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Polarographic Minimum Wave of Tetraiodocadmate(II) Complex in Acetonitrile

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Synopsis. Tetraiodocadmate(II) anion gives a polarographic minimum wave at potentials above −1.1 V *vs.* Ag/AgCl, when tetrabutylammonium iodide is used as a supporting electrolyte. The experimental results show that the minimum wave appears as a result of electrostatic repulsion between the cadmate(II) anion and the negatively charged mercury surface.

It is well-known that a normal polarographic wave is produced for metal complexes in acetonitrile of an inert aprotic solvent.[1–3] A polarographic minimum wave was observed for tetraiodocadmate(II) anion over the potential range from −1.1 to −1.5 V, when it was extracted into an acetonitrile phase containing 0.1 mol dm^{-3} tetrabutylammonium iodide as the supporting electrolyte and as the extracting agent. An electrochemical interpretation is attempted on the minimum wave in the presence of quaternary ammonium salts, based on the experimental evidence of the electrocapillary curves, the current-time (*i–t*) curves and the effect of different surfactants or inorganic salts. Until now, there has been little reported on the minimum wave in acetonitrile in contrast with the aqueous solutions.[4,5] Further, we should pay attention to the choice of supporting electrolytes in the anodic stripping analysis,[6] because the pre-electrodeposition efficiency is decreased at the potential range inducing such a minimum wave.

Experimental

Cadmium(II) in aqueous solution (20.0 cm^3) is quantitatively extracted into the aqueous phase (10.0 cm^3) containing 0.1 mol dm^{-3} quaternary ammonium iodide, when 10.0 g of ammonium sulfate and a small amount of ascorbic acid were added. A Yanako P-8 polarograph was used for all polarographic work. The electrochemical cell was equipped with a silver–silver chloride reference electrode, a platinum wire counter electrode and the dropping mercury electrode which had the capillary characteristics: m= 0.932 mg s^{-1} and t=6.01 s at an open circuit in acetonitrile. A Watanabe Sokki WTR-2C oscillograph linear corder was used for measuring *i–t* curves, in which a 1 kΩ resistor was inserted into the platinum counter electrode in a series. The chemicals used were available from Wako Junyaku Co., Ltd. The other experimental procedures were similar to that described earlier.[7]

Results and Discussion

Figure 1 shows d.c. polarograms for the teraiodocadmate(II) ion which was extracted into acetonitrile phases containing different kinds of quaternary ammonium iodide (0.1 mol dm^{-3}). Normal well-defined waves were obtained with tetraethylammonium iodide (TEAI) and tetrapropylammonium iodide (TPrAI) at $E_{1/2}$=−0.77 V *vs.* Ag/AgCl, while polarographic minimum waves appeared from about −1.1 V with tetrabutylammonium iodide (TBAI) and tetrapentylammonium iodide (TPeAI). The limiting current on the four polarographic waves were all diffusion-controlled. To clarify the difference in the polarographic wave, we investigated the electrode reaction between the cadmate(II) ion and the mercury electrode by means of the conventional polarographic analysis.[8] The plots of log $i/(i_d-i)$ *vs.* E for the d.c. waves yield straight lines with reciprocal slopes of 30.9 and 34.1 mV for TEAI and TBAI at 25 °C, respectively. It is obvious that the reversibility of the electrode reaction is lowered for TBAI. The electrocapillary and *i–t* curves were examined to ascertain whether the cadmate(II) ion was adsorbed onto the mercury electrode on electrolysis or not. From the electrocapillary curves

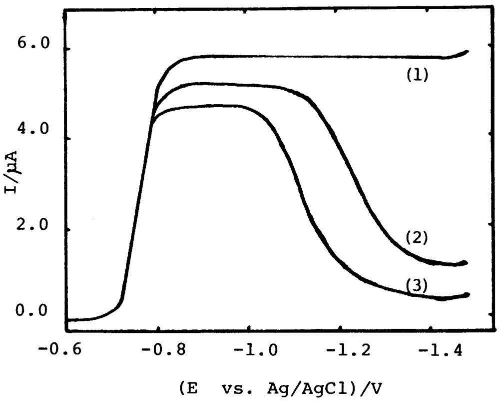

Fig. 1. D.c. polarograms of 8.8×10^{-4} mol dm^{-3} tetraiodocadmate(II) complex in acetonitrile. Supporting electrolyte: (1) 0.1 mol dm^{-3} TEAI or TPrAI; (2) 0.1 mol dm^{-3} TBAI; (3) 0.1 mol dm^{-3} TPeAI.

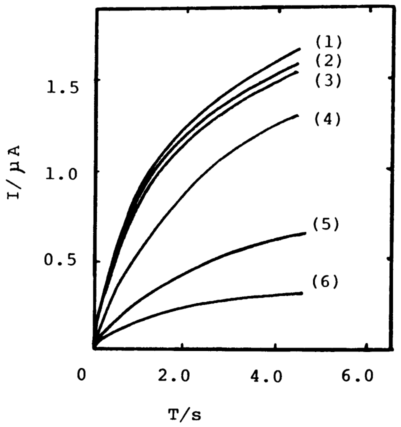

Fig. 2. *i–t* curves for 8.8×10^{-4} mol dm^{-3} tetraiodocadmate(II) complex at various potentials.
(1): 0.1 mol dm^{-3} TEAI at potentials from −1.0 to −1.5 V; (2): 0.1 mol dm^{-3} TBAI at −1.0 V; (3): −1.1 V; (4): −1.2 V; (5): −1.3 V; (6): −1.4 V.

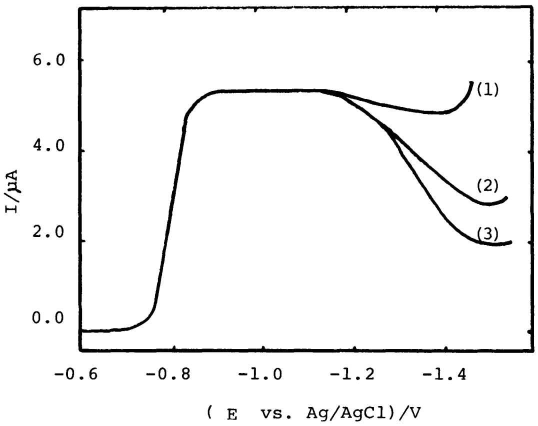

Fig. 3. Effect of inorganic salts on d.c. polarogram of 8.8×10^{-4} mol dm^{-3} tetraiodocamate(II) complex in acetonitrile containing 0.1 mol dm^{-3} TBAI. (1): 0.08 mol dm^{-3} $Al(ClO_4)_3$, (2): 0.07 mol dm^{-3} $LiClO_4$, (3): 0.04 mol dm^{-3} $LiClO_4$.

obtained, it was found that the drop-time was gradually decreased at the potential range from −0.8 to −1.5 V, and that no sharp decrease of drop-time was observed in both cases of TEAI and TBAI. The *i–t* curves shown as in Fig. 2 indicate that the current is almost proportional to $t^{1/6}$ at all potentials investigated, even above −1.1 V for TBAI. These results reveal that no adsorption of the ionic species onto the mercury electrode occurs. There seems to be other reasons for the appearance of the polarographic minimum wave in acetonitrile containing 0.1 mol dm^{-3} TBAI.

The effect of various surfactants and inorganic salts on the minimum wave was investigated for TBAI. It was observed that the addition of triton X-100 and hexadecyltrimethylammonium chloride to the acetonitrile solution recovered the diminution of the reduction current for the cadmate(II) ion at potentials above −1.1 V, but that of sodium dodecylbenzenesulfonate does not. It is interesting to note from Fig. 3 that more positive effect of recovering the minimum wave was obtained with the addition of cations of higher valency (Al^{3+}>Li^{+}). It is also noted that the degree of depression on the minimum wave was decreased as the concentration of salts added was increased.

Y. Umezawa *et al.* have discussed the polarographic behavior of minimum waves for inorganic anions in aqueous medium, based on the quantum mechanical effect and the electrostatic one.[9] In the present study, the appearance of the minimum wave can merely be explained in terms of the electrostatic model:[10] the minimum wave takes place with the electrostatic repulsion between the cadmate(II) anion and the negatively charged mercury surface. This is because the presence of cationic substances gives rise to normal reduction waves. When the large TBA^+ ion was exchanged with a small cation near the mercury electrode, the cadmate(II) ion is possible to approach to the electrode where as a result the electron transfer occurs to a more greater extent. We also consider that the large TBA^+ ion interfere sterically with the approach of the cadmate(II) ion to the electrode. It seems that a slightly negative shift of $E_{1/2}$ by addition of Li^+ or Al^{3+} is attributed to the ion-pair formation with the cadmate(II) ion, or to the salt effect due to increasing supporting electrolyte.[11]

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