Potentiometric and Thermodynamic studies of p-nitro benzaldehyde and o-amino phenol and its metal complexes

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INTRODUCTION

The dissociation constants of Schiff base (derived from p-nitro benzaldehyde and o-amino phenol) and metal-ligand stability constants of its complexes with some transition metal ions have been determined potentiometricaly 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 (ΔG, ΔH, ΔS) 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 p-nitro benzaldehyde and o-amino phenol) complexes with bivalent metals like Cu^{+2}, Ni^{+2}, Co^{+2}, Cu^{+2}.

EXPERIMENTAL

Chemicals and solvents used were dried and purified by standard methods and moisture was excluded from the glass apparatus using $CaCl_2$ drying tubes.

The Schiff base (fig 1) was prepared by the condensation of p- nitro benzaldehyde and o-amino phenol in 1:1 ratio in ethanolic medium. After condensation solid precipitate was formed then it was washed by ethanol for several times, then it was recrystallised by hot ethanol. Then it was dried and weighed.

The purity of ligand was checked by thin layer chromatography and elemental analysis:
(Found):-   66.64%C,   4.392%H, 12.30%N
(Calculated):-   66.18%C,   4.372%H, 12.38%N

The IR spectrum was recorded using KBr discs (400-4000cm^{-1}). A strong band at 1596cm^{-1} due to -C=N bond, which is shifted to lower wave number in the spectra of metal complexes due to formation of a co-ordinate link between nitrogen and

metal, like the band appear at 1576cm^{-1} due to L-Cu[+2] complex and bands appear at 1562cm^{-1}, 1555cm^{-1}, 1542cm^{-1} due to L-Ni[+2], L-Co[+2], L-Mn[+2] complexes respectively. The band corresponding to the υ (OH) appears at 3373.4cm^{-1}. A band corresponding to the υ (aromatic-CH) appears at above 3000cm^{-1}.

The ^{1}HNMR spectra were recorded in DMSO solution using TMS as internal standard. The Schiff base show the –OH proton signal at 13.04 ppm which is absent in the spectra of the corresponding metal complexes. The –C=NH (azomethine) proton appear at 8.89ppm, which is shifted to the downfield in the spectra of complexes due to formation of co-ordinate bond with metals, like the signals appear at 8.72ppm, 8.52ppm, 8.46ppm, 8.32ppm due to L-Ni[+2], L-Co[+2], L-Mn[+2] and L-Cu[+2] complexes respectively. The signal at 8.40-7.32 ppm appears due to aromatic –CH proton of ligand.

Potentiometric studies

Metal ion solutions (C = 0.0002 moldm[-3]) were prepared from analar metal chlorides in bidistilled water and were standardized with EDTA (13). The ligand solution (C =0.001moldm[-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 bidistilled water. A carbonate free sodium hydroxide in ethanol-water mixture (30vol %) was used as titrant and standardized against oxalic acid (Analar).

The apparatus, general conditions, and methods of calculations were the same as in the previous work[14].

The following mixtures (I-III) were prepared and titrated potentiometricallly at 298K against standard 0.004M NaOH in ethanol-water mixture (30vol.%).
- 5cm[3] 0.001M HCl +5cm[3] 1M NaCl +20cm[3] ethanol
- 5cm[3] 0.001M- HCl + 5cm[3] 1M NaCl + 5cm3 0.001M- ligand +15cm[3] ethanol.
- 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 bidistilled 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].

RESULT AND DISCUSSION

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-

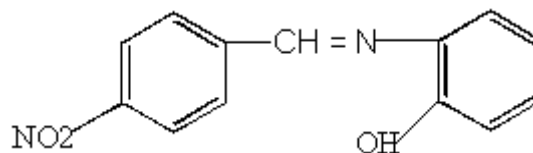$$\eta_A = Y + \frac{(V_1-V_2)(N+E^0)}{(V_0+V_1)C^0_L} \qquad ...(1)$$

Fig. 1: Structure of ligand

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 reagent, respectively. V[0] is the initial volume (50cm[3]) of the mixture, C[0]$_L$ is the total concentration of the reagent, N[0] is the concentration of sodium hydroxide solution and E[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 protons (the hydrogen ion of the –OH group) in the o-amino phenol moiety of the ligand. 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[16]. The data obtained are listed in table 1.

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 (pL), according to Irving and Rosotti[17].

The average number of the reagent molecules attached per metal ion, ç and free ligand exponent, P_L, can be calculated using the equations.

$$\eta = \frac{(V_3 - V_2)(N + E^0)}{(V^0 + V_2)\eta_A C^0} \qquad ...(2)$$

and

$$P_L = \log_{10} \frac{\Sigma \beta_n^H (1/\text{antilog } p^H)^n}{C_L^0 - \eta \ C_M^0} \cdot \frac{V^0 + V_3}{V^0} \quad ..(3)$$

Where C^0_M 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. These curves were analyzed and the successive stability constants were determined using different computational methods [18]. The values of the stability constants (log {k_1} and log {k_2}) are given in table 2.

The following general remarks can be made.

˘ The maximum value of η was 1 indicating the formation of 1:1 (n [metal]: n [ligand]) complexes only.

˘ The metal ion solution used in the present study was very dilute (2×10^{-5} mol dm^{-3}), hence there was no possibility of formation of polynuclear complexes[19].

˘ 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[20].

˘ In most cases, the colour of the solution after

Table 1: Thermodynamic function for the dissociation of ligand in ethanol-water (30vol. %) mixtures and 0.1 M- NaCl at different temperature

T/K	p(dissociation Constant) pKa	(Gibbs Energy Change) KJmol^{-1}	(Ehthalpy Change) KJmol^{-1}	[-Entropy Change]i Jmol^{-1}K^{-1}
298	7.72	44.04		45.10
308	7.52	44.34	30.63	44.61
318	7.40	45.05		45.44

Table 2: Stepwise Stability Constants for ML Complexes of L in ethanol-water (30vol %) mixtures and 0.1 M- NaCl at different temperature

M^{n+}	298K		308 K		318 K	
	Log(K$_1$)	Log (K$_2$)	Log(K$_1$)	Log (K$_2$)	Log(K$_1$)	Log (K$_2$)
Mn^{+2}	6.88	2.98	6.98	3.15	7.18	3.25
Co^{+2}	6.97	3.10	7.15	3.25	7.30	3.38
Ni^{+2}	7.28	3.26	7.47	3.48	7.46	3.55
Cu^{+2}	7.48	3.58	7.67	3.68	7.81	3.78

complex formation was found to be different from the colour of the ligand at the same pH.

For the same ligand at constant temperature, the stability of the chelates increases in the order Mn^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2} (21). 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 (pka) 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, and are given in table 1 and 2. The enthalpy change (ΔH) for the dissociation and complexation process was calculated from the slope of the plot pka or log {k} vs. 1/ (T) (Fig. 2-4) using the graphical representation of von't hoff equations.

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

Or

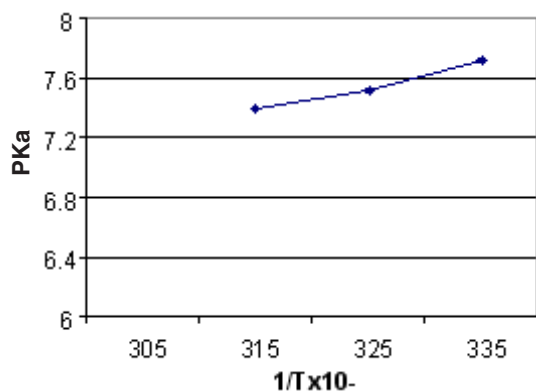$$\text{Log } K = (\text{-}\Delta H/2.303R)(1/T) + (\Delta S+2.303R) \quad ...(5)$$

Fig. 2: Vant Hoff Plot pKa of Schiff base NBAP against 1/T

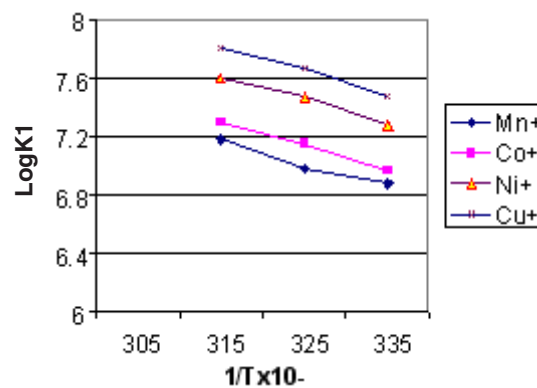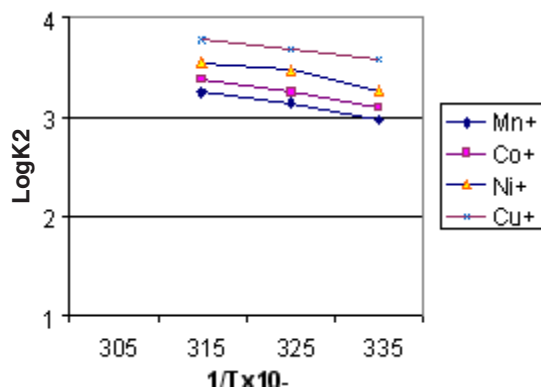**Fig. 3: Vant Hoff plot of log {K₁} of M⁺ⁿ complexes with NBAP against 1/T**

Fig. 4: Van't Hoff plot of log {K₂} of M⁺ⁿ complexes with NBAP against 1/T.

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

$$\Delta G= \text{-}2.303\,RT \log \{K\} \quad ...(6)$$
$$\Delta S= (\Delta H - \Delta G)/T \quad ...(7)$$

Where the gas constant R= 8.314JK⁻¹ 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 L are recorded in table 1. From these result the following conclusions can be made.

˘   The pka values decreases with increasing

temperature revealing that their acidity increases with increasing temperature[22].

ˇ   A positive value of ΔH indicates that the process is endothermic.

ˇ   A large positive value of ΔG indicates that the dissociation process is not spontaneous[23].

ˇ   The dissociation process for L has negative values of ΔS due to the increased order as a result of salvation processes[24].

All the thermodynamic parameters of the stepwise stability constants of complexes are recorded in table 3. It is known that the metal ions exist in solution as octahedrally hydrated species[25] and the obtained values of ΔH and ΔS can then be considered as the sum of two contributions.

ˆ   Release of H_2O molecules and
ˆ   Metal- ligand bond formation.

Examination of these values showed that.

ˆ   The stepwise stability constants (log $\{K_1\}$ and log $\{K_2\}$) for ligand complexes decrease with increasing temperature.

ˆ   The negative value of ΔG for the complexation process suggests that spontaneous nature of such process[26].

ˆ   The ΔH values are negative, meaning that these processes are exothermic and favourable at lower temperature.

(4) The ΔS values for the ligand complexes are positive confirming that the complex formation is entropically favourable[27].

Table 3: Thermodynamic functions for ml complexes of l in ethanol-water (30vol %) mixtures and 0.1 m- nacl at different temperature

M^{n+}	T/K	(Gibbs Energy Change)i $KJmol^{-1}$		(Ehthalpy Change)i $KJmol^{-1}$		[-Entropy Change)i $Jmol^{-1}K^{-1}$	
		1	2	1	2	1	2
Mn^{+2}	298	39.25	17.00			228.08	143.75
	308	41.16	18.57	28.72	25.84	226.88	144.18
	318	43.71	19.78			227.76	143.75
Co^{+2}	298	39.76	17.68			239.42	149.26
	308	42.16	19.16	31.59	26.80	239.44	149.22
	318	44.44	20.57			239.08	148.96
Ni^{+2}	298	41.53	18.60			242.14	155.57
	308	44.05	20.52	30.63	27.76	242.46	156.75
	318	46.27	21.61			241.82	155.25
Cu^{+2}	298	42.67	20.42			249.19	164.89
	308	45.23	21.70	31.59	28.72	249.41	163.70
	318	47.55	23.01			248.86	162.67

CONCLUSION

The dissociation process is non-spontaneous, exothermic and entropically unfavourable while the complexation process is spontaneous, exothermic and entropically favourable.

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