

Landskoener and Laidler¹⁷ have derived another equation for the dielectric constant dependence of

(17) P. A. Landskoener, Dissertation submitted to the Graduate School of Arts and Sciences of the Catholic University of America, Washington, D. C.

the rate of ion-dipole reaction rates. This equation purportedly takes proper cognizance of the charge distribution in the reactants and activated complex.

FAYETTEVILLE, ARK.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE STATE COLLEGE OF WASHINGTON]¹

Polarographic Investigation of the Ethylenediamine, 1,2-Propanediamine and Diethylenetriamine Complexes of Mercury(II)

BY C. J. NYMAN, D. K. ROE AND D. B. MASSON

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The complex ions formed by mercury(II) ion with three polyamines at 25° were investigated by a modification of the polarographic method. The data were interpreted as indicating the existence of the ions $[\text{Hg}(\text{en})_2]^{++}$, $K_2 = 1.5 \times 10^{23}$; $[\text{Hg}(\text{pn})_2]^{++}$, $K_2 = 3.4 \times 10^{23}$; and $[\text{Hg}(\text{dien})_2]^{++}$, $K_2 = 1.15 \times 10^{25}$. A value of 1.2×10^{18} was calculated for the formation constant of the ion $[\text{Hg}(\text{dien})]^{++}$. These complex ions alone do not allow a complete interpretation of the data. An interpretation based on the possible existence of complexes containing more than two amine molecules per mercury(II) ion is presented.

There are several reports of investigations of the complex ions of mercury(II) ion with polyamines which are pertinent to this investigation. A report of the stability of complex ions formed between mercury(II) ion and ethylenediamine² was made by Bjerrum.³ For the logarithm of the mean complexity constant, Bjerrum reported the value 11.71. Thus, for the ion $[\text{Hg}(\text{en})_2]^{++}$, an over-all formation constant of 2.6×10^{23} is indicated. A polarographic investigation by Mason and Watters⁴ indicated the formation constant of this same ion to have a value of 4.5×10^{22} .

Prue and Schwarzenbach^{5,6} have investigated by pH methods the complex ions formed by mercury(II) ion with diethylenetriamine. In chloride and in bromide media, the complex ion formed appeared to contain both halide and diethylenetriamine. In 0.5 N sodium perchlorate, the data could not be interpreted to obtain a formation constant for $[\text{Hg}(\text{dien})]^{++}$. However, an equilibrium constant of approximately 1×10^7 for the reaction of $[\text{Hg}(\text{dien})]^{++}$ with diethylenetriamine to form $[\text{Hg}(\text{dien})_2]^{++}$ was obtained.

This paper reports the results of a polarographic investigation of the complexes of mercury(II) ion with three polyamines. A preliminary investigation of the ethylenediamine complexes⁷ was completed about the time that the work of Mason and Watters was reported. It was undertaken initially in order to compare the formation constants obtained by the method employed with those obtained by Bjerrum, presumably from pH measurements. The diethylenetriamine system was reinvestigated in an attempt to obtain a value for the

formation constant of $[\text{Hg}(\text{dien})_2]^{++}$ from mercury(II) ion and diethylenetriamine in the absence of halogen. There appeared to be no reports of previous investigations of the stability of mercury-1,2-propanediamine complexes, and so this system was also studied.

Data and Discussion

General.—The usual procedure followed in the polarographic investigation of complex ions is to determine the effect of different concentrations of complexing agent on the half-wave potential of the metal ion. In such a case, the relationship between the half-wave potential of the metal ion and the concentration of complexing agent is given by eq. 1. $(E_{1/2})_c$ and $(E_{1/2})_s$ are half-wave potentials of

$$(E_{1/2})_s = (E_{1/2})_c + \frac{RT}{nF} \ln (C_x)^j K_j \quad (1)$$

the complex and simple metal ions; C_x is the concentration of the complexing agent; and K_j is the formation constant of the complex ion MX_j from the simple metal ion and j molecules of the complexing agent.^{8,9}

In this investigation, the effect of changing the concentration of complexing agent on the oxidation potential of mercury to mercuric ion was determined. The difference in oxidation potentials of the complex and simple mercuric ions is given by an equation entirely analogous to equation 1, with the exception that the potentials involved are not half-wave potentials, but the potentials of the electrode at an arbitrary current. As has been pointed out by Kolthoff and Miller,¹⁰ the potential of a mercury electrode in equilibrium with the surrounding liquid is given by equation 2. In this expression

$$E_{\text{d.e.}} = E_{\text{Hg}^{2+}}^0 + \frac{RT}{nF} \ln [\text{Hg}^{2+}]_0 = E_{\text{Hg}^{2+}}^0 + \frac{RT}{nF} \ln [\text{Hg}^{++}]_0 \quad (2)$$

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(2) The names of ethylenediamine, 1,2-propanediamine and diethylenetriamine have been abbreviated (en), (pn) and (dien), respectively.

(3) J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

(4) J. Mason and J. I. Watters, Paper No. 91 presented before the Division of Physical and Inorganic Chemistry at the 125th National A.C.S. Meeting, Kansas City, Mo., March 23 to April 1, 1954.

(5) G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 947 (1950).

(6) J. E. Prue and G. Schwarzenbach, *ibid.*, **33**, 985 (1950).

(7) C. J. Nyman, Progress Report No. 7 to Office of Ordnance Research, Project No. DA-04-200-ORD-65, March 1, 1953.

(8) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946.

(9) D. D. DeFord and D. N. Hume, *THIS JOURNAL*, **73**, 5321 (1951).

(10) I. M. Kolthoff and C. S. Miller, *ibid.*, **63**, 1405 (1941).

$E_{d.e.}$ is the potential of the dropping mercury electrode; $E_{\text{Hg}_2^{++}}^{\circ}$ and $E_{\text{Hg}^{++}}^{\circ}$ are the standard oxidation potentials of the mercury-mercury(I) ion and mercury-mercury(II) ion couples, respectively; $[\text{Hg}_2^{++}]_0$ and $[\text{Hg}^{++}]_0$ are the surface concentrations of mercury(I) and mercury(II) ions, respectively.

On electrooxidation of mercury in the absence of a complexing agent, mercury is oxidized primarily to mercury(I) ion, the mercury(II) ion concentration being relatively small. The concentration of mercury(I) ion at the electrode surface is proportional to the current flowing; this proportionality can be expressed in the form of equation 3. In equation 3, i is the current which is flowing

$$i = k_{\text{Hg}_2^{++}}[\text{Hg}_2^{++}] \quad (3)$$

in microamperes (an anodic current is considered here to have a positive sign), and $k_{\text{Hg}_2^{++}}$ is a constant dependent in part on the electrode characteristics. By combining equations 2 and 3 and combining constants, the resulting equation 4 describes the polarographic curve for the oxidation process. In equation 4, the potential quantity $E'_{\text{Hg}_2^{++}}$ is a constant which is equal to the potential

$$E_{d.e.} = E'_{\text{Hg}_2^{++}} + \frac{RT}{nF} \ln i \quad (4)$$

of the dropping mercury electrode when the current flowing is one microampere. A plot of $E_{d.e.}$ vs. $\log i$ should produce a slope of 0.0296 volts at 25°. An experimental test of this equation by Kolthoff and Miller yielded a slope of 0.032 volt, indicating that the polarographic oxidation process is a reversible one. In the present investigation, the average value of $E'_{\text{Hg}_2^{++}}$ was found to be 0.423 ± 0.002 volt vs. S.C.E.

If mercury were to be oxidized to the simple mercury(II) ion, an equation similar to equation 4 would describe the polarographic curve, the difference being the replacement of the constant $E'_{\text{Hg}_2^{++}}$ by another constant $E'_{\text{Hg}^{++}}$. Since mercury is more easily oxidized to mercury(I) ion than to mercury(II) ion, the constant $E'_{\text{Hg}^{++}}$ cannot be evaluated directly. It can, however, be easily calculated. The difference between $E'_{\text{Hg}^{++}}$ and $E'_{\text{Hg}_2^{++}}$ should be equal to the difference between their standard electrode potentials, provided the assumption is made that the differences in diffusion current constants is negligible. From the diffusion coefficients determined by Kolthoff and Miller, the calculated effect of the difference in diffusion current constants is less than 1 mv. The polarographic oxidation potential of mercury, $E'_{\text{Hg}^{++}}$, is calculated to be 0.488 volt vs. the S.C.E.

In the presence of a substance which complexes mercury(II) ion, but not mercury(I) ion, mercury is oxidized to the divalent state. The equation for the polarographic curve is given by equation 5

$$E_{d.e.} = (E'_{\text{Hg}^{++}})_c + \frac{RT}{nF} \ln i \quad (5)$$

where $(E'_{\text{Hg}^{++}})_c$ is a constant equal to the potential $E'_{d.e.}$ when the current flowing is one microampere. A plot of $E_{d.e.}$ vs. $\log i$ should have a reciprocal slope of 0.0296 volt for a reversible two-electron oxidation at 25°. Experimentally it was found that this

slope varied between 0.030 and 0.034 volt. The value of $(E'_{\text{Hg}^{++}})_c$ is best obtained from such plots. Equation 5 is valid only when the assumption can be made that the concentration of the complexing agent in the bulk of the solution and at the electrode surface are the same.

The potential $(E'_{\text{Hg}^{++}})_c$ is related to concentration of complexing agent and the formation constant of the complex ion by equation 6. If the quantity

$$(E'_{\text{Hg}^{++}})_c = E'_{\text{Hg}^{++}} - \frac{RT}{nF} \ln K_f(C_x)^i \quad (6)$$

$[E'_{\text{Hg}^{++}} - (E'_{\text{Hg}^{++}})_c]$ is plotted against $\log C_x$, a straight line should be obtained if only one species of complex ion exists over the concentration range investigated. The slope of this line should be $2.303 jRT/nF$, or for a two-electron oxidation at 25°, 0.0296j volts.

Ethylenediamine Solutions.—In Table I are presented the data for the variation of $[E'_{\text{Hg}^{++}} - (E'_{\text{Hg}^{++}})_c]$ with ethylenediamine concentration. The free amine concentration in the solutions was calculated¹¹ by making use of the known values for the total ethylenediamine added, the pH, and the values of the acid dissociation constants ($pK_1 = 7.18$, $pK_2 = 9.96$) obtained by Murbach¹² for ionic strength 0.2 at 25°.

TABLE I
EXPERIMENTAL VALUES OF $[E'_{\text{Hg}^{++}} - (E'_{\text{Hg}^{++}})_c]$ AS A
FUNCTION OF ETHYLENEDIAMINE CONCENTRATION FOR 25°
IN 0.1 M KNO₃

(en)total (mole/l.)	pH	(en) (moles/l.)	$[E'_{\text{Hg}^{++}} - (E'_{\text{Hg}^{++}})_c]$ (volts)
0.0204	11.09	0.0191	1.585
.0409	11.27	.039	.602
.0613	11.35	.059	.614
.0818	11.43	.079	.621
.1022	11.48	.099	.628
.164	11.67	.160	.640
.204	11.70	.201	.645
.307	11.89	.303	.659
.409	11.73	.402	.666
.511	11.80	.504	.673
.715	11.89	.707	.683
1.022	12.02	1.013	.694
1.533	12.18	1.525	.707
1.939	12.23	1.929	.715
2.49	12.52	2.48	.726
3.59	12.85	3.58	.745

By a plot of $[E'_{\text{Hg}^{++}} - (E'_{\text{Hg}^{++}})_c]$ vs. $\log(en)$, it was found that the ion $[\text{Hg}(\text{en})_2]^{++}$ is the predominant complex ion present in the solution below approximately 1.0 M amine concentration. Above 1.0 M, the plot deviates from a straight line. This is usually taken to indicate the presence of one or more additional species of complex ions.

If the data in Table I are interpreted by the graphical method of DeFord and Hume,⁹ the formation constant K_2 of the ion $[\text{Hg}(\text{en})_2]^{++}$ is found to be 1.5×10^{28} , a value in reasonable agreement with that reported by Bjerrum and by Mason and Wat-

(11) J. Bjerrum, "Metal Amine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p. 202.

(12) E. W. Murbach, unpublished results.

ters. The ion $[\text{Hg}(\text{en})_3]^{++}$ is also indicated, with a formation constant $K_3 \cong 1.15 \times 10^{23}$. Above 2.0 M there is some indication of still another species of complex ion, possibly $[\text{Hg}(\text{en})_4]^{++}$.

Some support is given this interpretation by a study of the refractive index of solutions of mercury(II) chloride and ethylenediamine reported by O'Brien.¹³ In a plot of refractive index *vs.* ratio of moles of ethylenediamine to moles of mercury, breaks in the curve occur at 3 and 4 moles of ethylenediamine per mole of mercury. This might be interpreted as indicating the existence of the ions $[\text{Hg}(\text{en})_3]^{++}$ and $[\text{Hg}(\text{en})_4]^{++}$.

The acceptance of the presence of $[\text{Hg}(\text{en})_3]^{++}$ and $[\text{Hg}(\text{en})_4]^{++}$ should be made with caution. In the first place, the activity coefficients of the ions and the free amine have not been included since no values appear to be available. Secondly, several assumptions are involved relative to the constancy of the diffusion current constants of the simple and complex ions. Thirdly, an interpretation of the data based on the existence of the ion $[\text{Hg}(\text{en})_2(\text{OH})]^+$ along with the $[\text{Hg}(\text{en})_2]^{++}$ ion is possible, although the data are not fitted so well as with the added ethylenediamine groups.

1,2-Propanediamine Solutions.—As was expected, the mercury(II)–1,2-propanediamine system was found to be analogous to the ethylenediamine system. In Table II are recorded the data obtained for the solutions investigated. The free propylenediamine concentration was estimated

TABLE II
EXPERIMENTAL VALUES OF $[E'_{\text{Hg}^{++}} - (E'_{\text{Hg}^{++}})_c]$ AS A FUNCTION OF 1,2-PROPANEDIAMINE CONCENTRATION FOR 25° IN 0.1 M KNO_3

(pn) total (mole/l.)	pH	(pn) (mole/l.)	$[E'_{\text{Hg}^{++}} - (E'_{\text{Hg}^{++}})_c]$ (volts)
0.0215	11.01	0.0196	0.596
.0429	11.18	.0403	.616
.0644	11.29	.0613	.627
.1072	11.40	.1032	.641
.150	11.50	.146	.648
.215	11.62	.210	.658
.329	11.72	.316	.668
.429	11.80	.423	.677
.537	11.87	.530	.683
.751	11.88	.741	.693
1.073	12.01	1.065	.704
1.609	12.20	1.599	.717
2.04	12.36	2.03	.728
2.94	12.53	2.94	.742
4.11	12.92	4.10	.767

(13) T. D. O'Brien, *THIS JOURNAL*, **70**, 2771 (1948).

using values of $pk_1 = 7.13$ and $pk_2 = 10.00$, as reported by Basolo, Murmann and Chen.¹⁴

A plot of $[E'_{\text{Hg}^{++}} - (E'_{\text{Hg}^{++}})_c]$ *vs.* $\log(\text{pn})$ indicates that the predominant ion below about 1.0 M amine has the formula $[\text{Hg}(\text{pn})_2]^{++}$. Above this concentration, the points deviate from a straight line, indicating the presence of higher species of complex ions. Using the method of DeFord and Hume, the ions $[\text{Hg}(\text{pn})_2]^{++}$ and $[\text{Hg}(\text{pn})_3]^{++}$ are indicated, and the formation constants of these ions are $K_2 = 3.4 \times 10^{23}$ and $K_3 \cong 1.8 \times 10^{23}$. Again there was some indication of an additional species, possibly $[\text{Hg}(\text{pn})_4]^{++}$. The values of the formation constants of these ions are entirely reasonable and of the order of magnitude expected by analogy with the ethylenediamine complexes.

Diethylenetriamine Solutions.—The values of $[E'_{\text{Hg}^{++}} - (E'_{\text{Hg}^{++}})_c]$ for various concentrations of amine are recorded in Table III. The free amine concentration was calculated using values of $pk_1 = 4.34$, $pk_2 = 9.13$ and $pk_3 = 9.94$ as reported by Prue and Schwarzenbach⁶ for 0.1 M potassium chloride at 25°. The ions $[\text{Hg}(\text{dien})_2]^{++}$ and $[\text{Hg}(\text{dien})_3]^{++}$ appear to be present, and to have the formation constants $K_2 = 1.15 \times 10^{25}$ and $K_3 \cong 1 \times 10^{24}$, respectively. There is also some indication of a complex of the formula $[\text{Hg}(\text{dien})_4]^{++}$.

TABLE III
EXPERIMENTAL VALUES OF $[E'_{\text{Hg}^{++}} - (E'_{\text{Hg}^{++}})_c]$ AS A FUNCTION OF DIETHYLENETRIAMINE CONCENTRATION FOR 25° IN 0.1 M KNO_3

(dien) total (mole/l.)	pH	(dien) (mole/l.)	$[E'_{\text{Hg}^{++}} - (E'_{\text{Hg}^{++}})_c]$ (volts)
0.0200	11.00	0.0184	0.637
.0399	11.12	.0374	.658
.0599	11.30	.0574	.668
.0988	11.42	.0955	.682
.1397	11.53	.1362	.690
.1996	11.58	.195	.701
.299	11.59	.293	.711
.399	11.72	.393	.719
.499	11.71	.490	.725
.700	11.85	.692	.736
.998	12.00	.990	.748
1.497	12.20	1.490	.763

By combining the value of K_2 obtained here with the second complexity constant ($k_2 = 1 \times 10^7$) obtained by Prue and Schwarzenbach,⁶ the value of the formation constant K_1 of the ion $[\text{Hg}(\text{dien})]^{++}$ is calculated to be 1.2×10^{18} .

PULLMAN, WASHINGTON

(14) F. Basolo, R. K. Murmann and Y. T. Chen, *ibid.*, **75**, 1478 (1953).