Polarographic Studies of the Anodic Oxidation of Mercury. III. The Adsorption of the Mercury(II) Complexes of Ammonia and Alkylamines on the Mercury Electrode Surface

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A solution of ammonia, methylamine, *n*-propylamine, isopropylamine, or *n*-butylamine in *N,N*-dimethylformamide gives an anodic prewave due to the adsorption of the oxidation product, $Hg(amine)_2^{2+}$, on the dropping mercury electrode. The shape of the prewave of each amine can be well interpreted by an equation derived on the basis of the assumptions that the adsorption follows the Langmuir isotherm and that the adsorption coefficient of the adsorbate complex decreases exponentially as the electrode potential becomes more positive. Some physicochemical properties of the mercury(II) complexes, such as the overall stability constants and the adsorption coefficients at 0.0 V *vs.* SCE, were determined by analyses of the polarographic waves.

In a previous paper,[1] it was shown that the shape of the anodic adsorption prewave given by ethylamine in *N,N*-dimethylformamide (DMF) can be well interpreted by an equation which is derived on the basis of the assumptions that the adsorption of the oxidation product, $Hg(EtNH_2)_2^{2+}$, follows the Langmuir isotherm and that the adsorption coefficient of the product decreases exponentially as the electrode potential becomes more positive. The change in the adsorption coefficient was attributed to the change in the energy of the electrostatic repulsion between the ionic adsorbate and the positively-charged electrode with a potential. However, it is still uncertain whether or not the treatment can be generally applied to the prewaves due to the adsorption of ionic species. The present study was undertaken in order to extend the previous study to the prewaves of ammonia and alkylamines other than ethylamine, *i.e.*, methyl-, *n*-propyl-, isopropyl-, and *n*-butylamine.

Experimental

The solvent (DMF) and the supporting electrolyte (tetraethylammonium perchlorate) were purified as had been described previously.[2] The *n*-propylamine, isopropylamine, and *n*-butylamine were commercially-obtained and were used after distillation. Aqueous solutions of ammonia and methylamine obtained commercially (28 and 30% respectively) were used for polarography without removing the water.

The DC polarography was carried out with a Yanagimoto polarograph, model P8-DP. A cadmium-cadmium chloride electrode proposed by Marple[3] was used as the reference electrode instead of the bridged saturated calomel electrode which had been used in the previous studies.[1,2] The cadmium electrode was connected with a cell solution by a DMF-methylcellulose bridge containing 0.5 M tetraethylammonium perchlorate. The reference electrode gave a stable and reproducible potential of −0.667 V *vs.* SEC. All the measurements were carried out at 25°C.

Results and Discussion

Electrode Reaction Mechanism. The polarographic behavior of *n*-propylamine, isopropylamine, and *n*-butylamine was examined over the wide concentration range from 0.1 to 100 mM. Similarly, the behavior of ammonia and methylamine, which had been examined previously,[2] was reinvestigated, since none of them had been examined at concentrations higher than 5 mM. The results for these depolarizers were very similar to one another and to that for ethylamine.[1] Thus, a dilute solution of each amine (below 0.5 mM) gave a single anodic wave. At concentrations higher than 1.0 mM, another anodic wave appeared in each amine, except ammonia, at a potential less positive than that of the main wave. In the case of ammonia, no prewave appeared until the concentration exceeded 5.0 mM. In every case, however, the prewave had the nature of an adsorption, whereas the total anodic wave was diffusion-controlled; this conclusion was confirmed by an examination of the dependence of the limiting currents on the amine concentrations and on the effective mercury pressure.

When mercury(II) perchlorate was added to each of the amine solutions, the polarographic wave of the resulting solution became partly cathodic. However, the half-wave potential of the total wave was scarcely influenced by the addition of the mercury(II) ion. When the concentration of the mercury(II) ion added becomes equal to half that of the amine, the total wave became completely cathodic. These results are similar to those for methyl- and ethylamine reported previously,[1,2] and it can likewise be considered that the anodic wave given by each amine in the present study is also due to the polarographically reversible oxidation of mercury to the 1 : 2 complex of mercury(II) with the amine (Eq. (1)):

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

Figure 1 shows the results of log-plots ($\log i/(i_d - i)^2$ *vs.* potential) for the anodic waves given by dilute solutions of *n*-propylamine, isopropylamine, and *n*-butylamine. Similar plots have been reported in a previous paper[2] for the cases of ammonia and methylamine. A straight line with a reciprocal slope of 0.030 V was obtained at the more positive potentials of the wave in each amine, as had been expected from the current-potential equation derived from Eq. (1).[2] The deviation of the plot from the straight line at the less positive potentials of each wave may be caused by the adsorption of the oxidation product, $Hg(am)_2^{2+}$,

1) Y. Matsui and Y. Date, This Bulletin, **46**, 460 (1973).
2) Y. Matsui, Y. Kurosaki, and Y. Date, This Bulletin, **46**, 147 (1973).
3) L. W. Marple, *Anal. Chem.*, **39**, 844 (1967).

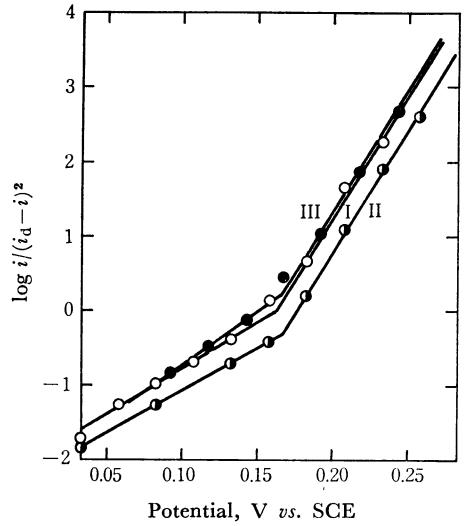

Fig. 1. Plots of log $i/(i_d-i)^2$ *vs.* potential for the waves of 0.44 mM *n*-$PrNH_2$ (I), 0.82 mM *iso*-$PrNH_2$ (II), and 0.50 mM *n*-$BuNH_2$ (III).

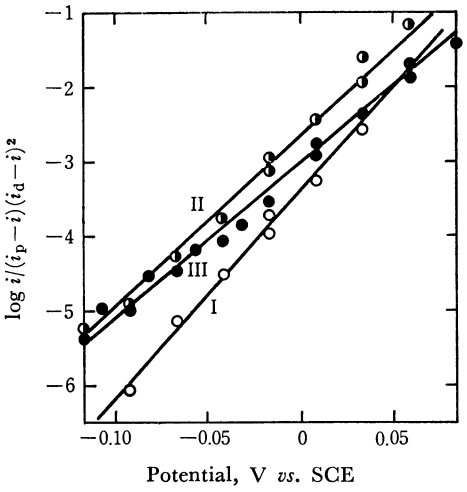

Fig. 2. Plots of log $i/(i_p-i)(i_d-i)^2$ *vs.* potential for the prewawes of NH_3 (I), *n*-$PrNH_2$ (II), and *n*-$BuNH_2$ (III). Reciprocal slope: I; 0.036 V, II; 0.044 V, III; 0.047 V.

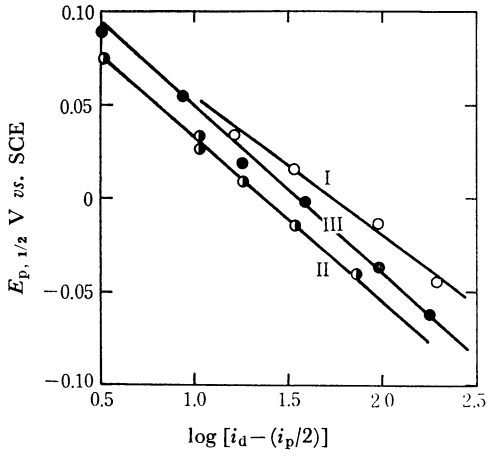

Fig. 3. Plots of the half-wave potentials of the prewaves of NH_3 (I), *n*-$PrNH_2$ (II), and *n*-$BuNH_2$ (III). *vs.* log $[i_d-(i_p/2)]$. Slope: I; −0.072 V, II; −0.088 V, III; −0.090 V.

on the electrode surface.

Analyses of the Adsorption Prewaves. According to a previous paper,[1] if the adsorption of the oxidation product, $Hg(am)_2^{2+}$, follows the Langmuir isotherm, and if the adsorption coefficient of the complex exponentially decreases as the electrode potential becomes more positive, the plot of log $i/(i_p-i)(i_d-i)^2$ *vs.* the potential for the adsorption prewave of each amine should give a straight line with a reciprocal slope of $0.030/(1-\gamma)$ V at 25°C, where γ is a proportionality constant in the equation relating the adsorption energy of the mercury(II) complex to the electrode potential,[1] and where i_p is the height of the prewave. Likewise, the plot of the half-wave potential ($E_{p,1/2}$) of the prewave *vs.* log$[i_d-(i_p/2)]$ should be linear, with a slope of $-0.060/(1-\gamma)$ V at 25°C. These plots for ammonia, *n*-propylamine, and *n*-butylamine are shown in Figs. 2 and 3. In fact, the plot of log $i/(i_p-i)(i_d-i)^2$ *vs.* the potential was virtually linear at any concentration of any amine. The plot of $E_{p,1/2}$ *vs.* log$[i_d-(i_p/2)]$ was also virtually linear for each amine. Similar results were also obtained for methylamine and isopropylamine.

It is interesting that, in each amine, the absolute value of the slope in the plot of $E_{p,1/2}$ *vs.* log$(i_d-(i_p/2))$ is virtually equal to double that of the reciprocal slope in the plot of log $i/(i_p-i)(i_d-i)^2$ *vs.* the potential. This result agrees exactly with that expected theoretically. The values of γ evaluated from the slopes are listed in Table 1. Except for ammonia, all of them are virtually equal to one another. In ammonia, the value of γ is significantly smaller than those for alkylamines. This indicates that the mercury(II) complex of ammonia is more easily desorbed than those of alkylamines from the electrode surface as the electrode potential becomes more positive. In the adsorption of the mercury(II) complexes on the electrode, the electric repulsion between the positively-charged mercury (II) and the positively-charged electrode may be lowered by the shielding of the ligands present between them. In the complex of ammonia, however, the shielding effect may be small, probably because of the small size of the ligand. Therefore, the complex of ammonia may be more subject to the effect of the change in electric field in the vicinity of the electrode than the complexes of alkylamines. We will discuss this problem further later. In any event, all the results shown above clearly indicate that the present method of the analysis of an adsorption prewave is

Table 1. The proportionality constants, γ, for the complexes of mercury(II) with ammonia and alkylamines

Complexes	γ
$Hg(NH_3)_2^{2+}$	0.17
$Hg(MeNH_2)_2^{2+}$	0.32
$Hg(EtNH_2)_2^{2+}$	0.36[a]
$Hg(n\text{-}PrNH_2)_2^{2+}$	0.32
$Hg(iso\text{-}PrNH_2)_2^{2+}$	0.36
$Hg(n\text{-}BuNH_2)_2^{2+}$	0.36

a) Ref. 1.

applicable at least to the prewaves given by any alkylamines.

Some Physicochemical Properties of Alkylamines and Their Mercury(II) Complexes in DMF. Table 2 shows the diffusion coefficients (D_a) of several amines in DMF. They were evaluated from the total height of the anodič wave of each amine on the basis of the Ilkovič equation. The value of D_a decreases with an increase in the molecular weight of the amine. According to Kolthoff and Lingane,[4] the diffusion coefficient of uncharged substances is inversely proportional to the cube root of the molecular weight (M) of the substances. In fact, the plot of log D_a *vs.* log M for the amines studied was roughly linear, with a slope of -0.33 (Fig. 4). This shows that no alkylamines are essentially subject to solvation in DMF.

Table 3 shows the diffusion coefficients (D_c) of the mercury(II) complexes of ammonia and several alkylamines, as well as that of the mercury(II) ion. They were also evaluated from the height of the reduction wave of each mercury(II) complex or the mercury (II) ion on the basis of the Ilkovič equation. It is interesting that no values of D_c are so different from one another as the values of D_a are. It even seems that

Table 2. Diffusion coefficients of ammonia and alkylamines in DMF at 25°C

Compounds	Diffusion coefficients (cm^2/s)
NH_3	19.9×10^{-6} a)
$MeNH_2$	19.0×10^{-6}
	18.8×10^{-6} a)
$EtNH_2$	16.3×10^{-6}
n-$PrNH_2$	15.2×10^{-6}
isoPrNH_2	15.1×10^{-6}
n-$BuNH_2$	13.0×10^{-6}
Ethylenediamine	15.0×10^{-6} a)
1,2-Diaminopropane	12.9×10^{-6} a)

a) Ref. 2.

Table 3. Diffusion coefficients of the simple mercury(II) ion and the complexes of mercury(II) with ammonia and alkylamines in DMF at 25°C

Compounds	Diffusion coefficients (cm^2/s)
Hg^{2+}	3.9×10^{-6} a)
$Hg(NH_3)_2^{2+}$	3.7×10^{-6} b)
$Hg(MeNH_2)_2^{2+}$	4.0×10^{-6} b)
$Hg(EtNH_2)_2^{2+}$	3.6×10^{-6}
$Hg(n\text{-}PrNH_2)_2^{2+}$	4.4×10^{-6}
$Hg(iso\text{-}PrNH_2)_2^{2+}$	4.1×10^{-6}
$Hg(n\text{-}BuNH_2)_2^{2+}$	4.1×10^{-6}
$Hg(en)_2^{2+}$ c)	5.6×10^{-6} b)
$Hg(pn)_2^{2+}$ c)	4.8×10^{-6} b)

a) Y. Matsui and Y. Date, This Bulletin, **43**, 2052 (1970). b) Ref. 2. c) en: Ethylenediamine; pn: 1,2-Diaminopropane

4) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, New York, N. Y. (1952), p. 57.

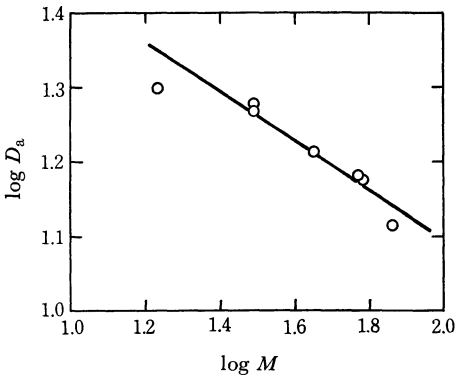

Fig. 4. Plot of log D_a *vs.* log M. Slope: -0.33

the values of D_c are virtually equal to one another. Since the mercury(II) ion usually forms a complex in which four ligands coordinate in the tetrahedral configuration, the "simple" mercury(II) ion may actually be coordinated by four molecules of the solvent, DMF. This idea is supported by the fact that the value of D_c is too small for the "simple" mercury (II) ion to be really simple. When the solvated mercury(II) ion forms a complex with ammonia or alkylamine, two of the four molecules of DMF coordinating to the mercury(II) ion are replaced by two molecules of the ammonia or the amine. In this case, however, it seems that the molecular weight or the size of the mercury(II) complex does not significantly change with the change in the kind of ligand. This may be the reason why the value of D_c is virtually invariant, irrespective of the kind of ligand in the mercury(II) complex.

Table 4 shows the overall stability constants (β_2) of the $Hg(am)_2^{2+}$ complex. They were evaluated from the results of the log-plots given in Fig. 1 in a manner which has been described previously.[2] All the values obtained are approximately equal to one another. There is no apparent tendency for the value of β_2 to increase or decrease with an increase in the size of the alkyl groups of the amines. According to Bjerrum,[5] the value of β_2 in an aqueous solution increases with an increase in the basic strength of

Table 4. Overall stability constants (β_2) of the complexes of mercury(II) with ammonia and alkylamines in DMF at 25°C

Complexes	β_2, $l\cdot mol^{-1}$
$Hg(NH_3)_2^{2+}$	$10^{17.0}$ ($10^{16.9}$ a))
$Hg(MeNH_2)_2^{2+}$	$10^{17.0}$ ($10^{17.1}$ a))
$Hg(EtNH_2)_2^{2+}$	$10^{16.5}$ b)
$Hg(n\text{-}PrNH_2)_2^{2+}$	$10^{16.7}$
$Hg(iso\text{-}PrNH_2)^{2+}$	$10^{16.3}$
$Hg(n\text{-}BuNH_2)_2^{2+}$	$10^{16.8}$
$Hg(en)_2^{2+}$ c)	$10^{23.5}$ a)
$Hg(pn)_2^{2+}$ c)	$10^{24.0}$ a)

a) Ref. 2. b) Ref. 1. c) en: Ethylenediamine; pn: 1,2-Diaminopropane

5) J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950).

Table 5. Adsorption characteristics of the complexes of mercury(II) with ammonia and alkylamines on the mercury electrode in DMF at 25°C

Complexes	Z[a] mol/cm²	a[b] Å²/molecule	w_0[c] l/mol
$Hg(NH_3)_2^{2+}$	1.28×10^9	13.0	0.2×10^6
$Hg(MeNH_2)_2^{2+}$	1.24×10^9	13.4	0.8×10^6
	1.41×10^9 [d]	11.8[d]	
$Hg(EtNH_2)_2^{2+}$	1.17×10^9 [e]	14.2[e]	4.6×10^6
$Hg(n\text{-}PrNH_2)_2^{2+}$	0.79×10^9	21.0	2.5×10^6
$Hg(iso\text{-}PrNH_2)_2^{2+}$	0.87×10^9	19.1	1.6×10^6
$Hg(n\text{-}BuNH_2)_2^{2+}$	0.82×10^9	20.2	1.0×10^6

a) Z: The maximal amount of the adsorbate per unit area. b) a: The area of the electrode surface occupied by one adsorbate molecule. c) w_0: The adsorption coefficient of the adsorbate complex at 0.0 V *vs.* SCE. d) Ref. 2. e) Ref. 1.

amine. However, no such relation was observed in the present case. It is notable that the mercury(II) complexes of diamines are more stable than those of monoamines by a factor of about 10^7. This may be due to the chelate formation in the former complexes.

Table 5 shows the adsorption characteristics for the mercury(II) complexes of ammonia and alkylamines on the mercury electrode. The maximal amount of the adsorbate per unit of area (Z) and the area (a) of the electrode surface occupied by one adsorbate molecule were evaluated from the heights of the prewaves of ammonia and alkylamines by the use of an equation described previously.[2] The adsorption coefficients (w_0) of the adsorbates at 0.0 V *vs.* SCE were evaluated from the results of the log-plots in Fig. 2 in a manner which has previously been reported.[1] The values of a thus obtained are reasonable for the size of the mercury(II) complexes. They increase with an increase in the size of the alkyl groups of the amines. It is uncertain whether the alkyl groups in the mercury(II) complexes are oriented horizontally or vertically to the electrode surface. However, the values of a are large enough to suggest that the alkyl groups are horizontally oriented to the electrode surface.

An interesting result was obtained with regard to the value of w_0. Thus, the value for the complex of ammonia was the smallest of all, whereas that for the complex of ethylamine was the largest. With a further increase in the size of the alkyl groups of amines, the value of w_0 decreased. It seems that the value of w_0 is a measure of the adsorptivity of the mercury(II) complexes on the electrode surface. The larger the value of w_0, the stronger is the adsorptivity, and *vice versa*. In the adsorption of the mercury(II) complex on the mercury electrode immersed in a DMF solution, the hydrophobic interaction between the alkyl groups of the adsorbate complexes and the electrode may play no important role because of the high solubility of the aliphatic groups in the solution, although such an interaction is very important for the adsorption in an aqueous solution.[6] The interaction between the amino groups of the ligands and the electrode may also be negligible, for no alkylamines are significantly adsorbed on the electrode. Therefore, the adsorption of the mercury(II) complexes on the electrode may be caused by the attractive interaction between the mercury(II) ion and the electrode mercury. If so, the attractive force may decrease with an increase in the size of the ligand alkylamines present between the mercury(II) ion and the electrode. This may be responsible for the fact that the value of w_0 decreases in the order of the mercury(II) complexes of ethylamine, *n*-propylamine, isopropylamine, and *n*-butylamine. On the other hand, the w_0 values of the mercury(II) complexes of ammonia and methylamine are smaller than that of the ethylamine complex. In these cases, the ligands are so small that the mercury(II) ion in the complexes may be subject to the strong force of electrostatic repulsion from the electrode which is positively charged at 0.0 V *vs.* SCE. This presumption is in agreement with that derived above on the basis of the values of γ. Thus, the adsorptivity of each complex of mercury(II) with alkylamine may eventually be determined by the relative values of the two kinds of force, *i.e.*, the chemical attractive force and the electrostatic repulsive force of the electrode mercury acting on the mercury(II) ion.

In the present study, only ammonia and primary alkylamines have been examined. However, secondary alkylamines also give an anodic adsorption prewave, as has been reported previously.[2] This will be dealt with in a succeeding paper.

6) B. B. Damaskin and A. N. Frumkin, "Reactions of Molecules at Electrode," ed. by N. S. Hush, John Wiley & Sons, London (1971), p. 1.