

Solvation of Tris-maltolatoaluminium(III) and Related Complexes in Methanol–Water Mixtures

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Abstract

Solubilities in methanol–water mixtures have been obtained at 298.2 K for the tris-maltolato complexes of aluminium(III) and iron(III), and for two analogous tris-pyridinonatoaluminium(III) complexes. Transfer chemical potential trends derived from these measurements are discussed in terms of preferential solvation and hydrophilic/lipophilic properties of the peripheries of the respective complexes.

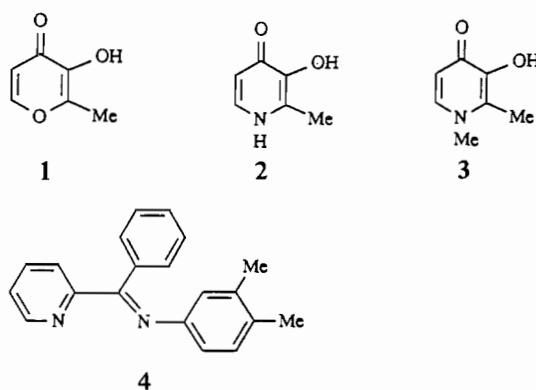
Introduction

We have for some time been interested in the monitoring of solvation of inorganic complexes in binary aqueous solvent mixtures [1]. In particular we have been investigating, through appropriate solubility measurements, how transfer chemical potential trends reflect preferential solvation in such mixtures. In this manner one can obtain a quantitative estimate of the effect of the hydrophilic or hydrophobic character of the periphery of complexes on their solvation characteristics. Thus, for instance, the resultant of favourable hydration of the cyanide ligands and of favourable solvation by an alcohol of the 2,2'-bipyridyl ligands is clear from plots of transfer chemical potentials of $\text{Fe}(\text{CN})_2(\text{bipy})_2$ against solvent composition [2]. Sometimes such plots reflect not only the various ligand periphery–solvent component interactions but also intercomponent interactions in, for example, *t*-butyl alcohol–water solvent mixtures.

We are currently concerned with establishing solvation properties of species containing aluminium, zinc and technetium in regard to how such properties will determine transport across gastrointestinal and blood–brain barriers. We believe that the traditional measure provided by water–octanol partition coefficients may be too simple to reflect the relevant inorganic complex/biological environment interactions. Indeed it has proved

impossible to determine reliable partition coefficients for some complexes of the type discussed in this paper due to hydrogen-bonding complications [3].

In this present paper we report solubilities and transfer chemical potentials for the tris-ligand(LL)–aluminium(III) complexes of 3-hydroxy-2-methyl-4H-pyran-4-onate (LLH = maltol, 1), 3-hydroxy-2-



methyl-4-pyridinonate (LLH = mpp, 2) and 3-hydroxy-1,2-dimethyl-4-pyridinonate (LLH = dpp, 3), and for tris-maltolatoiron(III), in each case in a range of methanol–water solvent mixtures. These complexes have peripheries with areas of hydrophilic and of hydrophobic (lipophilic) character, so that the consequences of modifying the balance between these properties can be assessed. These complexes have the additional advantage that they are uncharged, and thus the problems over the extrathermodynamic assumptions required to obtain single ion transfer chemical potentials [4] for charged inorganic complexes do not arise.

Experimental

The complexes were prepared by published methods [3, 5, 6]; their purity was checked by CHN microanalysis. Numbers of waters of crystallisation were deduced from these analyses and from thermogravimetric measurements (Stanton-Redcroft

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Model TG750). This latter technique was used to examine solid phases in equilibrium with solvent mixtures of various compositions, to check that such solid phases did not change as the proportion of methanol increased. Obviously it was not sensible to measure solubilities in anhydrous methanol, since the solid phase in equilibrium with saturated solution would not be the hydrate in equilibrium with saturated solutions in water-rich solvent mixtures.

Saturated solutions at 298.2 K were generated and analysed by methods described earlier [7]. Concentrations of the various complexes were monitored spectrophotometrically, using a Shimadzu Model UV-160 spectrophotometer. The aluminium complexes of maltol (1), mpp (2) and dpp (3) have $\epsilon(305) = 18\,800$ (ref. [5]), $\epsilon(280) = 21\,200$ and $\epsilon(290) = 30\,000$ respectively. The last two results were obtained in the course of the present investigation.

Results

Absorbances of saturated solutions (measured absorbances multiplied by the respective dilutions) and derived transfer chemical potentials are given in Table 1. The transfer chemical potentials were calculated from the absorbances (i.e. solubilities) assuming that the ratio of the activity coefficient in the mixed solvent to that in water was in each case one. This seems to us to be an acceptable approximation here since the complexes are uncharged, and moreover the solutions are dilute. It is unlikely that errors larger than $\pm 1 \text{ kJ mol}^{-1}$ will have been introduced as a consequence. It has also been assumed, on the basis of the experiments mentioned above, that the same hydrate is in equilibrium with

TABLE 1. Absorbances of saturated solutions and transfer chemical potentials (kJ mol^{-1} ; molar scale; 298.2 K)

	MeOH (vol.%)					
	0	20	40	60	80	100
Al(maltol) ₃						
Absorbance	560	720	1270	2830	5535	2285
$\delta_m \mu^\theta$	0	-0.6	-2.0	-4.0	-5.6	-3.4
Al(mpp) ₃						
Absorbance	918	1217	1431	1293	734	300
$\delta_m \mu^\theta$	0	-0.7	-1.0	-0.8	+0.5	+2.7
Al(dpp) ₃						
Absorbance	109	160	429	1548	12705	9802
$\delta_m \mu^\theta$	0	-0.9	-3.3	-6.5	-11.7	-11.1
Fe(maltol) ₃						
Absorbance	73	83	140	246	308	195
$\delta_m \mu^\theta$	0	-0.3	-1.6	-2.9	-3.5	-2.4

the saturated solution throughout the solvent composition range. If this is not the case, then errors of the order of 2 or 3 kJ mol^{-1} may well have been introduced at the methanol-rich end [8]. This does not affect the general discussion of selective solvation, but it does mean that the small up-turn at 80 to 100% methanol in the lower plots of Fig. 1 may not be significant.

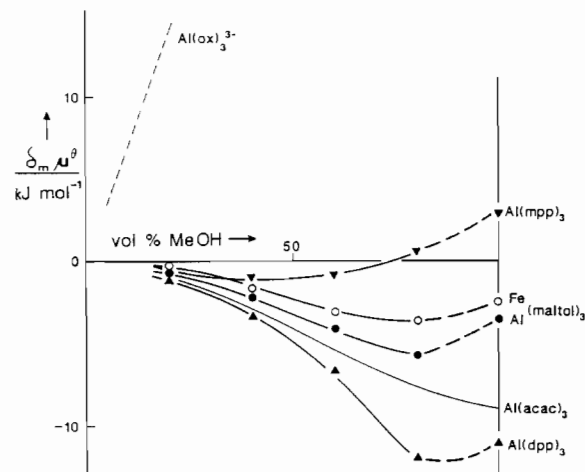


Fig. 1. Transfer chemical potentials from water into methanol–water mixtures. Dashed lines indicate some uncertainty – see text for details.

Discussion

The derived transfer chemical potentials for the four complexes studied are plotted against solvent composition in Fig. 1. The very similar trends for the tris-maltolato–aluminium(III) and –iron(III) complexes are consistent with identical peripheries and similar radii for these two species. The aluminium complex of ligand 2 is considerably less hydrophobic than maltol, but the addition of a second methyl group to ligand 2, to give ligand 3, results in a marked increase in hydrophobicity. As befits species with both modestly hydrophilic and modestly hydrophobic areas on their surfaces, transfer chemical potentials do not change dramatically with solvent composition. The modest effects established here should be compared with the large stabilisation (c. -50 kJ mol^{-1} [9]) for the very hydrophobic cation $[\text{Fe}(\text{Me}_2\text{bsb})_3]^{2+}$, $\text{Me}_2\text{bsb} = 4$, on transfer from water into methanol, and the correspondingly large destabilisation of aqua-metal ions and of tris-oxalato-metallates on transfer from water into binary aqueous solvent mixtures. The plot for the $[\text{Al}(\text{ox})_3]^{3-}$ anion in Fig. 1 is estimated from that for the $[\text{Cr}(\text{ox})_3]^{3-}$ anion [10], the closest related species for which data are available.

Figure 1 also contains the trend for tris-pentane-2,4-dionatoaluminium(III), $\text{Al}(\text{acac})_3$ [11]. It is

interesting that over much of the solvent composition range the plot for this complex is close to that for tris-maltolatoaluminium(III), indicating similar solvation characteristics. However whereas the plots for the four complexes of the present investigation curve upwards at high methanol proportions (the exact amount of destabilisation as pure methanol is approached is a little uncertain, cf. above), that for $\text{Al}(\text{acac})_3$ continues to indicate stabilisation on increase of methanol content up to 100%. $\text{Al}(\text{acac})_3$ is only moderately hydrophobic, but has no hydrophilic areas on its periphery. In contrast, the maltolate and related complexes do have hydrophilic areas. Thus when a little water is added to methanol, favourable interaction between this added water and the hydrophilic centres causes a reduction in transfer chemical potential on going from methanol into methanol-water. Complementarily, these complexes are stabilised by the additional methanol-hydrophobic areas interactions on going from aqueous solution into methanol-water mixtures.

This pattern of increased solvational stabilisation of complexes with mixed hydrophilic/lipophilic character in aqueous/organic media may be important in biochemical contexts as well as in relation to interfacial chemistry at micelles and in (micro)-emulsions. In relation to the possibility of absorption of ingested aluminium, there are strong indications that absorption of aluminium is increased when hydrophilic/lipophilic ligands such as citrate [12] or natural products such as those in Norwegian tap water in the autumn [13] are ingested concurrently with inorganic aluminium. In such cases, and indeed in cases where potential ligands such as maltol may be produced during digestive processes [3], there is the distinct possibility of generating an uncharged and predominantly hydro-

phobic species [14] which could readily move across biological membranes.

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