# *The Polarographic Behavior of Mercuric Diethyldithiocarbamate in a Ternary Solvent Mixture*

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Sodium-diethyldithiocarbamate has long been used as one of the most useful analytical reagents in methods involving solvent extraction for the separation and concentration of the trace constituents of a sample.

As is well known, the method of solvent extraction has been widely applied to the analysis of trace elements, particularly in colorimetric determinations. However, in order to apply the extraction method to electrochemical analyses, either the sample solution has to be evaporated and the residue redissolved in water or, alternatively, the solution must be reextracted with water after a suitable adjustment of the physico-chemical conditions.

The present authors, in a previous paper,(1) proposed a third method, in which a ternary mixture is used as a solvent for the polarographic analysis after extraction; they applied the method to the determination of traces of lead in sodium chloride of analytical grade. In this procedure, the chloroform layer, into which the lead chelate of diethyldithiocarbamate had been extracted, was mixed directly with a solution consisting of ethylene glycol monomethyl ether (methyl-cellosolve), and aqueous hydrochloric acid as the supporting electrolyte. Even though chloroform is insoluble in water, the addition of methyl-cellosolve makes it possible to obtain a homogeneous solution. It was found that this homogeneous ternary mixture had a dielectric constant high enough to ensure the electrolytic dissociation of dissolved salts. The ohmic drop in this solution was about the same as that in a purely aqueous solution. Hence, it was possible to carry out the polarographic analysis directly, without any further treatment.

In the present work, the polarographic reduction of mercuric-diethyldithiocarbamate has been investigated in a ternary solvent mixture consisting of chloroform, methyl-cellosolve and water, in the presence of 0.5 M perchloric acid as a supporting electrolyte. In this solution, $Hg(DDTC)_2$ usually gives two d.c. cathodic waves, though a small anodic step appears at a more positive potential when the temperature is lowered below 15°C. The first cathodic step (step A in Fig. 1, curve 1) was found to be proportional to the bulk concentration of $Hg(DDTC)_2$ over the concentration range of 0.1 mM to 0.4 mM; it is probably due to the reduction of unadsorbed $Hg(DDTC)_2$. The height of the second step (step B in Fig. 1, curve 1), on the other hand, was almost constant and independent of the concentration of $Hg(DDTC)_2$ and, hence, seems due to the reduction of $Hg(DDTC)_2$ adsorbed onto the surface of the dropping electrode. Step B, therefore, represents a so-called anomalous polarographic step.(2) In the present case, the oxidised form of the depolarizer, $Hg(DDTC)_2$, is adsorbed strongly onto the electrode surface and, consequently, a post-step B appears at a more negative potential than the normal step A. Though many

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1) T. Fujinaga, H. Brodowsky, T. Nagai and K. Yamashita, *Review of Polarography* (*Japan*), 11, 217 (1963).

examples of anomalous waves[2-6] have been found for the adsorption of the reduced form which produces a prewave, examples of the present case have rarely been reported.

## Experimental

The reagents and the apparatus used were the same as those reported on in the previous paper.[1] Throughout the experiments, two dropping mercury electrodes with the following characteristics were used: Electrode A: $m=0.73$ mg./sec., $t=3.75$ sec., and $h=65$ cm., and Electrode B: $m=0.64$ mg./sec., $t=4.63$ sec., and $h=65$ cm. in an air-free ternary solvent mixture at open circuit. The polarographic measurements were carried out in the absence of air; the potential values quoted refer to the saturated calomel electrode, which was connected to the electrolyte solution through an agar bridge (5% agar, 7.5% sodium perchlorate).

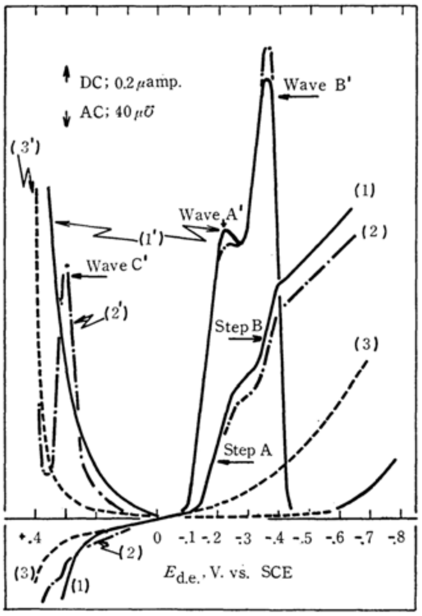

Fig. 1.

(1) D. C. polarogram of $3\times10^{-4}$ M mercuric-diethyldithiocarbamate $Hg(DDTC)_2$ and 0.5 M perchloric acid in the ternary solvent mixture at 25°C.
(1′) A. C. polarogram of the same solution as in (1).
(2) D. C. polarogram of the same solution as in (1) at 10°C.
(2′) A. C. polarogram of the same solution as in (1) at 10°C.
(3) D. C. polarogram of 0.5 M perchloric acid in the ternary mixture at 25°C
(3′) A. C. polarogram of the same solution as in (3).

## Results

It is well known that $Hg(DDTC)_2$ can be extracted completely into chloroform from an aqueous solution over a wide pH range.[7,8] The solution of $Hg(DDTC)_2$ in the ternary solvent mixture was prepared as follows: 1 ml. of an aqueous solution of 0.4% sodium diethyldithiocarbamate was added to 2 ml. of water which contained from 1 mM to 10 mM mercuric ions. To this solution 5 ml. of chloroform were added. After this mixture had been shaken for five minutes, 11 ml. of methyl-cellosolve and 1 ml. of concentrated perchloric acid were added and the solution was shaken until a clear solution was obtained. The proportion of water, methyl-cellosolve and chloroform in the final solution was 4:11:5 by volume.

**D. C. Polarography.**—With a solution of less than 0.1 mM $Hg(DDTC)_2$, only a single step is observed around −0.4 V. vs. SCE. When the concentration of $Hg(DDTC)_2$ is raised above 0.1 mM, however, two steps appear, one at −0.2 and the other at −0.4 V., as is shown by curve 1, Fig. 1.

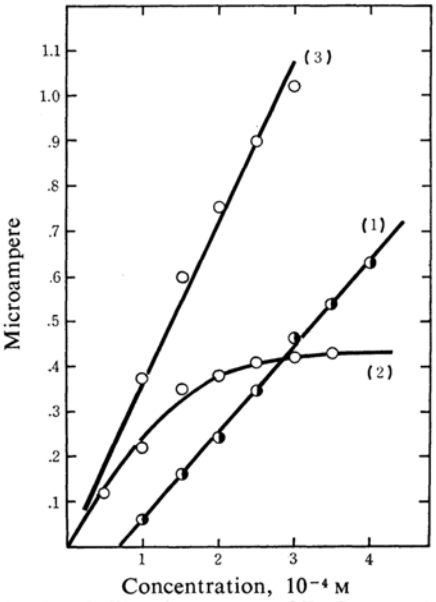

Fig. 2. Calibration curves of D. C. steps (1) A, (2) B and (3) the total step height in 0.5 M perchloric acid, and in ternary solvent mixture, $h=65$ cm,; $m=0.64$ mg./sec.; $t=4.63$ sec.; $T$, 25°C.

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2) R. Brdicka, *Collection Czechoslov. Chem. Communs.*, **12**, 522 (1947).
3) O. H. Müller, *Trans. Electrochem. Soc.*, **87**, 441 (1941).
4) R. C. Kage and H. I. Stonehill, *J. Chem. Soc.*, **1942**, 3244.
5) Y. Asahi, *Review of Polarography*, **8**, 1 (1960).
6) B. Breyer and T. Biegler, *Collection Czechoslov. Chem. Communs.*, **25**, 3348 (1960).
7) H. Bode, *Z. anal. Chem.*, **142**, 414; **143**, 182 (1954).
8) Y. Hamamoto and M. Kotakemori, *J. Agr. Chem. Soc. Japan*, **34**, 885 (1960).

TABLE I. EFFECT OF THE HEIGHT OF THE MERCURY COLUMN ABOVE THE CAPILLARY TIP, $h_{Hg}$, ON THE CURRENTS OF STEPS B AND TOTAL FOR 0.3 mM SOLUTION OF $Hg(DDTC)_2$ IN 0.5 M PERCHLORIC ACID IN THE TERNARY MIXTURE

| $h_{Hg}$ cm. | $m$, mg./sec. | $t$, sec. at −0.4 V. | $\bar{i}$(mm.) | | $h_{corr.}$ cm. | $\bar{i}_B/h_{corr.}$ | $\bar{i}_T/h^{1/2}_{corr.}$ |
|---|---|---|---|---|---|---|---|
| | | | $\bar{i}_B$ | $\bar{i}_T$ | | | |
| 60.2 | 0.667 | 4.52 | 35.5 | 72.0 | 58 | $0.61_2$ | $9.4_6$ |
| 65.2 | 0.717 | 4.12 | 38.0 | 75.5 | 63 | $0.60_3$ | $9.5_1$ |
| 70.2 | 0.771 | 3.88 | 41.5 | 79.0 | 68 | $0.61_0$ | $9.5_8$ |
| 75.2 | 0.823 | 3.57 | 45.0 | 83.0 | 73 | $0.61_6$ | $9.7_1$ |
| 80.2 | 0.874 | 3.32 | 48.0 | 86.0 | 78 | $0.61_5$ | $9.7_3$ |
| 85.2 | 0.928 | 3.10 | 52.5 | 90.0 | 83 | $0.63_2$ | $9.8_7$ |

Figure 2 illustrates the dependence of the heights of step A (1), step B (2) and of the total step height (3) on the concentration of $Hg(DDTC)_2$. The limiting currents of step A, step B and of the total step height were measured at −0.25 and at −0.40 V., respectively. The height of step B increases with the concentration of $Hg(DDTC)_2$ in a fashion corresponding to a Langmuir adsorption isotherm; it shows a limiting value when the concentration of $Hg(DDTC)_2$ reaches a value of 0.3 mM. The height of step A increases linearly with the concentration of $Hg(DDTC)_2$, but the step does not appear at concentrations of $Hg(DDTC)_2$ below 0.1 mM because of its adsorption onto the electrode surface which produces step B. The total wave height (curve 3) also increases approximately linearly with the concentration of $Hg(DDTC)_2$.

The electrocapillary curves obtained are shown in Fig. 3. In the presence of $Hg(DDTC)_2$, a marked decrease of the drop time is observed between +0.4 and −0.4 V. (curve 3). At more negative potentials than −0.4 V., the drop time in the presence of $Hg(DDTC)_2$ is equal to that in its absence (curve 2). This indicates that the substance is adsorbed between +0.4 and −0.4 V. and is desorbed from the electrode surface at about −0.4 V. The potential at which $Hg(DDTC)_2$ is desorbed corresponds to that at which step B appears.

The relationship between the heights of steps A and B and the concentration of $Hg(DDTC)_2$ also confirms the supposition that step B is due to the reduction of the adsorbed form of $Hg(DDTC)_2$, whilst step A is due to the reduction of the unadsorbed form. This assumption is also confirmed by experimental results to be reported on below.

The temperature coefficients of the heights of steps A and B and of their sum were +1.63%, +1.28% and +1.46% respectively in the 15∼30°C range (Fig. 4).

The effect of the height of the mercury reservoir was also studied. The results are shown in Table I. The height of step B was approximately linearly proportional to $h$, whilst the total step height was approximately proportional to $h^{1/2}$. This agrees well with the assumption that step B is anomalous. The fact that surfactants, such as polyacrylamide (PAM 75) or gelatine, had little effect on the polarograms shows that $Hg(DDTC)_2$ is more strongly adsorbed than these surfactants.

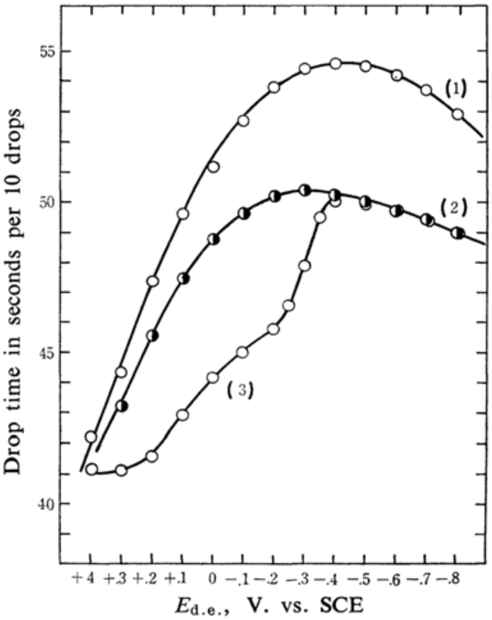


Fig. 3. Electrocapillary curves of (1) 0.5 M perchloric acid in water, (2) 0.5 M perchloric acid in ternary solvent mixtures and (3) $3\times10^{-4}$ M concentration of $Hg(DDTC)_2$, $h=$ 65 cm.; $m=0.73$ mg./sec.; $t=3.75$ sec.; $T$, 25°C.

**A. C. Polarography.**—A. C. polarograms obtained with a solution of 0.3 mM $Hg(DDTC)_2$ in the ternary solvent mixture are shown in Fig. 1. At 25°C, two a. c. waves were observed (curve 1′, A′ and B′) at potentials corresponding to the two d. c. steps.

Below 15°C, however, a new a. c. wave (wave C′) was observed at about +0.3 V., a wave which corresponds to the small anodic wave in the d.c. polarogram (Fig. 1). The height of wave A′ increased linearly with the concentration of Hg(DDTC)$_2$ at concentrations below 0.5 mM (Fig. 5, curve 1). The calibration curves of waves B′ and C′ have the shape of a Langmuir adsorption isotherm (Fig. 5, curve 2, and Fig. 6). Hence, these two waves seem to be connected with the adsorption and desorption of Hg(DDTC)$_2$.

The effects of temperature are shown in Figs. 7 and 8. The height of wave A′ increases with the increasing temperature (Fig. 7, curve 1); the height of wave B′, however, decreases with the increasing temperature. This behavior shows that the a.c. current of wave B′ has both a tensammetric and a faradaic component

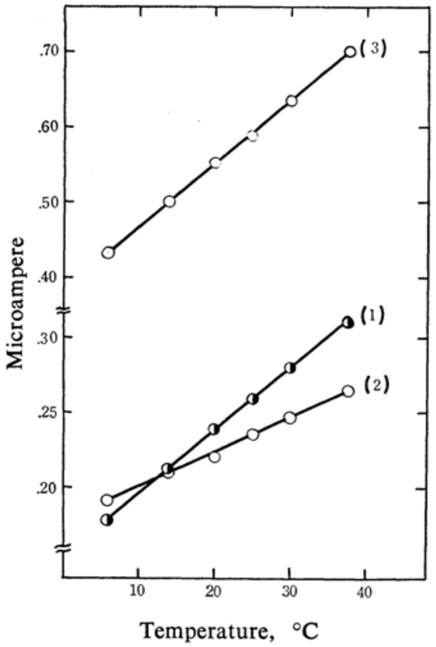


Fig. 4. Effect of temperature on heights of steps (1) A, (2) and (3) total step height in 0.5 M perchloric acid in the ternary solvent mixture, $h$=65 cm.; $m$=0.73 mg./sec.; $t$=3.75 sec.; $T$, 25°C.

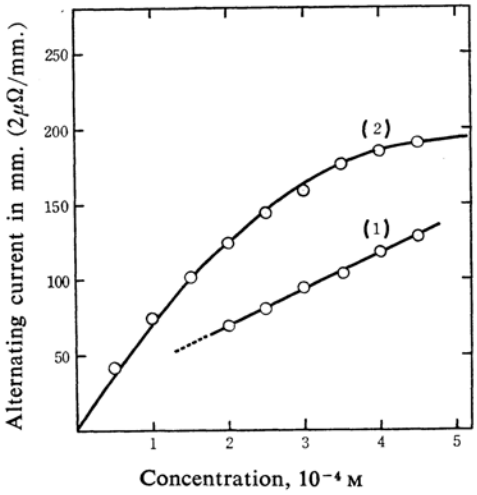


Fig. 5. Calibration curves of waves (1) A′ and (2) B′ of Hg(DDTC)$_2$ in 0.5 M perchloric acid in the ternary solvent mixture, $h$=65 m.; $m$=0.64mg./sec.; $t$=4.63 sec. at open circuit; $T$, 25°C; A.C. 15 mV. r. m. s.

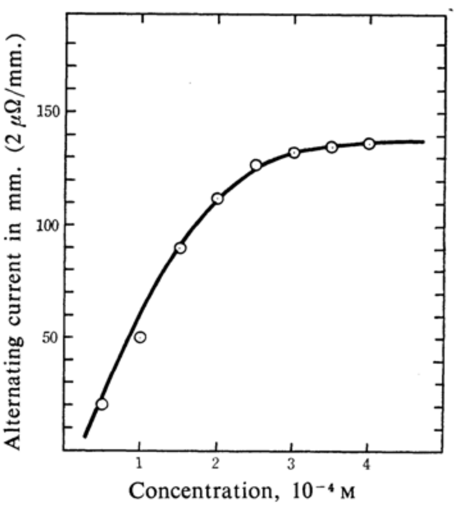


Fig. 6. Calibration curves of tensammetric wave (wave C′) of Hg(DDTC)$_2$ in 0.5 M perchloric acid in the ternary solvent mixture, $h$=65 cm., $m$=0.64 mg./sec., $t$=4.63 sec., at zero applied potential, $T$, 10°C; A.C. 15 mV. r. m. s.

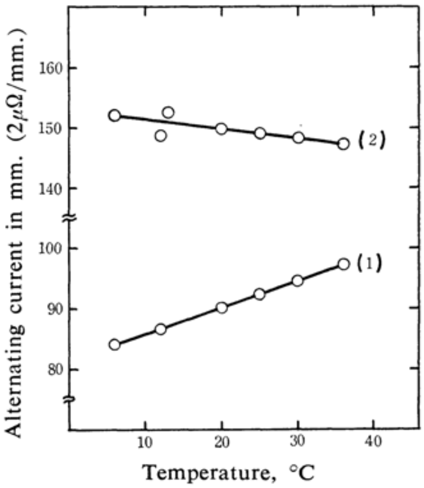


Fig. 7. Effect of temperature on the heights of A. C. waves (1) A′ and (2) B′; $h$=65 cm.; $m$=0.64 mg./sec.; $t$=4.63 sec.; $T$, 25°C; A. C. 15 mV. r. m. s.

(" rearrangement current "[9]). The results obtained by the a. c. polarographic method are also in good agreement with the assumption that waves **B** and **B′** are anomalous, that is, that they are due to the fact that the strongly adsorbed Hg(DDTC)$_2$ is reduced and desorbed from the electrode surface.

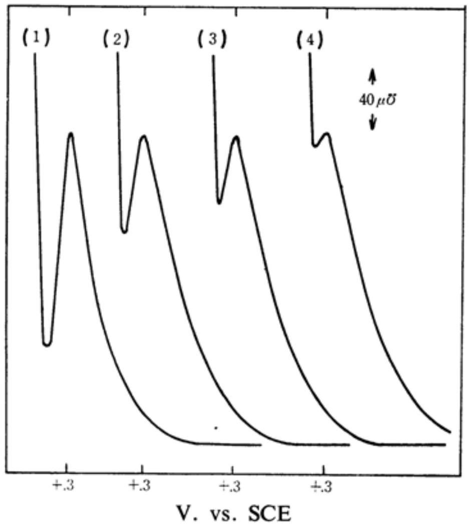


Fig. 8. Effect of temperature on the appearance of the tensammetric wave (wave **C′**) in 0.5 M perchloric acid in the ternary solvent mixture; $h$=65 cm; $m$=0.64 mg./sec.; $t$=4.63 sec.; A. C. 15 mV. r. m. s. (1) 10°C, (2) 13°C, (3) 14°C, (4) 15°C.

## Discussion

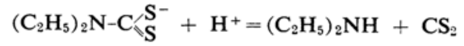
The appearance of wave C′ in the a. c. polarogram in the absence of a d. c. polarographic step indicates that this a. c. wave is tensammetric in nature. The adsorption of Hg(DDTC)$_2$ onto the dropping mercury electrode, therefore, begins at this potential.

When the concentration of Hg(DDTC)$_2$ is small (below about 0.1 mM), all the molecules which diffuse to the electrode surface are adosorbed to be reduced at the B potential corresponding to step in d. c. polarography. If the concentration of Hg(DDTC)$_2$ becomes larger than that sufficient for the electrode surface to be completely covered with adsorbed molecules, unadsorbed molecules reach the electrode surface and are reduced, forming wave A. In d. c. polarography, wave B is called an anomalous polarographic wave. As has been pointed out already, the current of the a. c. wave B′ is a rearrangement current, that is, it contains both a faradaic and a tensammetric component; this is in good agreement with the postulate that it is due to the reduction of adsorbed Hg(DDTC)$_2$. Incidentally, we believe that this is one of the first instances where the existence of the theoretically-predicted rearrangement current has been proved experimentally.

If we assume that the reduction of Hg(DDTC)$_2$ proceeds according to:

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

we would expect that the (DDTC)$^-$ anion so formed would give rise to an oxidation step. However, it has been reported by Bode[7] and by Gregg[10] that the (DDTC)$^-$ anion is decomposed immediately in a strongly acidic solution, such as 0.5 M perchloric acid, according to:



$$\mathrm{(C_2H_5)_2N\text{-}C\overset{S^-}{\underset{S}{\lessgtr}} + H^+ = (C_2H_5)_2NH + CS_2}$$

In fact, we did not observe an oxidation step of DDTC$^-$ ions in 0.5 M perchloric acid, though we did see one in a basic solution.

If the concentration of Hg(DDTC)$_2$ in the solution is large enough, the electrode surface is completely covered with a mono-layer of Hg(DDTC)$_2$ and the excess of Hg(DDTC)$_2$ produces step A.

The average current ($\bar{i}$) at the potential of wave A can be expressed as:

$$\bar{i}=\bar{i}_{\mathrm{I}}-\bar{i}_{\mathrm{B}} \qquad (2)$$

where $\bar{i}_{\mathrm{I}}$ is the theoretical current, that is, that calculated from the Ilkovič equation under the assumption that Hg(DDTC)$_2$ is unadsorbed. $\bar{i}_{\mathrm{I}}$ is defined by:

$$\bar{i}_{\mathrm{I}}=2Km^{2/3}t^{1/6}(C_0{}^*-C_0{}^0) \qquad (3)$$

where $C_0{}^*$ is the concentration of Hg(DDTC)$_2$ in the bulk of the solution and $C_0{}^0$, that at the electrode surface, while $\bar{i}_{\mathrm{B}}$ is the current corresponding to step B, i. e., the current due to the reduction of adsorbed Hg(DDTC)$_2$. $\bar{i}_{\mathrm{B}}$ is practically independent of the concentration of Hg(DDTC)$_2$ and can be expressed by the following equation:

$$\bar{i}_{\mathrm{B}}=2Fz\Delta q \qquad (4)$$

where $F$: Faraday constant, $z$: maximum number of moles adsorbed per unit area, and $\Delta q$: the mean increase of the surface area per time unit ($\Delta q=0.85\,m^{2/3}t^{-1/3}$).

From Eqs. 2 and 3, we obtain:

$$\bar{i}\doteq 2Km^{2/3}t^{1/6}(C_0{}^*-C_0{}^0)-\bar{i}_{\mathrm{B}}$$

$$C_0{}^0=C_0{}^*-(\bar{i}+\bar{i}_{\mathrm{B}})/2Km^{2/3}t^{1/6} \qquad (5)$$

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[9] B. Breyer and H. H. Bauer, "Alternating Current Polarography and Tensammetry," Interscience Publishers, New York (1963), pp. 74, 268.

[10] E. C. Gregg and W. P. Tyler, *J. Am. Chem. Soc.* **72**, 4561 (1950).

Since, as has already been explained, $(\mathrm{DDTC})^-$ ions cannot exist in an acid solution, we can write:

$$\bar{\imath}=K'm^{2/3}t^{1/6}C_{\mathrm{R}}{}^0$$

where $C_{\mathrm{R}}{}^0$ is the surface concentration of $(\mathrm{DDTC})^-$.

Therefore,

$$C_{\mathrm{R}}{}^0=\bar{\imath}/K'm^{2/3}t^{1/6} \tag{6}$$

Assuming that the redox reaction 1 occurs reversibly, the potential at any point of wave A is given by the Nernst equation:

$$E_{\mathrm{d.e.}}=E_0-0.0295\log(C^\circ{}_{\mathrm{DDTC^-}})^2/C^\circ{}_{\mathrm{Hg(DDTC)_2}} \tag{7}$$

Solving Eqs. 5, 6 and 7, we obtain

$$E_{\mathrm{d.e.}}=$$
$$E_0'-0.0295\log(\bar{\imath}^2/(2C_0{}^*Km^{2/3}t^{1/6}-\bar{\imath}-\bar{\imath}_{\mathrm{B}}))$$

where $E_0'$ is equal to $E_0-0.0295\log(K/K'm^{2/3}t^{1/6})$ and is almost constant at a constant $m^{2/3}t^{1/6}$. $2C_0{}^*Km^{2/3}t^{1/6}$ is equal to the total limiting current and is given by the sum of $\bar{\imath}_{\mathrm{B}}$ and $\bar{\imath}_{\mathrm{A}}$ (average limiting current of step A).

Hence, we can write:

$$E_{\mathrm{d.e.}}=E_0'-0.0295\log\bar{\imath}^2/(\bar{\imath}_{\mathrm{A}}-\bar{\imath}) \tag{8}$$

Thus a plot of $E_{\mathrm{d.e.}}$ vs. $\log\bar{\imath}^2/(\bar{\imath}_{\mathrm{A}}-\bar{\imath})$ of wave A should have a slope of 29.5 mV. The experimental results agreed well with this prediction, as Fig. 9 shows; log-plots were found to have a slope between 28 and 31 mV. This fact suggests that the reduction of $\mathrm{Hg(DDTC)_2}$ is a reversible, two-electron process.

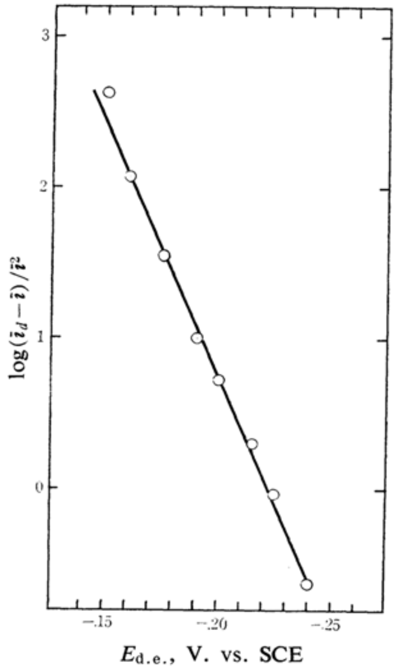

Fig. 9. Relationship between $\log(\bar{\imath}^2/\bar{\imath}_{\mathrm{A}}-\bar{\imath})$ and $E_{\mathrm{d.e.}}$ of the D. C. step A $T$, 25°C.

Relationship 4 makes it possible to evaluate directly the maximum number of molecules per unit area of the electrode surface. At a concentration of 0.3 mM of $\mathrm{Hg(DDTC)_2}$, the number of moles of $\mathrm{Hg(DDTC)_2}$ adsorbed per unit area of the electrode surface was calculated as:*

$$Z_1=5.7\times10^{-10}\ \mathrm{mol./cm^2}$$

Similary, at a concentration of 0.1 mM, when wave A begins to appear:

$$Z_2=2.3\times10^{-10}\ \mathrm{mol./cm^2}$$

From the value of $Z_1$, the area which one molecule of $\mathrm{Hg(DDTC)_2}$ occupies is 30 Å²/molecule, assuming that the adsorbed molecules form a monolayer. If we consider that $\mathrm{Hg(DDTC)_2}$ is adsorbed vertically upon the electrode surface, this value seems reasonable, considering the area calculated from the crystal data reported by Simonsen and Wah Ho.[11] From the $Z_2$ value, the occupied area is found to be 75 Å²/molecule; this value is in fairly good agreement with the value calculated by assuming that the chelate is adsorbed horizontally onto the electrode. We think that the difference between $Z_1$ and $Z_2$ might be due to a different orientation of the adsorbed chelate molecule at the electrode surface. However, it is also possible that the adsorbed film may be a multi- and not a monolayer.

The behavior of the $\mathrm{Hg(DDTC)_2}$ dimethylformamide solution will be reported on in a subsequent paper.

The authors wish to acknowledge the helpful suggestions of Visiting Professor Bruno Breyer, formerly of the University of Sydney.

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[11] S. H. Simonsen and u. J. Wah Ho, *Acta Cryt.* 6, 430 (1953).

* For the calculation, the following data were used:

$$\bar{\imath}_{\mathrm{B}}=(\bar{\imath}_{\mathrm{total}})_{\mathrm{corr.}}-\bar{\imath}_{\mathrm{A}},$$
$$(\bar{\imath}_{\mathrm{total}})_{\mathrm{corr.}}=(\bar{\imath}_{\mathrm{total}})_{\mathrm{obs.}}\,(t_{\mathrm{A}}/t_{\mathrm{B}})^{1/6}$$

where $t_{\mathrm{A}}=4.66$ sec., $\bar{\imath}_{\mathrm{A}}=0.475$ microampere at −0.29., $t_{\mathrm{B}}=4.97$ sec., and $(\bar{\imath}_{\mathrm{total}})_{\mathrm{obs.}}=0.905$ microampere at −0.40 V.