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Effect of ionic strength on stability constant of chelates of azoles in 70% DMF-Water system

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ABSTRACT

The stability constants of Cu (II), La (III) metal ions with substituted azoles has been studied by pH-metric technique at 0.1 M (KNO_3) ionic strength at 27 ± 0.1^{0}C in aqueous medium. Also the effect of ionic strength on stability constants of chelates of azoles in 70% DMF-Water system with pH-metric technique has been studied. The data obtained was used to study the correct mechanism of complexation, to determine thermodynamic properties and to study proton-ligand and metal-ligand stability constants.

Key words: Ionic strength, stability constants, chelates, azoles.

INTRODUCTION

Ionic strength is an electrical current produced by the ions of an inert salt in solution. It affects proton ligand stability constant (pK) and metal ligand stability constant (log K.) Recently the study of effect of ionic strength on stability constant by pH-metric method has now become of considerable interest. Narwade etal[1] have studied the stability constants of Th (IV) complexes with some substituted pyrozolines. Ali-Asgar et al.,[2] have investigated the metal ligand stability constants of Cu (II) complexes with some substituted isoxazolines at different ionic strengths. Agrawal et al.,[3] studied the stability constants of Co (II), Sr (II), Pr (II) complexes with substituted azoles at various ionic strength.

In the present paper, the interactions of Cu (II) and La (III) metal ions with 2- (4-amino – 5 – mercapto – [1, 2, 4] triazol – 3- yl) – phenol (AMTP) at various ionic strength in 70% DMF Water mixture medium have been investigated by Calvin Bjerrum pH-metric technique at 27 ± 0.1^{0}C.

EXPERIMENTAL

All the chemicals used were of AR grade. The solvents were purified by standard procedures[4]. The solute used in the present investigation were synthesized by standard methods[5, 6]. All the weightings were made on one pan digital balance (Adair Dutt-180) and the solutions ere made in doubly distilled water.

The pH-metric measurement were carried out by using Equiptronics digital pH-meter model EQ 610 with combined glass electrode with an accuracy of ± 0.01 of pH unit at 27 ± 0.1^{0}C. The pH-meter was standardized against 0.05 M potassium hydrogen phthalate solution in acid medium and 0.01 M borax solution in alkaline medium.

RESULTS AND DISCUSSION

In the present investigation the dependence of stability constants on the ionic strength of the medium was examined by taking

Table 1: Proton-ligand stability constant at various Ionic strength

Ionic strengthμ	μ	pK
0.04 M	0.2000	11.24
0.06 M	0.2449	10.95
0.08 M	0.2828	10.75
0.10 M	0.3162	10.50

fixed concentration of metal nitrates and nitric acid during pH-metric titrations. The system has been studied at 0.04 M, 0.06 M, 0.08 M and 0.1 M. ionic strengths by varying the concentration of potassium nitrate. The total ionic strength of the medium was calculated by following expression.

$$\mu = \frac{1}{2}\sum c_1 Z_1^2 \qquad ...(1)$$

Table 2: Log K_1 and log K_2 values of Cu (II)-AMTP complex at different Ionic strengths

Ionic strength μ	μ	pK	Log K_1	Log K_2
0.04 M	0.2000	11.24	10.94	7.02
0.06 M	0.2449	10.95	10.72	6.61
0.08 M	0.2828	10.75	10.14	6.38
0.10 M	0.3162	10.50	9.48	5.42

Table 3: Log K_1 and log K_2 values of La (II)-AMTP complex at different Ionic strengths

Ionic strength μ	μ	pK	Log K_1	Log K_2
0.04 M	0.2000	11.24	11.151	6.233
0.06 M	0.2449	10.95	10.891	6.094
0.08 M	0.2828	10.75	10.624	5.872
0.10 M	0.3162	10.50	10.323	5.525

Table 4: Thermodynamic Dissociation constant at zero Ionic strengths

Plots	pK°
pK Vs μ	12.49
pK Vs μ /1 + μ	12.88
pK V [μ /(1 + μ)] – 0.3 μ	13.24

The proton ligand stability constant (pK values) and metal ligand stability constant (log K values) has been obtained for ligand (AMTP) and Cu (II) – AMTP, La (III) – AMTP complexes.

The pK-values and log K values at various ionic strengths are presented in Table 1 to 3. It is observed from experimental data that an increase in the ionic strength of the system causes a decrease in pK and log K values.

The data of pK and log K values are employed to calculate the thermodynamic constants with the help of Bronsted equation[7].

$$\text{Log } K = \log K^\circ + A\ Z^2\ \mu \qquad ...(2)$$

$$pK = pK^\circ - A\ Z^2\ \mu \qquad ...(3)$$

Where Z^2 is the difference in the square of charges of product and reactant ion.

Newton Arcand[8] has used a similar formula for the study of complex formed between Ce (III) and sulphate ions.

The data obtained of pK and log K values were utilized to study thermodynamic dissociation constants at zero ionic strength presented in table 4 and to know the mechanism of complexation equillibria. The plots of pK /log K versus μ gave straight line over entire range of ionic strengths for the ligand which shows that Bronsted relation is valid for the dissociation equillibria. The value of Z^2 were calculated from the slops of the straight lines. The values of A was taken to be 0.5161[9].

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