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Studies of binary complexes of metal ions with Mandelic acid by Potentiometry

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Abstract: The binary complexes of Mandelic acid (MA) with transition metal ions metal ligand ratio (1:2) are studied potentiometrically in aqueous solution using Irving Rosotti method. The Proton ligand constant and metal ligand stability constants are studied at 27^0C. Ionic strength is maintained by using 1N $NaNO_3$.1:1 and 1:2 complexes are reported. Stability constant values are calculated by SCOGS computer programme. The values are verified by half integral and point wise method. High values of stability constant are reported. The order is in agreement with Irving-Williams order.
Keywords: Studies of binary complexes of metal ions with Mandelic acid by Potentiometry.

Introduction

Mandelic acid is an aromatic hydroxy acid. It has molecular formula C_6H_5 (CHOH) COOH. Mandelic acid (MA) has a long history of use in the medicinal community as an antibacterial, particularly in the treatment of urinary tract infections. It has also been used as an oral antibiotic. In Skin care, it is also an alternative to glycolic acid in skin care products. It has antiseptic properties. In continuation with earlier studies[1] the paper reports the complexation of MA with transition metal having metal ligand ratio 1:2 in aqueous solution.

Experimental

The metal solutions were prepared by dissolving transition metal nitrates in double distilled water. Sodium hydroxide, Sodium nitrate and nitric acid, MA used of AR grade SD Fine. Sodium hydroxide, Sodium nitrate and nitric acid solution were prepared in double distilled water and standardized by usual methods. Glass electrode with digital potentiometer (ELICO-120) used for potentiometric measurement. Potentiometer was calibrated using buffer solution of pH = 4 and pH = 7 before titration. All necessary precautions were taken for smooth operation of potentiometric titration. The experimental procedure involved three titrations I) HNO_3 (A) II) HNO_3 + Ligand (A+L) III) HNO_3 + Ligand + metal (A+L+M) against 0.2 N NaOH. Proton ligand and metal ligand stability constant were determined by using SCOGS computer programme.

Results and discussion

The Mandelic acid has two ionizable groups –OH and –COOH**.** The ionization of strong carboxylic group occurs at lower pH, due to the high stability of the carboxylate ion by resonance and hydroxylic group occur at higher pH. For the present work the protonation constant obtained are 2.944 and 9.425. These values are in agreement with pKa values with earlier work in which ligand possess carboxylic and hydroxyl group. [2-4]. Jain et al [5] studied complexation of Eu(III) with humic acid and its model compounds. They reported

formation of 1:1 and 1:2 complexes and pKa value 3.19 for Mandelic Acid. Calderia et al [6] has reported high stability values for tungeston complexes of the MA.

The complexation of Mandelic Acid with metal ions under study gives metal ligand stability constants which are shown in the table1.1.When the stabilities of metal complexes under study with MA are compared on the basis of stability constant following sequence obtained is

1:2 complexes is Cu (II) > Ni (II) > Zn(II) > Co(II) > Cd(II).

Since the size of Ni (II) is smaller than Co(II), Ni(II) forms stronger bond with α-hydroxy group of mandelate ligand than Co(II), similar results were reported by Ki Young et al. [7]. Agrawal et al [8] studied interaction of transition metal ions with benzoic acid at 25^0C and evaluated 4.19 value of pKa for –COOH group of benzoic acid, according to them Copper and Nickel complexes shows high stability during formation of 1:1 complexes. The order of stability towards complexation with benzoic acid observed by them was Cu (II) > Zn (II) > Mn (II).

R. Sundersanan [9] studied Indium metal complexes of glycollic acid, mandelic acid and lactic acid polarographically and reported pKa values as 3.3,3.00 and 3.86, the order of stability of complexes as mandelate < lactate < Glycollate. According to them increased substitution leads to lowering stability due to presence of hindering groups. Formation of 1:1 and 1:2 complexes for mandelic acid was predicted. The pKa value of mandelic acid is less than benzoic acid, this may be due to substituents present. Hydroxyl carboxylic acid contain two donor groups, the carboxyl and hydroxyl group therefore act as bidentate ligand. The proton and metal ion complexation constants of these ligands strongly depend upon the relative position of the two donor groups. The 2-hydoxy acids form stronger metal complexes than simple carboxylic acids. Hydroxyl group has marked effect on dissociation behaviour of carboxylic group. The electron withdrawing effect of hydroxyl group induce an increase in acid strength of the carboxylic group.e.g. 2- hydroxy acetic acid is 10 times stronger than acetic acid .[10]. Similar effect is observed in case MA ligand, it has pKa value as 2.9444 which correspond to –COOH group (our results) and phenyl acetic acid has value of 4.28. Mehta B.H. [11] studied the complexes of various carboxylic acids with transition metals and reported values of pKa for malic acid as 8.8828, 11.873, assigned higher pKa for –OH group. Order of stability as Mn(II) > Fe(III) < Ni(II) < Cu(II) < UO_2(II). Basavraj et al [12] studied complexation of Schiffs bases (SB) with transition metal ions in water ethanol medium, reported pKa for SB as 12.85 and 4.05 corresponding to –OH and –COOH group respectively. They have reported coordination of metal ions through oxygen of –OH group and carboxylate of –COOH group. Order of stability shown by them was

Zn (II) < Cu(II) > Ni (II) > Co(II) = Cd(II) > Mg(II)

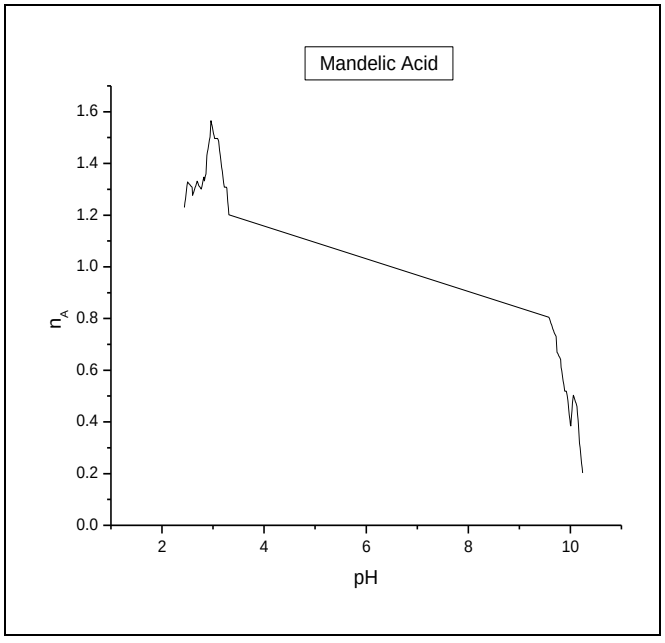
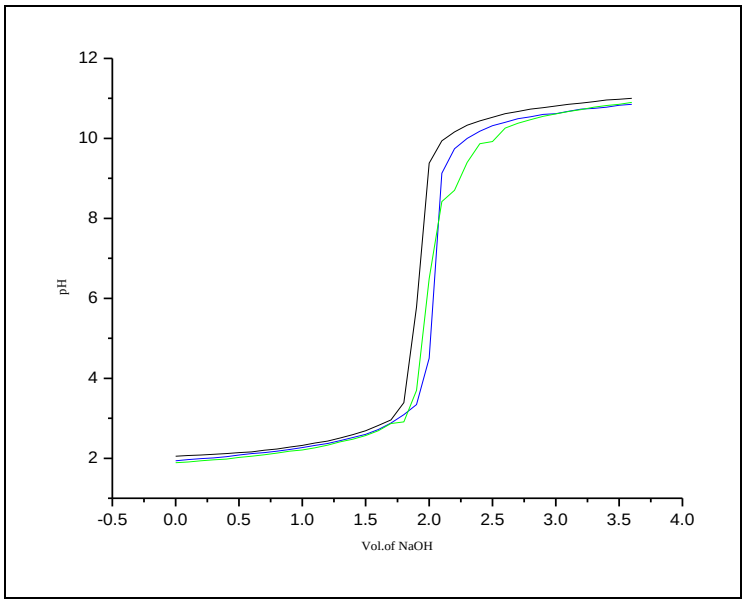


Fig. 1.1a n_A vs pH for Mandelic Acid



Graph 1.1b pH metric titration curve for Co (II) + Mandelic Acid in 1:2 ratio

Table 1.1 Proton ligand and metal ligand stability constants of Mandelic acid (1:2)

Proton ligand stability constant	**Metal ion**	Metal Ligand stability constants		
		Log K_1	**Log K_2**	**Log â**
Half integral	**Cu**(II)	7.5067	7.1232	14.6300
pK_1 = 2.9444	**Zn**(II)	6.3857	6.0603	12.4461
pK_2 = 9.9425	**Ni**(II)	7.1127	5.5842	12.6969
Point wise	**Fe**(III)	-	-	-
pK_1 = 2.6200	**Co**(II)	5.8731	5.3747	11.2478
pK_2 = 9.9852	**Cd**(II)	5.5844	-	5.5844

Regression Analysis

A linear regression analysis of stability constant of complexes against physical properties of metal ions has been carried out considering the equation y = Bx + A. The regression coefficient r is calculated using computer software Origin 6.0. The physical properties which are considered in the present study is given in the table 1.3. It was observed that none of the physical property of the metal ion shows above 0.2 regression coefficient for stability constant of metal ligand complexes. Ionization potential (I.P.) is one of the important properties of metal ions. For present work second I.P. was considered. It was observed that in case of Metal – Mandelic acid does not have significantly good co-relation with any of the physical property under study. A poor corelation is observed.

Table 1.2 : Physical properties of metal ions

Metal ion	Atomic number	Atomic mass	Atomic radius(ppm)	Ionic radius (ppm)	I.P.(KJ/mol)	Electronegativity
Fe	26	55.85	126	64	1561	1.64
Co	27	58.93	125	74	1648	1.70
Ni	28	58.71	128	72	1753	1.75
Cu	29	63.54	128	69	1958	1.75
Zn	30	65.38	138	74	1733	1.66
Cd	48	112.4	154	109	1631	1.46

Table 1.3: Correlation coefficient for stability constant vs. physical properties of metal

Ligand	Atomic number	Atomic mass	I.P. KJ/mol	Atomic radius **(**ppm)	Ionic radius **(**ppm)	Electrone gativity
MA	-0.327734	-0.309631	0.096551	0.076273	-0.384331	0.14392

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