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# CHELATE FORMATION BETWEEN ALUMINIUM (III) AND 2,5-DIHYDROXYBENZOIC ACID SPECTROPHOTOMETRIC STUDIES OF THE COMPOSITION AND STABILITY

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2,5-Dihydroxybenzoic acid ($H_3L$) has been extensively used as a complexing agent for many metal ions[1-4]. Tanabe and Hata[5] studied colour reactions of this acid with cobalt and copper in presence of ammonia. It has been found that $H_3L$ also forms a colourless complex with aluminium which is used as analgesic and antipyretic[6]. In the present paper the authors have re-

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\* The work done during the author's stay at the Department of Analytical Chemistry, Purkyně University, Brno.

ported the results of spectrophotometric studies of the complex in aqueous medium on which no data are available in literature.

A recrystallized sample of 2,5-dihydroxybenzoic acid (T. Schuchardt, Germany) was used for preparing stock solution. Sodium perchlorate was used for maintaining ionicstrength. Ammonium acetate (B.D.H., A.R.) was used in buffer solutions.

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

Light absorption measurements were made by Hilger Uvispek spectrophotometer (Model H700—308) using cells of one cm effective light path. The cell compartment was fitted with a water jacket through which water could be circulated from a thermostat (Townson & Mercer). The variation of temperature was less than $0.1°C$ over a period of time much longer than that needed for measuring the absorbance.

Conductance measurements were made using a conductivity meter (type LBR, Wissenschafftlich-Technische Werkstätten, Germany) with a titration cell type LTI. Beckman pH meter (type H2) was used for measuring pH of solutions. All solutions and subsequent dilutions were made with double distilled water.
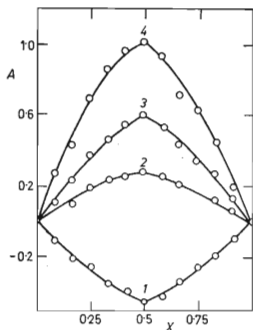


Fig. 1

Job Method of Continued Variation
pH 4·5, $I = 0.01$. Curves 1—4 at 300, 325, 330 and 340 nm respectively. $A$ difference between absorbance of the solution and that which is shown by acid alone if no reaction occurs at the same pH. $X$ mol fraction of aluminium.
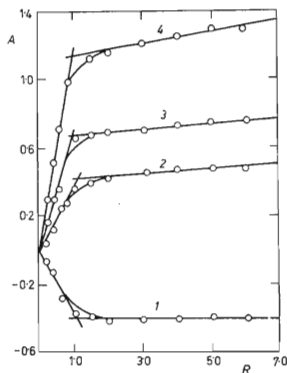


Fig. 2

Mol Ratio Method
pH 4·5, $I = 0.01$. Curves 1—4 at 300, 325, 330 and 340 nm respectively. $A$ difference between absorbance of the solution and that which is shown by 2,5-dihydroxybenzoic acid alone if no reaction occurs at the same pH, $R$ mol of aluminium/mol of $H_3L$.

RESULTS AND DISCUSSION

2,5-Dihydroxybenzoic acid solution (pH 4·5) absorbs strongly in UV region with an absorption maximum at 320 nm, whereas aluminium perchlorate solution is transparent round this wavelength. Addition of aluminium perchlorate to 2,5-dihydroxybenzoic acid solution causes a small bathochromic shift in the absorption maximum (325 nm), suggesting interaction between aluminium and $H_3L$ in the solution. A series of solutions containing aluminium ions and $H_3L$ was prepared at various pH values and light absorption was measured. It was found that the complex was stable in the pH range 3·0—5·5. Investigation above pH 5·5 could not be made because of precipitation of aluminium presumably as hydroxide. Therefore, pH 4·5 was selected for subsequent studies.

Composition of the Complex

*Job method of continued variation.* The molecular composition of the complex at pH 4·5 was determined using equimolar solutions. The absorption measurements were made at the total molarity $9·6 . 10^{-4}$M and at wavelengths 300, 325, 330 and 340 nm. The values of absorbance were plotted against the mole fraction of aluminium. The results obtained have been presented in Fig. 1. The maxima in all the four casas indicate the formation of 1 : 1 complex.

*Mol-ratio method.* A series of solutions was prepared from aluminium perchlorate and 2,5-dihydroxygenzoic acid at pH 4·5 varying the mol ratio of 2,5-dihydroxybenzoic acid to aluminium from 1 : 0·2 to 1 : 6. Fig. 2 showes breaks at a ratio of one mol of aluminium to one mol of 2,5-dihydroxybenzoic acid.

Attempts have also been made to determine molecular composition of the complex by titrating 2,5-dihydroxybenzoic acid against aluminium perchlorate solution conductometrically. From these observations, the same ratio (1 : 1) has also been found.

Molecular Extinction Coefficient and Stability Constant

The molecular extinction coefficient of the complex and 2,5-dihydroxybenzoic acid and stability constant of the complex have been calculated in a similar way as described earlier[7,8]. The values of molecular extinction coefficients of the complex and that of 2,5-dihydroxybenzoic acid at 340 nm and at pH 4·5 are 3 710 ± 10 and 1280 ± 20 respectively. Table I records stability constant of the complex at different ionic strengths. It is interesting to note that the stability constant decreases with the increase of ionic strength. The ionic atmosphere about the complex ions are denser in salt solution and screening effect reduces theri rate of recombination[9]. The stability constant has also been determined at various temperatures and the results are shown in Table II.

The thermodynamic functions like changes of free energy, entropy and enthalpy of the com-

TABLE I

Effect of Ionic Strength on the Stability Constant of Al L
   20°C, pH 4·5, 340 nm.

| $I$ | 0·01 | 0·03 | 0·06 | 0·09 | 0·11 | 0·15 | 0·20 |
|---|---|---|---|---|---|---|---|
| $K . 10^4$ | 3·23 | 2·34 | 1·60 | 1·10 | 0·80 | 0·59 | 0·34 |

TABLE II

Effect of Temperature on the Stability Constant of Al L
pH 4·5, 340 nm, $I$ 0·01.

| $T$, °K | 293·16 | 303·16 | 313·16 | 323·16 | 333·16 |
|---|---|---|---|---|---|
| $K \cdot 10^4$ | 3·23 | 3·75 | 5·62 | 7·81 | 12·00 |

plex formation have also been calculated. The value of $\Delta G$ was found to be 4·95 kcal/mol. The change of enthalpy $\Delta H$ was calculated with the help of isolar equation and was found to be 5·44 kcal/mol ($\Delta S = 41·5$ eu).

The present investigation clearly reveals the formation of 1 : 1 complex between aluminium and 2,5-dihydroxybenzoic acid. On the basis of the above observation the probable structure of the complex may be assigned as
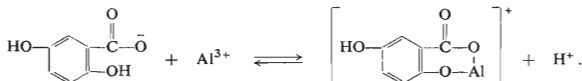
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