



Potentiometric and thermodynamic studies of schiff base hydrazone metal complexes

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ABSTRACT

The synthesis and structural features of some Bidentate Schiff base complexes of the type $[M(OON)_2]$ (where $M = Cu^{+2}, Ni^{+2}, Co^{+2}, Mn^{+2}$ and O represents the salicylaldehyde moiety) are reported. The ligand was derived by the condensation of Cinnamaldehyde hydrazone with substituted salicylaldehyde. These metal complexes were characterized by elemental analysis, molar conductance, magnetic momentum measurements, IR, 1H NMR spectral data. An octahedral geometry was proposed for all metal complexes. Stability constants of these metal complexes were determined using a potentiometric method at constant ionic strength (0.1μ) and at different temperature ($25^0C, 30^0C, 35^0C$) in 50% v/v ethanol-water mixture by calculating the values of η_A, η and P_L , it has been found that ligand forms complexes in 1:2 ratio.

Key words- Schiff base, stability constant and IR conductance.

INTRODUCTION

The dissociation constants of Schiff base (derived from Cinnamaldehyde hydrazone with substituted salicylaldehyde) and metal-ligand stability constants of its complexes with some transition metal ions have been determined potentiometrically in 0.1M NaCl and ethanol-water mixture (30vol%). The order of the stability constants of the formed complexes increases in the sequence $Mn^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}$. The effect of temperature was studied and the corresponding thermodynamic parameter ($\Delta G, \Delta H, \Delta S$) were derived and discussed. The dissociation process is non-spontaneous, endothermic and entropically unfavorable. The formation of the metal complexes was found to be spontaneous, exothermic and entropically favorable. The versatile chelating ability of Schiff base (Thiosmicabazone) with various metals is very well established [1-6].

Structural studies have shown that Schiff base exhibit different types of bonding depending on the nature of the metal ion and the reaction condition [7-9]. The interest in such complexes continues increasing due to the possibility of their use as models to explain some intricate reaction in biological systems such as- antiviral, antimalarials, antiulcer, anticancer[10-12].

In this paper, we are reporting the synthesis, characterization and thermodynamic studies of Schiff base (derived from Cinnamaldehyde hydrazone with substituted salicylaldehyde) complexes with bivalent metals like Cu^{+2} , Ni^{+2} , Co^{+2} , Mn^{+2} .

MATERIALS AND METHODS

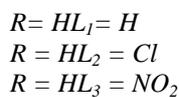
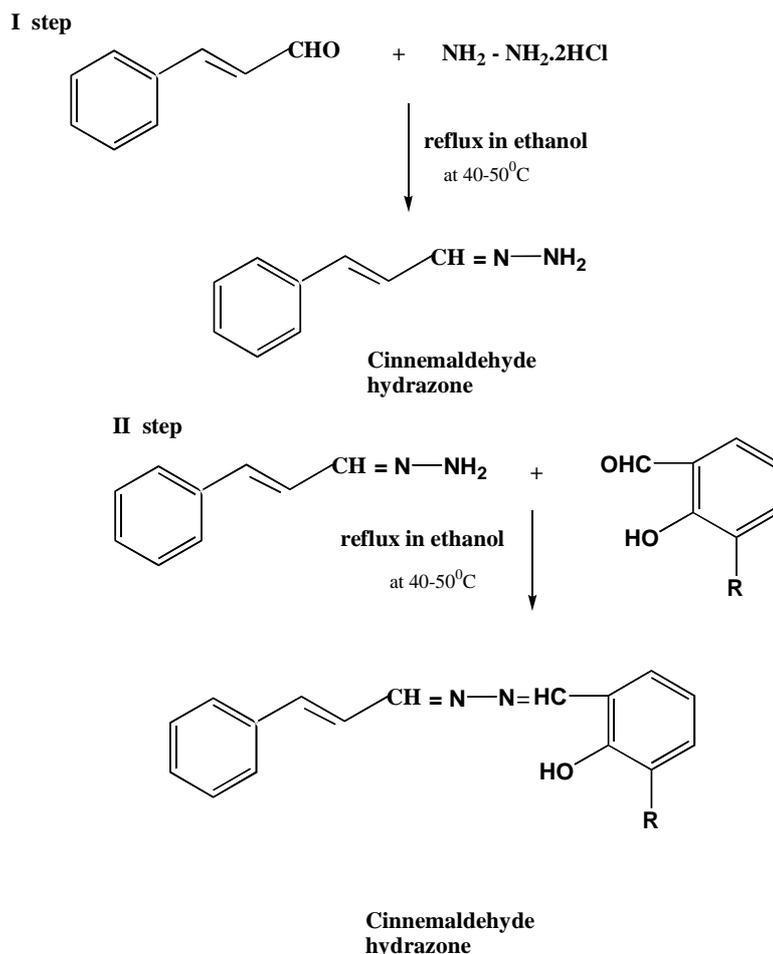
2.1 Material, analytical methods and physical measurements

All chemicals used were of reagent grade. Solvents were distilled prior to use. The metal content of the complexes were estimated gravimetrically, copper metal was estimated by ammonium thiocyanate gravimetrically. Nickel, cobalt and manganese were estimated by gravimetrically using dimethylglyoxime, ammonium thiocyanate and iron with triethanolamine respectively [13]. Magnetic susceptibility of complexes was measured at room temperature on a faraday balance using Hg $[\text{Co}(\text{SCN})_4]$ as a calibrant. Electronic spectra were recorded using digital spectrophotometer in DMSO. The IR spectra of ligands and their complexes were recorded as KBr pallets in the region $4000\text{-}400\text{cm}^{-1}$ on FT IR spectrophotometer Shimadzu 8201. ^1H NMR spectra of ligands and their Cu (II), Ni (II), Co (II) and Mn (II) complexes were recorded in DMSO- d_6 at room temperature using TMS as internal standard on a Bruker Advance 400 MHz FT NMR. Elemental analyses were carried out on a Vario EL III Elementar Carlo- Erba 1108. Conductivity measurements were made on 10^{-3} M solutions of the complexes in DMSO using Equiptronics model no Eq-660A conductivity meter, provides with a dip type cell having cell constant 1.0. EPR spectra of metal complexes of Schiff base hydrazones were recorded at room temperature on E-112 X-band spectrometer using TCNE as g-marker. Melting points of the ligands and their metal complexes were determined by open capillary method using Sunsim electric melting point apparatus and uncorrected. Molecular weight of ligands and their metal complexes were determined by Rast camphor method. The purity of ligands and their metal complexes was checked by thin layer chromatography using n-hexane-ethyl acetate mixture (3:1).

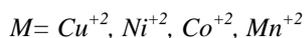
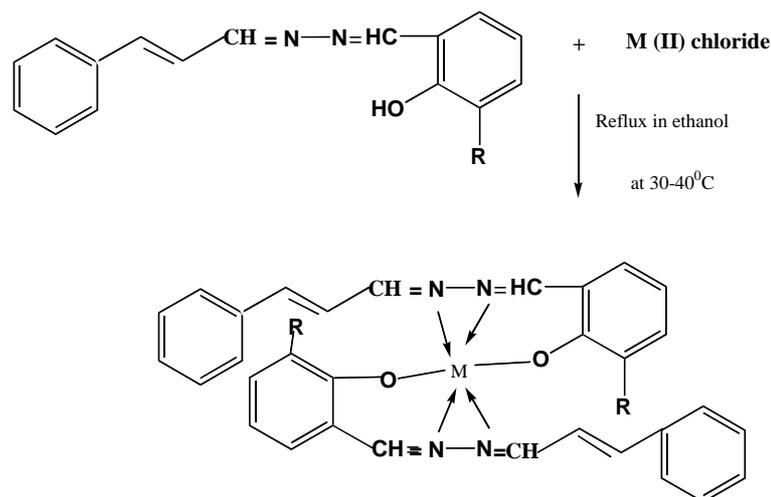
2.2 Synthesis of the ligands

The ligand was synthesized in two steps. The first step is the synthesis of Cinnamaldehyde monohydrazone according to the reporting method [14], followed by the Cinnamaldehyde hydrazones (II) in the second step from monohydrazone.-

Cinnamaldehyde monohydrazone (2gm, 1m mol) (80% yield, mp 120°C , yellow crystal) was dissolved in absolute ethanol (10ml). To this solution salicylaldehyde, chloro salicylaldehyde and nitro salicylaldehyde (1m mol 1.22ml, 1.32ml, 1.42ml) were added for preparing HL_1 [Cinnamaldehyde-(2-hydroxybenzylidene)hydrazineCHBH], HL_2 [Cinnamaldehyde-(2-hydroxy,3-hlorobenzylidene)hydrazine CHCBH] and HL_3 Cinnamaldehyde-(2-hydroxy,3-nitrobenzylidene)hydrazine CHNBH] respectively. The reaction mixture was refluxed for 4hrs. After cooling, the formed yellow precipitate was collected, filtered and finally washed with absolute ethanol (10ml) and purified by recrystallization from ethanol (77%yield mp 130°C) (Scheme-1).



SCHEME-1 SYNTHESIS OF LIGAND



SCHEME-2 SYNTHESIS OF METAL COMPLEXES

2.3 Synthesis of metal complexes

Warm ethanol solution (20ml) of the respective Schiff base (0.002M) were added to a magnetically stirred solution of the metal (II) salts (0.001M) in ethanol (25ml).

Table-1: Micro analytical data of the ligands and their metal complexes

Table-2: IR, ¹HNMR and UV spectra of ligand LH₁ and its metal complexes

Compounds	Molecular weight Found (calc.)	Found (calc) %				M.P °C	Molar cond. Δm $Cm^{-2}mol^{-1}ohm^{-1}$	Magnetic moment	Colour	Yield	Molecular formulae
		Carbon	Hydrogen	Nitrogen	Oxygen						
HL ₁	248 (250)	76.0 (76.8)	5.58 (5.6)	11.1 (11.2)	6.38 (6.4)	130°C	12	-	Yellow	77%	C ₁₆ H ₁₄ N ₂ O
HL ₂	280 (284)	67.51 (67.6)	4.45 (4.57)	9.82 (9.85)	5.61 (5.63)	140°C	15	-	Dark yellow	80%	C ₁₆ H ₁₃ N ₂ OCl
HL ₃	292 (295)	65.0 (65.08)	4.35 (4.40)	14.21 (14.23)	16.22 (16.27)	135°C	11	-	Yellow	75%	C ₁₆ H ₁₃ N ₄ O ₃
L ₁ -Cu ⁺²	554 (556)	68.9 (69.06)	4.65 (4.67)	10.0 (10.07)	5.72 (5.75)	150°C	20	1.98	Dark Brown	70%	C ₁₆ H ₁₃ N ₂ O ₂ Cu
L ₁ -Ni ⁺²	552 (554)	69.28 (69.31)	4.67 (4.69)	10.0 (10.10)	5.70 (5.72)	160°C	24	2.98	Brownish black	65%	C ₁₆ H ₁₃ N ₂ ONi
L ₁ -Co ⁺²	550 (552)	69.54 (69.56)	4.7 (4.71)	10.11 (10.14)	5.77 (5.79)	170°C	26	4.98	Black	73%	C ₁₆ H ₁₃ N ₂ OCo
L ₁ -Mn ⁺²	546 (548)	69.98 (70.07)	4.72 (4.74)	10.18 (10.21)	5.81 (5.83)	175°C	32	5.25	Dark black	80%	C ₁₆ H ₁₃ N ₂ OMn
L ₂ -Cu ⁺²	620 (624)	61.51 (61.53)	3.80 (3.84)	8.92 (8.97)	5.11 (5.12)	145°C	22	1.88	Dark Brown	78%	C ₁₆ H ₁₂ N ₂ OCICu
L ₂ -Ni ⁺²	621 (622)	61.88 (61.93)	3.84 (3.87)	9.0 (9.03)	5.13 (5.16)	165°C	25	3.01	Brownish black	84%	C ₁₆ H ₁₂ N ₂ OCINi
L ₂ -Co ⁺²	618 (620)	62.11 (62.13)	3.85 (3.88)	9.01 (9.06)	5.13 (5.17)	173°C	28	5.01	Black	88%	C ₁₆ H ₁₂ N ₂ OCICo
L ₂ -Mn ⁺²	613 (616)	62.52 (62.54)	3.85 (3.90)	9.08 (9.12)	5.16 (5.21)	180°C	31	5.52	Dark black	72%	C ₁₆ H ₁₂ N ₂ OCIMn
L ₃ -Cu ⁺²	652 (656)	59.41 (59.44)	3.69 (3.71)	12.98 (13.0)	14.84 (14.86)	147°C	21	2.01	Dark Brown	67%	C ₁₆ H ₁₂ N ₄ O ₃ Cu
L ₃ -Ni ⁺²	651 (654)	59.59 (59.62)	3.68 (3.72)	13.0 (13.04)	14.88 (14.90)	186°C	27	3.15	Brownish black	72%	C ₁₆ H ₁₂ N ₄ O ₃ Ni
L ₃ -Co ⁺²	650 (652)	59.79 (59.81)	3.71 (3.73)	13.02 (13.08)	14.92 (14.95)	190°C	33	4.87	Black	82%	C ₁₆ H ₁₂ N ₄ O ₃ Co
L ₃ -Mn ⁺²	646 (648)	60.11 (60.18)	3.73 (3.76)	13.14 (13.16)	15.0 (15.04)	200°C	38	5.3	Dark black	66%	C ₁₆ H ₁₂ N ₄ O ₃ Mn

Compounds	I.R. spectra cm ⁻¹			¹ H.N.M.R. spectra ppm		U.V. spectra nm	
	v(C=N)	v(M-N)	v(C-O-C)	δ(Ar-H)	δ(HC=N)	(-C=C-)	(-C=N)
HL ₁	1623, 1613	-	1202	7.2	7.68	250	300
HL ₂	1612, 1605	-	1207	7.0	7.61	240	295
HL ₃	1608, 1603	-	1210	7.5	7.54	245	310
L ₁ -Cu ⁺²	1588, 1593	450	1220	6.8	7.58	250	355
L ₁ -Ni ⁺²	1580, 1577	447	1225	6.85	7.45	250	350
L ₁ -Co ⁺²	1572, 1568	443	1224	6.75	7.32	250	345
L ₁ -Mn ⁺²	1565, 1562	462	1229	6.60	7.28	250	340
L ₂ -Cu ⁺²	1594, 1588	455	1230	6.65	7.22	240	365
L ₂ -Ni ⁺²	1586, 1583	463	1217	6.72	7.18	240	360
L ₂ -Co ⁺²	1576, 1572	470	1227	6.68	7.08	240	358
L ₂ -Mn ⁺²	1570, 1566	478	1232	6.57	7.99	240	344
L ₃ -Cu ⁺²	1604, 1600	465	1214	6.52	7.47	245	372
L ₃ -Ni ⁺²	1600, 1595	472	1234	6.97	7.39	245	366
L ₃ -Co ⁺²	1590, 1580	481	1225	6.86	7.26	245	350
L ₃ -Mn ⁺²	1584, 1577	486	1221	6.67	7.18	245	348

Table-3: Thermodynamic function for the dissociation of ligand in ethanol-water (50vol %) mixtures and 0.1 M- NaCl at different temperature

T/K	p(dissociation Constant) pKa	(Gibbs Energy Change)i KJmol ⁻¹	(Ehthalpy Change)i KJmol ⁻¹	[-Entropy Change]i Jmol ⁻¹ K ⁻¹
298	7.54	43.22		61.51
308	7.40	43.63	24.89	60.84
318	7.28	44.32		61.11

Table-4: Stepwise Stability Constants for ML Complexes of L in ethanol-water (50vol %) mixtures and 0.1 M- NaCl at different temperature

M ⁿ⁺	298K		308K		318K	
	Log(K ₁)	Log (K ₂)	Log(K ₁)	Log (K ₂)	Log(K ₁)	Log (K ₂)
Mn ⁺²	6.5	3.53	6.6	3.61	6.72	3.74
Co ⁺²	6.1	3.6	6.2	3.7	6.29	3.8
Ni ⁺²	7.1	3.85	7.15	4.01	7.25	4.12
Cu ⁺²	7.2	4.0	7.25	4.1	7.32	4.19

Table-5: Thermodynamic Functions for ML Complexes of L in ethanol-water (50vol. %) mixtures and 0.1 M-NaCl at different temperature

M ⁿ⁺	T/K	(-Gibbs Energy Change) _i KJmol ⁻¹		(Enthalpy Change) _i KJmol ⁻¹		(Entropy Change) _i Jmol ⁻¹ K ⁻¹	
		1	2	1	2	1	2
Mn ⁺²	298	37.08	20.14			161.34	135.03
	308	38.92	21.28	11.48	18.18	162.07	134.35
	318	40.91	22.77			163.23	134.81
Co ⁺²	298	34.17	19.93			177.78	133.15
	308	34.8	20.54	14.36	25.84	177.72	132.95
	318	36.56	21.81			177.57	132.92
Ni ⁺²	298	38.29	23.13			184.12	160.40
	308	40.51	21.96	18.18	19.14	183.5	160.64
	318	42.16	23.64			183.96	160.12
Cu ⁺²	298	44.14	25.08			198.85	137.58
	308	42.78	24.17	11.00	20.10	197.82	137.5
	318	44.56	25.51			197.29	137.38

The mixture was refluxed for 1hr and cooled at room temperature. On cooling, precipitates of metal complexes were formed, which were filtered from Buckner funnel, washed with ethanol and dried. Recrystallization in aqueous ethanol (30:70) gave the pure metal complexes. The analytical data of ligands and their metal complexes are given in table-1. (Scheme-2)

2.4 Potentiometric studies-

Metal ion solutions ($C = 0.0002 \text{ moldm}^{-3}$) were prepared from analar metal chlorides in bidistilled water and were standardized with EDTA. The ligand solution ($C = 0.001 \text{ moldm}^{-3}$) was prepared by dissolving the accurate mass of the solid in ethanol (Analar). Solutions of 0.001M HCl and 1M NaCl were also prepared in double distilled water. A carbonate free sodium hydroxide in ethanol-water mixture (30vol %) was used to titrate and standardized against oxalic acid (Analar).

The following mixtures (i-iii) were prepared and titrated potentiometrically at different temperatures 298K, 308K and 318K against standard 0.004M NaOH in ethanol-water mixture (50vol%): -

- (i) 5cm^3 0.001M HCl + 5cm^3 1M NaCl + 20cm^3 ethanol
- (ii) 5cm^3 0.001M- HCl + 5cm^3 1M NaCl + 5cm^3 0.001M- ligand + 15cm^3 ethanol.
- (iii) 5cm^3 0.001M-HCl + 5cm^3 1M NaCl + 15cm^3 ethanol + 5cm^3 0.001M- ligand + 5cm^3 0.0002M- Metal salt.

For each mixture, the volume was made up to 50cm^3 with double distilled water before the titration. The pH measurements were carried out using Equiptronics- 610 pH meter accurate to ± 0.01 units. The pH meter readings in ethanol- water (50vol. %) are corrected according to Van-Uitert and Hass relation [15].

RESULTS AND DISCUSSION

3.1 Characterization of ligand and their metal complexes

Structure of ligands and their metal complexes were established by microanalytical and spectral methods like $^1\text{H NMR}$, UV, IR, Mass and ESR, which confirm the structure which is nearly same as reported earlier [16-20].

3.2 Stability constant

The average number of the protons associated with the ligand molecule L, η_A , was determined at different pH values applying the following equation.

$$\bar{\eta}_A = y + \frac{(V_2 - V_1)(N^0 + E^0)}{(V^0 + V_1)(T_{CL^0})}$$

Where Y is the number of available protons in L (Y=1) and V_1 and V_2 are the volumes of alkali required to reach the same pH on the titration curve of hydrochloric acid and organic ligand respectively. V^0 is the initial volume (50cm^3) of the mixture; N^0 is the concentration of sodium hydroxide solution and C_{L^0} is the initial concentration of free acid. The titration curves (η_A vs. pH) for the proton- ligand systems were constructed and found to extend between 0 and 1 on the η_A scale. This means that L has one ionisable proton. It can be seen that for same volume of NaOH added the ligand titration curves had a lower pH value than the acid titration curve. The displacement of a ligand titration curve along the volume axis with respect to the acid titration curve is an indication of proton dissociation. The proton-ligand stability constants were calculated using the method of Irving and Rossoti [21]. The data obtained are listed in table-3.

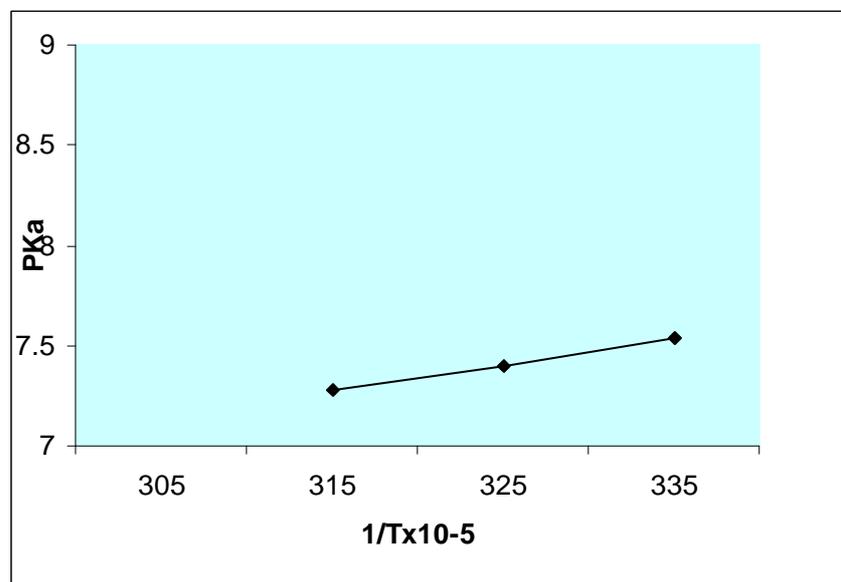


FIG-1 Vant Hoff Plot pKa of Schiff base HL₁ against 1/T

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ions (η) vs. the free ligand exponent (p_L), according to Irving and Rosotti [22]. The average number of the reagent molecules attached per metal ion, η and free ligand exponent, p_L , can be calculated using the equations.

$$\bar{\eta} = \frac{(V_3 - V_2)(N^0 + E^0)}{(V^0 + V_2)(T_{CM^0})(\bar{\eta}_A)}$$

$$\text{And } P_{L=} \log_{10} \frac{\sum \beta_n^H (1/\text{antilog } p^H)^n}{C_{L-}^0 - \eta C_M^0} \cdot \frac{V^0 + V_3}{V^0}$$

Where C_M^0 is the total concentration of the metal ions present in the solution, β_n^H is the overall proton-reagent stability constant. V_1, V_2, V_3 are the volumes of alkali required to reach the same pH on the titration curves of hydrochloric acid, organic ligand and complex, respectively.

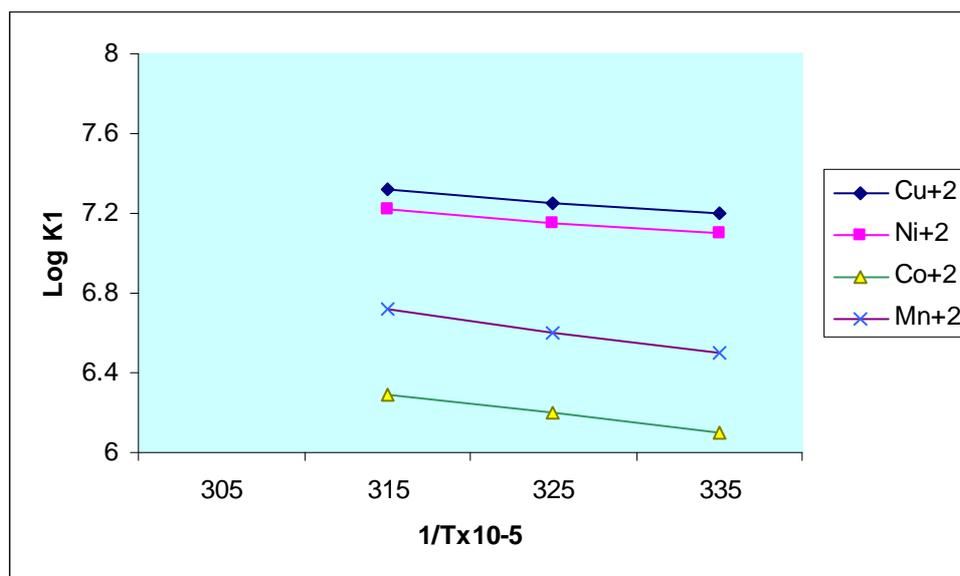


FIG-2 Van't off plot of log {K₁} of M⁺² complexes with HL₁ against 1/T

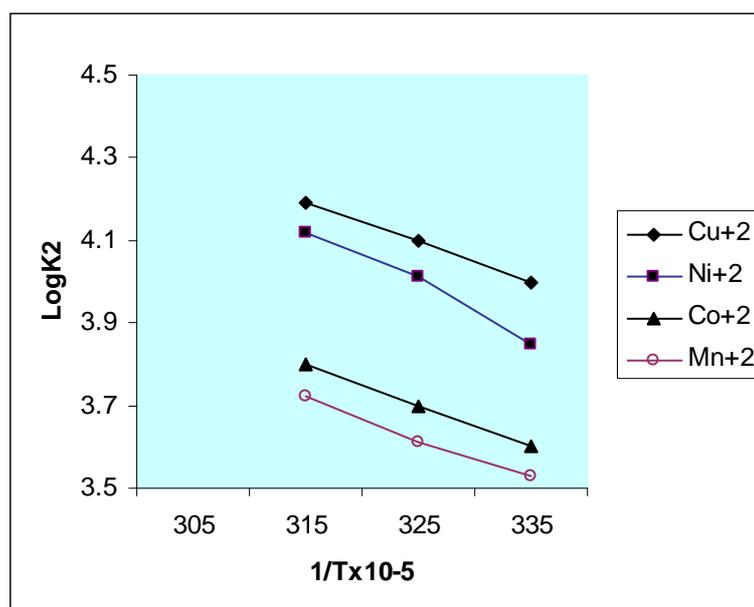


FIG-3 Van't Hoff plot of log {K₂} of M⁺² complexes with HL₁ against 1/T.

These curves were analyzed and the successive stability constants were determined using different computational methods [23]. The values of the stability constants (log {K₁} and log {K₂}) are given in table 4.

The following general remarks can be made:-

- (i) The maximum value of η was 2 indicating the formation of 1:2 (n [metal]: n [ligand]) complexes only.
- (ii) The metal ion solution used in the present study was very dilute ($2 \times 10^{-5} \text{ mol dm}^{-3}$), hence there was no possibility of formation of polynuclear complexes [24].
- (iii) The titration curve of the metal ion complexes were displaced to the right hand side of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion and ligand. The large decrease in pH for the metal ion complexes titration curves relative to ligand titration curves points to the formation of strong metal ion complexes [25].
- (iv) In most cases, the colour of the solution after complex formation was found to be different from the colour of the ligand at the same pH.
- (v) For the same ligand at constant temperature, the stability of the chelates increases in the order Mn^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} [26]. This can be attributed to the decrease of charge on the central metal ion which decreases the electronic attraction between the cation and the ligand.

The dissociation constants (pK_a) for L, as well as the stability constants of its complexes with Mn^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} have been evaluated at 298K, 308K and 318K. The enthalpy change (ΔH) for the dissociation and complexation process was calculated from the slope of the plot pK_a or $\log \{k\}$ vs. $1/T$ using the graphical representation of von't hoff equations (FIG-1).

$$2.303RT \log \{K\} = \Delta H - T\Delta S \quad (4)$$

Or

$$\log K = (-\Delta H/2.303R) (1/T) + (\Delta S + 2.303R) \quad (5)$$

From the Gibbs energy change (ΔG) and (ΔH) values one can deduce the entropy changes (ΔS) using the well known relationships.

$$\Delta G = -2.303 RT \log \{K\} \quad (6)$$

$$\Delta S = (\Delta H - \Delta G) / T \quad (7)$$

Where the gas constant $R = 8.314 \text{ JK}^{-1} \text{ Mol}^{-1}$, K is the dissociation constant for the ligand or the stability constant of the complexes, and T absolute temperature. All thermodynamic parameter of the dissociation process of M L are recorded in table 5.

From these result the following conclusions can be made.

- (i) The pK_a values decreases with increasing temperature revealing that their acidity increases with increasing temperature [27].
- (ii) A positive value of ΔH indicates that the process is endothermic.
- (iii) A large positive value of ΔG indicates that the dissociation process is not spontaneous [28].
- (iv) The dissociation process for L has negative values of ΔS due to the increased order as a result of solvation processes [29].

All the thermodynamic parameters of the stepwise stability constants of complexes are recorded in table 5. It is known that the metal ions exist in solution as octahedral hydrated species [30] Examination of these values showed that:

- (i) The stepwise stability constants ($\log \{K_1\}$ and $\log \{K_2\}$) (FIG-2,3) for ligand complexes decrease with increasing temperature.
- (ii) The negative value of ΔG for the complexation process suggests that spontaneous nature of such process [31].
- (iii) The ΔH values are negative, meaning that these processes are exothermic and favorable at lower temperature.

(iv) The ΔS values for the ligand complexes are positive confirming that the complex formation is entropically favorable [32].

CONCLUSION

The dissociation process is non-spontaneous, exothermic and entropically unfavorable while the complexation process is spontaneous, exothermic and entropically favorable.

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