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Polarography of Ammonium 1-Pyrrolidinecarbodithioate and Ammonium 2-Carboxy-1-pyrrolidinecarbodithioate at the Dropping Mercury Electrode

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Direct current and alternating current polarographic behaviors of ammonium 1-pyrrolidinecarbodithioate (APCD) and ammonium 2-carboxy-1-pyrrolidinecarbodithioate (ACPCD) were investigated at the dropping mercury electrode. APCD showed an adsorption pre-wave (−0.70 V *vs.* SCE) and one-electron oxidation wave (−0.42 V). ACPCD showed only an adsorption wave (−0.65 V). These results were also confirmed by the investigation of the electrocapillary curves and the current-time curves. The surface excess of APCD or ACPCD on the surface of mercury drop electrode at the potential which the adsorption process was observed were 5.76×10^{-10} mol/cm^2 and 2.62×10^{-10} mol/cm^2, respectively.

APCD forms insoluble complexes with various metal ions and these complexes are much more stable than 1,1-diethylcarbodithioate complexes for heat and acidity. This reagent has been used for colorimetric determinations[1] and atomic absorption spectrophotometric determinations[2] since it was found that these precipitates were extracted with organic solvents.[3] On the other hand, ACPCD forms soluble complexes with various metal ions in aqueous solution.

This paper concerns the polarographic behaviors of APCD and ACPCD at the dropping mercury electrode. The mechanism of electrode reactions and the number of moles adsorbed per unit area of the electrode surface of these substances are also discussed.

Experimental

APCD was prepared according to Mallisa and Schöff-

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[1] R. W. Looyenga and D. F. Boltz, *Talanta*, **19**, 82 (1972).

[2] R. R. Brooks, B. J. Presley, and I. R. Kaplan, *ibid.*, **14**, 809 (1967).

[3] W. Doll und H. Specker, *Z. Anal. Chem.*, **161**, 354 (1958).

mann.[4]

ACPCD was prepared by the following procedure. Dissolve 0.1 mol of 2-carboxypyrrolidine(L-proline) in the minimum amount of methanol and add 6 ml of carbon disulfide. Saturate the solution with ammonia gas at 0 °C. Filter off the product and recrystallize twice by dissolving in methanol and precipitating with ethyl ether. Found: C, 32.05; H, 6.80; N, 18.37%. Calcd for $C_6H_{15}O_2N_3S_2$: C, 31.98; H, 6.71; N, 18.65%. All other reagents were A.R. grade.

Polarographic curves were recorded using Yanagimoto P-8 type Polarograph in conjunction with a H-type cell with a saturated calomel electrode and a spiral platinum wire as an auxiliary electrode. The dropping mercury electrode used had the following characteristics; mercury flow rate $m=1.32$ mg/s, drop time $t=5.57$ s at open circuit and at a height of mercury reservoir 65 cm in 0.1 M sodium hydroxide. The current-time curves were recorded using National Oscilloscope VP-546A in conjunction with the polarograph.

A freshly prepared sample solution which contained 0.1 M sodium hydroxide as a supporting electrolyte, was taken into the H-type cell. The dissolved oxygen was removed by bubbling with highly purified nitrogen and then the polarogram was recorded. Experiments were carried out in alkaline solution at 25.0±0.1 °C in order to prevent the decomposition of the sample.[5,6]

Results

Ammonium 1-Pyrrolidinecarbodithioate (APCD).

Direct Current (DC) Polarography: Figure 1 shows the DC and AC polarograms of 5×10^{-4} M APCD in 0.1 M sodium hydroxide solution. Only one DC wave A is observed at −0.70 V in APCD solution less than 1.5×10^{-4} M. When the concentration of APCD exceeds 1.5×10^{-4} M, however, another DC wave B appears at −0.42 V. The limiting current of wave A does not change with increasing concentration of APCD above 1.5×10^{-4} M. The limiting current of total wave (A+B), however, increases linearly with the concentration of APCD less than 2×10^{-3} M as shown in Fig. 2. The effect of the height of the mercury reservoir is shown in Table 1. The height of wave A is approximately proportional to $h_{corr.}$ linearly, while the total wave height is approximately proportional to $h_{corr.}^{1/2}$ The temperature coefficient of the limiting current of the total wave is +1.3% per degree in the temperature range of 5 to 40 °C (Fig. 3). These results show that

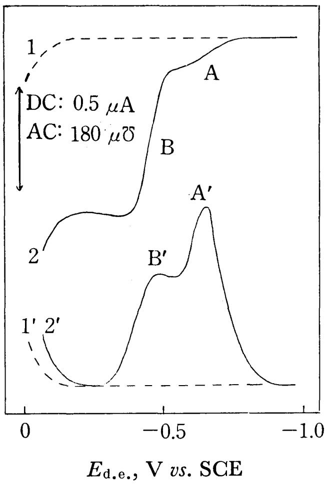

Fig. 1. Polarograms of APCD in 0.1 M NaOH at 25 °C. 1, 1′: 0 M APCD, 2, 2′: 5×10^{-4}M APCD, 1,2: DC polarograms, 1′, 2′: AC polarograms.

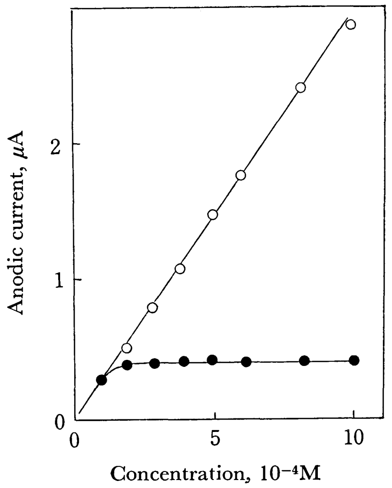

Fig. 2. Calibration curves of DC waves of APCD in 0.1 M NaOH at 25 °C.
(●—●): pre-wave A, (○—○): total wave (A+B)

Table 1. The effect of the height of the mercury reservoir on the pre-wave A and the total wave (A+B) of 5×10^{-4} M APCD in 0.1M NaOH at 25 °C

h, cm	$\bar{i}_A$, nA	$\bar{i}_{A+B}$, nA	$\bar{i}_A/h_{corr.}$	$\bar{i}_{A+B}/\sqrt{h_{corr.}}$
45.0	220	1450	5.0	210
55.0	280	1580	5.2	210
65.0	320	1770	5.0	220
75.0	380	1920	5.1	220
85.0	420	2060	5.0	230
95.0	480	2200	5.1	230

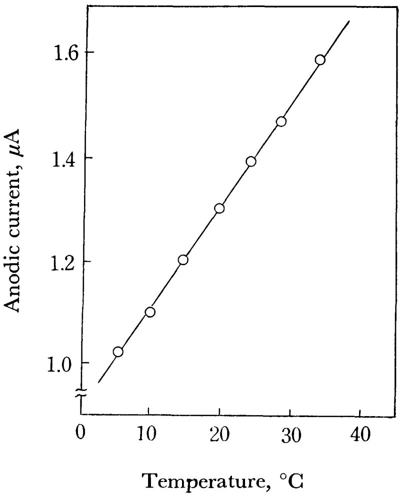

Fig. 3. The effect of temperature on the height of DC total wave of 5×10^{-4}M APCD in 0.1M NaOH.

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[4] H. Malissa und E. Schöffmann, *Mikrochim. Acta*, **1**, 187 (1955).

[5] S. J. Joris, K. I. Aspila, and C. L. Chakrabarti, *J. Phys. Chem.*, **74**, 860 (1970).

[6] S. J. Joris, K. I. Aspila, and C. L. Chakrabarti, *Anal. Chem.*, **43**, 1529 (1971).

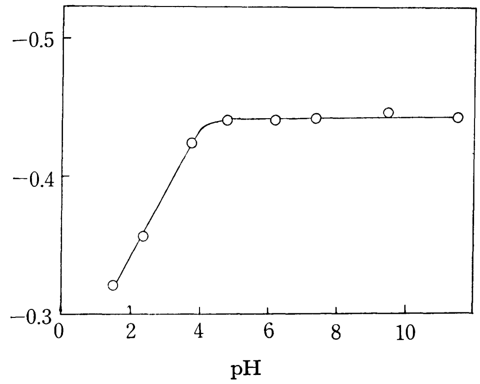

Fig. 4. The effect of pH on the half-wave potential of the wave B of APCD (Britton-Robinson buffers).

wave A is an adsorption wave and that the total anodic wave of APCD is diffusion controlled. The effect of pH on the half-wave potential was also studied. The results are shown in Fig. 4. The half-wave potential of wave B shifts to more negative potential with increasing pH in the pH range less than 4.2 and at higher pH value the half-wave potential of wave B is almost pH independent. This result shows that hydrogen ion participates in the anodic oxidation process of APCD in the pH range less than 4.2.

Alternating Current (AC) Polarography. Two AC waves are observed (Fig. 1, curve 2′, A′ and B′). AC peak A′ is observed in the potential region in which DC wave A is observed, and AC peak B′ in the region of DC wave B. The peak height of A′ is considerable high in comparison with the corresponding small DC wave A.

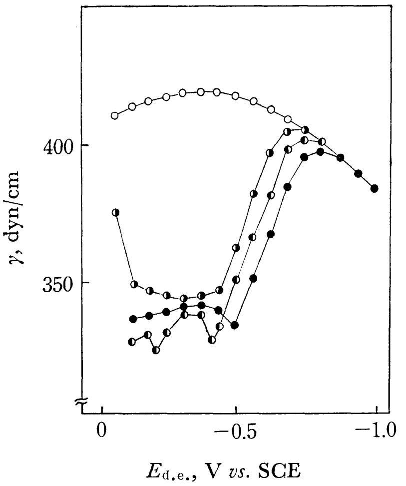

Fig. 5. Electrocapillary curves of APCD in 0.1M NaOH at 25 °C.
(○—○): 0 M, (◑—◑): 10^{-4}M, (◐—◐): 2×10^{-4}M, (●—●): 10^{-3}M.

Electrocapillary Curves. The electrocapillary curves of APCD are shown in Fig. 5. In the presence of APCD, marked decrease of the surface tension of mercury is observed in the potential range between 0 and −0.7 V. At more negative potential than −0.7 V, the surface tension of mercury in the presence of APCD is almost equal to that in its absence. This indicates that APCD adsorbs on the mercury surface strongly in the potential region between 0 and −0.7 V.

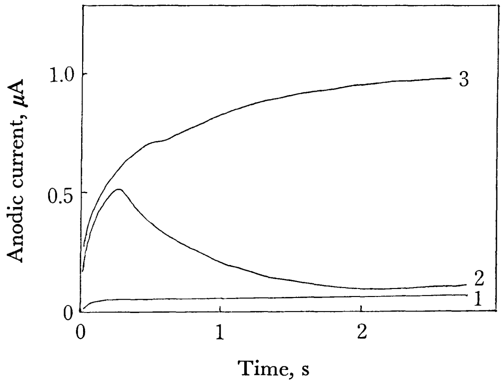

Fig. 6. The effect of the potential on *i-t* curves of 3×10^{-4}M APCD in 0.1M NaOH at 25 °C.
1: −0.80 V, 2: −0.47 V, 3: −0.20 V.

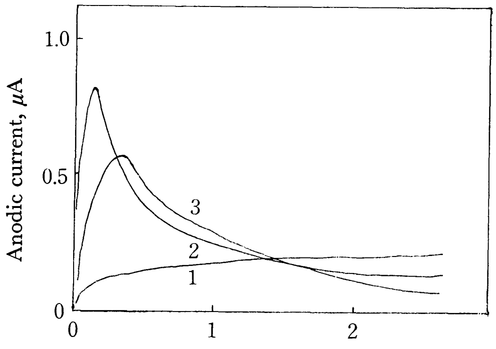

Fig. 7. The effect of the concentration on *i-t* curves of APCD at −0.47 V.
1: 10^{-4}M, 2: 3×10^{-4}M, 3: 5×10^{-4}M.

Current-Time Curves. A series of the current-time (*i-t*) curves of APCD during single mercury drop life was measured. The results are shown in Figs. 6 and 7. At the potential more positive than −0.4 V, the *i-t* curves of 5×10^{-4} M APCD show the diffusion current, which are approximately proportional to $t^{1/6}$. At the potential −0.47 V, however, the *i-t* curves are deformed anomalously. The current increases rapidly for a short time, and then decreases slowly. The time t_{m}, at which the *i-t* curves reaches maximum, decreases with increasing concentration of APCD, and the height of the maximum current i_{m} increases with increasing concentration of APCD. These facts are discussed later. This shape of *i-t* curve is the same as that for 1,1-diethylcarbodithioate.[7]

From DC and AC polarograms, electrocapillary curves and *i-t* curves, it seems to be considered that the wave A is adsorption controlled and the total wave is diffusion controlled.

According to Ilkovič equation, the diffusion current constant I of APCD can be calculated; $I=1.77\ \mu\mathrm{A}\cdot\mathrm{mg}^{-2/3}\cdot\mathrm{s}^{1/2}\cdot\mathrm{mM}^{-1}$. This value indicates that the number of electron in the oxidation process of APCD is one and the diffusion coefficient of APCD is $8.52\times10^{-6}\ \mathrm{cm}^2\cdot\mathrm{s}^{-1}$.

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[7] Unpublished data.

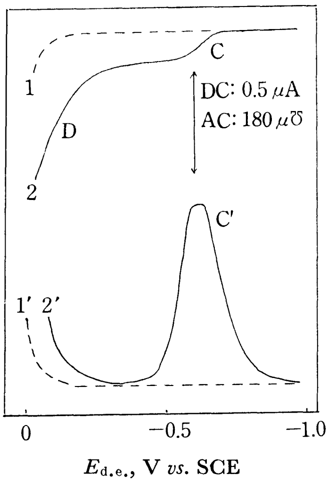

Fig. 8. Polarograms of ACPCD in 0.1M NaOH at 25 °C. 1, 1': 0 M ACPCD, 2, 2': 5×10^{-4}M ACPCD, 1, 2: DC porlarograms, 1', 2': AC polarograms.

Ammonium 2-Carboxy-1-pyrrolidinecarbodithioate (ACPCD). DC and AC Polarography: Figure 8 shows the DC and AC polarograms of 5×10^{-4} M ACPCD in 0.1 M sodium hydroxide. ACPCD shows DC wave C at −0.65 V, and the limiting current becomes constant above 10^{-4} M. Another DC wave D which appears at more positive potential is overlapped with the anodic dissolution of mercury and can not be analyzed. An AC peak C' is observed at the potential corresponding to the DC wave. The height of the AC peak is considerably high in comparison with the corresponding DC wave.

From these results, it is found that the DC wave C of ACPCD corresponds to the DC wave A of APCD and that the wave C is also adsorption controlled. The fact that the DC wave D of ACPCD shifts to more positive potential than the DC wave B of APCD may be attributed to the difference of the formation constant of their mercuric complexes, that is, mercury(II) PCD complex is more stable than mercury(II) CPCD complex.

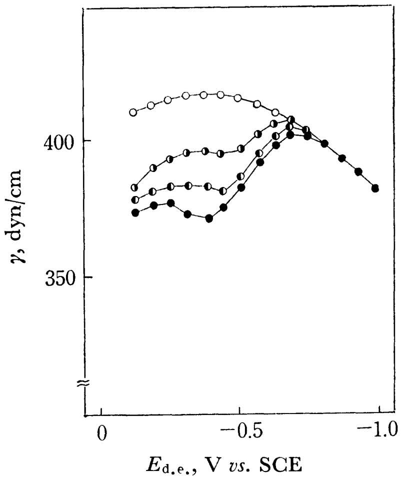

Fig. 9. Electrocapillary curves of ACPCD in 0.1 M NaOH at 25 °C.
(○—○): 0 M, (◑—◑): 10^{-4}M, (◐—◐): 5×10^{-4}M, (●—●): 10^{-3}M.

Electrocapillary Curves. The electrocapillary curves of ACPCD are shown in Fig. 9. ACPCD also causes a decrease of the surface tension of mercury in the potential range between 0 and −0.65 V. However, the degree of decrease of the surface tension is not so remarkable as that of APCD.

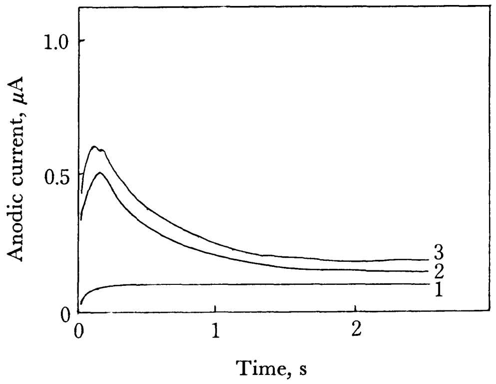

Fig. 10. The effect of the potential on *i-t* curves of 4×10^{-4}M ACPCD in 0.1 M NaOH at 25 °C.
1: −0.75 V, 2: −0.49 V, 3: −0.38 V.

Current-Time Curves. The results of the *i-t* curves of ACPCD are shown in Fig. 10. The *i-t* curves of ACPCD are similar to those of APCD, and it is found that ACPCD also adsorbs on the surface of mercury electrode in the potential range below −0.5 V.

Discussion

The Electrode Reaction Mechanism. The following electrode reactions are considered at the potential which the adsorption process occurs

$$\mathrm{Hg} \xleftrightarrow{\text{reversible}} \mathrm{Hg^{2+}} + 2\mathrm{e^-} \tag{1}$$

$$\mathrm{Hg^{2+}} + 2\mathrm{L} \rightleftharpoons \mathrm{HgL_2} \tag{2}$$

where L stands for a ligand (*e.g.*, $\mathrm{PCD^-}$ or $\mathrm{CPCD^{2-}}$). It is assumed that $\mathrm{Hg^{2+}}$ and $\mathrm{HgL_2}$ are absent in the bulk of the solution and that the mass transfer of L and $\mathrm{HgL_2}$ is controlled by diffusion.

The current is expressed in a following equation.[8]

$$i = i_{\mathrm{d}}/(1+\xi\theta) \tag{3}$$

$$i_{\mathrm{d}} = 7.08\times10^4 nm^{2/3}t^{1/6}D^{1/2}C \tag{4}$$

$$\xi = \exp\frac{nF}{RT}(E^0-E_{1/2}) \tag{5}$$

$$\theta = \exp\frac{nF}{RT}(E-E^0) \tag{6}$$

The net current until the surface of the mercury electrode is completely covered with $\mathrm{HgL_2}$ is;

$$i = \int_0^{t_{\mathrm{m}}} i\mathrm{d}t = nF\Gamma_{\mathrm{m}}A \tag{7}$$

$$A = 0.85m^{2/3}t^{2/3} \tag{8}$$

where Γ_{m} is a surface excess of L and A is a surface area of electrode.

From Eqs. (3)—(8), the time t_{m} till which the current reaches maximum is;

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[8] E. Laviron and C. Dogrand, *Bull. Soc. Chim. Fr.*, **1964**, 864.

$$t_m = 1.82\Gamma_m{}^2(1+\xi\theta)^2/C^2D \qquad (9)$$

and at $t=t_m$, the maximum current i_m is;

$$i_m = 7.08\times10^4nm^{2/3}D^{1/3}\Gamma_m{}^{1/3}C^{2/3}/(1+\xi\theta)^{2/3} \qquad (10)$$

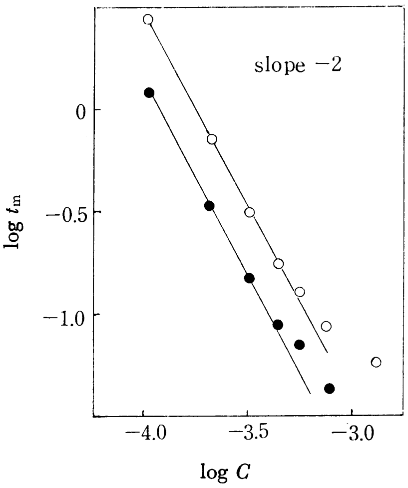

Fig. 11. The effect of concentration on the time till which the current reaches maximum.
(○—○): APCD, (●—●): ACPCD.

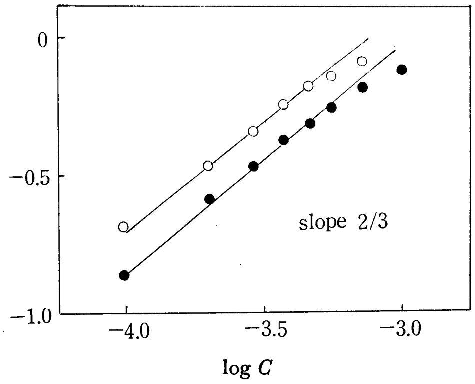

Fig. 12. The effect of concentration on the maximum currents.
(○—○): APCD, (●—●): ACPCD.

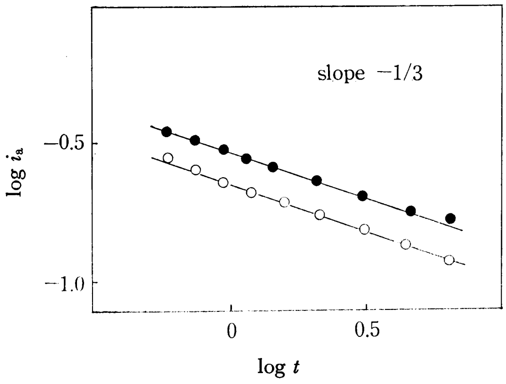

Fig. 13. Log plots of i-t curves of 10^{-3}M of APCD (○—○) and ACPCD (●—●) in 0.1M NaOH at 25 °C.

and in case of $t>t_m$, the adsorption controlled current i_a is;

$$i_a = 5.47\times10^4nm^{2/3}\Gamma_m/t^{1/3} \qquad (11)$$

then the values of

$$\partial \log t_m/\partial \log C = -2,$$

$$\partial \log i_m/\partial \log C = 2/3,$$

and $$\partial \log i_a/\partial \log t = -1/3$$

can be obtained. In Figs. 11—13, the log plots of these experimental values are shown and the results are in accordance with the theoretical values.

Surface Excess. The values of surface excess of APCD and ACPCD can be calculated from the following three methods.

The first method is based upon a mean adsorption current of DC polarogram using the following equation.[9)]

$$\Gamma_s = i_a\tau^{1/3}/8.17\times10^4nm^{2/3} \qquad (12)$$

where τ is a drop time.

The second method is a calculation from the surface tensions at the constant potential E using the following equation.[10)]

$$\Gamma_i = -(1/RT)(\partial\gamma/\partial \ln C)_E \qquad (13)$$

where γ is the surface tension.

Third method is a calculation from the maximum currents of the i-t curves using Eq. (9).

TABLE 2. SURFACE EXCESS OF CARBODITHIOATES

Substance	Γ, 10^{-10} mol/cm^2
APCD	6.9[a)]
	5.8[b)]
	3.7[c)]
ACPCD	4.8[a)]
	2.6[b)]
	2.5[c)]

a) Calculated from adsorption wave (i_a).
b) Calculated from surface tention (γ).
c) Calculated from current-time curve (t_m).

The results are shown in Table 2. The second method seems to be the most accurate experimentally. In all cases, the values of the surface excess of APCD are larger than that of ACPCD. This will be due to the steric hindrance of mercuric CPCD complex owing to the presence of carboxy group at 2 position.

The authors thank the Ministry of Education for financial support.

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9) K. Hasebe and T. Kambara, *Rev. Polarog.* (Kyoto), **15**, 37 (1968).

10) B. B. Damaskin, O. A. Petrii, and V. V. Batrakov, "Adsorption of Organic Compounds on Electrodes," Plenum Press, New York-London, (1971), p. 22.