

**Spectrophotometric Studies on Fe(III) Complexes**

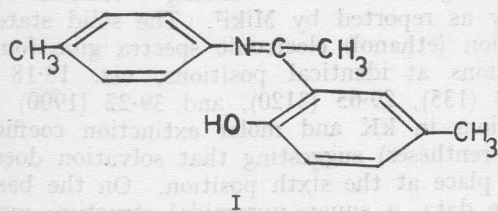
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Fe(III) complex with Schiff base derived from *p*-toluidine and 2-hydroxy-5-methylacetophenone has been studied spectrophotometrically. Both the Job's and the slope ratio methods indicate the formation of a 1:1 complex. The complex is stable for several days at room temperature. The apparent stability constant ( $\log K$ ) of the complex at the optimum pH and room temperature is 4.34. The Schiff base has been used as an auxiliary ligand also to determine the composition of the colourless complexes of Fe(III) with carboxylic acids. All the acids form 1:1 complex.

IN continuation of our previous work<sup>1</sup> on Cu(II) complexes of Schiff base (I) derived from 2-hydroxy-5-methylacetophenone and *p*-toluidine, we report now the results of our studies on a violet coloured Fe(III) complex in solution. Compositions of colourless complexes formed by Fe(III) with malonic, citric and oxalic acids have also been determined using the Schiff base (I) as an auxiliary ligand.



All absorbance measurements were carried out with a Zeiss-Specol spectrophotometer using 1 cm matched cells at room temperature. All the measurements were done in a methanol-water medium adjusted to 0.005M with respect to nitric acid.

The Schiff base (I) was prepared by refluxing equimolar quantities of the amine and 2-hydroxy-5-methylacetophenone in ethanol<sup>2</sup>. The separated Schiff base was filtered and recrystallized from ethanol as a yellow solid.

Standard reagent solution was prepared by dissolving weighed quantity in methanol.

All the other chemicals used were of AR quality. The stock solution of Fe(III) was prepared as described earlier<sup>3</sup>. The stock solutions of carboxylic acids were prepared by dissolving the calculated amount of each in 0.01M HNO<sub>3</sub>.

The nature of complexes in Fe(III)-Schiff base (SB) system was determined by the method of Vosburgh and Cooper<sup>4</sup>. The absorbance curves of the mixtures containing Fe(III) and the ligand in the ratio 1:1, 1:2 and 1:3 [Fe(III):ligand] showed only one maximum at 580 nm which indicates that only one complex is formed. At this wavelength the

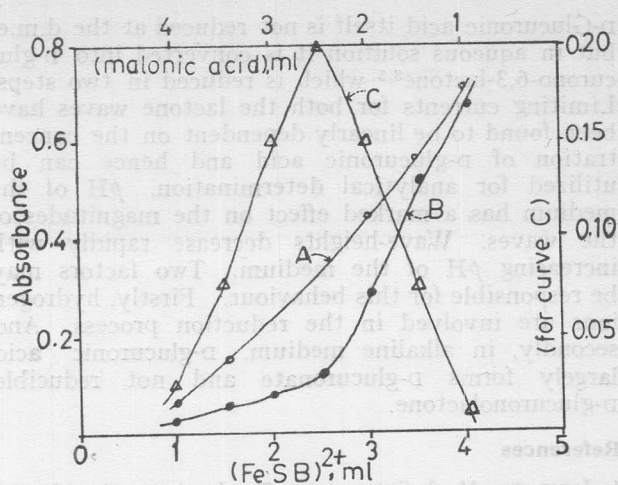


Fig. 1 — Job's curve for (FeSB)<sup>2+</sup>-malonic acid complex [Curve A, (FeSB)<sup>2+</sup>-0.01M HNO<sub>3</sub>; curve B, (FeSB)<sup>2+</sup>-malonic acid; curve C, difference of curves A and B]

Schiff base (I) does not show any appreciable absorbance.

In order to study the effect of pH on complex formation, a series of solutions containing fixed amounts of Fe(III) and constant excess of the reagent were prepared. Constant absorbance is exhibited in the pH range 2.0-2.5. Subsequent studies were, therefore, carried out in this pH range.

Job's method of continuous variations<sup>5</sup> and slope ratio<sup>6</sup> method indicate the formation of a 1:1 complex (metal:ligand). The apparent stability constant of the complex ( $\log K = 4.34$ ) was calculated from absorbance data by the method of Mukherji and Dey<sup>7</sup>.

Compositions of the colourless complexes were determined by the method of Babko *et al.*<sup>8</sup>. A solution containing Fe(SB)<sup>2+</sup> ( $2.5 \times 10^{-3}M$ ) was prepared by mixing equal volumes of Fe(III) ( $5 \times 10^{-3}M$ ) and SB ( $5 \times 10^{-3}M$ ) solutions. Job's method<sup>5</sup> was adopted using  $2.5 \times 10^{-3}M$  Fe(SB)<sup>2+</sup> and  $2.5 \times 10^{-3}M$  carboxylic acid solutions. The absorbances were measured at 580 nm.

Two sets of solutions for each equilibrium, one with and the other without the carboxylic acid, were prepared. The difference in the absorbances of the pair of corresponding solutions for the two sets corresponds to the Y function in Job's curve. Appearance of a maximum in Y indicates 1:1 composition for the colourless complexes of Fe(III) with citric, oxalic and malonic acids. Typical results are shown in Fig. 1 for Fe(III)-SB-malonic acid system.

It can be seen from Fig. 1 that the maximum decolourization is observed at a Fe(III): malonic acid ratio of 1:1. This indicates the formation of a complex corresponding to the formula Fe(malonic acid)<sup>+</sup> under the experimental conditions. Results obtained with citric and oxalic acid also indicate that Fe(III) forms 1:1 complexes with these acids.

In order to study whether mixed ligand complex formation occurs, increasing amounts of carboxylic acid were added to a solution containing Fe(III) and excess SB and the absorbance measured. The

absorbance over the entire visible range decreased as the concentration of the added carboxylic acid increased. This indicates a progressive conversion of the Fe-SB complex to a Fe-carboxylate complex. It was, therefore, concluded that no mixed ligand complexes are formed in these systems.

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#### Stabilities of Pr(III), Nd(III) & Sm(III) Complexes with Girard T Derivative of Resacetophenone

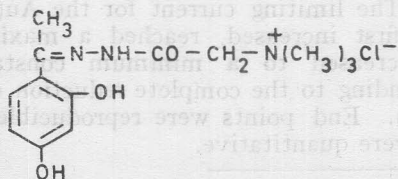
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The dissociation constant of the ligand and stability constants of complexes of Pr(III), Nd(III) and Sm(III) with Girard's T-derivative of resacetophenone have been determined potentiometrically using Calvin-Bjerrum pH-titration technique at  $27 \pm 0.1^\circ$  and  $\mu = 0.1M$  ( $\text{NaClO}_4$ ) in aqueous medium.  $\log K_1$ ,  $\log K_2$  and  $\log K_3$  values have been calculated for Pr(III), Nd(III) and Sm(III) complexes ( $\log \beta_3 = 11.31, 11.60$  and  $11.82$  respectively).

THE oxime of resacetophenone<sup>1</sup> was used for the determination of Cu(II) and Ni(II) in the presence of certain cations. The phenylhydrazone of resacetophenone<sup>2</sup> was used as a spot test reagent for Cu(II). The study of the stabilities of metal complexes in solution is facilitated by introducing a solubilizing group like quaternary ammonium group into the ligand. In the present investigations trimethylammoniumacetylhydrazine chloride (Girard T-reagent) derivative (I) of resacetophenone, containing azo methine group and solubilizing quaternary ammonium group has been prepared



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and the stability constants of its complexes with Pr(III), Nd(III) and Sm(III) have been determined in aqueous medium at  $\mu = 0.1M$  ( $\text{NaClO}_4$ ) and  $27^\circ \pm 0.1^\circ$  employing Calvin-Bjerrum pH titration technique.

Resacetophenone, Girard T-reagent, sodium perchlorate, etc., were of AR grade. Metal solutions were prepared from their respective nitrates (BDH, analar). Sodium perchlorate (BDH, analar, 1.0M) was used for maintaining the ionic medium constant at 0.1M. An aqueous solution of carbonate-free sodium hydroxide (analar) was prepared and standardized against potassium hydrogen phthalate.

A Cambridge bench type pH-meter (accuracy 0.02) with glass and calomel electrodes was used. The measurements were checked before and after the titration with standard buffers.

*Synthesis of the ligand (GTRP)*—Equimolecular proportions of resacetophenone and Girard T-reagent were taken in absolute ethyl alcohol. A small quantity of glacial acetic acid was added to it to dissolve Girard T-reagent. The reaction mixture was boiled under reflux for 2 hr. On cooling overnight, yellow crystals of the reagent (GTRP) appeared. The crystals were filtered and recrystallized from absolute ethanol. The yield was almost quantitative.

The substance does not have a sharp melting point but decomposed at  $245-48^\circ$ . It is fairly soluble in water but sparingly in alcohol [Found: C, 51.64; Cl, 11.80; N, 14.02; O, 15.87. Req'd: C, 51.74; Cl, 11.77; N, 13.93; O, 15.92%].

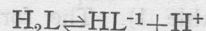
The molecular weight of the compound was found to be 300 which is very near to the theoretical value (301.5).

*pH-Titration procedure*—The following solutions (total volume 50 ml) were prepared and titrated against carbonate-free 0.1M NaOH (i) 1.0 ml of 0.1M perchloric acid + 5.0 ml of 1M sodium perchlorate. (ii) 1.0 ml of 0.1M perchloric acid + 5.0 ml of 1.0M sodium perchlorate + 5.0 ml of 0.02M ligand solution. (iii) 1.0 ml of 0.1M perchloric acid + 5.0 ml of 1.0M perchlorate + 5.0 ml of 0.02M ligand solution + 2.0 ml of 0.01M metal solution.

The metal and the ligand were taken in the ratio 1:5. The metal-ligand titration curves for the three metal ions under study are similar.

The acid dissociation constant of GTRP was calculated to be  $pK_1 = 6.1$  and  $pK_2 = 8.05$  by Irving and Rossotti method<sup>3</sup>. Formation curves for the metal-ligand systems (Fig. 1) were drawn between  $\bar{n}$  and  $pA$  where  $\bar{n}$  is the average number of ligands associated with each metal ion and  $pA$  is the free ligand exponent. The values of these terms were obtained from Bjerrum's method<sup>4</sup> as modified by Calvin and Wilson<sup>5</sup>.

In the complex formation there was no liberation of second proton and so the second phenolic proton has not taken part in complexation. Thus, GTRP acts as a biprotic bidentate ligand and neutralizes one equivalent of base to yield one buffer region in the potentiometric equilibrium curve.



Complex formation was evident from the drop in pH when metal solutions were added to ligand solution.