

## Effect of various mixed aqueous solvents on the stability constants of Cu(II) chelates with piperidine-2-carboxylic acid

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**Abstract.** The ligand dissociation constants and the formation constants of Cu(II) piperidine-2-carboxylic acid chelates have been measured in varying proportions of methanol-water, ethanol-water, acetone-water, isopropanol-water and dioxane-water at 30°C and 0.10 M ionic strength. The results are discussed with reference to the change in the dielectric constant of water in the presence of the organic solvent, change in structure and hydrogen bonding in water, relative solvent basicity and proton solvation by the organic solvent. The relatively greater contribution to the stability of the metal chelate by the O-M link as compared to the N-M link has been suggested on the basis of the observed solvent effects on stabilities.

**Keywords.** Piperidine-2-carboxylic acid; mixed aqueous solvents; solvent effects; formation constants.

### 1. Introduction

Very little work has been reported on the systematic investigation of dissociation equilibria of ligands and metal chelate formation constants in mixed aqueous solvents. Yet, on the addition of organic solvents, the properties of water undergo marked changes. It has been reported (Irving and Rossotti 1956) that the stabilities of N-M bonds are much less affected than those of the O-M link, on addition of an organic solvent to water. In the present study, we report the effect of solvent characteristics on the formation constants of Cu(II) with piperidine-2-carboxylic acid to determine the relative importance of the effect of solvent properties on compounds containing both O-M and N-M bonds.

### 2. Experimental

All reagents were AR or GR grade. pH measurements were made using a 'Century' pH meter with a combined glass and calomel electrode. The following solutions (total volume 50 ml) were titrated against standard 0.1 M KOH:

- (i)  $\text{HNO}_3$  ( $4.00 \times 10^{-3}$  M) + solvent
- (ii)  $\text{HNO}_3$  ( $4.00 \times 10^{-3}$  M) + ligand ( $2.00 \times 10^{-3}$  M) + solvent
- (iii)  $\text{HNO}_3$  ( $4.00 \times 10^{-3}$  M) + ligand ( $2.00 \times 10^{-3}$  M) +  $\text{Cu}(\text{NO}_3)_2$  ( $4.00 \times 10^{-4}$  M) + solvent

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The ionic strength was maintained at 0.10 M by adding calculated amounts of 1 M  $\text{KNO}_3$  solution. The metal ligand ratio was maintained at 1 : 5. Titrations were carried out in 0, 30, 40, 50, 60 and 70% v/v organic solvent-water mixtures. The organic solvents used were methanol, ethanol, isopropanol, acetone and dioxane. The highest limits of the volume proportions were restricted by the solubility of the complex. The titration cell was flushed with pure nitrogen gas previously saturated with the particular solvent used in the titration cell. The pH correction factor (Van Uitert *et al* 1953) at 30°C was obtained for each composition of the five different organic solvents following the procedure of Gentile and Dadgar (1968).

The dissociation constants of piperidine-2-carboxylic acid and Cu(II)-ligand formation constants in the various mixed aqueous solvents were computed using the least squares treatment of the Irving and Rossotti formulae applicable to mixed aqueous solvents, the data is presented in table 1. The average error is  $\pm 0.04$ . The values of dielectric constant of the different organic solvent-water mixtures were calculated or obtained from the data given by Akerlof (1932) and Hall and Gibson (1953).

### 3. Results and discussion

There is apparently no simple relationship between the stability of complexes and different solvent characteristics. As reviewed by Franks and Ives (1966) the structural and related properties of organic solvent-water mixtures are influenced by a complex array of parameters. Bates *et al* (1966) have indicated that both electrostatic and non-electrostatic effects must be considered to describe adequately the observed trends in acid dissociation and chelate formation constants. In subsequent work they have characterized the latter effect as the 'solvent basicity' effect. In fact, the non-electrostatic component is probably best characterized in terms of the separate contributions of proton solvation and solvation of the conjugate acid and the base species to the overall changes in dissociation constants. Rorabacher *et al* (1971) have concluded that solvation effects on the conjugate acid and base, while sensitive to short range structural changes, are much less influential in determining the gross solvent effects. The electrostatic component of the solvent effect is assumed to be significant primarily for the protonation of charged bases as a result of the changing solvent dielectric.

In the present study, the expected linear relationship between  $pK_a$  and the mole fraction of the organic solvent is observed for each of the five two-component solvent systems. Plots of  $pK_a$  vs. mole fraction yield straight lines of different slopes for each solvent system. A plot of  $pK_a$  vs. the reciprocal of dielectric constant ( $1/D$ ) likewise, gives rise to linear relationships upto 60% (v/v) organic solvent-water mixtures. This shows that the relationship advanced by Wynne-Jones (1933) is also valid for a single ligand in various mixed solvents throughout a dielectric constant range of 65 to 30. Below a dielectric constant of 30, the  $pK_a$  as a function of  $1/D$  deviates from linearity. This deviation has been attributed to the fact that the organic solvent-water mixtures are generally treated as homogeneous media of uniform dielectric constant (Glasstone *et al* 1941). However, it is possible that in such solutions, there are preferential orientations of the water molecules around the ions, thus placing them in an environment of higher dielectric constant. Since the measured dielectric constant is that of the bulk of the medium, a lower  $pK_a$  is expected and observed in the present study.

Log K for Cu(II) piperidine-2-carboxylic acid was plotted against the reciprocal of

**Table 1.** Formation constants of Cu(II) chelates of piperidine-2-carboxylic acid in different mixed aqueous solvents at 30°C and 0.10 M ionic strength.

Solvent composition (% v/v)	Mole fraction	Reciprocal of dielectric constant $1/D$	$pK_a$	$\log K_1$	$\log K_2$	$\log \beta_2$
<i>Isopropanol</i>						
0	0	0.013	10.47	7.49	6.04	13.53
30	0.09	0.017	10.56	8.15	6.33	14.48
40	0.13	0.018	10.57	8.41	6.51	14.92
50	0.19	0.021	10.59	8.68	6.68	15.36
60	0.26	0.026	10.65	9.09	7.33	16.42
70	0.28	0.0348	10.71	9.20	7.24	16.44
<i>Dioxane</i>						
0	0	0.013	10.47	7.49	6.04	13.53
30	0.08	0.019	10.53	8.60	6.42	15.02
40	0.12	0.023	10.56	8.72	6.80	15.52
50	0.17	0.029	10.60	8.94	7.83	16.77
60	0.24	0.038	10.75	9.37	7.75	17.12
70	0.25	0.056	10.81	9.92	8.52	18.44
<i>Acetone</i>						
0	0	0.013	10.47	7.49	6.04	13.53
30	0.09	0.016	10.50	7.01	6.40	13.41
40	0.14	0.017	10.55	7.61	6.80	14.41
50	0.19	0.019	10.60	9.19	7.48	16.67
60	0.27	0.225	10.63	9.30	7.80	17.10
70	0.29	0.028	10.67	9.46	8.54	18.00
<i>Ethanol</i>						
0	0	0.013	10.47	7.49	6.04	13.53
30	0.116	0.016	10.53	8.47	7.09	15.56
40	0.169	0.017	10.61	8.58	7.18	15.76
50	0.231	0.019	10.68	8.78	7.25	16.03
60	0.318	0.021	10.73	9.02	7.72	16.74
70	0.355	0.026	10.76	9.37	8.13	17.50
<i>Methanol</i>						
0	0	0.013	10.47	7.49	6.04	13.53
30	0.16	0.015	10.50	8.51	6.94	15.45
40	0.23	0.016	10.52	8.62	6.91	15.53
50	0.30	0.017	10.55	8.74	7.03	15.77
60	0.40	0.019	10.59	8.95	7.23	16.18
70	0.47	0.022	10.63	9.14	7.86	17.00

dielectric constant for the different organic solvent-water mixtures. A linear relationship is noted upto 60% (v/v) of the organic solvent-water mixtures after which deviations are observed. However, due to solubility restrictions, the  $\log K$  vs.  $1/D$  relationship could not be investigated beyond 70% v/v. An interesting feature of the linear relationship is that for the alcohol water mixtures (methanol, ethanol and isopropanol-water), the slopes of the straight lines are identical, but are markedly different from those for the acetone, dioxane-water mixtures. This observation reveals that methanol, ethanol and isopropanol may be placed in one group whereas acetone

and dioxane are in another group with respect to their solvent effect on metal chelation (Gentile *et al* 1963).

A plausible explanation for the above behaviour on the basis of the bulk and local dielectric constants of the media has been advanced by Gentile and Dadgar (1968). It appears that for the alcohol-water mixtures, the local dielectric constant is lower than that of acetone-, dioxane-water mixtures. The lower the local dielectric constant, the higher is the expected  $\log K$  value and this was found to be true experimentally. However, it would be naive to justify this observed trend in  $\log K$  values on the basis of the above explanation alone, and hence, a better understanding of the influence of the other factors is essential.

It has been suggested (Irving and Rossotti 1956) that since O-metal bonds are more influenced by the composition of the solvents than N-metal bonds, the effect of solvent composition on the stabilities of chelates containing the O-metal-N link might give an indication of the relative importance of these bonds. The  $\log \beta_2$  of Cu(II) with piperidine-2-carboxylic acid in aqueous medium at 30°C and 0.1 M ionic strength is 13.53. The highest value for  $\log \beta_2$  observed for the same system in 70% v/v dioxane-water is 18.44. The overall stability constant  $\log \beta_2$  in the aqueous and the dioxane-water mixtures varies by 4.91 log units. This may suggest that the O-M bond in the chelate is stronger than the N-M bond.

#### 4. Conclusions

The different solvent characteristics mentioned above influence the  $pK_a$  of the ligand in the following manner:

- (1)  $pK_a$  increases with decrease of the dielectric constant and vice versa;
- (ii) on decreasing the extent of hydrogen bonding in water by adding an organic solvent, the proton accepting property of water increases. Hence the dissociation constant ( $K_a$ ) increases or the ligand becomes a weaker base;
- (iii) increased proton solvation by the organic solvent increases the  $pK_a$  of the ligand.

For a particular composition of solvent-water mixture say 60% v/v, the reciprocal of the dielectric constant changes in the following order:

dioxane-water > isopropanol-water > acetone-water > ethanol-water > methanol-water.

For the same v/v percentage of the organic solvent-water mixture, the order of  $pK_a$  is in the order:

dioxane-water > isopropanol-water > ethanol-water > acetone-water > methanol-water.

This is the same as the order of the reciprocal of dielectric constants except that acetone and ethanol have exchanged places.

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## References

- Akerlof J 1932 *J. Am. Chem. Soc.* **54** 4180  
Bates R G, Paabo M and Robinson R A 1966 *J. Phys. Chem.* **70** 247  
Franks F and Ives D G J 1966 *Q. Rev.* **20** 1  
Gentile P S, Cefora M and Alfred V G 1963 *J. Phys. Chem.* **67** 1083  
Gentile P S and Dadgar A 1968 *J. Chem. Eng. Data* **13** 236  
Glasstone S, Laidler and Eyring T 1941 *The theory of rate processes* (New York: McGraw Hill) p. 432  
Hall J L and Gibson J R 1953 *J. Am. Chem. Soc.* **75** 1991  
Irving H and Rossotti H S 1956 *Acta Chem. Scand.* **10** 72  
Rorabacher D B, Mackellar W J, Shu F R and Bonavita M 1971 *Anal. Chem.* **43** 561  
Van Uitert L G, Fernelius W C and Douglas B E 1953 *J. Am. Chem. Soc.* **75** 2736  
Wynne-Jones W F K 1933 *Proc. R. Soc. (London)* **A140** 440