Technical Paper

The Ion Selectivity of a Liquid Membrane Electrode with Partial Ion Association in the Membrane

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The intrinsic selectivity values of dichloromethane and 2,2'-dichlorodiethylether membranes, in which the ion-exchange site and its counter ion associated partly, were determined by the method similar to the bi-ionic potential measurement. The selectivity of the membranes was mainly governed by the solvent species of the membrane, and was scarcely affected by the kind of the ion-exchange site and the extent of the ion association in the membrane. A good correlation in accordance with the theoretical expectation was observed between the selectivity values determined and the extraction constants in different manner from the correlation reported by Bäck *et al.* The influence of interfacial diffusion phenomena on the selectivity was also discussed.

1 Introduction

It has been pointed out that the selectivity of a liquid membrane electrode was largely dependent on solvent extraction parameters^{1)~7)}. As is well known, however, selectivity coefficients of a liquid membrane electrode are not constant, and vary with the methods and conditions of a selectivity evaluation^{8),9)}. Then the physicochemical meaning of selectivity values thus obtained seems to be obscure.

Bäck *et al.*⁹⁾ and we⁷⁾ have reported that such variation of selectivity values could be ascribed to the formation of interfacial diffusion layers accompanied with the ion-exchange reaction between the electrode membrane and the sample solution. In previous papers⁷⁾, we have shown that an intrinsic selectivity value of a liquid membrane could be obtained by a particular method similar to a bi-ionic potential measurement of a liquid ion-exchanger membrane proposed by Shean *et al.*¹⁰⁾. A good correlation between selectivity values determined by this proposed method and ion partition parameters was observed in the liquid membrane of the completely dissociated type⁷⁾.

In this work, we have determined selectivity values of the liquid membrane in which the ion-exchange site and its counter ion associated partly, and will discuss on the relationship between the selectivity of the membranes and physicochemical properties of the membrane system.

2 Experimental

2.1 Selectivity evaluation of liquid membranes

The selectivity of liquid membranes was evaluated by the EMF measurement of the following electrochemical cell (1):

The reference solution was an aqueous solution of sodium bromide. A liquid membrane consisted of an organic solution of an electrolyte S-Br. Here, S denotes an ion-exchange site in the liquid membrane. Crystal violet (CV), tetraphenylarsonium (TPA), tetraphenylphosphonium (TPP), or methyltricaprylammonium (MTA) ion was used as the ion-exchange site. Dichloromethane and 2,2'-dichlorodiethylether were used as the solvent of the membrane. The sample solution was an aqueous solution of a sodium salt of a monovalent anion *j*, such as

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nitrate, iodide and salicylate. Procedures of the potential measurement were described in detail elsewhere¹¹⁾.

2.2 Conductivity measurement of liquid membrane solutions

Conductivity of membrane solutions was measured at 25°C by means of a conductivity cell with a cell constant of 0.286 cm⁻¹, using a Yanagimoto Conductivity Meter MY-8. The solvent of the membrane was purified by double distillations. Salts of ion-exchange sites with monovalent anions were prepared by a precipitation method or an extraction method. The salts were recrystallized twice from the aqueous media. The results of elemental analysis are listed in Table 1.

2.3 Solvent extraction

Extraction constants K_{ex} and dissociation constants k_{diss} of the following notation (2) were evaluated by using the relation (3).

$$\left. \begin{aligned} K_{ex} &= [Sj]_{org}/[S]_{aq}[j]_{aq} \\ k_{diss} &= [S]_{org}[j]_{org}/[Sj]_{org} \end{aligned} \right\} \quad (2)$$

$$\begin{aligned} D &= ([Sj]_{org} + [S]_{org})/[S]_{aq} \\ &= K_{ex}[S]_{aq} + (K_{ex}k_{diss})^{1/2} \end{aligned} \quad (3)$$

The partition ratio D was estimated by the spectrophotometric measurement of the concentration of the ion S in the equilibrated aqueous phase $[S]_{aq}$ after 30 min shaking of the organic solution of the salt Sj with an equal volume of water, or after 30 min shaking of the aqueous solution of the salt with an equal volume of the organic solvent.

3 Results

3.1 Selectivity of liquid membranes of partly associated ion type

When the i ion-sensitive electrode with a liquid membrane is immersed in the sample solution containing a foreign ion j as well as an objective ion i , the exchange reaction of the ions i and j takes place between the membrane and the sample solution. Since diffusion coefficients have equal orders of magnitude in both membrane and aqueous phases in the case of the liquid membrane electrode, diffusion layers, in which an interdiffusion of the ions i and j occurs, are formed near the membrane-sample solution interface. Accordingly, an ionic composition in the sample solution near the interface, which determines mainly the membrane potential, may change from an ionic composition in the *bulk* of the sample solution. The following Nikolsky equation (4) does not hold for the electrode response in such cases:

$$E_M = -RT/F \ln((a_i'' + K_{i,j}^{pot} a_j'')/a_i') \quad (4)$$

where a_i'' and a_j'' are activities of respective ions i and j in the bulk of the sample solution, and a_i' denotes the activity of the i ion in the bulk of the reference solution.

Hereafter, we consider the case that the sample solution initially contains the only j ion as a counter ion. In this case, Equation (4) can be reduced to:

$$E_M = -RT/F \ln(K_{i,j}^{pot} a_j''/a_i') \quad (5)$$

As pointed out in a previous paper⁷⁾, equation (5) holds for the electrode response under such conditions where the ionic composition in the sample solution near the interface is equal to that in the bulk of the sample solution, namely, the $K_{i,j}^{pot}$ is greater than unity and the concentration of the j ion in the sample solution C_j''

Table 1 Results of elemental analysis

Salt	Calcd. (%)			Observed (%)		
	C	H	N	C	H	N
(C ₆ H ₅) ₄ PClO ₄	65.68	4.59	—	65.44	4.54	—
(C ₆ H ₅) ₄ PSCN	75.54	5.07	3.52	75.36	5.21	3.44
(C ₆ H ₅) ₄ PBr	68.75	4.81	—	67.91	5.00	—
(C ₆ H ₅) ₄ PC ₆ H ₅ SO ₃ *	72.56	5.07	—	72.51	5.11	—
(C ₆ H ₅) ₄ PC ₁₀ H ₇ SO ₃ **	74.71	4.98	—	74.52	4.92	—
(C ₆ H ₅) ₄ AsClO ₄	59.58	4.16	—	59.62	4.18	—
(C ₆ H ₅) ₄ AsC ₁₀ H ₇ SO ₃ **	69.03	4.60	—	68.97	4.58	—

*: Benzenesulfonate, **: 1-Naphthalenesulfonate

Table 2 Selectivity of the dichloromethane membrane

Liquid membrane: Dichloromethane solution of S-Br ($1.0 \times 10^{-3} M$), Reference solution: $1.00 \times 10^{-1} M$ NaBr, Sample solution: $1.00 \times 10^{-1} M$ Na-*j*, Temp.: $27 \pm 2^\circ C$

Ion (<i>j</i>)	Ion-exchange site (S)							
	CV		TPA		TPP		MTA	
	E_M (mV)	$\log K_{Br,j}^{pot}$	E_M (mV)	$\log K_{Br,j}^{pot}$	E_M (mV)	$\log K_{Br,j}^{pot}$	E_M (mV)	$\log K_{Br,j}^{pot}$
NO ₃ ⁻	-30	0.50	-30	0.50	-30	0.50	-30	0.50
ClO ₃ ⁻	-45	0.76	-45	0.76	-44	0.74	-43	0.72
I ⁻	-113	1.90	-113	1.90	-114	1.92	-111	1.87
SCN ⁻	-120	2.02	-122	2.05	-118	1.98	-118	1.98
ClO ₄ ⁻	-188	3.16	-187	3.14	-185	3.11	-182	3.06
Benzenesulfonate*	-37	0.62	-38	0.64	-39	0.66	-38	0.64
Salicylate	-87	1.44	-84	1.39	-84	1.39	-85	1.41
1-Naphthalenesulfonate*	-119	2.00	-119	2.00	-121	2.03	-117	1.97

*: Concentrations of S-Br in the membranes were $1.0 \times 10^{-4} M$, and concentrations of reference and sample solutions were $1.00 \times 10^{-2} M$. Selectivity values were calculated by using a concentration instead of an activity.

Table 3 Selectivity of the 2,2'-dichlorodiethylether membrane

Liquid membrane: 2,2'-dichlorodiethylether solution of S-Br ($1.0 \times 10^{-4} M$), Reference solution: $1.00 \times 10^{-2} M$ NaBr, Sample solution: $1.00 \times 10^{-2} M$ Na-*j*, Temp.: $27 \pm 2^\circ C$

Ion (<i>j</i>)	Ion-exchange site (S)							
	CV		TPA		TPP		MTA	
	E_M (mV)	$\log K_{Br,j}^{pot}$	E_M (mV)	$\log K_{Br,j}^{pot}$	E_M (mV)	$\log K_{Br,j}^{pot}$	E_M (mV)	$\log K_{Br,j}^{pot}$
NO ₃ ⁻	-46	0.77	-47	0.79	-47	0.79	-46	0.77
ClO ₃ ⁻	-54	0.91	-55	0.92	-56	0.94	-56	0.94
SCN ⁻	-143	2.40	-143	2.40	-143	2.40	-145	2.44
ClO ₄ ⁻	-219	3.68	-219	3.68	-219	3.68	-218	3.66
Benzenesulfonate*	-50	0.84	-50	0.84	-51	0.86	-51	0.86
Salicylate	-104	1.73	-105	1.74	-106	1.76	-106	1.76
1-Naphthalenesulfonate*	-143	2.40	-144	2.42	-145	2.44	-143	2.40

*: A concentration was used in calculation of selectivity values instead of an activity

is sufficiently higher than the concentration of the ion-exchanger in the liquid membrane C_{S-i}^* . In this work, consequently, we have selected bromide ion as the *i* ion, and the concentration ratio C_j^*/C_{S-Br}^* was kept as 100/1. Under these conditions, one can evaluate an intrinsic selectivity value of the membrane from the membrane potential E_M and the activity of the *j* ion in the bulk of the sample solution a_j^* using the relation (5).

In Tables 2 and 3, selectivity values of dichloromethane and 2,2'-dichlorodiethylether membranes thus obtained are summarized together with membrane potentials of Cells (1). The selectivity sequence and selectivity values are

scarcely dependent on the kind of the ion-exchange site. As is shown in Fig. 1, the selectivity is nearly independent of the concentration of the ion-exchanger in the membrane, that is, the extent of the ion association in the membrane. From these results, we can conclude that the selectivity of the liquid membrane of the partly associated ion type is also mainly governed by the solvent species of the membrane, analogous to the case of the liquid membrane of the completely dissociated type.

3.2 Ionic equilibria in the membrane system

Limiting molar conductances Λ_0 and dissociation constants k_{diss} of the membrane solutions

Concn. of TPP-Br in membrane C_{S-Br}^*
 Fig. 1 Dependence of selectivity on concentration of ion-exchanger in membrane
 Liquid membrane: Dichloromethane solution of TPP-Br. The ratio C_j''/C_{S-Br}^* was kept as 100/1
 ●—●—●: ClO_4^- , ◐—◐—◐: SCN^-
 ○—○—○: I^- , ○—○—○: NO_3^-

Table 4 Conductivity parameters of organic solutions of salts S-Br and S-j at 25°C

Solvent	Salt	Λ_0 (ohm ⁻¹ cm ² mole ⁻¹)	log k_{diss}
CH_2Cl_2	$(\text{C}_6\text{H}_5)_4\text{PClO}_4$	122	-3.61
	$(\text{C}_6\text{H}_5)_4\text{PSCN}$	122	-3.71
	$(\text{C}_6\text{H}_5)_4\text{PBr}$	118	-3.64
	$(\text{C}_6\text{H}_5)_4\text{AsClO}_4$	126	-3.77
	$(\text{C}_6\text{H}_5)_4\text{AsC}_{10}\text{H}_7\text{SO}_3^*$	102	-3.67
$(\text{ClCH}_2-\text{CH}_2)_2\text{O}$	$(\text{C}_6\text{H}_5)_4\text{AsClO}_4$	28.5	-2.54

*: 1-Naphthalenesulfonate

were estimated by the Shedrovsky's method¹²⁾ using conductance data. The results are listed in Table 4. Both parameters Λ_0 and k_{diss} for the salts of the same ion-exchange site are not so different among counter ion species tested.

Extraction parameters K_{ex} and k_{diss} obtained are listed in Table 5. Dissociation constants have the same orders of magnitude as those obtained

Table 5 Extraction parameters of the dichloromethane-water system at 11 °C

Salt	log K_{ex}	log k_{diss}
$(\text{C}_6\text{H}_5)_4\text{PBr}$	3.39	-3.79
$(\text{C}_6\text{H}_5)_4\text{PC}_6\text{H}_5\text{SO}_3^*$	3.99	-3.52
$(\text{C}_6\text{H}_5)_4\text{PC}_{10}\text{H}_7\text{SO}_3^{**}$	5.58	-3.51

*: Benzenesulfonate, **: 1-Naphthalenesulfonate

from the conductivity measurement. Although dissociation constants are not so different among the counter ions tested, extraction constants are largely dependent on the counter ion species.

4 Discussion

According to Bäck *et al.*⁶⁾, the theoretical expression of the membrane potential of the system (1) can be written as follows:

$$E_M = -RT/F \ln(\alpha_j K_{\text{ex}}^j a_j'' / \alpha_{\text{Br}} K_{\text{ex}}^{\text{Br}} a_{\text{Br}}') \quad (6)$$

Here, α is a side reaction coefficient of the site with the counter ion in the membrane. Subscripts and superscripts denote respective counter ion species.

If no side reaction occurs between the site and the counter ion in the membrane except for the dissociation of the site-counter ion pair, and if we can assume that the dissociation constant of the site-counter ion pair in the membrane is not dependent on counter ion species, we can obtain the relation:

$$K_{\text{Br},j}^{\text{pot}} = K_{\text{ex}}^j / K_{\text{ex}}^{\text{Br}} \quad (7)$$

In Equations (6) and (7), mobilities of ions do not appear. This is due to the fact that mobilities of counter ions in the organic phase are nearly equal as judged from conductance data in

Fig. 2 Relationship between selectivity values and extraction constants

Selectivity values: Values of the dichloromethane membrane containing TPP-Br,

Extraction constants:

Filled circle; Taken from Ref. 13,

Open circle; Determined in this work

a previous section. It is expected from Equation (7) that the plot of $\log K_{Br,j}^{pot}$ vs. $\log (K_{ex}^i/K_{ex}^{Br})$ would be a straight line with a slope of unity. As is shown in Fig. 2, a sufficiently good correlation was observed between both parameters. This suggests the validity of the relation (7).

Equation (7) can be rewritten as :

$$K_{Br,j}^{pot} = k_j k_{diss}^{Br} / k_{Br} k_{diss}^j \quad (8)$$

where k denotes a partition coefficient of a counter ion between the solvent of the membrane and water. As it can be assumed that k_{diss} is not so different as k among counter ion species, $K_{Br,j}^{pot}$ is approximately equal to the ratio k_j/k_{Br} . The k is usually governed by the solvent species of the membrane, then the selectivity of the liquid membrane of the partly associated ion type is mainly governed by the solvent species of the membrane, in analogy with the selectivity of the liquid membrane of the completely dissociated type.

Bäck *et al.* have reported that the selectivity of the dichloromethane membrane is related to the extraction constant by a square root dependence⁶⁾. They have emphasized that such results could be ascribed to interfacial diffusion phenomena induced by the following ion-exchange reaction :

In their work, picrate ion was used as the i ion to which the membrane showed the highest selectivity among ions examined. In such a case, the reaction (9) will not proceed completely to the right hand side. This leads to the deviation of the ionic composition in the sample between the interface and the bulk of the solution owing to the formation of diffusion layers near the interface. The observed selectivity of the membrane may deviate from the intrinsic selectivity under such conditions.

On the other hand, we have used bromide

ion as the i ion to which the membrane showed the lowest selectivity among ions tested, and measured the membrane potential under conditions where C_j'' is much greater than C_{S-Br}^* . Accordingly, bromide ion within the membrane near the interface may be completely exchanged by the j ion, *i. e.*, the membrane layer adjacent to the sample solution is converted to the membrane responsive to the j ion from initially responsive to bromide ion. It is also expected that the contribution of bromide ion eluted from the membrane to the membrane potential can be neglected because of its lower concentration and selectivity compared with those of the j ion. The membrane potential is thus determined by the activity of the j ion in the bulk of the sample solution. We have, then, been able to observe the good correlation between the selectivity values and the extraction constants.

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