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Stability Constants of Cu(II)/Ni(II) of Binary Chelates with 4-Hydroxypicolinic Acid N-Oxide in Aquo-Organic Media

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The proton ligand constants of 4-hydroxypicolinic acid N-oxide and the complexation equilibria of corresponding binary chelates of Cu(II) and Ni(II) have been measured at 30° ± 1°C and 0.1 M ionic strength in varying percentages of dioxane-water, acetone-water, ethanol-water and *iso*propanol-water media. The results are discussed with reference to the change in dielectric constants of water in the presence of organic solvent, change in the structuredness of water, change in hydrogen bonding ability of the organic solvent in water, solvent basicity and proton solvation by organic solvent. The values have been compared with aqueous and mixed aqueous systems of picolinic acid N-oxide and 4-aminopicolinic acid N-oxide.

INTRODUCTION

The formation constants of transition metal chelates with picolinic acid N-oxide (PicO) and substituted compounds in aqueous media reported earlier[1] revealed the substitution in the fourth position by groups such as hydroxy, amino, methoxy, ethoxy and propoxy increased the stabilities. Shashikala and Ram Reddy[2, 3] and Sarala Devi *et al.*[4] studied these systems in aquo-organic media and observed increased stabilities compared to aqueous systems. The present study emphasizes the effect of various aquo-organic solvents on the formation constants of Cu(II)/Ni(II)-4-hydroxy picolinic acid N-oxide systems. The different trends observed have been explained in terms of solvent basicity, structuredness of water and protonation of organic solvents.

EXPERIMENTAL

The ligand 4-hydroxy picolinic acid N-oxide was prepared in our laboratory by known procedures[5]. The solvents used were dioxane, *iso*propanol, acetone and ethanol with percentages ranging from 30 to 70% v/v organic solvent-water mixtures. All solvents were purified by standard procedures[6]. The pH correction factor[7] and the values of dielectric constants[8–10] for different organic solvent-water mixtures calculated from literature data. The proton-ligand and metal-ligand constants were determined using the graphical method of Irving and Rossotti[11] applicable to mixed aqueous solvents. The data are presented in Table 1.

TABLE 1
SOLVENT EFFECT ON BINARY COMPLEXES OF M(II)-4-OHPicO IN VARIOUS AQUO-ORGANIC MEDIA

Metal ion	Stability constants	Percentage				
		30	40	50	60	70
		Dioxane-water				
H^+	pKa	4.30	4.65	4.92	5.30	5.52
Cu(II)	log K_1	4.98	5.87	5.99	6.08	6.11
	log K_2	3.76	4.12	4.72	5.12	5.72
Ni(II)	log K_1	3.97	4.41	4.87	4.93	5.17
	log K_2	3.09	3.38	3.72	3.86	3.97
		Acetone-water				
H^+	pKa	4.17	4.20	4.28	4.64	5.21
Cu(II)	log K_1	4.61	4.98	5.71	5.89	5.98
	log K_2	3.49	3.70	4.12	4.69	3.77
Ni(II)	log K_1	3.67	3.98	4.42	4.56	4.71
	log K_2	2.81	3.18	3.02	3.47	3.59
		Isopropanol-water				
H^+	pKa	4.26	4.28	4.36	4.50	4.47
Cu(II)	log K_1	4.51	4.69	5.03	5.72	5.72
	log K_2	3.38	3.52	4.27	4.72	3.69
Ni(II)	log K_1	3.65	3.76	3.80	3.57	4.70
	log K_2	2.97	3.00	2.96	2.99	3.61
		Ethanol-water				
H^+	pKa	4.10	4.65	4.92	5.30	5.52
Cu(II)	log K_1	4.45	4.70	4.95	5.05	5.20
	log K_2	4.11	4.28	4.20	4.30	3.48
Ni(II)	log K_1	3.68	3.69	3.71	3.97	4.62
	log K_2	2.82	3.09	3.35	3.68	3.71

The ionic strength was maintained at 0.1 M by addition of calculated amounts of 1 M KNO_3. The plots of pKa vs 1/ε and mole fraction (N) and log K vs 1/ε and mole fraction (N) for Cu(II)-4-hydroxy picolinic acid N-oxide chelates are given in Figures 1 and 2, to represent the systems studied.

RESULTS AND DISCUSSION

The pKa values of the ligand in the present study increased with increase in v/v percentages of each of the four mixed aqueous solvents. The pKa values of 4-OH picolinic acid N-oxide are higher than the corresponding values of picolinic acid N-oxide in all aquo-organic media. This is due to the presence of the electron-donating OH group in the fourth position. The pKa values of 4-NH_2 picolinic acid N-oxide increased both in aqueous and aquo-organic media when compared to PicO and 4-OH PicO values reported earlier[12]. This is due to more electron donating NH_2 group present in the fourth position. The

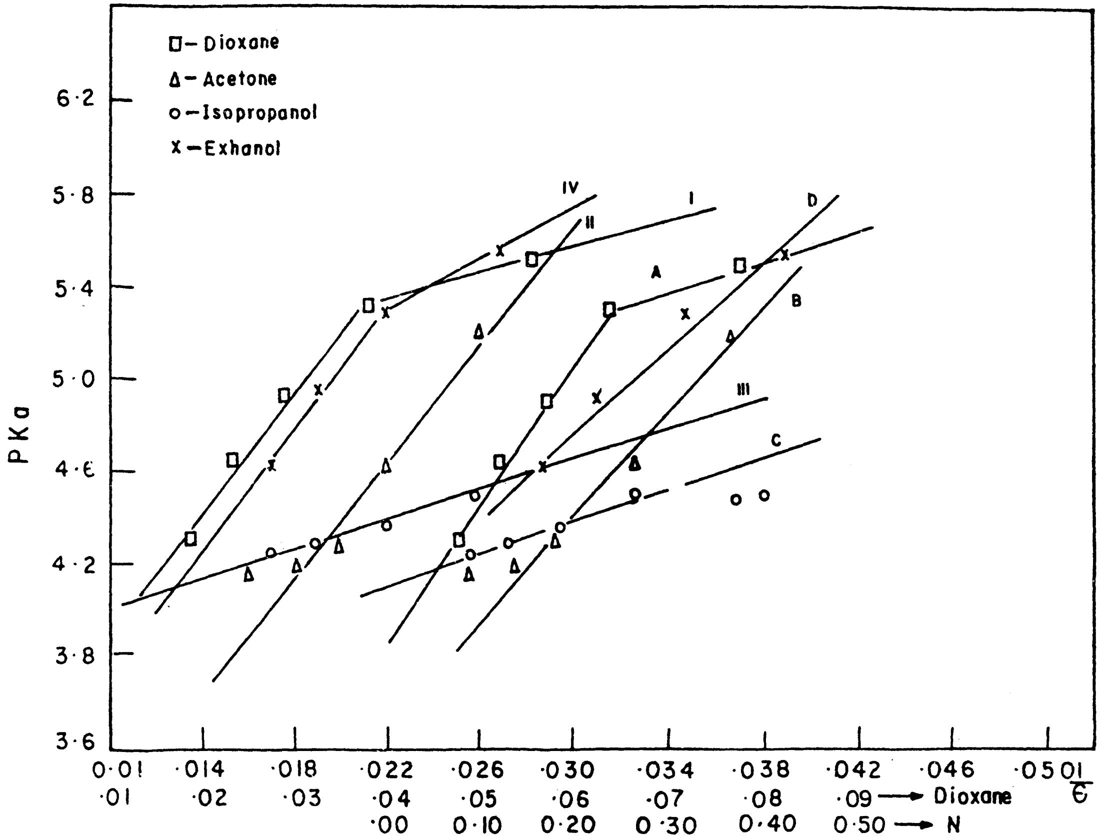

Fig. 1 Variation of pKa of 4-OH Pica with dielectric constant and molefraction of solvents Dielectric constants of solvents (I) Dioxane (II) Isopropanol (IV) Ethanol Molefraction of solvents (A) Dioxane (B) Acetone (C) Isopropanol (D) Ethanol.

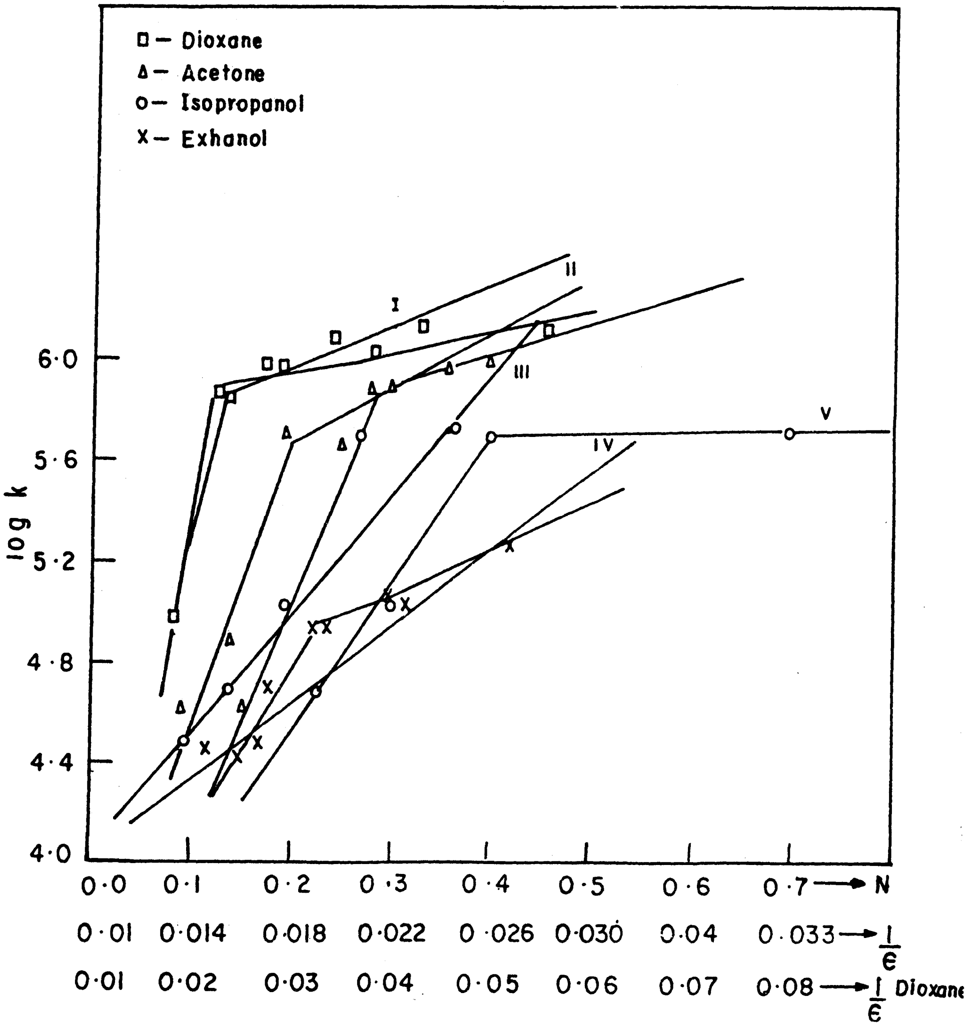

Fig. 2 Variation of log k of Cu(II)-4-OH PicO with dielectric constants and molefraction of solvents. Molefraction of solvents (I) Dioxane (II) Acetone (III) Isopropanol (IV) Ethanol Dielectric constants of solvents (A) Dioxane (B) Acetone (C) Isopropanol (D) Ethanol.

increase in pKa values with dielectric constant of the medium may be due to increased proton solvation by the organic solvent. The plots of pKa of ligands vs mole fraction (Fig. 1) reveal that there is a linear relationship upto 60% v/v dioxane-water. Above this percentage another straight line with different slope is observed. For acetone-water, *iso*propanol-water and ethanol-water linearity is observed upto 70% v/v percentage. The plots of pKa vs 1/ε in Fig. 1 reveal that there is a linear relationship upto 60% v/v of dioxane-water and ethanol-water. Above these percentages another straight line with different slope is observed. For acetone-water and isopropanol-water linearity is observed upto 70% v/v percentage. This indicates that the structuredness of water remains upto this composition. Thereafter the aqueous solvation shell is dispersed and the organic solvent molecules participate in the solvation of water molecules. For the same 50% v/v composition the pKa of the ligand studied follow the sequence

Dioxane-water > Ethanol-water > *Iso*propanol-water > Acetone-water

It is observed that the pKa values of ligands in mixed aqueous solvents do not follow either the order of dielectric constants or the order of basicity of solvents. This shows that in addition to the dielectric constant of the medium, other factors such as the hydrogen bonded structure and proton solvation capacity have to be taken into consideration in the interpretation of data. The pKa values are maximum in 70% dioxane-water which may be attributed to the fact that the dioxane has a low dielectric constant and no hydrogen bonded structure. Similar observations were made by Sarala Devi *et al.*[4] in their studies of PicO and 4-OCH_3PicO systems.

The formation constants of 4-OHPicO in aquo-organic media are higher than the corresponding values in water. The stabilities increase with increasing composition in all the four mixed aquo-organic solvents studied. Plots of log K vs mole fraction and 1/ε show linearity upto a certain percentage composition of the organic solvent. From the observed log K values, the composition that corresponds to maximum structuredness of water at 30°C are close to 0.318 mole fraction of ethanol-water, 0.195 of acetone-water and 0.174 mole fraction of dioxane-water for 4-amino PicO systems. But in the case of Cu-4-OHPicO systems it is observed that the maximum structuredness of water is close to 0.31 mole fraction of ethanol-water, 0.20 mole fraction of acetone-water and 0.11 mole fraction of dioxane-water. The deviations observed at high solvent composition may be due to gradual displacement of water molecules in the hydration sphere of the metal ion by organic solvents. The formation constant values of Cu(II)/Ni(II) -4-OHPicO chelates in iso-dielectric mixtures at 1/ε = 0.0195 follow the sequence

Acetone-water > Ethanol-water > Isopropanol-water > Dioxane-water.

The corresponding mole fraction of various aquo-organic media at 1/ε = 0.0195 follow the sequence

Ethanol-water > Acetone-water > Isopropanol-water > Dioxane-water.

The fact that ethanol and acetone have exchanged places may be attributed to smaller solvation capacity of acetone compared to ethanol. Similar observations were made by Chaudhary and coworkers[13-15]. From these observations, it may be concluded that pKa and log K are influenced by the dielectric constant, mole-fraction and solvation capacity of the medium. The stability order of metal chelates in mixed aqueous solvents appears to be influenced by the nature of metal ions, properties of ligands as well as various characteristics. Both water and cosolvent molecules could be involved in solvation. Thus in mixed aqueous solvents, molecules of both kinds may be regarded as ligands that are coordinated to or associated with each metal ion.

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