

## Spectrophotometric Studies of Gallium, Indium and Thallium Chelates with Solochrome Cyanine R

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The formation of reddish violet coloured chelates between trivalent gallium, indium and thallium with sodium salt of *o*-sulfohydroxydimethyl fuchsonic dicarboxylic acid (SCR) have been reported. By studying the absorption spectra of the chelates in the entire visible range at different pH values, it was ascertained that only one complex is formed in all the cases. The composition of the chelates have been determined by the Job's method of continuous variations, mole ratio and slope ratio methods using absorbance measurements. The chelates have the composition of 1:1. The stability constants of the chelates have been calculated by four different methods, viz. (a) the method of Anderson and coworkers modified by Dey and coworkers using equimolecular solutions, (b) method of continuous variations using non-equimolecular solutions, (c) method of mole ratio and (d) by using the values of molecular extinction coefficient. The average values of log K are 5.8, 5.5 and 5.1 for Ga(III)-SCR, In (III)-SCR and Tl (III)-SCR chelates respectively.

Sodium salt of *o*-sulfohydroxydimethylfuchsonic dicarboxylic acid, commonly known as Eriochrome Cyanine R or Solochrome Cyanine R (abbr. SCR, forms coloured chelates with many metal ions. The photometric determination of Al<sup>1-8</sup>, Be<sup>9-12</sup>, Sc<sup>13-14</sup>, and Cr (III)<sup>15</sup> have been reported by various workers. Determination of fluoride with Zr-SCR lake has also been reported<sup>16-17</sup>. Langmyhr and Stumpe have reported the complex formation of Fe (III) with Eriochrome Cyanine R<sup>18</sup>.

Little work is available in literature regarding the photometric determination of Ga and In<sup>19-22</sup>. The authors have used SCR for the photometric determination

1. F. Richter, *Z. Anal. Chem.* 1944, **126**, 426.
2. S. Henry, and P. Hanisci, *Ind. Chem. Belge.*, 1962, **27**, 24.
3. A. J. Hegedus, *Mikrochim. Acta*, 1963, 831.
4. W. E. Thrun, *Anal. Chem.*, 1948, **20**, 1117.
5. Y. L. Lelchuk, V. B. Sokolovich and O. A. Dreolina, *Izv. Tomskogo Politekhn. Inst.*, 1954, **128**, 101.
6. A. Bacon, *Analyst*, 1952, **77**, 90.
7. Ko Jen Hu and Chih Hung Chen., *Wu Han Ta Hsueh, Tzu Jan Ko Hsueh Hsueh Pao*, 1959, **5**, 83.
8. R. P. H. Scholes, and Valerie, D. Smith, *Analyst*, 1958, **83**, 615.
9. P. R. Mohilner, *Anal. Chem.*, 1963, **35**, 1103.
10. S. Umemoto, *Bull. Chem. Soc., Japan.*, 1956, **29**, 845.
11. P. W. West and P. R. Mohilner, *Anal. Chem.* 1962, **34**, 558.
12. C. H. Wood and H. Isherwood, *Metallurgia*, 1949, **39**, 321.
13. T. Fuginaga, T. Kuwamoto and K. Kuwabara, *Bunseki-Kagaku*, 1963, **12**, 399.
14. T. Fuginaga, T. Kuwamota, S. Tsurubo and K. Kuwabara, *Bunseki Kagaku*, 1964, **13**, 127.
15. M. Malat, *Naturwiss.*, 1961, **48**, 569.
16. S. Meeregian, *Anal. Chem.* 1954, **26**, 1161.
17. P. L. Sarma, *Anal. Chem.*, 1964, **36**, 1684.
18. F. J. Langmyhr and T. Stumpe, *Anal. Chim. Acta*, 1965, **32**, 535.
19. M. K. Akhmedli and E. L. Gluskchenko, *Zh. Analit. Khim.*, 1964, **19**, 556.
20. A. K. Babko and P. P. Kish, *Dopovidi Akad. Nauk. Ukr. R. S. R.*, 1961, 1323.
21. A. K. Babko and P. P. Kish, *Zh. Analit. Khim.*, 1962, **17**(6), 693.
22. P. V. Sakellaridis and B. S. Roufogalis, *Chim. Chronika*, 1964, **29**(5), 113.

of Ga, In and Tl<sup>23</sup>. Sakellaridis and Roufogalis<sup>24</sup> have reported the composition of Ga and In complexes to be 1 : 1 and have also reported the reaction constant K. The present paper describes the systematic study of the composition, stability constants and other characteristics of the chelates of gallium and indium with SCR and the Tl-SCR chelate for the first time.

## EXPERIMENTAL

Standard solutions of SCR were prepared by dissolving known weights of SCR (BDH indicator) in water. gallium nitrate, indium nitrate and thallic oxide (Johnson Matthey and Company) were dissolved in water or acid and acidified with suitable acids. The solutions were standardized by the usual methods.

The absorbance measurements were done with a Beckman model B Spectrophotometer using 1 cm glass cells.

The pH of the solutions were measured by a Beckman pH meter using glass-calomel electrode system. All the experiments performed were at room temperature 27°. The total volume in all cases was 25 ml. The solutions of metal ion and reagent individually were adjusted to pH 3.5 by addition of HCl or NaOH. All the solutions were kept for ½ hr. to equilibrate before absorbance measurements. Various electrolytes were tried to maintain the ionic strength but were not found suitable because either they produce lakes or the solutions fade considerably with time.

## RESULTS AND DISCUSSION

*Characteristics of the reagent:* Effect of pH on reagent alone was studied by taking  $1 \times 10^{-4}$ M SCR and studying absorption spectra in the entire visible range. The following shifts in  $\lambda_{\max}$  were found.

TABLE I

*Effect of pH on SCR*

pH	Wavelength of maximum absorption (m $\mu$ )
1.0-2.0	500
3.0-3.5	520
4.0-4.5	540
5.0-7.0	550
7.5-12.0	440

The reagent solution was found to be colloidal in nature and hence extremely dilute solutions of the order of  $10^{-4}$  to  $10^{-5}$ M were used.

*Characteristics of the complexes formed :* Red-violet coloured water soluble complexes are formed when the SCR solution was added to the metal ion solution of Ga(III), In(III)

23. A. P. Joshi and K. N. Munshi, *Microchem.* 1967, **12**, 447.

24. P. V. Sakellaridis and B. S. Roufogalis, *Chim. Chronika*, 1962, **27**, 123.

and Tl(III) at pH 3.5. No changes were observed if the order of addition of reagents were changed. The colour formation is instantaneous and the absorption values of the complexes remain constant even after 48 hr.

*Number of complexes formed* : Three series of mixtures were prepared with reagent: metal ratio of 4 : 1, 1 : 1, and 1 : 4. The pH of each series containing 6 mixtures were adjusted to different pH values. The absorption spectra of each mixture was studied from 400-600 m $\mu$  and the following results were obtained.

TABLE II

 $\lambda_{\max}$  of the Chelates

System	Ratio Reagent : Metal	Wavelength of maximum absorbance (m $\mu$ ) at pH					
		2.0	3.0	3.5	4.0	5.0	6.0
Ga (III)-SCR	4:1	500	560	560	560	560	560
	1:1	500	570	570	570	560	560
	1:4	500	570	570	570	560	560
In (III)-SCR	4:1	500	550	550	550	550	550
	1:1	500	560	560	560	560	560
	1:4	500	560	560	560	560	560
Tl (III)-SCR	4:1	500	550	550	550	550	550
	1:1	500	560	560	560	560	560
	1:4	500	560	560	560	560	560

At pH 2.0, the  $\lambda_{\max}$  of the above chelates correspond to the  $\lambda_{\max}$  of the reagent alone, indicating that the complex has completely decomposed at this pH. In case of Ga(III)-SCR chelates the results show that the complex is stable from pH 3.0 to 4.0 having a  $\lambda_{\max}$  570 m $\mu$ . In the 1st series  $\lambda_{\max}$  however shifts to 560 m $\mu$  due to a large excess of reagent. Studies at this wavelength revealed the existence of the same complex, whereas studies at pH 5.0 and 6.0 and at 560 m $\mu$  gave confusing results indicating the instability of the complex. Indium and Thallium-SCR complexes show a stability from pH 3.0 to 6.0, the  $\lambda_{\max}$  being 560 m $\mu$  in both the cases. However, in the first series of both the complexes the  $\lambda_{\max}$  of the complexes formed tends to shift to 550 m $\mu$ . This may be attributed due to an excess of reagent. Studies at this wave length and from pH 3.0 to 6.0 revealed the existence of the same complex.

Hence it may be concluded that SCR forms only one complex with Ga(III), In(III) and Tl(III) under the conditions studied. However, the studies are performed at 570 m $\mu$  and 580 m $\mu$  for all the chelates.

*Composition of the complex formed* : The compositions of chelates formed were studied by three methods, (1) Job's method of continuous variations, (2) Mole ratio method and (3) Slope ratio method.

The methods showed the chelates to be 1 : 1 at pH 3.5 (at 570 m $\mu$  and 580 m $\mu$ ).

*Evaluation of stability constant* : The stability constants were calculated by four different methods namely, (a) the method of Anderson and coworkers<sup>25</sup>, modified by Dey and coworkers<sup>26</sup> using equimolecular solutions, (b) the method of continuous variations using non-equimolecular solutions, (c) the method of mole ratio<sup>27</sup> and (d) by the measurements of molecular extinction coefficient.

The values of log *K* calculated by various methods are shown in Table III.

TABLE III

*Stability constants of the Chelates. pH=3.5, Temp. 27°*

Method	Ga(III)-SCR	In (III)-SCR	Tl (III)-SCR
(a)	5.0±0.1	4.8±0.1	4.7±0.1
(b)	5.8±0.1	4.9±0.1	4.9±0.2
(c)	6.4±0.1	6.2±0.2	5.9±0.2
(d)	5.6±0.2	5.8±0.2	5.8±0.2

*Suggestions on the structure of chelate* : Some tentative suggestions may be made about the position of the chelate ring in the chelates. All the three chelates of SCR are anionic in character as shown by adsorption measurements. When the solutions of the chelates are passed through a column of ion exchange resin, Amberlite IR-45 (OH), the chelate is completely adsorbed. The electrophoretic measurements further support the anionic nature of the complexes. The anionic nature of the complexes shows chelation involving phenolic hydrogen and the adjacent-COOH group, with the dissociation of other-COOH and-SO<sub>3</sub>H group.

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25. R. T. Foley and R. C. Anderson, *J. Amer. Chem. Soc.*, 1948, **70**, 1195; 1949, **71**, 909.

26. A. K. Mukherji and A. K. Dey, *J. Inorg. Nucl. Chem.*, 1958, **6**, 314, *Anal. Chim. Acta*, 1958, **18**, 324.

27. J. H. Yoc and A. L. Jones, *Ind. Eng. Chem. Anal. Ed.*, 1944, **16**, 111.