Thermodynamics of Complex Formation of Transition Metal Ions with Schiff Bases in Mixed Sovent Media

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A series of Schiff bases derived from 2-hydroxy-5-methyl acetophenone and *p*-toluidine, *p*-anisidine and *p*-phenetidine have been synthesized. Their chelating tendencies towards Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II) metal ions have been investigated potentiometrically at various temperatures in 50 : 50 ethanol-water medium and 0.1 M (NaClO$_4$) ionic strength. Thermodynamic parameters for metal-ligand stability constants have been determined by temperature coefficient method.

INTRODUCTION

Schiff bases and their metal complexes have been the subject of intensive research due to their novel structural features, interesting spectral and magnetic properties and their industrial and biological importance. The biological activity, catalytic properties and analytical applications can be correlated to the structure of Schiff bases. The optimum conditions required for the maximal or complete formation of a complex may be predicted on the basis of its stability constants in solution. Extensive data on the stabilities of transition metal complexes in solution are available with differently substituted Schiff bases[1-4]. Howerver, there is no systematic solution study of the complexes of transition metals with these Schiff bases. In view of the above facts, the study of their binary complexes with some transition metals has been undertaken.

EXPERIMENTAL

All the chemicals used were of AR grade. The Schiff bases were prepared by the condensation of 5-methyl-2-hydroxy acetophenone with *p*-toluidine, *p*-anisidine and *p*-phenetidine. The metal nitrates were dissolved in doubly distilled water and standardized by the known methods. All the other solutions were also prepared in doubly distilled water.

A digital pH meter (Elico, Model LI–120) in conjunction with a combined electrode was used for pH measurements. The method of Calvin and Bjerrum modified by Irving and Rossotti[5] was used to obtain pK and log K values. The measurements were made at 25°, 35° and 45°C at $\mu = 0.1$ M (NaClO$_4$) in 50% aqueous ethanol.

The pK and log K values were determined by half integral method, pointwise

calculations and also by the method of least squares wherever the difference[6] between log K_1 and log K_2 was less than 1.75 .In all the calculations, pH correction and volume correction factors have been applied for the ethanol-water mixture. The average log K values were used to calculate the free energy (ΔG) from the van't Hoff's isotherm. The ΔH and ΔS values were calculated from the van't Hoff's isochore and the equation $\Delta G = \Delta H - T \Delta S$ respectively. The data are listed in Table-1.

TABLE-1

FORMATION CONSTANTS, FREE ENERGY, ENTHALPY AND ENTROPY CHANGES IN THE COMPLEXATION EQUILIBRIA OF TRANSITION METAL IONS WITH LIGANDS R_1, R_2 and R_3.

Temp. $25 \pm 0.1°C$, $\mu = 0.1$ M (NaClO$_4$)

Complex		log K_1	log K_2	log β	$-\Delta G_1$	$-\Delta G_2$	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	ΔS_2
					(kJ mol^{-1})					
Cu(II)	R_1	7.82	6.89	14.71	44.622	39.315	12.620	13.563	107.380	86.416
Cu(II)	R_2	8.01	6.90	14.91	45.706	39.372	11.836	14.569	113.658	83.732
Cu(II)	R_3	8.04	7.38	15.42	45.877	42.111	14.774	13.897	104.373	94.679
Ni(II)	R_1	5.85	4.45	10.30	33.380	25.392	9.576	8.045	79.880	58.211
Ni(II)	R_2	7.76	6.66	14.42	44.279	38.002	10.444	16.130	113.541	73.398
Ni(II)	R_3	6.86	5.34	12.20	39.144	30.470	16.950	15.557	74.477	50.046
Cd(II)	R_1	5.80	4.92	10.72	33.095	28.074	10.052	14.259	77.325	46.359
Cd(II)	R_2	7.62	6.46	14.08	43.480	36.861	15.044	10.257	95.420	89.274
Cd(II)	R_3	6.45	5.69	12.14	36.804	32.468	12.700	15.117	80.888	58.224
Co(II)	R_1	5.70	4.62	10.32	32.525	26.362	11.967	13.677	68.985	42.567
Co(II)	R_2	6.64	5.56	12.30	37.888	31.726	10.637	10.444	91.446	71.416
Co(II)	R_3	6.36	5.39	11.75	36.291	30.756	15.318	12.222	70.379	62.195
Mn(II)	R_1	5.62	4.60	10.22	32.068	26.248	12.185	13.962	66.723	41.228
Mn(II)	R_2	6.59	5.46	12.05	37.603	31.155	15.666	10.770	73.613	68.408
Mn(II)	R_3	5.11	4.55	9.66	29.158	25.962	17.160	12.487	40.263	45.221
Zn(II)	R_1	6.41	5.46	11.87	36.576	31.155	12.487	16.716	80.834	48.453
Zn(II)	R_2	7.64	6.78	14.42	43.595	38.687	14.910	10.530	96.257	94.488
Zn(II)	R_3	6.98	6.27	13.25	39.828	35.777	15.318	15.956	82.251	66.515

R_1 = 5-Methyl-OHA-N-(4-methylphenyl) imine ($C_{16}H_{17}ON$)
R_2 = 5-Methyl-OHA-N(4-methoxyphenyl) imine ($C_{16}H_{17}O_2N$)
R_3 = 5-Methyl-OHA-N-(4-ethoxyphenyl) imine ($C_{17}H_{19}O_2N$)

RESSULTS AND DISCUSSION

The pK_1 and pK_2 values of Schiff bases which represent the deprotonation of NH group at azomethine nitrogen atom and phenolic OH group were determined at $\bar{n}_A = 1.5$ and 0.5 respectively. The values were further checked from the plots of log $\{(2 - \bar{n}_A)/(\bar{n}_A - 1)\}$ vs B and log $n_A/(1 - n_A)$ *vs.* B (B = pH meter reading) and are given in Table-2.

TABLE-2

	Temperature (°C)		
	25	35	45
Ligand I (R_1)			
pK_1	4.66	4.51	4.41
pK_2	11.25	10.96	10.68
Ligand II (R_2)			
pK_1	4.91	4.43	4.01
pK_2	11.27	11.07	10.87
Ligand III (R_3)			
pK_1	5.00	4.79	4.60
pK_2	11.26	11.01	10.77

The pK_1 value of R_1 is lower than that of R_2 and R_3. The ligand R_1 is having methyl substituent at *para* position to amine group and the other ligands are having —OCH_3 and —OC_2H_5 groups respectively. This can be explained on the basis of domination nature of +M effect of —OCH_3/—OC_2H_5 group over +I effect of —CH_3. This may be attributed to the fact that the methoxy and ethoxy group increases the electron density on the azomethine nitrogen to a greater extent than methyl group resulting in stronger bonding.

The metal-ligand titration curve deviates from the acid-dissociation curve in the pH range 5.0 to 8.2, indicating that the complexation takes place in this pH range. The maximum value of $\bar{n}$ is found to be 2.0 in all the complexes which suggest the formation of 1 : 1 and 1 : 2 complexes. The values of log K_1 and log K_2 were determined by the half integral method and least squares method (Table-1).

The stability constants of Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II) complxes with R_1 follow the order Cu > Zn > Cd > Co > Ni > Mn and with R_2 and R_3 the order is Cu > Zn > Ni > Cd > Co > Mn. These stabilities are similar to the observations made by a number of workers[7-10] and are in accordance with Irving-Williams order[11].

The linear relation log K = a pK + b has been found out by some workers[12, 13] to hold for transition metal complexes of a series of closely related ligands. Similar plots of pK_1 vs log K_1 and pK_1 + pK_2 vs log β shows no linear relationship. Ionization potential of the metal ion and donor atoms, tendency of metal ions to form π-bonds, ligand-field stabilization of ligand and the nature of ligands[14] are some of the factors which affect the linear relationship.

The direct correlation of stabilities of metal complexes with ligand basicities is shown by comparing the stability per unit base strength, *i.e.*, log β/ΣpK. The ratios of all metals are approximately same except Cu(II) complexes, which are significantly larger. These greater values of copper complexes indicate the extensive π-interactions.

It is evident from Table-1 that the stability constants of the complexes decrease

with the increase in temperature which indicates that the high temperature does not favour the formation of stable complexes. The ΔH and ΔS values of the metal complexes with the same ligand do not show any regularity which is in accordance with the Basolo and Pearson order[15]. The ΔS_1 and ΔS_2 values of Cu(II) complexes are relatively higher than those of all other metal complexes and follow the order of basicity of ligands. The high entropy values in copper complexes many be attributed to Jahn-Teller distortion of the octahedral symmetry in copper which may result in greater covalent character of the metal ligand bond. The negative values of ΔG_1 and ΔG_2 indicate that the formation of 1 : 1 and 1 : 2 metal-ligand complexes in all the cases are thermodynamically favoured processes. The negative values of ΔH_1 and ΔH_2 also lead to the same inference. The high positive values of ΔS_1 and ΔS_2 in all cases indicate that the entropy effect is predominant over the enthalpy effect.

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