TABLE I

Compound	Copper, % Theoretical	Copper, % Found	Chloride, % Theoretical	Chloride, % Found
Bis-methylammoniumtetrachlorocuprate(II)	23.58	23.50 ± 0.06	52.63	52.50 ± 0.10
Bis-dimethylammoniumtetrachlorocuprate(II)	21.35	21.18 ± .06	47.65	47.28 ± .10
Bis-trimethylammoniumtetrachlorocuprate(II)	19.51	19.53 ± .08	43.56	43.50 ± .12
Bis-tetramethylammoniumtetrachlorocuprate(II)	17.97	17.97 ± .06	40.09	39.90 ± .12
Bis-ethylammoniumtetrachlorocuprate(II)	21.35	21.26 ± .07	47.65	47.66 ± .09
Bis-triethylammoniumtetrachlorocuprate(II)	15.53	15.51 ± .08	34.66	35.68 ± .10
Bis-*n*-butylammoniumtetrachlorocuprate(II)	17.97	17.84 ± .07	40.09	40.15 ± .12
Bis-isobutylammoniumtetrachlorocuprate(II)	17.97	17.94 ± .08	40.09	40.00 ± .12
1,6-Hexane-di-ammoniumtetrachlorocuprate(II)	19.95	20.13 ± .08	43.81	44.22 ± .10

sorption spectra of these compounds give some rather unusual results. The spectra are quite different in methanol, acetone and isopropyl alcohol, indicating the compounds are reacting with the solvent.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Polarographic and Solubility Studies on Mercuric Oxycyanide[1]

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Studies on the solubility of mercuric oxide in aqueous mercuric cyanide solutions indicate the product to be HgOHCN. The equilibrium constant, K_m, of the reaction $Hg(CN)_2 + Hg(OH)_2 = 2HgOHCN$ was found to be 260 at 23° and an ionic strength of 2.0 by this method. Polarographic reduction of mercuric oxycyanide solution gave a value of 280 for K_m. The dissociation constant of mercuric hydroxide, measured polarographically, was found to be 4.0×10^{-22}. The formation constant of mercuric hydroxycyanide is 7.3×10^{28}.

Introduction

Mercuric cyanide solutions have long been known to dissolve significant amounts of mercuric oxide,[2] and from these solutions solid mercuric oxycyanide, usually written $HgO \cdot Hg(CN)_2$, can be obtained. Friend[3] gives numerous references on the preparation and reactions of the solid, which has been used extensively in pharmacy. Little or nothing appears to have been done about determining the properties of the compound in solution other than some early cryoscopic studies[4] and the present investigation deals with this problem.

Materials and Methods

All the chemicals were of reagent grade and deionized distilled water was employed throughout. The mercuric oxide was Mallinckrodt "mercuric oxide, yellow." Solubility studies were carried out by shaking mercuric oxide in excess with mercuric cyanide solutions for five days in a constant temperature room. Total dissolved mercury was determined by pipetting an aliquot into 50 ml. of a mixture containing 0.2 *M* sodium cyanide, 1.8 *M* sodium nitrate and 0.008% gelatin. The *p*H of this mixture was 11.5. The sample then was made up to 100 ml. with 2.0 *M* sodium nitrate for measurement of the diffusion current of mercury. Under these conditions, the diffusion current is linear with mercury concentration and independent of small changes in cyanide ion concentration. Polarographic measurements were carried out using the apparatus and technique described in a previous communication.[5]

Solubility Studies.—Excess mercuric oxide was shaken at 23° for five days with 2 *M* sodium nitrate solutions containing various known concentrations of mercuric cyanide. The *p*H before and after shaking was approximately 6.5. Filtered samples were taken for polarographic analysis. The time allowed was found to be more than sufficient to attain equilibrium. The results are summarized in Table I.

TABLE I

SOLUBILITY OF HgO IN $Hg(CN)_2$ SOLUTIONS, 2.0 *M* IN $NaNO_3$[a]

a	*t*	*a* − *x*	*x*
0	0.39	..	..
1.00	2.35	0.04	0.96
2.00	4.22	.17	1.83
5.00	9.57	.82	4.18
10.0	18.2	2.18	7.82
50.0	77.2	23.2	26.8

[a] All concentrations in millimoles per liter. *a* = initial concentration of $Hg(CN)_2$, *t* = total concentration of Hg(II) in equilibrium mixture, *a* − *x* = concentration of free $Hg(CN)_2$ at equilibrium, *x* = formal concentration of $HgO \cdot Hg(CN)_2$ at equilibrium.

The simplest equation which can be written for the reaction is

$$HgO(s) + Hg(CN)_2 \longrightarrow HgO{\cdot}Hg(CN)_2 \quad (1)$$

assuming that the reactants combine in a ratio of 1:1. This assumption is in accord with the composition of the solid product which can be obtained by evaporation and it was found that the data do not fit other assumptions such as 1:2 or 2:1 combining ratios. If *a* is the initial concentration of mercuric cyanide and *x* is the formal concentration of the product, $(a - x)$ becomes the equilibrium concentration of mercuric cyanide. The total analytical concentration of mercury in solution, *t*, if corrected for the solubility of mercuric oxide in the absence of mercuric cyanide may be designated t', which is then seen to be $t' = (a - x) + 2x = (a + x)$. Thus *x* is readily determinable from the known values of *a*, the solubility of mercuric oxide and the corresponding measured values of *t*. If dissolved mercuric oxy-

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(1) Taken in part from the Ph.D. Thesis of Leonard Newman, Massachusetts Institute of Technology, June, 1956. This work was supported in part by the Atomic Energy Commission under Contract AT(30-1)905.

(2) J. F. W. Johnston, *Phil. Trans.*, 113 (1839).

(3) J. Newton Friend, "A Textbook of Inorganic Chemistry," Vol. III, Part 2, Griffin and Co., London, 1926.

(4) K. Holdermann, *Arch. Pharm.*, **244**, 133 (1906).

(5) L. Newman, J. deO. Cabral and D. N. Hume, THIS JOURNAL, **80**, 1814 (1958).

cyanide exists as written in eq. 1, the quantity $x/(a - x)$ will be a constant, whereas if it is actually HgOHCN, the quantity $(2x)^2/(a - x)$ will be constant. This is most readily tested by plotting log x *versus* log $(a - x)$. When this was done with the data of Table I, a good straight line with a slope of 0.55 was obtained, indicating clearly that the product in solution should be written HgOHCN.

It was shown by Garrett and Hirshler[6] that dissolved mercuric oxide exists essentially completely as undissociated mercuric hydroxide. Accordingly, one may write for the formation of the mercuric hydroxycyanide in solution

$$Hg(OH)_2 + Hg(CN)_2 \longrightarrow 2HgOHCN \qquad (2)$$

and from the data in Table I evaluate the corresponding equilibrium constant, K_m, for the formation of the compound in a medium having an ionic strength of two. The solubility of mercuric oxide in 2.0 M sodium nitrate was found to be 3.9×10^{-4} M, in good agreement with the value of 4.0×10^{-4} observed by Garrett and Hirshler, who also worked at an ionic strength of two. Utilizing our value of the solubility of mercuric oxide to determine the values of x and $a - x$ from the observed values of i in Table I, an average value of K_m equal to 260 ± 30 was obtained.

Polarographic Studies

Theory.—Exploratory polarograms of mercuric hydroxy cyanide solutions showed the presence of a cathodic wave at approximately +0.05 v. *versus* the S.C.E., and falling between the anodic wave of hydroxide ion and the cathodic wave of free mercuric cyanide (Fig. 1). This wave can be attributed to reduction of the species HgOHCN. The equation of the wave is derived readily.

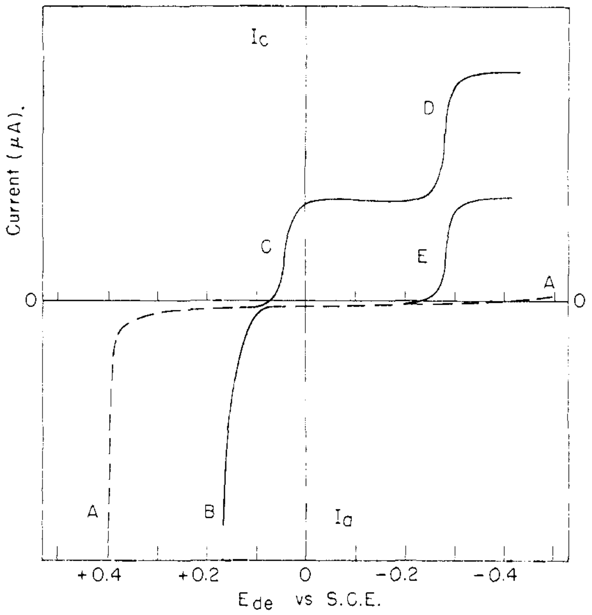

Fig. 1.—Polarographic characteristics of mercuric hydroxycyanide and related substances: A, residual current of sodium nitrate; B, anodic wave of hydroxide ion; a diffusion plateau is formed at low concentrations; C, mercuric hydroxycyanide wave; D, E, mercuric cyanide wave.

The net electrode reaction for the reduction of the basic cyanide in the potential region between the hydroxide and mercuric cyanide waves is

$$2HgOHCN + 2e^- = Hg^0 + 2OH^- + Hg(CN)_2 \qquad (3)$$

If the electrode reaction is reversible, we may substitute for the activity of mercuric ion in the equation for the potential of the dropping electrode

$$E_{de} = E_0 + 0.030 \log (a_{Hg^{++}}/a_{Hg^0}) \qquad (4)$$

the value obtained by combining K_m, the equilibrium constant of eq. 2, with K_{OH}, the formation constant of mercuric hydroxide. This leads to the expression

$$E_{de} = E_0 + 0.030 \log \frac{[C^0_{HgOHCN}]^2}{[C^0_{OH^-}]^2[C^0_{Hg(CN)_2}]\,K_{OH}K_m} \qquad (5)$$

in which the symbol C^0 is used to indicate concentration at the surface of the drop. Equation 5 involves the usual assumption of constancy of activity coefficients in a medium of constant ionic environment. The proportionalities between electrode surface concentrations and current are seen to be $C^0_{HgOHCN} = (i_d - i)/d_m$; $C^0_{OH^-} = i/d_{OH^-}$, and $C^0_{Hg(CN)_2} = i/d_c$, and substitution in eq. 5 gives the equation of the wave

$$E_{de} = E_{f,m} + 0.030 \log \frac{(i_d - i)^2}{i^3} \qquad (6)$$

Here $E_{f,m}$ is the concentration-independent potential of the wave, which is analogous in the reduction of mercury compounds to the half-wave potential in ordinary polarograms.[5] Explicitly, $E_{f,m}$ is related to E_0 by the expression

$$E_{f,m} = E_0 + 0.030 \log \frac{d_{OH}{}^2 d_c}{K_{OH}K_m d_m{}^2} \qquad (7)$$

where d_{OH}, d_c and d_m are the proportionality constants between diffusion current and concentration for hydroxide ion, mercuric cyanide and mercuric hydroxycyanide, respectively. These are approximately proportional to the square roots of the corresponding diffusion coefficients.

In the special case where mercuric cyanide is added in large excess, the amount formed by the reduction of the basic cyanide can be considered negligible and the equation of the wave reduces to

$$E_{de} = E_{f,m}' + 0.060 \log \frac{i_d - i}{i} \qquad (8)$$

where

$$E_{f,m}' = E_0 + 0.030 \log \frac{d_{OH}{}^2}{K_{OH}K_m d_m{}^2[Hg(CN)_2]} \qquad (9)$$

Conversely, for the polarographic oxidation of mercury in hydroxide solutions containing an excess of mercuric cyanide, eq. 8 becomes

$$E_{de} = E_{f,m}' + 0.060 \log \frac{i}{i - i_a} \qquad (10)$$

where i_a is the anodic diffusion current of hydroxide ion. Combination of eq. 8 and 10 gives the equation of the mixed anodic–cathodic wave where hydroxide and basic mercuric cyanide are present in comparable concentrations and mercuric cyanide is in large excess

$$E_{de} = E_{f,m}' + 0.060 \log \frac{i_d - i}{i - i_a} \qquad (11)$$

A large second wave will be present due to the reduction of mercuric cyanide.

The polarographic characteristics of the hydroxide ion enter into the equations and must therefore be determined. Kolthoff and Miller[7] showed the anodic wave of hydroxide to be due to the formation of mercuric hydroxide and derived the equa-

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[6] A. B. Garrett and A. E. Hirshler, THIS JOURNAL, **60**, 299 (1938).

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

tion of the wave in terms of half-wave potential. In terms of E_f

$$E_{de} = E_{f,\mathrm{OH}} + 0.030 \log \frac{i}{(i - i_a)^2} \qquad (12)$$

and

$$E_{f,\mathrm{OH}} = E_0 + 0.030 \log \frac{d_{\mathrm{OH}}^2}{d_h K_{\mathrm{OH}}} \qquad (13)$$

in which d_h is the constant for mercuric hydroxide. The equation for the reduction wave of mercuric hydroxide is

$$E_{de} = E_{f,\mathrm{OH}} + 0.030 \log \frac{i_d - i}{i^2} \qquad (14)$$

Hydroxide.—Equations 12, 13 and 14 were first tested by analysis of polarograms of hydroxide ion and mercuric hydroxide. Plots of E *vs.* the logarithmic terms in equations 12 and 14 gave straight lines with the theoretical slope of 30 mv. The data and results are summarized in Table II. The value of $E_{f,\mathrm{OH}}$ is constant and independent of concentration and whether the polarogram is anodic or cathodic. From the values of $E_{f,\mathrm{OH}}$, d_{OH} and d_h in Table II and the standard potential of the mercury–mercuric ion couple[8] K_{OH} was calculated as 2.5×10^{21} at 30° and an ionic strength of 2.0. This may be considered in satisfactory agreement with the values 5.5×10^{21} from solubility measurements of Garrett and Hirshler,[6] 5.0×10^{21} from potentiometric data of Hietanen and Sillén[9] and 2.3×10^{21} from potentiometric measurements of Anderegg.[10]

TABLE II

POLAROGRAPHIC CHARACTERISTICS OF HYDROXIDE ION AND MERCURIC HYDROXIDE[a]

(OH^-),[b] $M \times 10^4$	$\mathrm{Hg(OH)_2}$, $M \times 10^4$	$E_{f,\mathrm{OH}}$ *vs.* S.C.E., v.	d_{OH},[b] μa./mM	d_h, μa./mM	$K_{\mathrm{OH}} \times 10^{-21}$
1.0	..	+0.116	27	..	2.9
3.2	..	.118	23	..	2.2
..	1.7	.117	..	8.0	2.5
Average		+0.117	25		2.5

[a] At 30° in 2.0 M sodium nitrate, 0.004% gelatin. [b] From measured pH.

Mercuric Hydroxycyanide.—Polarograms were run on mercuric hydroxycyanide solutions at a number of concentrations. Samples from the solubility study were used and diluted if necessary with sodium nitrate to keep the ionic strength constant at 2.00 M. The data and results are summarized in Table III. Plots of E_{de} *versus* $\log [(i_d - i)^2/i^3]$ gave good straight lines with slopes ranging between 28 and the theoretical 30 mv. $E_{f,m}$ should be independent of the concentration of mercuric hydroxycyanide and drop time; the data in Table III confirm this. All the observable characteristics of the wave indicate the electrode reaction to be reversible.

TABLE III

POLAROGRAPHY OF HgOHCN

All samples in 2.0 M sodium nitrate with 0.004% gelatin. Temperature 30°.

HgOHCN, $M \times 10^4$	$E_{f,m}$ *vs.* S.C.E., v.	d_m, μa./mM	K_m	t, sec./drop
0.84	+0.045	7.9	270	4.3
2.5	.043	7.5	310	4.3
5.0	.045	7.7	270	4.3
8.4	.045	7.9	270	4.3
8.4	.044	..	290	8.6
8.4	.045	..	270	4.4
8.4	.046	..	250	2.7
Av.	+0.045	7.8	280	

By subtraction of eq. 7 from eq. 13, an expression convenient for the calculation of K_m is obtained

$$E_{f,\mathrm{OH}} - E_{f,m} = 0.030 \log \frac{d_m^2 K_m}{d_c d_h}$$

From the experimentally measured values in Tables II and III, and $d_c = 8.2$μa./mM from ref. 5, K_m was calculated using this relation. The resulting values, given in Table III, are as expected, independent of the concentration of mercuric hydroxycyanide and agree well with the value determined from solubility data. The values for K_m and K_{OH} may be combined with K_2, the formation constant of mercuric cyanide, to give a value for the formation constant of mercuric hydroxycyanide, $K_{\mathrm{OH,CN}} = (\mathrm{HgOHCN})/(\mathrm{Hg^{++}})(\mathrm{OH^-})(\mathrm{CN^-})$. Taking 270 (the average of polarographic and solubility determinations) for K_m and 7.9×10^{33} for K_2[5], $K_{\mathrm{OH,CN}}$ was estimated to be 7.3×10^{28} at 30° and ionic strength of two.

Attempts were made to check the results by polarography of hydroxide ion in the presence of a large excess of mercuric cyanide. Tenth to six tenths millimolar hydroxide in millimolar to centimolar mercuric cyanide gave waves of the expected shape and having the theoretical slope characteristics according to eq. 10. The $E_{f,m}$ values, however, showed a great deal of scatter and the calculated K_m values were consistently low, sometimes by as much as a factor of ten. Studies on mercuric hydroxycyanide and on mixtures of hydroxide ion and mercuric hydroxycyanide in the presence of a large excess of mercuric cyanide gave more consistent results, but the $E_{f,m}$ data obtained led to values for K_m of only about 140. In view of the possibility of interference by the large excess of mercuric cyanide, these results were excluded from the averages.

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(8) W. M. Latimer, "Oxidation Potentials," 2nd Edition, Prentice-Hall, New York, N. Y., 1952.

(9) S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **6**, 747 (1952).

(10) G. Anderegg, *J. Inorg. Nuc. Chem.*, **8**, 360 (1958).