Int. J. Chem. Sci.: 12(4), 2014, 1299-1304
ISSN 0972-768X
www.sadgurupublications.com

BINARY COMPLEXES OF NICOTINIC ACID WITH TRANSITION METAL IONS IN AQUEOUS MEDIUM

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ABSTRACT

The aim of present study is to investigate the complexation tendency and stability values of transition metal ions with nicotinic acid (NA) in aqueous media at room temperature using simple technique of potentiometry. 1N $NaNO_3$ was used to maintain ionic strength. The stability constants were evaluated by SCOGS computer programme. 1:1 and 1:2 complexes were reported. Metal ligand ratio kept is 1:2. Order of stability was compared and found to follow Irving-William natural order.

Key words: Complexation, Stability constants.

INTRODUCTION

Nicotinic acid is pyridine -3 carboxylic acid. Pyridine carboxylic acids are of very much interest because of their physiological activities shown by natural as well as synthetic acids. These acids are mainly present in many natural products like vitamins, alkaloids and coenzymes. Pyridine carboxylic metal complexes are interesting model systems. It has various pharmacological properties. In continuation of our previous studies on the solution equilibria of binary complexes[1], the paper reports the complexation of nicotinic acid with transition metal complexes having metal ligand ratio 1:2. Literature survey reveals that many workers worked on complexation of the NA in different ways[1-19].

EXPERIMENTAL

The metal solutions were prepared by dissolving transition metal nitrates in double

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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 potentiometer (ELICO-120) was used for potentiometric measurement. Potentiometer was calibrated using buffer solution of pH = 4 and pH = 7 before 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 complexation of nicotinic acid with transition metal ions has been studied under the experimental condition as described in experimental section. These results are presented in Table 1. The titration curves were plotted for ligand, and ligand + metal system (Fig. 1). The values were analysed to get protonation constant and metal-ligand stability constant. The value of $\bar{n}_A$ lies in the range of 0-1 indicating that ligand has only one replaceable proton**.** The pK_H value obtained are 5.425 and 5.200 considering the pointwise and half integral method. In case of 1:2 ratio of metal and ligand, Co(II) complexes are exceptionally more stable than Cu(II) complexes. For the present investigation, the order of stability may be assigned as follows:

Fe(III) > Zn(II) > Co(II) > Cu(II) > Cd(II) > Zn (II)

Turel et al.[2] have studied complexation of ciprofloxacin in aqueous solution at 25^{o}C. They reported two pKa values, 6.17 for 3-carboxylic group and 8.54 for nitrogen of piperazine group. They also reported formation of 1:1 complexes. Degim et al.[3] compared stabilities of naproxen and salicylic acid and reported value 6.512 and 4.325 for carboxyl group in naproxen and salicylic acid. Khalil et al.[4] studied complexes of dipicolinic acid and amino acids with bivalent metal ions in aqueous medium, evaluated pK_a 4.53 and 2.32 for dipicolinic acid. They also reported high stabilities for copper and nickel complexes. Patil et al.[5] studied interaction of transition metal ions with ibuprofen and paracetamol. They assigned pK_a value for –COOH group in ibuprofen is 5.32. They also reported formation of 1:1 complexes and high value of stabilities for copper and zinc complexes. Sekhon et al.[6] reported pK_a value 5.709 (carboxyl group) and 8.044 (piperazinyl group) for ciprofloxacin. Gamerio et al.[7] reported pKa values 6.25, 8.44 and 6.10, 8.60 for norfloxacin and ofloxacin. Patil[8] reported two pKa values for NA as 9.05 and 4.95. He also reported high value of stability constant for complexes of copper (II) and zinc ion (II), Hence, the order of stability is in agreement with our results. Patil[9] studied interaction of transition metal ions with NA and reported pKa value 4.74 for NA. They have found that the sequence of stability complexes with respect to metal ions is due to decreasing atomic radius and increasing

second ionization potential. Janrao et al.[10] have recently observed 4.90 pKa value for the NA and 6.4790 for metal ligand stability constant of zinc complex. They also reported formation of 1:1 complexes. Zaid et al.[11] studied stabilities of ciprofloxacin moiety and observed high values of stability for copper complexes. Farooqui et al.[12] evaluated two pKa values for picolinic acid as 10.95 and 8.83 in aqueous medium using potentiometry. They also reported high values of stability constants for cobalt than nickel complex. Nair et al.[13] observed two stability constants for NA as 4.69 and 7.02 at 37°C. They reported formation of 1:1 and 1:2 complexes. They also reported NA as a bidentate ligand and binding of ligand to metal ion through is N-pyridine and O of carboxalato atoms like that of pyridine-2-carboxylic acid.

Table 1: Protonation constant and metal-ligand stability constant values for NA

Proton-ligand stability constant	Metal ion	Metal ligand stability constants		
		Log K_1	**Log K_2**	**Log β**
Half integral	Cu (II)	3.1144	3.1032	6.2176
pK_1 = 5.200	Zn (II)	3.1080	3.0983	6.2064
Point wise	Ni (II)	3.1099	3.1491	6.2591
pK_1 = 5.4254	Fe (III)	4.1094	3.8639	7.9733
	Co (II)	3.1029	3.1311	6.2341
	Cd (II)	3.1057	3.1027	6.2084

Gupta[14] studied stability of ampicillin trihydrate in water-ethanol medium (50% V/V) maintaining ionic strength at 0.1 M KNO_3 with bivalent metal ions. She reported pKa value of 6.98 and formation of 1:1 complexes. The stability constants should be in the range of 3-5 for drugs to remain in biologically active form. The stability values are found to be in biologically active range and highest value was found for copper (II) ion. These stability values may be informative for biochemist during drug design or drug discovery. Hernowo[15] reported two values of pKa as 2.22 and 4.59 for carboxylic acid group and pyridine nitrogen and also compared stability constants of NA with GA (Gallic acid) and proved that NA is a weaker ligand.

Rasheed and Maqsood[16] studied solid state complexes of NA with Cu(II) and reported that NA complexes are water insoluble, octahedral in nature. The formation of 1:1 and 1:2 complexes was detected. Cu(II)-nicotinate complexes reported to exert diverse bioactivities. Monodentate nature of NA and possibility of bonding through nitrogen was also observed. Low values of stability of NA-Cu(II) complexes are due to weak nature of NA ligand. Kayande et al.[17] also studied the complexation of NA with Cu(II) and observed pKa 3.48. Interactions of insulin-mimetic zinc complexes of 2-picolinic acid was studied by

Ebedy et al.[18]. They also reported complexation through pyridine nitrogen and carboxylate oxygen for pKa 1.00 and 5.19. Solution behaviour of enrofloxacin (erf) complexes with transition metal ions in the presence of 1, 10-phenanthroline was investigated by Saraiva et al.[19] The results obtained show that at physiological condition, only copper form stable complexes. They reported pKa values 6.17 and 9.34 for -COOH group and piperazine in erf, respectively.

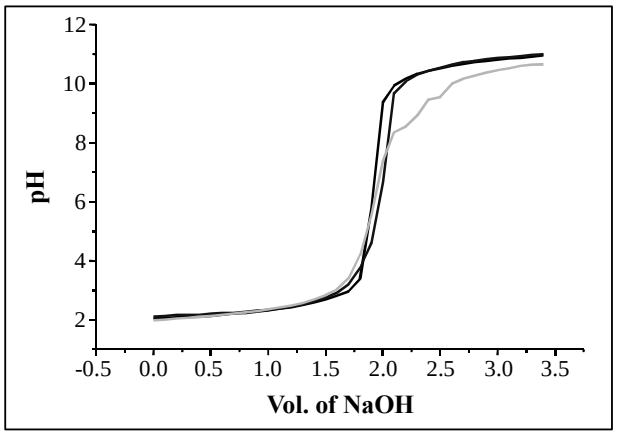

Fig. 1: pH metric titration curve for Zn (II) + Nicotinic acid (1:2 ratio)

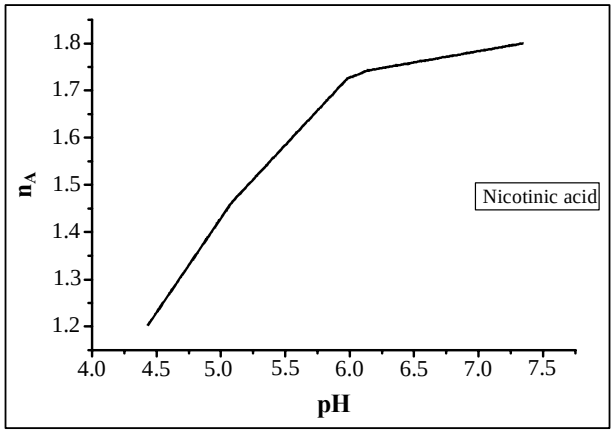

Fig. 2: Graph of $\bar{n}_A$ vs. pH for NA

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. These are shown

in Tables 3. The physical properties, which are considered in the present study, is given in the Table 2. It was observed that none of the physical property of the metal ion shows above 0.9 regression coefficient for stability constant of metal ligand complexes.

Table 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 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)	Electronegativity
NA	-0.764786	-0.763148	0.887634	-0.763148	-0.747816	0.842044

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-nicotinic acid and metal complexes, a positive correlation exists. The ionic radius of metal ions used in the present investigation shows good negative correlation with metal-nicotinic acid complexes. Again the complexes of nicotinic acid with metal ions show good positive correlation with electronegativity of metal ions. Considering the atomic mass, it shows good negative correlation with nicotinic acid complexes. Similarly, atomic radii of metal ions with metal, nicotinic acid complexes shows good correlation.

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Accepted : 08.07.2014