

mole fraction curves at different temperatures.

An equation was derived for calculating $B_C - B_D$ and was shown to be in agreement with the re-

sults of this investigation and with data recorded in the literature.

UNIVERSITY, LA.

RECEIVED MAY 12, 1941

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Contributions to the Chemistry of Indium. III. An Electrometric Study of the Precipitation of Hydrous Indium Hydroxide¹

BY THERALD MOELLER

Attention already has been directed to the fact that, while the term "neutral" as applied to aqueous indium salt solutions often appears in the literature, such usage is incorrect because any attempt to bring a solution containing indium ion to the neutral point will result in precipitation of the hydrous hydroxide.²

Inasmuch as reported quantitative investigations of the changes in pH during the addition of bases to indium salt solutions appear to be limited to a single titration of an indium nitrate solution with sodium hydroxide,³ it was deemed advisable to make more extensive observations of this nature with the ultimate aim of estimating the solubility and solubility product of indium hydroxide.

Furthermore, since the solubility of hydrous indium hydroxide in concentrated sodium and potassium hydroxide solutions has been thought of as involving indate formation,⁴ it was hoped that data from such titrations might either support or refute this contention.

Experimental

Materials Used.—Pure anhydrous indium sulfate was prepared from indium metal (stated to be 99.98% pure) as previously indicated.² Anhydrous indium chloride was obtained by chlorinating the metal and repeatedly subliming the product in dry nitrogen.⁵ Crystals of the hydrated nitrate, corresponding by analysis to $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$, were prepared by treating the pure oxide with dilute nitric acid in slight excess, evaporating to crystallization on the steam-bath, and drying the product over anhydrous calcium chloride for two months. Solutions obtained by dissolving these salts in distilled water and standardized by gravimetric determination of the indium as oxide² were of the following concentrations: $\text{In}_2(\text{SO}_4)_3$, 0.0493 *M*; $\text{In}(\text{NO}_3)_3$, 0.1000 *M*; InCl_3 , 0.1000 *M*.

Tenth-normal solutions of sodium, potassium and am-

monium hydroxides were obtained by diluting concentrated, carbonate-free solutions with carbon dioxide-free water. The sodium and potassium hydroxide solutions were standardized against primary standard potassium acid phthalate, using phenolphthalein as indicator, while the ammonium hydroxide was standardized against 0.1 *N* hydrochloric acid (using methyl red) which had previously been standardized against sodium hydroxide. All bases were protected against carbon dioxide with soda lime.

Experimental Procedure.—A 10-ml. portion of the indium salt solution was diluted to 40 ml. and placed in a thermostat controlled to $\pm 0.5^\circ$ of the desired temperature. While the solution was vigorously stirred, the base was added in small increments, the changes in pH being followed with a Beckman laboratory model G pH meter, the glass electrode of which had been calibrated against a standard 0.05 *M* potassium acid phthalate buffer. No attempt was made to protect the titration vessel from the carbon dioxide of the air because the only changes in pH due to carbonate formation were in regions of high pH where the alkali ion error becomes appreciable. In all instances, except where the pH changed markedly with small increases in added hydroxyl ion, equilibrium was attained rapidly.

Titrations were made at 40, 25 and 10°, and the effects of initial indium ion concentration were studied at 25°.

Results and Discussion

Studies at 25°.—Plotted in Fig. 1 as pH *vs.* the mole ratio of hydroxyl ion added to indium ion initially present are data obtained from titrations of indium nitrate, chloride and sulfate solutions with sodium, potassium and ammonium hydroxides. For each curve, the point (av.) at which precipitation began and the point (av.) at which flocculation of the colloidal suspension produced by the addition of the base occurred are indicated, respectively, by singly and doubly barbed arrows. For each indium salt agreement among the data for the three bases is excellent, particularly in the precipitation region bounded by the arrows.

Although with both the nitrate and sulfate solutions precipitates appeared only after the ratio of OH^- to In^{+++} reached 0.84, whereas with

(1) Presented before the Division of Physical and Inorganic Chemistry on April 8, 1941, at the 101st meeting of the American Chemical Society at St. Louis, Missouri.

(2) Moeller, *THIS JOURNAL*, **62**, 2444 (1940).

(3) Oka, *J. Chem. Soc. Japan*, **59**, 971 (1938).

(4) Renz, *Ber.*, **34**, 2763 (1901).

(5) Moeller, *THIS JOURNAL*, **63**, 1206 (1941).

the chloride the necessary ratio was 0.02, precipitation began uniformly at a pH of 3.41 to 3.43.

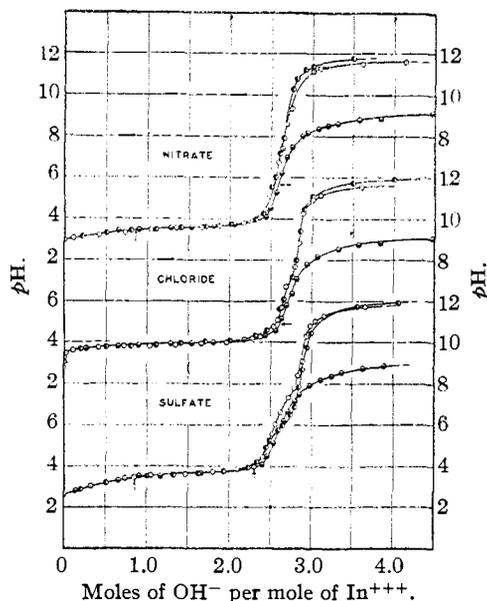


Fig. 1.—Titrations of indium nitrate, chloride and sulfate solutions at 25°: ○, sodium hydroxide; ●, potassium hydroxide; ●, ammonium hydroxide.

As is indicated in Fig. 1, flocculation always occurred before a $3OH^-$ to $1In^{+++}$ equivalence was attained, suggesting the formation of basic salts. If the OH^- to In^{+++} ratio at the point of flocculation be considered to be the same in the precipitate existing at that point, these precipitates were then of the compositions $In(OH)_{2.59}(NO_3)_{0.41}$ (compare with results of Oka³), $In(OH)_{2.62}Cl_{0.38}$ and $In(OH)_{2.32}(SO_4)_{0.34}$, the lower basicity of the sulfate being due to the greater flocculating power of the sulfate ion on the positive sol first produced. Confirmation of the existence of such basic salts, however, would require more information than can be supplied by electrometric titration data.

Even though flocculation was noted before the theoretical ratio of $3OH^-$ to $1In^{+++}$ was reached, the facts that equilibrium was always attained somewhat more slowly in the OH^-/In^{+++} region of 2.5 to 3.0, that none of the curves became abruptly steep in this region, and that significant changes in pH ceased only when a $3OH^-$ to $1In^{+++}$ ratio had been attained, plus the observation of Milligan and Weiser⁶ that indium hydroxide is precipitated as such, warrant the conclusion that the ultimate precipitate was probably hydrous indium hydroxide and justify appli-

(6) Milligan and Weiser, *THIS JOURNAL*, **59**, 1670 (1937).

cation of the conventional solubility product principle to the precipitation regions of these curves.

Summarized in Table I are values for the solubility product constant for hydrous indium hy-

TABLE I
SOLUBILITY PRODUCT DATA AT 25°

OH^-/In^{+++}	Indium nitrate Sol.		Indium chloride Sol.		Indium sulfate Sol.	
	pH	prod. of $In(OH)_3 \times 10^{33}$	pH	prod. of $In(OH)_3 \times 10^{33}$	pH	prod. of $In(OH)_3 \times 10^{33}$
1.00	3.43	0.3	3.90	7	3.55	0.6
1.25	3.50	.4	3.95	8	3.60	.7
1.50	3.57	.5	3.97	7	3.62	.7
1.75	3.65	.7	4.00	7	3.65	.6
2.00	3.72	.8	4.05	8	3.72	.8
	Av.	.5		7		.7

droxide calculated (without use of activity coefficients and thus upon the assumption of complete dissociation of each of the indium salts) from the pH values at OH^- to In^{+++} ratios selected from the curves in Fig. 1 (the ion product of water being taken as 1×10^{-14} at 25°) and indium ion concentrations at those points corrected for the volumes of base added. Although values for the constant vary somewhat with the OH^- to In^{+++} ratio and are larger for the chloride data than for the nitrate and sulfate, they approach 10^{-33} quite closely and are thus in agreement with the results of Oka,³ who reported an average value of 0.8×10^{-33} , and of Heyrovsky,⁷ who, from polarographic data, calculated the solubility product of freshly precipitated indium hydroxide to be 10^{-33} .

From the relation $S = \sqrt[3]{K/27}$, the average solubility, S , of indium hydroxide in water at 25° is calculated to be 2.1×10^{-9} , 4.1×10^{-9} and 2.3×10^{-9} gram moles per liter from the nitrate, chloride and sulfate data, respectively.

The higher values for the solubility product constant and solubility obtained from the chloride data as well as the fact that the precipitation range for the hydroxide lay at higher pH values in the chloride solutions than in the nitrate and sulfate (Fig. 1) can doubtless be explained as resulting from the tendency of indium chloride to exist in aqueous solution as anionic complexes,⁸ as demonstrated by the abnormally low electrical conductivities⁹ of such solutions, with concomitant reductions in the concentration of indium ion as such. The indium ion concentrations used in the calculations were thus too large. Indium sul-

(7) Heyrovsky, *Chem. Listy*, **19**, 168 (1925).

(8) Friend, "Textbook of Inorganic Chemistry," Vol. 4, 2nd ed., Charles Griffin and Company, Ltd., London, 1921, p. 155.

(9) Thiel, *Z. anorg. Chem.*, **40**, 280 (1904).

fate and nitrate apparently do not exhibit this anomaly.

Effects of Temperature.—Plotted in Fig. 2 are data obtained at 40, 25 and 10° when indium sulfate solutions were titrated with sodium and ammonium hydroxides. As indicated by the arrows, an increase in temperature lowered both the *pH* and the amount of hydroxyl ion necessary for initial precipitation. For the titrations with sodium hydroxide, these values were: 40°, *pH* 3.15, $\text{OH}^-/\text{In}^{+++} = 0.73$; 25°, *pH* 3.43, $\text{OH}^-/\text{In}^{+++} = 0.84$; 10°, *pH* 3.56, $\text{OH}^-/\text{In}^{+++} = 0.94$. Nearly identical values resulted with ammonium hydroxide.

In Table II are given solubility product constants and water solubilities for indium hydroxide

TABLE II

EFFECTS OF TEMPERATURE UPON THE SOLUBILITY PRODUCT AND SOLUBILITY OF INDIUM HYDROXIDE

Temp., °C.	$\text{OH}^-/\text{In}^{+++}$	<i>pH</i>	Sol. prod. $\times 10^{33}$	Sol. g. mole/liter $\times 10^3$
(a) With NaOH				
10	1.50	3.70	0.03	1.0
10	2.00	3.85	.05	1.2
25	1.50	3.62	.7	2.3
25	2.00	3.72	.8	2.3
40	1.50	3.30	2.0	2.9
40	2.00	3.40	2.4	3.0
(b) With NH_4OH				
10	1.50	3.70	0.03	1.0
10	2.00	3.80	.04	1.1
25	1.50	3.62	.7	2.3
25	2.00	3.67	.6	2.2
40	1.50	3.32	2.4	3.0
40	2.00	3.40	2.6	3.1

calculated from Fig. 2, the ion product of water being taken as 0.295×10^{-14} and 3.02×10^{-14} at 10 and 40°, respectively. In the temperature interval between 10 and 40°, the solubility of indium hydroxide in water trebles.

Effects of Initial Indium Ion Concentration.—Data for the beginning of precipitation obtained

TABLE III

EFFECTS OF INITIAL INDIUM ION CONCENTRATION

Init. In^{+++} concn., mole/liter	Initial <i>pH</i>	Sodium hydroxide pptn. began		Ammonium hydroxide pptn. began	
		$\text{OH}^-/\text{In}^{+++}$	<i>pH</i>	$\text{OH}^-/\text{In}^{+++}$	<i>pH</i>
0.02466	2.60	0.84	3.43	0.84	3.43
.02250	2.63	.82	3.41
.02000	2.70	.88	3.39	.83	3.42
.01500	2.79	.82	3.42	.83	3.42
.01000	2.90	.82	3.43	.83	3.40
.00500	3.10	.82	3.53	.77	3.43
	Av.	.83	3.43	.82	3.42

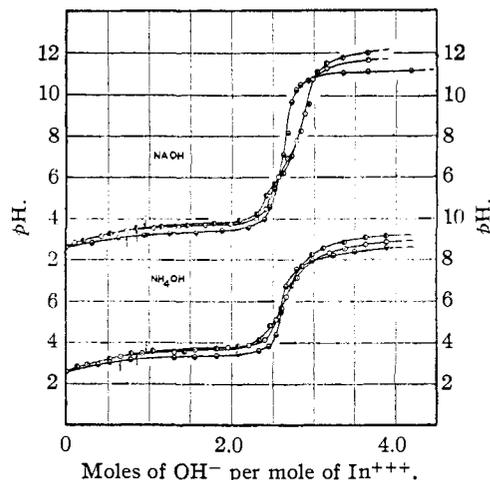


Fig. 2.—Effects of temperature using indium sulfate and sodium and ammonium hydroxides: ●, 10°; ○, 25°; ●, 40°.

at 25° during titrations of indium sulfate solutions varying in indium ion concentration from 0.00500 to 0.02466 *M* with sodium and ammonium hydroxides are summarized in Table III.

It is apparent that Britton's contention¹⁰ that the initial metal ion concentration (within the limits of ordinary analytical practice) has little or no effect upon the incidence of precipitation of the metal hydroxide holds true for indium hydroxide. Furthermore, the titration data when plotted fall along a single curve regardless of the initial indium ion concentration.

Data given in Table III for the initial *pH* values of the sulfate solutions agree well with those reported by Hattox and De Vries.¹¹

Amphoteric Nature of Indium Hydroxide.—In no instances have titration data given any indication of the dissolution of indium hydroxide with the formation of indiate solutions. When hydrous indium hydroxide was treated with a large excess of either sodium or potassium hydroxide, the solid dispersed to slightly opalescent suspensions which flocculated on the addition of various salts. Electrophoretic migration observations indicated that such "solutions" contained negatively charged colloidal particles of the hydroxide, presumably stabilized by adsorbed hydroxyl ions.

Summary

1. When indium sulfate, chloride, or nitrate solution is titrated with sodium, potassium, or ammonium hydroxide, precipitation begins at a

(10) Britton, "Hydrogen Ions," D. Van Nostrand Company, Inc., New York, N. Y., 1929, p. 249.

(11) Hattox and De Vries, *THIS JOURNAL*, **58**, 2126 (1936).

pH of 3.41–3.43, and the colloidal sol thus produced flocculates before the theoretical ratio of 3OH^- to 1In^{+++} is attained.

2. At 25° a mole ratio of 0.84OH^- to 1In^{+++} must be reached before indium hydroxide can be precipitated from sulfate or nitrate solutions. From a chloride solution, this ratio is only 0.02.

3. On the assumption that the ultimate precipitate is indium hydroxide, the solubility product constant at 25° is calculated to be of the order of 10^{-33} and the corresponding water solubility 2.2×10^{-9} g. moles of indium hydroxide per

liter (slightly higher from chloride solutions).

4. In the temperature range 10 to 40° , the solubility of hydrous indium hydroxide in water trebles.

5. Variation in the initial indium ion concentration between 0.00500 and 0.02466 M has no effect on the pH at which precipitation begins.

6. When indium hydroxide is treated with excess sodium or potassium hydroxide, at least part of the indium hydroxide is peptized to a negative sol.

URBANA, ILLINOIS

RECEIVED APRIL 21, 1941

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Chromatography of Solutions Containing a Single Solute

BY HAROLD G. CASSIDY AND SCOTT E. WOOD

The theory of chromatography proposed by Wilson¹ is based, as he has pointed out, on the assumption of instantaneous equilibrium between the solution and the adsorbent, and on the assumption that the effects of diffusion can be neglected. The theory might therefore be called one of ideal chromatography. It seemed of interest to compare the theory in a simple case with data which had been obtained in this Laboratory. Quite good agreement was found, on the whole, between experiment and theory in this comparison.

The outstanding predictions about the adsorbed zone according to the theory are that the leading and following edges of the zone will be infinitely sharp and that the adsorbed material will be in equilibrium with the solution at the original concentration, c_0 . If the adsorption isotherm is written as $Q = Mf(c)$, where Q is the moles of adsorbed material per cm. length of column, M , the grams of adsorbent per cm. length of column, and c , the equilibrium concentration, then the length of the zone, x , in cm., after V cc. of solution have passed into the column is given by $x = Vc_0/(ac_0 + Q_0)$. Here a is the interstitial volume per cm. length of the column, and $Q_0 = Mf(c_0)$. The rate in cm. per cc. of liquid passed into the column at which the edges of the zone move down the column when the same solvent is used for developing is given by $c_0/(ac_0 + Q_0)$.

In these experiments the form of the zone was determined by analyzing the solution passing

from the column. Sufficient solution of concentration c_0 was used so that the front edge of the zone attained the bottom of the column of adsorbent before all of the solution had been passed into the column. Under these conditions, and with the assumption that the molal volume of the solution is equal to the molal volume of the pure solvent, the volume, V_1 (Table I), of liquid which must pass through the column in order to bring the front edge of the zone to the bottom of the adsorbent is lQ_0/c_0 , where l is the length of the column of adsorbent. The total volume, V_2 , which must pass through the column to completely remove the entire zone of adsorbed substance is $V_0 + V_1$, where V_0 is the volume of the original solution.

Experiment.—The materials were the same as have been described in previous papers.² Solutions of lauric acid in petroleum ether were passed at room temperature through tubes, 1.3 cm. in diameter, packed with Darco G-60 carbon. In each case 1 g. of carbon was used, and in all cases but "b" (Table I) 1 g. of filter aid (which does not adsorb^{2b}) was mixed with the carbon. Fresh solvent was added to the column just when the last of the lauric acid solution passed into the adsorbent. The liquid passing from the column was collected in fractions of varying sizes, depending on the exigencies of the experiment. The solvent was then evaporated from each fraction and the residue weighed.

Data for the chromatography of solutions of lauric acid of several concentrations are shown in Table I and Fig. 1. In the figure the solid lines show the experimental results; the broken lines indicate those predicted by the theory using the adsorption isotherm given below. It was ob-

(1) J. N. Wilson, *THIS JOURNAL*, **62**, 1583 (1940).

(2) H. G. Cassidy, *ibid.*, **62**, 3073 (1940); (b) **62**, 3076 (1940).