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Response and Application in Dipolar Aprotic Solvents of Ion-Selective Electrodes Based on Polyacrylamide Modified with Acyclic Poly(oxyethylene) Derivatives

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The response of organic polymer membrane electrodes, constructed by coating a platinum disk with polyacrylamide (PAA) coupled to acyclic poly(oxyethylene) derivatives, tetraethylene glycol monododecyl ether (POE4) and hexaethylene glycol monododecyl ether (POE6) was studied in acetonitrile (AN) and *N,N*-dimethylformamide (DMF). The PAA-POE4 electrode showed Nernstian response to the lithium ion in AN and the magnesium and barium ions in DMF, while the PAA-POE6 electrode showed near Nernstian response to the barium ion in DMF. The PAA-POE4 electrode was applied to study the complexation of the lithium ion in AN with DMF. The formation constants, $\beta_1=17$ and $\beta_2=1.2\times10^2$, obtained agreed well with the values obtained previously with an univalent cation sensitive glass electrode. The response of the PAA-POE4 electrode in barium bis(2-ethylhexyl) sulfosuccinate ($Ba(DSS)_2$)-DMF solution has been studied and the results are explained by taking the conductometrically determined association constant ($K_{1A}=5.2\times10^2$) between Ba^{2+} and DSS^- ions.

Some types of ion-selective electrodes have been successfully used in physicochemical as well as in analytical studies of nonaqueous solutions.[1] Recently, we have developed some ion-selective electrodes for use in dipolar aprotic solvents.[2] One of these electrodes was used to study the complexing of the magnesium and barium ions in acetonitrile (AN) with other dipolar aprotic solvent molecules.[3] In the present paper the response and the application of the same type of ion-selective electrodes[2] constructed by coating a platinum disk with polyacrylamide (PAA) coupled to tetraethylene glycol monododecyl ether (POE4) or hexaethylene glycol monododecyl ether (POE6) are reported. The response behavior of the PAA-POE4 and PAA-POE6 electrodes to the lithium, magnesium and barium ions were investigated in several nonaqueous chemical systems. The PAA-POE4 elctrode was used to obtain the successive complex formation constants of the lithium ion in AN with *N,N*-dimethylformamide (DMF) to compare with the values obtained previously with a values obtained previously with a univalent cation sensitive glass electrode.[4] The response behavior of the PAA-POE4 electrode to barium bis(2-ethylhexyl) sulfosuccinate ($Ba(DSS)_2$) in DMF has been studied and the results are explained by taking the conductometrically determined association constant of the compound.

Experimental

Reagents. The sodium bis(2-ethylhexyl)sulfosuccinate was the product of Tokyo Kasei Kogyo Co., Ltd. and the barium bis(2-ethylhexyl) sulfosuccinate, $Ba(DSS)_2$, was prepared and purified according to the method of Kitahara et al.[5] Other reagents and solvents were the same as those in the previous report.[3]

Potentiometric Measurements. Most of the methods of the potentiometric measurements and the electrode construction were the same as those described in the previous report.[3] The responses of the electrodes were tested in the following Cell I,

$$\begin{array}{l}\mathrm{Ag/10\ mM\ AgNO_3{+}10\ mM\ Et_4NClO_4\ (D)//}\\ \quad\mathrm{50\ mM\ Et_4NClO_4(D)//}C\ \mathrm{M(ClO_4)}_x\ \text{or}\ \mathrm{Ba(DSS)_2{+}}\\ \qquad\mathrm{10\ mM\ Et_4NClO_4\ (D)/PAA\text{-}POE4\ or\ 6/Pt}\cdots\cdots\text{Cell I,}\end{array}$$

where $M(ClO_4)_x$ was the perchlorate of the cation to be tested (lithium, magnesium, or barium ion), D was AN or DMF, and *C* in $mol\,dm^{-3}$. A standard addition method was employed in obtaining calibration curves. Steady state potentials were read to ±0.1 mV. The electrode potentials were not significantly affected by change in the rate of the solution.

Conductivity Measurements. A conductivity meter of Toa Denpa Kogyo, Type CM-40S, equipped with an interval time unit IT-1S and a Yanagimoto conductivity cell, Type C, was used. The conductivity was also monitored simultaneously with a strip chart recorder, Yokogawa Denki type 3056. The $Ba(DSS)_2$-DMF solution of known concentration was added to the conductometric cell (cell constant 0.368_5) with a microburette (Gilmont Instruments, Inc., S1100A and S1200A).

Determination of the Complex Formation Constants. The successive complex formation constants of the lithium ion in AN with DMF were determined by potentiometric measurement in Cell II. The complexing solvent DMF was added to the cell with a microburette, 10 µl in each step, until its volume per cent reached 1%.

$$\begin{array}{l}\mathrm{Ag/10\ mM\ AgNO_3{+}10\ mM\ Et_4NClO_4(AN)//}\\ \quad\mathrm{50\ mM\ Et_4NClO_4(AN)//0.1\ mMLiClO_4{+}}\\ \qquad\mathrm{10\ mM\ Et_4NClO_4(AN{+}DMF)/PAA\text{-}POE4/Pt}\cdots\text{Cell II.}\end{array}$$

The potentiometric data were analyzed by the same method as that described in the previous report.[3]

Results

Responses of the Electrodes. The PAA-POE4 and PAA-POE6 electrodes were durable in AN and DMF for at least two weeks. The responses of these electrodes to lithium, magnesium, and barium ions are summarized in Table 1 and Fig. 1. The activity of

Table 1. The Responses of Organic Polymer Membrane Electrodes to Some Metal Ions in Nonaqueous Solvents at 25 °C

Ion	r_c/Å[a)]	Solvent	Slope (mV/$pa_{M^{n+}}$)	The activity range of the linear response
			PAA-POE4	
Li^+	0.60	AN	57.4	8×10^{-5}—6×10^{-3}
Mg^{2+}	0.65	DMF	30.4	2×10^{-5}—2×10^{-3}
Ba^{2+}	1.35	DMF	27.3	3×10^{-6}—3×10^{-4}
			PAA-POE6	
Ba^{2+}	1.35	DMF	26.1	1×10^{-5}—4×10^{-4}

a) r_c: Crystallographic ionic radius.

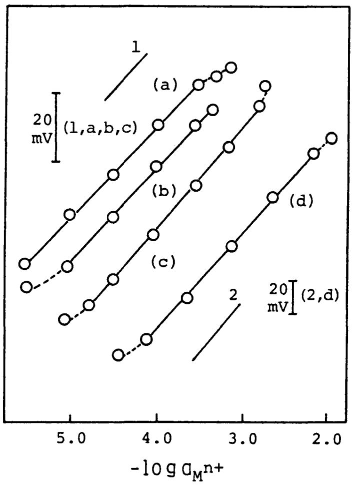

Fig. 1. Calibration curves in nonaqueous solvents at 25 °C. Lines 1 and 2, theoretical slope for bivalent cations (29.6 mV/$pa_{M^{2+}}$) and for univalent cation (59.2 mV/pa_{M^+}), respectively. (a) Ba^{2+} in DMF with PAA-POE4, (b) Ba^{2+} in DMF with PAA-POE6, (c) Mg^{2+} in DMF with PAA-POE4, (d) Li^+ in AN with PAA-POE4.

the metal ion, $a_{M^{x+}}$, was calculated by using the Debye-Hückel second approximation equation as previously described.[6)] The results in Table 1 have not been corrected for the change in the liquid junction potential between the sample solution and the salt bridge of Cells I and II, but its effect seems to be small. The PAA-POE4 electrode could respond in a Nernstian way to the activities of the lithium ion in AN between the concentration range 7×10^{-5}—7×10^{-3} M (1M=1 mol dm^{-3}). The electrode could respond in Nernstian ways to the activities of the magnesium and barium ions in DMF between the concentration ranges 5×10^{-5}—1×10^{-2} M and 1×10^{-5}—1×10^{-3} M, respectively. The PAA-POE6 electrode showed near Nernstian response to the activity of the barium ion in DMF between the concentration range 3×10^{-5}—2×10^{-3} M.

Complexing of the Lithium Ion in AN with DMF. The complex formation constants of the lithium ion in AN with DMF were determined by measuring the emf change of Cell II. The relations between the potential change ΔE and the concentration of DMF, [D], and between R_1 and [D] (see Ref. 3) obtained in this experiment are shown in Fig. 2(a) and (b), respectively. Here $R_1\equiv\{10^{\Delta E/59.16}-1\}/[D]=\beta_1+\beta_2[D]+\beta_3[D]^2+\cdots$. From the intercept and the slope of the straight line, $\beta_1=16$ and $\beta_2=1.5\times10^2$ are obtained (β_1 and β_2; see Ref. 3). The average values obtained in this experi-

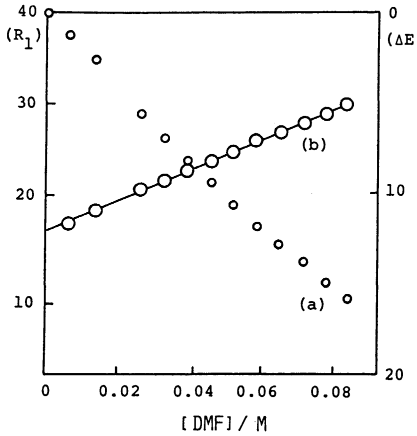

Fig. 2. The relations of ΔE-[DMF] and R_1-[DMF] for Li^+ ion in AN with PAA-POE4 at 25 °C.

Table 2. Complex Formation Constants of Li^+ in AN with DMF

Indicator electrode	Stability constant	
	β_1	$\beta_2(K_2)$
Cation-sensitive glass electrode[a)]	16	1.1×10^2(6.9)
PAA-POE4 electrode	17	1.2×10^2(7.0)

a) See Ref. 4.

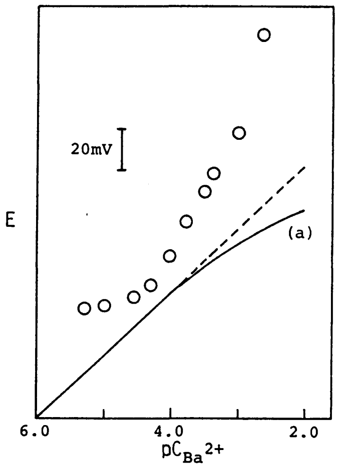

Fig. 3. Calculated potential curve vs. $\log C_{Ba^{2+}}$ (curve (a)) and E (O) vs. $\log C_{Ba^{2+}}$ relations of $Ba(DSS)_2$ in DMF with PAA-POE4 electrode under the coexistence of 10 mM Et_4NClO_4.

ment are shown in Table 2 with the results obtained previously by the use of an univalent cation-sensitive glass electrode.[4] The agreement between the results obtained with the two electrodes is excellent.

Potentiometric and Conductometric Behavior of $Ba(DSS)_2$ in DMF. (i) Potentiometry: The response of the PAA-POE4 electrode to the amphiphilic substance, $Ba(DSS)_2$, in DMF was measured using Cell I. The result is shown in Fig. 3 and curve (a) shows the calculated potential response to the barium ion in the solution of $Ba(DSS)_2$. The association constant of $Ba(DSS)_2$ in DMF used to elucidate the barium ion activity was obtained by the conductometric measurement shown below. When the concentration of the barium ion in DMF increased, the slope of the E-$pC_{Ba^{2+}}$ relation became steeper. The situation of the potential response of the PAA-POE4 electrode to the barium ion in $Ba(DSS)_2$-DMF solution, in which there was no Et_4NClO_4, was similar to that in Fig. 3 , but the potential change suddenly ceased at the highest concentration of the $Ba(DSS)_2$. **(ii) Conductometry:** The conductometric measurement was carried out to determine the association constant of $Ba(DSS)_2$ in DMF. The equivalent conductivities obtained are shown in Table 3. These values were used to get the association constant of Ba $(DSS)_2$ in DMF using the method of the Modified Fuoss-Edelson.[7] The activity coefficient of Ba^{2+}, y, was calculated using the Debye-Hückel second approximation equation[6] with ion-size parameters, a, of 10 Å and dielectric constant, ε, of 36.71 of DMF. The Modified Fuoss-Edelson plot obtained is shown in Fig. 4. Here the ΔF on the ordinate and the X on the abscissa in Fig. 4 are the same as those in Ref. 7 reported by Doe and Kitagawa. From the intercept and the slope of the straight line in Fig. 4, the limiting equivalent conductivity, Λ_0 of $Ba(DSS)_2$ in DMF and the 1 : 1 association constant between Ba^{2+} and DSS^-, K_{1A}, were obtained to be $54._8$ and $5.2_4 \times 10^2$, respectively. The limiting equivalent conductivity of the barium ion in DMF used for the above calculation was 39.0[8] and that of the DSS^- in DMF was calculated to be $15._8$.

Table 3. Equivalent Conductivity of $Ba(DSS)_2$ in DMF at 25 °C

10^4C/mol dm^{-3}	S/cm^2 mol^{-1}
0.6458	53.50
0.9901	52.20
2.248	48.98
4.031	46.99
6.279	44.86
9.091	42.79
12.28	40.96
19.35	37.91

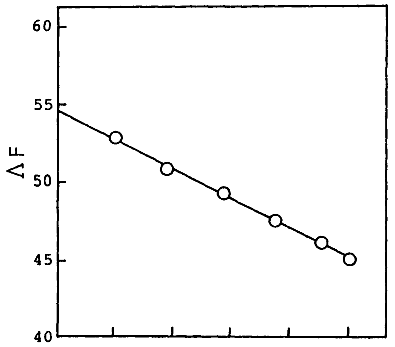

Fig. 4. Modified Fuoss and Edelson plot for $Ba(DSS)_2$ in DMF at 25 °C.

Discussion

The PAA-POE4 electrode can respond to the activities of the lithium ion in AN and the magnesium and barium ions in DMF. The PAA-POE6 electrode may also be used to measure the barium ion activity in DMF.

The PAA-POE4 electrode was used to determine the successive complex formation constants of the lithium ion in AN with DMF and the results agreed well with those obtained previously[4] by the use of an univalent cation-sensitive glass electrode. The glass electrode has been proved to respond in the same way as the amalgam electrode to the variation in solvation energies of the lithium ions.[9] In the previous paper,[3] we also showed that the PAA-POE4 electrode and the barium amalgam electrode could give similar formation constants for the complexation of the barium ion in AN with DMF. These results show that at least in an AN-rich region the electrode can respond thermodynamically to the variation in solvation energies of these ions and can be applied to study the complex formation reaction of alkali and alkaline earth metal ions in AN with other basic aprotic solvents.

In the present study the association constant of the barium ion with DSS^- in the $Ba(DSS)_2$-DMF solution was found to be of the same order of magnitude as that of the barium ion with p-toluenesulfonate and more associated than with perchlorate.[8] Using the association constant, the response of the PAA-POE4 electrode in the $Ba(DSS)_2$-DMF solution was estimated theoretically. But, as in Fig. 3, the slope of the potential change was larger than the theoretical one. It may be due to the localization of the barium ion at the PAA-POE4 membrane surface: the hydrophilic sulfonate of the DSS^- seems to be directed to the hydrophilic organic membrane and to concentrate the counter ion, Ba^{2+}, to the vicinity of the membrane. In the absence of Et_4NClO_4 in Fig. 3, the potential suddenly ceased to change at the highest concentration of the $Ba(DSS)_2$ as shown in the Results section. The difference in the electrode responses in the presence and absence of Et_4NClO_4 might be explained by the role of anions. In order to investigate the response mechanism of the PAA-POE4 electrode we prepared a glass filter membrane impregnated with PAA-POE4 and measured the ion transport across the membrane. A conductometric method was used to monitor the ionic transport. From the experiment, we found that the perchlorate ion can enter the membrane freely, while the entrance of the DSS^- into the membrane is fairly limited due to its larger size.[10] The sudden stop of the potential change in the absence of Et_4NClO_4 might be related to the difficulty for DSS^- to enter into the membrane. Probably sufficient anions should be present in the membrane to counterbalance the barium ion necessary for the proper electrode response. Some deficiency of anions would occur in the absence of Et_4NClO_4. In addition to this, it should also be taken into account that surface active substances (DSS^-) may change the property of the electrode surface and may interupt the response of the electrode.

Further studies are now being continued in this laboratory in order to elucidate the mechanism of the potential response at the polymer based ion-selective electrodes.

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