Polarographic Behavior of Iodide and Its Mercury and Cadmium Compounds in Acetone

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The polarographic behavior of iodide ion, its mercury compounds and tetraiodocadmiate(II) ion have been investigated in acetone containing the supporting electrolyte of 0.1 M sodium perchlorate. Iodide ion produces two anodic waves, the first step of which is due to the oxidation of mercury to form triiodomercurate(II) ion HgI_3^- and the second step to form mercury iodide HgI_2 . The tetraiodocadmiate(II) ion produces a cathodic wave and three anodic waves, all of which are reversible process. The cathodic wave is ascribed to the reduction of cadmium(II)-iodide complex. The first and third anodic waves are identical to those of iodide ion. The second anodic step is ascribed to the electrode process: $3\text{CdI}_2 + 2\text{Hg} - 4\text{e} \rightleftharpoons 2\text{HgI}_3^- + 3\text{Cd}^{2+}$.

1 Introduction

It is well known that the anion forming stable complex with mercury ion facilitates anodic dissolution of the mercury electrode. The halogen-halide systems have been studied by means of voltammetry in non-aqueous solvent such as dimethylformamide (DMF)¹⁻³, acetonitrile (AN)⁴⁻⁶, dimethylsulfoxide (DMSO)⁷, acetic anhydride⁸, acetic acid⁹, pyrrolidone-2⁹, N-methylpyrrolidone¹⁰ and tetrahydrofuran¹¹. The electrode reaction of halide ions at the dropping mercury electrode has been reported by Matsui *et al.*^{3,12}. Polarographic reduction of metal-halide compounds have also been studied in different non-aqueous solvents¹³⁻¹⁵. However, only small set of data^{16,17} on the anodic process of metal-halide complex in non-aqueous media is available.

In the present work, polarographic behavior of iodide and tetraethylammonium tetraiodocadmiate(II) $\{(\text{Et}_4\text{N})_2(\text{CdI}_4^{2-})\}$ in acetone are investigated. Acetone has been recommended as a solvent for anodic polarography of alkylxanthate ion¹⁸.

2 Experimental

The electrolysis cell was assembled as described by Misumi and Aihara¹⁹, except that two electrode system was employed. Polarograms were recorded with a Yanagimoto polar-

ograph PA-102. The dropping mercury electrode has the following characteristics: $m = 1.058 \text{ mg s}^{-1}$ and $t = 6.32 \text{ s}$ at open circuit in an acetone solution of 0.1 M sodium perchlorate when $h = 50 \text{ cm}$. The reference electrode was an aqueous SCE with an agar salt bridge of 0.1 M sodium perchlorate. After polarograms were recorded at $16 \pm 0.1^\circ\text{C}$, conductivity of the electrolysis solution was measured with a TOA conductometer, model CM-2 A, in order to correct potentials for the iR drop¹⁹. Liquid junction potential was found to be almost constant through all of measurements as evaluated employing aqueous SCE and acetone saturated calomel electrode²⁰. Therefore, potentials were corrected only for the iR drop. The electrolysis solution was deaerated by introducing nitrogen which passed through two traps containing acetone and Drilite (anhydrous calcium sulfate), respectively.

Acetone (Kanto Chemicals Co., extra pure grade) was purified according to Coetzee and Siano²¹ and stored in a desiccator with silica gel. Commercially available tetraethylammonium iodide (Et_4NI) and mercury iodide (HgI_2) were recrystallized from ethanol-water mixture. Preparation of tetraethylammonium triiodomercurate(II) $[\text{Et}_4\text{N}^+\text{HgI}_3^-]$ was similar to that of tetraethylammonium tribromomercurate(II)³. The yellow precipitate obtained was recrystallized from DMF-ethanol solution. Cadmium perchlorate was prepared from cadmium nitrate by the method using cation exchange resin Dowex 50-X 8 (50-100 mesh) and the evaporation was carried out under reduced pressure at

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60°C. Cadmium perchlorate thus obtained was dried in vacuum at 60°C for a week¹⁵⁾. The acetone solution of cadmium (II) perchlorate was standardized by EDTA titration. Tetraethylammonium tetraiodocadmiate(II) $[(Et_4N^+)_2(CdI_4^{2-})]$ was prepared by the following procedure. Potassium iodide (10.5 g) and cadmium nitrate hexahydrate (2.0 g) were added to 50 cm³ of water and agitated until they were in solution. The solution was added to 90 cm³ of aqueous solution containing 1.5 g of Et_4NI . The precipitate obtained was collected by filtration, washed with water and recrystallized from acetone-water. Found: Cd 12.63%, I 56.39%. Calculated for $[(C_2H_5)_4N]_2CdI_4$: Cd 12.77%, I 57.65%. Sodium perchlorate used as supporting electrolyte was dried in vacuum at 60°C for 6 h. All of glass wares and materials were kept in a desiccator with silica gel or sulfuric acid.

3 Results and Discussion

3.1 Polarographic behavior of iodide ion and its mercury compounds

Anodic polarogram of iodide ion in acetone

Fig. 1 Polarograms of (1) 0.6 mM iodide ion, (2) 0.2 mM triiodomercurate(II) ion and (3) 0.3 mM HgI_2 in acetone containing 0.1 M sodium perchlorate

Potentials were not corrected for the iR drop

containing 0.1 M sodium perchlorate as the supporting electrolyte is shown in Fig. 1. Two anodic waves are observed, half-wave potentials of which are -0.434 (step I) and -0.135 (step II) V vs. SCE, respectively, for 0.6 mM iodide ion. The limiting current of steps I and II is proportional to the square root of mercury column height corrected for the back pressure. The relative temperature coefficient of wave height at 16°C is 1.10% for step I and 0.83% for step II. The results indicate that both waves I and II are diffusion-controlled. The limiting current of steps I and II increases linearly with increasing concentration of iodide ion. The ratio $I_d(I)/I_d(II)$ of diffusion current constants of steps I and II, as tabulated in Table 1, is approximately 2:1, suggesting that the number of electrons transferred at step I is twice as much as step II. With increasing concentration of iodide ion, the half-wave potential of step I shifts to a more negative value and that of step II to a more positive.

Electrode reaction of iodide ion in DMF has been reported by Misumi and Date³⁾. It may be assumed that the similar electrode process as in DMF proceeds also in acetone; namely, for the step I

Table 1 Polarographic data for iodide ion and its mercury compounds

	Concentration C/mM	Half-wave potential ^{a)}		Diffusion current constant ^{b)}	
		1st wave	2nd wave	1st wave	2nd wave
$Et_4N^+I^-$	0.4	-0.421	+0.129	1.86	0.81
	0.6	-0.434	+0.135	1.95	0.88
	0.8	-0.440	+0.138	2.00	0.95
	1.0	-0.445	+0.140	1.97	0.91
	1.2	-0.455	+0.143	2.03	0.92
$Et_4N^+HgI_3^-$	0.2	-0.443	+0.130	5.46	2.39
	0.3	-0.460	+0.136	5.74	2.56
	0.4	-0.469	+0.138	5.94	2.68
	0.5	-0.476	+0.142	5.96	2.75
	0.6	-0.484	+0.146	5.94	2.77
HgI_2	0.2	+0.117	-0.427	1.53	3.58
	0.3	+0.122	-0.436	1.75	3.83
	0.4	+0.129	-0.446	1.76	3.78
	0.5	+0.131	-0.453	1.83	3.78
	0.6	+0.135	-0.467	1.78	3.83

a) $E_{1/2}$ vs. SCE, corrected for iR drop

b) $I_d = i_a C^{-1} m^{-2/3} t^{-1/6}$

Fig. 2 A plot of $\log \{i^2/(i_d - i)^b\}$ vs. E at 16°C for 1.4 mM iodide ion

(1) wave I, (2) wave II

and for the step II

The current-potential relationships of these electrode reactions are given by eqns. (3) and (4), respectively.

$$E = E_0' + 0.03 \log \frac{i}{(i_d - i)^3} \quad (3)$$

$$E = E_0'' + 0.03 \log \frac{i^3}{(i_d - i)^2} \quad (4)$$

where E_0' and E_0'' are the formal standard potentials. The results of logarithmic analysis according to eqns. (3) and (4) are shown in Fig. 2. The plot has a slope of 27 mV for step I and 30 mV for step II, which are in agreement with the theoretical values.

The polarograms of mercury iodide complexes HgI_3^- and HgI_2 are also shown in Fig. 1. The HgI_3^- ion gives a cathodic wave (step I') and an anodic wave (step II'), and the HgI_2 produces two cathodic waves (steps I'' and II''). The half-wave potentials of steps I' and I'' coincide with that of the anodic step I of iodide ion and those of steps II' and II'' with the step II of iodide ion, indicating the reversible electrode process. The diffusion current constants of the respective waves are given in Table 1. As the ratio of diffusion current constant, $I_d(\text{I}) : I_d(\text{I}') : I_d(\text{I}'') = 1 : 3 : 2$ was found. The half-wave potentials of HgI_3^- and

HgI_2 waves were plotted against the logarithm of their concentrations. The plot gives a straight line whose slope is in agreement with the theoretical value. Namely, we obtained -68 mV for step I', $+33$ mV for step II', $+33$ mV for step I'' and -69 mV for step II''. These results indicate that the electrode reaction of iodide ion in acetone follows the eqs. (1) and (2).

3.2 Polarographic behavior of cadmium (II)-iodide complex

Polarograms of cadmium(II)-iodide system in acetone are shown in Fig. 3. The free cadmium (II) ion gives a cathodic wave at around -0.35 V. The limiting current diminishes when the concentration of iodide ion is increased, owing to the formation of cadmium (II)-iodide complexes which are reduced at a more negative potential. On the other hand, anodic waves IV and V appear at the concentration ratio of $[\text{I}^-]/[\text{Cd}^{2+}] = 1, 2$ and 3. At $[\text{I}^-]/[\text{Cd}^{2+}] = 4$ and 5, an additional anodic wave III appears. A polarogram of 0.2 mM cadmium (II) salt $\{(\text{Et}_4\text{N}^+)_2(\text{CdI}_4^{2-})\}$ is identical to (5) in Fig. 3. Further experiments were carried out by using the cadmium (II) salt. The wave heights III, IV and V are proportional to the square root of mercury column height.

Fig. 3 Polarograms of cadmium (II)-iodide system

$[\text{Cd}(\text{II})] = 0.2 \text{ mM}$. Concentration ratio: (1) $[\text{I}^-]/[\text{Cd}^{2+}] = 0$, (2) = 1, (3) = 2, (4) = 3, (5) = 4, (6) = 5, (7) Supporting electrolyte only (0.1 M NaClO_4)

Table 2 Polarographic data for tetraethyammonium tetraiodocadmiate(II) $\{(\text{Et}_4\text{N}^+)_2(\text{CdI}_4^{2-})\}$

Concentration mM	Diffusion current constant			
	$I_d(\text{cathodic})$	$I_d(\text{III})$	$I_d(\text{IV})$	$I_d(\text{V})$
0.10	5.06	1.74	5.53	3.36
0.15	4.88	1.75	5.65	3.33
0.20	5.06	1.79	5.72	3.62
0.30	4.81	1.70	5.50	3.78
0.40	4.94	1.82	5.46	3.72
0.55	4.83	1.78	5.36	3.55
average	4.93	1.76	5.54	3.56

$I_d(\text{cathodic})$, $I_d(\text{III})$, $I_d(\text{IV})$ and $I_d(\text{V})$ are diffusion current constants of cathodic wave, wave III, wave IV and wave V, respectively.

The relative temperature coefficient of limiting current at 16°C is 0.99% for the cathodic wave, 0.94% for the anodic wave III, 1.48% for wave IV and 1.10% for wave V. Since AC peaks corresponding to the respective DC steps are observed, the electrode reactions are reversible. The diffusion current constants of the waves III, IV and V of the cadmium(II) salt were tabulated in Table 2. If the diffusion current constant of wave III is regarded as 1, the ratio $I_d(\text{cathodic}) : I_d(\text{III}) : I_d(\text{IV}) : I_d(\text{V}) = 2.8 : 1 : 3.1 : 2.1$ was found. Moreover, the half-wave potential of anodic wave III is in fairly good agreement with that of anodic step I of iodide ion and the wave V with the step II.

Assuming that the tetraiodocadmiate(II) ion CdI_4^{2-} in acetone dissociates to liberate iodide ions according to

the cathodic wave of the cadmium(II) salt may be attributed to the reduction of iodo complexes of cadmium(II).

where i is the number of ligands bound to cadmium(II).

From a comparison of half-wave potentials of iodide and cadmium(II) salt and their diffusion current constants, it was thought that waves III and V are identical to the step I and II of iodide ion, respectively. As shown in Fig. 4, the slope of a plot $E_{1/2}$ vs. $\log[(\text{Et}_4\text{N}^+)_2(\text{CdI}_4^{2-})]$ is -54 mV for wave III and +30 mV for wave V, which are in good accordance with those expected from

eqs. (3) and (4). The results of logarithmic analysis, as shown in Fig. 5, indicate that the electrode reactions follow eqs. (1) and (2), respectively.

For the anodic wave II, the following electrode reaction was assumed.

where j and k are the number of ligands coordinated to cadmium(II). The Nernst equation corresponding to equ. (7) is given by

Fig. 4 A plot of $E_{1/2}$ vs. $\log[(\text{Et}_4\text{N}^+)_2(\text{CdI}_4^{2-})]$ (1) wave III, (2) wave IV, (3) wave V

Fig. 5 A plot of $\log \{i^a/(i_d-i)^b\}$ vs. E at 16°C for (1) wave III, (2) wave V and (3) wave IV of 0.7 mM $\{(\text{Et}_4\text{N}^+)_2(\text{CdI}_4^{2-})\}$

$$E = E_{0,a} + \frac{0.03}{n} \log \frac{[\text{CdI}_k^{2-k}]^m [\text{HgI}_3^-]^n}{[\text{CdI}_j^{2-j}]^m} \quad (8)$$

The current-potential relationship is expressed as

$$E = E'_{0,a} + \frac{0.03}{n} \log \frac{i^{m+n}}{(i_d - i)^m} \quad (9)$$

The half-wave potential $E_{1/2,a}$ is given by

$$E_{1/2,a} = E''_{0,a} + 0.03 \log i_d \quad (10)$$

A plot of $E_{1/2,a}$ vs. $\log [(\text{Et}_4\text{N}^+)_2(\text{CdI}_4^{2-})]$ for wave IV is linear, as shown in Fig. 4, and has a slope of +30 mV.

Logarithmic analysis was carried out for possible six cases in order to determine m and n values in equ. (9). When $m=3$ and $n=2$, assuming the equ. (11) or (12),

the plot has a slope of +15 mV, which is in agreement with the theoretical value (Fig. 5).

When $m=1$ and $n=1$, assuming the equation:

the slope was found to be +49 mV, which does not agree with the theoretical value +30 mV.

When $m=3$ and $n=1$, assuming the following three cases:

The slope was +23 mV, which is smaller than the theoretical one +30 mV.

3.3 Polarographic behavior of Cd^{2+} - HgI_3^- and Cd^{2+} - HgI_2 systems

Polarograms of the HgI_3^- ion in the presence of various amounts of cadmium(II) perchlorate are shown in Fig. 6. The wave height VIII increases linearly with increasing concentration of cadmium(II) up to 3 mM, i.e., $[\text{Cd}^{2+}]/[\text{HgI}_3^-]=3/2$ and above 3 mM cadmium(II), it becomes constant, the wave VII appearing. The wave VIII is ascribed to the reduction of cadmium(II)-iodide complex and the wave VII to the reduction of free cadmium(II) ion. The wave height VI increases with increasing concentration of cadmium(II) and becomes constant at above $[\text{Cd}^{2+}]/[\text{HgI}_3^-]=3/2$. The

anodic wave height II' is independent of cadmium(II) concentration. The height of cathodic wave I' of HgI_3^- ion decreases linearly with increasing amount of cadmium(II) and it disappears completely at the ratio of $[\text{Cd}^{2+}]/[\text{HgI}_3^-]=3/2$. The results imply that the following electrode reaction may take place.

The cadmium(II) complex CdI_2 formed is further reduced at the potential of wave VIII.

Figure 7 shows the polarograms of Cd^{2+} - HgI_2 system whose behavior are very similar to the Cd^{2+} - HgI_3^- system. If the polarograms of

Fig. 6 Polarograms of Cd^{2+} - HgI_3^- system

$[\text{HgI}_3^-]=0.2 \text{ mM}$. Concentration ratio: (1) $[\text{Cd}^{2+}]/[\text{HgI}_3^-]=0$, (2)=1/2, (3)=2/2, (4)=3/2, (5)=4/2, (6)=5/2 and (7)=6/2. Potentials were not corrected for iR drop

Fig. 7 Polarograms of Cd^{2+} - HgI_2 system

$[\text{HgI}_2]=0.3 \text{ mM}$. Concentration ratio: (1) $[\text{Cd}^{2+}]/[\text{HgI}_2]=0$, (2)=1/3, (3)=2/3, (4)=3/3, (5)=4/3 and (6)=5/3. Potentials were not corrected for iR drop

Cd^{2+} - HgI_2 system are shifted toward an anodic direction by about $0.6 \mu\text{A}$, they overlap with those of Cd^{2+} - HgI_3^- system at the equivalent concentration of cadmium (II), as might be expected from the eqn. (2).

From the results described above, it is confirmed that the anodic process of wave IV of cadmium (II) salt $\{(\text{Et}_4\text{N}^+)_2(\text{CdI}_4^{2-})\}$ is given by eqn. (12).

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