

Sodium Alizarin 3-Sulphonate as a Chromophoric Reagent. IV

## Chelate Formation of Indium (III) with Alizarin Red S and its Application to the Determination of Indium

By KAILASH N. MUNSHI, KRISHNA K. SAXENA and ARUN K. DEY

With 6 Figures

### Abstract

The composition and stability of Indium-Alizarin Red S has been studied. The pink coloured chelate has a  $\lambda_{\max}$  530 m $\mu$  and a composition of 1:2 (metal:chelating agent). The chelate is stable between pH 3.0 to 6.5. The value of log K (K = stability constant) as calculated by two different methods using absorbance data is 9.0 and 9.4 respectively at pH 4.0 at 25°C. A method for the determination of indium using this reagent has been described. The coloured complex conforms to BEER's law over the indium concentration of 0.23 to 27.54 ppm. The suitable pH for the measurement of absorbance is 3.8 to 4.5. Temperature has no effect on the intensity of the colour. The sensitivity is 0.046  $\gamma/\text{cm}^2$ . The interferences by added foreign ions have also been investigated.

### Introduction

Sodium alizarin 3-sulphonate (1:2 dihydroxy 3-anthraquinone sulphonate, trivial name Alizarin Red S, Colour Index 58005, abbr. ARS) reacts with several metal ions to form coloured complexes which have been used for the colorimetric determination of microamounts of metals. DEY et al.<sup>1)</sup> reported the formation of stable coloured chelates of sodium alizarin 3-sulphonate with a large number of metal ions including copper, uranium, lead, thorium, hafnium, molybdenum, tungsten, chromium, and aluminium. Recently they observed the chelate formation of palladium, rhodium, ruthenium and other platinum metals, scandium, yttrium and rare earths with Alizarin Red S<sup>2)</sup>.

In this communication we have described the composition, stability and characteristics of the chelate formed between Alizarin Red S and indium(III). Only a few satisfactory chromogenic reagents are known for indium. Aliza-

<sup>1)</sup> A. K. DEY, A. K. MUKHERJI, S. K. BANERJI, S. C. SRIVASTAVA, R. L. SETH and S. N. SINHA, *J. Sci. Ind. Research* **21** A, 373 (1962).

<sup>2)</sup> A. K. DEY and coworkers, Unpublished Work.

rin Red S appears to be sensitive but not at all selective for its determination. We have also described in this paper the conditions for the colorimetric determination of indium when present alone, using this reagent.

## Experimental

### Apparatus

A unicam SP 500 spectrophotometer was used for absorbance measurements using 1 cm. thickness of solutions in each case. A KLETT SUMMERSON photoelectric colorimeter (test tube model) was used for colorimetric measurements using test tubes of uniform diameter of 1 cm.

### Reagents

Alizarin Red S (B. D. H. indicator) and indium chloride (JOHNSON and MATTHEY) were used for preparing the solutions. All other reagents used were of analytical grade.

### Conditions of study

All experiments were performed at 25 °C. The total volume of the mixture prepared for the measurements was kept at 25 ml. The pH of all the solutions and mixtures was adjusted to  $4.0 \pm 0.2$  by the addition of sodium hydroxide or hydrochloric acid.

## Results and Discussion

### Properties of the reagent and absorption spectra

In view of the observations of MUKHERJI and DEY<sup>3)</sup> that Alizarin Red S behaves as a colloidal electrolyte, dilute solutions of the order of  $10^{-4}$  M were employed. With variation in hydrogen ion concentration Alizarin Red S changes its colour and its region of maximum absorption is found to shift as shown in the table below:

Table I  
Shift of  $\lambda_{\max}$  with change in pH

pH	Region of maximum absorption in $\mu$ .
1.0— 5.0	430
5.0—12.0	520
12.0 and above	560

It may be seen from above that there are three distinct regions of maximum absorption and it may be concluded that the reagent exists in three diffe-

<sup>3)</sup> A. K. MUKHERJI and A. K. DEY, Kolloid-Z. 158, 147 (1958).

rent forms depending upon the pH of the solution as described by RAGHAVA RAO and coworkers<sup>4)</sup><sup>5)</sup>).

### Nature of the Complex

The method of VOSBURGH and COOPER<sup>6)</sup> was employed to determine the nature of the complexes formed in solution. Mixtures containing different ratio of In:ARS were prepared at pH 4.0 and absorbances were measured. It was found that only one complex having wavelength of maximum absorption 530 m $\mu$  is formed under the conditions of study.

### Composition of the Alizarin Red S complex of Indium

To estimate the empirical formula of the complex species formed under the present conditions, the continuous variations, mole ratio and the slope ratio methods were used. For the former method solutions of indium and ARS of the same concentrations were mixed in varying proportions and the series of solutions thus prepared were adjusted to pH 4.0 and absorbances were measured at 530 and 540 m $\mu$ . Figs. 1 and 2 (in the figures  $c$  = concen-

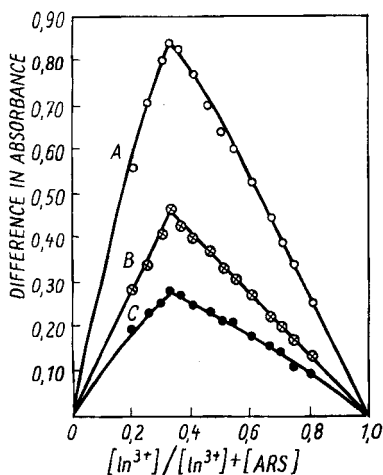


Fig. 1. Determination of the composition by the method of continuous variations at 530 m $\mu$  ( $p = 1$ ; pH 4.0). Curve A:  $c = 5.00 \cdot 10^{-4}$  M; Curve B:  $c = 2.50 \cdot 10^{-4}$  M; Curve C:  $c = 1.67 \cdot 10^{-4}$  M

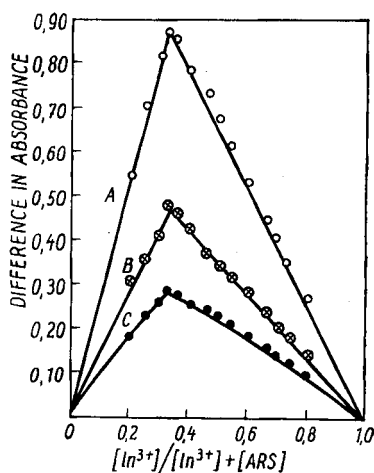


Fig. 2. Determination of the composition by the method of continuous variations at 540 m $\mu$  ( $p = 1$ ; pH 4.0). Curve A:  $c = 5.00 \cdot 10^{-4}$  M; Curve B:  $c = 2.50 \cdot 10^{-4}$  M; Curve C:  $c = 1.67 \cdot 10^{-4}$  M

<sup>4)</sup> D. V. N. SARMA and BH. S. V. RAGHAVA RAO, *Anal. Chim. Acta* **13**, 142 (1955).

<sup>5)</sup> K. S. VENKATESWARLU and BH. S. V. RAGHAVA RAO, *Anal. Chim. Acta* **13**, 79 (1955).

<sup>6)</sup> W. C. VOSBURGH and G. R. COOPER, *J. Amer. chem. Soc.* **63**, 437 (1941).

tration of indium,  $c'$  = concentration of ARS;  $p = c'/c$ ) shows that the combining ratio of indium to ARS can reasonably be regarded as 1:2. The following table summarises the results on the composition as arrived at when the method of continuous variations was employed:

Table II  
Composition of the Indium-ARS chelate  
Total Volume = 25 ml

Figure	Curve	Conc. of the reactants $\cdot 10^4$ (M)	Wavelength (m $\mu$ )	Volume of InCl <sub>3</sub> at peak (ml)	Composition of the chelate In <sup>3+</sup> :ARS
1	A	5.00	530	8.33	1:2
	B	2.50	530	8.33	1:2
	C	1.67	530	8.33	1:2
2	A	5.00	540	8.33	1:2
	B	2.50	540	8.33	1:2
	C	1.67	540	8.33	1:2

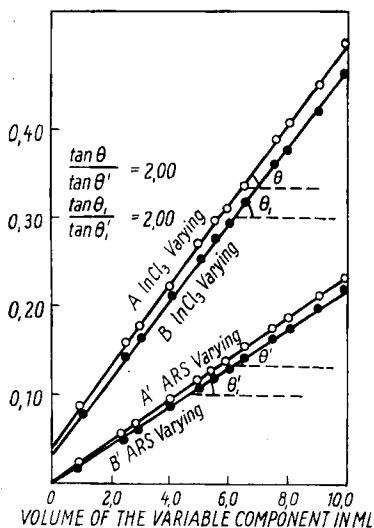


Fig. 3. Determination of the composition by the slope ratio method (pH 4.0). A, A' = 530 m $\mu$ ; B, B' = 540 m $\mu$ . 10 ml of  $6.66 \cdot 10^{-4}$  M excess component  $\cdot$  ml of  $2.22 \cdot 10^{-4}$  M variable component (15 - x) ml of H<sub>2</sub>O

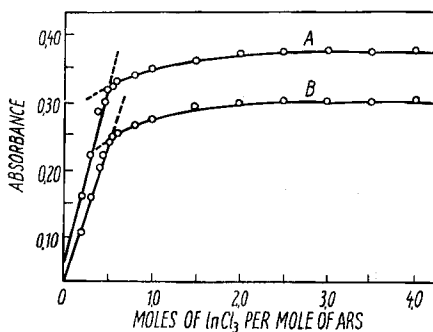


Fig. 4. Determination of the composition by the mole ratio method at 530 m $\mu$  (pH 4.0) Final concentration of ARS, A: ARS =  $1.33 \cdot 10^{-4}$  M; B: ARS =  $1.00 \cdot 10^{-4}$  M

In the slope ratio method two series of solutions were prepared, in the first, various amounts of indium were added to a large excess of ARS and in the second, different quantities of ARS were added to a large excess of

indium. The absorbances of the solutions were measured and plotted against the concentration of the variable component. The combining ratio of the complex is equal to the ratio of the slopes of the two straight lines which are shown in fig. 3, which shows the formation of 1:2 (In:ARS) species.

The composition of the chelate is also confirmed by the mole ratio method, which also suggests the existence of 1:2 (In:ARS) chelate in the solution. Fig. 4 shows the break at this ratio.

#### Evaluation of stability constant

The apparent stability constant was calculated from the absorbance data by the method of DEY et al.<sup>7)</sup> and also by the mole ratio method and the results are as below. The value of free energy change of formation is also shown in the last column:

Table III

Method employed	pH	log K	$\Delta G^\circ$ at 25 °C. (K. Cals.)
Method of DEY et al	4.0	$9.0 \pm 0.2$	$12.5 \pm 0.3$
Mole ratio method	4.0	$9.4 \pm 0.1$	$13.0 \pm 0.2$

#### Conformity to Beer's law

The linearity between the colour intensity of indium-ARS complex and indium concentration was tested by varying indium concentration and measuring the colour intensity at pH 4.0 by a photoelectric colorimeter with green filter No. 54 (transmission 520–580 m $\mu$ ). The system was found to adhere to BEER's law in the range of 0.23 to 27.54 ppm of indium.

#### Sensitivity

The sensitivity of the colour reaction as defined by SANDELL at 530 m $\mu$  is 0.046  $\gamma/\text{cm}^2$ . The practical sensitivity based on an absorbance of 0.10 unit is 0.46  $\gamma/\text{cm}^2$ .

#### Reaction rate and effect of standing time

The rate of colour formation does not depend upon reaction time and is almost instantaneous. A mixture of indium chloride and excess of ARS solution retained its absorbance even after 72 hours of standing at room temperature.

<sup>7)</sup> A. K. MUKHERJI and A. K. DEY, *J. Inorg. Nucl. Chem.* **6**, 314 (1958).

<sup>8)</sup> A. K. MUKHERJI and A. K. DEY, *Anal. Chim. Acta* **18**, 324 (1958).

### Effect to temperature

There was no marked change in the intensity of the colour with the change in temperature from 5° to 90 °C.

### Influence of pH

The  $\lambda_{max}$  of the chelate, 530  $m\mu$ , remains the same between pH 3.0 to 6.5 showing the stability of chelate within this range of pH (Fig. 5), but the intensity of the colour was found to remain constant between pH 3.8 and 4.5 as is evident from fig. 6.

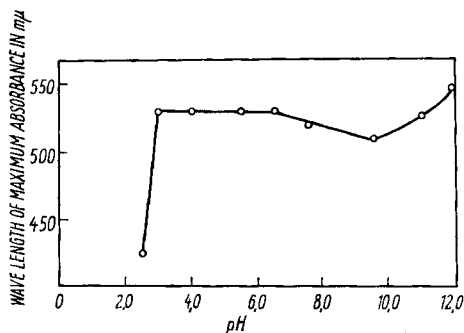


Fig. 5. Variation in the region of maximum absorption with change in hydrogen ion concentration  $c = 1.0 \cdot 10^{-4} M$ ,  $0 = 2.0$

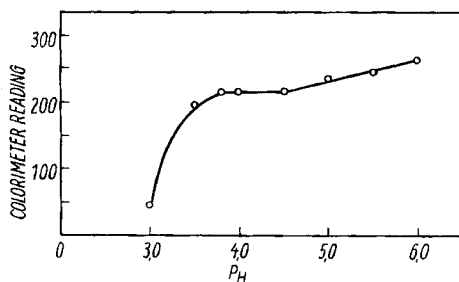


Fig. 6. Variation of colour intensity with change in hydrogen ion concentration  $c = 6.67 \cdot 10^{-5} M$ ,  $c' = 1.33 \cdot 10^{-4} M$

### Effect of diverse ions

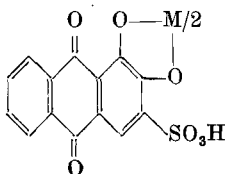
The effect of various cations and anions was studied with KLETT SUMMERSON photoelectric colorimeter and tolerance limit in each case were determined. For tolerance limit has been chosen the concentration of foreign ions which effects the absorbance of the system under investigation by less than  $\pm 2.0$  percent. It was found that Cu(II), Fe(III), Fe(II), Al(III), Be(II), Th(IV), Ce(III), Mo(VI), V(V),  $UO_2(II)$ , Ti(IV), Se(III), Y(III), La(III) interfere seriously. Of the common anions chloride, bromide, acetate, iodide, chlorate, nitrate, nitrite, thiocyanate, thio-sulphate, and phosphate do not interfere at all. Tartarate, citrate, carbonate, borate and oxalate must be absent.

### Recommended procedure

For the determination of indium by this method the interfering substances as described above should be removed by usual methods. The pure solution of indium salt (chloride, nitrate or sulphate) should then be treated directly with a freshly prepared Alizarin Red S solution. The reagent should always be kept in large excess, pH should be maintained between 3.8 and 4.5 and the colour intensity may be measured with a spectrophotometer or a photoelectric colorimeter using a green KLETT filter No. 54.

### Suggestions on the structure of the chelate

Some tentative suggestions may be made about the position of the metal in the chelate. It appears that the metal ion is chelated between the two phenolic oxygens as shown below, leading to the formation of anionic complex. This is corroborated by the anionic nature of the chelate as has been found by electrophoresis experiments and also by complete adsorption of the chelate by ion exchange resin Amberlite IR-45 (OH). It, therefore, appears that the structure is as follows:



The work has been supported by a grant from the Council of Scientific and Industrial Research, India, and the authors are thankful for the financial assistance and for the award of research fellowships to two of them (K. N. M. and K. K. S.).

Allahabad (India), Chemical Laboratories, University of Allahabad.

Bei der Redaktion eingegangen am 11. Oktober 1963.