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Behavior of Polyacrylamide-Acyclic Poly(oxyethylene)-coated Ion-selective Electrodes in Nonaqueous Solvents

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Synopsis. Ion-selective electrodes constructed with polyacrylamide(PAA) coupled to acyclic poly(oxyethylene) neutral carriers, tetraethylene glycol monododecyl ether (POE4) or hexaethylene glycol monododecyl ether (POE6), were reported. Nernstian responses were obtained to magnesium and barium ions in AN with the PAA–POE4 membrane and to copper(II) and silver(I) ions in DMSO with the PAA–POE6 membrane.

Ion-selective electrodes have been shown to be useful for analytical and physicochemical studies in nonaqueous and mixed solvents[1] and their applications are steadily increasing. Ion-selective electrodes applicable in nonaqueous solutions, however, have mainly been limited to those with glass- or crystalline- sensing elements because of possible damage to or dissolution of the electrode components by organic solvents. Development of other types of ion-selective electrodes for use in nonaqueous solutions is desirable.

Recently we showed that a gelatine membrane electrode coated on a copper disk was durable in dimethyl sulfoxide(DMSO) and could respond in a Nernstian way to the activities of the magnesium and calcium ions in DMSO.[2] We also showed that a platinum disk electrode coated with polyacrylamide (PAA) polymer coupled to macrocyclic polyether neutral carrier (dibenzo-18-crown-6) could serve as a barium ion sensor durable for at least twenty days in acetonitrile(AN).[3] In the present report, we will report the behavior of electrodes which have been prepared by coating a platinum disk with a membrane of PAA coupled to acyclic poly(oxyethylene) neutral carriers. As the acyclic poly(oxyethylene), tetraethylene glycol monododecyl ether (POE4) and hexaethylene glycol monododecyl ether (POE6) were used. The PAA–POE4 electrode showed a Nernstian response to the activities of the magnesium and barium ions in AN and the PAA–POE6 electrode showed a Nernstian response to those of the copper(II) and silver(I) ions in DMSO.

Experimental

Apparatus. Potentiometric measurements were carried out at 25 °C with a Beckman Φ71 digital pH/mV meter and a Yokogawa Denki type 3056 strip chart recorder. Construction of the indicator electrode is similar to that reported before.[3] The silver/silver ion reference electrode and the salt bridge were as shown below in Cell I.

Reagents. The POE4 and POE6 were obtained from Tokyo Kasei Kogyo Co. Ltd. All other chemicals were the same as those used in the previous reports.[2,3]

Preparation of PAA-POE4 and PAA-POE6 Conjugates. The acyclic neutral carriers, POE4 and POE6, were conjugated at the carboxyl group of the carboxyl-modified polyacrylamide by esterification in benzene under the coexistence of *p*-toluenesulfonic acid as a catalysis.[4] The products were washed with tetrahydrofuran and dried under high vacuum.

Construction and Preparation of the Indicator Electrode. The indicator electrodes were constructed using either PAA–POE4 or PAA–POE6. Small amounts of the respective materials were dissolved in 5 µl of water and spread on the end surface of a 3 mm platinum disk. After flushing with nitrogen gas to volatile water, it was placed in a desiccator with silica gel for a few hours. The electrode was then conditioned in 0.01 M Et_4NClO_4–AN (1 M=1 mol dm^{-3}) or 0.01 M Et_4NClO_4–DMSO for 1 d. The electrodes should be stored in the same solution for repeated use.

Measurements of the Electrode Potential. The response of the electrodes was tested in the following cell,

$$\begin{gathered}\mathrm{Ag}\,|\,0.005\ \mathrm{M\ AgNO_3} + 0.01\ \mathrm{M\ Et_4NClO_4(D)}\ \vdots\vdots \\ 0.05\ \mathrm{M\ Et_4NClO_4(D)}\ \vdots\vdots\ C\ \mathrm{M(ClO_4)}_x + 0.01\ \mathrm{M} \\ \mathrm{Et_4NClO_4(D)}\,|\,\text{Polymer Membrane}\,|\,\mathrm{Pt} \cdots \text{Cell I}\end{gathered}$$

where D denotes AN or DMSO. $M(ClO_4)_x$ is the perchlorate of the cation to be tested (sodium, potassium, silver(I), magnesium, barium, copper(II) or zinc(II) ion). All the solutions were freshly prepared daily. The concentration, C in mol dm^{-3}, of the metal perchlorate was usually increased by the standard addition method to obtain calibration curves. Steady state potentials were read to ±0.1 mV. The electrode potentials were not significantly affected by a change in stirring rate.

Results and Discussion

The membrane electrodes, PAA–POE4 and PAA–POE6, constructed in this experiment were durable in AN and DMSO for at least about a week. The responses of these electrodes to the magnesium, barium, copper(II), and silver(I) ions in AN or DMSO are summarized in Table 1. Some typical calibration curves are also shown in Fig. 1. The activity of the metal ion, $a_{M^{x+}}$, was calculated by using the Debye-Hückel equation as previously described.[2] The results in Table 1 have not been corrected for the change of the liquid junction potential between the sample solution and the salt bridge of Cell I, but its effect seems to be small. In AN, the PAA–POE4 membrane electrode could respond in a Nernstian way to the activities of the magnesium and barium ions between the concentration ranges 5.0×10^{-7} M—5.0×10^{-3} M and 6.8×10^{-6} M—1.5×10^{-3} M, respectively. In DMSO, the PAA–POE6 electrode could respond in a Nernstian way to the activities of copper(II) and silver(I) ions between the concentration ranges 1.5×10^{-5} M—1.6×10^{-3} M and 6.2×10^{-5} M—1.1×10^{-2} M, respectively. The response of the PAA–POE4 electrode to the activity of the silver(I)

Table 1. The responses of the polymer membrane electrodes to some metal ions in nonaqueous solvents at 25 °C[a)]

PAA-POE4

Ion	$2r_c$,Å	Solvent	Slope ($mV/pa_{M^{x+}}$)	Range of the linear response ($pa_{M^{x+}}$)
Mg^{2+}	1.30	AN	29.2±1.1 (5)	6.7—3.0
Ba^{2+}	2.70	AN	26.8±2.1 (4)	5.7—3.4
Ag^+	2.52	DMSO	48.5±2.1 (3)	4.3—2.3

PAA-POE6

Ion	$2r_c$,Å	Solvent	Slope ($mV/pa_{M^{x+}}$)	Range of the linear response ($pa_{M^{x+}}$)
Cu^{2+}	1.44	DMSO	30.4±1.5 (10)	5.2—3.2
Ag^+	2.52	DMSO	61.3±1.5 (3)	4.3—2.1

a) The figures in parentheses denote the number of experiments. r_c : crystallographic ionic radius.

ion in DMSO was sub-Nernstian between the concentration of 6.2×10^{-5} M and 6.5×10^{-3} M. In all cases, the steady state potential was reached within ten minutes after each increase of the ionic concentration. Both electrodes of PAA-POE4 and PAA-POE6, however, showed poor responses to sodium and potassium ions in AN. These electrodes also showed poor responses to sodium, potassium, and zinc(II) ions in DMSO. The approximate selectivity coefficient obtained for the magnesium ion *vs.* barium ion, $\log k_{Mg^{2+},Ba^{2+}}$, was 1.2 by the mixed solution method in AN in the case of PAA-POE4 electrode.

Yanagida *et al.*[5)] showed a specific interaction of the magnesium ion with POE4 in acetone and suggested that the so called "hole-size rule" in the complexation of metal ions with crown ethers could be applicable to complexation with such acyclic polyethers as POE4 and POE6. If we consider that the magnesium ion in AN reacts with POE4 to form a stable complex, the response of the PAA-POE4 electrode to a wide concentration range of the magnesium ion in AN may be reasonable. But the electrode could also respond, though in a narrower concentration range, to the barium ion with a larger ionic size. The fact that the response to the silver(I) ion in DMSO was Nernstian with the PAA-POE6 electrode but was sub-Nernstian with the PAA-POE4 electrode may also be related to the hole sizes of POE4 and POE6. It seems reasonable to assume that complexation of the metal ions with POE4 or POE6 is essential for the electrode response. For correlation between the electrode response and the hole size concept, however, more detailed data will need to be obtained. In connection with this, solvents may play important roles on the electrode behavior through their solvation to the metal ions and also to the electrode materials. The extremely slow and poor response behavior of the electrode constructed of polyacrylamide polymer alone in AN has been reported before.[3)] The present experiment confirms that the presence of the neutral carrier, POE4 or POE6, in the membrane serves to stabilize the electrode potential and to improve the reproducibility and dynamic response behavior. Further experiments concerning the response behavior of these electrodes in other aprotic organic solvents and the application of these electrodes to obtain information about the solvent effect on the cations used in this experiment are now under investigation in this laboratory.

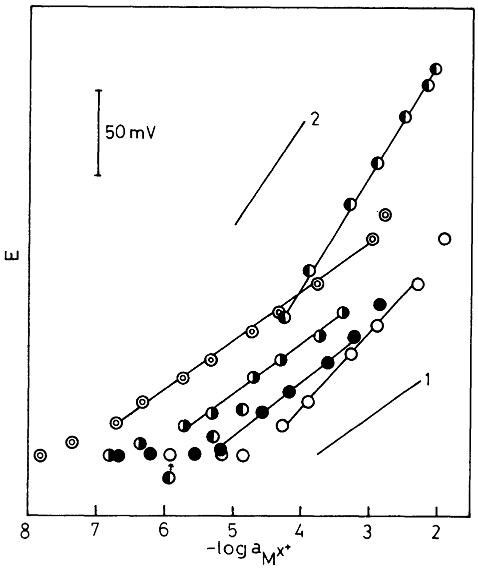

Fig. 1. Calibration curves in nonaqueous solvents at 25 °C. Lines 1 and 2, theoretical slope for divalent cations (29.6 $mV/pa_{M^{2+}}$) and for univalent cations (59.2 mV/pa_{M^+}), respectively. ◎, Mg^{2+} in AN with PAA-POE4; ◑, Ba^{2+} in AN with PAA-POE4; ○, Ag^+ in DMSO with PAA-POE4; ◐, Ag^+ in DMSO with PAA-POE6; ●, Cu^{2+} in DMSO with PAA-POE6.

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