Solvent Effects on the Protonation Constants of *N,N'*-Bis(2-carbamoylethyl)ethylenediamine and the Equilibrium Constants for Its Copper(II) Complexes in Methanol–Water Mixtures

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The interactions of *N,N'*-bis(2-carbamoylethyl)ethylenediamine (bcen) with copper(II) have been investigated as a function of solvent composition in methanol–water mixtures by a potentiometric technique. Each of the two protonation constants of the ligand passes through a minimum at 80% (w/w) methanol. The stability constant of the copper(II) complex exhibits an accelerating increase with increasing methanol content in the solvent, the net increase being 2 000-fold on going from water to 99% (w/w) methanol. Each of the deprotonation constants for $[Cu(bcen)]^{2+}$ and $[Cu(H_{-1}bcen)]^+$ passes through a maximum at 80% (w/w) methanol. These patterns are interpreted in terms of electrostatic effects, base solvation, and proton solvation as a function of the solvent composition.

Chemical reactions are strongly influenced by the solvent medium in which they proceed. The potential advantages of utilizing non-aqueous solvents for improving analytical methods involving metal complex formation have been noted previously.[1] However, the lack of reliable data for protonation and complex-formation constants in other than aqueous media has largely hindered the exploitation of non-aqueous approaches except on an occasional empirical basis.[1] Recent interest in this laboratory involving the influence of solvent on the kinetics of complexation and dissociation has led us to obtain information in this area. In previous studies of copper(II) complexes of diamino diamides in aqueous solution[2] and in 50% (w/w) methanol–water[3] it was noted that copper(II), after complexation with these ligands, can induce ionization of the amide protons, and the Cu–O to Cu–N bond rearrangements at the two amide sites occur in a stepwise fashion with an increase in pH. In order to gain a more detailed understanding of the effects on these reactions attributable to solvation, the protonation of *N,N'*-bis(2-carbamoylethyl)ethylenediamine, bcen, the formation of its copper(II) complex, and the Cu–O to Cu–N bond rearrangements of $[Cu(bcen)]^{2+}$ and $[Cu(H_{-1}bcen)]^+$ in several methanol–water mixtures have been studied by a potentiometric technique.

Experimental

The ligand, bcen, was the same as that reported previously.[3] All other chemicals used were of GR grade from Merck.

Measurements.—For pH measurements a Radiometer PHM 64 pH meter equipped with a GK 2401B combined electrode was used. The pH was standardized for each methanol-water solvent with an oxalate buffer (0.01 mol dm^{-3} oxalic acid + 0.01 mol dm^{-3} ammonium hydrogenoxalate in the same methanol–water solvent) and a succinate buffer (0.01 mol dm^{-3} succinic acid + 0.01 mol dm^{-3} lithium hydrogensuccinate in the same methanol–water solvent).[1] The hydrogen- and hydroxide-ion concentrations in these solvents were determined by the method of Rorabacher *et al.*[1]

Appropriate aliquots of standard solutions of the ligand or the ligand and metal ion were titrated with a standard CO_2-free sodium hydroxide solution prepared by the method of Rorabacher *et al.*[1] In all titrations the ionic strength was maintained constant by using 0.10 mol dm^{-3} $NaClO_4$ as supporting electrolyte. The solutions were protected from air by a stream of humidified prepurified nitrogen which had first been bubbled successively through two towers containing solvent of identical composition to the titration solution in order to facilitate saturation of the gas with the solvent vapour and thereby minimize evaporation. The temperature was maintained at 25.0 ± 0.1 °C during measurements. The equilibrium constants were obtained by a linear least-squares fit of the data by using an Apple II microcomputer.

Results and Discussion

Protonation Constants.—The values of the protonation constants of bcen, K_1^H and K_2^H in methanol–water solvents are listed in the Table together with values reported for this ligand in aqueous solution and in 50% (w/w) methanol–water.[2,3] As shown, each of these protonation constants passes through a minimum at approximately 80% (w/w) methanol.

The comparative trend in $\Delta \log K_j^H$ values for successive protonation of bcen as a function of solvent composition is given in Figure 1. Each of the protonation constants passes through a minimum at *ca.* 80% (w/w) methanol. A Born–Haber-type analysis indicates that $\Delta \log K_j^H$ decreases as the relative solvation of the product decreases, and as the relative solvation of the reagent increases.

The extremely small H^+ ions are strongly stabilized by solvation and very sensitive to the nature of the solvent medium. The addition of methanol to an aqueous solution initially increases the solvation stability of H^+ due to the increasing number of basic water molecules formed by breakdown of the complex water structure, resulting in a higher basicity for a methanol–water mixture relative to pure water.[4] The solvation stability of H^+ reaches a maximum at approximately 65% (w/w) methanol.[5] At higher methanol contents its molecules can replace the water molecules in the inner solvation sphere,[5] resulting in a decrease in the solvation stability of H^+. Still further increase in the methanol content decreases the solvation stability of H^+ markedly, as the central ion becomes $CH_3OH_2^+$

Table. Protonation constants for bcen and equilibium constants for its copper(II) complexes in methanol–water mixtures at 25.0 ± 0.1 C and $I = 0.10$ mol dm^{-3} ($NaClO_4$)

Methanol content (%, w/w)	log K_1^H	log K_2^H	log K_f	log K_A	log K_B
0*	8.78 ± 0.04	5.82 ± 0.03	12.58 ± 0.07	−8.08 ± 0.05	−9.33 ± 0.04
25	8.71 ± 0.04	5.63 ± 0.02	12.70 ± 0.03	−7.91 ± 0.04	−9.29 ± 0.04
50*	8.50 ± 0.03	5.05 ± 0.02	12.92 ± 0.04	−7.23 ± 0.04	−9.13 ± 0.04
65	8.17 ± 0.03	4.71 ± 0.02	13.41 ± 0.09	−6.82 ± 0.03	−8.77 ± 0.03
80	8.01 ± 0.04	4.55 ± 0.02	13.72 ± 0.01	−6.65 ± 0.04	−8.58 ± 0.03
90	8.22 ± 0.04	4.76 ± 0.03	14.33 ± 0.04	−7.00 ± 0.05	−8.81 ± 0.04
95	8.57 ± 0.04	5.10 ± 0.03	14.91 ± 0.03	−7.35 ± 0.03	−9.11 ± 0.02
99	9.25 ± 0.03	5.88 ± 0.03	15.92 ± 0.02	−8.14 ± 0.04	−9.91 ± 0.03

* From ref. 3.

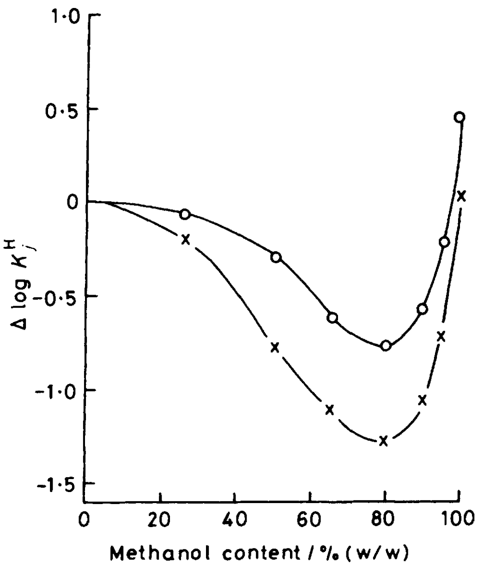

Figure 1. Trend in log K_j^H values for bcen at 25 °C as a function of the solvent composition: ○, $j = 1$; ×, $j = 2$

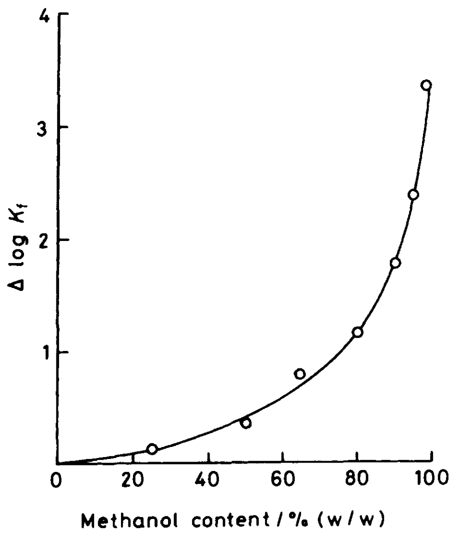

Figure 2. Trend in log K_f values for $[Cu(bcen)]^{2+}$ at 25 °C as a function of solvent composition

instead of H_3O^+.[6] The solvation of $Hbcen^+$ or bcen increases continuously with increasing methanol content. The comparative trend in K_1^H of bcen as a function of solvent composition in Figure 1 results primarily from the change in solvation of the proton, with minor contributions from changes in the solvation of $Hbcen^+$ and bcen.

Like Δ log K_1^H, Δ log K_2^H also shows a minimum at *ca.* 80% (w/w) methanol as shown in Figure 1. This behaviour is attributed to the relative solvation stabilities of H^+, $Hbcen^+$, and H_2bcen^{2+}. The solvent effect upon K_2^H is more pronounced than upon K_1^H.[7] This phenomenon arises from the increased electrostatic repulsion between an approaching proton and the positively charged sites of the protonated species, and is a function of the dielectric constant of the solvent.

Equilibrium Constants for the Interactions of Copper(II) *with bcen.*—The complexation reactions of copper(II) with bcen in methanol–water mixtures are very fast. During titration the colour of the solutions changed from blue to deep blue and finally to violet. These reactions can be described[8] by the equilibria (1)—(3), where L represents the unprotonated ligand,

$$Cu^{2+} + L \rightleftharpoons [CuL]^{2+};\ K_f = [CuL^{2+}]/[Cu^{2+}][L] \quad (1)$$

$$[CuL]^{2+} \rightleftharpoons [CuH_{-1}L]^+ + H^+;$$
$$K_A = [CuH_{-1}L^+][H^+]/[CuL^{2+}] \quad (2)$$

$$[CuH_{-1}L]^+ \rightleftharpoons [CuH_{-2}L] + H^+;$$
$$K_B = [CuH_{-2}L][H^+]/[CuH_{-1}L^+] \quad (3)$$

bcen, and the negative subscript to H represents the number of amide protons lost from the complex. The structures of the three complexes $[CuL]^{2+}$, $[CuH_{-1}L]^+$, and $[CuH_{-2}L]$ have been given previously.[3] The equilibrium constants obtained by the methods reported previously[8,9] are listed in the Table.

As shown in Figure 2, the stability constants exhibit an accelerating increase with increasing methanol content in the solvent, the net increase being 2 000-fold on going from water to 99% methanol. This trend is attributed mainly to the change in the solvation of the metal ion, with minor contributions from changes in the solvations of bcen and $[Cu(bcen)]^{2+}$. The Born equation indicates that the solvation energy of a metal ion decreases with decreasing dielectric constant of the solvent.[10] The addition of methanol to an aqueous solvent decreases the bulk dielectric constant. Thus the solvation stability of Cu^{2+} decreases and log K_f increases with increasing methanol content. This trend leads us to think that there may be a relationship between the stability constant of the complex and the macroscopic dielectric constant D of the solvent. A plot of

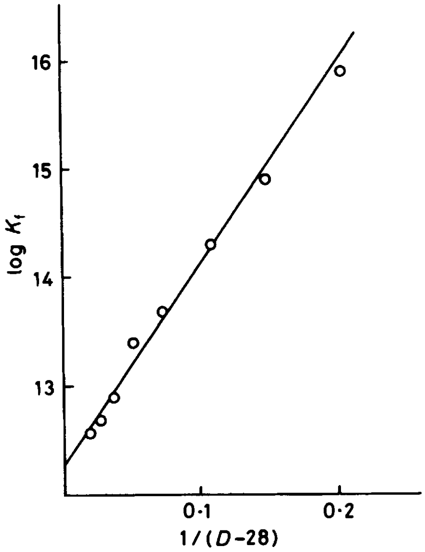

Figure 3. Plot of log K_f for $[Cu(bcen)]^{2+}$ at 25 °C against $1/(D - 28)$

log K against $(D-28)^{-1}$ is linear as shown in Figure 3. Thus the stability constant of the complex and the macroscopic dielectric constant of the solvent can be related by the empirical relation (4). This relation indicates that the effective dielectric constant

$$\log K = 17.6 \frac{1}{(D - 28)} + 12.3 \qquad (4)$$

of the solvent in the neighbourhood of the ion is significantly different from the ordinary macroscopic dielectric constant of the solvent.[11]

It is significant that the protonation constants of bcen in 80% (w/w) methanol–water are much smaller than those in aqueous solution, while the stability of $[Cu(bcen)]^{2+}$ in 80% (w/w) methanol is much higher than that in aqueous solution. These results imply that Cu^{2+} may compete more successfully with the proton for the ligand in 80% (w/w) methanol than is the case in aqueous solution.

As shown in Figure 4, each of the deprotonation constants for $[Cu(bcen)]^{2+}$ and $[Cu(H_{-1}bcen)]^{+}$, K_A and K_B, passes through a maximum at *ca.* 80% (w/w) methanol. This behaviour results primarily from the change in solvation of the proton, with a minor contribution from changes in the solvation of $[Cu(bcen)]^{2+}$ and $[Cu(H_{-1}bcen)]^{+}$, or of $[Cu(H_{-1}bcen)]^{+}$ and $[Cu(H_{-2}bcen)]$. The solvent effect upon K_A is more pronounced than that upon K_B. This large solvent effect upon K_A arises from the increased electrostatic repulsion between H^+ and $[Cu(H_{-1}bcen)]^{+}$, and is a function of the dielectric constant of the solvent.

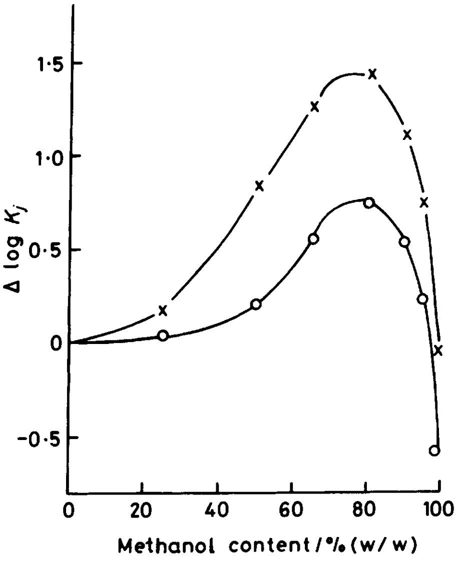

Figure 4. Trends in log K_A (×) and log K_B (○) for $[Cu(bcen)]^{2+}$ at 25 °C as a function of solvent composition

Acknowledgements

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