

Influence of dielectric constant of medium on stability constants of 4-amino-3-naphthol-sulphonic acid and its complex with Cu (II) ions

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ABSTRACT

In the present investigation the influence of dielectric constant of the medium on complex equilibria have been studied by determining the pK and logK values of 4-amino-3-naphthol-sulphonic acid and its complex with Cu (II) metal ions in different percentage of ethanol-water mixtures at constant ionic strength ($\mu=0.01M$). The formation of 1:1 and 1:2 complex of 4-Amino-3-Naphthol-Sulphonic Acid with Cu (II) metal ion have been observed. The data obtained is used to know the exact nature of the electrostatic forces of attraction between metal ion and negatively charged ligand by calculating the $\Delta\log K$.

Key words: Dielectric constant, Stability constants. Cu (II) ions.

INTRODUCTION

Specific variations in relative strengths of acids and bases with changing solvents should be a function of the charge, the radius of the ion and the dielectric constants of the medium. The dielectric constant is one of the characteristics of liquid. The pK and logK values are strongly depend on the dielectric constant (D) of the medium because of the fact that at least one of the constituents is charged and other is either changed or has a dipole moment.

The dielectric constant of a medium is not solely responsible for the extent of dissociation; there is at least an additional factor of the chemical role of the solvent in most cases. It has been reported that an acid in solvents of similar dielectric constants exhibits different strengths.

The determinations of pK and log K values at various percentages of dioxane-water, methyl alcohol-water and other organic solvent-water mixtures have been made by a number of workers¹⁻⁶.

Reddy et al⁷ have showed the effect of dielectric constant on the stability of Co (II) and Ni (II) with 2-mercaptoethyl benzimidazole, glycine, ethylene diamine and salicylic acid in various proportions of ethanol-water mixtures at 30°C and $\mu= 0.1 M$ ($NaClO_4$).

EXPERIMENTAL

All chemicals used in the present investigation were of AR grade and the glassware's used were of Pyrex quality. Metal nitrate was dissolved in perchloric acid and its concentration was determined by standard method⁸. Concentrations of metal nitrate and nitric acid taken were fixed. Solutions of ligand, metal ions and alkali etc. were prepared in double distilled water and were always used a fresh. The pH measurements were carried out with ELICO-L1-10 (accuracy ± 0.05 units) using combined electrode at constant temperature of 28°C. Ionic strength of the solution was maintained constant at ($\mu = 0.01M$) by adding an appropriate amount of KNO_3 solution.

RESULTS AND DISCUSSION

The proton-ligand and metal-ligand stability constant of 4A-3N-SA and its complexes with Cu (II) metal ions are given in Table 1. It could be seen that log K values increased with increase of the percentage of ethanol, this is due to the effect of bulk solvent.

The linear relationship between pK_1 and pK_2 versus $1/D$ holds for low percentage of organic solvent is in agreement with the observation of many workers⁹⁻¹¹. The plots of pK versus mole fraction exhibit a linear relationship for 50%-75% of organic solvent. Sawalakhe et al¹² and Mandakmare et al¹³ have observed the same linear relationship for the plots between pK_1 and pK_2 versus mole fraction.

The value of $(pK_2 - pK_1)$ can be regarded as a measure of interaction between charges at both ends of a diprotic acid. The pK values in different percentages of ethanol-water for $-SO_3H$ group in 4A-3N-SA were determined and used to

calculate $(pK_2 - pK_1)$. It could be seen that the difference shows a continuous decrease with increasing the percentage of ethanol. The decrease in ΔK with increasing the percentage of ethanol may be due to the different environmental effects during the dissociation of $-NH_3^+$ and $-OH$ group. The pK values in various percentages of ethanol obtained by Agrawal¹⁴ for substituted thiadiazoles and methyl-5-carboxylates.

Bhattacharya *et al*⁹ have studied equilibrium constants and other properties of ferric salicylate and ferric sulphosalicylate complexes in dioxane-water mixtures. The difference between log K_1 and log K_2 values in different percentages of ethanol-water mixtures are calculated and given in table 2. This difference continuously decreases with the increase in ethanol percentage. This means that either log K_1 is relatively decreasing or log K_2 is relatively increasing as the dielectric constant is decreased. The lowering of dielectric constant would increase the electrostatic forces of attraction

Table 1: pK and LogK values of 4A-3N-SA and its complex with Cu (II)ion in different percentage of Ethanol-Water mixtures at 0.01M ionic strength

% Ethanol	D	1/D	Mole-Fraction	4A-3N-SA		Cu (II)-4A-3N-SA	
				pK_1	pK_2	Log K_1	Log K_2
50	49.00	0.0204	0.2333	3.52	9.68	10.37	8.04
55	46.60	0.0215	0.2711	3.89	10.00	10.77	8.46
60	43.40	0.0230	0.3134	4.27	10.36	11.21	8.96
65	40.90	0.0244	0.3660	4.7	10.75	11.77	9.58
70	38.00	0.0263	0.4153	5.15	11.15	12.31	10.24
75	36.10	0.0277	0.4773	5.67	11.60	13.05	11.13

Table 2: (Log K_1 - Log K_2) values for Cu (II)-4A-3N-SA in Ethanol-Water

% Ethanol	(Log K_1 - Log K_2) Cu (II)- 4A-3N-SA
50	2.33
55	2.31
60	2.25
65	2.19
70	2.07
75	1.92

between metal ion and negatively charged ligand to from 1:1 complex. The formation of 1:2 complexes on the other hand is due to the reaction.

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