

## A study of stability constant for co-ordination compounds of Cu (II) using potentiometric method

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### ABSTRACT

The log  $K_H$  values of  $\pm$  aryloxyacetic acid, malonic acid,  $\pm$  amino butyric acid, picolinic acid and maleic acid were determined in aqueous 25% ethanol, 50% and 75% ethanol solutions, Binary and ternary metal-ligand stability constants were determined in aqueous and 25%, 50% and 75% ethanol solutions.

**Key words:** Cu(II), Potentiometric method

### INTRODUCTION

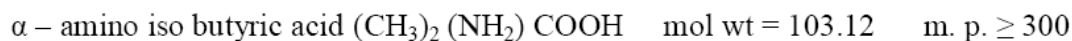
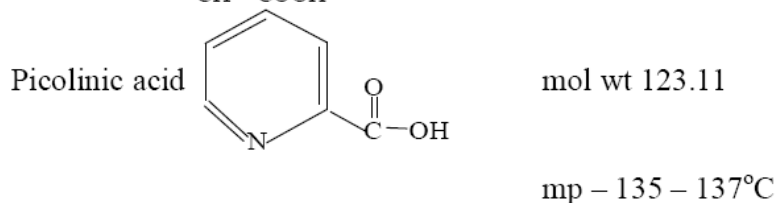
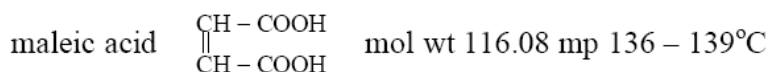
Solvent mixture are important reaction media as one can tune the polarity, solubility etc of a solution by altering the composition solvation environment around a reactant affects the barrier crossing rate. Interdiffusion and preferential solvation significantly slows down the dynamic in binary mixtures than in pure solvent. The solvent effect on a chemical reaction in a pure solvent and binary mixture is entirely different. The polarity and ion mobility in liquid mixture is different than in pure solvent. Therefore, we decided to study the effect of solvent, on the stability of complex formed between metal ion and some acids. We selected aryloxyacetic acid, picolinic acid and dicarboxylic maleic acid and malonic acids as ligands and investigated their stability constants with Cu (II) ion in aqueous, 25% 50% and 75% alcoholic solution. The stability constants were determined pH metrically. The mixed ligand titration curve  $M_{xy}$  involved simultaneous equilibrium.

### EXPERIMENTAL

Appropriate amount of ligand picolinic acid, maleic acid, malonic acid, aryloxyacetic acid and 2 amino isobutyric acid (S.D. fine Ltd.) of analar grade were dissolved in distilled water and diluted to definite volume to prepare solutions of known concentrations. The pH metric measurements were carried out with Elico digital pH meter (LI - 612) and combined glass electrode. The titrations were carried out at  $27 \pm 0.5^\circ\text{C}$  and on inert atmosphere were maintained by bubbling oxygen free nitrogen gas throughout the course of titration. The Calvin Bjerrum pH titration technique as modified by Irving and Rossotti<sup>1-4</sup> was applied to determine formation constant. The titrations were carried out with carbonate free 0.221 M sodium hydroxide solution. The ionic strength was maintained to 1.0 M with the help of  $\text{NaClO}_4$ . The metal to ligand ratio was 1:5. There is several advantages of potentiometer study over other methods such as speed, low cost, ease of preparation, simple instrumentation,

relatively fast response, very low reasonable selectivity etc. The potentiometry may be considered as the most accurate technique for the evaluation of complex equilibrium constants. The Literature

survey reveals that various papers appear on the study of complexation using potentiometry. Malonic acid  $\text{CH}_2(\text{COOH})_2$  mol wt 104.06 mp 134 – 135°C



## RESULTS AND DISCUSSION

The potentiometric data was analyzed using computer programme. The values of protonation constants are given in table 1.

Maleic acid and malonic acid contains two dissociable protons whereas aryloxy acetic acid releases one proton.  $\alpha$ -amino butyric acid contain two protons one at  $\text{NH}_2$  group and one of carboxylic group the low  $\log H_1 K$  is due to carboxylic group and higher value is for amino group. Using the binary titration, keeping 1:5 metals to ligand ratio, metal-ion stability constant was determined. (Table 2).

There are various interacting forces presents when we use solvent mixtures. Ion – dipole forces are important for solutions of ionic compounds in dipolar solvents, where solvated species such as  $\text{M}(\text{OH}_2)_m$  and  $\text{L}(\text{H}_2\text{O})_n$  exist. In case of some metal ions, these solvated species can be sufficiently stable. Liquid water consist of ordered regions of a regular lattice as well as regions in which the water molecules are hydrogen bonded in a random array, It is permeated by monomeric water and intrespored with random holes, lattice

vacancies and cages. When a binary mixture of solvent is taken, the solute is get preferentially solvated, the interaction may be non specific, involving solute / solvent association caused due to dielectric enrichment in the solvent shell of solute ions or dipolar solute molecules and the interaction may be specific involving solute / solvent association due to hydrogen bonding or electron pair donar electron pair acceptor interactions.

The statistical value of  $\Delta \log K$  depends of the geometry of the complex and for the distorted octahedral coordination sphere of  $\text{Cu}^{2+}$  with two different bidentate ligands was deduced (4) as – 0.9. The calculated values of  $\Delta \log K$  are given in table – 3. It is observed that  $\Delta \log K$  is 0.90 for Cu (Maleic acid) (PA) complex in 50% ethanol solution the highest 3.39 is observed for Cu (Maleic acid) (Picolinic acid) in 25% ethanol.

The metal ligand stability constant indicates that in ethanolic solution at 50% ethanol + water higher values are obtained. The dissociation constant of ligand depends on solvents. It is reported<sup>9</sup> that  $\text{pK}_1$  of amino acid increased as the concentration of ethanol increases. On the contrary

pK<sub>2</sub> values decreases upto 40% ethanol (w/w) and increases afterwards with the increasing concentration of ethanol in the solvent mixtures.

Changes in the ion-solvent interactions on transfer of electrolytes between solvents are small

but are sufficiently large to cause dramatic changes in chemical reactions involving ions. The solvents S<sub>1</sub> (water) and S<sub>2</sub> (ethanol) interact to give a structure S<sub>1-2</sub> and mixed solvents, three solvent structures S<sub>1</sub>, S<sub>2</sub> and S<sub>1-2</sub> may coexist. pK values in any solvent mixture has been assumed to be

**Table 1: Protanation constants of ligand**

Ligand	Aqueous		25 % Ethanol		50 % Ethanol		75 % Ethanol	
	log K <sub>1</sub> <sup>H</sup>	log K <sub>2</sub> <sup>H</sup>	log K <sub>1</sub> <sup>H</sup>	log K <sub>2</sub> <sup>H</sup>	log K <sub>1</sub> <sup>H</sup>	log K <sub>2</sub> <sup>H</sup>	log K <sub>1</sub> <sup>H</sup>	log K <sub>2</sub> <sup>H</sup>
Aryloxy acetic acid	10.308	-	7.424	-	6.148	-	7.095	-
Malonic acid	5.017	-	6.416	-	5.436	-	5.0442	-
α-amino butyric acid	7.656	10.987	4.760	2.843	7.843	5.549	8.542	2.698
Picolinic acid	5.056	-	4.097	-	2.699	-	5.112	-
Maleic acid	9.596	10.937	10.696	4.985	7.147	5.699	4.491	8.659

**Table 2: Metal ligand stability constants**

Ligand	Aqueous	25 % ethanol	50 % ethanol	75 % ethanol
Aryloxy acetic acid	4.757	4.668	7.281	4.349
Malonic acid	2.058	2.753	5.506	3.40
α-amino isobutyric acid	3.030	2.870	4.039	2.047
picolinic acid	5.202	2.821	6.006	2.50
maleic acid	3.467	2.233	3.234	4.718

**Table 3: Stability constants of mixed ligand complexes**

Mix Ligand	Aqueous		25 % Ethanol		50 % Ethanol		75 % Ethanol	
	log K <sub>Mxy</sub>	ΔlogK	log K <sub>Mxy</sub>	ΔlogK	log K <sub>Mxy</sub>	ΔlogK	log K <sub>Mxy</sub>	ΔlogK
Maleic acid + Aryloxy acetic acid	5.72	2.51	4.096	3.00	3.096	2.25	5.81	2.55
Maleic acid + malonic acid	5.60	2.60	3.859	2.59	4.795	2.69	5.59	2.30
Maleic acid + α amino isobutyric acid	6.01	1.00	4.775	3.71	5.055	3.40	6.58	0.59
Maleic acid + picolinic acid	5.09	3.23	3.964	3.39	4.985	2.00	6.00	0.90

weighted average of the ones in three solvents<sup>10</sup>  
i.e.

$$pK = \frac{n_1 pK_1 + n_2 pK_2 + n_{1-2} pK_{1-2}}{n_1 + n_2 + n_{1-2}}$$

$n_1$  and  $n_2$  and  $n_{1-2}$  are the number of molecules of solute solvated by each of the three respective solvents, Potentiometric titration method is not capable of determining simultaneously  $pK_1$ ,  $pK_2$  and  $pK_{1-2}$ , pH-measurement is unable to ascertain the preferential solvation of  $H^\pm$  ion in different solvents and can give no idea about the preferential solvent of anions and natural molecules.

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