

## Formation Constants of Metal Complexes of Cu(II) and Dy(III) with N-Substituted Anthranilic Acids in Different Aquo-Organic Solvents

B. KRISHNA RAO†, K. LAXMI and CH. SARALA DEVI\*  
Department of Chemistry, Nizam College, Osmania University  
Hyderabad-500 001, India  
E-mail: dr\_saraladevich@yahoo.com

The formation constants of Cu(II) and Dy(III) with N-substituted anthranilic acids have been determined potentiometrically by varying proportions of dioxane-water, acetone-water, isopropanol-water and ethanol-water at 30 °C and 0.1 M ionic strength. The results are discussed with reference to the change in dielectric constant of water in the presence of organic solvent, change in structure and hydrogen bonding in water, relative solvent basicity and proton solvation by the organic solvent.

**Key Words:** Formation constants, N-Substituted anthranilic acids, Cu(II) and Dy(III) complexes.

### INTRODUCTION

The study of formation constants of N-substituted anthranilic acids with lanthanides have been reported earlier<sup>1</sup>. The stability constants of ternary complexes of lanthanides with N-substituted anthranilic acids in presence of aminopolycarboxylic acids have also been reported earlier<sup>2</sup>. The survey of literature reveals that the formation constants were determined in mixed aqueous solvents as many organic reagents and their metal complexes were sparingly soluble in water. The present paper reports formation constants of Cu(II) and Dy(III) complexes of N-substituted anthranilic acids in different solvent compositions.

### EXPERIMENTAL

All the chemicals used were of AR Grade. The N-methyl anthranilic acid and N-phenyl anthranilic acid were synthesized in laboratory by known methods<sup>3,4</sup>. The solutions of these ligands were prepared in doubly distilled water. The metal ion solutions were standardized by known methods<sup>5</sup>.

---

†Department of Chemistry, University College of Engineering, Kakatiya University, Warangal-506 009, India.

The metal-ligand ratio was maintained at 1:5. The ionic strength was maintained as 0.1 M by adding KNO<sub>3</sub> solution (1 M). Titrations were carried out in 30, 40, 50, 60 and 70 % v/v organic solvent-water mixtures. The organic solvents used were dioxane, acetone, isopropanol and ethanol. The pH correction factor<sup>6</sup> at 30 °C was obtained for each composition of the four different organic solvents following the procedures of Gentile and Dadger<sup>7</sup>. The values of dielectric constants of the different organic solvent-water mixtures were calculated from the data given by Akerlof<sup>8</sup> and Gibson<sup>9</sup>. The pK<sub>a</sub> values of ligands employed in the present study and their respective formation constants with Cu(II) and Dy(III) were calculated using the expressions of Irving and Rossotti. These values were further refined using the BEST programme<sup>10</sup>.

## RESULTS AND DISCUSSION

The 1:1 formation constants of Cu(II) and Dy(III) with N-methyl anthranilic acid (N-Me.An.A) and N-phenyl anthranilic acid (N-Ph.An.A) in different aqueous solvents have been determined using Irving and Rossotti method. The dissociation constants and stability constants of the corresponding binary systems are presented in Tables 1 and 2, respectively. Cu(II) for transition metals, Dy(III) for lanthanides have been chosen for the above study due to their greater stability. The data could not be obtained for N-phenyl anthranilic acid in 30 and 40 % (v/v) composition of isopropanol-water and ethanol-water medium on account of precipitation.

Solvent effects on proton-ligand and metal-ligand formation constants are mainly interpreted in terms of electrostatic and non-electrostatic effects such as dielectric constant of the medium, structure and basicity of solvent, hydrogen bonding between solute and solvent-interactions. On the addition of organic solvent, the structure of water is gradually broken down, when the concentration of the organic solvent is very high, it solvates protons. The electrostatic effect is assumed to be significant primarily for the protonation of charged bases as a results of changing solvent dielectric<sup>11</sup>.

In the present study, it is observed that there is a linear relationship between the pK<sub>a</sub> of N-substituted anthranilic acids and mole fraction of organic solvent and also reciprocal of dielectric constant of the medium (Figs. 1 and 2). A linear relationship is found between mole fraction of each solvent and pK<sub>a</sub> of ligand (Fig. 1). The plot of reciprocal of dielectric constant against pK<sub>a</sub> for N-Me.An.A (Fig. 2) reveals that there is nearly linear relationship up to 60 % (v/v) percentage of each organic solvent-water mixture. Above these percentages, another straight line with a different slope is observed. Below 30 % (v/v) composition in the plot of pK<sub>a</sub> vs. 1/ε, a deviation from linearity is observed. This may be attributed to preferential orientations of water molecules around the ligand species, thus resulting in high dielectric constant environment around.

TABLE-1  
 FORMATION CONSTANTS OF METAL COMPLEXES OF N-METHYL  
 ANTHRANILIC ACID IN DIFFERENT (v/v) PERCENTAGES OF  
 AQUO-ORGANIC SOLVENTS AT 303 K AND 0.10 M IONIC STRENGTH

AA	BB	CC	pK <sub>a</sub>	Cu(II)			Dy(III)		
				log K <sub>1</sub>	log K <sub>2</sub>	log β <sub>2</sub>	log K <sub>1</sub>	log K <sub>2</sub>	log β <sub>2</sub>
Dioxane-water									
30	0.083	0.019	5.72	4.24	3.00	7.24	3.49	3.16	6.65
40	0.123	0.023	6.12	4.38	3.07	7.45	3.72	3.19	6.91
50	0.174	0.029	6.44	4.56	3.45	8.01	4.03	3.49	7.52
60	0.240	0.038	6.94	4.82	3.59	8.41	4.19	3.52	7.71
70	0.329	0.056	7.42	5.36	3.80	9.16	4.49	3.76	8.25
Acetone-water									
30	0.094	0.016	5.67	4.12	2.92	7.04	3.41	3.15	6.56
40	0.140	0.017	5.98	4.21	3.01	7.22	3.62	3.18	6.80
50	0.195	0.019	6.25	4.39	3.34	7.73	3.78	3.38	7.16
60	0.270	0.022	6.74	4.58	3.49	8.07	3.97	3.44	7.41
70	0.365	0.026	7.13	5.08	3.68	8.76	4.26	3.57	7.83
Isopropanol-water									
30	0.092	0.017	5.63	3.92	2.86	6.78	3.35	3.12	6.47
40	0.132	0.019	5.90	3.99	2.99	6.98	3.45	3.15	6.60
50	0.191	0.022	6.10	4.03	3.29	7.32	3.54	3.21	6.75
60	0.262	0.026	6.34	4.15	3.37	7.52	3.62	3.29	6.91
70	0.370	0.038	6.54	4.52	3.47	7.99	4.06	3.45	7.51
Ethanol-water									
30	0.116	0.016	5.40	3.81	2.82	6.63	3.34	3.16	6.50
40	0.169	0.017	5.52	3.89	2.94	6.83	3.40	3.25	6.65
50	0.231	0.019	5.62	3.94	3.26	7.20	3.47	3.28	6.75
60	0.318	0.022	5.94	4.10	3.29	7.47	3.66	3.30	6.96
70	0.420	0.027	6.08	4.35	3.35	7.70	3.85	3.36	7.21

AA = Solvent composition % (v/v); BB = Mole fraction (N); CC = Reciprocal of dielectric constants (1/ε).

The linear variation of pK<sub>a</sub> with 1/ε for 30-60 % (v/v) composition of all solvent-water mixtures indicates that the structuredness of water remains to an appreciable content up to this composition. The protons are accommodated in the interstices of the tetrahedral lattice. The plot of pK<sub>a</sub> vs. 1/ε in the region of above 60 % (v/v) gives a straight line with different slope for all solvent-water mixtures. In this region aqueous solvation shell is dispersed by the interposition of the organic solvent molecules and the participation of the organic solvent molecules in the solvation of water cannot be ignored.

For a particular composition of solvent-water mixtures, the reciprocal of dielectric constant changes in the following order:

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

TABLE-2  
 FORMATION CONSTANTS OF METAL COMPLEXES OF N-PHENYL  
 ANTHRANILIC ACID IN DIFFERENT (v/v) PERCENTAGE OF  
 AQUO-ORGANIC SOLVENTS AT 303 K AND 0.10 M IONIC STRENGTH

Solvent composition % (v/v)	pK <sub>a</sub>	Cu(II) system log K <sub>f</sub>	Dy(III) system log K <sub>f</sub>
Dioxane-water			
30	5.18	3.31	3.80
40	5.47	3.43	3.83
50	5.90	3.58	3.90
60	6.40	3.85	4.02
70	6.88	4.12	4.24
Acetone-water			
30	5.07	3.22	3.47
40	5.32	3.31	3.62
50	5.68	3.40	3.78
60	6.12	3.53	3.92
70	6.48	3.82	4.13
Isopropanol-water			
30	—	—	—
40	—	—	—
50	5.37	3.24	3.48
60	5.64	3.34	3.74
70	5.96	3.39	3.91
Ethanol-water			
30	—	—	—
40	—	—	—
50	5.10	3.03	3.27
60	5.46	3.15	3.62
70	5.60	3.30	3.72

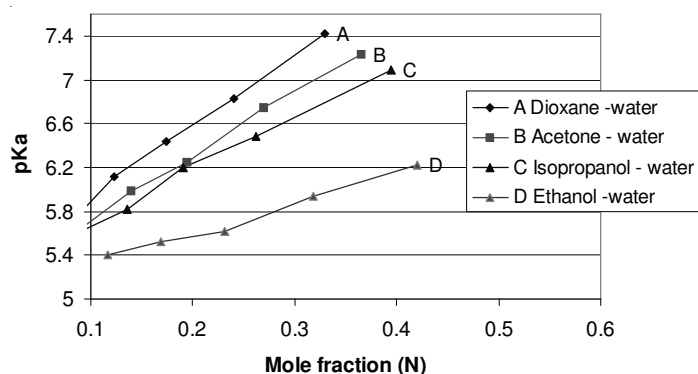


Fig. 1. Plot of pK<sub>a</sub> N-methyl anthranilic acid vs. mole fraction

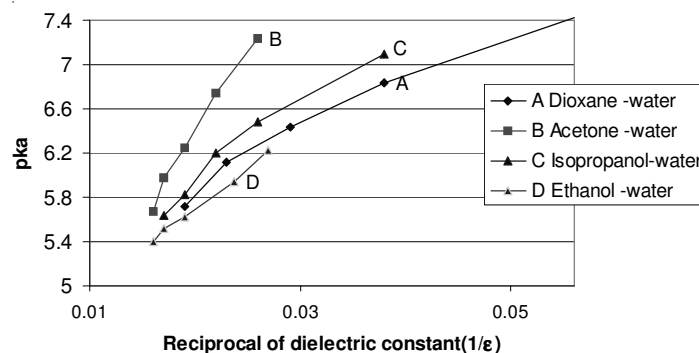


Fig. 2. Plot of  $pK_a$  N-phenyl anthranilic acid vs. Reciprocal of dielectric constant

However, when the stabilities of proton-ligand complexes are considered, the stability order does not follow the sequence of dielectric constant of the solvent. For the same v/v composition, the  $pK_a$  of the ligands in the present study follows the sequence.

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

The sequence order is similar to that of dielectric constant except that acetone and isopropanol have exchanged places.

The stabilities of proton-ligand complexes of N-methyl anthranilic acid and N-phenyl anthranilic acid are maximum in dioxane-water. This may be ascribed to the fact that dioxane in comparison to other solvents has low dielectric constant. As expected, the stability is least in the case of ethanol-water mixture because of high dielectric constant.

The stability constants of complexes of N-methyl anthranilic acid and N-phenyl anthranilic acid with Cu(II)/Dy(III) of this study increase with the increase of mole fraction of solvent. Plots of  $\log K_1$  vs. mole fraction (or)  $1/\epsilon$  for N-methyl anthranilic acid complexes (Figs. 3 and 4) are generally linear, but some deviations are observed with high solvent composition. This deviation may be due to gradual displacement of water molecules in the hydration sphere of metal ions by the organic solvent molecules at higher concentration of the latter, which may further influence the non-electrostatic interactions.

The order of dielectric constants of the mixed aqueous solvents is: dioxane-water > isopropanol-water > acetone-water > ethanol-water. A comparison of the values of formation constants of metal-ligand complexes in different organic solvent mixtures follows the sequence: dioxane-water > acetone-water > isopropanol-water > ethanol-water. The above order is in accordance of the order of reciprocal of dielectric constants of solvents under study except acetone has taken second place. This may be ascribed to lack of hydrogen bonding and the least proton solvation capacity. Such observation have also been made by other workers<sup>12-22</sup>.

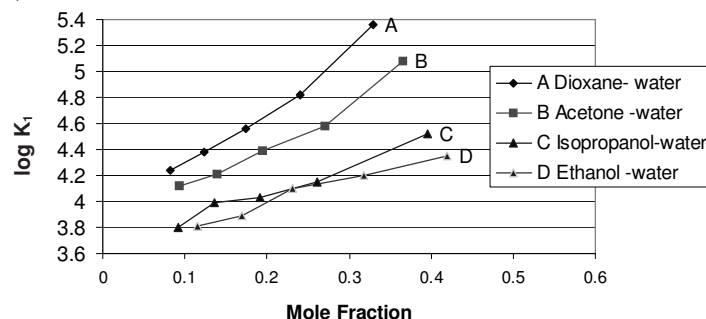


Fig. 3. Plot of log K<sub>1</sub> of Cu(II) N-methyl anthranilic acid vs. mole fraction of solvents

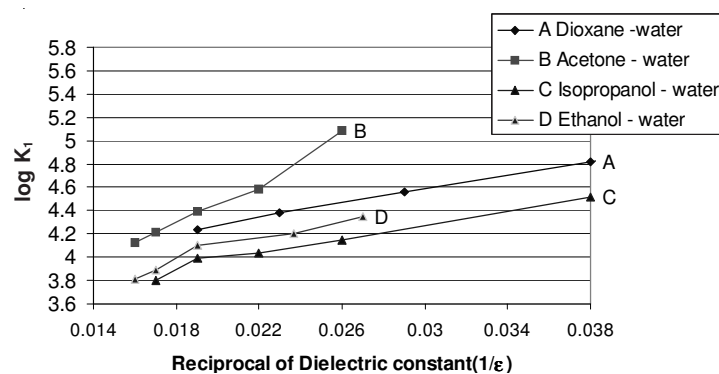


Fig. 4. Plot of log K<sub>1</sub> of Cu(II) N-methyl anthranilic acid vs. Reciprocal of dielectric constant

### Conclusion

It is observed that 1:2 complexes are formed only for N-methyl anthranilic acid with Cu(II) and Dy(III) studied in various aquo-organic solvents employed, while N-phenyl anthranilic acid formed 1:1 complexes only with Cu(II) and Dy(III). The log K<sub>1</sub> values in Cu(II)-N-methyl anthranilic acid are greater than the values of Dy(III)-N-methyl anthranilic acid systems in all aquo-organic solvents. In the case of N-phenyl anthranilic acid, the order of stabilities with respect to metals is in reverse *i.e.* Dy(III) > Cu(II). This may be ascribed to the monodentate nature of N-phenyl anthranilic acid which can form more stable complexes with tripositive Dy(III) ion compared to dipositive Cu(II) ion.

### REFERENCES

1. B.K. Rao, K. Ram and M.G.R. Reddy, *Acta Cien. Indica*, **14C**, 153 (1988).
2. B.K. Rao, Ch. S. Devi and M.G.R. Reddy, *Acta Cien. Indica*, **14C**, 27 (1988).
3. P.A. Petyunin, V.S. Shkiyaav and M.E. Konshin, *Zhur Priklad Khim.*, **33**, 1428 (1960).

4. C.F.H. Allen and C.H.W. MacKee, *Org. Synth.*, **19**, 16 (1939).
5. A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, Longman London, edn. 3, p. 160 (1971).
6. L.G. Van Uitert, W.C. Fermeois and B.E. Douglas, *J. Am. Chem. Soc.*, **75**, 2736 (1953).
7. P.S. Gentile and A. Dadger, *J. Chem. Eng. Data*, **13**, 236 (1968).
8. J. Akerlof, *J. Am. Chem. Soc.*, **54**, 4180 (1932).
9. F.E. Critchfield, J.L. Hall and J.R. Gibson Jr., *J. Am. Chem. Soc.*, **75**, 1991 (1953).
10. R.I. Motekaitis and A.E. Martell, *Can. J. Chem.*, **60**, 2403 (1982).
11. D.B. Rorabacher, W.J. MacKellar, F.R. Shu and M.S. Bonavita, *Anal. Chem.*, **43**, 561 (1971).
12. A.K. Chaudhury and N. Kole, *J. Indian Chem. Soc.*, **58**, 368 (1981).
13. A.K. Chaudhury, N. Kole and S.P. Ghosh, *J. Indian Chem. Soc.*, **58**, 243 (1981).
14. N. Kole and A.K. Chaudhury, *J. Inorg. Nucl. Chem.*, **43**, 2474 (1981).
15. G. Shashikala, C.C. Rebello and M.G.R. Reddy, *Proc. Nat. Acad. Sci. (India)*, **57A** (1987).
16. Shivaraj, Ch. S. Devi, G. Shashikala and M.G.R. Reddy, *Proc. Nat. Acad. Sci. (Chem. Sci.)*, **104**, 15 (1992).
17. Ch. V.R. Reddy and M.G.R. Reddy, *Indian J. Chem.*, **32A**, 233 (1993).
18. C.N. Reddy, Ch. S. Devi, Shashikala and M.G.R. Reddy, *Indian J. Chem.*, **34A**, 716 (1995).
19. G.S. Reddy, B. Sireesha, Ch. S. Devi, R. Mohiuddin, C.G. Kumari and M.G.R. Reddy, *J. Indian Chem. Soc.*, **75**, 20 (1998).
20. G.S. Reddy, B. Sireesha, K. Laxmi and Ch. S. Devi, *Bull. Pure Appl. Sci.*, **24C**, 57 (2005).
21. G.S. Reddy, B. Sireesha, K. Laxmi and Ch. S. Devi, *J. Teach. Res. Chem.*, **13**, 47 (2006).
22. K. Laxmi, G. Bhargavi, B. Sireesha and Ch. S. Devi, *Bull. Chem. Soc. Ethiopia*, **20**, 161 (2006).

(Received: 6 September 2007;

Accepted: 2 May 2008)

AJC-6558