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### Summary

1. Measurements of the partial vapor pressure of hydrogen chloride from its solutions in  $\beta, \beta'$ -dichloroethyl ether and in anisole at four temperatures in the range of 20–40° are reported.

2. The vapor pressure measurements are used to calculate the mole fraction solubility of hydro-

gen chloride in these solvents at a partial pressure of 1 atm. These calculated solubilities, which fit an equation of the form  $\log N = A/T + B$ , are used to obtain the differential heat and entropy of solution. The entropy values so obtained are in agreement with those derived from pertinent infrared absorption data and an equation connecting the thermodynamic with the spectroscopic quantity.

3. The question of the applicability of this equation to hydrogen chloride solutions in carbon tetrachloride, arising from a value for the heat of solution obtained from recent solubility measurements in this system, is considered.

OMAHA, NEBRASKA

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

## Contributions to the Chemistry of Indium. V.<sup>1</sup> Hydrolysis Constants for Indium Tribromide and Triiodide Solutions

BY THERALD MOELLER

In a previous communication,<sup>2</sup> the hydrolysis constant for indium trichloride solutions was evaluated from pH measurements at various concentrations upon the assumption that the governing hydrolytic reaction results in the formation of  $[\text{In}(\text{H}_2\text{O})_6(\text{OH})]^{++}$  and  $\text{H}_3\text{O}^+$  ions. Inasmuch as no similar literature data exist for solutions of the tribromide and triiodide, it has been of interest to extend such observations to these materials.

### Experimental

**Preparation of Anhydrous Indium Trihalides.**—Anhydrous indium tribromide was prepared and purified by the method of Baxter and Alter.<sup>3</sup> The white crystalline product was preserved in dry nitrogen until used.

Although anhydrous indium triiodide has been obtained by heating the metal in a stream of dry carbon dioxide laden with iodine vapor,<sup>4,5</sup> a similar procedure using nitrogen instead of carbon dioxide proved to be less effective than a modification of the method of Meyer<sup>6</sup> in which indium metal was warmed with an excess of iodine in an atmosphere of dry nitrogen. The triiodide was obtained as a brown liquid which, after removal of the excess iodine by sublimation, was purified by slow distillation in a current of nitrogen. Upon cooling, the distillate solidified to

a mass of bright yellow crystals containing none of the red monoiodide.

**Experimental Procedure.**—The procedure followed exactly duplicated that previously reported<sup>2</sup> and is, therefore, not included. The results obtained at 25 ± 0.05° with the glass electrode are summarized in Tables I and II for the bromide and iodide, respectively.

The indium tribromide solutions were unchanged upon standing, but the iodide solutions slowly turned yellow.

### Results

Employing the assumption that the ions  $[\text{In}(\text{H}_2\text{O})_6(\text{OH})]^{++}$  and  $\text{H}_3\text{O}^+$  are formed in each instance, values for the degree of hydrolysis ( $x$ ) and the hydrolysis constant ( $K_h$ ) have been cal-

TABLE I  
HYDROLYSIS OF INDIUM TRIBROMIDE SOLUTIONS AT 25°

| Moles of $\text{InBr}_3$ per liter | pH   | Degree of hydrolysis $x$ | Hydrolysis constant $K_h \times 10^4$ |
|------------------------------------|------|--------------------------|---------------------------------------|
| 0.002500                           | 3.42 | 0.152                    | 6.8                                   |
| .005000                            | 3.33 | .094                     | 4.8                                   |
| .01000                             | 3.25 | .056                     | 3.3                                   |
| .02000                             | 3.18 | .033                     | 2.3                                   |
| .04000                             | 3.10 | .020                     | 1.6                                   |
| .06000                             | 3.03 | .0155                    | 1.5                                   |
| .08000                             | 2.98 | .0130                    | 1.4                                   |
| .1000                              | 2.94 | .0115                    | 1.3                                   |
| .1500                              | 2.86 | .0092                    | 1.3                                   |
| .2000                              | 2.80 | .0079                    | 1.3                                   |
| .2500                              | 2.74 | .0073                    | 1.3                                   |
| .3000                              | 2.69 | .0068                    | 1.4                                   |
| .3500                              | 2.64 | .0065                    | 1.5                                   |
| .4000                              | 2.59 | .0064                    | 1.6                                   |

(1) For the fourth paper in this series see Moeller, *J. Phys. Chem.*, **45**, 1285 (1941).

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

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

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

(5) Klemm, *Z. anorg. allgem. Chem.*, **152**, 252 (1926).

(6) Meyer, *Ann.*, **150**, 137 (1869).

TABLE II  
HYDROLYSIS OF INDIUM TRIIODIDE SOLUTIONS AT 25°

| Moles of InI <sub>3</sub><br>per liter | pH   | Degree of<br>hydrolysis<br>$\alpha$ | Hydrolysis<br>constant<br>$K_h \times 10^6$ |
|--|------|-------------------------------------|---|
| 0.002500                               | 3.37 | 0.170                               | 8.7   |
| .005000                                | 3.28 | .105                                | 6.2   |
| .01000                                 | 3.18 | .066                                | 4.7   |
| .02000                                 | 3.09 | .041                                | 3.5   |
| .04000                                 | 3.02 | .024                                | 2.4   |
| .06000                                 | 2.96 | .018                                | 2.0   |
| .08000                                 | 2.92 | .0150                               | 1.8   |
| .1000                                  | 2.88 | .0130                               | 1.7   |
| .1500                                  | 2.81 | .0103                               | 1.6   |
| .2000                                  | 2.75 | .0089                               | 1.6   |
| .2500                                  | 2.70 | .0080                               | 1.6   |
| .3000                                  | 2.64 | .0076                               | 1.7   |

culated<sup>2,7</sup> for both the bromide and iodide solutions. These are summarized in Tables I and II. If the results for the four most dilute solutions be

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

neglected in each case,<sup>2</sup> the remaining values for  $K_h$  are then reasonably constant with means of  $1.4 \times 10^{-5}$  and  $1.8 \times 10^{-5}$  for the bromide and iodide respectively.

Comparison of these averages with the mean value of  $1.2 \times 10^{-5}$  reported for solutions of indium trichloride<sup>2</sup> indicates that the extent of hydrolysis is only slightly increased in the series chloride to bromide to iodide.

### Summary

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

2. Calculation of hydrolysis constants on the assumption that the hydrolysis products are  $[\text{In}(\text{H}_2\text{O})_6(\text{OH})]^{++}$  and  $\text{H}_3\text{O}^+$  yields average values of  $1.4 \times 10^{-5}$  and  $1.8 \times 10^{-5}$  for the bromide and iodide solutions, respectively.

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## Ionic Competition in Base-Exchange Reactions<sup>1</sup>

BY R. H. BRAY

A knowledge of the equilibria between exchangeable cations and electrolytes in colloidal systems has assumed new importance in recent years. The properties of clays in many of their ceramic uses, particularly castings, the weathering of minerals, the physical properties of soils, the softening of water and the recent application of new cation-exchange resins to numerous purposes are regulated by cation-exchange equilibria.

### Exchange Equilibria in Soils

The equilibria between the exchangeable cations on the soil clays and electrolytes in the soil water influence many important processes concerned with soil leaching and plant nutrition. The most important of these equilibria are those which involve relatively small amounts of electrolyte and relatively large amounts of cation-exchange material. However, cation-exchange studies usually have concerned themselves with the range within which clay and electrolyte are present in equivalent amounts or almost so.

A second aspect, little studied, is the influence of a mixed cation composition on the release or

adsorption of an individual cation, as for example where exchangeable calcium, magnesium, potassium, and hydrogen are present on the exchange complex and a mixture of potassium and sodium chlorides is added to the system.

A third aspect, likewise little studied, is the influence of relatively large amounts of exchangeable cations on the release of relatively small amounts of complementary ions and *vice versa*, as for example where 0.1 m. e. of exchangeable potassium occurs in a soil containing 10 m. e. of calcium, 5 of magnesium, and 5 of hydrogen as complementary exchangeable cations.

These aspects of cation-exchange may be summed up as follows. (a) The ratio of exchangeable cation to electrolyte is wide. (b) The ratio between complementary ions is wide. (c) The number of different kinds of ions present is large. The purpose of the present study is to present experimental cation-exchange data obtained under the above conditions and to evaluate the data in terms of exchange adsorption isotherms.

### General Considerations

The exchangeable cation composition of a clay system containing a relatively small amount of

(1) Presented before the Colloid Section of the American Chemical Society, St. Louis, Missouri, April, 1941. Published with the approval of the Director of the Agricultural Experiment Station.