

## Composition and Stability of the Chelate between Aluminium (III) and Sodium Alizarin 3-Sulphonate: Spectrophotometric and Electrical Conductance Studies

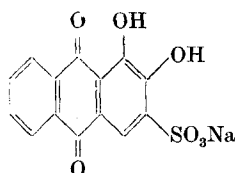
By ROSHAN LAL SETH and ARUN K. DEY

With 14 Figures

### Abstract

The composition and stability of aluminium-alizarin 3-sulphonate chelate has been studied by spectrophotometric and electrical conductance measurements. The red coloured chelate ( $\lambda_{\max}$  470 m $\mu$ ) has a composition 1:2 (metal: chelating agent). The chelate is stable between pH 2.5 and 4.5. The values of log K as calculated by two different methods are  $7.2 \pm 0.3$  and  $7.5 \pm 0.2$  at 25°C (pH  $3.5 \pm 0.2$ ). Suggestions have also been made about the position of the chelate ring in the metal chelate.

Sodium alizarin 3-sulphonate, commonly known as Alizarin Red S, is a member of the hydroxy anthraquinone group of dyes and has the following structure:



Alizarin Red S

In a number of publications from these laboratories, metal chelates with sodium alizarin 3-sulphonate have been described. Thus, the composition and stability of chelates involving copper<sup>1)</sup>, lead<sup>2)</sup>, uranium<sup>3)</sup>, thorium<sup>4)</sup>, hafnium, molybdenum<sup>5)</sup>, vanadium<sup>6)</sup>, tungsten<sup>7)</sup> and chromium<sup>8)</sup>

- 1) A. K. MUKHERJI and A. K. DEY, J. Ind. Chem. Soc. **34**, 461 (1957).
- 2) A. K. MUKHERJI and A. K. DEY, Proc. Natl. Acad. Sci. (India) **26 A**, 19 (1957).
- 3) S. K. BANERJI and A. K. DEY, J. Sci. Ind. Research (India) **20 B**, 375 (1961).
- 4) S. K. BANERJI and A. K. DEY, J. Sci. Ind. Research (India) **20 B**, 58 (1961).
- 5) S. K. BANERJI and A. K. DEY, Z. phys. Chem. **218**, 173 (1961).
- 6) S. K. BANERJI and A. K. DEY, Z. anorg. Chem. **309**, 226 (1961).
- 7) S. K. BANERJI and A. K. DEY, Z. anal. Chem. **179**, 30 (1961).
- 8) S. K. BANERJI and A. K. DEY, J. Ind. Chem. Soc. **38**, 121 (1961).

have been reported. Alizarin Red S has been known as a colorimetric reagent for aluminium since a long time<sup>9</sup>). In spite of the wide application of the aluminium alizarin 3-sulphonate in analysis<sup>10</sup>), details of its composition and stability have not been fully worked out. This paper records our work in this direction

## Experimental

### Materials used

Standard solutions of aluminium sulphate (BDH AnalaR) and Alizarin Red S (BDH indicator, abbreviated as ARS), were prepared in double distilled carbon dioxide free water and standardised by the usual methods. Other chemicals employed were of the reagent grade.

### Absorbance and Electrical Conductance Measurements

Absorbance measurements were carried out with a Unicam SP 500 spectrophotometer, operated by a Doran Mains Unit connected to 220 V/50 cycles a. c. mains, further stabilised by a constant voltage transformer. 1 cm. thickness of the solution was employed in all the cases by using matched glass cells supplied along with the instrument. All absorbance measurements were noted against a distilled water blank.

The electrical conductance measurements were done with Leeds and Northrup Kohlrausch Slidewire with an audio-frequency oscillator in the circuit, operated on the same mains and using a dip type measuring cell having a cell constant of 0.580.

Hydrogen-ion concentrations were measured with Leeds and Northrup direct reading pH indicator operated on the same mains. The electrode system was glass-calomel supplied by the same manufacturers.

All experiments were carried out in an airconditioned room maintained at  $25^{\circ} \pm 1^{\circ}\text{C}$ . The total volumes of all the mixtures prepared for the measurements were kept at 50 ml. The individual solutions and mixtures were kept immersed in a Townson and Mercer's Precision thermostat maintaining a temperature of  $25^{\circ} \pm 0.01^{\circ}\text{C}$ , for about two hours, a time which was sufficient for acquiring equilibrium and for attaining the temperature of the bath. pH of the solutions and mixtures was adjusted to  $3.5 \pm 0.2$  by the addition of suitable amounts of hydrochloric acid.

The composition of the chelate has been studied by (i) the method of continuous variations using absorbance and electrical conductance measurements, (ii) mole ratio method and (iii) the slope ratio method.

### Evaluation of the Stability Constant

The apparent stability constant was calculated from the absorbance data by the method of Anderson and coworkers<sup>11</sup>) as modified by Dey and associates<sup>1-8</sup>). For this, the method of continuous variations is employed using equimolecular solutions and the total volume is kept constant. The absorbance of the mixtures is measured at the wavelength of maximum absorbance of the complex and is plotted against  $[M]/[M] + [Ke]$ , (where  $[M]$  is the concentration of the metal ion and  $[Ke]$  that of the chelating agent). Metal ions, mostly being colourless

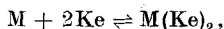
<sup>9</sup>) F. W. ATACK, J. Soc. Chem. Ind. **34**, 936 (1915).

<sup>10</sup>) E. B. SANDELL, Colorimetric Determination of Traces of Metals, 2nd Ed., Interscience, New York (1950).

<sup>11</sup>) R. C. ANDERSON and S. E. TURNER, J. Amer. chem. Soc. **71**, 912 (1949).

at high dilution, the absorbance of the mixtures is due to the colour of the chelate and the reagent only. With the progressive increase in the concentration of the metal ions, [Ke] decreases and in the descending portions of the curves, where [M] is in excess, the whole of the reagent may be assumed to be bound up in the complex. Thus, the absorbance in these portions is due to the chelate alone. When a number of curves are plotted, then at the same value of absorbance the respective amounts of the complex formed in each case are identical.

The concentration of the chelate can be calculated from the following procedure. In an equilibrium of the type, involving a metal ion and a chelating agent in the ratio of 1:2,



the stability constant is given by

$$K = \frac{x}{(a-x)(b-2x)^2} \dots\dots\dots (i).$$

Taking two concentrations having the same absorbance, i. e., the same value of x, we have

$$K = \frac{x}{(a_1-x)(b_1-2x)^2} = \frac{x}{(a_2-x)(b_2-2x)^2} \dots\dots (ii)$$

$$\text{or } 4x^2 [(a_1 + b_1) - (a_1 + b_1)] + x [b_2^2 - b_1^2 + 4(a_2 b_2 - a_1 b_1)] + (a_1 b_1^2 - a_2 b_2^2) = 0 \dots\dots\dots (iii)$$

$$x = \frac{-[b_2^2 - b_1^2 + 4(a_2 b_2 - a_1 b_1)] \pm \sqrt{[b_2^2 - b_1^2 + 4(a_2 b_2 - a_1 b_1)]^2 - 16[(a_1 + b_1) - (a_2 + b_2)](a_1 b_1^2 - a_2 b_2^2)}}{8 [(a_1 + b_1) - (a_2 + b_2)]}$$

Knowing the value of x from (iii), the value of K can be found out in the equation (i) by substitution. The stability constant has also been calculated from the mole ratio method through a calculation of the degree of dissociation.

### Results and Discussion

#### Nature of the Complexes Formed

The method of VOSBURGH and COOPER<sup>12)</sup> was followed to determine the nature of the complexes formed in solution. Mixtures containing varying proportions of 1/2 Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>: Alizarin Red S (1:1, 2:1, 1:2, 1:3 and 1:4), were prepared and the absorbance in each case was measured at suitable intervals between a range of wavelength from 350 mμ to 650 mμ. The results are graphically plotted in Fig. 1. It may be seen that the reagent has its maximum absorption at 420 mμ as is evident from curve A. In curves B, C, D and E the wavelength of maximum absorbance shifts to 470 mμ. However, in curve F it lies at 440 mμ owing to the presence of a large excess of the reagent. This indicates that only one complex is formed in solution under the conditions of study.

#### Stoichiometry of the Components

The composition of the chelate was established by all the methods. A large number of observations were taken and some of the typical results are plotted in Figs. 2 to 11.

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

The following table summarises the results on the composition as arrived at from the examination of Figs. 2 to 5, when the method of continuous

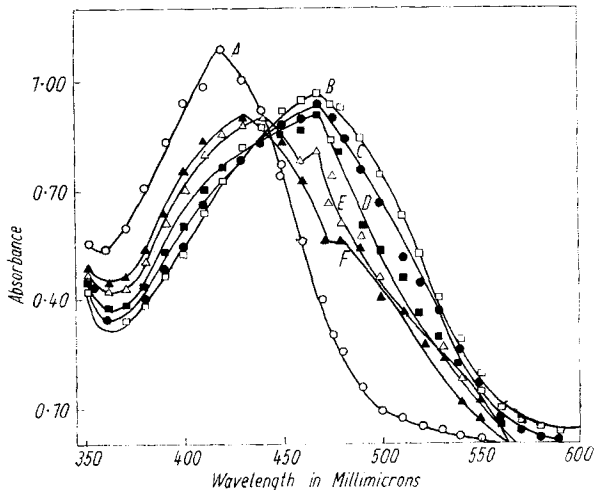


Fig. 1. Absorption spectra studies of mixtures of Aluminium sulphate and Alizarin Red S (pH  $3.5 \pm 0.2$ ). Curve A, Alizarin Red S  $4.00 \times 10^{-4}$  M; Curve B,  $c = 8.00 \times 10^{-4}$  M,  $p = 0.50$ ; Curve C,  $c = 4.00 \times 10^{-4}$  M,  $p = 1.00$ ; Curve D,  $c = 2.00 \times 10^{-4}$  M,  $p = 2.00$ ; Curve E,  $c = 1.33 \times 10^{-4}$  M,  $p = 3.00$ ; Curve F,  $c = 1.00 \times 10^{-4}$  M,  $p = 4.00$

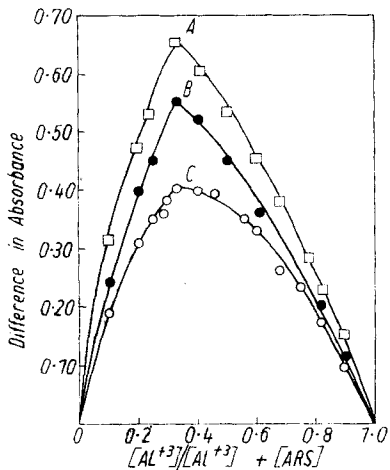


Fig. 2. Determination of the composition from absorption spectra studies of equimolecular solutions at  $470 \text{ m}\mu$  ( $p = 1$ ; pH  $3.5 \pm 0.2$ ). Curve A,  $c = 10.00 \times 10^{-4}$  M; Curve B,  $c = 6.66 \times 10^{-4}$  M; Curve C,  $c = 5.00 \times 10^{-4}$  M

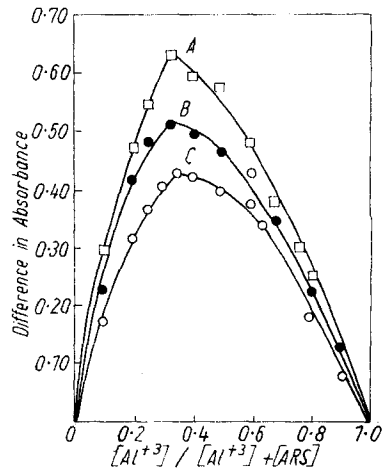


Fig. 3. Determination of the composition from absorption spectra studies of equimolecular solutions at  $490 \text{ m}\mu$  ( $p = 1.0$ ); Concentrations and pH same as in Fig. 2

variations was employed using absorbance measurements. In the table,  $c$  represents the concentration of  $\frac{1}{2} \text{Al}_2(\text{SO}_4)_3$  and  $p$ , the ratio  $c'/c$ ,  $c'$  being the concentration of Alizarin Red S.

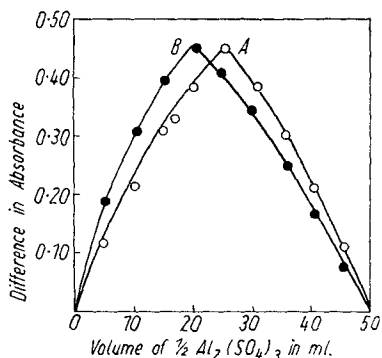


Fig. 4. Determination of the composition from absorption spectra studies of non-equimolecular solutions at  $470 \text{ m}\mu$  ( $\text{pH } 3.5 \pm 0.2$ ). Curve A,  $c = 5.00 \times 10^{-4} \text{ M}$ ,  $p = 2.00$ ; Curve B,  $c = 6.66 \times 10^{-4} \text{ M}$ ,  $p = 1.50$

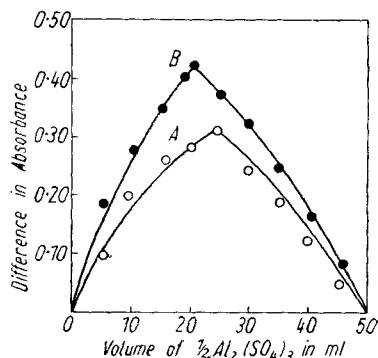


Fig. 5. Determination of the composition from absorption spectra studies of non-equimolecular solutions at  $490 \text{ m}\mu$ . Concentrations and pH same as in Fig. 4

Table I

Figure	Curve	$c \times 10^4$ (M)	P	$\lambda$ ( $\text{m}\mu$ )	Peak occurs at volume of $\frac{1}{2} \text{Al}_2(\text{SO}_4)_3$ (ml)	Composition of the chelate Al(III):ARS
4.4	A	10.00	1.0	470	16.7	1:2
4.4	B	6.66	1.0	470	16.7	1:2
4.4	C	5.00	1.0	470	16.7	1:2
4.5	A	10.00	1.0	490	16.7	1:2
4.5	B	66.6	1.0	490	16.7	1:2
4.5	C	5.00	1.0	490	16.7	1:2
4.6	A	5.00	2.0	470	25.0	1:2
4.6	B	6.66	1.5	470	21.5	1:2
4.7	A	5.00	2.0	490	25.0	1:2
4.7	B	6.66	1.5	490	21.5	1:2

The results of the method of continuous variations using electrical conductance (Figs. 6–7) are summarised below.

It is clear from the above tables that the ratio of aluminium to Alizarin Red S in the chelate is 1:2 and hence, it may be represented as  $\text{Al}(\text{ARS})_2$ . Results obtained by the other methods also, viz., the mole ratio method (Figs. 8 and 9) and the slope ratio method (Figs. 10 and 11) corroborate the same composition of the chelate.

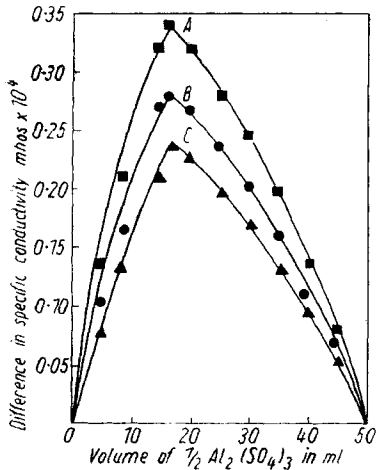


Fig. 6. Determination of the composition from electrical conductance studies of equimolecular solutions. (p = 1). Curve A, c = 6.66 × 10<sup>-4</sup> M; Curve B, c = 5.00 × 10<sup>-4</sup> M; Curve C, c = 4.00 × 10<sup>-4</sup> M

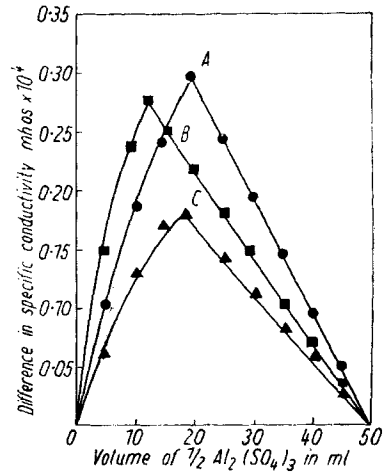


Fig. 7. Determination of the composition from electrical conductance studies of non-equimolecular solutions. Curve A, c = 5.00 × 10<sup>-4</sup> M, p = 1.33; Curve B, c = 6.66 × 10<sup>-4</sup> M, p = 0.75; Curve C, c = 4.00 × 10<sup>-4</sup> M, p = 1.25

Table II

Figure	Curve	c × 10 <sup>4</sup> (M)	p	Peak occurs at volume of 1/2 Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (ml)	Composition of the chelate Al(III):ARS
6	A	6.66	1.00	16.7	1:2
	B	5.00	1.00	16.7	1:2
	C	4.00	1.00	16.7	1:2
7	A	5.00	1.33	20.0	1:2
	B	6.66	0.75	13.7	1:2
	C	4.00	1.25	19.2	1:2

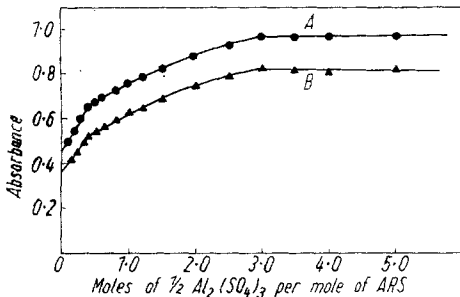


Fig. 8

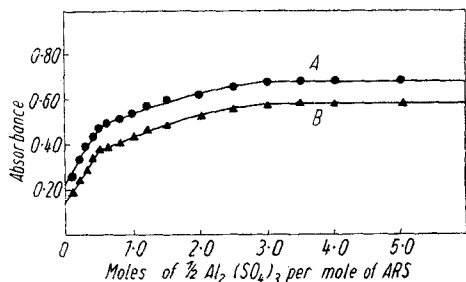


Fig. 9

Fig. 8 and Fig. 9. Determination of the composition from absorbance studies by the mole ratio method at 470 mμ (Fig. 8) and 490 mμ (Fig. 9) respectively, pH 3.5 ± 0.2. Concentration of ARS, A = 4.0 × 10<sup>-4</sup> M; B = 3.2 × 10<sup>-4</sup> M

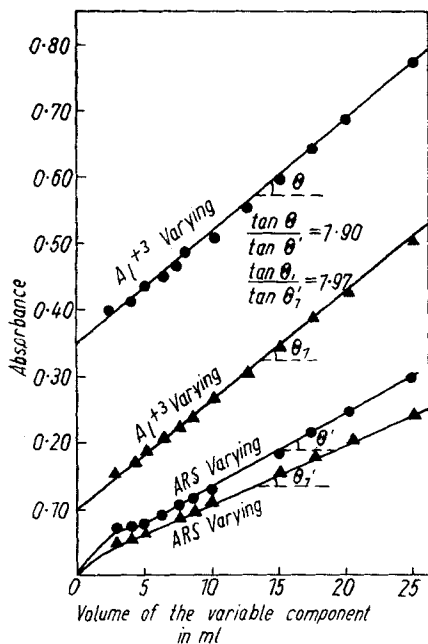


Fig. 10. 20 ml of  $1.00 \times 10^{-3}$  M excess component + x ml of  $2.00 \times 10^{-4}$  M variable component + (30 - x) ml  $H_2O$

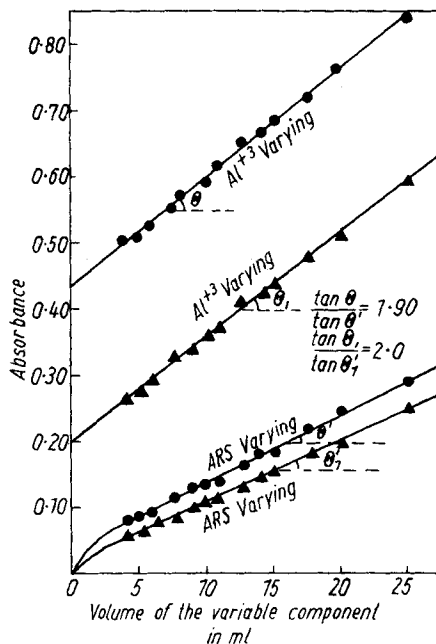


Fig. 11. 25 ml of  $1.00 \times 10^{-3}$  M excess component + x ml of  $2.50 \times 10^{-4}$  variable component + (25 - x) ml  $H_2O$

Fig. 10 and Fig. 11. Determination of the composition from absorbance studies by the slope ratio method. ● 470  $m\mu$ , ▲ 490  $m\mu$ , pH  $3.5 \pm 0.2$

### Effect of Hydrogen-ion Concentration on the Stability of the Chelate

The absorbances of mixtures containing  $\frac{1}{2} Al_2(SO_4)_3$  and Alizarin Red S in the ratio 1:2 ( $c = 2.00 \times 10^{-4}$  M,  $c' = 4.00 \times 10^{-4}$  M) at different pH

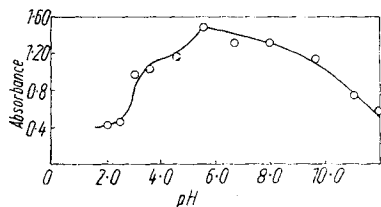


Fig. 12. Variation in colour intensity with change in pH at 470  $m\mu$ .  
 $c = 2.00 \times 10^{-4}$  M,  $p = 2.00$

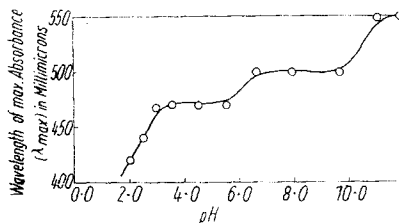


Fig. 13. Variation in the region of maximum absorption of the chelate with change in hydrogen-ion concentration.  
 $c = 2.00 \times 10^{-4}$  M,  $p = 2.00$

were measured at various wavelengths. Fig. 13 shows the results where it is clearly seen that the  $\lambda_{max}$  of the chelate which is 470  $m\mu$  holds good

from pH 2.5 to 4.5 showing thereby that the chelate is stable in this range of pH. Fig. 12 shows the variation in colour intensity of the chelate with change in pH at 470 m $\mu$ .

### Evaluation of the Stability Constant

The values of log K as determined by two different methods (Figs. 8, 9 and 14) are given in the following table. The particular value of pH is also mentioned. The free energy change of formation has also been calculated with the help of the expression:

$$\Delta F^\circ = -RT \ln K,$$

the terms having their usual meaning.

It is clear from the above table that the values obtained by both the methods are in close agreement with each other.

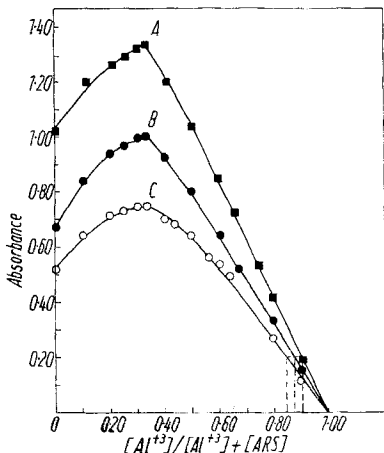
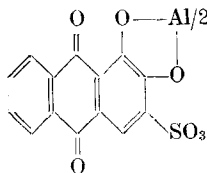


Fig. 14. Determination of the stability constant from absorbance data at 470 m $\mu$ .

Concentration and pH same as in Fig. 2

### Suggestions on the Structure of the Chelate

The metal ion may be chelated in two alternative positions viz., (i) between a pair of phenolic oxygens and (ii) between the quinoid oxygen and the adjacent phenolic oxygen. It is suggested that in the present case, chelation occurs between the phenolic oxygens, as shown below:



This yields an anionic complex which has been confirmed by the adsorption of the complex by ion exchange resin Amberlite IR 45 (OH).

Table III

Method employed	pH	log K	$\Delta F^\circ$ at 25°C (K. cal)
Method of DEY et al	3.5 $\pm$ 0.2	7.2 $\pm$ 0.3	- 9.9 $\pm$ 0.4
Mole ratio method	3.5 $\pm$ 0.2	7.5 $\pm$ 0.2	10.3 $\pm$ 0.3



The authors are thankful the Council of Scientific and Industrial Research, Govt. of India, for supporting the work and for the award of a research fellowship to one of them (R. L. S.)

Allahabad (India), Chemistry Department, University of Allahabad.

Bei der Redaktion eingegangen am 27. Juni 1962.