

Cadmium Sulfodichlorohydroxydimethylfuchsondicarboxylate Chelate—A Spectrophotometric Study

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Sulfodichlorohydroxydimethylfuchsondicarboxylic acid (trisodium salt; trivial name Chrome Azurol S; Color Index 43825) has extensively been used in these laboratories as a colorimetric reagent¹⁾ and as a chelating agent for metal chelate formation in aqueous solution.²⁻⁶⁾ The use of Chrome Azurol S as a chelatochromic indicator in the complexometric determination of thorium has also been reported.⁷⁾ The present communication reports our work on the composition and stability of the cadmium(II)-Chrome Azurol S chelate.

Experimental

Materials.—Solutions of cadmium sulfate and Chrome Azurol S (B. D. H.) were prepared in double distilled carbon dioxide free water.

Instruments.—For the absorbance measurements a Unicam SP 500 spectrophotometer was used.

pH measurements were done with a Leeds and Northrup direct reading pH indicator.

Results and Discussion

Behavior of the Reagent as a Colloidal Electrolyte.—Dey et al. reported earlier⁸⁾ that

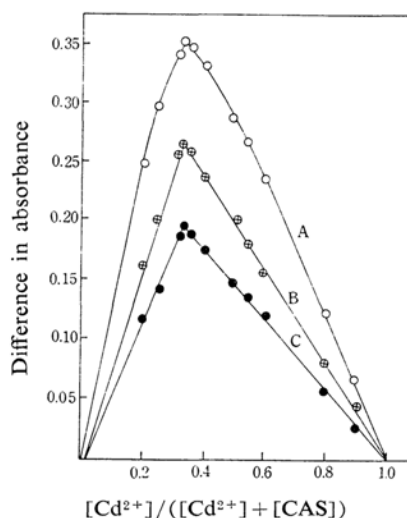


Fig. 1. Composition of the chelate using absorbance measurements by the method of continuous variations at 540 m μ , pH 11.0.
Curve A: Concn. of CdSO₄ 5.0×10^{-4} M
Curve B: Concn. of CdSO₄ 3.33×10^{-4} M
Curve C: Concn. of CdSO₄ 2.50×10^{-4} M

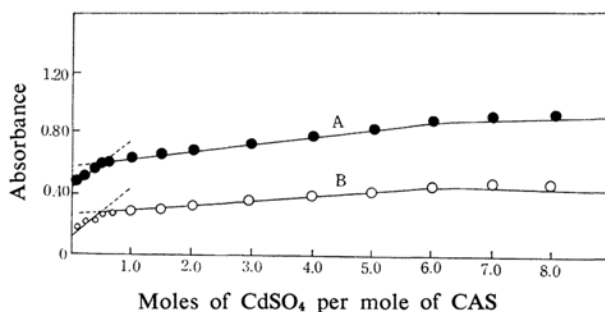


Fig. 2. Composition of the chelate using absorbance measurements by the mole ratio method at 540 m μ , pH 11.0.
Curve A: Concn. of CAS 2.0×10^{-4} M
Curve B: Concn. of CAS 1.0×10^{-4} M

1) A. K. Dey, S. C. Srivastava, R. L. Seth, S. N. Sinha and S. P. Sangal, 7th Int. Coord. Chem. Conf., Stockholm and Uppsala (Sweden), paper No. 7 B (1962).

2) S. C. Srivastava and A. K. Dey, *Inorg. Chem.*, **2**, 216 (1963).

3) S. C. Srivastava, S. N. Sinha and A. K. Dey, *J. prakt. Chem.*, (iv) **19**, 229 (1963).

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25, 217 (1963).

5) R. L. Seth and A. K. Dey, *J. Ind. Chem. Soc.*, **39**, 773 (1962).

6) S. P. Sangal and A. K. Dey, *ibid.*, **40**, 464 (1963).

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

TABLE I. THE COMPOSITION OF THE CHELATE BY THE CONTINUOUS VARIATIONS METHOD
 Total volume 50 ml.

Experiment	Curve	$c^* \times 10^{-4}$ M	p^\dagger	λ $m\mu$	Volume of CdSO_4 at peak, ml.	Composition of the chelate Cd : CAS
I (Fig. 1)	A	5.00	1.0	540	16.67	1 : 2
	B	3.33	1.0	540	16.67	1 : 2
	C	2.50	1.0	540	16.67	1 : 2
**Ia	A	5.00	1.0	560	16.67	1 : 2
	B	3.33	1.0	560	16.67	1 : 2
	C	2.50	1.0	560	16.67	1 : 2
**Ib	A	2.50	0.5	540	10.00	1 : 2
	B	5.00	2.0	540	25.00	1 : 2
**Ic	A	2.50	0.5	560	10.00	1 : 2
	B	5.00	2.0	560	25.00	1 : 2

** Figs. omitted to economise space.

CAS: Chrome Azurol S

* Concentration of cadmium sulfate

† The ratio c'/c , c' being the concentration of CAS.

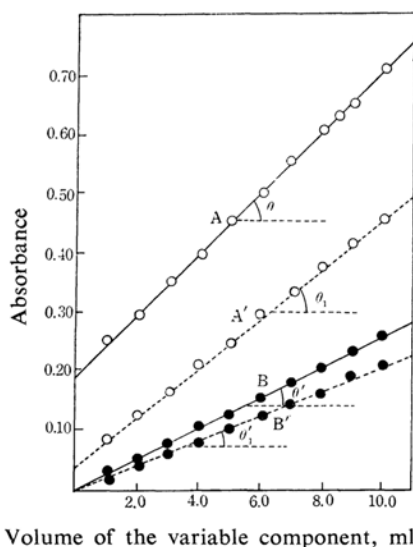


Fig. 3. Composition of the chelate using absorbance measurements by the slope ratio method at pH 11.0.
 20 ml. of $(2 \times 10^{-4} \text{ M})$ excess component + x ml. of $(2.5 \times 10^{-4} \text{ M})$ variable component + $(30 - x)$ ml. water.
 AA', CdSO_4 varying; BB', CAS varying; Solid line $540 \text{ m}\mu$ and broken line $560 \text{ m}\mu$.

$$\frac{\tan \theta}{\tan \theta'} = 1.9 \quad \frac{\tan \theta_1}{\tan \theta'_1} = 2.0$$

Chrome Azurol S behaves as a colloidal electrolyte in concentrated solutions. Therefore, during these investigations solutions were used of the order of 10^{-4} M so that the solutions may behave as true solution.

Effect of Time on the Chelate.—The chelate formation was found to be immediate and the absorbance values remained constant upto 48 hr. However, the solutions were kept for half an hour to attain equilibrium.

Nature of the Chelate Formed.—The method of Vosburgh and Cooper⁹⁾ was employed. Mixtures containing cadmium sulfate and Chrome Azurol S in the ratio of 0:1, 1:1, 1:2, 1:4 and 1:5 (pH 11.0) were prepared and their absorbances measured at various wavelengths. The results show that the region of maximum absorbance of Chrome Azurol S lies at $430 \text{ m}\mu$, whereas, that of the mixtures at $540 \text{ m}\mu$. This shows clearly that only one chelate having λ_{max} $540 \text{ m}\mu$ is formed under the conditions of study.

Stoichiometry of the Components.—The composition was studied using three different methods viz. (i) the method of continuous variations,¹⁰⁾ (ii) mole ratio method¹¹⁾ and the (iii) slope ratio method.¹²⁾ Measurements were made at pH 11.0, adjusted by ammonia added to the mixtures. The results obtained by the continuous variations method are summarized in Table I.

From Table I and Fig. 1 it is clear that the composition of the chelate is $\text{Cd}(\text{CAS})_2$. This is further corroborated by the mole ratio method (Fig. 2) and slope ratio method (Fig. 3).

TABLE II. STABILITY CONSTANTS K

Method employed	pH	$\log K$ at 25°C	ΔG (kcal.) at 25°C
Method of Dey et al.	11.0	9.1 ± 0.2	-12.7 ± 0.2
Mole ratio method	11.0	9.0 ± 0.2	-12.5 ± 0.2

9) W. C. Vosburgh et al. *J. Am. Chem. Soc.*, **63**, 437 (1941); **64**, 1630 (1942).

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Effect of pH on the Stability of the Chelate.

—Mixtures containing cadmium sulfate and Chrome Azurol S in the ratio of 1:2 were prepared, and their absorbances were measured at various wavelengths after adjusting their pH to different values. It was observed that the λ_{\max} of the chelate which is 540 m μ holds good between pH 9.5 to 11.5. This shows that the chelate is stable within this range of pH.

Calculations of the Stability Constant K .

The stability constants were calculated using the method of Dey et al.^{13,14} and the mole ratio method.¹¹ The results are given in Table II.

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Summary

Sulfodichlorohydroxydimethylfuchsondicarboxylate forms a 1:2 violet colored chelate (λ_{\max} 540 m μ) with cadmium(II). The chelate is stable between pH 9.5 and 11.5. The values of stability constant as determined by two different methods are 9.1 and 9.0, at 25°C.

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