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Voltammetric Investigation of the Response Mechanism of the Ion-Selective Electrodes Based on the Polymer Modified with Poly(oxyethylene) Derivatives in Acetonitrile

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The voltammetric behavior of barium and lithium ions in acetonitrile (AN) was studied at polymer membrane ion-selective electrodes which showed Nernstian responses to those metal ions in AN, in order to elucidate the mechanism of their potentiometric responses. The membrane electrodes consisted of polyacrylamide coupled to such poly(oxyethylene) derivatives as tetraethylene glycol monododecyl ether, dibenzo-18-crown-6, and cryptand222B and coated on platinum or gold disk. The cyclic voltammograms for barium and lithium ions, recorded repeatedly after setting the electrodes at the rest potentials, showed a cathodic peak at -1.5 ± 0.2 V vs. Ag/0.01 M Ag^+ (AN). The cathodic peak current (i_{cp}) decreased markedly between the first and second scans, but reached a steady value after the third scan. The i_{cp} values after the third scan were diffusion controlled and considered to be due to a transfer of the metal ions from the solution into the membrane. The differences in i_{cp} between the first and the third scans were proportional to the potential scan rate and attributed to a transfer of the metal ions which had been accumulated at or near the surface of the membrane by combining with the functional groups of the polymer. The accumulation occurred rather slowly and saturated with time. Based on the fact that the response processes of the ion-selective electrodes were very much similar to the accumulation processes, the response mechanism of the ion-selective electrodes is discussed.

Because ion-selective electrodes are useful for both analytical and physicochemical studies in organic solvents, many investigations have been carried out.[1] We recently developed ion-selective electrodes prepared by coating a platinum disk with polyacrylamide (PAA) coupled to such complexing reagents as dibenzo-18-crown-6 (DB18C6),[2] tetraethylene glycol monododecyl ether (POE4),[3] and cryptand222B (Cryp-222B).[4] They showed Nernstian responses to several cations in some organic solvents. One of them, the PAA-POE4 electrode, was also confirmed to respond in a Nernstian way to changes in the lithium and barium ion activities due to a solvent effect.[5,6] The PAA–POE4 electrode was applied in order to determine the successive formation constants of the complexing of the magnesium and barium ions in AN with such donor solvent molecules as DMF, DMSO, and HMPA.[5] The present paper reports on the cyclic voltammetric behavior of the lithium, sodium, potassium, magnesium, and barium ions in AN at such polymer membrane ion-selective electrodes as PAA–POE4, PAA–DB18C6, and PAA–Cryp222B, investigated to elucidate the mechanism of their potentiomeric responses.

Experimental

Apparatus. Cyclic voltammograms were measured with a potentio-galvanostat (Model HA501) and a function generator (Model 104) of Hokuto Denko Co. Ltd. and an X-Y recorder (Model RW-11) of Rika Denki Kogyo Co., Ltd. Cell I was used to study the voltammetric behavior of the polymer membrane-coated platinum or gold disk electrode and the auxiliary electrode was a platinum wire (1 M=1 mol dm^{-3}).

Ag/10 mM $AgNO_3$+10 mM Et_4NClO_4(AN)//
50 mM Et_4NClO_4(AN)//C $M(ClO_4)_x$+10 mM Et_4NClO_4(AN)/Polymer membrane/Pt or Au disk……Cell I

where $M(ClO_4)_x$ is the perchlorate of the cation to be tested (lithium, sodium, potassium, magnesium, or barium) and C is its concentration in mmol dm^{-3}. Measurements were carried out at 25 °C. The methods for constructing and conditioning of the polymer membrane electrodes were the same as those described in previous reports.[3,6] The thickness of the polymer membrane was ca. 50 μm.

Reagents. Polymer-neutral carrier conjugate, PAA-Cryp-222B, was obtained by the same method as described in a previous report.[2] Cryptand222B was a Merck product. All other chemicals were the same as those used previously.[3,6]

Results

The voltammetric behavior of the lithium, sodium, potassium, magnesium, and barium ions in AN at the PAA–POE4, PAA–DB18C6, and PAA–Cryp222B electrodes were studied cyclic voltammetrically. Typical cyclic voltammograms for the barium ion in AN recorded repeatedly at the PAA–DB18C6 electrode are shown in Fig. 1. Before the recording of the voltammograms, the electrode was kept at the rest potential for ten minutes with the solution being stirred and deaerated with nitrogen gas. Then, after stopping the stirring, the voltammogram was recorded cyclically from -0.8 V to -1.8 V at 100 mV s^{-1}. A cathodic peak was obtained at about -1.7 V vs. Ag/Ag^+ reference electrode. The peak current for the first scan, corrected for the background current, is designated as i_1 and that for the third scan, i_3. Between the first and third scans, the peak current decreased markedly. The voltammograms obtained after the third scan, however, almost overlapped the third one, showing that they were in the steady state. A small decrease in the peak current was also observed between the second and third scans, but did not significantly influence the discussions hereafter. Similar cyclic

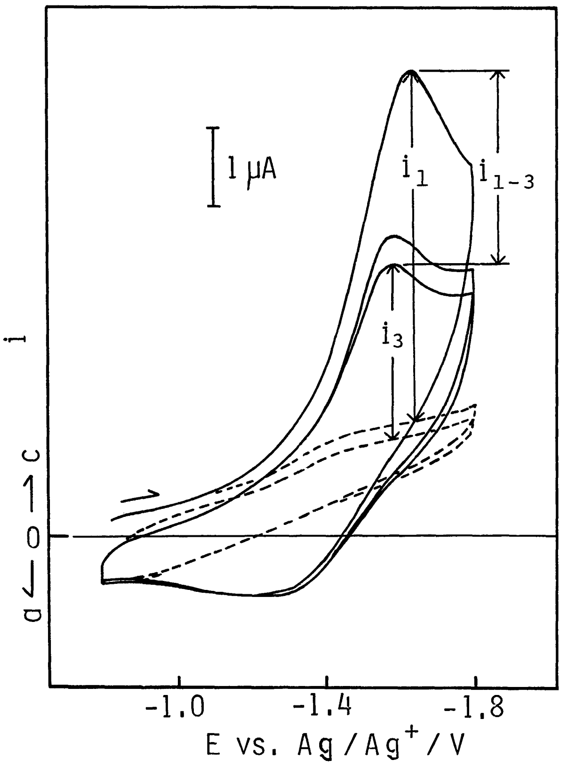

Fig. 1. Typical cyclic voltammograms in AN recorded continuously at PAA-DB18C6 electrode after standing for ten minutes at the rest potential: (——) 1 mM Ba^{2+}; (- - -) 0 mM Ba^{2+}; i_1, the cathodic peak height (i_{cp}) for the first scan; i_3, i_{cp} for and after the third scan; i_{1-3}, the difference between i_1 and i_3. Scan rate 100 mV s^{-1}.

voltammograms were obtained for the barium and lithium ions at the PAA-POE4 electrode and for the barium ions at the PAA-Cryp222B electrode. In all cases the cathodic peak appeared at approximately the same potentials (−1.5±0.2 V). When the gold disk was used instead of the platinum one, similar voltammograms were also obtained. The voltammetric behavior of the sodium, potassium, and magnesium ions at the PAA-POE4 electrode and that of the lithium and barium ions at a platinum disk electrode without any polymer coat was also investigated. However, no clear peak was obtained in the potential range between −0.5 and −1.9 V. Curves (a), (b), and (c) in Fig. 2 show the relations between i_1 and the barium ion concentrations at the PAA-POE4, PAA-DB18C6, and PAA-Cryp222B electrodes, respectively. Corrections have been made for the background currents. The relations between the lithium ion concentration and i_1 at the PAA-POE4 electrode (curve (d)) and the barium ion concentration and i_1 at the PAA electrode (free of functional compound) are also shown in Fig. 2. The repetitive fourteen measurements carried out for 2 mM barium ion at the PAA-DB18C6 electrode showed the coefficient of variation of i_1 of 2.4%. The cyclic

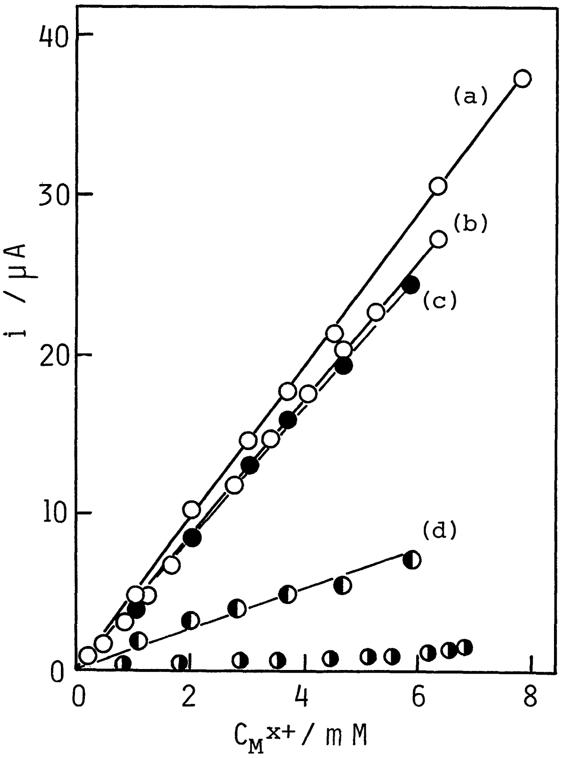

Fig. 2. The relation between the M^{x+} concentration in AN and the cathodic peak height (i_1): (a) Ba^{2+} at PAA-POE4 electrode; (b) Ba^{2+} at PAA-DB18C6 electrode; (c) Ba^{2+} at PAA-Cryp222B electrode; (d) Li^+ at PAA-POE4 electrode; (◑) Ba^{2+} at PAA electrode (scan rate: 100 mV s^{-1}, standing time: 10 min).

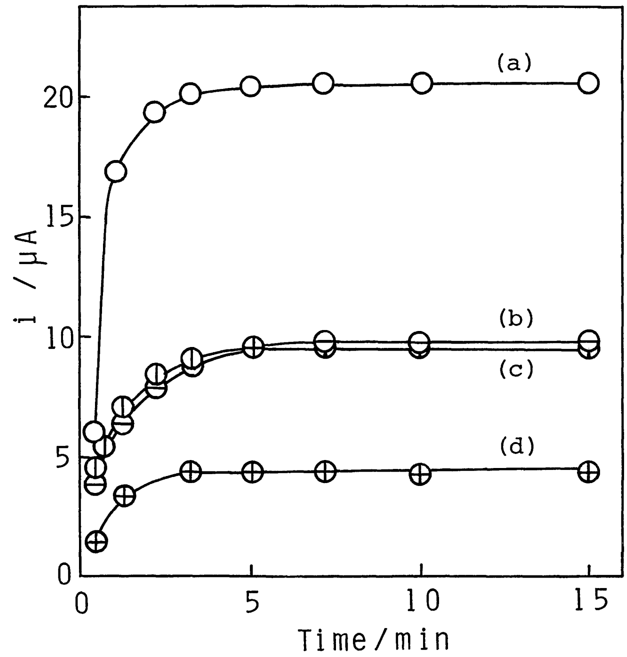

Fig. 3. The relation between the cathodic peak height (i_1) and the standing time: (a) Ba^{2+} (4 mM) at PAA-POE4 electrode; (b) Ba^{2+} (2 mM) at PAA-DB18C6 electrode; (c) Ba^{2+} (2 mM) at PAA-Cryp222B electrode; (d) Li^+ (2 mM) at PAA-POE4 electrode (scan rate: 100 mV s^{-1}).

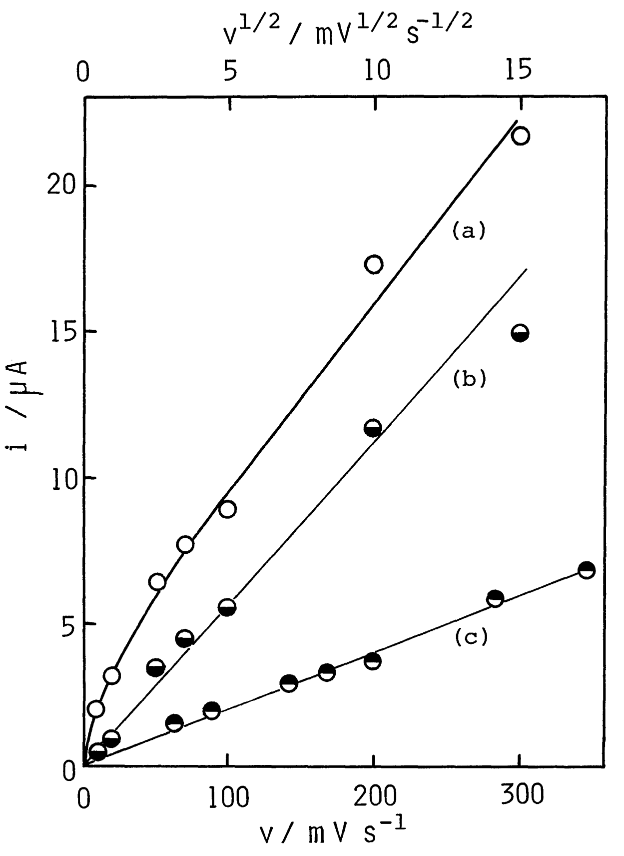

Fig. 4. The effect of the scan rate (v) to i_1, i_{1-3}, and i_3 for Ba^{2+} (2 mM) in AN at PAA-POE4 electrode (standing time: 10 min): (O) and curve (a), measured and calculated i_1–v relations; (b) i_{1-3}–v relation; (c) i_3–$v^{1/2}$ relation.

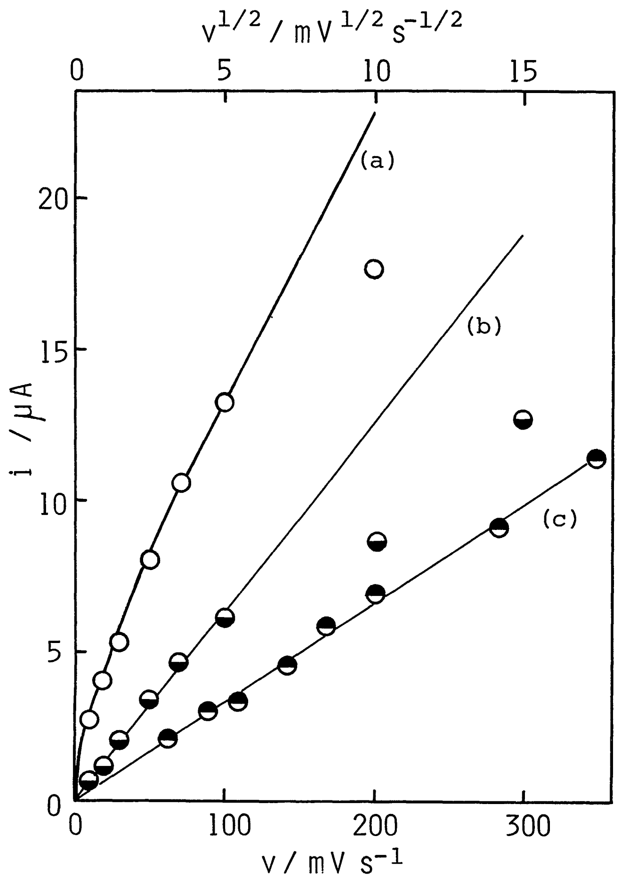

Fig. 5. The effect of the scan rate (v) to i_1, i_{1-3}, and i_3 for Ba^{2+} (3 mM) in AN at PAA-DB18C6 electrode (standing time: 10 min): (O) and curve (a), measured and calculated i_1–v relations; (b) i_{1-3}–v relation; (c) i_3–$v^{1/2}$ relation.

valtammograms were quite reproducible. The i_3 was proportional to the lithium and barium ion concentrations at the PAA-POE4 electrode and to those of barium ion at the PAA-DB18C6 and PAA-Cryp222B electrodes, respectively.

Figure 3 shows the relation between i_1 and the time of standing the electrode at the rest potential. Curves (a), (b), and (c) are for barium ions at the PAA-POE4, PAA-DB18C6, and PAA-Cryp222B electrodes, respectively, and curve (d) is for lithium ions at the PAA-POE4 electrode. The i_1 for barium ions became saturated after three to seven minutes and that for lithium ions after about three minutes. The i_3, on the contrary, was constant independent of the standing time.

Curves (a) in Figs. 4—6 show the relation between i_1 and the scan rate (v in mV s^{-1}) for barium ions at the PAA-POE4, PAA-DB18C6, and PAA-Cryp222B electrodes, respectively. Curve (a) in Fig. 7 is the i–v relation for lithium ions at the PAA-POE4 electrode. All these i–v relations were somewhat curved. In Figs. 4—7, Curves (b) show the $i_{1-3}(\equiv i_1 - i_3)$–$v$ relation and curves (c) the i_3–$v^{1/2}$ relation. It is interesting that both the i_{1-3}–v and the i_3–$v^{1/2}$ relations are approximately linear. This fact is discussed in the next section.

A similar voltammetric investigation as described here was also carried out for barium ions in propylene carbonate using the PAA-POE4 electrode; no clear cathodic peak, however, could be obtained.

Discussion

In Figs. 2 and 3, the i_1 for the barium ions at the PAA-POE4, PAA-DB18C6, and PAA-Cryp222B electrodes and that for lithium ions at the PAA-POE4 electrode were proportional to the metal ion concentrations, irrespective of the standing time of the electrode at the rest potential.

From the results in Figs. 4—7, current i_1 seems to consist of two different terms, as can be expressed by

$$i_1 = pv + qv^{1/2}, \tag{1}$$

where p and q are the proportional constants. The first term is proportional to the scan rate, while the second is proportional to the square root of the scan rate. Curve (a) in Fig. 4 (PAA-POE4-Ba^{2+}) was obtained using the values p=0.046 and q=0.47 in Eq.

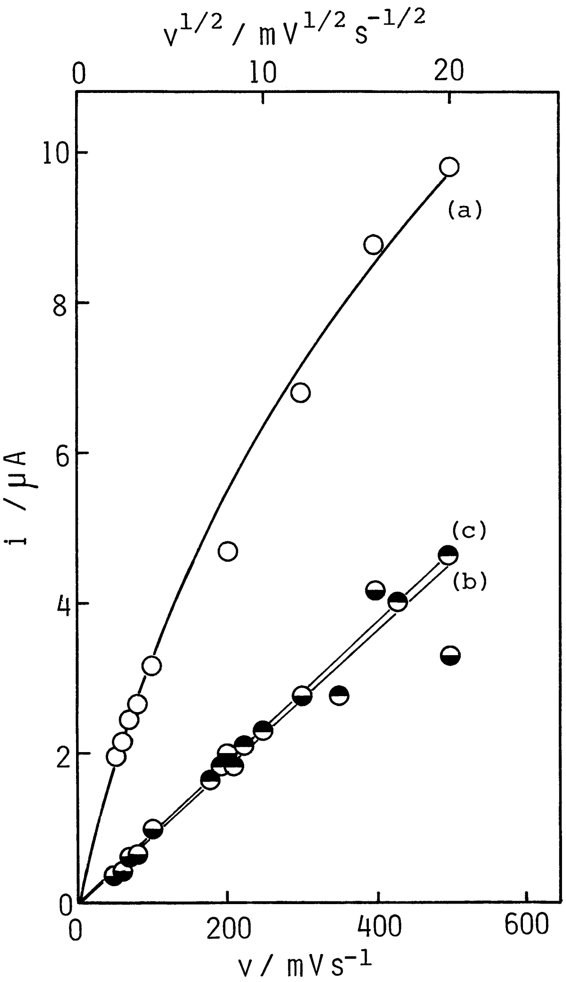

Fig. 6. The effect of the scan rate (v) to i_1, i_{1-3}, and i_3 for Ba^{2+} (1 mM) in AN at PAA-Cryp222B electrode (standing time: 10 min): (○) and curve (a), measured and calculated i_1-v relations; (b) i_{1-3}-v relation; (c) i_3-$v^{1/2}$ relation.

1. Curves (a) in Fig. 5 (PAA-DB18C6-Ba^{2+}), Fig. 6 (PAA-Cryp222B-Ba^{2+}), and Fig. 7 (PAA-POE4-Li$^+$), were obtained using $p=0.069$ and $q=0.63$, $p=0.010$ and $q=0.22$, and $p=0.006$ and $q=0.19$, respectively. The calculated i_1 values agreed fairly well with the experimental values. It is apparent that the i_1 consists of both a diffusion current (i_3) and a non-diffusion current (i_{1-3}). We consider that the diffusion current i_3 was produced by a transfer of barium or lithium ions from the bulk of the solution into the polymer membrane. The current i_{1-3}, on the other hand, seems to be related to the metal ions which were accumulated near the surface of the membrane by complexing with the functional groups on the polymer. Probably i_{1-3} is the current due to a transfer of accumulated metal ions into the membrane. As shown in Fig. 3, the accumulation process was rather slow, showing that a considerable part of the accumulation occurred by complexing with the functional groups near the surface, but not directly exposed to the bulk of the solution.

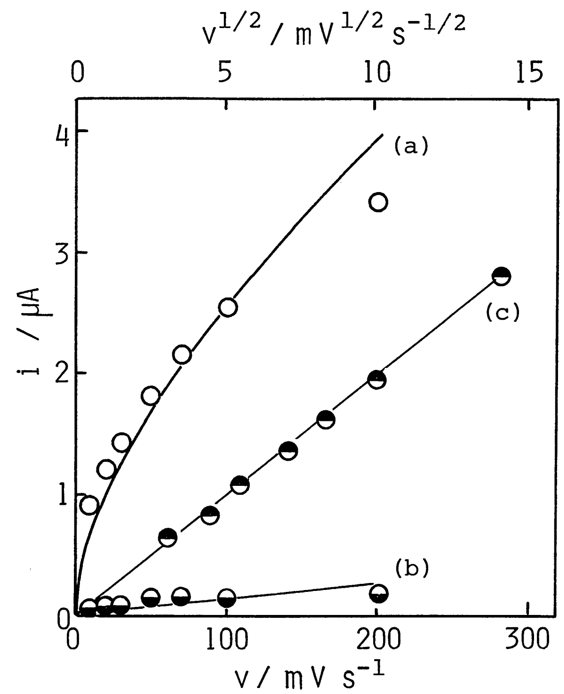

Fig. 7. The effect of the scan rate (v) to i_1, i_{1-3}, and i_3 for Li$^+$ (1 mM) in AN at PAA-POE4 electrode (standing time: 10 min): (○) and curve (a), measured and calculated i_1-v relations; (b) i_{1-3}-v relation; (c) i_3-$v^{1/2}$ relation.

This voltammetric behavior of polymer membrane ion-selective electrodes had similarities with the characteristics of their potentiometric responses. In potentiometry, the electrodes responded to variations in metal ion activities very quickly halfway to the equilibrium potentials, but then slowly. The time to reach the equilibrium potentials was six to eight minutes for barium ions at the PAA-POE4[3] and PAA-DB18C6[2] electrodes, three to four minutes for barium ions at the PAA-Cryp222B electrode[4] and three to four minutes for lithium ions at the PAA-POE4 electrode.[3] We consider from these voltammetric and potentiometric results that the steady state potential of the ion-selective electrodes are established in two steps. The first step is fast and related to a fast complexation of the metal ions with the functional groups directly exposed to the bulk of the solution. The second step is slow and related to the accumulated metal ions which showed the current i_{1-3} in voltammetry.

Similar voltammetric measurements were carried out for sodium, potassium, and magnesium ions in AN at the PAA-POE4 electrode. However, no clear cathodic peaks were obtained for them. The potentiometric response of the electrode was also sluggish to those metal ions. Probably, complexing with the functional groups at or near the surface of the polymer membrane plays important roles both in voltammetry and in potentiometry.

In order to further investigate the response mechanism of the ion-selective electrodes, we prepared glass filter membranes impregnated with PAA–POE4, PAA–DB18C6, and PAA–Cryp222B and now are studying the ion-transport across the membranes. The results, which support the above discussion, will be reported in the near future.

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