Solochrome Dark Blue as a Sensitive Reagent for Spectrophotometrie Determination of Gallium and Indium

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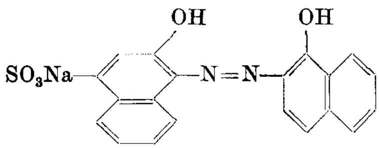
With 5 Figures

Summary

Spectrophotometric study of the colour reaction of sodium salt of 3 hydroxy-4-((-2-hydroxy-1-naphthyl)azo)-1-naphthalene sulfonic acid (SDB) with gallium and Indium is described for the determination of micromaounts of gallium and indium. The absorbance curves of the complexes at pH 3.0 show λ max of SDB alone at 550 mμ while for ga-chelate λ max is 580 mμ and for In-chelate it is 570 mμ. The study was made at 590 mμ where the reagent absorbs very little. The optimum conditions for the microdetermination of gallium and indium using this reagent have been described and include the effect of pH on colour intensity of chelate, effect of excess of reagent, range of adherence to BEER's law, sensitivity, molar absorption coefficient, rate of colour formation and stability of colour at room temperature. The effects of various diverse ions have also been studied and it was found that many ions do not interfere in the spectrophotometric determination of Gallium and Indium using SDB.

Introduction

Sodium salt of 3-hydroxy-4-((2-hydroxy-1-naphthyl)azo)-1-naphthalene sulfonic acid, commonly known as Solochrome Dark Blue (abbreviated here as SDB) forms coloured complexes in aqueous solution with some metal ions and has been used for their microdeterminations.



Solochrome Dark Blue

KORKISCH described it as one of the sensitive azo dyes for photometric determination of titanium[1]), zirconium[2]) and molybdenum[3]).

[1]) J. KORKISCH, Microchim Acta 16 (1962).
[2]) J. KORKISCH, Z. analyt. Ch. **182**, 253 (1961).
[3]) J. KORKISCH, Microchim. Acta 564 (1961).

Various colour reactions and photometric procedures have been reported for Gallium[4–7] and Indium[4)5)8–10]. In the present communication the formation of reddish violet chelates of gallium and indium with SDB have been noted for the first time and detailed studies have been made to use this chromogenic property for the spectrophotometric determination of gallium and indium using the above reagent.

Experimental

Instruments

Beckman model B spectrophotometer was used for absorbance measurements. It was operated by 110 volts AC current which was further stabilized by a constant voltage transformer. In the experiment 1 cm. glass cells were used and absorbance readings were noted against distilled water blank.

For pH measurements, a Beckman direct reading pH meter with glass calomel electrode system was used.

The colorimetric measurements were done using a Klett-Summerson photoeletric colorimeter which was connected to 220 volts ACmain. 1 cm diameter pyrex tube and filter no. 54 were used in all cases.

Materials

The solution of Ga (III) and In (III) was prepared by dissolving the chloride and nitrate (Johnson Matthey) repsectively in distilled water and acidified suitably.

SDB (BDH) solution was prepared by dissolving known weight of it in distilled water.

The solutions of required concentrations were prepared time to time by suitable dilution.

Buffer Solution

In the experiments, buffer solution used was obtained by adding 50 ml of 0.2 M potassium hydrogen phthalate + 20.4 ml of 0.2 M HCl, diluted to 200 ml. The pH of the mixtures were made to 3.0 by adding the suitable quantity of buffer solution.

Conditions of Study

All measurements were done at room temperature (27 °C). The pH of all the solutions was maintained to 3.0 by adding buffer solution. The total volume maintained in all the cases was 25 ml.

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5) C. D. Dwivedi, K. N. Munshi and A. K. Dey, Chemist-Analyst, **55**, 13 (1966).
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9) J. E. Johnson, M. C. Lavine and A. J. Rosenberg, Anal. Chem. **30**, 2055 (1958).
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Results and Discussion

Characteristics of colour

The reddish violet colour appears instantaneously by adding SDB to metal ion solution. However, there was no effect on absorbance values if the order of addition of the reactantes is changed. All mixtures were kept for 1 hour for equilibration before absorption measurements. The effect of temperature was studied and it was found that intensity is constant for both the chelates between 10° to 60° c.

The mixtures containing $8 \cdot 10^{-5}$ M metal ion solution and $2.4 \cdot 10^{-4}$ M SDB were kept at room temperature and stability of colour against time was measured. It was found that colour intensity remains constant even after 10 hours of standing at room temperature. This stability is quite sufficient for spectrophotometric determination.

Wavelength of maximum absorption

The λ max of SDB at pH 3.0 was found to be 550 mμ. The λ max of chelates was obtained by mixing the reagent and metal ion in various ratios and taking complete absorption spectra. They were found to be 580 mμ [for Ga(III)-SDB chelate] and 570 mμ [for In(III)-SDB chelate] at pH 3.0. Fig. 1 shows λ max of both the chelates and the reagent alone.

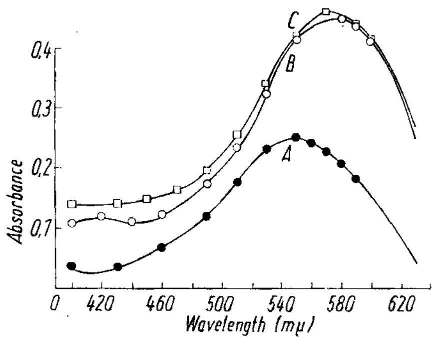

Fig. 1. λ_{max} of reagent and chelates. Curve A: of SDB. final concentration of SDB $5 \cdot 10^{-5}$ M. Curve B: Ga(III)—SDB chelate final concentration of Ga(III) $2 \cdot 10^{-5}$ M, final concentration of SDB $8 \cdot 10^{-5}$ M. Curve C: In(III)—SDB chelate final concentration of In(III) $2 \cdot 10^{-5}$ M, final concentration of SDB $8 \cdot 10^{-5}$ M

However, in all the cases the absorbance values were recorded at 590 mμ, where the differences in absorbance values of chelates and reagent alone were appreciable.

Influence of pH

A series of mixtures containing SDB and metal ion in the ratio of 4:1 were prepared at different pH values. The absorbance values were measured at 590 mμ and the results are graphically shown in Fig. 2 and 3.

It is observed that the absorbance of Ga(III)-SDB chelate is constant between pH 2.5 to 3.5 and that of In(III)-SDB chelate is also between pH 2.5 to 3.5.

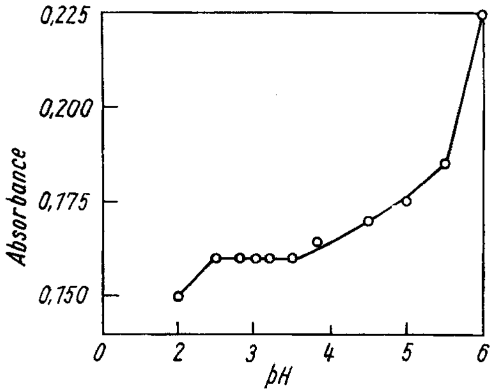

Fig. 2. Effect of pH on Ga(III)—SDB chelate at 590 mμ. final concentration of Ga(III)—$1 \cdot 10^{-4}$ M, final concentration of SDB—$4 \cdot 10^{-4}$ M

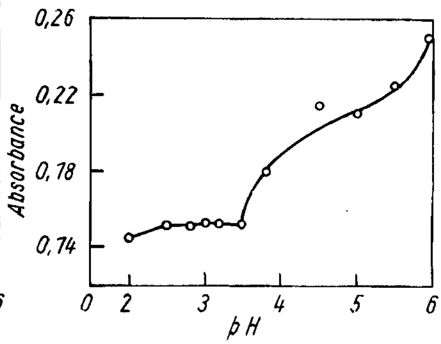

Fig. 3. Effect of pH on In(III)—SDB chelate at 590 mμ. Final concentration of In(III) $1 \cdot 10^{-4}$ M, Final concentration of SDB $4 \cdot 10^{-4}$ M

Conformity to Beer's Law

The linearity between the absorbance of chelates and metal concentration was tested by varying the metal ion concentration and keeping the concentration of SDB constant. The absorbances were measured at 590 mμ and at pH 3.0 for both the chelates. Range for adherence to BEER's law and the range for most effective photometric determination of each metal is listed in table 1.

Table 1
Range for adherence to BEER's Law and photometric determination of SDB chelates

Metal ion (III)	Range of conc. for adherence to BEER's law (p.p.m.)	Range of conc. for effective photometric determination (p.p.m.)
Ga	0.44—2.2	0.8—1.8
In	0.73—4.8	1.0—4.2

Effect of reagent concentration

The absorbance values of different mixtures of metal ion (3 ml of $1.33 \cdot 10^{-4}$ M) with varying ratio of SDB at pH 3.0 and at 590 mμ show that maximum colour formation is only attained when the mixture contains greater than 6-fold excess of the reagent with respect to metal ion. Fig. 4 and 5 show the results.

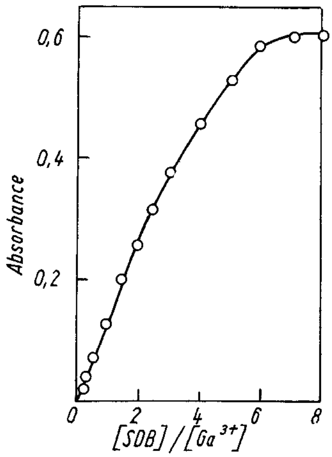

Fig. 4

Fig. 2

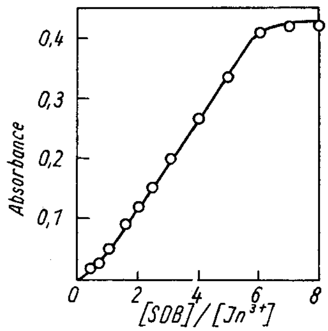

Fig. 4. Effect of Reagent concentration on the absorbance of Ga(III)—SDB chelate at 590 mμ, pH 3.0. Final concentration of Ga(III)—$1.6 \cdot 10^{-4}$ M

Fig. 5. Effect of Reagent concentration on the absorbance of In(III)—SDB chelate at 590 mμ, pH 3.0. Final concentration of In(III) $1.6 \cdot 10^{-4}$ M

Sensitivity

The values of practical as well as the Sandell sensitivity are given in table 2.

Table 2
Sensitivity and Molar absorption coefficient of the chelates

System	Practical sensitivity (μg/cm²)	Sandell sensitivity (μg/cm²)	Molar absorption coefficient
Ga(III)—SDB	0.013	0.0013	10,130
In(III)—SDB	0.030	0.0030	8,250

Molar absorption coefficient

5 ml of ($6.6 \cdot 10^{-5}$ M) metal ion was taken in each flask and to it 10, 15 and 20 ml of SDB solution ($1.33 \cdot 10^{-4}$ M) was added. Total volume made upto 25 ml with buffer solution. The average value for molar absorption coefficient calculated at 590 mμ and at pH 3.0 are given in table 2.

Effect of diverse ions

The effect of various anions and cations on the systems was studied with klett-summerson colorimeter using filter 54 and the tolerence limit in each case is determined. For tolerence limit, has been chosen the concentration of foreign ion which affects the absorbance of the system by less than $\pm$ 2 per cent. It was found that Fe(III), Fe(II), Ce(III), Cr(III), Tl(III), Ga(III), In(III), oxalate and nitrite interfere at all concentrations.

Table 3
Effect of diverse ions
concn. of metal ion: $2 \cdot 10^{-5}$ M
concn. of SDB: $4 \cdot 10^{-5}$ M
pH of mixture: 3.0

Foreign ion	Added as	Tolerence limit concn. of ions in p.p.m. Ga(III)–SDB	In(III)–SDB
Cu^{+2}	$CuSO_4\,5\,H_2O$	200	Interferes at all concentrations
Ni^{+2}	$NiSO_4\,6\,H_2O$	158	210
Co^{+2}	$CoSO_4\,7\,H_2O$	56	225
Zn^{+2}	$ZnSO_4\,7\,H_2O$	230	115
Mg^{+2}	$Mg(NO_3)_2\,6\,H_2O$	205	205
Cd^{+2}	$3\,CdSO_4\,8\,H_2O$	205	154
UO_2^{+2}	$UO_2(NO_3)_2\,6\,H_2O$	201	402
TeO_6^{-6}	$K_2O_4TeO_6\,3\,H_2O$	144	288
Be^{+2}	BeO	10	20
Al^{+3}	$Al(NO_3)_3\,9\,H_2O$	300	165
Pt^{+4}	$PtCl_4$	135	269
Acetate	Sodium Acetate	109	109
Citrate	Tri Sodium citrate	118	118
Chloride	NaCl	117	117
Bromide	KBr	48	96
Iodide	KI	266	266
Thiocyanate	NH_4SCN	152	60
Tartarate	$KNaC_4H_4O_6$	226	226
Sulphite	Na_2SO_3	101	101
Sulphate	Na_2SO_4	129	129
Thiosulphate	$Na_2S_2O_3 5H_2O$	99	198
Nitrate	KNO_3	89	44
Phosphate	Na_3PO_4	608	152

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