

zoic acid is essentially constant and not altered by substituents in the 4- or 5-position.

Comparison of the  $\sigma$ -constants for the reactions of the 2-methyl- with 2-unsubstituted benzoic acids is particularly interesting. In the diphenyldiazomethane reaction the 2-methyl lowers the reaction rate for each member of the 2-methyl over the 2-unsubstituted series but does not alter the relative influence of a 4- or 5-substituent. In the ionization reaction,  $\rho$  for the 2-unsubstituted acids (+1.46) is significantly smaller than for the 2-methyl acids (+1.67). A simple explanation for the apparent anomaly is possible. The influence of a given substituent on the rate of the diphenyldiazomethane reaction is exerted in the slow step which involves proton transfer from the

undissociated acid to the diazo compound.<sup>3</sup> In the transition state, the O-H bond of the benzoic acid is at most only partially ionized. Consequently, ionic solvation effects on the reaction are expected to be of relatively minor importance. In the acid ionizations, where equilibria between carboxylate ions and undissociated acids are involved, the effect of the ionic solvating power of the solvent is particularly important and it seems reasonable that  $\rho$  for the stabilization of 4- and 5-substituted 2-methylbenzoate ions by solvent molecules could be different than for the corresponding 2-unsubstituted acids.

(3) J. D. Roberts, W. Watanabe and R. E. McMahon, *THIS JOURNAL*, **73**, 760 (1951).

CAMBRIDGE 39, MASSACHUSETTS RECEIVED AUGUST 11, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW MEXICO SCHOOL OF MINES]

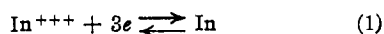
## A Study of Indium(III) Chloride Complexes by Polarographic Methods

BY JOSEPH A. SCHUFLE, MORRIS F. STUBBS AND RICHARD E. WITMAN

The polarographic reduction of the indium(III) ion has been studied by Lingane<sup>1</sup> and the shift in the half-wave potential of the indium ion with different chloride ion concentrations has been noted by Kolthoff and Lingane.<sup>2</sup> It was believed that the shift in half-wave potential with change in chloride ion concentration was due to formation of an indium chloride complex ion in solution. Aiken, Haley and Terrey<sup>3</sup> have proposed that indium dichloride is derived from  $\text{HInCl}_4$  and that  $\text{InCl}_2$  is probably better written  $\text{In}_2\text{Cl}_4$ , or  $\text{In}^+(\text{InCl}_4^-)$ , thus suggesting the existence of the chloro-indium complex,  $\text{InCl}_4^-$ .

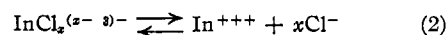
Theoretical treatment of this subject by Heyrovsky,<sup>4</sup> by Stackelberg and Freyhold<sup>5</sup> and by Lingane,<sup>6</sup> has shown that the shift in half-wave potential with change in concentration of the complex-forming substance may be used to determine the formula of the complex ion and, in some cases, the value of the dissociation constant for the metal complex. Stackelberg and Freyhold,<sup>5</sup> for example, found the formula for the zinc hydroxide complex ion to be  $\text{Zn}(\text{OH})_4^{2-}$  by determining half-wave potential ( $E_{1/2}$ ) values for zinc solutions at varying hydroxide ion concentrations.

In the case of the indium reduction studied in the present work the trivalent indium ion is reduced in one reversible step to metallic indium at the surface of the mercury electrode

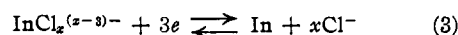


It is proposed that in the presence of chloride ion

in solution, however, the indium(III) ion is partly combined in the form of an indium chloride complex which must also dissociate reversibly if indium(III) is to be present to take part in the reduction indicated in equation (1).



Combining equations (1) and (2)



The value of  $E_{1/2}$  for this reaction, as shown by Stackelberg and Freyhold,<sup>5</sup> is given by the equation

$$E_{1/2} = E_s - \frac{0.0591}{n} \log \frac{a_{\text{InCl}_2^{(x-3)-}}}{(a_{\text{In}})} \quad (4)$$

where  $E_s$  is closely related to the normal reduction potential of the simple metal ion, but is more appropriately represented in this case by the half-wave potential for the reduction of the simple indium(III) ion in a non-complex-forming medium.

The dissociation constant ( $K_d$ ) for the indium chloride complex ion, obtained from equation (2), is given as

$$K_d = \frac{(a_{\text{In}^{+++}})(a_{\text{Cl}^-})^x}{(a_{\text{InCl}_2^{(x-3)-}})} \quad (5)$$

Substituting the value of  $a_{\text{InCl}_2^{(x-3)-}}$  obtained from equation (5) into equation (4)

$$E_{1/2} = E_s - \frac{0.0591}{n} \log \frac{(a_{\text{In}^{+++}})(a_{\text{Cl}^-})^x}{(a_{\text{In}})(K_d)} \quad (6)$$

Since the value of  $E_{1/2}$  for a metal ion is practically independent of the concentration of the metal ion,  $a_{\text{In}^{+++}}$  may be taken equal to unity. The activity of indium in the metallic state also may be assumed equal to unity ( $a_{\text{In}} = 1$ ). Thus equation (6) becomes

$$E_{1/2} = E_s - \frac{0.0591x}{n} \log (a_{\text{Cl}^-}) + \frac{0.0591}{n} \log K_d \quad (7)$$

(1) Lingane, *THIS JOURNAL*, **61**, 2099 (1939).

(2) Kolthoff and Lingane, *Chem. Revs.*, **24**, 1-94 (1939).

(3) Aiken, Haley and Terrey, *Trans. Faraday Soc.*, **32**, 1617 (1936).

(4) Heyrovsky, "Physikalische Methoden der analytischen Chemie," Bd. II, W. Böttger, Leipzig, 1936.

(5) Stackelberg and Freyhold, *Z. Elektrochem.*, **46**, 120 (1940).

(6) Lingane, *Chem. Revs.*, **39**, 1 (1941).

Thus a straight line should be obtained when values of  $E_{1/2}$  are plotted against values of  $\log(a_{\text{Cl}^-})$  for solutions of indium(III) ion in varying activities of chloride ion. The slope of the line obtained should be equal to  $-0.059x/n$ .

**Experimental.**—It was decided to study indium solutions in hydrochloric acid media, since accurate values of mean activity coefficients for hydrochloric acid solutions over a wide range of concentrations were available.<sup>7</sup> 0.001 *N* solutions of  $\text{InCl}_3$  were made up by dissolving weighed amounts of indium metal (99.97% pure In, obtained from the Indium Corporation of American, Utica, N. Y.) in 15.4 molal hydrochloric acid and diluting this stock solution with the calculated amounts of standardized hydrochloric acid and distilled water to make the required acid concentrations.

Polarographs were run on a Sargent model XII photographic recording polarograph, using an H-type polarographic cell so that all potentials were measured against an external saturated calomel electrode. The cell was immersed in a water-bath maintained at  $25.0 \pm 0.1^\circ$ . Four drops of 0.2% gelatin solution were added in each case to suppress maxima in the polarographic curves. Purified hydrogen gas was bubbled through the solution for 10–15 min. immediately preceding each run to remove dissolved oxygen from the solution. In most cases duplicate runs, and in some cases triplicate runs, were made on each different acid concentration and the average value of  $E_{1/2}$  determined for each solution. The average deviation of individual results from the average was  $\pm 0.004$  v.

The experimental data are given in Table I.

TABLE I

Concn. HCl (N)	Concn. HCl (molarity)	$\log \gamma$ (ref. 7)	$\log a_{\text{Cl}^-}$ ( $a = m\gamma$ )	$-E$ (vs. S.C.E.)	$n$
11.63	15.4	1.575	2.763	0.772 v.	3.0
11.0	14.3	1.470	2.625	.760	3.2
10.0	12.65	1.305	2.407	.746	3.3
9.0	11.09	1.140	2.185	.723	2.9
8.5	10.35	1.055	2.070	.727	2.8
8.0	9.62	0.970	1.953	.712	2.9
7.0	8.21	.795	1.709	.702	2.8
6.0	6.86	.620	1.456	.681	2.7
5.0	5.58	.450	1.197	.667	2.8
4.0	4.36	.290	0.930	.645	2.8
3.0	3.20	.140	.645	.632	2.6
2.0	2.09	.010	.330	.622	2.9
1.0	1.02	-.092	-.083	.599	2.8
0.50	0.506	-.121	-.417	.590	2.5
0.10	0.100	-.099	-1.099	.559	2.8
0.010 <sup>a</sup>	0.0100	-.161 <sup>b</sup>	-2.161	.540	2.5

<sup>a</sup> Solution was also made 0.1 *N* with respect to  $\text{KNO}_3$ .

<sup>b</sup>  $\log \gamma = 0.509 \sqrt{\mu}$ , where  $\mu = 0.1$ .

**Treatment of Results.**—Values of  $n$ , the number of electrons involved in the reduction of one indium ion to indium metal, were determined from the slope of the straight line obtained by plotting the potential of the dropping mercury electrode against the values of  $\log i/(i_d - i)$ , as proposed by Kolthoff and Lingane.<sup>8</sup> The fact that  $n$  is found to be somewhat less than the ideal value of 3 is in agreement with the findings of Davidson and Kleinberg.<sup>9</sup> These authors found that electrolysis carried out with an indium anode in acetic acid solution resulted in weight losses considerably greater than those corresponding to Faraday's

law if the product is assumed to be the indium(III) ion alone. To date, however, we have found no polarographic evidence for a second step in the reduction of indium which would indicate the existence in solution of a stable indium ion of oxidation state lower than three. In view of this uncertainty, the value of  $n$  was taken as an even 3 in subsequent calculations.

A graph of  $E_{1/2}$  values plotted against  $\log(a_{\text{Cl}^-})$  is shown in Fig. 1. The data for hydrochloric acid solutions of concentrations greater than approximately 8 *N* fall along the theoretical straight line corresponding to a value of  $x = 4$ . This indicates that the formula of the indium chloride complex existing in strong hydrochloric acid solution is  $\text{InCl}_4^-$ . The experimental points begin to fall off the line corresponding to  $x = 4$  at hydrochloric acid concentrations less than about 8 *N* and, starting at about 4 *N*, conform to a new straight line the slope of which corresponds to  $x = 2$ . This would indicate an indium chloride complex ion of formula  $\text{InCl}_2^+$ , not previously proposed, as existing in more dilute solutions of hydrochloric acid. Carter and Lea<sup>10</sup> made potentiometric measurements (not polarographic) of the potential of the cupric-cuprous electrode in varying concentrations of hydrochloric acid. They found a change in slope similar to ours occurring at hydrochloric acid concentrations of about 7–8 *N* when oxidation potentials of cupric and cuprous chloride were plotted against acid concentration and roughly attributed the change in slope to changes in the formula of copper chloride complexes in solution.

According to the work of Bjerrum,<sup>11</sup> the formation of complex ions in aqueous solution always occurs stepwise, and the stability of the various species  $\text{MA}_n$  existing in solution is characterized by a series of consecutive mass action constants,  $K_1, K_2, \dots, K_n$ . The existence of an  $\text{InCl}_3$  complex in solution in hydrochloric acid concentrations between 4 and 8 *N* might be proposed on this basis but we are not able to lend substantial support to this theory on the basis of the experimental data in the present work.

For the value of  $E_s$  in equation (7) we determined the value of  $E_{1/2}$  for the reduction of indium perchlorate in solutions of 0.1 *N* perchloric acid, because of the probable absence of complex formation between indium and perchlorate ions. Hughes and Hush,<sup>12</sup> for example, found no evidence of complex formation for the thallium ion in perchloric acid solutions. Kolthoff and Lingane<sup>13</sup> reported that solutions of indium perchlorate in perchloric acid were reduced irreversibly at an  $E_{1/2}$  value of about  $-0.95$  v. vs. S.C.E. We could not confirm this, but found instead that the reaction proceeded for a 0.001 *N*  $\text{In}(\text{ClO}_4)_3$  solution in 0.10 *N*  $\text{HClO}_4$ , at an  $E_{1/2}$  value of  $-0.573$  v. vs. S.C.E. The standard reduction potential for the indium-(III) ion given by Latimer<sup>14</sup> is  $-0.582$  v. vs. S.C.E.

(10) Carter and Lea, *J. Chem. Soc.*, 127, 499 (1925).

(11) Jannik Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase & Son, Copenhagen, 1941.

(12) Hughes and Hush, *Austral. J. Sci.*, 10, 184 (1948).

(13) Kolthoff and Lingane, "Polarography," Interscience Publishers, N. Y., 1946, p. 274.

(14) Latimer, "Oxidation States of the Elements," Prentice-Hall, N. Y., 1938, p. 150.

(7) Randall and Young, *THIS JOURNAL*, 50, 989 (1928).

(8) Kolthoff and Lingane, *Chem. Rev.*, 24, 1 (1939).

(9) Davidson and Kleinberg, paper presented before the Division of Physical and Inorganic Chemistry, 117th Meeting, A. C. S., Detroit, Mich., April 19, 1950.

The plot of  $E$  vs.  $\log i/(i_d - i)$  for the polarographic wave in this case gave a straight line from the slope of which the value of  $n$  was calculated to be 2.8.

The values of  $K_d$  from equation (7) were calculated for the two indium chloride complexes.  $K_d$  for the  $\text{InCl}_4^-$  ion for hydrochloric acid concentrations of 8–11.6  $N$  was calculated to vary between 6 and 13. This would indicate that the  $\text{InCl}_4^-$  ion is quite unstable in aqueous solution.  $K_d$  for the  $\text{InCl}_2^+$  ion for hydrochloric acid concentrations of 1 to 4  $N$  was calculated to vary between the limits  $1.5 \times 10^{-2}$  and  $3.3 \times 10^{-2}$ , indicating this latter complex to be more stable than the former by a factor of  $10^2$ .

**Acknowledgment.**—The authors wish to express their appreciation to the Office of Naval Research for their support of the work, part of which is covered in this report.

### Summary

Polarographic reduction of indium(III) ion in solutions of varying chloride ion activities has been studied. Evidence has been presented for the possible existence of two indium chloride complex ions in aqueous solution,  $\text{InCl}_4^-$  and  $\text{InCl}_2^+$ . The  $\text{InCl}_4^-$  complex is found to be relatively unstable and to exist only in solutions of high chloride ion concentration.

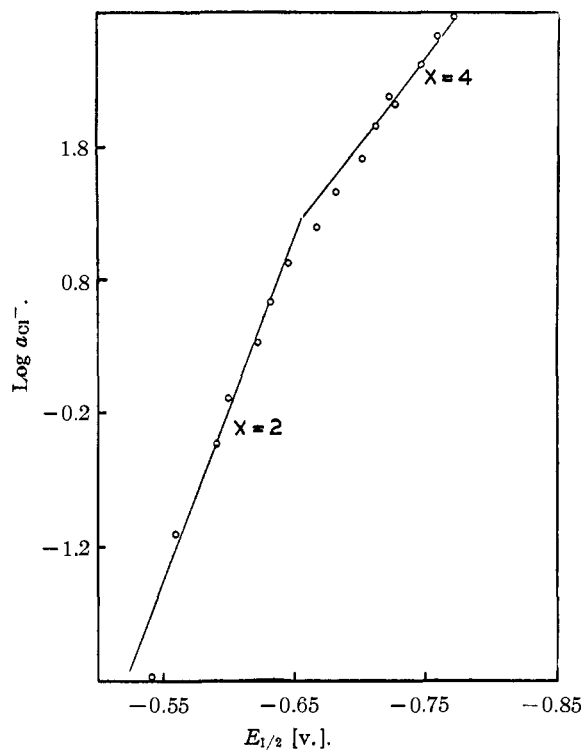


Fig. 1.

SOCORRO, NEW MEXICO

RECEIVED JULY 31, 1950

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

## Some Aspects of Reactions between Ammonia and Mercury(I) Compounds

BY SRINATH D. ARORA,<sup>1</sup> WILLIAM N. LIPSCOMB AND M. C. SNEED

The action of excess 0.1  $N$  aqueous ammonia on mercury(I) nitrate and perchlorate is described by the reaction  $2\text{Hg}_2^{++} + \text{X}^- + 4\text{NH}_4\text{OH} \rightarrow 2\text{Hg} + \text{Hg}_2\text{NX} + 3\text{NH}_4^+ + 4\text{H}_2\text{O}$  where  $\text{X}^-$  is  $\text{NO}_3^-$  or  $\text{ClO}_4^-$ . A similar reaction occurs with mercury(I) chloride  $2\text{Hg}_2\text{Cl}_2 + 4\text{NH}_4\text{OH} \rightarrow 2\text{Hg} + \text{Hg}_2\text{NCl}\cdot\text{H}_2\text{O} + 3\text{H}_2\text{O} + 3\text{NH}_4^+ + 3\text{Cl}^-$ . When about 0.7  $N$  ammonia is used, the ratio of  $\text{Hg}_2\text{Cl}_2$  to solution may be chosen to give the reaction  $\text{Hg}_2\text{Cl}_2 + 2\text{NH}_4\text{OH} \rightarrow \text{Hg} + \text{HgNH}_2\text{Cl} + \text{NH}_4^+ + \text{Cl}^- + \text{H}_2\text{O}$  which proceeds through intermediate formation of  $\text{Hg}_2\text{NCl}\cdot\text{H}_2\text{O}$ . The product,  $\text{HgNH}_2\text{Cl}$ , may be transformed to  $\text{Hg}_2\text{NCl}\cdot\text{H}_2\text{O}$  by 0.1  $N$  aqueous ammonia. The reaction of gaseous ammonia with  $\text{Hg}_2\text{Cl}_2$  yields  $\text{Hg} + \text{Hg}(\text{NH}_3)_2\text{Cl}_2$ , while that of liquid ammonia yields  $\text{Hg}$  plus some  $\text{HgNH}_2\text{Cl}$  and some  $\text{Hg}(\text{NH}_3)_2\text{Cl}_2$ . The compounds  $\text{Hg}_2\text{NNO}_3$ ,  $\text{Hg}_2\text{NClO}_4$ ,  $\text{Hg}_2\text{NOH}\cdot 2\text{H}_2\text{O}$ ,  $\text{Hg}_2\text{NCl}\cdot\text{H}_2\text{O}$ ,  $\text{Hg}_2\text{NBr}\cdot\text{H}_2\text{O}$  and  $\text{Hg}_2\text{NI}$  are shown to be isomorphous by means of X-ray diffraction photographs. The structure of the  $\text{Hg}_2\text{N}^+$  framework is very similar to that of cristobalite,  $\text{SiO}_2$ . Bonds from Hg are linear, while those from nitrogen are tetrahedral, and the Hg-N distance is 2.07 Å.

**Introduction**—The many different conclusions reached by various investigators in studies of the reactions of ammonia with mercury(I) compounds suggest that the reactions and products may vary considerably with the conditions employed for both reactions and analyses. The black solids produced in the reactions have been assigned many different formulas for which the most commonly accepted is  $\text{Hg} + \text{HgNH}_2\text{Cl}$ , but intermediates such as  $\text{Hg}_2\text{NH}_2\text{Cl}$  and  $\text{Hg}_2\text{O}$  have been claimed by the more recent investigators.<sup>2</sup>

(1) Jaswant College, Jodhpur, India.

(2) Description of older work may be found in the standard reference books of Inorganic Chemistry. The most recent work is that of E. Gleditsch and T. F. Egidius, *Compt. rend.*, **202**, 574 (1936); *Z. anorg. Chem.*, **226**, 265 (1936); *ibid.*, **228**, 249 (1936). Also T. F. Egidius,

Under other conditions Egidius<sup>2</sup> has claimed that compounds  $\text{Hg}_4\text{NCl}$  and  $\text{Hg}_2(\text{NH}_3)_2\text{Cl}_2$  decompose into  $\text{Hg} + \text{Hg}_2\text{NCl}$  and  $\text{Hg} + \text{Hg}(\text{NH}_3)_2\text{Cl}_2$ , respectively.

The present study is intended to elucidate the reactions in dilute aqueous ammonia. Both chemical and physical methods, particularly X-ray diffraction, are used in order to search for possible intermediates or other reactions, and in order to describe more completely the known compounds.

### Results and Discussion

**1. Action of 0.1  $N$  Aqueous Ammonia.**—The black solid, first formed upon reaction with a *ibid.*, **240**, 97 (1938), and H. Freche and M. C. Sneed, *THIS JOURNAL*, **60**, 518 (1938).