

Spectrophotometric Determination of the Stability Constants of Cu(II) and Fe(III) Complexes with some Aryl Schiff Bases

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Summary: Stability constants of Cu(II) and Fe(III) with some aryl Schiff bases derived from salicylaldehyde and aniline, 3-hydroxy and 3-chloro anilines were determined spectrophotometrically using "Chattopadhyaya and Singh" method at 25°C in methanol. Cu(II) forms 1:1 and 1:2 complexes, and Fe(III) forms 1:3 complexes with these Schiff bases. The order of stability constants of the ligands used for these complexes was as follows: salicylidene-3-hydroxyaniline > salicylidene aniline > salicylidene-3-chloroaniline. The effects of substituent groups on the stability constants were discussed.

Introduction

The well-known Schiff base compounds were extensively studied because of their biological and structural importance [1,2]. In addition, the importance of these compounds lies mainly on their specific and selective reactions with metal ions [3]. Although the synthesis, electronic properties and the structural characterization of Schiff-base complexes were extensively investigated [4], studies of stability were limited and are based on potentiometric techniques studies [5,6]. Potentiometry is one of the most convenient and successful techniques employed for metal complex equilibrium measurements. When complex formation is practically complete at the initial low pH, or proton-involving equilibrium occur above pH 12 or when spectral changes indicate reactions that occur at the pH is varied, spectrophotometry can be important auxiliary technique for determining stability constant. In addition, potentiometry does not provide microscopic information involving identification of protonation and metal coordination sites on a ligand. For such information spectroscopic measurements studies are needed. Stability constant of any metal complexes of our ligands have not been reported in the literature. The aim of the work is to determine both the stoichiometry and stability constants of the metal ions Cu(II) and Fe(III) with salicylidene-3-hydroxyaniline (hpsa), salicylideneaniline (psa), salicylidene-3-chloro aniline (cpsa). Stability constants of these complexes were determined from spectrophotometric data, using the Chattopadhyaya and Singh methods [7] at 25°C in methanol. This

method is based on the elimination of one of the two unknown and is applicable to both weak and stable complexes.

Results and Discussion

The absorption spectra of solutions with equimolar amounts of metal ion and Schiff bases, or with an excess of one component were investigated at different concentrations. Cu(II) reacted with Schiff bases to form two complexes, depending on the reagent concentrations. At $ca. 4 \times 10^{-5} M$, we showed maximum absorption in the vicinity of 380 nm and no absorption above 400 nm in Fig. 1, but at approx. $2 \times 10^{-3} M$, the second λ_{max} was observed at $ca. 650$ nm in Fig. 2. However, only one λ_{max} around 580 nm was observed for Fe(III)-Schiff base solution in the range of 850-200 nm at different concentration in Fig. 3. The composition of metal to ligand ratio determined by using mole ratio methods are shown in Table-1. The solutions are completely stable and no spectral changes with time were observed. Absorbance data at the above mentioned wavelengths strictly obey Beer-Lambert's law. Consequently, in the light of the above investigation Cu(II) forms both 1:1 and 1:2 complexes but Fe(III) forms only 1:3 complexes in the range of 850-200 nm.

Stability constants were calculated from seven different concentration between the ranges given in Table-1. The stability constants of these

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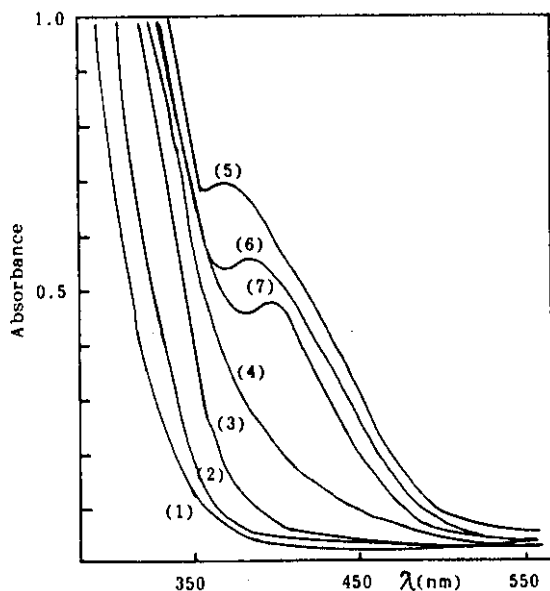


Fig. 1: Ultraviolet absorption spectra of 1:1 complexes with Cu(II) in methanol at 25°C. Key; (1) free Cu(II), (2) hpsa, (3) psa, (4) cpsa, (5) $[\text{Cu}(\text{hpsa})]^+$, (6) $[\text{Cu}(\text{psa})]^+$, (7) $[\text{Cu}(\text{cpsa})]^+$, $C_M=4 \times 10^{-4}$, $C_L=4 \times 10^{-4}$.

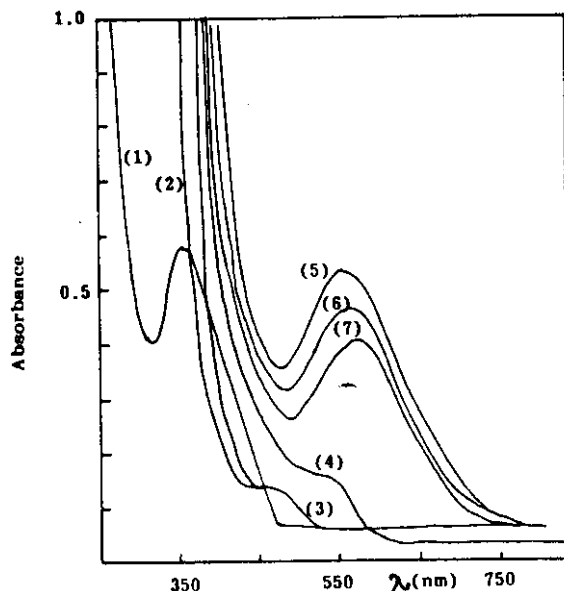


Fig.3: Ultraviolet absorption spectra of 1:3 complexes with Fe(II) in methanol at 25°C. Key; (1) free Cu(II), (2) hpsa, (3) psa, (4) cpsa, (5) $\text{Cu}(\text{hpsa})_3$, (6) $\text{Cu}(\text{psa})_3$, (7) $(\text{cpsa})_3$, $C_M=4 \times 10^{-4}$, $C_L=4 \times 10^{-4}$.

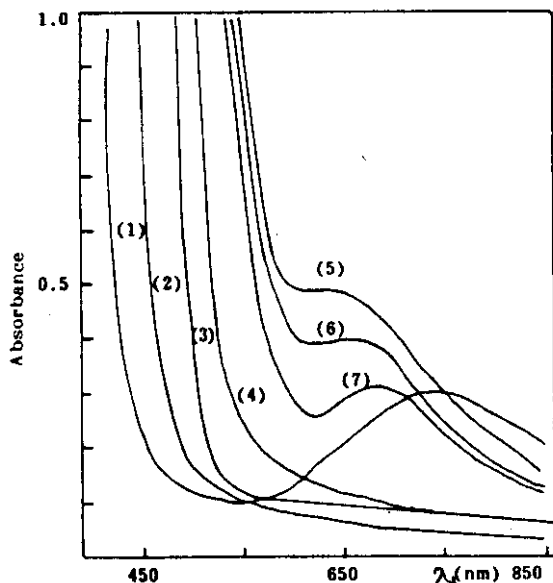


Fig. 2: Ultraviolet absorption spectra of 1:2 complexes with Cu(II) in methanol at 25°C. Key; (1) free Cu(II), (2) hpsa, (3) psa, (4) cpsa, (5) $\text{Cu}(\text{hpsa})_2$, (6) $\text{Cu}(\text{psa})_2$, (7) $\text{Cu}(\text{cpsa})_2$, $C_M=2 \times 10^{-3}$, $C_L=4 \times 10^{-3}$.

Table-1: Metal-to-ligand ratio and λ_{max} of the metal-Schiff base complexes at the definite concentration range.

Ion	$\lambda_{\text{max}}/\text{nm}$			M:L	Concentration range/M
	hpsa	psa	cpsa		
Cu(II)	370	385	398	1:1	$4.00 \times 10^{-5} - 7.00 \times 10^{-5}$
Cu(II)	636	657	688	1:2	$2.00 \times 10^{-3} - 5.00 \times 10^{-3}$
Fe(III)	562	576	582	1:3	$4.00 \times 10^{-5} - 7.00 \times 10^{-5}$

Table-2 Stability constants of the metal complexes with Schiff-bases at their adsorption maxima at 25°C in methanol

Ion	Symbol	Log β		
		hpsa	psa	cpsa
Cu(II)	β_1	6.74 ± 0.03	5.61 ± 0.03	4.06 ± 0.05
Cu(II)	β_2	10.74 ± 0.04	9.46 ± 0.02	8.81 ± 0.03
Fe(III)	β_3	12.21 ± 0.05	10.65 ± 0.01	9.96 ± 0.02

metal complexes calculated from computer program are listed in Table-2.

As can be seen in Table-2, stability of the psa complexes are higher than that of opsa complexes and lower than that of hpsa complexes, the order of stability constant with respect to ligand is as follows:



This order can be explained by considering the effect of substituents, hydroxy groups being electron-donating, enhances the electron density on the donor atoms of the Schiff bases with increase in nucleophilicity. However, chlorine atom as an electron-withdrawing group reduces the electron density, and as a result, the Schiff base becomes less basic. The Schiff bases coordinates to the metal ion via the phenolic oxygen and the imino nitrogen. The M-L bond with the hydroxy group is more stronger than that of chlorine group.

Experimental

All chemicals used were of analytical reagent grade, without further purification. 10^{-2} M stock solution of the Schiff bases and metal salts ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9(\text{H}_2\text{O})$) were prepared by dissolving the accurately weighted amounts in appropriate volume of absolute methanol.

Ligands were synthesized by mixing equimolar amounts of salicylaldehyde and the appropriate amine in methanol solution. All ligands showed satisfactory agreement of their elemental analyses with the theoretical content of their particular elemental composition.

Spectral data were measured with 1.00 cm matched quartz cells and Bosh-Lomb 2000 UV-Vis spectrometer thermostated at 25.0 ± 0.1 °C. Absorbance data were recorded under equilibrium conditions. Computations were performed on a Escort 386-SX computer.

Chattopadhyaya and Singh technique [7] was followed to determine the stability constants. Frequently encountered equilibria may be written as



Stability constants for the complexes can be expressed as

$$\beta_n = \frac{[\text{ML}_n]}{[\text{a}_M - \text{ML}_n][\text{a}_L - n\text{ML}_n]} \quad (2)$$

where a_M and a_L are the analytical concentrations of metal ion and ligands, respectively. If the metal ion, ligand and complex absorb light in the region of study, the absorbance can be expressed as

$$A = (\text{M}^0 - [\text{ML}_n])\epsilon_M + (\text{L}^0 - n[\text{ML}_n])\epsilon_L + [\text{ML}_n]\epsilon_C \quad (3)$$

where ϵ_M , ϵ_L and ϵ_C are the molar absorptivities of the species M, L and ML_n respectively.

Combining Eq. (3) with Eq. (2) and rearranging we get

$$\frac{[\text{a}_M \text{a}_L]}{[\text{A} - \text{A}^0]} \left[\epsilon^2 + (\text{a}_M - \text{a}_L)\epsilon + (\text{A} - \text{A}^0) \right] = \frac{\epsilon}{\beta_1} \quad (4)$$

$$\frac{[\text{a}_M \text{a}_L^2]}{[\text{A} - \text{A}^0]} \left[\epsilon^3 - 4(\text{a}_M \text{a}_L + \text{a}_L^2)\epsilon^2 + 4(\text{a}_M - \text{a}_L)(\text{A} - \text{A}^0)\epsilon - 4(\text{A} - \text{A}^0)^2 \right] = \frac{\epsilon^2}{\beta_2} \quad (5)$$

$$\frac{[\text{a}_M \text{a}_L^3]}{[\text{A} - \text{A}^0]} \left[\epsilon^4 - (9\text{a}_M \text{a}_L^2 + \text{a}_L^3)\epsilon^3 + (27\text{a}_M \text{a}_L + 9\text{a}_L^2)(\text{A} - \text{A}^0)\epsilon^2 + (27\text{a}_M + \text{a}_L)(\text{A} - \text{A}^0)^2 \epsilon + 27(\text{A} - \text{A}^0)^3 \right] = \frac{\epsilon^3}{\beta_3} \quad (6)$$

These three equations for 1:1 (4), 1:2 (5) and 1:3 (6) complexes, respectively.

where,

$$\text{A}^0 = \text{a}_M \epsilon_M + \text{a}_L \epsilon_L \text{ and } \epsilon = \epsilon_C - \epsilon_M - n\epsilon_L$$

The right-hand term of equation (4,5,6) is constant for all mixtures containing different analytical concentrations of metal and ligand. These equation (4,5,6) can be solved by simultaneous treatment of the values of a_M , a_L , A and A^0 for two different solutions at the same wavelength, thus the constant term would be eliminated. If n measurement have been made at a specified wavelength with different mixture solutions C(n,2) different values for ϵ may be obtained. Each ϵ value may then be substituted in corresponding pair of equations to give β_n . This calculations were carried out by computer for different analytical concentrations at several wavelengths to give statistical validity to the results. Errors in determination and computation of stability constants will arise from two principal sources, the quality of the measured data, and the model provided to the program. In this model, ambiguity may be possible if there are relatively

large errors in the data or no previous analogies exist. Our results obtained with this model have good reproducibility and Chattopadhyaya and Singh reported that there is good agreement between values calculated by this method and some of the values reported in the literature [7]. It is considerable to compare our results to the literature values for testing the reliability of stability constants for these complexes, but the available data about the stability of other Schiff-base complexes are very scarce.

Acknowledgements

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