

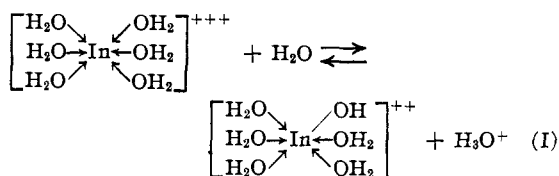
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Contributions to the Chemistry of Indium. II. The Hydrolysis of Indium Trichloride Solutions

BY THERALD MOELLER

Quantitative observations concerning the hydrolysis of soluble indium salts have been limited to indium sulfate solutions. Seward¹ measured the pH values of three such solutions, and Hattox and de Vries² determined the pH values of a number of solutions and calculated hydrolysis constants on the assumptions that $In(OH)^{++}$ and InO^+ ions were produced, the former hypothesis giving the better results.

Such observations are here extended to indium trichloride solutions. Since such solutions (like all simple In^{+++} salt solutions) are acidic, it can be assumed, as a first step, that the solvent water accepts a proton from the hydrated trivalent indium ion as follows:



the coordination number of the indium ion being taken as six.³ This reaction is comparable to that suggested by Hattox and de Vries and can, of course, be followed by subsequent reactions.

Hydrolysis constants calculated from pH values of indium chloride solutions support this equation.

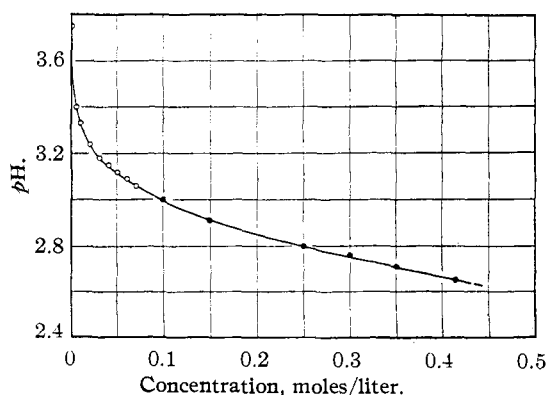


Fig. 1.—Change in pH with concentration of indium chloride: \circ , $InCl_3$ prep. from In metal; \bullet , $InCl_3$ prep. from In_2O_3 .

(1) Seward, *THIS JOURNAL*, **55**, 2740 (1933).

(2) Hattox and de Vries, *ibid.*, **58**, 2126 (1936).

(3) Morgan and Burstall, "Inorganic Chemistry. A Survey of Modern Developments," W. Heffer and Sons, Ltd., Cambridge, 1936, p. 96.

Experimental

Preparation of Anhydrous Indium Trichloride.—One sample of anhydrous indium trichloride was prepared by passing a stream of dry chlorine diluted with dry carbon dioxide⁴ over pieces of 99.98% pure indium metal⁵ heated just below its melting point in an apparatus similar to that used by Baxter and Alter.⁶ An apparently step-wise reaction yielded lustrous plates of the trichloride. The product was purified by repeated sublimations in a current of dry nitrogen⁶ and was pure white in color.

A second sample was obtained by heating an intimately ground mixture of pure indium oxide (prepared from the sulfate⁶ through intermediate conversion to the hydroxide) and excess charcoal in a stream of dry chlorine and nitrogen in the same type of apparatus. White crystals of the trichloride formed at once and were sublimed as before. Both samples were preserved in sealed Pyrex tubes in atmospheres of dry nitrogen.

Experimental Procedure.—The sample tubes were broken and immediately immersed in carbon dioxide-free distilled water. The salts dissolved rapidly to clear solutions, much heat being evolved. These solutions were standardized by gravimetric determination of the indium as oxide⁵ and diluted to the desired concentrations with carbon dioxide-free water. All resulting solutions were thermostated to $25 \pm 0.05^\circ$ and the pH values determined with a glass electrode, using a Beckman Laboratory Model G pH Meter. The results are summarized in Table I and in Fig. 1, the solutions 0.0700 molar and less concentrated being made from indium trichloride prepared from indium metal and those more concentrated than 0.0700 molar from indium trichloride prepared from indium oxide. Data for the two samples agree nicely.

The indium trichloride solutions showed no change in pH on long standing at room temperature. The use of the anhydrous chloride eliminated the possibility of the presence of any free hydrochloric acid in the solutions.

Results

Through application of the conventional procedure⁷ to equation (I), values for the degree of hydrolysis (x) and the hydrolysis constant (K_h) have been calculated. These are given in Table I. If the results for the three most dilute solutions (*i. e.*, those where the curve in Fig. 1 is becoming asymptotic to the pH axis) be neglected, the values for K_h are seen to be reasonably constant with a mean of 1.2×10^{-5} . The hydrolysis hypothesis given in equation (I) is thus supported.

(4) Mathers, *THIS JOURNAL*, **29**, 485 (1907).

(5) Moeller, *ibid.*, **62**, 2444 (1940).

(6) Baxter and Alter, *ibid.*, **55**, 1943 (1933).

(7) Britton, "Hydrogen Ions," D. Van Nostrand Company, Inc., New York, N. Y., 1929, pp. 168-170.

TABLE I
HYDROLYSIS OF INDIUM TRICHLORIDE SOLUTIONS AT 25°

Moles of InCl ₃ per liter	pH	Degree of hydrolysis α	Hydrolysis constant $K_h \times 10^6$
0.000500	3.75	0.3560	9.8
.005000	3.40	.0796	3.4
.01000	3.32	.0479	2.4
.02000	3.24	.0288	1.7
.03000	3.18	.0220	1.5
.04000	3.15	.0177	1.3
.05000	3.12	.0152	1.2
.06000	3.09	.0135	1.1
.07000	3.06	.0125	1.1
.1000	3.00	.0100	1.0
.1500	2.91	.0082	1.0
.2500	2.80	.0063	1.0
.3000	2.76	.0058	1.0
.3500	2.71	.0056	1.1
.4141	2.65	.0054	1.2

In this connection, it is interesting to note that a number of organic salts containing the $\text{In}(\text{OH})^{++}$ group have been prepared.⁸

Calculations similar to those made by Hattox

(8) Ekeley and Johnson, *THIS JOURNAL*, **57**, 773 (1935).

and de Vries² assuming the formation of InO^+ or $\text{In}(\text{H}_2\text{O})_4(\text{OH})_2^+$ ions yield hydrolysis constants of the order of 10^{-8} but of less constancy. That such ions be produced in the primary hydrolytic reaction seems unlikely, however, and it appears more probable that a constant so calculated would apply to a secondary reaction.⁹

The values for K_h are smaller than those obtained for indium sulfate solutions but more constant. Furthermore, indium sulfate solutions of a given concentration are more acid than indium trichloride solutions of the same concentration.

Summary

1. Variations of pH with concentration at 25° are given for pure indium trichloride solutions.

2. Hydrolysis constants are calculated for such solutions, assuming that the hydrolysis products are $\text{In}(\text{H}_2\text{O})_5(\text{OH})^{++}$ and H_3O^+ .

(9) Denham, *J. Chem. Soc.*, **93**, 41 (1908).

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Properties of the Electrical Double Layer at a Mercury Surface. I. Methods of Measurement and Interpretation of Results

BY DAVID C. GRAHAME

Measurements of the electrical capacity of the system formed when a metal is immersed in a solution of some chemically indifferent electrolyte such as aqueous potassium chloride are of much interest because of their intimate relation to other surface properties such as the surface tension of the metal, the specific surface charge or the electrokinetic zeta-potential. Although many experimenters¹⁻¹⁰ have measured the capacity of a mercury surface in contact with solutions of various electrolytes, an intercomparison of the results obtained reveals many examples of serious disagreement. Proskurnin and Frumkin showed in 1935 that a considerable part of the disagree-

ment existing in the literature at that time could be attributed to the effects of traces of surface-active impurities, since these latter were shown to have a very large effect upon the measured capacities. Yet even in cases where such an explanation could not reasonably be invoked, discrepancies continued to exist. It will be the primary purpose of this paper to show that by the use of suitable techniques and methods of calculation, values of the capacity of the electrical double layer can be obtained by three independent methods, and the results so obtained stand in good agreement with one another. From the new results several significant conclusions can be drawn regarding the structure and behavior of the electrical double layer.

A comprehensive theory of the electrical double layer has been presented by Stern,¹¹ who assumes the double layer to be composed of two parts, a compact "two dimensional" layer of ions at the surface and a diffuse, three dimensional layer of

(1) Krüger, *Z. physik. Chem.*, **45**, 1 (1903).

(2) Bowden and Rideal, *Proc. Roy. Soc. (London)*, **A120**, 59 (1928).

(3) Erdey-Grúz and Kromrey, *Z. physik. Chem.*, **157A**, 213 (1931).

(4) Philpot, *Phil. Mag.*, **13**, 775 (1932).

(5) Ilkovic, *Coll. Czech. Chem. Commun.*, **8**, 170 (1936).

(6) Thon, *Compt. rend.*, **200**, 54 (1935).

(7) Proskurnin and Frumkin, *Trans. Faraday Soc.*, **31**, 110 (1935).

(8) Borissova and Proskurnin, *Acta Physicochim. U. R. S. S.*, **4**, 1819 (1936).

(9) Vorsina and Frumkin, *Compt. rend. acad. sci. U. R. S. S.*, **24**, 918 (1939).

(10) Frumkin, *Trans. Faraday Soc.*, **36**, 117 (1940).

(11) Stern, *Z. Elektrochem.*, **30**, 508 (1924).