Influence of ionic strength of medium on stability constants of Cu(II) complex of 2-amino-5-chloro benzene sulphonic acid at 301K

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ABSTRACT

The proton-ligand stability constants and metal-ligand stability constants of 2-Amino-5-Chloro Benzene Sulphonic Acid and its complexes with Cu (II) metal ions were investigated at different ionic strengths pH-metrically and the data were utilized to estimate the thermodynamic stability constants at zero ionic strength and 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, Bronsted equation, salt effect.

In view of analytical applications, it was an interest to know the effect of addition of an electrolyte on complex equilibria. 2-Amino-5-Chloro Benzene Sulphonic Acids act as strong chelating agent. Narwade and Agrawal[1], A. Gupta[2] and Fazlur Rahman et al[3] have studied the influence ionic strength of the medium on complex equilibria. V. Sood et al[4] have also obtained the stability constants of Zn (II), Cd (II), Hg (II) complexes with salicyloyl urea at various strengths in 80% water-methanol mixture. Newton and Arcand[5] have used a similar formula for the study of complex formed between Ce (III) and sulphate ions.

The present work deals with the study of effect of ionic strength of the medium on pK and log K values of complexes of 2-Amino-5-Chloro Benzene Sulphonic Acid with Cu (II) metal ions at 301K by Calvin-Bjerrum pH-metric titration technique and hence to study the primary kinetic salt effect. For this purpose values of pK and logK are plotted against $\sqrt{\mu}$. Literature survey reveals that logK versus $\sqrt{\mu}$ plots are generally linier up to 0.1 M ionic strength[6].

Concentrations of metal nitrates were determined by standard method. The pH meter has a built in internal electronic voltage stabilizer for ± 10% fluctuations in voltage supply with temperature compensator covering the range 0-100°C. The instrument could read pH in the range 0-14.0 in the steps 0.01. All the solutions were prepared in double distilled water and the solutions of ligand was always used a fresh in present investigation. The pH measurements were carried out with ELICO-L1-10 (accuracy ±0.05 units) using combined electrode. All chemicals used were of AR grade. All the glassware used in these experiments was of Pyrex quality. Concentrations of metal nitrate and nitric acid taken were fixed. The system has been studied at 0.02M, 0.04M, 0.06M, 0.08M, 0.1M ionic strength by varying the concentrations of KNO_3. In addition to KNO_3, the titrating system contained ions from nitric acid, metal nitrate and sodium hydroxide. Total ionic strength of the medium is calculated by-

$$\mu = \frac{1}{2} \Sigma C_i \cdot Z_i^2 \qquad ...(1)$$

In the present investigation it is observed that pK and logK values decrease with increase in ionic strength. The data of pK and logK values is employed to calculate the thermodynamic constants with the help of Bronsted equation-

$$pK = pK^0 - A\Delta Z^2 \sqrt{\mu} \qquad ...(2)$$

$$\log K = \log K^0 + A\Delta Z^2 \cdot \sqrt{\mu} \qquad ...(3)$$

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

equilibria. The values of ΔZ^2 were calculated from the slopes of the straight lines. The value of A was taken equal to 0.5161[7].

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. Narwade, Sathe[8] and Meshram[9] had also recorded same discrepancy. This discrepancy may be due to the fact that value for 'a' (closest distance approached) was fixed ($3.3A^0$).

Table 1: pK and logK values of 2A-5Cl-BSA at different ionic strength

μ	$\sqrt{\mu}$	$\sqrt{\mu}/(1+\sqrt{\mu})$	$\sqrt{\mu}/(1+\sqrt{\mu}) - 0.3\sqrt{\mu}$	pK	$logK_1$
0.02	0.1414	0.1238	0.0813	2.83	2.32
0.04	0.2000	0.1666	0.1066	2.76	2.23
0.06	0.2449	0.1967	0.1232	2.70	2.14
0.08	0.2888	0.2204	0.1355	2.65	2.06
0.10	0.3162	0.2402	0.1453	2.61	2.01

Table 2: ΔZ^2 from plots of pK or log K vs. $\sqrt{\mu}$

System	Const.	Reaction equilibria	ΔZ^2	
			Exp.	Obs.
2A-5Cl-BSA	pK	$HL \rightleftharpoons H^+ + L^-$	2.00	- 2.4243
Cu (II)- 2A-5Cl-BSA	$LogK_1$	$Cu^{2+} + HL \rightleftharpoons CuL^+ + H^+$	- 2.00	- 3.4798

Table 3: Thermodynamic stability constants of Cu (II)-2A-5Cl-BSA

Plots	pK^0	$logK_1^0$
pK vs. $\sqrt{\mu}$	3.0082	-
pK vs. $\sqrt{\mu}/(1+\sqrt{\mu})$	3.0708	-
pK vs. $(\sqrt{\mu}/(1+\sqrt{\mu})-0.3\sqrt{\mu})$	3.1181	-
$logK_1$ vs. $\sqrt{\mu}$	-	2.5799
$logK_1$ vs. $\sqrt{\mu}/(1+\sqrt{\mu})$	-	2.6688
$logK_1$ vs. $\sqrt{\mu}/(1+\sqrt{\mu}) -0.3\sqrt{\mu}$	-	2.7360

The thermodynamic stability constants at zero ionic strength obtained from various plots are listed in table 3. It can be observed that there is a good agreement of thermodynamic constants obtained from various plots for a particular system.

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