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NOTE

Spectrophotometric Studies of Various Fe(III)-1,3-Thiazine Systems

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Spectrophotometric investigation on Fe(III) complexes with substituted thiazines and phenylthiazines has shown 1 : 1 and 1 : 2 complex formation at pH 3.0 and 5.0 respectively. The change in colour of solution from light brown to dark brown showed the commencement of complex formation. 1 : 1 and 1 : 2 complex formation also confirmed by Job's variation method. Conditional stability constants of 1 : 1 and 1 : 2 complex are determined by spectrophotometric technique.

In view of analytical application, substituted thiazine and phenylthiazine ligands are selected in the present investigation. The metal-chelates of hydrazodimedone dyes are studied by Atef *et al.* [1]. Narwade *et al*[2] have investigated the stability constants of some lanthanide ions with sulphonic acid spectrophotometrically. Sunita and Gupta[3] have worked on spectrophotometric determination of cyanide in biological samples using a new reagent. Bhatt *et al.* [4] have shown 3-hydroxy-3-methyl-1-*p*-methoxyphenyl triazine as a new reagent for spectrophotometric determination of nickel. Raghuwanshi *et al.* [5] have shown 1 : 1 and 1 : 2 complex formation of Co(II), Ni(II) and Cu(II) with some substituted chalcones and isoxazolines potentiometrically and spectrophotometrically. Zabeen *et al.*[6] have investigated 1 : 1 complex formation of 2-hydroxy-3-methyl-1-O-carboxyphenyl triazine with palladium by using spectrophotometric technique. Agrawal *et al.*[7] have investigated 1 : 2 complex formation of Cu(II) with piroxicam by using Job's method. Chakravarty *et al.*[8] studied various Fe(III) substituted aminothiophenol systems spectrophotometrically. The study of metal-to-ligand ratio of substituted thiazines and phenyl thiazine was still lacking.

Therefore, the present work has been undertaken to study systematically the confirmation of complex of 4-(2-hydroxy-5-chlorophenyl)-6-(3-nitrophenyl)-2-imino-6-H-2,3-dihydro-1-3-thiazine (ligand 1); 4-(2-hydroxy-5-chlorophenyl)-6-(3-nitrophenyl)-2-iminophenyl-3,6-dihydro-1,3-thiazine (ligand 2); 4-(2-hydroxy-5-chlorophenyl)-6-(3-nitrophenyl)-2-iminophenyl-6-H-3-phenyl-1,3-thiazine (ligand 3) with Fe(III) metal ion using Job's variation method.

Chelating agents as 4-(2-hydroxy-5-chlorophenyl)-6-(3-nitrophenyl)-2-imino-6-H-2,3-dihydro-1,3-thiazine (ligand 1); 4-(2-hydroxy-5-chlorophenyl)-6-(3-nitrophenyl)-2-iminophenyl-3,6-dihydro-1,3-thiazine (ligand 2); 4-(2-hydroxy-5-chlorophenyl)-6-(3-nitrophenyl)-2-iminophenyl-6-H-3-phenyl-1,3-thiazine (ligand 3) have been synthesised in the laboratory using Raghuwanshi method[9]. The

structure of the compounds were confirmed by using properties and spectral analysis. The compounds were crystallised from ethanol before use.

Ferrous sulphate salt (BDH) and sodium perchlorate (BDH) were used and their solutions were prepared in double distilled water [*i.e.* Fe(III) = 0.01 M and $NaClO_4$ = 0.1 M]. Chelating agent solutions were prepared in purified 1,4-dioxane because chelating agents were insoluble in water medium.

pH measurements were carried out with ELICO-LI-10 pH-meter (accuracy ± 0.05 units) using glass and calomel electrodes. Instrument visible spectrophotometer was used in the present work for measurement of absorption of the solution.

Job's Method: Job's variation method was used to know the nature of complexes. The composition of Fe(III) [1×10^{-2} M] and ligands [1×10^{-2} M] were prepared in 1,4-dioxane and ionic strength was maintained constant (0.1 M) by adding an appropriate amount of either HCl solution or NaOH solution. λ_{max} was determined using one of the compositions at which there is maximum absorption.

The absorptions for all the compositions were recorded at a constant wave length (λ_{max}). The data of absorption and percentage composition are used to construct the curve between optical density and percentage composition for each ligand at constant pH. One of the curves was shown in Fig. 1.

It was observed that 1 : 1 complex formation occurs at pH 3.0 for Fe(III) complexes with all ligands and 1 : 2 complex formation at pH 5.0.

Conditional stability constants of metal-ligand complexes were calculated for all the systems and presented in Table 1.

TABLE-1
CONDITIONAL STABILITY CONSTANT OF COMPLEXES FOR ALL SYSTEMS

System	log K_1 at pH 3.0	log K_2 at pH 5.0
Fe(III)-ligand 1	2.7793	2.8891
Fe(III)-ligand 2	2.1274	2.4941
Fe(III)-ligand 3	1.9111	1.7617

It could be seen from Table 1 that there is no sufficient difference between log K_1 at pH 3.0 and log K_2 at pH 5.0. It showed that there will be formation of simultaneous complexes for all the systems. The change in colour of solution from light brown to dark brown showed the commencement of complex formation.

It is also observed from the above Table 1 that the values of log K_1 and log K_2 for 1 : 1 and 1 : 2 complexes respectively are greater for ligand 1 than ligand 2 and ligand 3. The reduction in log K values for ligand 2 and ligand 3 may be due to the fact of phenyl group which acts as an electron withdrawing group. As the number of electron withdrawing phenyl groups increases, the conditional stability constant decreases.

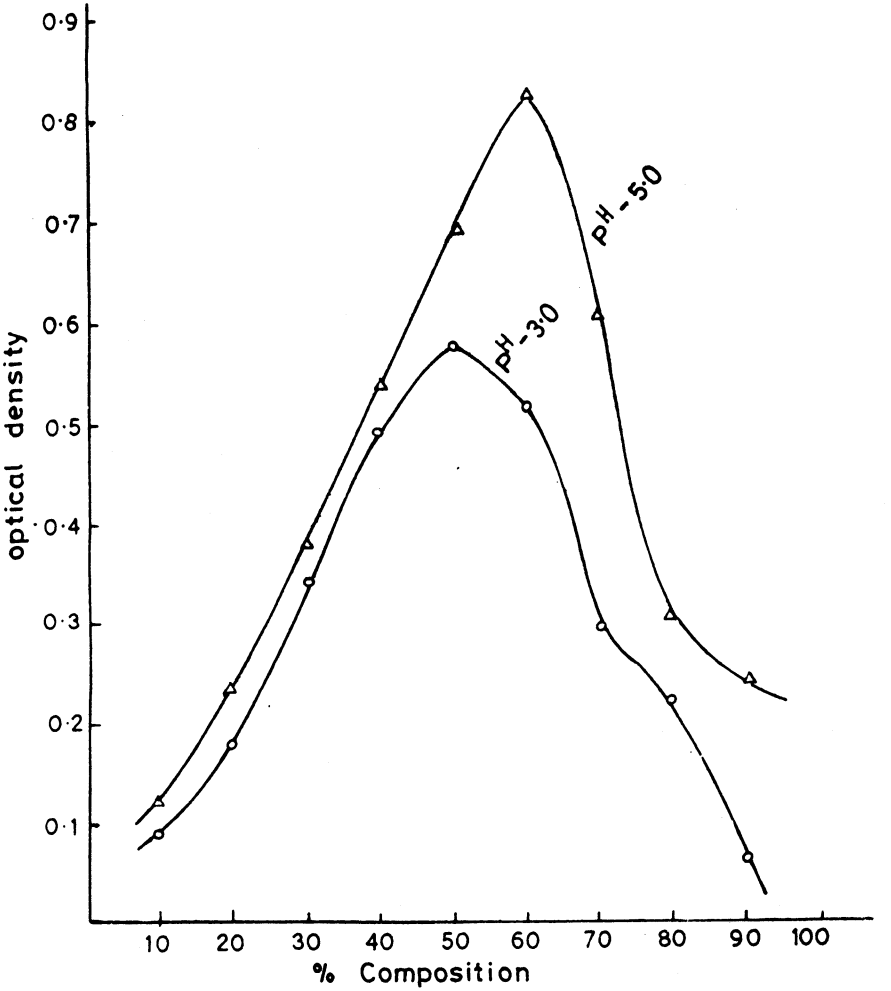

Fig. 1 Graph between percentage composition and optical density for ligand (I) with Fe(III) complex

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