

## Spectrophotometric and Conductometric Studies of the Complex between Aluminium and 2-hydroxy 3-naphthoic acid in Aqueous medium

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The colourless complex formed by 2-hydroxy 3-naphthoic acid with aluminium has been studied in aqueous solutions of different ionic strengths and at different temperatures spectrophotometrically. The molecular composition has been determined by Job's method of continued variation and is found to be  $AlR_3$  ( $R = \text{Reagent}$ ). The values of  $\Delta H$  and  $\Delta S$  are found to be  $-(9.45 \pm 0.15)$  k. cal/mole and  $(52.2 \pm 1.5)$  e.u. respectively. The probable structure of the complex is also suggested.

The blue coloured water soluble complex formed by 2-hydroxy 3-naphthoic acid with  $Fe^{3+}$  ion has been investigated by Gupta and Soni<sup>1</sup>. It is seen that aluminium forms a colourless complex with 2-hydroxy-3-naphthoic acid in aqueous medium. The present investigation, therefore, gives the results obtained in the study of the complex between aluminium and 2-hydroxy-3-naphthoic acid 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 variation<sup>2</sup>. The instability constant of the complex has been determined at various ionic strengths and at various temperatures.

### EXPERIMENTAL

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 required volume and sufficient perchloric acid was added to prevent hydrolysis. The aluminium content was estimated as oxide<sup>3</sup>.

2-Hydroxy-3-naphthoic acid was B. D. H., L. R. sample and was recrystallised before use. Sodium perchlorate (E. Merck) was used to adjust the ionic strength. Hydrochloric acid and sodium hydroxide used were of AnalaR quality of B. D. H.

Absorbance measurements were made by Hilger Uvispec spectrophotometer (Model H 700-308 of Hilger Watts Ltd., London) using one cm. effective light path. The cell compartment was fitted with jacket through which water could be circulated from a thermostat (Townson and Mercer Ltd., England). A thermometer inserted into the cell compartment and allowed to come to temperature equilibrium showed a variation of less

1. Gupta, S. L. and Soni, R. N., *This Journal*, 1966, 43, p. 473.

2. Job, P. *Ann. Chim.*, 1926, X, 9, 113.

3. Vogel, A. I., *A text book of Quantitative Inorganic Analysis*. Longmans Green & Co. Ltd, III Ed., p. 472.

than 0.1°C over period of time much longer than those needed to make measurement of optical density.

Conductometric measurements were made using conductivity meter (LBR of Wissenschaftlich Technische Werkstatton, Germany). The titrations were carried out in a titration cell (type LTI) which had a thermostatic jacket for temperature stability. The pH measurements were made by Beckman pH meter (Model H2). All the solutions and subsequent dilutions were made with conductivity water.

## RESULTS AND DISCUSSION

2-Hydroxy-3-naphthoic acid (pH 4.0) absorbs strongly in ultraviolet with an absorption maximum at 345 m $\mu$ , whereas aluminium perchlorate is transparent round this wavelength. The addition of aluminium perchlorate shifts the absorption maximum of 2-hydroxy-3-naphthoic acid from 345 m $\mu$  to 350 m $\mu$  indicating complex formation between aluminium and 2-hydroxy-3-naphthoic acid. This shift was found from pH 2.5 to 5.0. Investigations above pH 5.0 could not be carried out because of precipitation of aluminium presumably as hydroxide. Hence the pH of 4.0 was selected for subsequent studies.

*Composition of the Complex:* Fig.1 gives the molecular composition of the complex at pH 4.0 using Job's method of continued variation. The optical density measurements were made at 340, 355 and 360 m $\mu$  keeping total molarity of  $8.0 \times 10^{-4}M$ . The quantity,  $\bar{D}$  (the difference between the total optical density of the solution and that which is shown by the acid solution alone if no reaction occurs at the same pH), was plotted against  $[Al^{3+}]/\{[Al^{3+}]+[HOC_{10}H_6CO_2H]\}$ . At 355 and 360 m $\mu$  the complex has a higher absorption than that of free complexing agent and at 340 m $\mu$  the complexing agent has higher absorption than that of the complex. As such  $\bar{D}$  at 355 and 360 m $\mu$  passes through maximum and that at 340 m $\mu$  passes through a minimum. The maximum at 0.5 indicates the formation of 1:1 complex.

*Molecular Extinction Coefficient:* The molecular extinction coefficient of the complex was calculated from the optical density of the solutions containing aluminium and 2-hydroxy-3-naphthoic acid in which the metal ion was in excess so that the concentration of the complex could be taken to be equal to that of the ligand. The average value of extinction coefficient of the complex at 340, 355 and 360 m $\mu$  is  $(1589 \pm 4)$ ,  $(2457 \pm 3)$  and  $(2580 \pm 3)$  respectively whereas for the ligand it has been found to be  $(2132 \pm 5)$ ,  $(1855 \pm 2)$  and  $(1459 \pm 3)$  at the above wave lengths respectively.

*Instability Constant:* The instability constant of the complex

$$K_{in} = \frac{\{[Al^{3+}]_{total} - [Complex]\} \{[Acid]_{total} - [Complex]\}}{[Complex]}$$

has been calculated. The concentration of the complex is calculated from the optical density of the solution containing aluminium and the ligand using expression.

$$\text{Optical density} = \epsilon_c [Complex] l + \epsilon_l \{[Acid] - [Complex]\} l.$$

whereas  $\epsilon_c$  and  $\epsilon_l$  are the molecular extinction coefficients of the complex and the ligand respectively and  $l$ , the cell width.

At pH 4.0, the instability constant has been determined at different ionic strengths (vide Table I). Further the instability constant was determined at different temperatures. The results are recorded in Table II. The logarithm of the instability constants have been plotted against  $1/T$  which is linear and from the slope of the straight line,  $\Delta H$  has been found to be  $-(9.45 \pm 0.15)$  K. cal/mole. Assuming this to be constant over the range of experimental temperatures,  $\Delta S$  of the reaction has also been calculated and is  $(52.2 \pm 1.5)$  e. u.

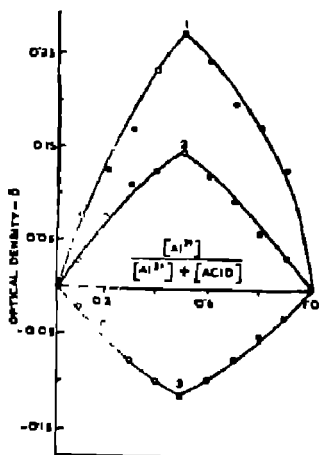


Fig. 1. Job's method of continued variation.  
Total molarity =  $8.0 \times 10^{-4} M$ ; pH = 4.0  
Curve 1-3. 360, 355 and 340 m $\mu$  respectively.

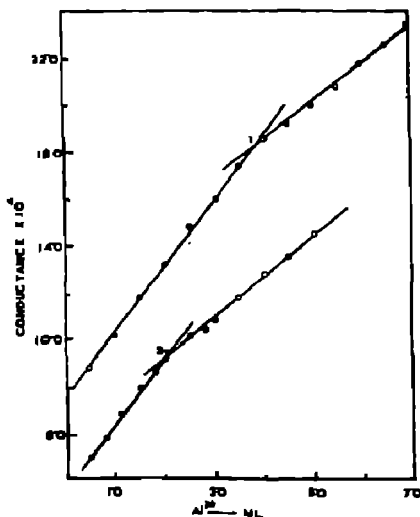


Fig. 2. Complex by conductivity method.  
Curve 1: 40 ml. of  $1.0 \times 10^{-3} M$  vs  
 $1.0 \times 10^{-3} M$   $Al^{3+}$  solution  
Curve 2: 40 ml. of  $5.0 \times 10^{-3} M$  vs  
 $1.0 \times 10^{-3} M$   $Al^{3+}$  solution.

*Conductometric Studies:* Curves 1 and 2, Fig. 2, give the titration curves of 40 ml. of  $1 \times 10^{-3} M$  and  $5.0 \times 10^{-3} M$  acid with  $1 \times 10^{-3} M$  solution of aluminium perchlorate respectively. From these curves also the ratio of the reagent to aluminium is found to be 1:1 which confirms the composition of the complex as obtained spectrophotometrically.

TABLE I

*Effect of ionic strength on the instability constant of the complex.*

$\lambda = 355$  m $\mu$ ; pH = 4.0; Cell width = 1 cm.; Temp. = 20°

| Ionic Strength | Instability Constant             |
|----------------|----------------------------------|
| 0.02           | $(2.80 \pm 0.09) \times 10^{-3}$ |
| 0.06           | $(4.16 \pm 0.20) \times 10^{-3}$ |
| 0.09           | $(5.45 \pm 0.15) \times 10^{-3}$ |
| 0.11           | $(6.72 \pm 0.04) \times 10^{-3}$ |
| 0.16           | $(8.45 \pm 0.15) \times 10^{-3}$ |
| 0.21           | $(1.08 \pm 0.24) \times 10^{-2}$ |

TABLE II

*Instability constant of the complex at different temperatures.*

| Ionic strength—0.02; | $\lambda=955 \text{ m}\mu$ ;     | $\text{pH}=4.0$ |
|----------------------|----------------------------------|-----------------|
| Temp.°K              | Instability Constant             |                 |
| 293.16               | $(2.80 \pm 0.09) \times 10^{-5}$ |                 |
| 303.16               | $(1.69 \pm 0.16) \times 10^{-5}$ |                 |
| 313.16               | $(1.26 \pm 0.23) \times 10^{-5}$ |                 |
| 323.16               | $(6.59 \pm 0.24) \times 10^{-6}$ |                 |
| 333.16               | $(9.79 \pm 0.37) \times 10^{-6}$ |                 |

*Structure of the Complex:* Curve 3, Fig. 3 shows that the pH of 2-hydroxy-3-naphthoic acid (25 ml. of  $10^{-3}\text{M}$   $\text{pH}=3.15$ ) is gradually decreased by the addition of aluminium perchlorate solution ( $10^{-2}\text{M}$   $\text{pH}=3.50$ ) and becomes constant at 2.90 when one equivalent of aluminium perchlorate (2.5 ml.) was added. This evidently shows an increase in the  $\text{H}^+$  ion concentration in the mixture. This is only possible when hydroxyl hydrogen of the 2-hydroxy-3-naphthoic acid is replaced by aluminium. This is in accordance with the view advanced by Owens and Yoc<sup>4</sup> in the structure of Be-phenoxyquinizarin sulphate (1:1) complex.

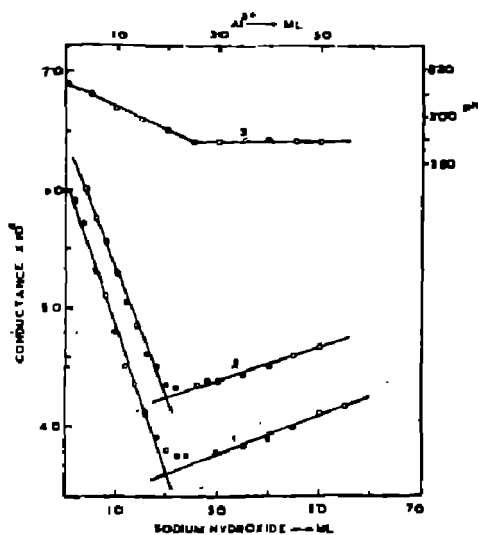


Fig. 3. Structure of the complex.

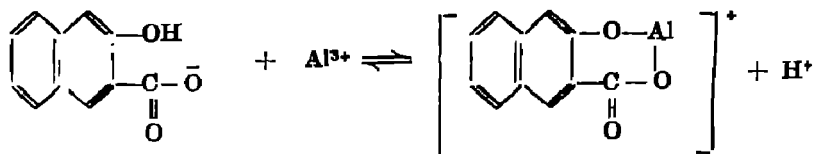
Curve 1: 1:1, Curve 2: 1:2.

mixtures of metal and ligand,  
titrated with 0.01 M NaOH.

Curve 3: 25 ml. of  $1.0 \times 10^{-3}\text{M}$  acid  
titrated with  $1.0 \times 10^{-2}\text{M}$   $\text{Al}^{3+}$  solution.

*Effect of addition of Sodium hydroxide solution:* Two sets of solutions were prepared by mixing  $10^{-3}\text{M}$  aluminium perchlorate with  $10^{-3}\text{M}$  sodium salt of 2-hydroxy-3-naphthoic acid in the ratio of 1:1 and 1:2 respectively. The total volume in each case being kept constant by the addition of conductivity water and the solutions were allowed to

stand for half an hour for attaining equilibrium. Varying amounts of  $10^{-3}M$  sodium hydroxide solutions were added to both samples and conductance values were noted down as usual. The observed data were plotted against the ml. of alkali added. It was interesting to note that in both the cases, conductance curves 1 and 2, Fig. 3 exhibited only one break corresponding to one equivalent of alkali added. Since the 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 of sodium hydroxide in both the cases, therefore, suggested that only 1:1 complex is formed in the system. On the basis of the above experimental observations the structure of the complex can be assigned as below:



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