



Co-ordination Studies of 3-Amino Phenol and Transition Metal Ions in Aqueous Media

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ABSTRACT

The study reflects the co-ordination properties of the 3-Amino Phenol (AMP) with transition metal ions in natural, ecofriendly media pH metrically by application of Irving Rossoti method. Ionic strength maintained by using cheap, easily available NaNO_3 . Protonation constant and stability constants were calculated by Microsoft excel programme. Protonation constant and stability constants calculated by half integral and pointwise method are in agreement. Stability orders were found in agreement with Irving and Williams natural order.

Keywords: Protonation constant, stability constants, Irving Rossoti

INTRODUCTION

Aminophenol isomers are primarily used as intermediates in the manufacture of dyes and pigments. The largest class of dyestuffs is that of the azo colours, which are made by diazotization. These isomers, which are crystalline solids of low volatility, act as skin sensitizers and cause contact dermatitis, which appears to be the greatest hazard arising from their use in industry. These compounds are also the main metabolites of aniline both in vivo and in vitro. [1] AMP is an isomer of 2-aminophenol and 4-aminophenol. One of the most relevant applications of the substance is the synthesis of 3-(diethylamino)phenol, key intermediate for the preparation of several fluorescent dyes (e.g., Rhodamine B).[2] It is used for fur, hair coloring, use for dyes, pharmaceutical intermediates and antioxidants, stabilizers and other reagents. It has been used as a stabilizer of chlorine-containing thermoplastics, although its principal use is as an intermediate in the production of 4-amino-2-hydroxybenzoic acid this isomer is also employed as a hair colorant and as a coupler molecule in hair dyes.[3] In continuation with our previous studies on solution equilibrium of binary complexes, the paper reports the metal ligand interaction between AMP and transition metal ions in aqueous media by the use of simple, cheap chemicals and simple method. Methodology is simple and may be performed in any lab. Our study focuses on bonding between AMP ligand and transition metal ions by using pH metric method.

MATERIALS AND METHODS

All the chemicals with SD fine AR grade were used. The metal solutions were prepared by dissolving transition metal nitrates in double distilled water. Sodium hydroxide, Sodium nitrate and nitric acid solution were prepared in double distilled water and standardized by usual methods. Glass electrode with digital pH meter (ELICO-120) used for pH metric measurement. pH meter was calibrated using buffer solution of pH = 4 and pH = 7 before titration. Irving Rossoti titrimetric method used for titration.[4] The experimental procedure involved three titrations I) HNO_3 (A) II) HNO_3 + Ligand (A+L) III) HNO_3 + Ligand + metal ion (A+L+M) against 0.2 N NaOH. Proton ligand and metal ligand stability constant were determined by using Microsoft Excel computer programme.

RESULTS AND DISCUSSION

The observed pH values from above three titrations are then plotted against the volume of alkali added. Three titration curves are obtained (Figure 1), corresponding to the titrations mentioned in the experimental part. The titration curves were separated from each other each taking approximately S shape. The end point for the titration increased in the order I > II > III. The maximum value of n did not exceed two for all complexes indicating the formation of 1:1 and 1:2 complexes. Considerable separation of metal complexes curve from reagent curve along volume axis is an evidence for complex formation. The use of very dilute solution ruled out the possibility of formation of polynuclear complexes. The order clearly indicates that log K value increases

with decreasing atomic radius. Stability values depends upon the ionic size of the metal ions, smaller ions have high stability therefore Cu has highest value.

The values of n_A suggests that ligand behaves as monoprotic acid due to deprotonation of –OH group. The higher pKa value indicate weak deprotonation of the ligand same as in the case of 2-hydroxy acetophenone and phenol.[4] From protonation constant values it appears that AMP dissociates at higher pH in the range of 9.00. Higher pKa value may be due to presence of aromatic ring. In our studies pKa value for –NH₂ group in AMP is undetectable this is in agreement with earlier studies.[5] The basicities of the –NH₂ groups in amino pyridines are too weak to be detected and certainly had no effect on the hydrogen ion concentration in a moderately acidic range. They observed no pKa value for –NH₂ group in 2-amino pyridine, it has shown only one pKa 6.14 due to protonation of the N of pyridine ring.

The proton ligand stability constant calculated are in agreement with the reported value. [6]. The pKa value for phenol is 10.00 and that of 3-aminophenol is 9.87. The decrease in pKa may be due to electron release by amino group. The –NH₂ group is an electron releasing group it weakens the phenol when present in the para position but strengthens it when in meta position. Binary complexes formed by M : L ratio 1:1 are more stable than 1:2 ratio. Minor difference between log K₁ and logK₂ indicates stepwise complex formation. (logK₁ – logK₂) values are positive, showing that the coordination of the first ligand molecule with the M⁺² ion is more favourable than its bonding to the second one because for M⁺² the coordination sites of the metal ions are more freely available for coordinating.[7] The order clearly indicates that log K value increases with decreasing atomic radius. Stability values depends upon the ionic size of the metal ions, smaller ions have high stability therefore Cu has higher value.

The order of stability for 1:1 complexes is Fe(III) > Ni(II) > Cu(II) > Cd(II) > Zn(II) > Co(II) and for 1:2 complexes is Cu(II) > Co(II) > Ni(II) > Zn(II) > Fe(III) > Cd(II) the order is in agreement with Irving and Williams natural order.

The metal–Ligand stability constants of 3-Amino Phenol with metal ions are shown in table 1 and 2.

Table 1

Proton Ligand Constant and Metal Ligand Stability Constants for AMP (1:1)

Proton Constant	Ligand	Metal Ligand Stability Constants			
		Metal ion	Log K ₁	Log K ₂	Log β
Half integral pK ₁ = 9.8423		Fe (III)	11.4881	10.5396	22.0277
		Ni (II)	13.0085	4.3775	17.3166
		Cu (II)	6.7243	6.4397	13.2129
Point wise pK ₁ = 9.8624		Cd (II)	6.8998	4.9594	11.8811
		Zn (II)	5.9446	5.5661	11.5107
		Co (II)	4.5264	4.3369	8.8634

Table 2

Metal Ligand Stability Constants for AMP (1:2)

Metal ion	Metal Ligand Stability Constants		
	Log K ₁	Log K ₂	Log β
Cu (II)	3.798823	3.230197	7.029021
Co (II)	3.740288	3.239687	6.979975
Ni (II)	3.737082	3.233206	6.970288
Zn (II)	3.72125	3.23214	6.953403
Fe (III)	3.706572	-	3.706572
Cd (II)	-	3.22753	3.22753

The literature values of pKa for aminophenol are 8.18 and 6.82.[8] Deosarkar and Narwade studied interaction of transition metal ions with 4-amino naphthol sulphonic acid and 6-amino naphthol sulphonic acid investigated potentiometrically.[9] There is formation of 1:1, 1:2 complexes, and two pKa values as 2.61(-NH₂), 9.27 (-OH) and 3.26 (-NH₂), 10.47(-OH). The order of stability reported by them was Cu (II) > Co (II) > Ni (II). Arbad et al [10] studied complex formation of methyl paraben (MP) and phenarbitone (PB) with transition metals in 50 % ethanol water. They reported formation of 1:1 complexes, with pKa 9.21 for –OH group in MP and 8.72 for –OH group in PB. The stability order for above ligands Mn(II) < Co(II) < Ni(II) < Cu(II) < Zn(II) was found by them. Atkas et al [11] studied dissociation of ten phenolic compounds in 10% acetonitrile –water mixture and reported pKa 9.79 for 4-fluorophenol.

Wankhede et al [12] studied chelation tendency of flavones in 70% acetone :water media and observed formation of 1:1 and 1:2 complexes. They reported higher pKa 10.60-11.00 for –OH group. The more stability of copper complexes than Nickel complexes is observed.

Mhaske and Patil[13] studied complexes of Paracetamol and determined pKa value 9.67 for –OH group in paracetamol. The formation of 1:1 and 1:2 complexes reported and observed the order of stability for metal chelate as Mn (II) < Co (II) < Ni (II) < Zn (II). Shaleva et al carried out measurement of pKa values of 105 organic compounds by multiplexed capillary electrophoresis technique, found 9.41 and 9.62 value for paracetamol, alprenol.[14] P. J. Parmar studied pKa values of pyrazoline (PYZ) and found that mono basic nature of PYZ due to presence of –OH group. He reported pKa values in the range of 8.00- 9.00.[15]

Rathod S.P. et al [16] synthesized substituted thiazine and studied their interaction with transition metal ions. These ligands are monobasic have –OH group and reported pKa value as 9.9 and 11.7. They also found that Cu (II) complexes are more stable than Co (II) complexes. Mittal et al [17] studied complexation of Schiff's bases of o-amino phenol in ethanolic medium with transition metal ions; pKa reported were in the range 7.40-7.72 due to ionization of –OH group.

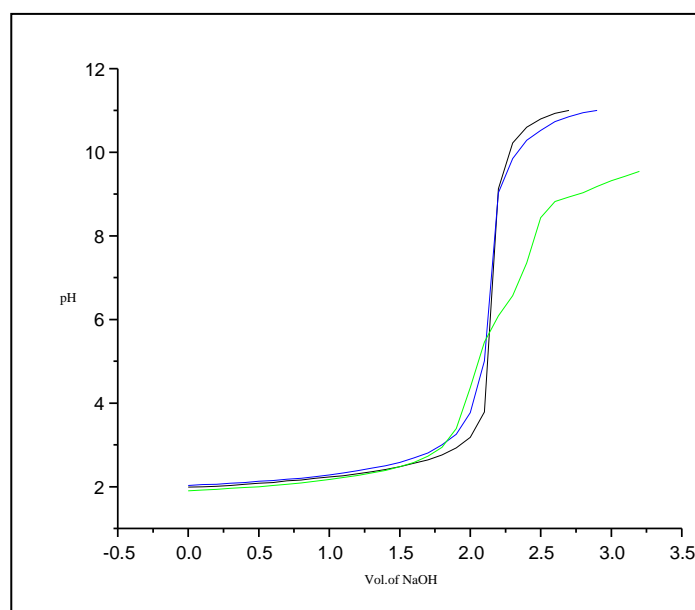


Fig.1. Titration curve

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Conflict of Interest Statement:

The authors have no conflicts of interest to declare.

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