Anodic Wave Polarography of *N*-2-Aminoethyl-*N*-2-hydroxyethylcarbodithioic Acid

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(Received August 21, 1974)

N-2-Aminoethyl-*N*-2-hydroxyethylcarbodithioic acid (Hahdtc) in an alkaline medium gives at the dropping mercury electrode an adsorption prewave due to the two-electron oxidation of mercury. The electrode reaction at pH=13.1—10.1 was inferred to proceed according to

$$\mathrm{Hg} + 2\mathrm{ahdtc}^- \rightleftharpoons \mathrm{Hg(ahdtc)_2} + 2\mathrm{e} \qquad (1)$$

The surface excess of the mercury(II) chelate was estimated to be 3.0×10^{-10} mol cm^{-2}.

The polarographic behavior of compounds containing carbodithioate group have been studied by many authors.[1–7)] These compounds give anodic waves corresponding to the mercury compound formation, in most cases, accompanied by adsorption phenomena. For sodium diethylcarbodithioate (Naddtc), the one-electron oxidation process was attributed to the formation of mercury complex Hg(ddtc), in which mercurous ion is present in the monomeric form, followed by rapid disproportionation to $\mathrm{Hg(ddtc)_2}$ and Hg.[1,4)] In the case of the anodic wave of ammonium 1-pyrrolidinecarbodithioate ($\mathrm{NH_4pcd}$), the electrode process was ascribed to the formation of the complex $\mathrm{Hg(pcd)_2}$.[7)]

In the present work, the polarographic behavior of *N*-2-aminoethyl-*N*-2-hydroxyethylcarbodithioic acid (Hahdtc) was investigated at the dropping mercury electrode.

Experimental

N-2-Aminoethyl-*N*-2-hydroxyethylcarbodithioic acid was synthesized as follows. To 80 g of carbon disulfide in 100 ml of ethanol, 24 g of 2-aminoethylaminoethanol dissolved in 100 ml of ethanol were added dropwise under cooling in a cold water bath. The product was filtered, washed with ethanol and recrystallized from water at 65 °C. After drying in air, the Hahdtc was stored in a desiccator containing silica gel as a desiccant. Found: C, 33.09; H, 6.74; N, 15.62; S, 35.58%. Calcd for $\mathrm{C_5H_{12}ON_2S_2}$: C, 33.31; H, 6.71; N, 15.54; S, 35.57%.

The Hahdtc in an aqueous solution was unstable and its limiting current decreased by 15% after 4 hr. Therefore, the Hahdtc solution was freshly prepared before each experiment. All other reagents used were of A. R. grade.

Direct current polarogram was recorded by means of a Shimadzu polarograph, type RP-2, and AC polarogram was recorded by using a Shimadzu AC attachment, type BF-1. The dropping mercury electrode used had the following characteristics; mercury flow-rate $m=1.50$ mg s^{-1} in deionized water, drop time $t=4.91$ s in 0.1 mol dm^{-3} sodium hydroxide solution at open circuit and at a height of the mercury reservoir $h=58.0$ cm. The potential values presented here refer to the saturated calomel electrode, which was connected to the electrolysis solution through an agar bridge (3% agar, satd. potassium nitrate). The mercury of SCE was connected to a mercury pool counterelectrode *via* a 2200 μF capacitor.

The pH measurements were carried out with a Hitachi-Horiba glass electrode pH meter, type F-5.

A portion of the freshly prepared electrolysis solution containing Hahdtc and 0.1 mol dm^{-3} sodium hydroxide as the supporting electrolyte was taken into a polarographic cell, and the polarogram was recorded at (25±0.1) °C after deaeration by bubbling nitrogen gas.

Results and Discussion

Direct Current Polarography. The DC and AC polarograms of 4.0×10^{-4} mol dm^{-3} Hahdtc in 0.1 mol dm^{-3} sodium hydroxide solution are shown in Fig. 1. At concentrations of the Hahdtc lower than 1.0×10^{-4} mol dm^{-3}, one DC prewave, A, at −0.65 V is observed. At concentrations higher than 1.0×10^{-4} mol dm^{-3}, the DC main wave B at −0.32 V appears, while the limiting current of the prewave remained constant. The sum of the limiting currents of the prewave and main wave is proportional to the concentration of Hahdtc between 1.0×10^{-4} and 8.0×10^{-4} mol dm^{-3} as shown in Fig. 2. The height of the prewave is approximately proportional to $h_{\mathrm{corr.}}$ and that of the total wave (A+B) is to $h_{\mathrm{corr.}}^{1/2}$ (Table 1). The limiting current

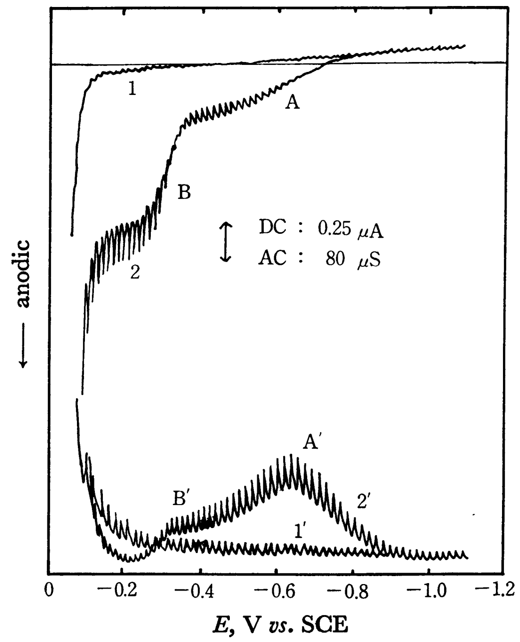

Fig. 1. Polarograms of Hahdtc in 0.1 mol dm^{-3} NaOH at 25 °C.
Concentration of Hahdtc 1, 1′: 0 mol dm^{-3}, 2, 2′: 4×10^{-4} mol dm^{-3}, 1, 2: DC polarogram, 1′, 2′: AC polarogram.

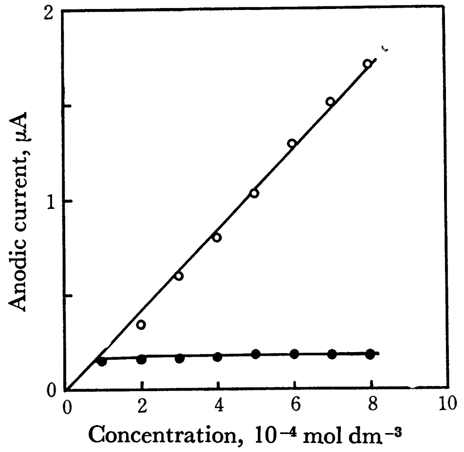

Fig. 2. Concentration dependence of the limiting currents of Hahdtc in 0.1 mol dm^{-3} NaOH at 25 °C.
●: prewave A, ○: total wave (A+B).

TABLE 1. THE EFFECT OF THE HEIGHT OF THE MERCURY RESERVOIR ON THE PREWAVE A AND THE TOTAL WAVE (A+B) OF 6×10^{-4} mol dm^{-3} Hahdtc IN 0.1 mol dm^{-3} NaOH

h (cm)	i_A (nA)	i_A+i_B (nA)	i_A/h_{corr} (nA cm^{-1})	$(i_A+i_B)/h_{corr}^{1/2}$ (nA cm$^{-1/2}$)
44.0	120	1150	2.8	180
49.0	130	1210	2.7	180
54.0	140	1310	2.7	180
59.0	150	1320	2.6	170
64.0	170	1340	2.7	170
69.0	180	1400	2.7	170
73.0	210	1510	2.9	180
78.0	230	1580	2.9	180

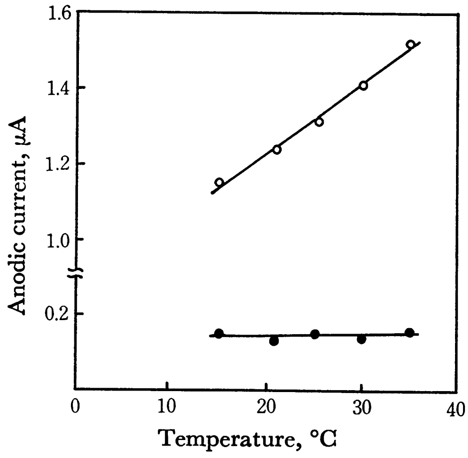

Fig. 3. The effect of temperature on the height of DC waves of 6×10^{-4} mol dm^{-3} Hahdtc in 0.1 mol dm^{-3} NaOH.
●: prewave A, ○: total wave (A+B).

of the total wave had the relative temperature coefficient of 1.60% K^{-1} in the temperature range from 15 to 35 °C; but the limiting current of the prewave was almost independent of temperature as shown in Fig. 3. These results indicate that the wave A is a typical adsorption prewave and the total wave is diffusion-controlled.

Logarithmic Analysis of DC Polarogram. If the electrode reaction in an alkaline medium is reversible and proceeds according to the following equation,

$$\mathrm{Hg} + 2\mathrm{ahdtc}^- \rightleftharpoons \mathrm{Hg(ahdtc)_2} + 2\mathrm{e} \tag{1}$$

the potential E of the electrode is given by

$$E = E_0 + \frac{RT}{2F}\ln\frac{1}{K} + \frac{RT}{2F}\ln\frac{[\mathrm{Hg(ahdtc)_2}]_\mathrm{o}}{[\mathrm{ahdtc}^-]_\mathrm{o}^2} \tag{2}$$

where K is the formation constant of $\mathrm{Hg^{II}(ahdtc)_2}$, and subscript o denotes the concentration at the surface of the electrode. If the concentration of the Hahdtc is large enough, the average current i of the main wave B is expressed as[5)]

$$i = i_t - i_A \tag{3}$$

$$i = k_1([\mathrm{ahdtc}^-]^* - [\mathrm{ahdtc}^-]_\mathrm{o}) - i_A \tag{4}$$

where i_t is the theoretical current which would flow if the adsorption did not occur, i_A the limiting current corresponding to the adsorption prewave, k_1 the proportionality factor, and asterisk means the concentration in the bulk of solution. The total limiting current (i_A+i_B) of the prewave A and main wave B is proportional to the concentration of the Hahdtc in the bulk of the solution. Therefore,

$$i_A + i_B = k_1[\mathrm{ahdtc}^-]^* \tag{5}$$

Since the complex $\mathrm{Hg(ahdtc)_2}$ is absent in the bulk of the solution, the current i is given by

$$i = k_2[\mathrm{Hg(ahdtc)_2}]_\mathrm{o} \tag{6}$$

where k_2 is the proportionality factor. By combination of Eqs. (2), (4), (5), and (6), the following equation is obtained (at 25 °C).

$$E = E_0' - 0.030\log\frac{(i_B - i)^2}{i} \tag{7}$$

$$E_0' = E_0 + 0.030\log\frac{1}{K} + 0.030\log\frac{k_1^2}{k_2} \tag{8}$$

Thus, the plot of E *vs.* $\log\{(i_B-i)^2/i\}$ should give a straight line with a slope of 30 mV. As shown in Fig. 4, the experimental result agreed well with the theoretical prediction. Moreover, the half-wave potential $E_{1/2}$ of the main wave is given by

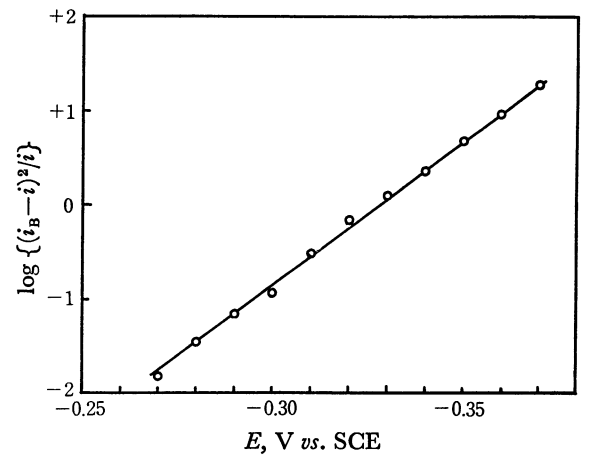

Fig. 4. Relationship between E and $\log\{(i_B-i)^2/i\}$ in 0.1 mol dm^{-3} NaOH at 25 °C.
Concentration of Hahdtc: 6×10^{-4} mol dm^{-3},
The plot has a slope of 33 mV.

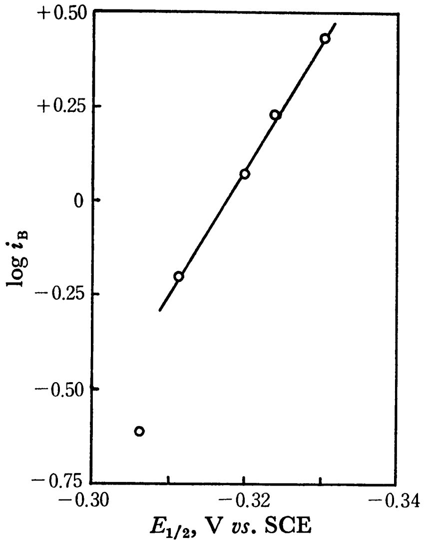

Fig. 5. Relationship between the half-wave potential $E_{1/2}$ of the main wave and log i_B in 0.1 mol dm^{-3} NaOH at 25 °C.

Concentration range of Hahdtc: (2.0—12)×10^{-4} mol dm^{-3},

The plot has a slope of 29 mV.

$$E_{1/2} = E_0' - 0.030 \log \frac{i_B}{2} \qquad (9)$$

A plot of $E_{1/2}$ *vs.* log i_B is given in Fig. 5. The plot has a slope of 29 mV, in accordance with the theoretical prediction. These results indicate that the electrode reaction is a reversible oxidation process corresponding to the formation of the mercury(II) complex, Hg(ahdtc)$_2$. The same equation as that given by Eq. (7) would be obtained if the electrode process corresponded to the formation of the mercurous complex, $Hg_2^I(ahdtc)_2$. However, it was found that a gray or black precipitation was formed instantaneously when mercurous nitrate was added to the solution of Hahdtc and the UV spectrum of the filtrate was in agreement with that of the mercuric complex. The result indicates that mercurous ion is rapidly disproportionates to mercuric ion and mercury in the presence of Hahdtc.

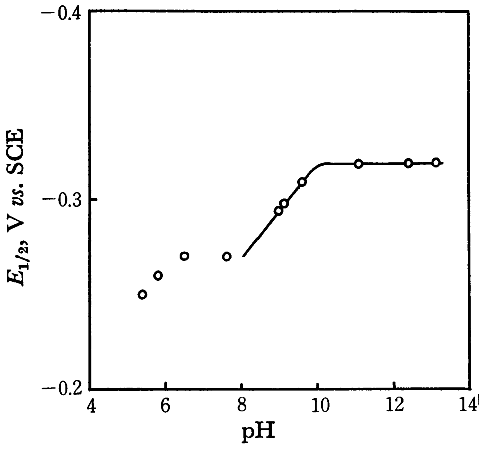

Fig. 6. Effect of pH on the half-wave potential $E_{1/2}$ of the main wave of the Hahdtc (Britton-Robinson buffer). In the pH range from 8.0 to 10.1, the plot has a slope of 25 mV.

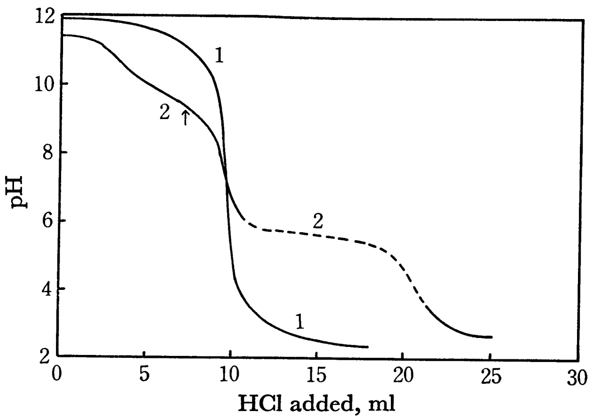

Fig. 7. Titration curve of the Hahdtc in sodium hydroxide solution with 0.104 mol dm^{-3} HCl.

Curve 1: 1 mmol NaOH; 2: 1 mmol NaOH+0.5 mmol Hahdtc, [KCl]=0.1 mol dm^{-3}.

The negative logarithm of the acid dissociation constant of amino group in the Hahdtc is estimated as 9.3, as indicated by arrow. The dashed line is the unstable region where the decomposition of Hahdtc into CS_2 and 2-aminoethylaminoethanol occurs.

Hence, it is safe to assume that the mercurous complex cannot give rise to the adsorption prewave.

Effect of pH. Effect of pH on the half-wave potential of the main wave is shown in Fig. 6. The half-wave potential is independent of pH between 10.1 and 13.1. However, at pH's lower than 10.1, the half-wave potential is shifted to more negative values with increasing pH. The pH value of the intersection of the extrapolated straight sections of the plot coincides approximately with 9.3, the value of the negative logarithm of acid dissociation constant of amino group in the Hahdtc obtained from the pH titration curve, shown in Fig. 7, which is very similar to those of other *N*-substituted carbodithioates.[8] The logarithmic analysis of DC polarogram obtained in a medium buffered at pH 9.1 indicated that a plot of E *vs.* $\log\{(i_B-i)^2/i\}$ gave a straight line with a slope of 35 mV. The result indicates that the electrode reaction is a reversible two-electron process also at the pH value. Moreover, the plot of $E_{1/2}$ *vs.* pH given in Fig. 6 had a slope of 25 mV in the pH range from 8.0 to 10.1. Therefore, the electrode reaction in the pH range from 8.0 to 10.1 may proceed according to the scheme

$$Hg + 2H^+ahdtc^- \rightleftarrows HHg(ahdtc)_2^+ + H^+ + 2e \qquad (1')$$

Further investigation in an acidic medium was impossible because Hahdtc decomposed rapidly.

Alternating Current Polarography. The Hahdtc gave two peaks on AC waves at potentials corresponding to the two DC waves (Fig. 1). The AC peak height of the prewave is considerably high in comparison with that corresponding to the main wave.

Electrocapillary Curves. The electrocapillary curves obtained in the presence and the absence of the Hahdtc are shown in Fig. 8. A marked decrease in drop time of the dropping mercury electrode is observed in the potential region between −0.2 and −0.7 V. At the potentials more negative than −0.7 V, the drop time

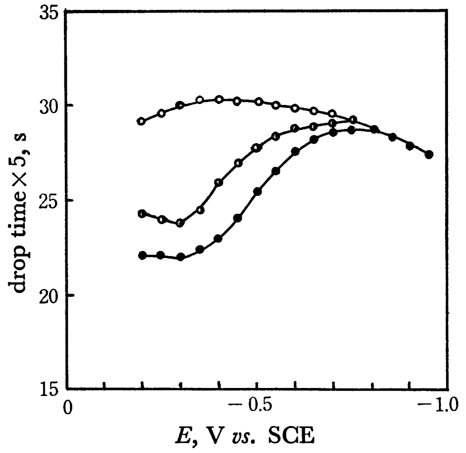

Fig. 8. Electrocapillary curves of Hahdtc in 0.1 mol dm^{-3} NaOH at 25 °C.
Concentration of Hahdtc ○: 0 ml dm^{-3}, ◑: 1×10^{-4} mol dm^{-3}, ●: 8×10^{-4} mol dm^{-3}, h=58.0 cm.

is almost equal to that in the supporting electrolyte. The results indicate that the electrode reaction product is adsorbed on the surface of mercury.

Surface Excess. The amount of substance of the adsorbed chelate molecules per unit area of the electrode surface was estimated to be 3.0×10^{-10} mol cm^{-2} by using the equation based upon the mean adsorption current of the DC polarogram.[9] From the above value, the area occupied by one molecule is calculated as 55×10^{-16} cm^2 under the assumption that a monolayer is formed.

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