

## The pH metric studies of complexes of 4-amino-3-naphthol-sulphonic acid and 6-amino-5-naphthol-sulphonic acid with transition metal ions

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(Received: February 10, 2008; Accepted: March 30, 2008)

### ABSTRACT

The interaction of Co (II), Cu (II) and Ni (II) metal ions with 4-Amino-3-Naphthol-Sulphonic Acid (4A-3N-SA) and 6-Amino-5-Naphthol-Sulphonic Acid (6A-5N-SA) has been investigated pH metrically. It showed the formation of 1:1 and 1:2 complexes. The values of pK (proton-ligand stability constant) and logK (metal-ligand stability constant) at 0.1M ionic strength and 28 °C ± 0.1° were calculated.

**Key words:** pH metric studies, transition metal ions.

### INTRODUCTION

The aromatic amino naphthol sulphonic acids are good complexing agents because they contain donor atoms like nitrogen and oxygen. Substituted sulphonic acids have been used as chelates forming agents because of the increased stability of these derivatives in water than the parent ligands. Many substituted sulphonic acids are well known for their enhanced biological activities and remarkable properties. Very recently, sulphonic acids are found to be an excellent anti-foggant for extended self-life. The metal complexes of dihydroxy naphthols, 8-amino-1-naphthol sulphonates, catechols, 8-hydroxy quinolines, nitroso naphthols etc. have been reported by number of workers. Narwade et al.,<sup>1</sup> studied the stability constants of Th (VI) with some substituted pyrazoline. Different substituted sulphonic acids are also used as an anti-inflammatory agent, insecticides, bactericidal and pharmaceutical fungicides.

In view of analytical applications of aromatic substituted sulphonic acids, it was of interest to know the physicochemical properties like stability complexes at particular ionic strength with some metal ions which is still lacking.

### EXPERIMENTAL

Metal nitrates (All BDH AnalaR) were dissolved in perchloric acid and its concentration was determined by standard method<sup>2</sup>. The instrument could read pH in the range 0-14.0 in the steps 0.01. This 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. All the solutions were prepared in double distilled water and the solutions of ligands were always used a fresh in present investigation. The pH measurements were carried out with ELICO-L1-10 (accuracy ±0.05 units) using combined (glass and calomel) electrode at 28°C ±

0.10. All chemicals used were of AR grade. All the glassware used in these experiments was of Pyrex quality.

#### Procedure

Titration of free acid, free acid and ligand and free acid, ligand and metal ion against standard carbonate free sodium hydroxide solution (0.195 to 0.203 N) in water medium were performed. The titrations were carried out in inert atmosphere by bubbling nitrogen gas. Ionic strength ( $\mu = \frac{1}{2} \sum Ci.Zi^2$ ) of the solution was maintained constant at ( $\mu = 0.1M$ ) by adding an appropriate amount of the  $KNO_3$  solution. The concentration of other ions in addition to  $K^+$  and  $NO_3^-$  ions were also taken into consideration.

## RESULTS AND DISCUSSION

The ligands used in the present investigation are dibasic i.e. having two replaceable  $H^+$  ions, one from  $-SO_3H$  and one from  $-OH$  group, which undergo dissociation at two different pH values. The deviation between free acid titration curve and ligand titration curve is the conformation of dissociation of acidic groups in the ligand i.e. the release of protons.

#### Proton-ligand stability constants

The pH metric titration data was used to draw the curves for Acid, Ligand and metal titration between volume of alkali and pH. The average number of protons associated with ligand was

**Table 1: Proton-ligand stability constants  
(pK)  $28^\circ C \pm 0.1^\circ$   $28^\circ C \pm 0.1^\circ$**

Ligand	Constant, the pK			
		Half integral	Pointwise	
	pK <sub>1</sub>	pK <sub>2</sub>	pK <sub>1</sub>	pK <sub>2</sub>
4A-3N-SA	2.67	2.61	9.31	9.27
6A-5N-SA	3.26	3.37	10.43	10.48

determined by Irving-Rossotti's expression<sup>3</sup>. The pK were calculated from the plots of proton-ligand formation number against pH (the formation curves) and are presented in Table 1. The pK values are calculated by both Half-integral and Pointwise method.

The pK<sub>1</sub> corresponds to the dissociation of proton from  $-SO_3H$  (actually from  $NH_3^+$ , as there is a formation of zwitter ion) and pK<sub>2</sub> corresponds to the dissociation of  $-OH$  proton, which happens at higher pH than former one. The difference in pK values of two ligands can be assigned to the relative position of the groups in the structure.

#### Metal-Ligand stability constants

Hiremath *et al.*,<sup>4</sup> have investigated metal-ligand stability constants of metal ions with

substituted amino 1,3,4-thiadiazoles. Agarwal *et al.*,<sup>5</sup> studied the metal ligand stability constants of complexes of transition metal ions with substituted pyrazole and thiodiazoles pH metrically. The metal-ligand stability constants of Co (II), Cu (II) and Ni (II) metal ions with 4-Amino-3-Naphthol-Sulphonic Acid (4A-3N-SA) and 6-Amino-5-Naphthol-Sulphonic Acid (6A-5N-SA) were determined by Calvin-Bjerrum pH metric titration technique used by Irving and Rossotti.

The significant departure of metal-ligand curve from ligand curve and the change in colour of solution indicated the formation of chelates between ligands and metal ions. The solutions used were very dilute and hence the possibility of existence of polynuclear species is very less.

**Table 2: Metal-Ligand stability constants (logK) at 28°C ± 0.1°**

System	logK <sub>1</sub>	logK <sub>2</sub>
Co (II) 4A-3N-SA	7.14	5.76
Co (II) 6A-5N-SA	8.12	6.05
Ni (II) 4A-3N-SA	6.32	4.21
Ni (II) 6A-5N-SA	4.15	3.09
Cu (II) 4A-3N-SA	9.47	7.38
Cu (II) 6A-5N-SA	8.65	5.43

The values of metal-ligand formation number were evaluated by using Irving-Rossotti's expression<sup>3</sup>. These values indicate the formation of 1:1 and 1:2 complexes in solution. Metal-ligand stability constants were calculated by half-integral method and are given in table 2. Raghuvanshi *et al.*,<sup>6,7</sup> have studied metal-ligand stability constants of transition metal ions with some substituted pyrazolines in 70% dioxane-water mixture.

The deviation of the metal complex titration curve from the reagent curve commenced from pH around 2.37 for Copper and 4.50 for Nickel and Cobalt for all the systems.

The result shows that the ratio logK<sub>1</sub>/logK<sub>2</sub> is positive in all cases which indicate that there is a little or no steric hindrance to the addition of secondary ligand molecules. The order of metal-ligand stability constants for both the ligands is- Cu (II) > Co (II) > Ni (II).

Meshram *et al.*,<sup>8</sup> have observed same order for substituted pyrazoline.

#### ACKNOWLEDGEMENTS

The authors wish to thank the Head of Deptt. Of chemistry and Director, Govt. V. I. S. H., Amravati for research facilities.

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