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Polarographic Studies of the Anodic Oxidation of Mercury. I. Anodic Waves of Ammonia and Several Amines in *N,N*-Dimethylformamide

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The behavior of ammonia and several amines at the dropping mercury electrode was studied in *N,N*-dimethylformamide containing 0.10M Et_4NClO_4 by means of DC polarography and amperometric titration. Ammonia gave a diffusion-controlled anodic wave, which was attributed to the reversible oxidation of mercury to the 1:2 complex of mercury(II) with ammonia. A dilute solution of methylamine or dimethylamine gave a diffusion-controlled anodic wave similar to that of ammonia. A concentrated solution of each amine gave a prewave due to the adsorption of the electrolysis product, $Hg(am)_2{}^{2+}$, on the electrode surface. Trimethylamine also gave an anodic wave, but it was attributed to the oxidation of the amine itself to the corresponding cation radical. Ethylenediamine and 1,2-diaminopropane each gave a well-defined anodic wave over the concentration range examined. The wave was diffusion-controlled and was attributed to the reversible oxidation of mercury to the chelate compound of the $Hg(diam)_2{}^{2+}$ type. No adsorption phenomena were observed in this case. Aromatic amines such as aniline and β-naphthylamine gave no anodic waves. The overall stability constants of the 1:2 complexes of mercury(II) with ammonia, methylamine, dimethylamine, ethylenediamine, and 1,2-diaminopropane were evaluated by the analyses of the waves to be $10^{16.9}$, $10^{17.1}$, $10^{15.0}$, $10^{23.5}$, and $10^{24.0}M^{-1}$ respectively.

When the dropping mercury electrode is polarized anodically in a solution containing an ion or a compound which can form a stable complex with mercury(I) or mercury(II), an anodic diffusion current is observed at a potential less positive than the potential at which the anodic current due to the free dissolution of mercury flows. This is due to the electrolytic oxidation of mercury to the mercury complex; such polarographic behavior make it possible not only to determine the complexing agents quantitatively, but also to investigate the chemical and physicochemical properties of both complexing agents and their mercury complexes. Among them, the halide, cyanide, thiocyanate, sulfide, and thiosulfate ions, the compounds containing the thiol group, and their mercury complexes have often been studied in aqueous and nonaqueous solutions.[1,2] The compounds containing an amino group are also known to form considerably stable complexes with mercury.[3] Nevertheless, their electrochemical behavior on the dropping mercury electrode has rarely been examined,[4-6] probably because amines are in general such strong bases that, in a dilute aqueous solution, they react with water to form the corresponding ammonium and hydroxide ions. On the other hand, amines are in the free state in aprotic solvents; this must be favorable for a polarographic study of free amines. Thus, Coetzee and Kolthoff[6] have reported that some amines give well-defined anodic waves in acetonitrile. However, they gave no details of the electrode reactions.

The present investigation was undertaken in order to survey the anodic behavior of amines on the dropping mercury electrode in detail by means of DC polarography and amperometric titration. Among amines, ammonia (NH_3), methylamine ($MeNH_2$), dimethylamine (Me_2NH), trimethylamine (Me_3N), ethylenediamine, 1,2-diaminopropane, aniline, and β-naphthylamine were chosen for the present study. *N,N*-dimethylformamide (DMF) was used as a solvent, for it is aprotic and is frequently used in polarography.

Experimental

Materials. The DMF obtained commercially was dried over potassium carbonate for several days and then distilled under reduced pressure in the presence of a few lumps of calcium hydride. The tetraethylammonium perchlorate (Et_4NClO_4) used as a supporting electrolyte was prepared as has been described by Fujinaga *et al.*[7] The NH_3, $MeNH_2$, Me_2NH, and Me_3N were obtained commercially in aqueous solutions; their concentrations were 28, 30, 40, and 30% respectively. They were diluted with DMF in order to prepare cell solutions of the amines without the removal of water.[8] The concentration of each amine was determined by titration with an aqueous hydrochloric acid. The other amines studied were commercially obtained and were used without further purification. A solution of mercuric perchlorate in DMF was prepared as has been described previously.[9]

Apparatus. The DC polarography was carried out at 25°C with a Shimadzu polarograph, model RP-50. An H-type cell was used for the polarography. The bridged

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[1] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, New York (1952), pp. 511, 541, 561, 577, and 781.

[2] C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York (1970), p. 476.

[3] J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950).

[4] C. J. Nyman, D. K. Roe, and D. B. Masson, *J. Amer. Chem. Soc.*, **77**, 4191 (1955).

[5] C. J. Nyman and R. A. Johnson, *Anal. Chem.*, **29**, 483 (1957).

[6] J. F. Coetzee and I. M. Kolthoff, *J. Amer. Chem. Soc.*, **79**, 6110 (1957).

[7] T. Fujinaga, K. Izutsu, K. Umemoto, T. Arai, and K. Takaoka, *Nippon Kagaku Zasshi*, **89**, 105 (1968).

[8] The amount of water introduced into the cell solutions with the amines was thought to be too small (below 0.04%) to affect the polarographic behavior of the amines. In fact, it was found for $MeNH_2$ that the anodic waves measured in the presence of water up to 0.40% were essentially the same as that measured after the removal of water.

[9] Y. Matsui and Y. Date, This Bulletin, **43**, 2052 (1970).

saturated calomel electrode proposed by Takaoka[10] was used throughout as a reference electrode. All the potentials were corrected automatically for the IR-drop across the electrolysis cell with a Shimadzu automatic potential corrector, model AIC-50. No cell solution was degassed, since some amines are so volatile that degassing would change the amine concentrations. The cathodic wave of oxygen appears at a potential too negative to influence the anodic wave of mercury. The current-time curves (*i-t* curves) were measured by means of the polarograph described above, with a minimum damping of amplitude and with a maximum chart speed of the recorder (160 mm/min). The response of the recorder was not very fast, but it was fast enough to observe qualitative features.

Results and Discussion

Anodic Waves of NH_3, $MeNH_2$, and Me_2NH. In polarographic behavior NH_3, $MeNH_2$, and Me_2NH are essentially similar to one another. Figures 1, 2, and 3 show their polarograms at various concentrations. Each of these depolarizers gave a single well-defined anodic wave at concentrations lower than 0.5 mM. At higher concentrations, $MeNH_2$ and Me_2NH gave prewaves, while NH_3 did not. For each depolarizer, as is shown, for example, in Tables 1 and 2 with respect to $MeNH_2$, the total limiting current (i_d) was virtually proportional to the bulk concentration of the depolarizer, and also to the square root of the effective pressure (h_{corr}) on the mercury drop; these facts indicate that the total limiting current is diffusion-controlled. On the other hand, the height (i_p) of each prewave of $MeNH_2$ and Me_2NH was virtually independent of the bulk concentration of the depolarizer and was proportional to h_{corr}; these facts indicate that the prewave

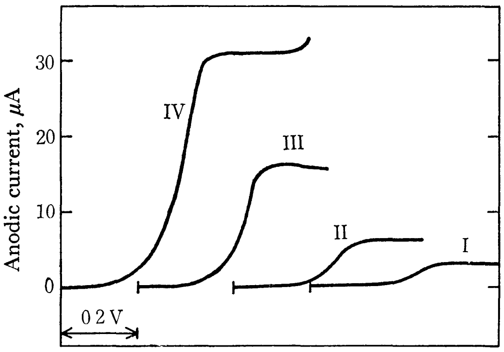

Fig. 1. DC polarograms of NH_3 in DMF at 25°C. Each polarogram was recorded from −0.10 V *vs.* SCE toward the positive potential.
I, 0.66 mM; II, 1.31 mM; III, 3.29 mM; IV, 6.57 mM

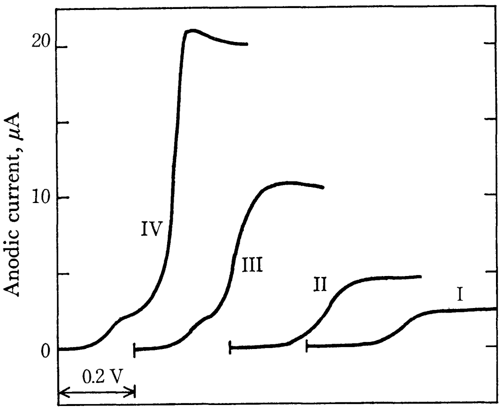

Fig. 2. DC polarograms of $MeNH_2$ in DMF at 25°C. Each polarogram was recorded from −0.10 V *vs.* SCE toward the positive potential.
I, 0.48 mM; II, 0.96 mM; III, 2.41 mM; IV, 4.82 mM

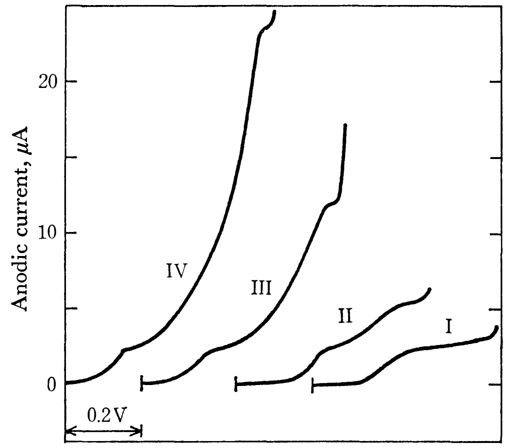

Fig. 3. DC polarograms of Me_2NH in DMF at 25°C. Each polarogram was recorded from 0.00 V *vs.* SCE toward the positive potential.
I, 0.53 mM; II, 1.06 mM; III, 2.65 mM; IV, 5.29 mM

TABLE 1. POLAROGRAPHIC CHARACTERISTICS OF METHYLAMINE AT VARIOUS CONCENTRATIONS AT 25°C

Concn. (mM)	$E_{1/2}$, V *vs.* SCE		i_p (μA)[a]	I_d[b]
	prewave	total wave		
0.10	—	+0.157	—	2.88
0.24	—	+0.155	—	2.54
0.48	—	+0.151	—	2.60
0.96	—	+0.142	—	2.66
2.41	+0.017	+0.166	1.80	2.52
4.82	+0.032	+0.213	1.90	2.52

a) The height of the prewave.
b) 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 1.26 mM METHYLAMINE AND EFFECTIVE PRESSURE ON THE DROPPING MERCURY ELECTRODE AT 25°C

h_{corr} (cm)	i_p[a] (μA)	i_d[b] (μA)	i_p/h_{corr} (μA/cm)	$i_d/h_{corr}^{1/2}$ (μA/cm$^{1/2}$)
38.2	1.0	4.3	0.026	0.70
44.2	1.2	4.6	0.027	0.69
54.2	1.5	5.2	0.028	0.71
64.2	1.8	5.7	0.028	0.71
74.2	2.1	6.1	0.028	0.71
84.2	2.4	6.5	0.029	0.71

a) The limiting current of the prewave.
b) The limiting current of the total wave.

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

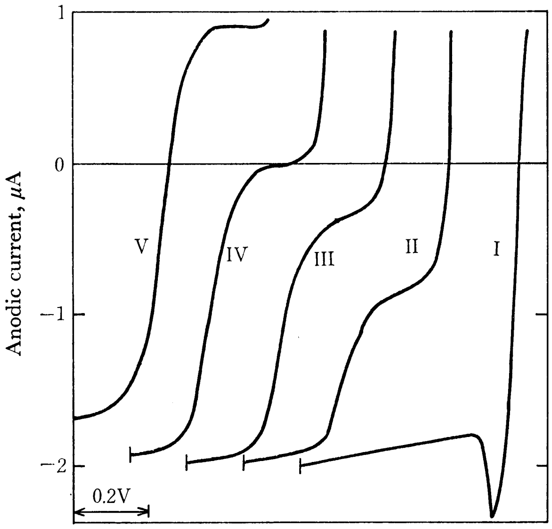

Fig. 4. The amperometric titration of 0.50 mM Hg(II) with $MeNH_2$ at 25°C. Each polarogram was recorded from −0.10 V *vs.* SCE toward the positive potential. The concentration of $MeNH_2$ added: I, 0.00 mM; II, 0.50 mM; III, 0.75 mM; IV, 1.00 mM; V, 1.25 mM

is characteristic of an adsorption current.

The composition of the mercury-amine complexes, which were considered to be formed during the electrode processes of the amines, was examined by the amperometric titration of the simple mercury(II) ion with each amine. The results for all three amines were virtually the same; as an example, the results of $MeNH_2$ are shown in Fig. 4. The simple mercury(II) ion gave a cathodic wave (accompanied by a maximum). The cathodic limiting current decreased with the amount of the amine added. At the same time, a second cathodic wave appeared at a less positive potential. The wave height increased in proportion to the amount of the amine added. When the quantity of the amine added was more than double that of mercury(II), the first cathodic wave disappeared, whereas an anodic limiting current appeared on the second wave. After that, the cathodic current of the second wave became virtually constant or decreased only slightly, while the anodic current increased in proportion to the excess amount of the amine. These results evidently show that the mercury(II) ion reacts with the amine (am) to form a complex of the $Hg(am)_2^{2+}$ type and that the complex is reduced at a potential corresponding to the second cathodic wave. The half-wave potential of this wave is approximately equal to that of the anodic wave of $MeNH_2$ shown in Fig. 2; this indicates that the electrode process is reversible. Thus, the electrode reaction can be expressed by the following equation:

$$Hg + 2am \rightleftharpoons Hg(am)_2^{2+} + 2e \qquad (1)$$

Although Coetzee and Kolthoff[6] attributed the anodic waves of NH_3 and some amines in acetonitrile to the formation of salts of the $HgNH_2ClO_4$ type, this is implausible, at least in the case of the electrode process in DMF.

The diffusion coefficients of NH_3, $MeNH_2$, Me_2NH, and their mercury(II) complexes were evaluated by using the Ilkovic equation. The results are shown in Table 3, together with those for the other amines and their mercury(II) complexes. Compared with the data that the diffusion coefficient of NH_3 in water is 14.6×10^{-6} cm²/s (20°C)[11] and that of the simple mercury(II) ion in DMF is 3.92×10^{-6} cm²/s (25°C),[9] the values here obtained seem to be reasonable.

TABLE 3. DIFFUSION COEFFICIENTS OF AMINES AND THEIR COMPLEXES WITH MERCURY (II) IN DMF AT 25°C

Compound	$D_a\times10^{6}$ [a] (cm²/s)	$D_c\times10^{6}$ [b] (cm²/s)
NH_3	19.9	3.68
$MeNH_2$	18.8	4.01
Me_2NH	18.9	2.76
Ethylenediamine	15.0	5.59
1,2-Diaminopropane	12.9	4.83

a) Diffusion coefficient of amine.
b) Diffusion coefficinet of the 1:2 complex of mercury (II) with amine.

If the electrode process (1) is reversible, the equation of the wave should be expressed by:

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

In this equation, E_0 represents the standard potential of the mercury-mercury(II) half-cell; β_2, the overall stability constant of the $Hg(am)_2^{2+}$ complex, and k_0 and k_2, the Ilkovic equation constants for the amine and $Hg(am)_2^{2+}$ respectively. Since the first three terms on the right-hand side of this equation are constant, a plot of $\log i/(i_d-i)^2$ *vs.* E should give a straight line, with a reciprocal slope of 0.030 V at 25°C. The results for the waves of 0.66 mM NH_3, 0.52 mM $MeNH_2$, and 0.24 mM Me_2NH are shown in Fig. 5. For each compound, a straight line with a 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. Similar plots were obtained for the waves of 0.33—1.32

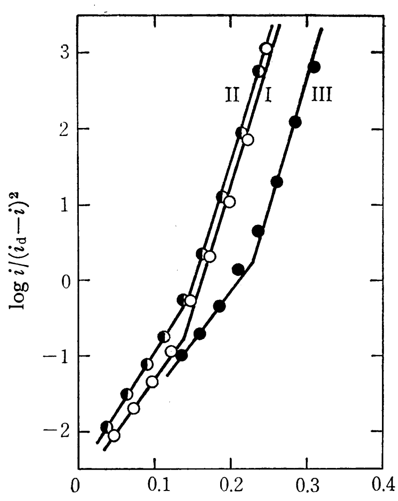

Fig. 5. The plots of $\log i/(i_d-i)^2$ *vs.* potential for the waves of 0.66 mM NH_3 (I), 0.52 mM $MeNH_2$ (II), and 0.24 mM Me_2NH (III).

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[11] D. M. Himmelblau, *Chem. Rev.*, **64**, 527 (1964).

mM NH_3, 0.10—0.66 mM $MeNH_2$, and 0.11—0.53 mM Me_2NH. The deviation of the plots can be attributed either to the partial formation of the higher amine complex, $Hg(am)_3^{2+}$, or to the adsorption of the electrolysis product, $Hg(am)_2^{2+}$, on the electrode surface. However, it was found that no equation derived by taking into account the formation of the higher complex[12] can explain the shape of the wave measured. Thus, at the less positive potentials of the wave a large part of the electrolysis product may be adsorbed on the electrode surface, and this may be responsible for the flowing of the extra anodic current. At the more positive potentials of the wave, the complex formed may cease to be adsorbed, and the polarographic curve may come to agree with that expressed by Eq. (2).

If Eq. (2) holds at the more positive potentials of each wave the value of β_2 can be estimated. For example, the potential at which the $\log i/(i_d-i)^2$ of the NH_3 wave equaled zero was graphically estimated to be 0.163 (average) V *vs.* SCE, E_0 is 0.557 V *vs.* SCE,[9] and the k_0 of NH_3 and the k_2 of $Hg(NH_3)_2^{2+}$ were 4.37×10^3 and 3.06×10^3 μA/M respectively. Consequently, β_2 was evaluated to be $10^{16.9}$M^{-1}. This value is comparable to that in water, that is, $10^{17.5}$M^{-1}.[13] The results of the other amines are listed in Table 4.

TABLE 4. OVERALL STABILITY CONSTANTS OF THE 1:2 COMPLEXES OF MERCURY (II) WITH AMINES IN DMF AT 25°C[a)]

Compound	β_2, M^{-1}
NH_3	$10^{16.9}$
$MeNH_2$	$10^{17.1}$
Me_2NH	$10^{15.0}$
Ethylenediamine	$10^{23.5}$
1,2-Diaminopropane	$10^{24.0}$

a) Ionic strength: 0.10M

Furthermore, from Eq. (2) the following equation can easily be derived:

$$E_{1/2} = K - (RT/2F)\ln c_0 \qquad (3)$$

where $E_1/_2$ and c_0 are the half-wave potential and the bulk concentration of each amine respectively, and where K is a constant. The observed $E_1/_2$'s of the NH_3 waves are plotted in Fig. 6. When the concentration of NH_3 was less than 2 mM, the $E_1/_2$ was shifted, exactly in accordance with Eq. (3), to the less positive potential with an increase in the concentration. This indicates that Eq. (2) is valid in the low concentration range. However, when the concentration exceeded 2 mM, the $E_1/_2$ was shifted to the more positive potential with an increase in the concentration. Similar plots were obtained for $MeNH_2$ and Me_2NH, too. These may be well explained in terms of the inhibition of the anodic process by the electrolysis product adsorbed on the mercury electrode. That is, the concentration of each depolarizer may be so high that the surface of the mercury electrode may be completely covered by the film of the electrolysis product, which may then continue to inhibit the further diffusion of the depolarizer to the electrode until the complex is desorbed from the electrode at the more positive potential.

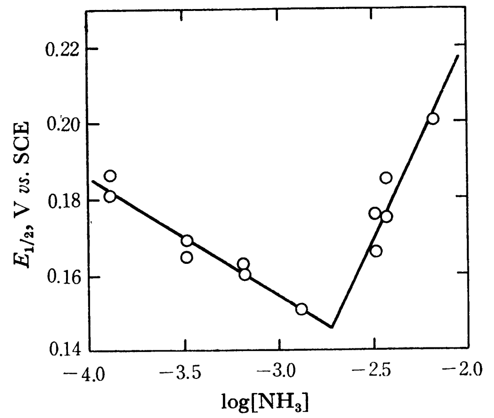

Fig. 6. Relation between the concentration of NH_3 and its half-wave potential.

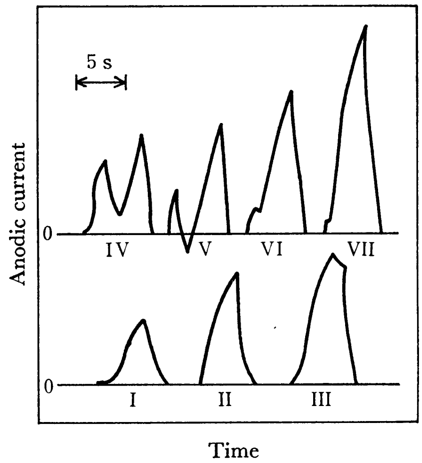

Fig. 7. The current-times curve of 1.5 mM Me_2NH at various potentials (25°C). Potential (V *vs.* SCE): I, 0.10; II, 0.15; III, 0.20; IV, 0.25; V, 0.30; VI, 0.40; VII, 0.50.

The inhibition of the electrode process by the adsorption was also observed by the measurement of the *i-t* curve during the growth of each mercury drop, especially in the case of Me_2NH (Fig. 7). In this case, the anodic current increased with the growth of a mercury drop at the potential of +0.15 V *vs.* SCE, corresponding to the mid-point of the Me_2NH prewave; this is characteristic of a diffusion-controlled process. On the other hand, at the potential of +0.20 V *vs.* SCE corresponding to the plateau of the prewave, the anodic current decreased somewhat before the dropping of mercury. At more positive potentials, the anodic current abruptly decreased in the course of the growth of a mercury drop. This is characteristic of an adsorption current and indicates that the electrode process is inhibited by the adsorbate layer. Similar results were observed in the case of $MeNH_2$, although that decrease in the current was not so great as in the case of Me_2NH.

If the adsorption of the mercury complexes obeys the

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[12] T. Murayama, T. Sawaki, and S. Sakuraba, This Bulletin, **43**, 2820 (1970).

[13] L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special. Publ. **17**, Chem. Soc., London (1964), p. 155.

Langmuir isotherm, the maximum amount of the adsorbate per unit area (Z) can be evaluated by the following equation:[14]

$$Z = i_p/(knFm^{2/3}t^{-1/3}) \qquad (4)$$

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

where n is the number of the electrons participating in the electrode process. For example, in the case of $MeNH_2$ n is equal to 2, and the mean value of i_p, measured when m and t are equal to 1.546 mg/s and 4.67 s respectively, is 1.85 μA. Therefore, Z is equal to 1.41×10^{-9} mol/cm^2, which indicates that one adsorbate molecule occupies an area of 11.8 Å^2 of the electrode surface. The value of Z for Me_2NH was 1.59×10^{-9} mol/cm^2 (10.4 Å^2/molecule).

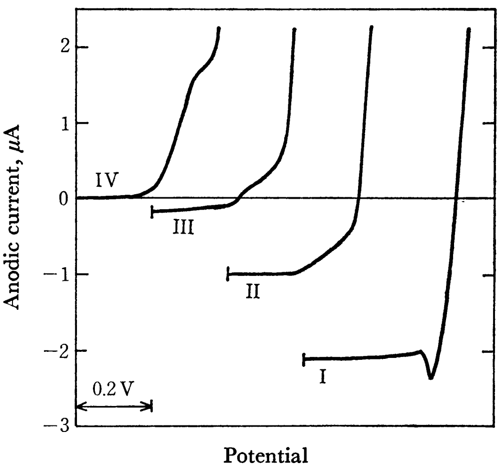

Fig. 8. The amperometric titration of 0.50 mM Hg(II) with Me_3N at 25°C. Each polarogram was recorded from +0.10 V *vs.* SCE toward the more positive potential. The concentration of Me_3N added: I, 0.00 mM; II, 0.50 mM; III, 1.00 mM; IV, 1.50 mM.

Anodic Wave of Me_3N. The polarogram of Me_3N was similar to that of $MeNH_2$. The wave height was virtually proportional to the bulk concentration of Me_3N and also to the square root of the effective pressure on the mercury drop; these facts indicate that the wave is diffusion-controlled ($I_d = 1.31\ \mu\mathrm{A \cdot mM^{-1}\,mg^{-2/3}s^{1/2}}$). However, the results of the amperometric titration of the simple mercury(II) ion with Me_3N were different from those with $MeNH_2$ and Me_2NH (Fig. 8). Although the height of the wave of the simple mercury(II) ion decreased with the increase in the amount of Me_3N, no reduction wave of the mercury complex appeared. The reduction wave of the simple mercury(II) ion almost disappeared when the concentration of the amine added exceeded twice that of the mercury(II) ion. It was also observed that the mercury(II) solution changed from colorless to a yellowish brown as the amine was added. These results indicate that the simple mercury(II) ion is chemically reduced by the amine to metallic mercury and the cation radical of the amine, which may then be liable to decompose to electro-inactive products. Thus, the anodic wave of Me_3N may not be due to the oxidation of mercury to its complex with the amine, but to the oxidation of the amine itself to the corresponding cation radical.

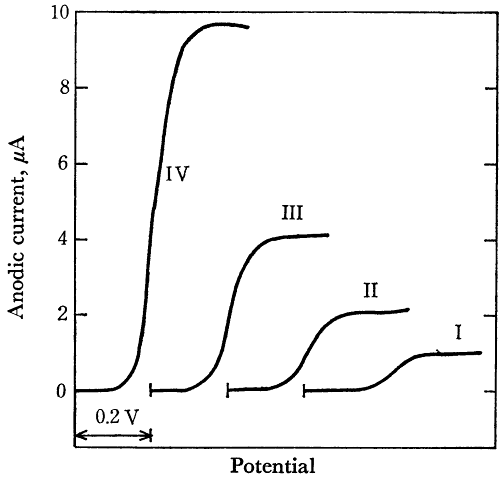

Fig. 9. DC polarograms of ethylenediamine in DMF at 25°C. Each polarogram was recorded from −0.25 V *vs.* SCE toward the positive potential. I, 0.25 mM; II, 0.51 mM; III, 1.01 mM; IV, 2.53 mM.

Anodic Waves of Ethylenediamine and 1,2-Diaminopropane. The polarographic behavior of ethylenediamine and that of 1,2-diaminopropane were similar to one another, but different from that of the monoamines examined above. Figure 9 shows the polarograms of ethylenediamine at various concentrations. Each diamine gave a well-defined anodic wave even in a concentrated solution. The height of the wave of each diamine was proportional to the bulk concentration of the diamine and also to the square root of the effective pressure on the mercury drop; these facts indicate that the wave is diffusion-controlled. The results of the amperometric titration of the simple mercury(II) ion with each diamine clearly indicated that the mercury(II) ion reacts with each diamine to form a complex of the $\mathrm{Hg(diam)_2}^{2+}$ type.

If the anodic wave of each diamine is due to the formation of the 1:2 complex in a reversible process, Eq. (2) should hold. The plots of $\log i/(i_d - i)^2$ *vs.* potential were linear, in good accordance with Eq. (2), over the entire potential range of the anodic wave of each diamine. This is different from the results obtained for NH_3, $MeNH_2$, and Me_2NH and suggests that the mercury(II) complex with each diamine is not adsorbed on the electrode. This argument was supported by the measurements of the i-t curve and of the electrocapillary curve of each diamine. The absence of adsorption may be related to the formation of the chelate complex of mercury(II) with each diamine. A plot of $E_{1/2}$ *vs.* the logarithmic concentration of each diamine was virtually linear, in accordance with Eq. (3), over the whole range of concentration studied. The diffusion coefficients of each diamine and its mercury(II) complex, and the overall stability constants of the 1:2 complex, are listed in Tables 3 and 4 respectively.

It was found that the mercury(II) complexes of the diamines are more stable than those of the mono-

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

amines by a factor of about 10^7. It was also found that the values of β_2 in DMF are very close to those in water ($10^{23.42}$M^{-1} for ethylenediamine and $10^{23.53}$M^{-1} for 1,2-diaminopropane in 0.10N KNO_3 at 25°C[4]); this suggests that solvents have little effect on the stability of the complexes.

Anodic Behavior of Aromatic Amines. Although Coetzee and Kolthoff[6] have reported that aniline gives a well-defined anodic wave in acetonitrile, it gives no anodic wave in DMF. β-Naphthylamine also gives no anodic wave in DMF. These results are in clear contrast to those of the aliphatic amines. The complexing ability of the aromatic amines with mercury(II) may be lower than that of the aliphatic amines, just as the basicity of the former is lower than that of the latter.