the nitrobenzene mem-

TABLE 5. SELECTIVITY COEFFICIENTS OF CARBOXYLATE ION-SELECTIVE ELECTRRODES, Temp. 20 °C

Electrode[a)] (i)	Interferant (j)	Selectivity coefficient (log $K_{i,j}^{pot}$)	
		Obtained by the mixed solution methods	Calculated value
Hydrogenmaleate[b)]	Cl^-	−2.5	−2.67
	Br^-	−1.0	−1.16
	NO_3^-	−0.2	−0.18
	I^-	0.9	1.19
	ClO_4^-	2.9	2.99
Hydrogenphthalate[b)]	Cl^-	−3.1	−3.51
	Br^-	−2.1	−2.00
	NO_3^-	−1.2	−1.02
	I^-	0.0	0.34
	ClO_4^-	1.8	2.15
Trifluoroacetate[c)]	Cl^-	−2.1	−2.24
	Br^-	−0.9	−0.73
	NO_3^-	0.0	0.25
	I^-	1.3	1.61
	ClO_4^-	3.2	3.42

a) Liquid membranes were nitrobenzene solutions of crystal violet salts of objective anions (1.0×10^{-4}). b) Selectivity values in first column were determined based on the mixed solution method II A in Ref. 5. c) Selectivity values in first column were determined by the mixed solution method II C in Ref. 5.

TABLE 6. SELECTIVITY COEFFICIENTS OF NITROBENZENE MEMBRANES CONTAINING TRIS(BATHOPHENANTHROLINE)-IRON(II) ION AS AN ION-EXCHANGE SITE (Temp. 20 °C).

Counter ion in membrane	Reference solution	Sample solution (as sodium salt)		Membrane potential in mV	Selectivity coefficient	
HMA^- [a]	NaHMA (1.00×10^{-2}M)	Salicylate	(1.00×10^{-2}M)	− 44	$\log K_{HMA,j}^{pot}$	0.76 (0.74)[c]
		HPA^-	(1.00×10^{-2}M)	− 49		0.84 (0.87)
		ClO_4^-	(1.00×10^{-2}M)	−177		3.04 (3.04)
HPA^- [a]	NaHPA (1.00×10^{-2}M)	ClO_4^-	(1.00×10^{-2}M)	−125	$\log K_{HPA,j}^{pot}$	2.15 (2.15)
NO_3^- [b]	$NaNO_3$ (1.00×10^{-1}M)	BF_4^-	(1.00×10^{-2}M)	−128	$\log K_{NO_3,j}^{pot}$	2.20 (2.15)

a) Concentrations of ion-exchangers were 1.0×10^{-4}M. HMA: hydrogenmaleate, HPA: hydrogenphthalate. b) The concentration of the ion-exchanger was 5.0×10^{-4}M. c) Figures on parentheses are values of the nitrobenzene membrane containing crystal violet as an ion-exchange site.

brane exhibits a slightly higher inter-ionic selectivity than the nitromethane membrane. The selectivity sequence of anions is approximately consistent with the Hofmeister anion series on the nitrobenzene and 1,2-dichloroethane membranes. The chloroform and 1-decanol membranes show a somewhat different order of anion selectivity from the nitrobenzene and 1,2-dichloroethane membranes. Relatively high selectivities for halide ions are observed on the chloroform membrane. On the 1-decanol membrane, the selectivities for perchlorate and borofluoride ions are lowered, while organic anions show a relatively higher selectivity than do inorganic anions.

From the selectivity values in Tables 3 and 4, one can obtain the selectivity coefficient of a given ion-selective electrode for any ion by using Relation (11). The selectivity coefficients of the hydrogenmaleate ion-selective electrode with the nitrobenzene membrane, for example, are thus calculated: the value for perchlorate over hydrogenmaleate (HMA), $\log K_{HMA,ClO_4}^{pot}$, is $\log K_{Cl,ClO_4}^{pot}$ minus $\log K_{Cl,HMA}^{pot}$, which is 2.29, while that for bromide, $\log K_{HMA,Br}^{pot}$, is $\log K_{Cl,Br}^{pot}$ minus $\log K_{Cl,HMA}^{pot}$, which is −1.16, and so on. In Table 5, the calculated selectivity values are compared with the values determined by the usual mixed-solution methods.[5] The values are consistent with each other in order of magnitude.

Relationship between the Selectivity Coefficient and Ionic Parameters. Sandblom and his co-workers have proposed theoretical expressions of the potentials arising across the liquid ion-exchanger membranes.[18,19] According to their theory, the membrane potential in the electrochemical system (1) is given by Eq. (12), when the site and counter ions dissociate completely in the liquid membrane:

$$E_M = \pm 2.303RT/F \log (u_j k_j a_j''/u_i k_i a_i') \qquad (12)$$

TABLE 7. COMPARISON OF SELECTIVITY COEFFICIENTS OBTAINED WITH THEORETICAL VALUES

Ion (j)	$\log (k_i/k_j)$	$\lambda°$ ($cm^2\Omega^{-1}$)[c]	Theoretical value $\log (k_i\lambda_j°/k_i\lambda_j°)$	Experimental value $\log K_{i,j}^{pot}$
Na^+ (i)	0.0[a]	16.02	0.0	0.00
K^+	1.9[a]	17.53	1.9	2.00
$(CH_3)_4N^+$	5.4[a]	17.0	5.4	5.12
$(C_2H_5)_4N^+$	7.0[a]	16.1	7.0	6.52
Cl^- (i)	0.0[b]	22.68	0.0	0.00
Br^-	1.6[b]	21.93	1.6	1.51
I^-	3.7[b]	21.25	3.7	3.85
ClO_4^-	5.4[b]	17.7	5.3	5.77

a) Taken from Ref. 22. b) Ref. 23. c) Ref. 24.

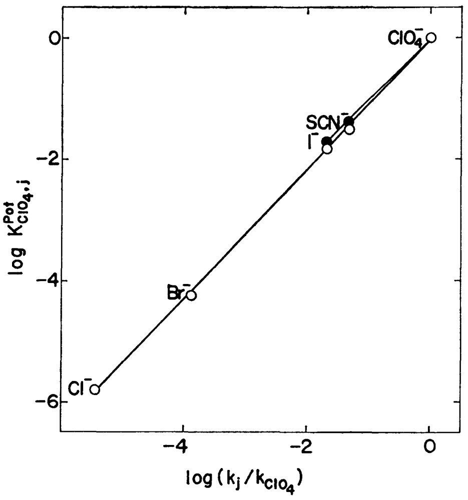

Fig. 3. Relationship between the selectivity coefficent and the ion partition coefficient.
○: nitrobenzene membrane,
●: 1,2-dichlorothane membrane.

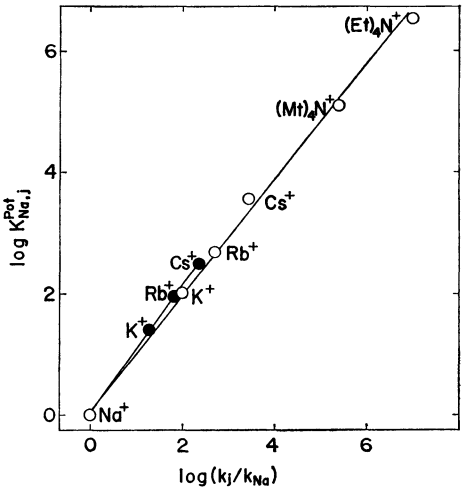

Fig. 4. Relationship between the selectivity coefficient and the ion partition coefficient.
○: nitrobenzene membrane,
●: nitromethane membrane.

TABLE 8. SELECTIVITY COEFFICIENTS OF 1,2-DICHLOROETHANE MEMBRANES CONTAINING TRIS(BATHOPHENANTHROLINE)IRON(II) AS AN ION-EXCHANGE SITE Temp. 20 °C

Counter ion in membrane	Reference solution	Sample solution (as sodium salt)		Membrane potential in mV	Selectivity coefficient	
HMA^- [a]	NaHMA $(1.00\times10^{-2}M)$	Salicylate	$(1.00\times10^{-2}M)$	-33	$\log K_{HMA,j}^{pot}$	0.57 (0.58)[c]
		HPA^-	$(1.00\times10^{-2}M)$	-42		0.72 (0.74)
		ClO_4^-	$(1.00\times10^{-2}M)$	-158		2.72 (2.75)
HPA^- [a]	NaHPA $(1.00\times10^{-3}M)$	ClO_4^-	$(1.00\times10^{-2}M)$	-117	$\log K_{HPA,j}^{pot}$	2.02 (1.99)
NO_3^- [b]	$NaNO_3$ $(1.00\times10^{-2}M)$	BF_4^-	$(1.00\times10^{-1}M)$	-117	$\log K_{NO_3,j}^{pot}$	2.02 (2.01)

a) Concentrations of ion-exchangers in membranes were $1.0\times10^{-4}M$. b) The concentration of the ion-exchanger was $5.0\times10^{-4}M$. c) Figures in parentheses are values of the 1,2-dichloroethane membranes containing crystal violet as an ion-exchange site.

where u_i and u_j are the mobilities of the i and j ions, respectively and where k_i and k_j are the partiton coefficients of the corresponding ions between water and the solvent of the membrane. From Eqs. (4) and (12), the selectivity coefficient for the membrane of the complete-dissociation type may be represented by ionic parameters as follows:

$$K_{i,j}^{Pot} = u_j k_j / u_i k_i = \lambda_j^\circ k_j / \lambda_i^\circ k_i \qquad (13)$$

where λ_i° and λ_j° are the limiting single-ion conductivities of the i and j ions respectively. Equation (13) implies that the selectivity coefficient of the ion-selective electrode with the liquid membrane of the complete-dissociation type is not dependent on the ion-exchange site species. The counter ion and site ion dissociate almost completely in the nitrobenzene membrane at such low concentrations of the ion-exchanger as 10^{-4} M, as judged from the dissociation constants in the literature.[11,20,21] In Table 6, the selectivity values of the nitrobenzene membranes containing the tris (bathophenanthroline)iron(II) ion as the ion-exchange site are compared with those of the membranes containing the crystal violet site. A good agreement is observed between the values of the two membranes. In Table 7, the selectivity values obtained are also compared with the theoretical values computed from Eq. (13) by employing ionic parameters quoted from the literature.[22-24] The experimental values are in good agreement with the theoretical ones. Since limiting single-ion conductivities are not so different among the ions, the selectivity coefficients may be said to be predominantly governed by the ion-partition coefficients. As is shown in Figs. 3 and 4, a good mutuality between the selectivity values and the reported ion-partition coefficients was also observed on the 1,2-dichloroethane and nitromethane membranes.[20,25] Table 8 shows a comparison of the selectivity values between the 1,2-dichloroethane membranes containing the tris(bathophenanthroline)iron(II) ion and the crystal violet ion as the ion-exchange sites. In these membranes, the selectivity values are also scarcely dependent on the site species.

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