

Spectrophotometric and Conductometric Studies of the Complex between Beryllium and 2:4 Dihydroxybenzoic Acid in Aqueous Medium

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The colourless complex formed by the interaction of beryllium with 2 : 4 dihydroxybenzoic acid has been studied spectrophotometrically in aqueous solutions of various ionic strengths and at different temperatures. The molecular composition of the complex has been determined by Job's method of continued variation and molar ratio method and is found to be 1 : 1. The values of ΔH and ΔS are calculated to be (1.49 ± 0.2) k.cal/mole and (24.7 ± 1.5) e.u. respectively. The probable structure of the complex is also suggested.

2 : 4 Dihydroxybenzoic acid forms a number of complexes with various metal ions. Complexes of 2 : 4 dihydroxybenzoic acid with Cu^{+2} , Fe^{3+} , Al^{3+} have been studied by Gupta and his coworkers^{1,2,3}. In course of our investigation on its complexes it was found that beryllium also forms a colourless complex. This paper therefore gives the results obtained in this study in aqueous medium on which no data are available in literature. The molecular composition of the complex has been determined by Job's method of continued variation⁴ and molar ratio method⁵.

EXPERIMENTAL

Beryllium perchlorate was prepared by heating beryllium chloride (E. Merck) with concentrated perchloric acid (E. Merck) until the solution no longer gave a test for chloride ion. It was diluted to required volume and sufficient perchloric acid was added to prevent hydrolysis. The beryllium content was estimated gravimetrically.

2 : 4 Dihydroxybenzoic acid was B.D.H., L.R. sample and recrystallised before use. Sodium perchlorate was used to maintain the ionic strength. Other chemicals were of AnalaR quality of B.D.H.

All the measurements of optical densities were made with a Hilger Uvispek spectrophotometer (Model H700-308 of Hilger Watts Ltd., London) using 1 cm. effective light path. The spectrophotometer was equipped with a thermostat (Townson and Mercer) and cell compartment was fitted in a jacket through which water could be circulated from the

1. S. L. Gupta, R. N. Soni and J. N. Jaitly, *Jour. Indian Chem. Soc.*, 1966, **43**, 331.
2. S. L. Gupta and R. N. Soni, *Jour. Indian Chem. Soc.*, 1965, **42**, 384.
3. S. L. Gupta and R. N. Soni, *Jour. Birla Inst. Tech. and Sci.*, 1968, **1**, 97.
4. P. Job, *Ann. Chim.*, 1928, **x**, 9, 113.
5. A. E. Harvey Jr. and D. L. Manning, *J. Amer. Chem. Soc.*, 1950, **72**, 4488.

thermostat to control the temperature. Conductances were measured with conductivity meter (LBR of Wissenschaftlich Technische Werkstätten, Germany) using titration cell (LTI). A Beckman pH meter (Model H2) was used to measure pH. All the solutions and subsequent dilution were made with conductivity water.

RESULTS AND DISCUSSION

2 : 4 dihydroxybenzoic acid ($pH = 5.0$) absorbs strongly in ultraviolet region with an absorption maximum at $290 m\mu$, whereas beryllium perchlorate is transparent round this wavelength. Addition of beryllium perchlorate to 2 : 4 dihydroxybenzoic acid solution causes the shift in the absorption maximum to higher wavelength $300 m\mu$ suggesting interaction between beryllium and 2 : 4 dihydroxybenzoic acid. This shift was found from 3.0 to 5.5 pH. Investigations above 5.5 could not be made because of precipitation of beryllium presumably as hydroxide. Hence the pH of 5.0 was selected for subsequent studies.

Composition of the Complex :

Job's Method.—A series of solutions was prepared from beryllium perchlorate and acid. The optical density measurements were made at total molarity of $4.8 \times 10^{-4} M$ at the wavelength 295, 300 and $305 m\mu$. The difference between total optical density of the

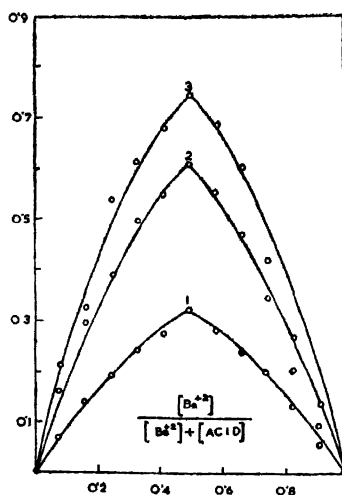


FIG 1

Fig. 1—Job's method of continued variation.

Total molarity = $4.8 \times 10^{-4} M$, $pH = 5.0$

Curves 1-3 : 295, 300 and $305 m\mu$ respectively.

solution and that which is shown by the acid solution alone if no reaction occurs at the same pH was plotted against $[Be]^{+2}/[Be]^{+2} + [Acid]$. Fig. 1 shows the maximum in all the three curves at 0.5 indicating the formation of 1 : 1 complex.

Molar ratio Method.—A series of solutions was prepared from acid in which varying amounts of beryllium were added such that the molar ratio of reagent to beryllium was varied from 1 : 0.2 to 1 : 7. Curves at 295 and 300 $m\mu$ (Fig. 2) show breaks at one mole of the reagent to one mole of beryllium.

Molecular extinction coefficient and instability constant : The molecular extinction coefficient of the complex and acid were calculated in the same way as described in our earlier

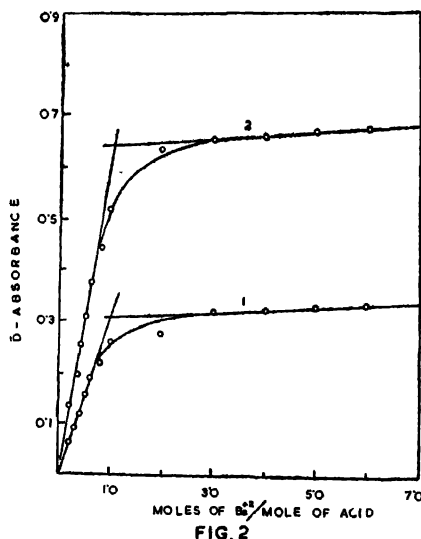


Fig. 2—Molar-ratio method.

Curves 1-2 : 295 and 300 $m\mu$ respectively.

communication³. The average values of extinction coefficient of complex and the acid at 300 $m\mu$ and at pH 5.0 are (6950 ± 13) and (2461 ± 10) respectively.

The instability constants of the complex at pH 5.0 were determined at various ionic strengths. These are recorded in the Table I. It was observed that the addition of a neutral salt increases the extent of dissociation of the complex. The ionic atmospheres about the

TABLE I

Effect of ionic strength on the instability constant of the complex between Be^{2+} and 2 : 4 dihydroxybenzoic acid.

$\lambda = 300 m\mu$; pH = 5.0; Cell width = 1 cm.; Temp. = 30°.

Ionic strength	Instability constant
0.01	$(4.68 \pm 0.15) \times 10^{-5}$
0.02	$(5.21 \pm 0.20) \times 10^{-5}$
0.05	$(5.64 \pm 0.12) \times 10^{-5}$
0.08	$(5.94 \pm 0.05) \times 10^{-5}$
0.10	$(6.33 \pm 0.20) \times 10^{-5}$
0.15	$(6.94 \pm 0.15) \times 10^{-5}$
0.20	$(7.27 \pm 0.15) \times 10^{-5}$

complex ions are denser in the salt solution. They screen the interaction between the ions of the complex and reduce their rate of recombination⁶. The instability constant was determined at different temperatures (Vide Table II).

TABLE II.

Instability constant of the complex at different temperatures.

Ionic strength = $0.01 \times$ $pH = 5.0$; $\lambda = 300 m\mu$.

Temp. °K	Instability constant
283.16	$(5.26 \pm 0.05) \times 10^{-5}$
293.16	$(4.84 \pm 0.06) \times 10^{-5}$
303.16	$(4.68 \pm 0.15) \times 10^{-5}$
313.16	$(4.30 \pm 0.02) \times 10^{-5}$
323.16	$(3.88 \pm 0.02) \times 10^{-5}$
333.16	$(3.56 \pm 0.20) \times 10^{-5}$

The logarithm of the instability constants have been plotted against $1/T$ which gives linear curve and from the slope of the straight line ΔH has been found to be $-(1.49 \pm 0.2)$ k.cal/mole. Assuming this to be constant over the range of experimental temperatures, ΔS of the complex has been calculated and is (24.7 ± 1.5) e.u.

Conductometric studies: Curves 1 and 2 (Fig. 3) give the conductometric titration (40 ml. of $7.5 \times 10^{-4}M$ and $5.0 \times 10^{-4}M$ beryllium solution with $1.0 \times 10^{-2}M$ solution of 2:4 dihydroxybenzoic acid respectively). From these curves also the ratio of beryllium to acid is found to be 1:1.

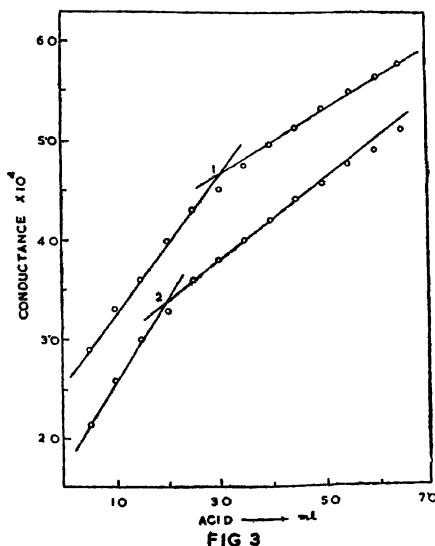


Fig. 3—Complex by conductivity method.

Curve 1—40 ml. of $7.5 \times 10^{-4}M$ Be^{+2} vs. $1 \times 10^{-2}M$ acid solution.

Curve 2—40 ml. of $5.0 \times 10^{-4}M$ Be^{+2} vs. $1 \times 10^{-2}M$ acid solution.

6. P. Debye, *Trans. Electrochem. Soc.*, 1942, **82**, 265,

Structure of the complex : Curve 4 (Fig. 4) shows that the pH of 2 : 4 dihydroxybenzoic acid (20 ml. of $10^{-3}M$; $pH = 3.40$) is gradually decreased by the addition of beryllium perchlorate ($10^{-2}M$; $pH = 3.70$) and became constant at 3.25 when one equivalent of beryllium perchlorate was added. Thus there is an increase in the hydrogen ion concentration. This is only possible when hydroxyl hydrogen of 2 : 4 dihydroxybenzoic acid is replaced by beryllium.

Further three sets of solutions were prepared by mixing beryllium perchlorate and sodium salt of the acid in the ratio of 1 : 1, 1 : 2 and 1 : 3 respectively. The total volume in each case being kept constant by the addition of conductivity water and the solutions

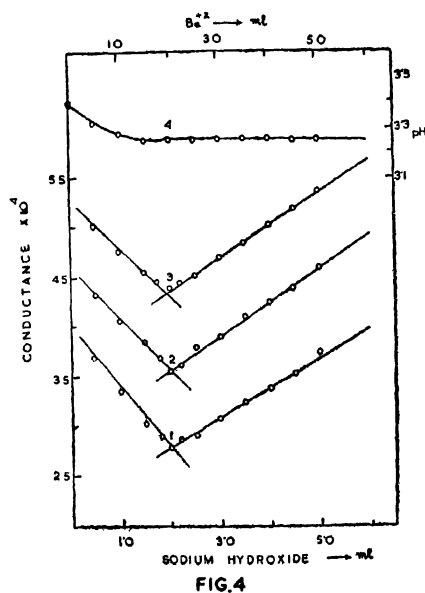


Fig. 4—Structure of the complex.

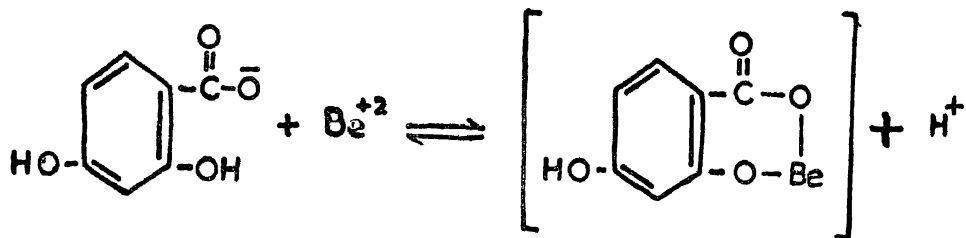
Curve 1 :—1 : 1, Curve 2 :—1 : 2, Curve 3 :—1 : 3

Mixtures of metal and ligand titrated with $1.0 \times 10^{-2}M$ NaOH.

Curve 4 : 20 ml. of $1.0 \times 10^{-3}M$ acid vs. $1.0 \times 10^{-2}M$ Be^{+2} solution.

were allowed to stand for half an hour for attaining equilibrium. These solutions were titrated with sodium hydroxide solution and conductance values were plotted against the volume of alkali added. It was observed that in all these cases conductance curves 1, 2, and 3, (Fig. 4) exhibited only one break at one equivalent of alkali added. Since sodium salt of the acid was used, the only proton which could be replaced as a result of chelation was the hydroxyl hydrogen. The break at one equivalent in all the cases, therefore, suggested

. 1 : 1 complex found in the system. On the basis of the above experimental observations, the structure of the complex may be assigned as—



The authors are grateful to the authorities of the Birla Institute of Technology and Science, Pilani, for providing facilities and to C.S.I.R. for the award of research fellowship to one of them (R.N.S.).

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Received December 12, 1967.