A Spectrophotometric Study of the Complex Formation of Vanadium(IV) with Chrome Azurol S

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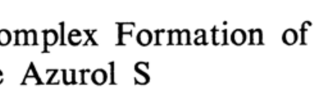
(Received October 13, 1965)

Chrome Azurol S (trisodium salt of 3′′-sulpho-2′′ : 6′′-dichloro-3 : 3′-dimethyl-4-hydroxy-fuchsone-5 : 5′-dicarboxylic acid; colour-index; mordent blue; C. I. 43825; abbr. CAS) is an important member of the hydroxy-triphenylmethane group of dyes. It has been extensively employed as a metal indicator and as a reagent for the photometric determination of various metals. Earlier workers, such as Revinson and Harley,1) Silvermann and Shideler,2) and Macnulty and Woolard,3) utilised CAS chelates for the microdetermination of fluoride. Recently Dey and his co-workers,4) and Langmyhr and Klausen5) have established the composition of the iron-CAS chelate. Sheyanova and Chelysheva6) have suggested the use of CAS for the determination of vanadium(IV) in steel, and in a recent communication Sanyal and Mushran7) have reported the formation of a violet-coloured chelate of varadium(IV) with the reagent.

The structure of Chrome Azurol S is as follows:



(Na-salt of Chrome Azurol S)

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1) D. Revinson and J. H. Harley, *Anal. Chem.*, **25**, 794 (1953).

2) L. Silvermann and M. E. Shideler, *ibid.*, **31**, 152 (1959).

3) B. J. Macnulty and L. D. Woolard, *Anal. Chim. Acta*, **14**, 452 (1956).

4) A. K. Dey and R. L. Seth, *J. Indian Chem. Soc.*, **39**, 772 (1962).

5) F. J. Langmyhr and K. S. Klausen, *Anal. Chim. Acta*, **29**, 149 (1963).

6) F. R. Sheyanova and S. F. Chelysheva *Trudy. Chim. i. Khin. Tekhnol (Gov. Ku)*, **3**, 579 (1960).

7) P. Sanyal and S. P. Mushran, *Mikrochim. Acta*, **5**, 959 (1965).

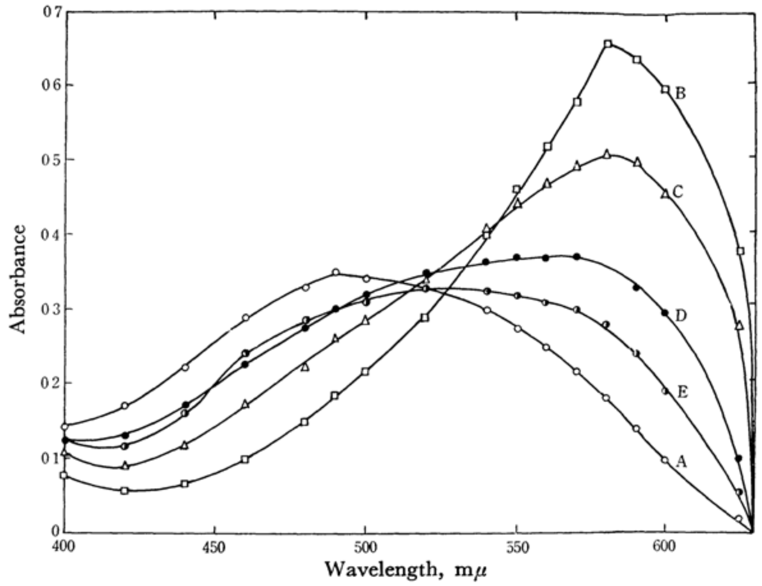

Fig. 1. Nature of the complex formed using absorbance measurements at pH 4.0. Absorption spectra of vanadium(IV)-CAS chelate

	Final concentration, $\mathrm{M}\times10^5$		Ratio
	$VOSO_4$	CAS	
A	0.00	4.0	0 : 1.0
B	8.00	4.0	1 : 0.5
C	4.00	4.0	1 : 1.0
D	2.00	4.0	1 : 2.0
E	1.33	4.0	1 : 3.0

The reagent has pronounced chelating properties due to the presence of donor groups such as –COOH, –OH and =O

In the present communication, a spectrophotometric method has been employed for the determination of the composition and the stability of the vanadium(IV)-CAS chelate.

Experimental

Reagents. B. D. H.-indicator reagent-grade CAS (trisodium salt) was dissolved in doubl-distilled water; fresh solutions were used for each set of experiments.

A. R., a B. D. H. sample of vanadyl sulphate was used; it was standardised by the usual methods.

Apparatus. For extinction measurements a Unicam SP 500 spectrophotometer (1 cm-thick solution) was used.

The pH measurements of the solutions were recorded with a direct-reading Leeds and Northrup pH indicator, with glass and calomel electrodes. The pH meter was standardised by a standard buffer solution of pH 6.8.

Conditions of Study. The reagent behaves as a colloidal electrolyte in concentrated solutions; therefore, very dilute solution of the order of 10^{-4} M were employed (*cf.* Seth, Srivastava and Dey).[8)]

All the measurements were carried out in an air-conditioned room maintained at 25±1°C. The total volume in every case was maintained at 25 *ml* for the absorbance measurements. The pH of the solutions was fixed by the addition of either sulphuric acid or caustic alkali in suitable concentrations.

Procedure. The composition of the chelate was established by two different methods (a) Job's method of continuous variations,[9)] and (b) the slope-ratio method.[10)] The absorbance measurements were made at pH 4.0 and at 580 mμ.

Results and Discussion

The Colour Formation and the Effect of the Temperature. The colour formation was found to be instantaneous at room temperature. However, above 40°C the colour intensity of the chelate generally diminished.

The Order of the Addition of Reagents. No appreciable change in the absorbance values was found when the order of the addition of the reagents was altered; however, slightly better results were obtained when the reagent solution was added to the metal ion solution at a fixed pH.

The Nature of the Complex Formed. The method of Vosburgh and Cooper[11)] was employed

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8) R. L. Seth, S. C. Srivastava and A. K. Dey, *J. Colloid Sci.*, **17**, 86 (1962); A. K. Dey, *ibid.*, **3**, 473 (1948).

9) P. Job, *Ann. Chim. (X)*, **9**, 113 (1928).

10) A. E. Harvey and D. L. Hanning, *J. Am. Chem. Soc.*, **72**, 4488 (1950); *ibid.*, **74**, 4744 (1952).

11) W. C. Vosburgh and G. R. Cooper, *ibid.*, **63**, 437 (1941); *ibid.*, **4**, 1630 (1942).

to determine the nature of the complex formed. Mixtures containing vanadyl sulphate: CAS in different stoichiometric ratios (0 : 1, 1 : 0.5, 1 : 1, 1 : 2 and 1 : 3) were prepared, and the absorbance of each of them was measured at suitable wavelengths within the range of 400 to 625 mμ. The results, represented graphically in Fig. 1, show that, at pH 4.0, the reagent has the maximum absorbance at 490 mμ (curve A), whereas for curves B, C, D and E the region of maximum absorbance shifts to 580 mμ. This indicates that only one complex, with a λ_{max} at 580 mμ, is formed under the specified conditions.

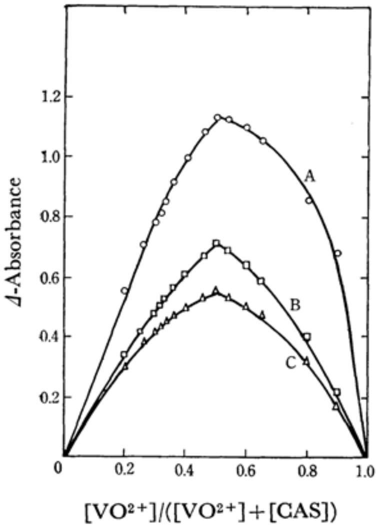

Fig. 2. Composition of the chelate using absorbance measurements by the method of continuous variations at 580 mμ, pH 4.0. $p=1$
Curve A: Concn. of $VOSO_4$ 2.0×10^{-4} M
Curve B: Concn. of $VOSO_4$ 1.33×10^{-4} M
Curve C: Concn. of $VOSO_4$ 1.00×10^{-4} M

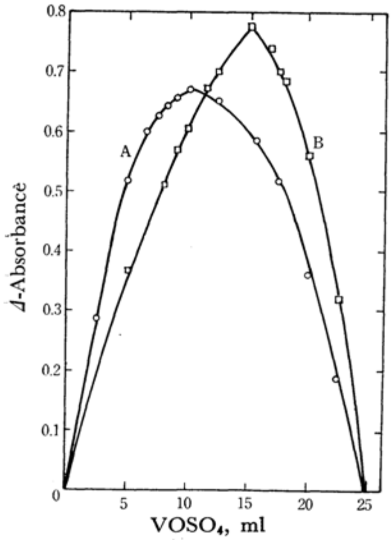

Fig. 2(a). Composition of the chelate using absorbance measurements by the method of continuous variations at 580 mμ, pH 4.0.
p=A, 0.5; B, 2.0
Curve A: Concn. of $VOSO_4$ 2.0×10^{-4} M
Curve B: Concn. of $VOSO_4$ 1.0×10^{-4} M

The Stoichiometry of the Components. The results obtained by the continuous variations method are represented graphically in Figs. 2 and 2(a) for the different equi and non-equimolar concentrations of the reactants. In the figures, the ratio p is c'/c, where c' is the concentration of CAS and c represents the concentration of vanadyl sulphate. From the peaks of the curves it is evident that a 1 : 1 chelate is formed. This is further supported by the slope ratio method (Fig. 3).

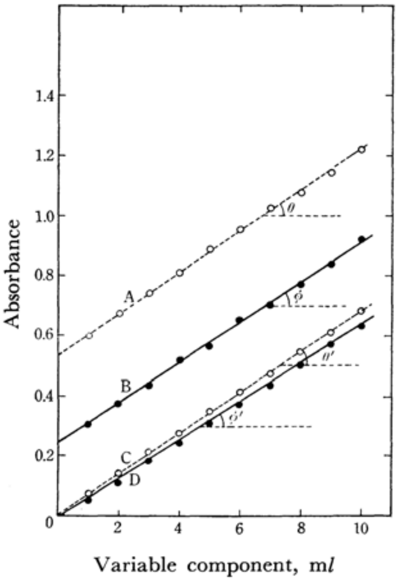

Fig. 3. Composition of the chelate using absorbance measurements by the slope ratio method at pH 4.0.
10 ml of 4.0×10^{-4} M excess component - x ml of 1.33×10^{-4} M variable component.
A, B: $VOSO_4$ varying; C, D: CAS varying; dotted line 580 mμ and solid line 600 mμ.

$$\frac{\tan\theta}{\tan\theta'} = 1.02 : \frac{\tan\phi}{\tan\phi'} = 1.05$$

An Evaluation of the Stability Constants. The values of the apparent stability constants, K, were determined using the method of Dey and his co-werkers[12] (Fig. 4). For the reaction of the type:

$$mA + nB \rightleftarrows A_mB_n, \text{ where } m/n = 1.$$

The formation constant is given by:

$$K = \frac{x}{(a-x)(b-x)} \tag{1}$$

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[12] A. K. Mukherji and A. K. Dey, *J. Inorg. Nucl. Chem.*, **6**, 314 (1958); *Anal. Chim. Acta*, **18**, 324 (1958).

where x is the concentration of the complex, while a and b are the initial concentrations of vanadyl sulphate and CAS. Taking two concentrations, a_1 and a_2, and b_1 and b_2, of the reactants where the value of the optical density is the same, we have:

$$K=\frac{x}{(a_1-x)(b_1-x)}=\frac{x}{(a_2-x)(b_2-x)}$$

or

$$x=\frac{a_1b_1-a_2b_2}{(a_1+b_1)-(a_2+b_2)} \quad (2)$$

The values of a_1, a_2, b_1 and b_2 are obtained from Fig. 4, and the value of x is obtained from Eq. (2). The substitution of the x value in Eq. (1) gives the value of K at pH 4.0.

Continuous variation data from Fig. 2(a) have also been used to evaluate the stability constant of the chelate. The values of log K, along with the values of $\Delta G°$, the free energy change during chelation, are given in Table 1.

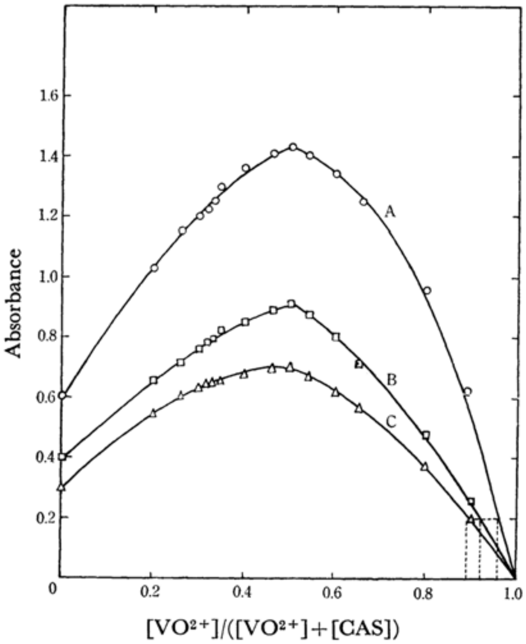

Fig. 4. Determination of the stability constant by the method of Dey and coworkers at pH 4.0.
Evaluation of K 580 mμ
Curve A: Concn. of $VOSO_4$ 2.0×10^{-4} M
Curve B: Concn. of $VOSO_4$ 1.33×10^{-4} M
Curve C: Concn. of $VOSO_4$ 1.00×10^{-4} M

TABLE 1. VALUES OF THE APPARENT STABILITY CONSTANT AND FREE-ENERGY CHANGE AT pH 4.0

Method employed	log K (25°C)	ΔG^0 at 25°C kcal
Dey *et al.* (Fig. 4)	4.0 ± 0.1	-5.6 ± 0.1
Continuous variation (Fig. 2(a))	4.6 ± 0.1	-6.3 ± 0.1

The Effect of the Hydrogen Ion Concentration on the Stability of the Chelate.—Several mixtures containing vanadyl sulphate and CAS in the ratio of 1 : 1 were prepared; after their pH values had been adjusted to different values, their absorbance were measured at various wavelengths. The results show that the λ_{max} of the chelate which is 580 mμ holds good between pH 3.0 to 5.5; this is therefore, the pH range over which the chelate is stable.

The Probable Structure of the Chelate.—From the structure of CAS as represented earlier, it may be seen that the trisodium salt is ionisable and that, in a neutral solution, the reagent in all probability exists as a trivalent ion. The reagent undergoes colour changes with variation in hydrogen ion concentration of the medium. It can, therefore, be concluded that it exists in three different structural forms, as has been discussed by Langmyhr⁵⁾ and by Malát¹³⁾. The wavelength of the maximum absorbance depends upon the pH as follows:

TABLE 2. THE VARIATION IN λ_{max} WITH THE pH

pH	Wavelength of maximum absorbance (λ_{max}), mμ
1.4—5.0	460, 490
5.3—11.5	430
11.5 and above	600

From the experimental results described in this paper, it is not possible to obtain definite information about the exact structure of the chelate, but some tentative suggestions may be pointed out. The chelation may either occur between quinoid oxygen and adjacent carboxylic oxygen, or the metal ion may coordinate between phenolic oxygen and the adjacent carboxylic oxygen. It is interesting to note that the λ_{max} of the chelate is 580 mμ, whereas the λ_{max} of CAS lies at 600 mμ in a strongly alkaline medium; this suggests a structure involving the removal of the phenolic hydrogen by ionisation. In neutral media, however, CAS has a λ_{max} at 430 mμ. It is, therefore, evident that, since the λ_{max} of the chelate, 580 mμ, is closer to the λ_{max} of the reagent in an alkaline medium, it is highly probable that, during chelation, the phenolic hydrogen is replaced, leading to the metal ion being attached to phenolic oxygen and adjacent carboxylic oxygen and not to the quinoid oxygen and the adjacent carboxylic oxygen. Further, we have observed a significant drop in pH during chelation; this undoubtedly supports the above contention. The nature of the charge on the chelate was obtained by passing the violet-coloured chelate through an Amberlite IR (45) OH resin bed. It was observed that an ion-exchange took place and

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13) M. Malát, *Anal. Chim. Acta*, **25**, 289 (1961).

that the eluted solution was colourless. Further, there was a significant increase in the pH of the solution, thus confirming the anionic nature of the vanadium(IV)-CAS chelate.

Thanks are due to the Council of Scientific and Industrial Research, New Delhi, India, for providing financial aid to one of us (P. S.) during the course of the investigation.