

Formation constants of binary chelates of Cu(II)/Ni(II) with 4-chloro and 4-amino picolinic acid N-oxide in aquo organic media

SHIVA RAJ, SARALA DEVI CH, SESHIKALA G
and RAM REDDY M G*

Department of Chemistry, Osmania University, Hyderabad 500007, India

MS received 27 May 1991; revised 9 December 1991

Abstract. The proton ligand constants of 4-chloro and 4-amino picolinic acid N-oxide and the formation constants of corresponding binary chelates of Cu(II) and Ni(II) have been measured at 30°C and 0.1 M ionic strength in varying percentages of dioxane–water, acetone–water, ethanol–water and isopropanol–water. 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-methoxy picolinic acid N-oxide.

Keywords. 4-Chloro and 4-amino picolinic acid N-oxide; mixed aqueous solvents; solvent effect; formation constants.

1. Introduction

The formation constants of transition metal chelates with picolinic acid N-oxide (picO) and its 4-substituted compounds reported earlier by Sudhakar Reddy and Ram Reddy (1981) revealed that substitution in the fourth position by groups such as hydroxy, methoxy, ethoxy and propoxy increased the stabilities. Seshikala and Ram Reddy (1986, 1987) and Sarala Devi *et al* (1990) 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-X-picolinic acid N-oxide systems (X = Cl and NH₂). The different trends observed have been explained in terms of solvent basicity, structuredness of water and protonation of organic solvents.

2. Experimental

The ligands were prepared in the laboratory by known procedures (Proft and Steinke 1961). The solvents used were dioxane, isopropanol, acetone and ethanol with percentages ranging from 30 to 70. The pH correction factor (Van Uitert *et al* 1953) and

* For correspondence

Table 1. Proton ligands constants of 4-X-picO and formation constants of Cu(II)/Ni(II)-4-X-picO in different aquo-organic solvents ($T = 30^\circ\text{C}$ and $\mu = 0.1 \text{ M}$ mole).

% v/v Organic component	Mole fraction	1/ ϵ	pK_a	4-Cl picO				4-NH ₂ picO				
				Cu(II)		Ni(II)		Cu(II)		Ni(II)		
				log K_1	log K_2	log K_1	log K_2	pK_a	log K_1	log K_2	log K_1	log K_2
<i>Dioxane-water</i>												
0	0	0.0130	3.32	3.50	2.97	3.38	2.91	5.20	5.00	3.48	3.70	3.27
30	0.083	0.0195	4.35	4.35	3.68	3.17	2.94	6.40	5.85	4.19	3.97	3.22
40	0.123	0.0234	4.68	4.61	3.65	3.32	2.97	6.60	5.96	4.62	4.35	4.16
50	0.174	0.0293	5.02	5.12	3.79	3.58	3.01	6.82	6.92	6.62	5.39	4.86
60	0.240	0.0388	5.21	5.27	3.71	3.87	3.11	7.39	7.09	5.96	6.17	5.36
70	0.329	0.0565	5.68	5.43	3.59	3.93	3.02	7.83	7.21	6.00	6.22	5.50
<i>Acetone-water</i>												
30	0.094	0.0160	4.09	3.99	3.12	3.01	2.06	6.11	5.78	4.07	4.52	3.45
40	0.140	0.0177	4.21	4.31	3.33	3.29	2.12	6.24	5.92	4.57	5.01	3.85
50	0.195	0.0197	4.57	4.58	3.69	3.67	2.95	6.51	6.58	4.42	5.38	4.13
60	0.270	0.0225	4.97	4.89	3.48	3.71	3.00	7.13	6.92	5.83	6.31	4.31
70	0.365	0.0264	5.45	5.05	3.15	4.00	3.06	7.38	7.11	5.92	6.81	4.81
<i>Isopropanol-water</i>												
30	0.092	0.0170	3.72	3.69	2.98	2.77	2.19	5.78	5.51	4.09	4.29	3.39
40	0.132	0.0190	3.92	3.91	3.09	2.97	2.22	5.87	5.55	4.28	4.32	3.19
50	0.192	0.0220	4.03	4.22	3.42	3.08	2.26	6.07	5.82	4.70	5.05	4.21
60	0.262	0.0260	4.28	4.23	3.50	3.12	3.32	6.32	6.04	4.51	5.83	4.52
70	0.370	0.0384	4.31	4.19	3.31	3.62	3.93	6.64	6.50	5.27	6.09	5.21
<i>Ethanol-water</i>												
30	0.116	0.0160	3.77	3.59	2.99	3.01	2.17	5.38	5.41	3.12	4.40	3.00
40	0.169	0.0175	3.81	3.81	3.39	3.17	2.26	5.87	5.54	4.19	4.50	3.52
50	0.231	0.0194	3.96	3.92	3.21	3.31	2.38	6.10	5.91	4.77	5.27	4.28
60	0.318	0.0220	4.01	4.01	3.71	3.42	3.12	6.24	6.41	4.92	5.98	4.72
70	0.470	0.0272	4.18	4.09	3.43	3.93	3.00	6.54	6.59	5.31	5.98	4.81

the values of dielectric constants for different organic solvent-water mixtures were calculated from literature data (Akerloff 1932; Hall and Gibbson 1953; Gentile and Dadger 1968). The proton ligand and metal ligand constants were determined using the graphical method of Irving and Rossotti (1954) applicable to mixed aqueous solvents. The data are presented in table 1. The ionic strength was maintained at 0.1 M by the addition of calculated amounts of 1 M KNO_3 . The plots of pK_a vs. $1/\epsilon$ and mole fraction (N) and $\log K_1$ vs. $1/\epsilon$ and mole fraction (N) for Cu(II)-4-NH₂picolinic acid N-oxide chelates are given in figures 1 and 2, to represent the systems studied.

3. Results and discussion

The pK_a values of the ligands in the present study increased with increase in v/v percentages of each of the four mixed aqueous solvents. The pK_a values of 4-Cl picolinic acid N-oxide are lower than the corresponding values of the unsubstituted compound (Seshikala and Ram Reddy 1986) in all aquo organic media. This is due to the presence of the electron-withdrawing chloro group in the fourth position. The pK_a values of 4-NH₂picO increased both in aqueous and aquo organic media when compared to picO and 4-OCH₃picO values reported by Seshikala and Ram Reddy (1986, 1987). This is attributed to the presence of the amino group in the fourth position. The increase in pK_a values with dielectric constant of the medium may be

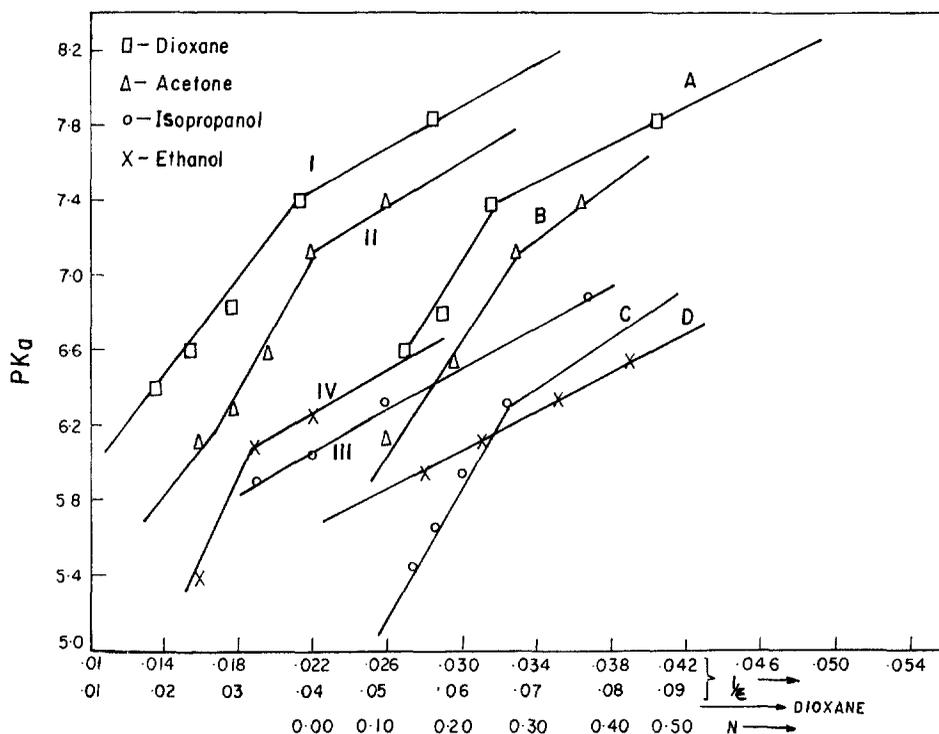


Figure 1. Variation of pK_a of 4-NH₂ picO with dielectric constant and mole fraction of solvents. Dielectric constants of solvents - (I) dioxane; (II) acetone; (III) isopropanol; (IV) ethanol. Mole fraction of solvents - (A) dioxane; (B) acetone; (C) isopropanol; (D) ethanol.

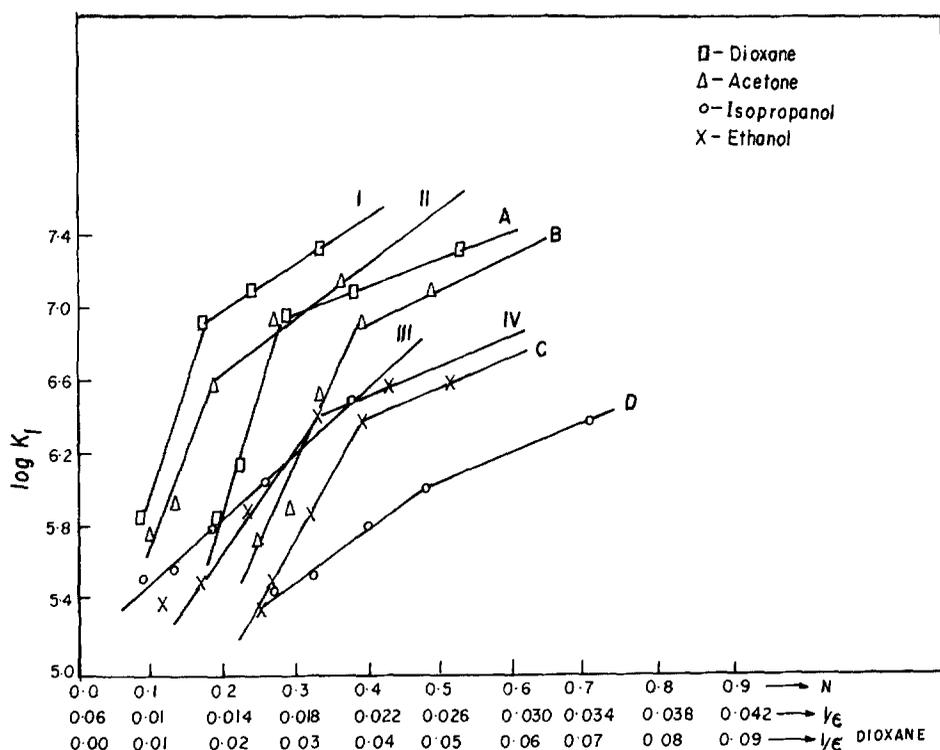


Figure 2. Variation of $\log K_1$ of Cu(II)-4-NH_2 picO with dielectric constant and mole fraction of solvents. Mole fraction of solvents – (I) dioxane; (II) acetone; (III) isopropanol; (IV) ethanol. Dielectric constants of solvents – (A) dioxane; (B) acetone; (C) isopropanol, (D) ethanol.

due to increased proton solvation by the organic solvent. The plots of pK_a of ligands vs. mole fraction and also the reciprocal of dielectric constant (figure 1) reveal that there is a linear relationship up to 60% v/v of dioxane–water, acetone–water and 50% v/v ethanol–water and for all the percentages of isopropanol–water. Above these percentages, another straight line with a different slope is observed. 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 pK_a of the ligands studied follow the sequence:

4-Cl picO: dioxane–water > acetone–water > isopropanol–water > ethanol–water.

4-NH₂ picO: dioxane–water > acetone–water > ethanol–water > isopropanol–water.

It is observed that the pK_a 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 pK_a values are maximum in 70%

dioxane–water which may be attributed to the fact that dioxane has a low dielectric constant and no hydrogen-bonded structure. Similar observations were made by Sarala Devi *et al* (1990) in their study of picO and 4-OCH₃ picO systems.

The formation constants of Cu(II)/Ni(II) 4-Cl/4-NH₂ picO 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_1 vs. mole fraction and $1/\epsilon$ show linearity upto a certain percentage composition of the organic solvent. From the observed log K_1 values, the compositions that correspond to maximum structuredness of water at 30°C are close to 0.318 mole fraction of ethanol–water, 0.195 mole fraction of acetone–water and 0.174 mole fraction of dioxane–water for both 4-chloro and 4-amino picO systems. 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 constants are generally higher in dioxane–water medium except for Ni(II)-4-NH₂ picO chelates, where the values are higher in the acetone–water medium. This may be due to the smaller solvation capacity of acetone compared to other solvents. The formation constant values of Cu(II)/Ni(II)-4-Cl/4-NH₂ picO chelates in isodielectric mixtures at $1/\epsilon = 0.0195$ follow the sequence:

acetone–water > ethanol–water > isopropanol–water > dioxane–water.

The corresponding mole fractions of various aquo-organic media at $1/\epsilon = 0.0195$ follow the sequence: ethanol–water > acetone–water > isopropanol–water > dioxane–water. The fact that ethanol and isopropanol have exchanged places may be attributed to smaller solvation capacity of acetone compared to ethanol. Similar observations were made by Choudhury and coworkers (Choudhury *et al* 1981, Choudhury and Kole 1981; Kole and Choudhury 1981). From these observations, it may be concluded that pK_a and log K_1 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 co-solvent 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.

1:2 chelates are formed with both the ligands studied and it is observed from the data that log K_2 values show trends similar to those observed for log K_1 .

Acknowledgement

The authors wish to thank Prof T Navaneeth Rao for his keen interest.

References

- Akerloff J 1932 *J. Am. Chem. Soc.* **54** 4180
- Choudhury A K and Kole N 1981 *J. Indian. Chem. Soc.* **58** 368
- Choudhury A K, Kole N and Ghosh S P 1981 *J. Indian Chem. Soc.* **58** 243, 368
- Gentile P S and Dadger A 1968 *J. Chem. Eng. Data* **13** 236
- Hall J L and Gibson J R 1953 *J. Am. Chem. Soc.* **75** 1991

- Irving H M and Rossotti R S 1954 *J. Chem. Soc.* 2904
Kole N and Choudhury A K 1981 *J. Inorg. Nucl. Chem.* **43** 2474
Proft E and Steinke W 1961 *J. Prakt. Chem.* **13** 58
Sarala Devi Ch, Seshikala G, Krishna Rao B and Ram Reddy M G 1990 *Orient. J. Chem.* **6** 173
Seshikala G and Ram Reddy M G 1986 *Indian J. Chem.* **A25** 295
Seshikala G and Ram Reddy M G 1987 *Proc. Natl. Acad. Sci. India* **57A** IV
Sudhakar Reddy M and Ram Reddy M G 1981 *Indian J. Chem.* **A20** 1134
Van Uitert L G, Cornelius W C and Douglas B E 1953 *J. Am. Chem. Soc.* **75** 2736