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Selective Ion Transport in Acetonitrile Across the Ionophore-Immobilized Polymer Membranes Used as the Sensor of the Ion-Selective Electrodes

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A conductometric study was carried out concerning the selective ion transport of alkali and alkaline earth metal ions, mainly in acetonitrile (AN), across a membrane of polyacrylamide (PAA) coupled to such ionophores as tetraethylene glycol monododecyl ether, hexaethylene glycol monododecyl ether, dibenzo-18-crown-6, and cryptand222B. A sintered glass filter membrane was impregnated with PAA-ionophores and the conductivity of the solution of one side of the membrane was measured in order to monitor the ion transport across the membrane from the opposite side. Alkali and alkaline earth metal ions could pass across the ionophore-free PAA membrane, but the ions were entrapped in the PAA-ionophore membranes. Tetraethylammonium and perchlorate ions, however, could pass across both the PAA and the PAA-ionophore membranes. The entrapped ions could pass across the PAA-ionophore membranes if a complexing reagent was added to the solution on one side of the membrane by forming complexes with the reagent. The limiting equivalent conductivities and the ion association constants of $(\mathrm{Li\text{-}12C4})^+\mathrm{ClO_4^-}$, $(\mathrm{Li\text{-}Cryp22})^+\mathrm{ClO_4^-}$, $(\mathrm{K\text{-}DB18C6})^+\mathrm{ClO_4^-}$, $(\mathrm{K\text{-}Cryp222})^+\mathrm{ClO_4^-}$, $(\mathrm{Mg\text{-}12C4})^{2+}2\mathrm{ClO_4^-}$, $(\mathrm{Ba\text{-}DB18C6})^{2+}2\mathrm{ClO_4^-}$, $(\mathrm{Ba\text{-}Cryp22})^{2+}2\mathrm{ClO_4^-}$, and $(\mathrm{Ba\text{-}Cryp222})^{2+}2\mathrm{ClO_4^-}$ were determined. The limiting equivalent conductivities were used to compare the relative conductivity values among different species obtained the conductometric measurements of ion transport across the membrane.

We recently developed ionophore-immobilized polymer membrane ion sensors which can respond to both alkali and alkaline earth metal ions,[1-3] as well as fluoride ion[4] in dipolar aprotic solvents. The electrodes were constructed by coating a platinum or gold disk with polyacrylamide (PAA) coupled to poly(oxyethylene) derivatives (POE) or to a phthalocyanine cobalt (PhCo) complex. One of the electrodes for the cations was applied in order to study complexing of magnesium and barium ions in acetonitrile (AN) with other donor solvent molecules,[5] and to obtain the Gibbs free energies of transfer of the barium ion from propylene carbonate (PC) to PC–*N*,*N*-dimethylacetamide mixtures.[6] The electrode for the anions was applied so as to determine the water content as well as the solubility products of the sodium fluoride in AN and PC.[4] The voltammetric behaviors of the electrodes[7] have also been studied to elucidate the mechanism of the potentiometric responses reported in previous papers.[1-3]

Studies concerning ion transport across a liquid membrane containing ionophores, which especially react with alkali and alkaline earth metal ions, have been widely carried out.[8-10] The selective ion transport of chloride and bromide ions across membranes comprising a synthetic polymer have also been reported;[11,12] these studies, however, were carried out in aqueous systems.

In the present paper we report on the selective ion transport of some monovalent and divalent cations in nonaqueous solvents in order to investigate the chemical characteristics of the PAA-ionophore membranes used as the sensor of ion-selective electrodes.[1-3]

Experimental

Reagents. Cryptand22 (Cryp22), cryptand222 (Cryp222), and 12-crown-4 (12C4) were the products of Merck. The other reagents, solvents, and PAA-ionophore membranes used in the experiment were the same as those used in previous studies.[1-3]

Measurement of Conductivity. The ion transport across the ionophore-immobilized polymer membranes was monitored by measuring the conductivity of the solution in compartment C_B in the cell shown below. Fig. 1 shows a schematic diagram of the cell:

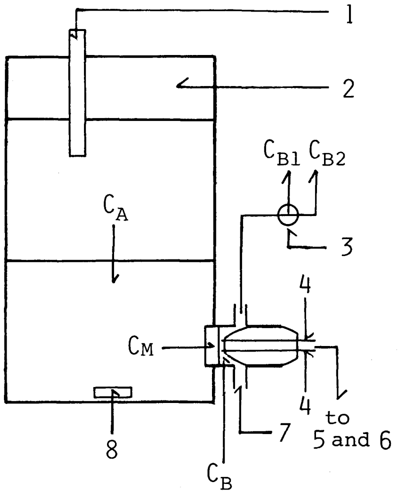

Fig. 1. Schematic diagram of the conductivity measuring cell for ion transport across the ionophore-immobilized polymer membrane. The assembly was in an air bath thermostated at 25±0.2 °C. 1; solution inlet, 2; Teflon stopper, 3; three way stop cock, 4; Pt electrode, 5; conductivity meter, 6; pen recorder, 7; solution outlet, 8; Teflon stirring bar. C_A, C_M, C_B; See text.

$\underline{10\ \mathrm{mM}\ Et_4NClO_4 + x\ \mathrm{mM}\ M^{y+}yX^-(D)}$ ·················· C_A

$\underline{/\mathrm{PAA, PAA\text{-}POE4, PAA\text{-}DB18C6, or\ PAA\text{-}Cryp222B}}$ ····· C_M

$\underline{/D(C_{B1})\ \mathrm{or\ POE\ Derivatives}\ (D)\ (C_{B2})}$ ················· C_B,

where M^{y+} denotes such cations as Et_4N^+, Li^+, K^+, Mg^{2+}, and Ba^{2+}. The perchlorate ion and the anion of diethyl sulfosuccinate (DSS^-) were also used as counter anions (X^-). D denotes AN, PC, and *N*,*N*-dimethylformamide (DMF); C_{B1} the reservoir of pure solvent D; and C_{B2} that of D containing such complexing reagents (ionophores) as 12C4, dibenzo-18-crown-6 (DB18C6), Cryp22, and Cryp222. C_M was a sintered-glass filter membrane made of G4 (3 mmϕ) and impregnated with such polymers as PAA, PAA-POE4, PAA-DB18C6, and PAA-Cryp222B. About 5 mg of dry powder of the respective polymer was swelled with 5 μl water and used to coat the glass filter; it was then stored for twenty minutes in an air bath at 40 °C. After setting the cell in a thermostated chamber at 25 °C the compartments of C_A and C_B were filled with an appropriate solvent or solution, and the conductivity of C_B was monitored with a conductivity meter (Toa Denpa Kogyo, Type CM-40S) equipped with an interval time unit (IT-1S). The signals of the conductivity and the temperature of C_B were recorded with a two-pen recorder (Yokogawa Denki Co. Ltd). The measurements of the equivalent conductivities of the chemical substances shown in Table 1 were carried out in the same manner as those in a previous paper.[3] The experimental results obtained by conductivity measurements were analyzed with a personal computer (NEC, PC9801).

Results

Limiting Equivalent Conductivities and Ion Association Constants. Conductometric measurements were carried out in order to determine the limiting equivalent conductivities (Λ_o) of such salts as $(Li\text{-}12C4)^+ClO_4^-$, $(Li\text{-}Cryp22)^+ClO_4^-$, $(K\text{-}DB18C6)^+ClO_4^-$, $(K\text{-}Cryp222)^+ClO_4^-$, $(Mg\text{-}12C4)^{2+}2ClO_4^-$, $(Ba\text{-}DB18C6)^{2+}2ClO_4^-$, $(Ba\text{-}Cryp22)^{2+}2ClO_4^-$, and $(Ba\text{-}Cryp222)^{2+}2ClO_4^-$ in AN. The results of the conductivity measurements were analyzed by the method of Shedlovsky[13] for monovalent cations, and by that of Modified Fuoss Edelson[14] for divalent cations, as shown in Ref. 3. The limiting equivalent conductivity (Λ_o) of complex ions and the 1:1 association constants between M^{n+} and ClO_4^-(K_1) were calculated simaltaneously. The values are summarized in Table 1. The values in the last column of Table 1 show the respective ratio of the conductivity, $\Lambda_o{}^{Ba(ClO_4)_2}/\frac{z}{2}\Lambda_o{}^{M(ClO_4)_z}$; here, M and *z* denote such cations as those shown in Table 1 and their charge, respectively.

Ion Transport Across the Membrane. In order to investigate the response mechanism of the PAA-POE electrodes, sintered-glass filter membranes impregnated with PAA-POEs were prepared and the transport of alkali and alkaline earth metal ions, tetraethylammonium ion, and perchlorate ion in AN across the membrane was measured. All of the conductivities were normalized to that of $Ba(ClO_4)_2$ according to the ratio (shown in Table 1). Fig. 2(1) shows the relation between the time and the conductivity in C_B, obtained by a transfer of tetraethylammonium perchlorate (Et_4NClO_4) in AN from C_A to C_B across the PAA and PAA-POE4 membranes. From Fig. 2(1), (A), (B), and (C), it can be found that Et_4N^+ and ClO_4^- ions could be transferred across the PAA membrane, but that the rate of transfer of the ions across the membranes decreased with time. The situation was almost the same in all membranes used in the experiment. At points 2 and 4 of curves C and D

Table 1. Limiting Equivalent Conductivities (Λ_o) and Ion Association Constants (K_1)[a] at 25 °C

Salt	Solvent	Λ_o	$10^{-2}K_1$ / $mol^{-1}\,dm^3$	Ratio[b]
		Shedrovsky's method		
$Li^+ClO_4^-$[c]	AN	172.4	1.14	2.3
$(Li\text{-}12C4)^+ClO_4^-$	AN	153.6	C.D.[d]	2.6
$(Li\text{-}Cryp22)^+ClO_4^-$	AN	150.7	C.D.	2.7
$K^+ClO_4^-$[c]	AN	184.3	0.27	2.2
$(K\text{-}DB18C6)^+ClO_4^-$	AN	160.4	C.D.	2.5
$(K\text{-}Cryp222)^+ClO_4^-$	AN	154.2	C.D.	2.6
$Et_4N^+ClO_4^-$[c]	AN	188.9	C.D.	2.1
$Et_4N^+ClO_4^-$[c]	DMF	87.5	C.D.	4.6
		Modified Fuoss Edelson method		
Salt	**Solvent**	**Λ_o**	**$10^{-2}K_1$ / $mol^{-1}\,dm^3$**	**Ratio[b]**
$Mg^{2+}2ClO_4^-$[c]	AN	167.7	0.17	1.2
$(Mg\text{-}12C4)^{2+}2ClO_4^-$	AN	171.6	5.20	1.2
$Ba^{2+}2ClO_4^-$[c]	AN	200.2	4.82	—
$Ba^{2+}2ClO_4^-$[c]	DMF	91.4	C.D.	2.2
$(Ba\text{-}DB18C6)^{2+}2ClO_4^-$	AN	124.4	5.42	1.6
$(Ba\text{-}Cryp22)^{2+}2ClO_4^-$	AN	134.6	8.51	1.5
$(Ba\text{-}Cryp222)^{2+}2ClO_4^-$	AN	133.1	3.61	1.5

a) and b) See text. c) Quoted from Ref. 15. d) Completely dissociated.

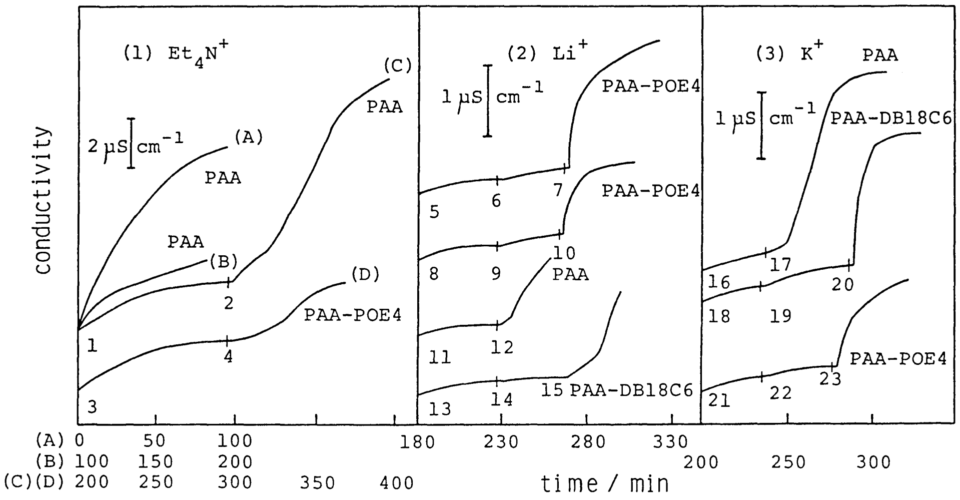

Fig. 2. Relation between time and the normalized conductivity[#] in AN. At the numbered points the salt solution or the solution containing the complexing reagent shown below was added to compartment C_A or C_B[#], respectively. 1, 3, 5, 8, 11, 13, 16, 18, 21; 0.1 mM Et_4NClO_4: 2, 4; 10 mM Et_4NClO_4: 6, 9, 12, 14; 10 mM $LiClO_4$: 7, 15; 1 mM 12C4: 10; 1 mM Cryp22: 17, 19, 22; 1 mM $KClO_4$: 20; 1 mM Cryp222: 23; 1 mM DB18C6. #) See text.

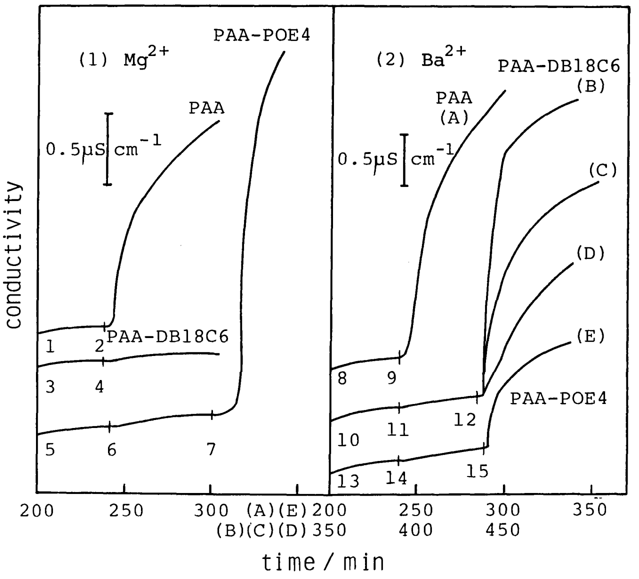

Fig. 3. Relation between time and the normalized conductivity[##] in AN. At the numbered points the salt solutions or the solution containing the complexing reagents shown below were added to compartment C_A or C_B,[##] respectively. 1, 3, 5, 8, 10, 13; 0.1 mM Et_4NClO_4: 2, 4, 6; 1 mM $Mg(ClO_4)_2$: 7; 1 mM 12C4: 9, 11, 14; 1 mM $Ba(ClO_4)_2$; 12; 1 mM Cryp222(B), 1 mM DB18C6(C), 1 mM Cryp22(D): 15; 1 mM DB18C6. ##) See text.

in Fig. 2(1) the concentration of Et_4NClO_4 in C_A changes from 0.1 to 10 mM (M=mol dm^{-3}); this result supports the idea that Et_4N^+ and ClO_4^- ions could be transferred across the PAA and PAA-POE4 membranes. Fig. 3(2) shows the results for the ion transport of the barium perchlorate in AN across PAA, PAA-POE4, and PAA-DB18C6 membranes. The barium ion could pass through the PAA membrane, but was trapped in the PAA-POE4 and PAA-DB18C6 membranes. At points 12 and 15 in Figs. 3(2) (B), (C), (D), and (E), the solution of C_B was switched into that containing such ionophores as Cryp222, DB18C6, Cryp22, or DB18C6. The ionophores interact specially with the barium ion. The barium ions trapped in PAA-POE4 and PAA-DB18C6 membranes were released into C_B. From the results shown in Figs. 2(2), 2(3), and 3(1), the PAA membrane could also transfer lithium, potassium, and magnesium ions in AN, but PAA-POE4 and PAA-DB18C6 membranes trapped the ions. The ions could be released, however, into C_B upon adding ionophores in C_B, as shown in the captions of Figs. 2 and 3. The barium perchlorate trapped in the PAA-Cryp222B membrane could also be made to pass the membrane by adding Cryp222 in C_B. When DMF was used as D in C_A, $Ba(DSS)_2$ was also able to pass the PAA membrane, but it was trapped in the PAA-POE4 membrane; it, however, released into C_B by adding DB18C6 in C_B. The results of the phenomena concerning ion transport are summarized in Table 2.

Discussion

Ion transport across ionophore-immobilized membranes was studied conductometrically. Since the conductivity data obtained carring out measurements in compartment C_B (Fig. 1) were normalized to that of $Ba(ClO_4)_2$ by using the ratio of the limiting equivalent conductivities (as can be seen in Table 1), the conductivities given in Figs. 2 and 3 correspond to the

Table 2. Results of the Ion Transport Across the Ionophore-Immobilized Polymer Membranes at 25 °C

Membrane		PAA	PAA-POE4		PAA-DB18C6		PAA-Cryp222B	
Ion	Situation Solvent	Pass[a]	Pass	Rel[b]	Pass	Rel	Pass	Rel
Et_4N^+	AN	Y[c]	Y		Y		Y	
ClO_4^-	AN	Y	Y		Y		Y	
DSS^-	DMF	Y						
Li^+	AN	Y	N[d]	Y(1,3)	N	Y(1)		
K^+	AN	Y	N	Y(2)	N	Y(4)		
Mg^{2+}	AN	Y	N	Y(1)	N			
Ba^{2+}	AN	Y	N	Y(4)	N	Y(2,3,4)	N	Y(4)
Ba^{2+}	PC	Y	N	Y(2)				
Ba^{2+}	DMF	Y	N	Y(2)				

(1): 12C4, (2): DB18C6, (3): Cryp22, (4): Cryp222. a) Pass means that ions could pass across the membrane. b) Rel means that the ions entrapped in the membrane were released from the membrane. c, d) Y and N denote yes and non, respectively.

relative concentration of the ions transported across C_M. We can consider from the experimental results that the ion transport across the membrane was more difficult for ions which had a complexing ability with the ionophore immobilized in the membrane. The tetraethylammonium and perchlorate ions, with no complexing ability, however, could transfer across the PAA-ionophore membranes. Since complexing of the Cryp222 with the barium ion in AN was very stable, the barium ions trapped in PAA-DB18C6 were quickly released and, thus, the ions could pass through the membrane when Cryp222 was added in C_B.

It can be seen from the results of Figs. 2 (A), (B), and (C) that the rate of transport of tetraethylammonium perchlorate across the PAA membrane gradually slowed down with time. In order to understand the role of water contained in the PAA membrane, the IR spectra with a streching band at 3450 cm^{-1} [16] were measured. Dry PAA powder was divided into several portions of similar weight, and each of them was allowed to soak up a constant volume of water. After becoming homogeneous gels, they were transferred into constant volume of dry AN in a closed bottle. The IR spectra of the PAA gels were measured at constant intervals one after another after a period of standing time. The intensity of the IR absorption at 3450 cm^{-1} was gradually weakened, showing that the water soaked in the PAA was drawn out while standing in AN. Since the water content in PAA was decreased and AN could not take the place of water, the swollen PAA might become contruct and the distance of the atoms might be shortened, so that the rate of transfer of the tetraethylammonium perchlorate across the PAA membrane might be decreased with time.

The results obtained by a cyclic voltammetric investigation,[7] had shown that the mechanism of the establishment of the steady state potential and dynamic response of the PAA-ionophore based ion sensors had been deeply affected by the ionophores immobilized in the membranes. The experimental results of the ion transport obtained in the present paper also showed that the ionophores immobilized in the membranes played important roles in the characteristics of the membranes.

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