

## Studies in Equilibria Involved in Complexation Reaction Between Zr(IV) & Some Organic Dyes

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Zirconium(IV) forms 1:2 complexes (Zr:Ligand) with Calmagite (CLM) and Solochrome Black 6 B (SBB) in 0.1M and 0.5M acid concentrations respectively and 1:1 chelate with Thoron and Nitroso-R-salt (NRS) at pH 2.0 and 1.5 respectively. At higher pH, NRS forms another complex whose composition could not be assigned due to uncontrolled hydrolysis of zirconium. On the basis of equilibrium study, the number of protons liberated during the chelation and the equilibrium constant have been evaluated for CLM and SBB chelates which are found to be anionic. The values of absolute stability constant ( $\log \beta'$ ) of CLM and SBB chelates are 49.0 and 46.2 respectively. The conditional stability constant ( $\log \beta$ ) of Thoron and NRS chelates are 5.2 and 5.1 respectively.

ALTHOUGH colour reactions of some organic reagents with zirconium have been studied, very few attempts have been made to study the quantitative equilibria involved in these complexation reactions<sup>1,2</sup>. In the present paper the results of a detailed study of Zr(IV) complexes formed with (i) 3-hydroxy-4-[(6'-hydroxy-*m*-tolylazo)]-1-naphthalene sulphonic acid (calmagite; abbr. CLM), (ii) sodium salt of 4-sulpho-2-hydroxy- $\alpha$ -naphthalene azo- $\alpha$ -naphthol (solochrome black 6B; abbr. SBB), (iii) disodium salt of 1-(*o*-arsonophenylazo)-2-naphthol, 3,6-disulphonate (Thoron), and (iv) disodium salt of  $\alpha$ -nitroso- $\beta$ -naphthol-3,6-disulphonic acid (nitroso R-salt, abbr. NRS) have been reported. Although CLM<sup>3</sup>, SBB<sup>4,5</sup> and Thoron<sup>6,7</sup> have been known to form coloured chelates with different metal ions, the study on Zr(IV) is being reported for the first time. NRS have been reported to form coloured chelates with Ti, Hf and Zr<sup>8</sup> and Gopal Krishna and Raghava Rao<sup>9</sup> have reported the formation of 3:2 (Zr:NRS) chelate at pH 2.0 having a  $\lambda_{\max}$  520 nm. However, in our studies we have observed formation of a 1:1 complex at about pH 1.5.

### Experimental Procedure

Beckman DU-2 spectrophotometer with cells of 1 cm path length were used. An Elico pH meter model LI-10 was used for pH measurement.

Solution of zirconium oxychloride (E. Merck) was prepared by dissolving the sample in a known quantity of HCl in such a way that after dilution the stock solution was  $10^{-3}M$  in 1M HCl. The zirconium content of this solution was estimated as pyrophosphate. Freshly prepared solutions were used. Samples of CLM (Fluka), SBB (BDH), Thoron (BDH) and NRS (E. Merck) were purified by converting these into free acid and then recrystallizing from 50% ethanol. The purity (99.7%) was further checked by titrating the free acid of these ligands potentiometrically. A stock solution ( $10^{-3}M$ )

was then prepared by dissolving the known weight in NaOH solution and then adjusting its pH suitably.

*Procedure* — To maintain the acid concentration of the mixtures in the range of 0.1M or above, calculated amount of HCl solution was added or it was obtained by diluting the stock solution. To adjust the pH of the solutions to 1.5 or 2.0, the pH-meter was used. The use of alkali was minimized to avoid hydrolysis of zirconium. The metal solutions were added to reagent solution while preparing mixtures, the pH of these solutions were preadjusted and it was further maintained after keeping the mixtures for some time. The absorbance values were recorded after equilibration for 1 hr. The range of final concentration of zirconium solution used was between  $10^{-4}$  and  $10^{-6}M$  where the chances of its polymerization is almost negligible.

### Results and Discussion

*Acid dissociation constants* — The dissociation of the ligands may be represented as shown in Eqs 1-4, neglecting the dissociation due to one sulphonic group in CLM and SBB and two sulphonic acid groups in Thoron and NRS, which dissociate at much lower pH and thus could not be determined under the present conditions of study. The values of  $pK_1 (\pm 0.02)$  and  $pK_2 (\pm 0.03)$  at room temperature (30°) as obtained by the method of Albert and Serjeant<sup>10</sup> are also given.

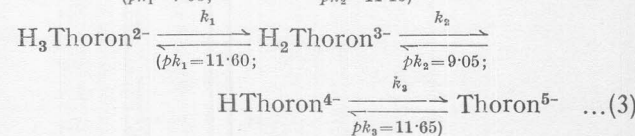
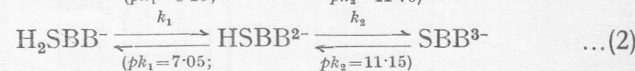
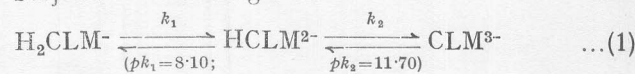


TABLE 1 — ABSORPTION SPECTRA OF THE CHELATES  
(Zr: LIGAND=4:1)

System	$\lambda_{\max}$ (nm) at different acid concentrations				
	1.0M HCl	0.5M HCl	0.1M HCl	1.5 pH	2.0 pH
Zr-CLM	530	540	540	540	540
Zr-SBB	ppt	560	560	560	ppt
Zr-Thoron	ppt	ppt	480	480	480
Zr-NRS	ppt	ppt	370	390	400

*Characteristics of the chelates formed* — The existence of various chelates at different acid concentrations was tested by recording the absorption spectra in the entire visible range of the chelates formed over the acid concentration range 1M HCl to pH 3.0 for a series of solutions containing 1:1, 1:4 and 4:1 (Zr: ligand). The  $\lambda_{\max}$  values for different systems obtained at different acid concentrations are shown in Table 1.

The wavelength of maximum absorbance of the reagents in the above acid concentration range is 530, 530, 470 and 370 nm for CLM, SBB, Thoron and NRS respectively. On the basis of the wavelength of maximum absorbance of chelates given in Table 1 and of ligands alone, it may be concluded that CLM does not form any complex in 1M HCl. It, however, forms one complex in 0.5M HCl which remains stable up to pH 2.0 and has a  $\lambda_{\max}$  540 nm. This chelate was studied in 0.1M HCl at 600 nm where the difference in absorbance of the complex and ligand alone is appreciable. The composition as determined by the Job's method of continuous variations and mole ratio method comes out to 1:2 (Zr: CLM). SBB, however, is less soluble in 1M HCl and a stable complex having a  $\lambda_{\max}$  560 nm is formed only in 0.5M HCl and remains stable up to pH 1.5. At pH 2.0, the hydrolysis of chelate starts. This chelate was studied in 0.5M HCl at 580 nm in order to get a better difference in absorbance between the complex and the ligand alone. The composition as determined by the above method has been found to be 1:2 (Zr: SBB).

Thoron and NRS are precipitated as their free acids in 1M and 0.5M HCl. Even in 0.1M HCl some turbidity appears after some time. From Table 1 it appears that the only chelate having a  $\lambda_{\max}$  480 nm is formed with thoron from pH 1.0 to 2.0. This was studied at pH 2.0 and at 540 nm and shows a composition of 1:1 as determined by all the above methods.

Zirconium forms no complex with NRS up to pH 1.0. At pH 1.5 the  $\lambda_{\max}$  shifts to 390 nm which further shifts to 400 nm at pH 2.0 to 2.5. A careful study at properly controlled pH conditions, shows that a fairly stable 1:1 (Zr: NRS) chelate is formed at pH 1.5 having maximum absorbance at 400 nm. As the pH is increased a second complex having the composition 3:2 (Zr: NRS) is formed at pH 2.0 as reported by earlier workers<sup>9</sup>. However, the results are not reliable as there is a gradual change in the composition to 4:1 (Zr: NRS) at pH 2.5. This does not appear to be correct considering the structure of

NRS. Thus only 1:1 chelate at pH 1.5 was studied at 400 nm.

*Study of equilibrium of CLM and SBB chelates* — Formation of 1:2 (Zr: ligand) complexes with CLM and SBB has been studied in 0.1M and 0.5M HCl where the chances of hydrolysis of zirconium is negligible. Hydrolysis is further suppressed in the presence of strong chelating agents like CLM and SBB. Thus the reacting species may be taken as  $Zr^{4+}$  in these reactions. Now, if we assume  $H_2L^-$  for ligands, where L = CLM or SBB, we can write  $Zr^{4+} + 2H_2L^- \rightleftharpoons [ZrL_2]^{2-} + 4H^+$  ... (5)

The equilibrium constant (K) for the above reaction may be written as

$$K = \frac{[ZrL_2]^{2-}}{[Zr^{4+}][H_2L^-]^2} \cdot [H^+]^4 \quad \dots(6)$$

the conditional stability constant,  $\beta$ , may be written as

$$\beta = [ZrL_2]^{2-} / [Zr^{4+}][H_2L^-]^2 \quad \dots(7)$$

Therefore, substituting  $\beta$  in Eq. (6) we get

$$K = \beta \cdot [H^+]^4$$

$$\text{Or } \log \beta = -4 \log [H^+] + \log K \quad \dots(8)$$

A plot of  $\log \beta$  versus  $\log [H^+]$  is linear with a slope equal to 4, which is the number of protons released during reaction (5), and the intercept equal to  $\log K$ .

A series of solutions were prepared by taking Zr:L in 1:2 ratio and the acid concentration of these solutions were adjusted to different values (the range of acid concentration is selected in such a way that in this range the extinction of ligand remains constant and the complexation should occur). The absorbance values were then noted at 600 nm for CLM and at 620 nm for SBB chelates.

If  $A_s$  is total extinction of mixture,  $E_c$  and  $E_a$  the molar absorptivity of the chelate and ligand respectively and  $A_T$  and  $A_i$  as the initial and equilibrium concentration of the metal and  $B_T$  and  $B_i$  as the initial and equilibrium concentration of ligand respectively, and if  $Q$  is the equilibrium concentration of the chelate, we can write

$$A_s = E_c \times Q + E_a \times B_i \quad \dots(9)$$

$$= E_c \times Q + E_a(B_T - 2Q)$$

$$Q = \frac{A_s - E_a B_T}{E_c - 2E_a} \quad \dots(10)$$

Since the composition of complex is 1:2 (Zr: ligand), in stoichiometric mixture,  $2A_T = B_T$  and  $2A_i = B_i$ . Therefore, the conditional stability constant ( $\beta$ ) is given by Eq. (11)

$$\beta = \frac{Q}{(A_i)(B_i)^2} = \frac{Q}{4(A_i)^3} = \frac{Q}{4(A_T - Q)^3} \quad \dots(11)$$

The concentration of complex  $Q$  and thus  $\beta$  was determined by the method of Zittel and coworkers<sup>1,2</sup> at different acid concentrations and a plot of  $\log \beta$  vs  $\log [H^+]$  was drawn as shown in Fig. 1. The slope values of the two linear plots are equal to about 4, confirming that the reaction (5) is the actual equilibrium reaction. The intercept for Zr-CLM chelate (Fig. 1, curve A) comes to 9.40 and for Zr-SBB chelate (Fig. 1, curve B) it is equal to 9.80.

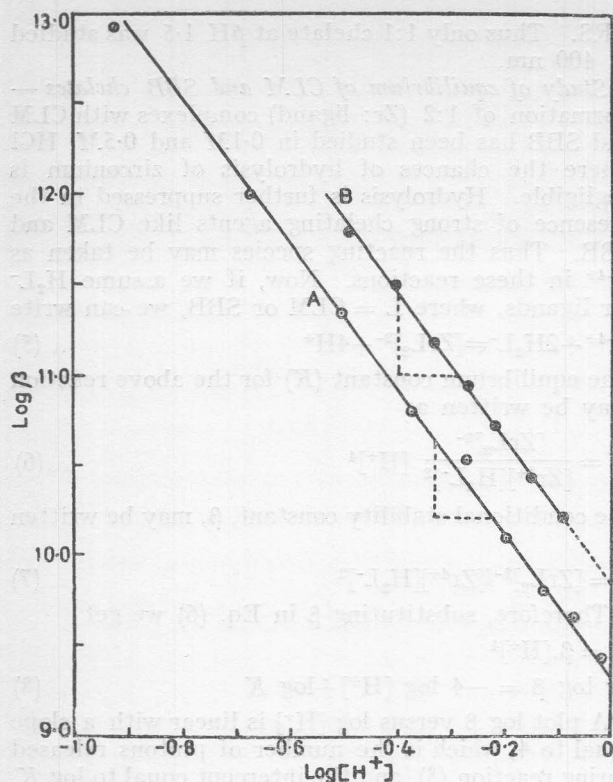


Fig. 1 — Relationship between [H<sup>+</sup>] and conditional stability constant (β) of CLM and SBB chelates of zirconium [Curve A, Zr<sup>4+</sup> = 3.0 × 10<sup>-5</sup>M, CLM = 6.0 × 10<sup>-5</sup>M curve B, Zr<sup>4+</sup> = 4.0 × 10<sup>-5</sup>M; SBB = 8.0 × 10<sup>-5</sup>M]

The absolute stability constant of the chelate (β') may be defined as

$$\beta' = \frac{[\text{ZrL}_2^-]}{[\text{Zr}^{4+}][\text{L}^3]^{-2}} \quad \dots(12)$$

Putting the value for [ZrL<sub>2</sub><sup>-</sup>] as obtained from Eq. (6) we get

$$\beta' = K \cdot \frac{[\text{Zr}^{4+}][\text{H}_2\text{L}^-]^2}{[\text{H}^+]^4[\text{Zr}^{4+}][\text{L}^3]^{-2}} = K \cdot \frac{[\text{H}_2\text{L}^-]^2}{[\text{L}^3]^{-2}[\text{H}^+]^4} \quad \dots(13)$$

where the quantity [H<sub>2</sub>L<sup>-</sup>]<sup>2</sup>/[L<sup>3-</sup>]<sup>2</sup>[H<sup>+</sup>]<sup>4</sup> (corresponding to the equation 2H<sub>2</sub>L<sup>-</sup> ⇌ 2L<sup>3-</sup> + 4H<sup>+</sup>) is equal to the product of the dissociation constants (k<sub>1</sub><sup>2</sup>k<sub>2</sub><sup>2</sup>) of the ligands for the groups involved in chelation. Hence we can write β' = K/(k<sub>1</sub><sup>2</sup>k<sub>2</sub><sup>2</sup>)

$$\text{or } \log \beta' = \log K + 2pk_1 + 2pk_2 \quad \dots(14)$$

For Zr-CLM chelate the absolute stability constant

$$\log \beta' = 9.40 + 2(8.1) + 2(11.70) = 49.0$$

And for Zr-SBB chelate

$$\log \beta' = 9.80 + 2(7.05) + 2(11.15) = 46.2$$

It appears from the above studies that these chelates are anionic in nature. This is confirmed by the complete adsorption of the chelate on the resin Amberlite IR-45 (OH) and is further confirmed by electrophoresis experiments.

**Zirconium chelates with thoron and NRS** — The complexation of zirconium with Thoron and NRS is a fast reaction, giving 1:1 chelates at pH 2.0 and 1.5 respectively. At this pH, the hydrolysis of zirconium is expected. It was, however, not possible to study either the kinetics of reaction or the number of protons released during chelation. Although these complexes have been found to be anionic in nature but due to the lack of evidences about the reacting species of zirconium, the structure of the chelates could not be assigned. However, the conditional stability constants of these chelates have been evaluated by the Job's and mole ratio methods at room temperature (30°). The average values of conditional stability constants are 5.25 ± 0.05 for Zr-Thoron chelate at pH 2.0 and μ = 0.1 and 5.10 ± 0.05 for Zr-NRS chelate at pH 1.5 and μ = 0.3.

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