Effect of Added Salt on Stability of 2,3-Dibromo-1-(5-chloro-2-hydroxy-phenyl)-3-phenyl-propan-1-one and Its Ni(II) Complex at 28 ºC

S.D. Deosarkar

Department of Chemistry, S.F.S. College, Nagpur-440 006, India
E-mail: sandeo24@yahoo.co.in

The proton-ligand stability constant of ligand (2,3-dibromo-1-(5-chloro-2-hydroxyphenyl)-3-phenyl-propan-1-one) and metal-ligand stability constants with Ni(II) metal ions were investigated in the presence of 0.02, 0.04, 0.06, 0.08 and 0.1 mol L^{-1} KNO_3 pH metrically at 28 ºC. The formations of binary 1:1, 1:2 ligand-Ni(II) complexes were reported. The data obtained was utilized to estimate the thermodynamic stability constants (pK^o and log K^o) for ligand and its complex with Ni(II) ions at zero ionic strength to know the exact nature of the complexation equilibria. The different possible reactions and expected values of ΔZ^2 for corresponding dissociation or association equilibria are determined.

Key Words: Ionic strength, Stability constants, Brønsted equation, Salt effect.

INTRODUCTION

In view of the analytical applications, it is interesting to know the effect of addition of an electrolyte on complex equilibria. Agarwal and Narwade[1] have studied influence of ionic strength of the medium on complex equilibria; El-Roudi and Latif[2] studied the effect of ionic strength on stabilities of N-[*tris*(hydroxymethyl)methyl] glycine and its metal complexes. Das and Chattopadhyay[3] have studied the effect of buffers and ionic strength on the stability constant of complexes of iron(III) with salicylic acid and its derivatives, Sondawale and Narwade[4], Meshram *et al.*[5] and Patil and Narwade[6] have studied the influence of ionic strength of the medium on complex equilibria.

Present work deals with the study of effect of ionic strength of the medium on pK value of 2,3-dibromo-1-(5-chloro-2-hydroxyphenyl)-3-phenyl-propan-1-one and log K value of its complex with Ni(II) metal ions by pH-metric titration technique and hence to study the primary kinetic salt effect. Literature survey reveals that log K *versus* $\sqrt{\mu}$ plots are generally linear up to 0.1 M ionic strength[7].

EXPERIMENTAL

All reagents were of analytic grade. Metal ion solution (c = 0.0004 mol dm^{-3}) was prepared from nickel(II) nitrate in doubly distilled water and standardized with EDTA. The ligand was prepared by proposed methods[5,6]. The ligand solution (c =

0.002 mol dm^{-3}) was prepared by dissolving the exact mass of the solid in solvent. Solution of 0.01 M HCl and 1 M KNO$_3$ were also prepared in doubly distilled water. A carbonate free sodium hydroxide solution in dioxane-water was used as titrant and standardized against oxalic acid (AnalaR). All the glassware's used in present experiment was of Pyrex quality.

Measurements: Potentiometric titrations were carried out in 70 % dioxane-water mixtures by using a digital ELICO-LI-10 pH meter (accuracy ± 0.05 units) with a combined Glass and Calomel electrode assembly. The electrode system was calibrated with buffer solutions at pH 4.00 and 9.2. The experimental procedure involved the potentiometric titrations of the solutions of (a) 5 mL 0.01 M HCl solution (b) 5 mL 0.01 M HCl and 10 mL 0.002 M ligand solution and (c) 5 mL 0.01 M HCl, 10 mL 0.002 M ligand solution and 5 mL 0.0004 M metal ion solution. The total volume of each mixture was adjusted to 100 mL by 70 % dioxane-water mixture and each of the mixture was titrated with NaOH solution. An appropriate correction was made to the glass electrode for non-aqueous-aqueous mixtures by using method of Van-Uitert and Fernelius[8].

The ionic strength of solutions was maintained constant by the addition of appropriation amount of 1.0 M KNO$_3$ stock solution. All of the potentiometric titrations were performed over the pH range 2.0-11.0.

Calculations: The number of proton associated with compound at different pH values $\bar{n}_A$ were calculated from the titration curves of the acid in absence and presence of a ligand by using following eqn. 1:

$$\bar{n}_A = \gamma + \frac{(E^o + N)(V_1 - V_2)}{(V^o + V_1) \cdot T^o_L} \tag{1}$$

where, γ is total proton number associated with the original ligand, V_1 and V_2 are the volumes of alkali required to reach the same pH on the titration curves of hydrochloric acid and organic ligand, respectively, V^o is initial volume of the acid and ligand solution, N is the normality of NaOH solution, E^o initial free acid concentration and T^o_L is total initial concentration of the ligand.

The proton-ligand formation number, $\bar{n}_A$ at various pH for the ligand was determined and the formation curves ($\bar{n}_A$ *vs.* pH) for the proton-ligand systems were constructed and are found to extend between 0 and 1 in the $\bar{n}_A$ scale. This means that ligand have one dissociable proton from the hydroxyl group. The value of pKa was read directly from $\bar{n}_A = f$ (pH) graph at $\bar{n}_A = 0.5$. The average number of ligands attached per metal ions $\bar{n}$ was calculated by using the eqn. 2:

$$\bar{n} = \frac{(E^o + N)(V_3 - V_2)}{(V^o + V_2) \cdot \bar{n}_A T_M^o} \tag{2}$$

where, V_2 and V_3 are the volumes of alkali required to reach the same pH on the titration curves organic ligand and complex, respectively and T^o_M is the total concentration of the metal ions present in the solution. The value of inverse of logarithm of free ligand concentrations (pL), were calculated by using following eqn. 3:

$$pL = \log_{10} \frac{1 + K_1^H[H] + K_1^H K_2^H[H]^2}{\{T^o_L - \bar{n}T^o_M\}} \times \frac{(V^o + V_3)}{V^o} \qquad (3)$$

The corresponding values of $\bar{n}$ and pL, the formation curve of the metal-ligand system is drawn according to Irving and Rossotti method and the stability constant is read directly at $\bar{n}$ = 0.5, 1.5. All calculations were done using excel program on a personal computer.

RESULTS AND DISCUSSION

It can be seen that for the same volume of NaOH solution 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 (x-axis) with respect to the acid titration curve is an indication of proton dissociation.

The metal ion solution used in the present study was very dilute (4×10^{-4} M), hence there was no possibility of formation of polynuclear complexes[9]. The maximum value of $\bar{n}$ was ≈ 2 indicating the formation of 1:1 and 1:2 (n (metal):n (ligand)) complexes only. The metal titration curves 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 with the ligand.

The large decrease in pH for the metal titration curves relative to ligand titration curves points to the formation of strong metal complexes[10]. The colour of the solution after complex formation was observed to be different from the colour of the ligand at the same pH.

When studied at different ionic strength of the solution, the proton-ligand and Ni(II)-ligand stability constants found to decrease with increase in ionic strength at 28 ºC as shown in Table-1. This decrease in pK and log K values may be due to the opposite charges on the reacting species. According to Bronsted equation, if the charges of reacting species are opposite then there is a decrease in the reaction rate with increasing ionic strength whereas if the charges are identical, an increase in the reaction rate will occur.

TABLE-1
pK AND log K VALUES AT DIFFERENT IONIC STRENGTH

μ	√μ	Ligand and Ni(II) complex of ligand		
		pK	log K$_1$	log K$_2$
0.02	0.1414	6.42	5.93	4.80
0.04	0.2000	6.32	5.83	4.69
0.06	0.2449	6.25	5.74	4.61
0.08	0.2888	6.17	5.68	4.52
0.10	0.3162	6.10	5.60	4.45

The data of pK and log K values were employed to calculate the thermodynamic stability constants with the help of Brønsted eqns. 4 and 5:

$$pK = pK^o + A \times \Delta Z^2 \cdot \sqrt{\mu} \tag{4}$$

$$\log K = \log K^o + A \times \Delta Z^2 \cdot \sqrt{\mu} \tag{5}$$

where, ΔZ^2 is difference between square of charges of product and reactant ions. The plots of pK and log K *versus* $\sqrt{\mu}$ gave straight line over the entire range of ionic strength which means, Brønsted relationship is valid for dissociation equilibria.

The values of ΔZ^2 were calculated from the slopes of the straight lines and are presented in Table-2. The value of A was taken equal to 0.5161[7]. The thermodynamic stability constants at zero ionic strength obtained from various plots are listed in Table-3.

TABLE-2
ΔZ^2 FROM PLOTS OF pK OR log K *vs.* $\sqrt{\mu}$

System	Constant	Reaction equilibria	Observed ΔZ^2
Ligand	pK	$HL = H^+ + L^-$	-3.4622
Ni(II) complex of ligand	$\log K_1$	$Ni^{2+} + HL = NiL^+ + H^+$	-3.5529
	$\log K_2$	$NiL^+ + HL = NiL_2 + H^+$	-3.8202

TABLE-3
THERMODYNAMIC STABILITY CONSTANT

System	Plots	pK^o	$\log K^o$
Ligand + Ni(II) complex	pK *vs.* $\sqrt{\mu}$	6.6778	–
	$\log K_1$ *vs.* $\sqrt{\mu}$	–	6.1929
	$\log K_2$ *vs.* $\sqrt{\mu}$	–	5.0838

It can be seen from Table-2 that, the observed ΔZ^2 values, in all the cases are different than expected. These values do not therefore give conclusive evidence regarding the magnitude of charge of the reacting species except the information that these are oppositely charged.

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