

Spectrophotometric Studies of Yttrium (III) Complexes with Solochrome Cyanine-R and Eriochrome Azurol-B.

SUNIL P. PANDE and KAILASH N. MUNSHI ,

Department of Chemistry, Nagpur University, Nagpur

Manuscript received 20 July 1972; revised 14 May 1973; accepted 6 August 1973

Solochrome Cyanine R (SCR) and Eriochrome Azurol B (ECAB) have been recommended as sensitive reagents for the spectrophotometric determination of yttrium (III) in aqueous solution. The composition has been found to be 1 : 1 and 1 : 2 (metal : reagent) for Y (III)-SCR and Y (III)-ECAB chelates respectively. The stability constants of the chelates have been determined by Job's method and limiting logarithmic method, at four different fixed values of ionic strength. The value of thermodynamic stability constant of the chelates have been determined to be 5.0 ± 0.2 for Y(III)-SCR chelate and 9.6 ± 0.2 for Y (III)-ECAB chelate respectively. The study also includes the analytical applications of the chelates.

SODIUM salt of *o*-sulphohydroxydimethyl fuchsone dicarboxylic acid, commonly known as Solochrome Cyanine R (abbreviated as SCR) forms coloured chelates with metal ions. Recently, Sommer and Kuban¹ have reported the spectrophotometric determination of beryllium, and Wille² has suggested SCR for the photometric determination of aluminium.

Sodium salt of (2'', 6''-dichloro-4'-hydroxy-3-3'-dimethyl fuchsone-5,5'-dicarboxylic acid), commonly known as Eriochrome Azurol B (abbreviated as ECAB) also forms coloured chelates with metal ions. Katsube, Vesugi and Yoe³ have reported the spectrophotometric determination of beryllium, copper and iron with ECAB. Chugreeva and Yampol'skii⁴ have suggested a spot test for yttrium with ECAB.

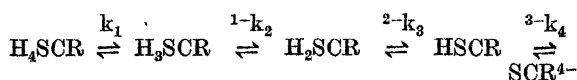
Experimental

Spectrophotometric measurements were made with a Beckman model DU-2 spectrophotometer, using glass cells of 1 cm. path length. For pH measurements, Beckman direct reading H-2 model pH meter with glass calomel electrode system was used. The solution of Y(III) was prepared by dissolving its chloride (E. Merck) in distilled water, acidified and estimated as usual⁵. All other solutions were prepared by using reagents of analytical grade.

Results and Discussion

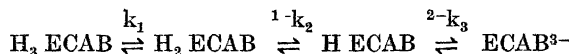
In the present communication a detailed study of the nature of the ligands and the complexes formed with Y(III) have been reported.

The dissociation of SCR may be given as :



In the present work (by the spectrophotometric method) three values of pK could be obtained. They are : pK₁ = pK₂ = 4.1, pK₃ = 7.1, pK₄ = 12.5. The one -SO₃H group present may be dissociating at lower pH value, thus, not permitting its determination under the present conditions of study.

The dissociation of ECAB may be given as :

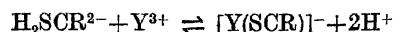


In the present work, three values of pK obtained are :

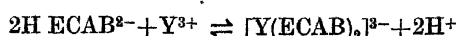
$$pK_1 = 3.5, \quad pK_2 = 4.6, \quad pK_3 = 11.6.$$

The Y(III)-SCR chelate has a λ_{max} 550 nm at pH 6.0 ± 0.1 (λ_{max} of SCR at pH $6.0 \pm 0.1 = 530$ nm), and Y(III)-ECAB chelate has a λ_{max} 550 nm at pH 6.0 ± 0.1 (λ_{max} of ECAB at pH $6.0 \pm 0.1 = 450$ nm). Both the chelates were studied at pH 6.0 ± 0.1 and the wavelength chosen for study was 560 nm for both the systems where the difference in the absorbance of the chelate and the reagent was appreciable. The Y(III)-SCR chelate has a composition 1 : 1 while the Y(III)-ECAB chelate has a composition 1 : 2 (metal : reagent) respectively. Studies by the "straight-line method" of Asmus⁶, as modified by Klausen and Langmyhr⁷, confirm the presence of only the mononuclear species.

In the complexation reaction of Y(III) with SCR, the following equilibria is considered to be present



while the complexation reaction of Y(III) with ECAB can be represented by the following equilibria



The values of log K of the chelates were calculated by two different methods: (a) Method of Foley and Anderson modified by Mukherji and Dey, and (b) Limiting logarithmic method. The experiments were performed at four different fixed values of ionic strength maintained by the addition of suitable quantity of sodium perchlorate solution. The values of log K obtained by different methods are summarised in Table 1.

TABLE 1—VALUES OF STABILITY CONSTANT OF THE CHELATES

Ionic strength (μ)	Temp. = 27°		Method
	log K Y(III)-SCR (1:1)	log K Y(III)-ECAB (1:2)	
0.05	4.7 ± 0.2	9.3 ± 0.2	(a)
	4.6 ± 0.2	9.1 ± 0.2	(b)
0.10	4.4 ± 0.2	9.2 ± 0.2	(a)
	4.5 ± 0.2	9.0 ± 0.2	(b)
0.15	4.3 ± 0.2	8.7 ± 0.2	(a)
	4.4 ± 0.2	8.7 ± 0.2	(b)
0.20	3.9 ± 0.2	8.6 ± 0.2	(a)
	4.1 ± 0.2	8.6 ± 0.2	(b)

For determining the value of thermodynamic stability constant of the chelates, a graph of average values of log K against $\sqrt{\mu}$ was plotted and the curves so obtained were extrapolated to zero ionic strength. The values so obtained are 5.0 ± 0.2 for Y(III)-SCR chelate and 9.6 ± 0.2 for Y(III)-ECAB chelate respectively.

It was found that Beer's law holds good in the concentration range of 0.53 to 2.85 ppm of Yttrium for Y(III)-SCR system, and 0.35 to 2.49 ppm of yttrium for Y(III)-ECAB system. The values of

sensitivity and molar absorptivity for both the chelates are given in Table 2.

TABLE 2—VALUES OF SENSITIVITY AND MOLAR ABSORPTIVITY OF THE CHELATES

System	pH	Wavelength of Study = 560 nm		
		Practical sensitivity ($\mu\text{g}/\text{cm}^2$)	Sandell sensitivity ($\mu\text{g}/\text{cm}^2$)	Molar absorptivity
Y(III)-SCR	6.0	0.089	0.0089	12,000
Y(III)-ECAB	6.0	0.071	0.0071	13,830

The effect of various anions and cations on the systems was also studied and the tolerance limit in each case was determined. Because of large number of interferences, Solochrome Cyanine R and Eriochrome Azurol B can be recommended as sensitive but not selective reagents for the spectrophotometric determination of yttrium (III) in aqueous solution.

Acknowledgement

The authors are thankful to Prof. R. H. Sahasrabudhey, Head of the Chemistry Department, Nagpur University for providing necessary facilities.

References

1. L. SOMMER and V. KUBAN, *Spisy Prirodoved*, 1969, 7, 193.
2. K. S. WILLE, *Fresenius' Z. Anal. Chem.*, 1970, 250 (1), 23.
3. Y. KATSUBE, K. VESUGI and J. H. YOE, *Bull. Chem. Soc. Japan*, 1971, 34, 72.
4. N. V. CHUGREEVA and M. Z. YAMPOL'SKII, *Uchenye Zapiski*, 1958, 11, 143.
5. JAMES FREDERICK SPENCER, *The Metals of the Rare Earths*, Longmans Green, London, 1919, p. 105.
6. E. ASMUS, *Z. Anal. Chem.*, 1960, 178, 104.
7. K. S. KLAUSEN and F. J. LANGMYHR, *Anal. Chim. Acta*, 1963, 28, 501.