Complex Formation between Mandelic Acid and Tervalent Indium in Aqueous Solutions

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pH and conductometric studies of the system indium-perchlorate-mandelic acid-water show the existence of three chelates in solution with a metal to ligand ratio of 1 : 1, 1 : 2, and 1 : 3. The 1 : 3 complex has been found to be most stable as it could be isolated in a crystalline state and its composition has been determined.

The studies on mandelate complexes of tervalent aluminium and gallium by utilising preparative and physico-chemical techniques have already been reported[1-2]. Two crystalline complex acids with a metal to ligand ratio of 1:2 and 1:3 for gallium and only one stable chelate for aluminium, the alumino-mandelic acid possessing a ratio of 1 : 2, were isolated.

A survey of the literature reveals that trivalent indium forms a diversified series of complex compounds containing inorganic and organic ligands[3-7]. Several indium complexes with simple organic acids, other than mandelic, have also been reported[8-11].

Cozzi and Raspi[12], during studies on the polarographic behaviour of indium (III) in presence of various organic acids, employed mandelic acid and inferred the fromation of a complex with a ratio of indium to mandelic acid 1 : 3. In view of the above results and lack of detailed information on the indium-mandelate complexes, it was considered worthwhile to undertake a physico-chemical investigation of the indium (III)—mandelic acid—water system and to isolate the complexes in a crystalline state. The present communication deals with the same study.

EXPERIMENTAL

A stock solution of indium perchlorate was prepared by dissolving freshly precipitated indium hydroxide in perchloric acid and standardised gravimetrically by "8-quinolinol".

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In each case, indium perchlorate solution was adjusted to an initial pH of 3.15 by adding a requisite quantity of a standard NaOH solution prior to the preparation of a particular set of mixture. An approximate quantity of mandelic acid (B. D. H. extra pure) was dissolved in conductivity water to provide a solution of the desired strength.

Procedure.—Electrometric and conductometric titrations were employed for the physico-chemical studies, using monovariation method. To constant volumes of $0.01M$ indium perchlorate solution varying amounts of $0.01M$ mandelic acid solution were added. Thus three sets of mixtures containing a metal to ligand ratio of 1:1, 1:2, and 1:3 were prepared. To these mixtures different quantities of the standard NaOH solution were added and the mixtures were made to a constant volume. The sets were left for about 24 hr. to attain equilibrium. The pH values and conductances of these solutions were measured at a constant temperature of $30° \pm 1°$. For purposes of comparison, solutions of indium perchlorate and mandelic acid were also separately titrated potentiometrically and conductometrically with the standard alkali under identical conditions.

The pH values were measured by a sensitive pH-meter (made by Leeds and Northrup Co., Philadelphia. U.S.A., Cat. No. 7667) having a glass and a saturated calomel electrode. The instrument was standardised with a standard buffer solution.

Conductance determinations were performed with a dip type conductivity cell (cell constant=1.03), using a battery-operated Serfass conductivity bridge (Model RCM 15B, made by Arthur H. Thomas Co., Philadelphia, U.S.A.), the null point being detected by a magic eye. The results of the investigations are graphically represented in Fig. 1 and 2.

DISCUSSION

Fig. 1 shows the variation of H^+-ion concentration with the progressive addition of alkali to various systems. Curve E represents the titration of mandelic acid alone and, as expected of a monobasic acid, shows a sudden rise in pH when nearly one equivalent of alkali has been added. In curve A, obtained for $0.01M$ indium perchlorate solution, precipitation of the hydroxide starts at a pH ∼ 4.0 and an abrupt increase in pH is observed when three moles of alkali are added, indicating complete precipitation of the hydroxide.

Curve B, obtained for the 1:1 mixture of indium perchlorate and mandelic acid, shows that the pH of the mixture (2.75) in the beginning, when no alkali is added, is lower than the pH of indium-perchlorate (3.15) and mandelic acid (3.25) separately. This clearly shows that chelation has taken place due to which the protonic hydrogen of the hydroxyl group of the mandelic acid has been released along with the replaceable hydrogen of the carboxylic group. Thus two moles of alkali should be expected to be consumed for the titration, but actually curve B possesses an inflection at three equivalents of alkali, indicating an overall consumption of three moles. If no chelation had taken place, four equivalents of alkali, however, should have been consumed. The experimental results could be explained by assuming the formation of an unstable 1:1 chelate which readily hydrolyses to
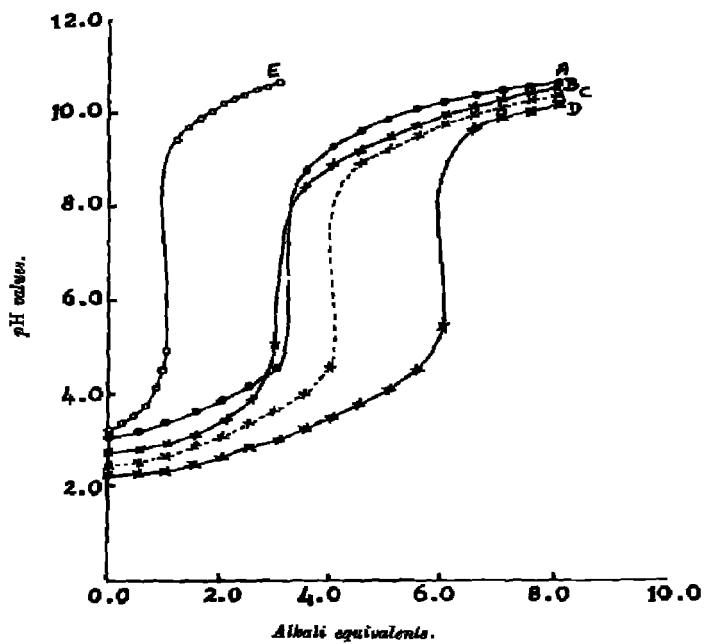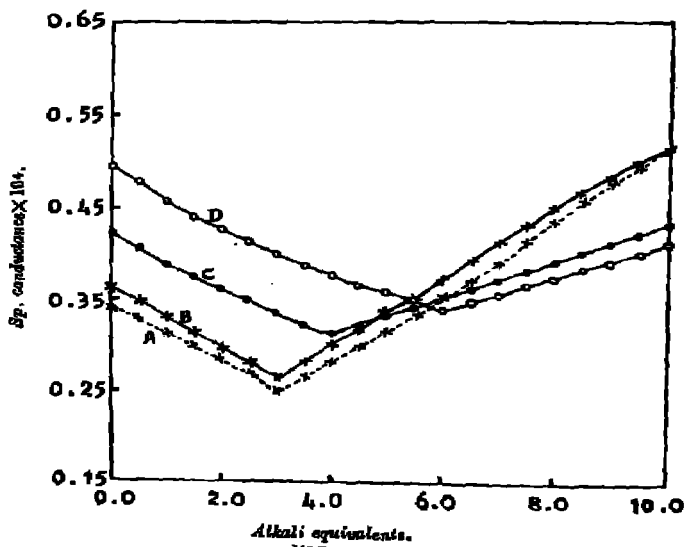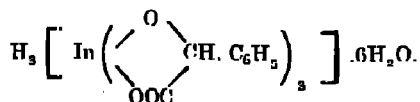
pH value.

Alkali equivalents.

FIG. 1

Sp. conductance×10⁴.

Alkali equivalents.

FIG. 2

afford a basic indium mandelate. The reactions taking place could be represented by the equation:

$$\ldots \quad (1)$$

Titrations of 1 : 2 and 1 : 3 mixtures, represented by curves C and D (Fig. 1), respectively, show an inflection at four and six equivalents of alkali. This corresponds to the formation of complexes with a metal to ligand ratio of 1 : 2 and 1 : 3, respectively, represented by the following equations:

$$+ 4H^+ + 4H_2O \quad \ldots \quad (2)$$

and

$$+ 6H^+ + 6H_2O \quad (3)$$

The results of the conductance measurements are shown graphically in Fig. 2. It is observed that both the curves A and B, representing the conductometric titration of indium parchlorate alone and its 1 : 1 mixture with mandelic acid, respectively, possess an inflection at three equivalents of alkali. The results are analogous to those obtained for the pH-titrations of these mixtures and confirm the formation of a 1 : 1 unstable complex which is hydrolysed to a basic indium mandelate.

Curves C and D, obtained for 1 : 2 and 1 : 3 mixtures respectively, show, however, minimum conductances at four and six equivalents of alkali. The decrease in conductance with addition of alkali solution in the beginning may be due to replacement of fast-moving H^+ by the slow-moving Na^+. When all the H^+ ions are removed, the conductance rises

abruptly due to the excess of Na^+ and OH^-, causing a break in the curve. Thus the curve is actually analogous to the titration curve of a strong acid and a strong base. Therefore, from the positions of inflections in curves C and D, the formation of 1:2 and 1:3 complexes is confirmed and is explained by the same equations for pH titrations (*vide supra*).

Isolation and Characterisation of the Compound

An excess of freshly precipitated indium hydroxide was shaken with concentrated mandelic acid solution (0.3 M) till no more of it dissolved. The unchanged indium hydroxide was filtered and the volume of the filtrate reduced in a vacuum desiccator. A white crystalline solid separating was washed with ethanol-water mixture and ether and air-dried.

The indium and mandelic acid contents of the compound were analysed[13]. Water molecules were also determined by heating a known weight of the air-dried sample in an oven at 110° and finding the loss in weight. (Found: In, 16.19; mandelate, 66.46; water, 16.07. Calc. for $C_{24}H_{21}O_9.In.6H_2O$: In, 16.96; mandelate, 66.60; water 15.97%). The compound is sparingly soluble in water and ethanol but insoluble in other common organic solvents. Its aqueous solution is acidic to litmus and requires three equivalents of alkali for complete neutralisation. Both the analytical data and properties of the compound are in agreement with the formulation :

$$H_3 \left[In \left(\overset{O}{\underset{OOC}{\diagup\diagdown}} CH.\,C_6H_5 \right)_3 \right].6H_2O.$$

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