Complex Compounds of Gallium with Mandelic Acid

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In a previous communication from this laboratory[1] it has been reported that aluminium hydroxide and mandelic acid form two compounds, an insoluble basic salt and a water-soluble chelate, both possessing a metal-to-ligand ratio of 1 : 2. Gallium, indium and thallium, other metals of the same group, are known to show a close resemblance to aluminium in their tendency to form coordination complexes. A study of the gallium chloride - mandelic acid - water system has been undertaken with a view of establishing the nature of the complex species. The results are communicated in this paper.

Experimental

pH and Conductivity Studies.—A stock solution of gallium chloride was prepared by dissolving freshly-precipitated gallium hydroxide in a minimum quantity of dilute hydrochloric acid. The metal content was determined gravimetrically by the use of 8-quinolinol. The gallium chloride solution was adjusted to an initial pH of 2.95 in each case by adding a requisite quantity of a standard sodium hydroxide solution prior to the preparation of a particular set of mixtures.

Mandelic acid (British Drug House, extra pure quality) was dissolved in conductivity water and used as such.

Using 0.004 M solutions of gallium chloride and mandelic acid, three sets of mixtures, with metal-to-ligand ratios of 1 : 1, 1 : 2 and 1 : 3, were prepared. To these solutions varying quantities of a standard alkali solution were added and the volumes made up to the same mark in each case. The mixtures were then shaken well and left overnight to attain equilibrium. The pH values and conductances of these solutions were measured at a constant temperature. For purposes of comparison, solutions of gallium chloride and mandelic acid of the same concentration were also separately titrated with the standard alkali under identical conditions.

The pH determinations were carried out with the help of a sensitive pH meter (made by Leeds and Northrup Co ; Philadelphia, U. S. A. Cat. No. 7667) equipped with a glass and a saturated calomal electrode. The pH values of all the sets are plotted against the amount of alkali added, and the curves obtained are shown in Fig. 1.

Conductivity experiments were performed with a dip-type conductivity cell (cell constant, 1.46 ml.)

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[1] T. N. Srivastava and D. C. Rupainwar, *J. prakt. Chem.*, to be published.

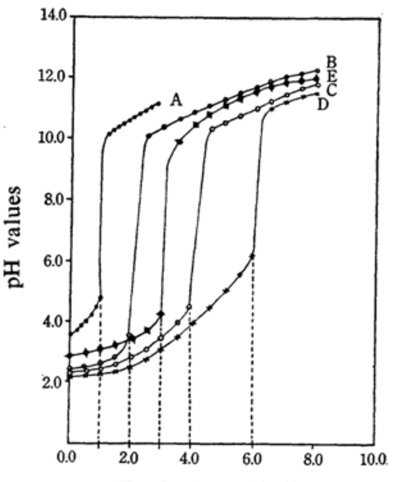


Fig. 1. Electrometric titration of mixtures of 0.004 M gallium chloride and 0.004 M mandelic acid at 30±1°C.
$GaCl_3$: Mandelic acid
A, 0 : 1 B, 1 : 1 C, 1 : 2 D, 1 : 3 E, 1 : 0

using an electrical Mullard Conductivity Bridge, the null point being detected by the use of a magic eye. The results are shown in Fig. 2, where the specific conductance is directly plotted against the equivalents of alkali added.

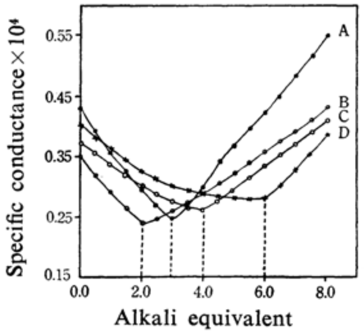


Fig. 2. Conductometric titrations of mixtures of 0.004 M gallium chloride and 0.004 M mandelic acid at 30±1°C.
$GaCl_3$: Mandelic acid
A, 1 : 0 B, 1 : 1 C, 1 : 2 D, 1 : 3

Solubility Measurements.—A set of ten samples containing almost the same weight of freshly-precipitated gallium hydroxide and a 100 ml. aqueous solution of mandelic acid of the different concentrations ranging from 0.005 M to 0.05 M, was prepared in 250 ml. Erlenmeyer flasks. The amount of the hydroxide was so chosen that in a few of the later samples the gallium-to-mandelic acid ratio exceeded 1 : 3, while in several sets in the beginning the amount of the hydroxide was always larger than that required for a 1 : 3 ratio. All the flasks were shaken in a mechanical shaker at room temperature for 24 hr. Known aliquots were taken out with cotton-plugged pipettes, and their metal and mandelic acid contents were analysed, the former gravimetrically by 8-quinolinol and the latter volumetrically with cerium(IV) sulphate.[2] The observations are represented graphically in Fig. 3.

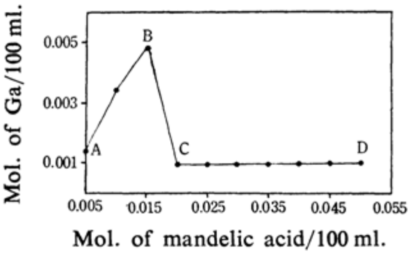
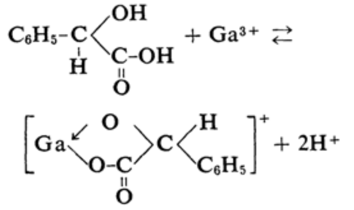


Fig. 3 Solubility of gallium hydroxide in aqueous mandelic acid solution (0.005—0.05 M) at 31±1°C.
Portion AB=Excess of gallium hydroxide
Portion CD=Excess of mandelic acid

Results and Discussion

pH and Conductivity Measurements.—Curve A (Fig. 1) represents the titration of mandelic acid alone; as is to be expected for a monobasic acid, it shows a sudden rise in pH when nearly one equivalent of alkali has been added. Curve B for a 1 : 1 mixture of gallium chloride and mandelic acid gives an inflection at 2 equivalents of alkali, indicating the formation of a 1 : 1 chelate. The chelation takes place by the donation of a lone pair of electrons from the hydroxyl oxygen atom, making the hydrogen atom attached to it more labile and causing a lowering of the pH value. Consequently, two equivalents of alkali are consumed in the titration. The overall equation may, then, be represented as follows:



$$C_6H_5\text{-}\underset{H}{C}(OH)\text{-}C(=O)\text{-}OH + Ga^{3+} \rightleftarrows \left[Ga\begin{smallmatrix}\swarrow O \\ \diagdown O\text{-}\underset{O}{\overset{}{C}}\end{smallmatrix}\!\!>C\!<\begin{smallmatrix}H\\C_6H_5\end{smallmatrix}\right]^+ + 2H^+ \qquad (1)$$

This is supported by the lower pH value of the mixture (2.40) as compared to that of individual gallium(III) chloride (2.95) and mandelic acid (3.60) solutions.

The further addition of alkali brings about a sudden increase in the hydroxide ion concentration, and the curve registers an abrupt rise in pH value.

Titrations of the 1 : 2 and 1 : 3 mixtures represented by curves C and D respectively

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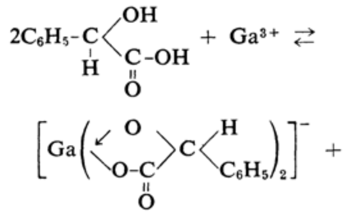
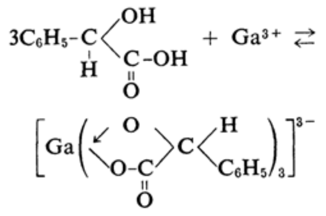
[2] M. R. Varma and S. D. Paul, *J. Sci. Ind. Res.*, **13B**, 347 (1954).

(Fig. 1) show inflection points at four and six equivalents of alkali. This corresponds to the formation of complexes with 1 : 2 and 1 : 3 metal-to-ligand ratios respectively; the complexes may be represented by the following equations:



(2)

and



(3)

Curve A (Fig. 2), representing the conductometric titration of a 0.004 M gallium chloride solution with sodium hydroxide, shows a well-defined inflection at 3 equivalents of alkali corresponding to the precipitation of the hydroxide. Curves B, C and D, obtained for 1 : 1, 1 : 2 and 1 : 3 mixtures respectively, show minimum conductances at two, four and six equivalents of alkali. The decrease in conductivity with the addition of an alkali solution in the beginning may be due to the replacement of the fast-moving H^+ by the slow-moving Na^+. When all the H^+ is removed, the conductance rises abruptly on account of the excess Na^+ and OH^- present in the solution, which cause a break in the curve. The formation of the three chelates may be explained by the same three equations given above for pH titrations.

Solubility.—The straight line marked AB in Fig. 3 represents a consistent ratio of 1 : 3 between the metal and the ligand, indicating the nature of the soluble species formed in this region. The curve registers an abrupt fall at point B, showing that almost all the gallium has gone out of the solution, forming an insoluble compound which separates as a white granular solid in the flasks. The CD portion of the curve may represent the solubility of this species in a solution with an excess of mandelic acid. The experiment thus shows the formation of two compounds, a soluble 1 : 3 chelate (compound I) when the hydroxide is present in excess and an almost insoluble white crystalline solid (compound II) when mandelic acid is present in excess.

The Isolation and Characterisation of the Compounds.—*Compound I.*—The combined filtrate obtained from the samples in the region AB of the solubility curve (Fig. 3) was concentrated by slow evaporation on a water bath, and then left for crystallisation when a white crystalline solid separated. This was washed with an ethanol-water mixture and with ether, and air-dried.

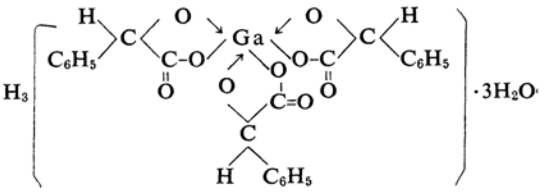
Compounds II.—Compound II obtained as a white insoluble granular solid from samples after the point B on the solubility curve was collected, washed with an ethanol-water mixture and with ether, and air-dried.

The gallium and mandelic acid contents of both the compounds were analysed. The water molecules were also examined by heating a known weight of the air-dried sample in an oven at 110°C and then ascertaining the loss in weight. The results of the analysis, along with the formulae tentatively assigned, are given below:

Tentative formula for the compound		% Gallium	% Mandelate	% Water
$C_{24}H_{27}O_{12}Ga$ (I)	Found	12.10	79.3	9.15
	Calcd.	12.07	79.1	8.89
$C_{16}H_{19}O_8Ga$ (II)	Found	16.80	71.92	8.68
	Calcd.	17.12	73.96	8.87

The good agreement between the calculated and the experimental values observed above indicates that the molecular formulae tentatively assigned are correct.

Compound I, with a metal-to-ligand ratio of 1 : 3, is soluble in water and ethanol, but insoluble in other common organic solvents. It is acidic to litmus and needs 3 equivalents of alkali for complete neutralisation. Taking three molecules of water as the water of crystallisation, its structure, in analogy with several other such chelates of tervalent metals,[3-6] may be given as:



Compound II, possessing a metal-to-ligand ratio of 1 : 2, is sparingly soluble in water, the solubility being 0.025 g./100 cc. at room temperature (30.5°C). It is insoluble in ethanol, ether and other common organic solvents. It is acidic to litmus and requires for complete

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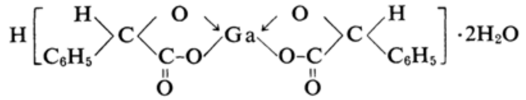
[3] T. Moellor, *J. Am. Chem. Soc.*, **62**, 2444 (1940).

[4] N. K. Dutta and P. Bose, *J. Indian Chem. Soc.*, **30**, 431 (1953).

[5] K. Peters, *Chem. Abstr.*, **53**, 13525 (1959).

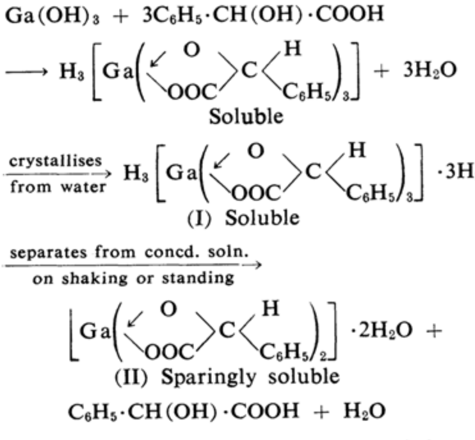
[6] E. N. Deichman and G. V. Rodicheva, *Zhur. Neorg. Khim.*, **9(4)**, 807 (1964).

neutralisation three equivalents of alkali, two of which are consumed by the released mandelic acid formed by the ready hydrolysis of the compound, and the remaining one, by the cationic hydrogen. The complex thus behaves as a monobasic acid. On being heated at 110°C, it loses two molecules of water. The structure of compound II may be written as:



The structures assigned to the two complexes support Eqs. 2 and 3, which represent the physico-chemical investigations. Attempts to isolate the 1 : 1 complex shown by Eq. 1 were, however, unsuccessful.

The reaction between gallium hydroxide and mandelic acid solutions represented by the portion CD of the solubility curve (Fig. 3) may now be reconsidered. It appears that when the concentration of the 1 : 3 chelate is relatively large in the solution and when it is vigorously shaken to induce precipitation, the more stable and less soluble 1 : 2 complex separates out. This was supported by separately taking a concentrated solution of the 1 : 3 chelate and shaking it vigorously for a few hours, a compound thereupon separated which, on analysis, was found to be identical with compound II. The change was found to be irreversible; no former species could be identified in solution when the latter was shaken with an excess of mandelic acid. The changes taking place may be represented by the following equation:



$$Ga(OH)_3 + 3C_6H_5\cdot CH(OH)\cdot COOH$$

$$\longrightarrow H_3\left[Ga\left(\begin{smallmatrix}\swarrow O\\ OOC\end{smallmatrix}>C<\begin{smallmatrix}H\\ C_6H_5\end{smallmatrix}\right)_3\right] + 3H_2O$$

Soluble

$$\xrightarrow[\text{from water}]{\text{crystallises}} H_3\left[Ga\left(\begin{smallmatrix}\swarrow O\\ OOC\end{smallmatrix}>C<\begin{smallmatrix}H\\ C_6H_5\end{smallmatrix}\right)_3\right]\cdot 3H_2O$$

(I) Soluble

$$\xrightarrow[\text{on shaking or standing}]{\text{separates from concd. soln.}}$$

$$\left[Ga\left(\begin{smallmatrix}\swarrow O\\ OOC\end{smallmatrix}>C<\begin{smallmatrix}H\\ C_6H_5\end{smallmatrix}\right)_2\right]\cdot 2H_2O +$$

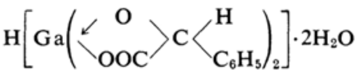
(II) Sparingly soluble

$$C_6H_5\cdot CH(OH)\cdot COOH + H_2O$$

The metal-to-ligand ratio obtained for compound II is similar to that of aluminomandelic acid reported previously.[1)] The compound differs from the aluminium complex in being more insoluble and thus is not converted into the corresponding basic salt. Further, unlike the Al^{3+} - mandelic acid - water system, the treatment of the mixture containing concentrated solutions of gallium chloride and mandelic acid with ammonia did not result in the precipitation of a basic salt. On the other hand, the above solution, when shaken and left overnight, gave a white crystalline compound, the analysis of which agreed with that of compound II.

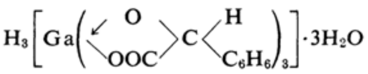
Summary

pH and conductometric studies of the gallium chloride - mandelic acid - water system show the existence of three chelates in solution with a metal-to-ligand ratio of 1 : 1, 1 : 2 and 1 : 3. The solubility of freshly-precipitated gallium hydroxide in aqueous solutions of mandelic acid of varying concentrations, however, indicates the presence of only, 1 : 2- and 1 : 3-type species. These two complexes have here been isolated in the crystalline state. Their structures may be represented by



$$H\left[Ga\left(\begin{smallmatrix}\swarrow O\\ OOC\end{smallmatrix}>C<\begin{smallmatrix}H\\ C_6H_5\end{smallmatrix}\right)_2\right]\cdot 2H_2O$$

and



$$H_3\left[Ga\left(\begin{smallmatrix}\swarrow O\\ OOC\end{smallmatrix}>C<\begin{smallmatrix}H\\ C_6H_6\end{smallmatrix}\right)_3\right]\cdot 3H_2O$$

respectively. The 1 : 1 complex indicated by electrometric titrations appears to be fairly unstable, as it could neither be inferred from solubility experiments nor isolated in the crystalline state.

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