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Spectrophotometric Study of Stability Constants of Cr(III), Ni(II) and Cu(II) Complexes with a Schiff Base in Different Solvents

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ABSTRACT

Complexation of Cr(III), Ni(II) and Cu(II) with para-dimethylaminoanil of ortho-hydroxyphenylglyoxal Schiff's base in methanol, ethanol and acetone solvents has been studied spectrophotometrically at room temperature (298K). The stoichiometry and stability of the complexes were determined using mole-ratio method. Stability data shows solvent-wise stability constants order as methanol > ethanol > acetone.

Key words: Free energy**,** Ortho-hydroxyacetophenone, para-dimethylaminoaniline, stability constant.

INTRODUCTION

Although owing to versatile properties of Schiff's bases they have multifarious roles in diverse fields, viz. industries[1], analytical[2,3], coordination[4-6] and organic chemistry[7-8], agriculture[9], medical sciences[10-12] etc. but ketoazomethines exhibiting novel ligation properties in forming heteropolynuclear[13] and isomeric complexes[14] and also adducts in unusual coordination numbers[15-16] with transition metals attract high attention as ligands.

The effective coordination of ligands with metal ions may have significance in biological implications[17]. The chelation therapy for intoxication of heavy metals depends upon the chelating agent being able to reach the intercellular site where the heavy metals are firmly bound[18]. For a pretty long time, varieties of ligands have been used as antidote to combat metal poisoning. As Cr(III), Ni(II) and Cu(II), essential trace elements of mammals, usually form stable complexes with N, O and S donor ligands, a bidentate Schiff's base, para-dimethylaminoanil of ortho-hydroxyphenylglyoxal (L), with N, O donor sites, therefore, has been used as ligand for spectrophotometric study of stability constants of complexes of Cr(III), Ni(II) and Cu(II) ions in different solvents (methanol, ethanol and acetone) and report in the present communication.

EXPERIMENTAL

Ortho-hydroxyacetophenone, para-dimethylaminoaniline, selenium dioxide and chlorides of Cr(III), Ni(II) and Cu(II) reagent grade chemicals of 97-98% purity obtained from CDH, Fluka and BDH were used in synthetic work without further purification. Solvents of analytical grade purity were used as supplied.

Spectrophotometric measurements were done on Shamdzu SP65 UV-Visible spectrophotometer in 200-800 nm range

Synthesis of Ligand

Ortho-hydroxyphenylglyoxal, precursor of the ligand, was prepared[16] by oxidation of ortho-hydroxyacetophenone with selenium dioxide in ethanol. The ligand was prepared by condensation of ortho-hydroxyphenylglyoxal and para-dimethylaminoaniline. On mixing equimolar quantities of the reactants (0.5 mol) in 100 ml of ether (predried with anhydrous Na_2CO_3) followed by stirring, precipitate[19] of product was obtained, washed with dry ether and dried in air.

Preparation of Standard Stock Solutions

Equimolar (1×10^{-2}M) stock solutions of ligand and metal chlorides were prepared by dissolving their requisite quantities in each of the solvents (methanol, ethanol and acetone) and diluting to 100 ml in volumetric flask.

Preparation of Working Solutions

Dilute solutions of the metal ions and ligand under study were obtained by appropriate dilution of stock solutions with their solvents.

Selection of Analytical Wavelength of the Complexes

For the selection of analytical wavelength Vosburgh and Cooper procedure was adopted[20]. A number of solutions are made by mixing different volumes of stock solutions of reactants in the same solvent. The absorbance were scanned between 200-800 nm at the difference of 10 nm to determine the λ_{max} using UV-Visible spectrophotometer. The wavelength of maximum absorbance for each complex is noted in Table 1.

Procedure for Mole-Ratio Method

The procedure described by Nardo and Dawson[21] was followed. 0.5 ml stock solution of each metal chloride in each solvent was pipetted into each of the sixteen test tubes and aliquot (0, 0.1, 0.2, 0.3, -1.5 ml) of stock solution of ligand was added. In each test tube of metal-ligand mixture total volume was raised to 2 ml by adding the solvent (1.5, 1.4, 1.3, -0 ml). The reaction mixtures were shacked. The absorbance of each of the mixture was taken at λ_{max} of the complexes in their solvents at room temperature (298K)

RESULTS AND DISCUSSION

Properties of Complexes

Ligand reacted with Ni(II), Cu(II) and Cr(III) to give orang red, orang yellow and greenish yellow complexes respectively in all the three solvents. Ligand showed λ_{max} at 250 nm, 290 nm, 300 nm whereas Cr(III), Ni(II) and Cu(II) chlorides exhibit λ_{max} at 515 nm, 510 nm and 415 nm in methanol, ethanol and acetone respectively. λ_{max} of complexes are noted in Table 1. On heating the metal and ligand

Table 1: The thermodynamic stability constant (logk), change in free energy (ΔG°), Em, Es, α and λ_{max} of Ni^{+2}, Cu^{+2} and Cr^{+3} complexes

Experimental	Cr(III)-L			Ni(II)-L			Cu(II)-L		
Data	MeOH	EtOH	Me_2CO	MeOH	EtOH	Me_2CO	MeOH	EtOH	Me_2CO
λ_{max}(nm)	440	440	490	460	460	500	430	430	530.0
Em	1.765	1.792	2.745	2.499	2.245	1.959	2.196	2.087	2.942
Es	1.669	1.678	2.551	2.129	1.775	1.532	1.986	1.882	2.714
α	0.054	0.064	0.070	0.148	0.209	0.218	0.096	0.098	0.417
Logk (L/mol)	7.477	7.250	7.130	3.89	3.56	3.520	6.407	6.37	4.303
-ΔG° (KJ/mol)	33.0	24.6	21.00	2.2195	2.0312	2.0084	36.58	36.42	24.56

mixture solution (stoichiometric ratio) up to 60^{0}C unchanged colour intensity reveals independence of stability of complexes upon temperature.

Composition and Stability Constant of the Complexes

The stoichiometric ratio of the ligand to Cr(III), Ni(II) and Cu(II) in their complexes was determined by mole-ratio method at constant metal ion concentration (1x10^{-2}M) and varying ligand concentrations (1x10^{-2}M) and optical density was measured at the λ_{max} of each complex in respective solvents. The intercepts of tangents on both arms of the graphs plotted between optical density and varying concentrations of ligand indicate 2:1, 1:1 and 2:1 ligand to metal interaction ratios in the complexes respectively in all the three solvents (Figures 1-3). The suggested metal ligand interactions are:

Cr^{3+} + 2 L [$Cr\text{-}L_2$]
Ni^{2+} + L [Ni-L]
Cu^{2+} + 2L [$Cu\text{-}L_2$]

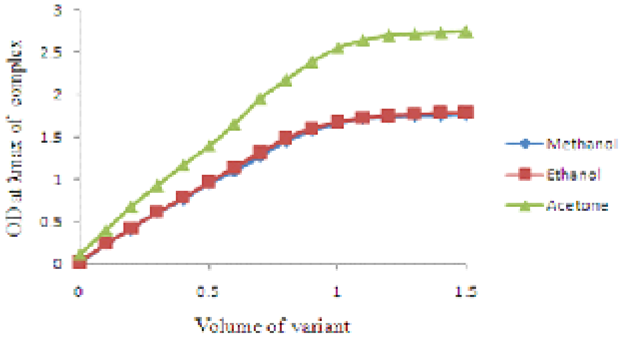

Fig. 1: Determination of composition of Cr(III)-DMAAHPG complexes by mole ratio method in methanol, ethanol and acetone solvents at room temperature (T=298K)

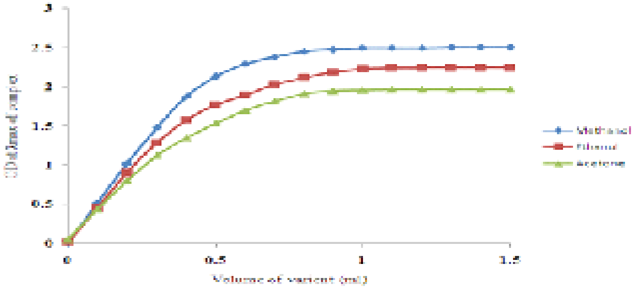

Fig. 2: Determination of composition of Ni(II)-DMAAHPG complexes by mole ratio method in methanol, ethanol and acetone solvents at room temperature (T=298K)

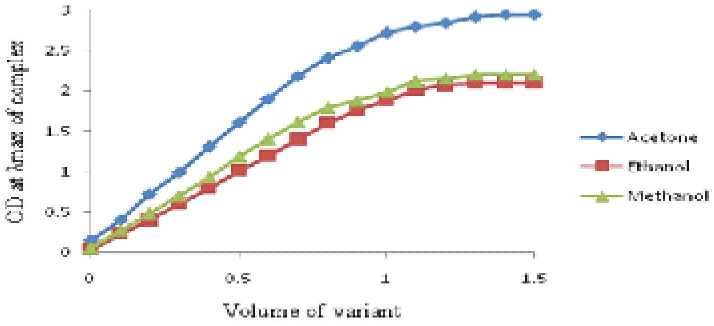

Fig. 3: Determination of composition of Cu(II)-DMAAHPG complexes by mole ratio method in methanol, ethanol and acetone solvents at room temperature (T=298K)

The stability constants of the complexes have been calculated by using the following equations:

$$\begin{array}{lll} MLn & \rightleftharpoons & M + nL \\ C & & 0 \qquad 0 \\ C(1-\pm) & & \pm C \qquad n\pm C \end{array}$$

Where C is the total molar concentration of the complex assuming no dissociation, ± is degree of dissociation and ±C and n±C are equilibrium concentrations of the metal and ligand respectively.

The stability constant (K_s) = $C(1-\pm)/\pm C.(n\pm C)^n$ ...(i)

and $\pm = (E_m - E_s)/(E_m)$ ...(ii)

Where E_m is maximum extinction ($Lmol^{-1}cm^{-1}$) obtained from intercept of tangents on both arms of the curve and E_s is extinction at equilibrium concentrations of complex and reactants obtained by intercept of mole ratio curve by the line parallel to y-axis through E_m. The value of n is number of ligand to metal.

The value of Gibbs free energy ("G^o) of the complexation reactions is calculated by

$$-\Delta G^0 = 2.303RT \log k_s$$

The perusal of stability data (Table 1) reveals solvent-wise stability order for each of the complex as methanol > ethanol > acetone in accordance of polarity (dielectric constant) of solvents which indicates high covalent character of metal-ligand bond(s) in the title complexes. The negative free energy values indicate thermodynamic stability of complexes i.e independence of stability upon temperature.

1. The values of stability constants and negative sign of entropy changes of the complexes in the solvents used indicate that metal-ligand reactions are endothermic and complexes are stable at higher temperatures.
2. Solvent-wise stability order of complexes, methanol > ethanol > acetone, in accordance of polarity of solvents indicates high covalent character of metal-ligand bond(s).
3. Stability constant results suggest that ligand used is a good chelator agent for all the three metals.

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