460 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 460—463 (1973) [Vol. 46, No. 2

Polarographic Studies of the Anodic Oxidation of Mercury. II. The Anodic Adsorption Wave of Ethylamine in *N*,*N*-Dimethylformamide

Yoshihisa Matsui and Yoshio Date

Department of Agricultural Chemistry, Shimane University, Nishikawazu, Matsue

(Received June 3, 1972)

Ethylamine at concentrations lower than 0.5 mM in N,N-dimethylformamide gives a diffusion-controlled anodic wave due to the reversible oxidation of the mercury to a 1 : 2 complex of mercury(II) with the amine. At higher concentrations, another anodic wave appears at a potential less positive than the main wave; this has been attributed to the adsorption of the oxidation product on the mercury electrode. The adsorption prewave was analyzed on the basis of Brdička's theory, in which the Langmurian adsorption was assumed. It was shown that the nature of the prewave can be well interpreted on the additional assumption that the adsorption coefficient of the adsorbed complex decreases exponentially as the electrode potential becomes more positive.

In a previous paper,[1] it was shown that ammonia, methylamine, and dimethylamine anodically depolarize the dropping mercury electrode in N,N-dimethylformamide (DMF) to form 1 : 2 complexes of mercury (II) with the amines. Furthermore, it was suggested that the complexes are adsorbed on the electrode surface to cause the flowing of the extra anodic current. However, the nature of the anodic adsorption current has not yet been examined in detail.

The present study was undertaken not only in order to extend the previous study to ethylamine, but also in order to examine the characteristics of the anodic adsorption current in detail.

Experimental

The solvent, DMF, and the supporting electrolyte, tetraethylammonium perchlorate, were purified as had been described previously.[1] Ethylamine, which had been separated from a commercial 70% aqueous solution by the addition of a saturated NaOH solution, was dried and distilled over granular NaOH. The concentration of the amine in DMF was determined by titration against an aqueous hydrochloric acid. A solution of mercury(II) perchlorate in DMF was prepared as has been described elsewhere.[2]

Polarograms were obtained in a manner similar to that described before.[1] All the potentials reported in the present paper refer to an aqueous, saturated calomel electrode connected with a cell solution by means of a DMF-agar salt bridge.[3]

Results and Discussion

The polarographic behavior of ethylamine was examined with a dropping mercury electrode over a wide concentration range from 0.1 to 100 mM in DMF. The amine gave a single well-defined anodic wave at concentrations lower than 0.5 mM. At higher concentrations, another anodic wave appeared at a potential less positive than the main wave. The polarographic characteristics of these waves are summarized in Tables 1 and 2. The total limiting current (i_d) was virtually proportional to the bulk concentration of the amine, and also to the square root of the effective pressure (h_{corr}) on the mercury drop; these findings indicate that the total limiting current is diffusion-controlled. On the other hand, the limiting current (i_p) of the prewave was virtually independent of the bulk concentration of the amine when it was lower than 20 mM. It was also shown that the value of i_p increases in proportion to h_{corr}. These results indicate that the prewave has the nature of an adsorption current. At concentrations higher than 20 mM, the value of i_p gradually increased with an increase in the concentration. This may be at-

Table 1. Polarographic characteristics of ethylamine at various concentrations[a)]

Concn. (mM)	$E_{1/2}$ (V *vs.* SCE) prewave	total wave	i_p[b)] (μA)	I_d[c)]
0.10	—	+0.184	—	2.22
0.26	—	+0.180	—	2.37
0.52	—	+0.160	—	2.42
1.02	+0.093	+0.176	1.62	2.35
2.18	+0.038	+0.176	1.80	2.55
5.50	−0.001	+0.167	1.80	2.52
10.9	−0.028	+0.166	1.85	2.67
21.8	−0.051	+0.179	1.97	2.55
54.4	−0.084	+0.272	3.10	2.42
100.0	−0.097	+0.333	4.85	2.35

a) $m=1.778$ mg/s, $t=3.79$ s.

b) The limiting current of the prewave.

c) Diffusion current constant: $I_d=i_d/C\cdot m^{2/3}t^{1/6}$ (μA·mM^{-1} mg$^{-2/3}$ s$^{1/2}$).

Table 2. Relation between the limiting current of 5.0 mM ethylamine and effective pressure on the dropping mercury electrode[a)]

$h_{corr.}$ (cm)	i_p[b)] (μA)	i_d[c)] (μA)	i_p/h_{corr} (μA·cm^{-1})	$i_d/h_{corr}^{1/2}$ (μA·cm$^{-1/2}$)
38.7	0.87	17.2	0.022	2.76
44.7	0.97	18.6	0.022	2.79
54.7	1.20	20.4	0.022	2.75
64.7	1.40	23.2	0.022	2.88
74.7	1.51	23.6	0.020	2.73
80.3	1.63	24.9	0.020	2.78

a) $m=1.460$ mg/s, $t=4.44$ s.

b) The limiting current of the prewave.

c) The limiting current of the total wave.

---

[1] Y. Matsui, Y. Kurosaki, and Y. Date, This Bulletin, **46**, 147 (1973).

[2] Y. Matsui and Y. Date, *ibid.*, **43**, 2052 (1970).

[3] K. Takaoka, *Rev. Polarog.* (Kyoto), **14**, 63 (1966).

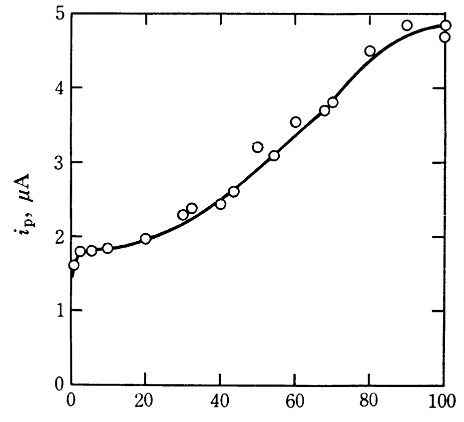

Fig. 1. Plot of the height of the prewave *vs.* the concentration of EtNH$_2$.

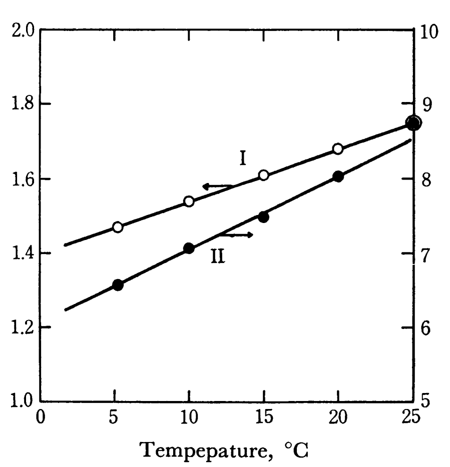

Fig. 2. Plot of the heights of the prewave (I) and the total wave (II) of EtNH$_2$ *vs.* temperature.
[EtNH$_2$] = 1.89 mM

tributed to the formation of additional superimposed layers of the adsorbate on the mercury surface, for the curve obtained by plotting i_p against the amine concentration resembles the B. E. T. isotherm (Fig. 1). The half-wave potential of the total anodic wave at high amine concentrations shifted toward the positive value as the concentration increased. The film of the adsorbate may inhibit the electrode process, thus causing the positive shift.

Figure 2 shows the effect of the temperature on the heights of the total wave and the prewave, which linearly increased with the temperature. The average rates of increase were 1.38% and 0.89% per degree respectively. These values also indicate that the former is controlled by diffusion, and the latter, by adsorption. The fact that the adsorption wave appeared at potentials less positive than the main wave suggests that the adsorbate is the oxidation product rather than the depolarizer.[4]

Figure 3 shows the effect of ethylamine on the electrocapillary curve in DMF containing 0.10 M tetraethylammonium perchlorate. A significant decrease in the surface tension of the mercury drop was

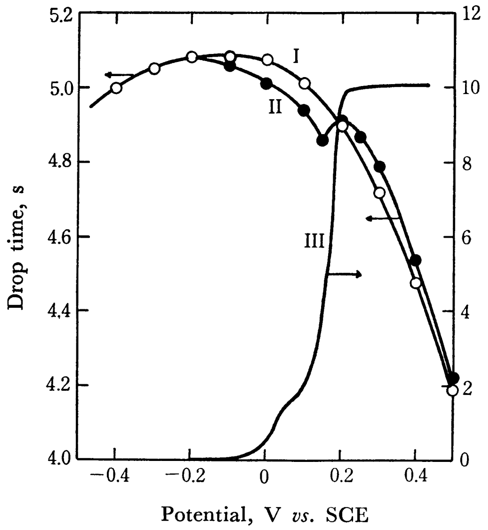

Fig. 3. Effect of EtNH$_2$ on the electrocapillary curve.
I, 0.10 M Et$_4$NClO$_4$; II, I+1.72 mM EtNH$_2$; III, Polarogram of 2.18 mM EtNH$_2$.

caused by the addition of a small amount of the amine. The decrease began at *ca.* 0.00 V *vs.* SCE, where the anodic prewave appeared, and finished at *ca.* +0.20 V *vs.* SCE, where the main wave just approached its plateau. It is obvious that the adsorption of the oxidation product on the electrode surface is responsible for the appearance of the prewave. It can also be presumed that the desorption of the product facilitates the electrolytic process.

Figure 4 shows the results of the amperometric titration of mercury(II) perchlorate against ethylamine. The limiting current of the mercury(II) ion decreased with the addition of ethylamine. At the same time, a second cathodic wave appeared at a more negative potential. The wave height increased in proportion to the ratio of the concentration of ethylamine to that of the mercury(II) ion, until the ratio exceeded 2.0. Thereafter, the wave of the mercury(II) ion disappeared, the height of the second cathodic wave reached a virtually constant value, and an anodic limiting current appeared and increased in proportion to the

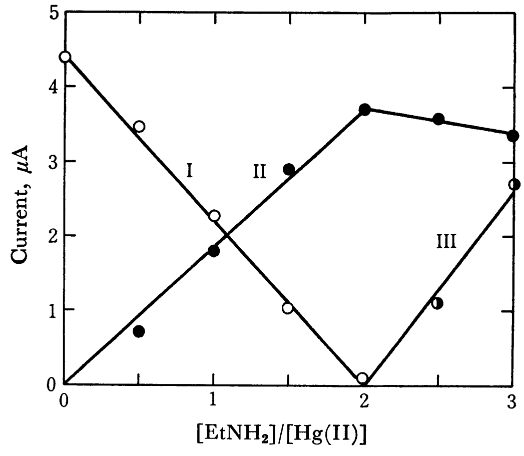

Fig. 4. Amperometric titration of Hg(II) with EtNH$_2$.
I : Wave height of the simple Hg(II) ion,
II : Wave height of the complex; Hg(EtNH$_2$)$_2^{2+}$,
III: Wave height of EtNH$_2$.

---

[4] R. Guidelli, *J. Phys. Chem.*, **74**, 95 (1970).

excess amount of the amine. These results are similar to those for methylamine reported in a previous paper;[1] it can likewise be thought that the mercury(II) ion reacts with ethylamine to form the 1 : 2 complex, $Hg(EtNH_2)_2^{2+}$, which then gives the second cathodic wave. It can also be considered that the anodic wave of the amine is due to the polarographically reversible oxidation of mercury to $Hg(EtNH_2)_2^{2+}$:

$$Hg + 2EtNH_2 \rightleftarrows Hg(EtNH_2)_2^{2+} + 2e \tag{1}$$

Provided that the electrode process is simply expressed in terms of Eq. (1), the equation for the current-potential curve should be given by:[1]

$$E = E_0 - (RT/2F)\ln\beta_2 + (RT/2F)\ln k_0^2/k_2 + (RT/2F)\ln i/(i_d-i)^2 \tag{2}$$

In this equation, E_0 represents the ordinary standard potential of the mercury-mercury(II) half-cell; β_2, the overall stability constant of the complex of $Hg(EtNH_2)_2^{2+}$, and k_0 and k_2, the Ilkovič equation constants for the amine and the complex, respectively. The plot of log $i/(i_d-i)^2$ *vs.* E for the wave of 0.46 mM ethylamine is shown in Fig. 5. A straight line with the reciprocal slope of about 0.030 V was obtained at the more positive potentials of the wave, whereas the plot deviated from the line at the less positive potentials of the wave. In analogy with the case of methylamine,[1] the deviation may be due to the adsorption of the oxidation product, $Hg(EtNH_2)_2^{2+}$, on the electrode surface. On the assumption that Eq. (2) holds for the more positive potentials of the wave, the value of β_2 was estimated to be $10^{16.5}$. In this calculation, E_0 was taken to be 0.557 V *vs.* SCE.[2]

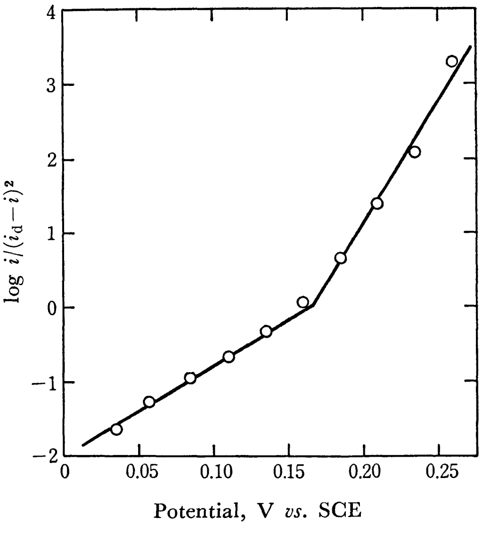

Fig. 5. Plot of log $i/(i_d-i)^2$ *vs.* potential for the wave of 0.46 mM $EtNH_2$.
Reciprocal slope: I; 0.030 V, II; 0.075 V.

The Analysis of the Adsorption Prewave. When the amine concentration was high enough, the adsorption prewave could be well resolved from the main wave. Furthermore, it seems, on the basis of the results shown in Fig. 1, that the adsorption obeys the Langmuir isotherm at amine concentrations lower than 20 mM. Therefore, we undertook to analyze the prewave on the basis of Brdička's theory of the adsorption wave. On assuming that the oxidation product, $Hg(EtNH_2)_2^{2+}$, is the only adsorbate, and that the adsorption obeys the Langmuir isotherm, the anodic current (i) can be related to the concentrations of the amine and the complex (a and x_2 respectively) on the electrode surface by the following equations:[5]

$$i_d - i = k_0 a \tag{3}$$

$$i = k_2 x_2 + (i_p w x_2/(1+wx_2)) \tag{4}$$

In this equation, w, is the adsorption coefficient of $Hg(EtNH_2)_2^{2+}$. The height of the prewave, i_p, is correlated with the maximum amount of substance adsorbed per unit area of the electrode (Z) by the following equation:

$$i_p = knFm^{2/3}t^{-1/3}Z \tag{5}$$

where

$$k = 0.85\ \mathrm{cm^2 g^{-2/3}}\ \text{at}\ 25^\circ\mathrm{C}$$

and where n is the number of the electrons participating in the electrode process; m, the mass of mercury flowing out of the capillary per unit time, and t, the drop time. The value of Z for $Hg(EtNH_2)_2^{2+}$ at amine concentrations lower than 10 mM was calculated from this equation to be 1.17×10^{-9} mol/cm²; this is slightly less than that for $Hg(MeNH_2)_2^{2+}$ (1.41×10^{-9} mol/cm² [1]).

When it is assumed that, at the potentials corresponding to the prewave, the amount of the oxidation product diffusing into the solution is negligibly small compared with that adsorbed on the electrode surface, Eq. (4) can be simplified as follows:

$$i = i_p w x_2/(1+wx_2) \tag{6}$$

Thus, a and x_2 are given by:

$$a = (i_d-i)/k_0 \tag{7}$$

$$x_2 = i/w(i_p-i) \tag{8}$$

On the other hand, the electrode potential is expressed by the equation:

$$E = E_0 - (RT/2F)\ln\beta_2 + (RT/2F)\ln x_2/a^2 \tag{9}$$

By introducing Eqs. (7) and (8) into Eq. (9), we obtain:

$$E = E_0 - (RT/2F)\ln\beta_2 + (RT/F)\ln k_0 - (RT/2F)\ln w + (RT/2F)\ln i/(i_p-i)(i_d-i)^2 \tag{10}$$

If the adsorption coefficient of $Hg(EtNH_2)_2^{2+}$ does not change with the potential, the first four terms on the right-hand side of Eq. (10) are constant. Then, the plot of log $i/(i_p-i)(i_d-i)^2$ *vs.* E should give a straight line with a reciprocal slope of 0.030 V at 25°C. The results for the prewaves given by 2.8—43.5 mM ethylamine are shown in Fig. 6. The plot gave a good straight line. However, the reciprocal slope (0.047 V) was significantly larger than the theoretical value. It might be considered that the increase in the reciprocal slope is due to the irreversibility of the electrode process. However, this can be ruled out in the present case, for the fact that the reciprocal slope of the log-plot was equal to 0.030 V for the wave

---

[5] R. Brdička, *Z. Elektrochem.*, **48**, 278 (1942).

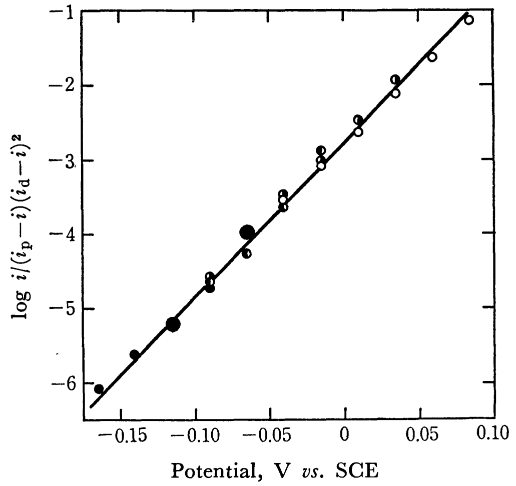

Fig. 6. Plot of $\log i/(i_p-i)(i_d-i)^2$ *vs.* potential for the prewave of $EtNH_2$.
Concentration of $EtNH_2$: ○; 2.75 mM, ◑; 5.50 mM, ◐; 21.8 mM, ●; 43.5 mM.

of the amine at a low concentration, and the fact that the half-wave potential of the oxidation wave of the amine was approximately equal to that of the reduction wave of $Hg(EtNH_2)_2^{2+}$ obtained in the amperometric titration, show that the electrode process is reversible. According to Guidelli,[4] it is possible that the increase in the slope of the adsorption wave is caused by the change in the adsorption coefficient with the potential. Since the adsorbed complex, $Hg(EtNH_2)_2^{2+}$, has a positive charge, it seems natural to consider that the adsorption energy (φ) of the complex may be lowered, as the electrode potential becomes more positive, by an increase in the electronic repulsion between the adsorbed complex and the electrode. In fact, it was found that the polarographic behavior of the prewave can be well explained on the basis of the assumption that the energy of the electronic repulsion between the divalent positive ion and the electrode is in proportion to $2FE$. Then, φ may be written as:

$$\varphi_0 - \varphi = 2F\gamma E \qquad (11)$$

where φ_0 is the adsorption energy at 0.00 V *vs.* SCE, and γ, the proportionality constant. On the other hand, w is generally proportional to $\exp(\varphi/RT)$,[5] so that:

$$w = w_0 \exp(-2F\gamma E/RT) \qquad (12)$$

In this equation, w_0 corresponds to the adsorption coefficient at 0.00 V *vs.* SCE. By combining Eqs. (10) and (12), we obtain:

$$(1-\gamma)E = E_0 - (RT/2F)\ln\beta_2 + (RT/F)\ln k_0 \\ - (RT/2F)\ln w_0 + (RT/2F)\ln i/(i_p-i)(i_d-i)^2 \qquad (13)$$

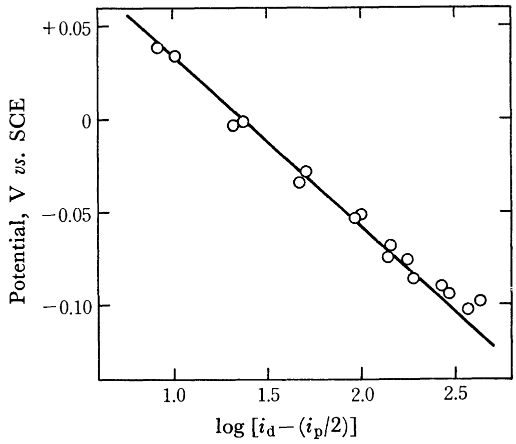

Fig. 7. Plot of the half-wave potential of the prewave of $EtNH_2$ *vs.* $\log [i_d-(i_p/2)]$.
Slope: -0.092 V

This equation indicates that the reciprocal slope of the plot of $\log i/(i_p-i)(i_d-i)^2$ *vs.* E is equal to $0.030/(1-\gamma)$ V at 25°C. By taking γ as 0.36, we obtain the slope of 0.047 V, which agrees with the observed value. From Eq. (13), Eq. (14) is readily derived:

$$E_{p,1/2} = C - (1/(1-\gamma))(RT/F)\ln(i_d - i_p/2) \qquad (14)$$

where $E_{p,1/2}$ is the half-wave potential of the prewave, and C, the constant. This equation shows that $E_{p,1/2}$ should shift toward a more negative potential with an increase in the amine concentration. The relation between $E_{p,1/2}$ and $\log(i_d - i_p/2)$ observed was virtually linear, with a slope of -0.092 V (Fig. 7); this is fairly well in agreement with the value, -0.094 V, calculated on the basis of Eq. (15), which γ is taken as 0.36. This is one evidence in support of the validity of Eq. (13). Since the numerical values of the constants and the variables in Eq. (13) are all either known or experimentally estimated except for w_0, it is possible to calculate the value of w_0. Thus, we obtained the value of w_0 as 4.6×10^6 l/mol for $Hg(EtNH_2)_2^{2+}$. This value is so large that it is consistent with the above assumption that the amount of the oxidation product diffusing into the solution is negligibly small compared with that adsorbed on the electrode surface at the potentials corresponding to the prewave of ethylamine.

Thus, it is obvious that the present method of treatment of an adsorption wave is plausible in this case. However, it is still uncertain whether or not it can generally be applied to the prewaves due to the adsorption of ionic compounds. This will be studied further in succeeding papers.