

## A Spectrophotometric Study of Iron(III) Complex of 1-hydroxy 2-naphthoic Acid

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With 7 Figures

### Abstract

The interaction between iron(III) and 1-hydroxy 2-naphthoic acid in pH range 2—5 results in the production of deep blue colour, which exhibits absorption maximum at 620 m $\mu$ . The composition and stability of the complex responsible for the appearance of colour has been studied spectrophotometrically at different pH values. Application of JOB's methods, slope ratio method and mole ratio method indicated the formation of 1:1 complex. The stability constant (log k) at pH 2.90 and 3.92 corresponded to 4.20 and 3.90 respectively.

The analytical behaviour of 1-hydroxy 2-naphthoic acid and some of its derivatives has been the subject of a number of recent investigations. DATTA<sup>1)</sup> has quantitatively determined thorium and zirconium using this acid. The remarkable chelatometric properties of 1-hydroxy 2-naphthoic acid are evidenced by the fact that it interacts with various cations viz. Ni<sup>II</sup>, Zn<sup>II</sup>, Cu<sup>II</sup>, Cd<sup>II</sup><sup>2)</sup>, UO<sub>2</sub><sup>II</sup><sup>3)</sup>, Cr<sup>II</sup><sup>4)</sup> and Fe<sup>III</sup><sup>5)</sup> etc. at proper pH conditions. More recently a significant use of its complexing property has been made by employing it as a complexometric indicator<sup>6)</sup> in the determination of Fe(III), by titrating against EDTA. The necessity of the value of stability constant for the iron(III) complex of 1-hydroxy 2-naphthoic acid and its variation with pH, became apparent in the course of studies connected with the perfection of a titrimetric method<sup>7)</sup> (in author's laboratory) for the estimation of Fe<sup>III</sup> in presence of aluminium, employing the complex as indicator. The existing values of stability constant reported by CHANLEY

1) S. K. DATTA, J. Ind. Chem. Soc. **33**, 257 (1956).

2) P. PFEIFFER and S. V. MULLENHEIM, J. prakt. Chem. **137**, 9 (1933).

3) S. C. TRIPATHI and SATYA PRAKASH, J. Ind. chem. Soc. **36**, 19 (1959).

4) G. SCHETTY and H. ACKERMANN, Angew. Chem. **70**, 222 (1958).

5) J. D. CHANLEY and E. FEAGESON, J. Amer. chem. Soc. **78**, 2237 (1956).

6) A. B. SEN and V. B. S. CHAUHAN, J. Ind. chem. Soc. (In Press).

7) S. S. KATIYAR and V. B. S. CHAUHAN, J. Ind. chem. Soc. (In Press).

and FEAGESON<sup>5</sup>) and AGARWAL and Coworkers<sup>8</sup>) are  $K \times 10^{-4}$  and  $K \times 10^{-2}$  respectively. The wide discrepancy between these values warranted a new investigation. The present investigation was undertaken to investigate in detail the nature and composition of the complex by slope ratio, mole ratio and continuous variation method in aqueous medium. The influence of pH of the medium on the stability has also been examined.

### Experimental

1-hydroxy 2-naphthoic acid of B.D.H. (L.R.) quality was purified<sup>9</sup>) by crystallisation from ethanol. The purified product had a m.p. 187°C (literature value 186–188°C<sup>10</sup>). Stock solution of the acid was made in double distilled water as its sodium salt.

Ferric ammonium sulphate of E. Merck G.R. grade was used for making stock solution of iron(III); this last was standardised spectrophotometrically using thioglycollate method<sup>11</sup>).

Sodium acetate-hydrochloric acid buffers were used for controlling the pH of the solutions containing the complex. The chemicals used for preparing the buffers were of analytical grade.

Absorption measurements were made with the help of a BECKMAN DU Spectrophotometer. Corex cells of 10 mm width were employed. The temperature in the cell compartment was maintained at the desired value by circulating water, in the dual thermostat set fixed in the spectrophotometer, from an externally maintained thermostat.

pH measurements of the solutions were carried out with Cambridge pH meter (bench pattern) with an accuracy of  $\pm 0.01$  unit. All the measurements were made at 35.5°C.

### Results and Discussion

The interaction between iron(III) and 1-hydroxy 2-naphthoic acid in pH range 2–5 is indicated by the development of intense blue colour. The species of the complex existing in this blue solution were determined by the method of VOSBURGH and COOPER<sup>12</sup>). Solutions containing varying proportions of iron(III) and reagent were prepared and their spectra were recorded in the wavelength range 400–700 m $\mu$ . The results obtained are reported in Fig. 1; in which curves 1, 2 and 3 refer to iron(III) to reagent molar ratio of 1:1, 1:2 and 1:3 respectively.

The absorption in Fig. 1 is seen to be maximum at  $\lambda = 620$  m $\mu$  in all the three compositions. This observation is of value as it points out towards the

<sup>5</sup>) R. C. AGARWAL, S. P. AGARWAL and T. N. SRIVASTAVA, *Z. anorg. allg. Chem.* **304**, 337 (1960).

<sup>9</sup>) I. HEILBRON and H. M. BUNBURY (Editors), "Dictionary of Organic Compounds", Eyre and Spottiswoode, London (1946) p. 302.

<sup>10</sup>) C. D. HODGMAN, R. C. WEAST and S. M. SELBY, "Hand-Book of Chemistry and Physics", The Chemical Rubber Publishing Co., Cleveland, Ohio (1960) p. 1110.

<sup>11</sup>) A. I. VOGEL, "A Text-Book of Quantitative Inorganic Analysis" Longmans Green and Co., Ltd. (1960), p. 647.

<sup>12</sup>) W. C. VOSBURGH and G. R. COOPER, *J. Amer. chem. Soc.* **63**, 437 (1941).

existence of only one species of the complex in the solution. It may be noted that neither the iron(III) nor reagent absorbs in the vicinity of the wavelength of maximum absorption.

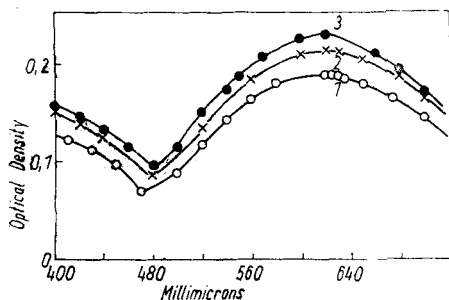


Fig. 1. Absorption spectra of mixtures of iron(III) and 1-hydroxy 2-naphthoic acid. [Fe(III): Acid for curve 1, 1:1, Curve 2, 1:2, Curve 3, 1:3]

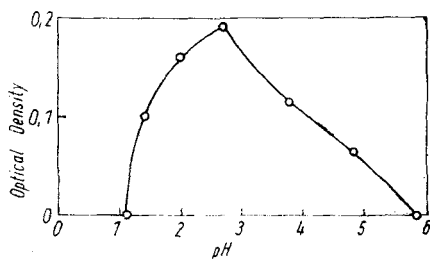


Fig. 2. Variation of absorbance of the iron(III) complex with pH at 620 mμ.

### Influence of pH on the complex

It was observed that addition of acid or alkali in the blue coloured complex resulted in the disappearance of colour. It appeared necessary therefore to examine the stability of the complex at different pH. Solutions containing  $1.6 \times 10^{-4}$  M iron(III) and  $3.2 \times 10^{-4}$  M 1-hydroxy 2-naphthoic acid in different buffers were prepared in 25 ml. measuring flasks. Their spectra were recorded. The wavelength of maximum absorption was not affected by the change of pH in the range 2–5. However, the absorbance was affected markedly by pH. The variation of absorbance with pH at  $\lambda = 620$  mμ is shown in Fig. 2. It becomes apparent from this figure that the maximum formation of the complex takes place near pH 2.80. At pH values lower or above than this, the optical density readings decrease rapidly and no complex is formed below pH 1 or above 5.8. The optimum pH range for the investigation of complex is 2–5.

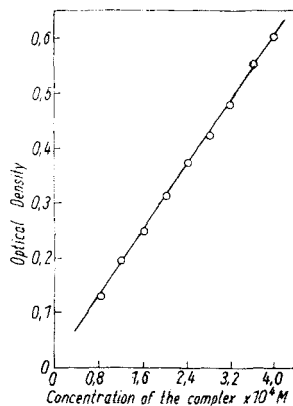


Fig. 3. Variation of optical density of the complex with concentration at 620 mμ.

### BEER'S LAW

The blue coloured complex obeyed BEER'S LAW. Fig. 3 gives the typical data showing the variation of optical density of complex with concentration.

The linear plot obtained indicates the applicability of BEER'S Law. The concentration of complex was taken to be equal to the concentration of iron(III) which was in completely complexed state due to the presence of a sufficient excess of 1-hydroxy 2-naphthoic acid. The extinction coefficient ( $\epsilon$ ) of complex at pH 2.90 corresponded to  $1.58 \times 10^3$  litre mole<sup>-1</sup> cm<sup>-1</sup>.

The composition of the complex was determined by JOB'S method as modified by VOSBURGH and COOPER<sup>12</sup>). It was further verified by the slope ratio and mole ratio methods.

The continuous variation method<sup>13</sup>): The studies by this method were made employing equimolar solutions (M/500) of iron(III) and 1-hydroxy 2-naphthoic acid. A series of solutions were prepared by mixing x ml. of iron and (10 - x) ml. of ligand, where x was varied from 1 to 10 ml. and total volume was kept 25 ml. The pH of these solutions was 2.70. The optical densities of these solutions were measured at  $\lambda = 620$  m $\mu$  against water as blank solution. The absorbance was taken to be due to the presence of complex only, since both the components iron(III) and ligand do not show any absorption near 620 m $\mu$ . The results are recorded in Fig. 4, which gives a variation of optical density with mole fraction of iron(III). The occurrence of a peak at 0.5 mole fraction of iron indicates the formation of 1:1 complex.

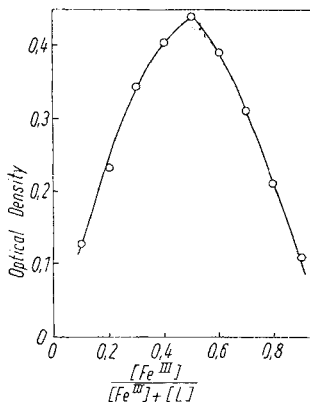


Fig. 4. Determination of composition of the complex by continuous variation method employing equimolar solutions ( $\lambda = 620$  m $\mu$ )

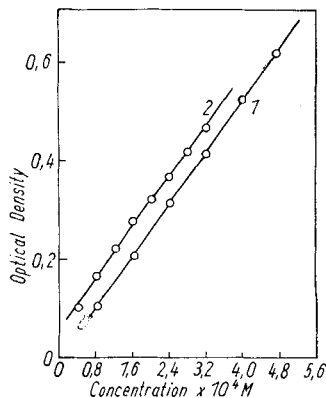


Fig. 5. Determination of composition of the complex by slope ratio method at 620 m $\mu$ . (Curve 2 shifted upwards on ordinate by 1 cm.)

The slope ratio method: Fig. 5 represents the typical data obtained by the use of slope ratio method<sup>14</sup>). Curve 1 represents the variation of

<sup>13</sup>) P. JOB, Ann. Chim. **9**, 113 (1928); **16**, 97 (1936).

<sup>14</sup>) A. E. HARVEY and D. L. MANNING, J. Amer. chem. Soc. **72**, 4488 (1950).

optical density with the increase in concentration of 1-hydroxy 2-naphthoic acid ( $M/500$ ), keeping the concentration of iron(III) constant and in sufficient excess. In the second series (curve 2) of solutions the concentration of ligand was kept constant and in sufficient excess while iron(III) ( $M/500$ ) was varied. The optical density measurements of the solutions were made at  $\lambda = 620 \text{ m}\mu$  taking water as reference. The resulting pH of the solutions was 2.72. The slopes of the plots 1 and 2 worked out to be

$$\text{Slope of plot 1} = 0.13 \times 10^4$$

$$\text{Slope of plot 2} = 0.13 \times 10^4$$

$$\text{Molar ratio of the complex} = \frac{0.13}{0.13} = 1.$$

Thus this method also suggests the formation of 1:1 complex.

**The mole ratio method:** This elegant method suggested by YOE and JONES<sup>15</sup>) gives information about the composition of the complex from the break observed in absorbance vs. molar concentration of the component (whose concentration is varied) curve. The concentration of iron(III) was kept constant ( $2.4 \times 10^{-4} \text{ M}$ ), while of the ligand was varied in the ratio 1:0.05, to 1:10, final pH of the solutions being 2.61. The data obtained are recorded in Fig. 6 (curve 1). It is seen from curve 1 Fig. 6 that a sharp break is not observed, which probably is due to the ionisation of the complex in dilute solutions. However, when the experiments were conducted in presence of 5 c.c. of 1.0 M KCl, a break was observed at 1:1 ratio of iron(III) to reagent (curve 2, Fig. 6). This observation also verifies the 1:1 composition of complex, as established by earlier methods (vide supra).

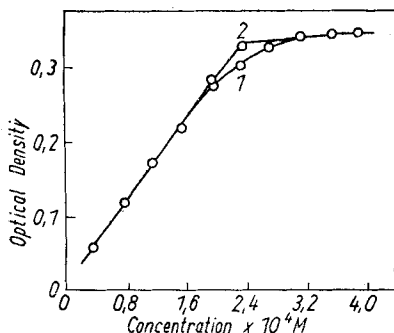


Fig. 6. Composition of the complex by mole ratio method at 620  $\text{m}\mu$ .

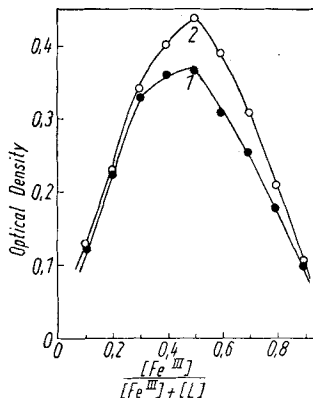


Fig. 7. Continuous variation curves at different pH. Curve 2 pH = 2.90; Curve 1 pH = 3.92

<sup>15</sup>) J. H. YOE and A. L. JONES, *Ind. Eng. Chem. Anal. Ed.* **16**, 111 (1946).

<sup>16</sup>) S. K. BANERJI and A. K. DEY, *J. Sci. Industr. Res. (India)* **20B**, 375 (1961).

### Stability constant of the complex and influence of pH on 'K'

The classical formation constant of iron(III) 1-hydroxy 2-naphthoic acid complex was computed from JOB's curves shown in Fig. 7. Curves 1, 2 and 3 here refer to the data obtained at pH values 1.93, 2.90 and 3.92 respectively.

The values of  $k$  are given in Table 1 below.

pH	Classical stability constant log K	Thermodynamic stability constant log K
2.90	4.20	5.18
3.92	3.90	4.86

The last column of this Table gives the values of  $K$ , the thermodynamic stability constant which was obtained by the equation of DEBYE and HUCKEL<sup>17)</sup>. The values of  $K$  were further utilised for the computation  $\Delta F^\circ$ , free energy of formation which is related to  $K$  as follows.

$$\Delta F^\circ = - RT \ln K \quad (3)$$

The value of  $\Delta F^\circ$  at 35.5 °C and pH 2.90 corresponded to -7.31 kcal.

The authors wish to thank Prof. P. K. KELKAR, Director, Indian Institute of Technology, Kanpur for his interest; to Director National Sugar Institute for the permission to use the spectrophotometer and Dr. A. B. SEN for the encouragement.

<sup>17)</sup> S. GLASSTONE, "A Text Book of Physical Chemistry" Mac-Millan and Co., Ltd. London (1956) p. 970.

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