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Solvation of Metal Ion Complexes

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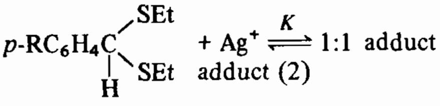
The solvation of metal ions in water has been intensively studied but the full extent of hydration of different ions is still uncertain [1]. Even less is known about the changes in hydration that occur when a hydrated metal ion, carrying no other ligands, forms a 1:1 adduct with a non-chelating neutral base in aqueous solution. This is a very common reaction, but one that has received little systematic study relevant to the question of hydration. It seems [1, 2] that when the base has a simple chemical structure (e.g. NH_3) adduct formation is normally exothermic and exhibits an entropy change close to zero. This could be interpreted as the net displacement by the base of just one water molecule from the hydration shell(s). For bases likely to undergo significant restriction of rotation or vibration, on adduct formation, ΔS is normally negative [2]: more freedom is lost by the base and the remaining solvating water molecules than is gained by the departing water molecules (some of which may have been attached to the base, see eqn. (1).

$$B(H_2O)_x + M^{n+}(H_2O)_y \rightleftharpoons B{:}M^{n+}(H_2O)_{x+y-z} + zH_2O \qquad (1)$$

We have studied the change in thermodynamic parameters for 1:1 adduct formation as the nature of B is changed in such a way as to weaken its basicity toward M^{n+} but minimally to alter its structure as a coordinating ligand. The *S,S*-diethylacetals of *para*-substituted benzaldehydes (**I**) form 1:1 adducts with Ag^+ ions in aqueous solution (eqn. (2)) in



$$p\text{-}RC_6H_4CH(SEt)_2 + Ag^+ \overset{K}{\rightleftharpoons} 1{:}1 \text{ adduct} \qquad (2)$$

adduct (2)

I

which Ag^+ is attached to sulphur [3]. Using a method developed in earlier work [3, 4]*, we find $K = 230$, 160 and 1.5 $mol^{-1}\ dm^3$ at 25 °C for the *p*-Me, *p*-MeO and *p*-NO_2 compounds, respectively. Determinations of K at (three) other temperatures permitted the calculation (to within ±12%) of ΔH and ΔS for adduct formation: we find $\Delta H = -41, -26$ and 77 kJ mol^{-1}, and $\Delta S = -92, -43$ and 259 J $K^{-1}\ mol^{-1}$ for the *p*-Me, *p*-MeO and *p*-NO_2 derivatives, respectively. There is thus a progression of values with substantial changes between the *p*-MeO and *p*-NO_2 compounds.

Any rationalisation of these values must surely invoke a significantly greater release of solvent on adduct formation for the *p*-NO_2 compound: only that could account for the large, positive ΔS value, whose magnitude suggests [1] that much of the silver-bound water is lost, together perhaps with any attached to the NO_2 group. The loss of significantly more water on adduct formation for the *p*-NO_2 compound is supported by the relative solvent deuterium isotope effects on K: for the *p*-Me compound $K(D_2O)/K(H_2O) \simeq 1$, whereas for the *p*-NO_2 derivative $K(D_2O)/K(H_2O) \simeq 2.5$. The more solvent molecules that are freed to return to the bulk, the greater would this isotope effect be expected to be [5].

More water may be released for the *p*-NO_2 compound because a chelate complex (involving both S atoms) is formed in this case only. However, the same (unfavourable) geometry is available to the *p*-Me and *p*-MeO compounds as to the *p*-NO_2 compound, as well as more electron density on sulphur, so that this explanation seems quite unlikely. We suggest that the loss of more solvent is necessary in forming the adduct with the *p*-NO_2 derivative because the residual solvent then leads to less dispersion of the positive charge. We predict that cationic adducts involving relatively weak, neutral bases will prove, in general, to be less solvated than structurally similar adducts involving stronger bases.

References

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*K values for the present systems are obtainable to within ±10%.