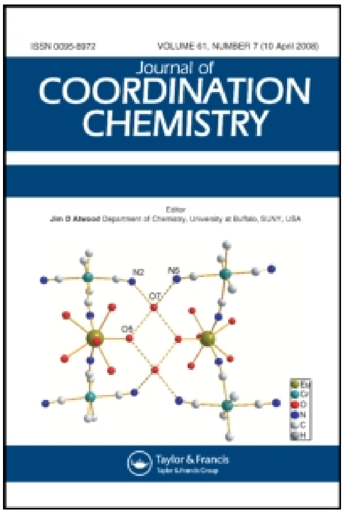

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SOLVATION OF ALUMINIUM(III) AND IRON(III) COMPLEXES OF HYDROXAMATE LIGANDS IN ALCOHOL-WATER MIXTURES

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Solubilities and derived transfer chemical potential trends are reported for several *tris*(hydroxamato)-aluminium(III) and iron(III) complexes in methanol-water and in *t*-butylalcohol-water solvent mixtures. These trends are discussed in terms of hydrophilic and hydrophobic characteristics of the peripheries of these complexes.

KEY WORDS: Aluminium(III), iron(III), hydroxamates, alcohol-water mixtures, solubilities.

INTRODUCTION

Hydroxamates have long been known to form very stable complexes with a number of metal(III) ions,[1] and indeed have been widely used as gravimetric reagents,[2,3] and in extractive metallurgy.[3] The metal-binding sites in several siderophores contain hydroxamate moieties, which facilitate the uptake of iron;[4] stability constants for some iron(III)-natural siderophore complexes have been determined.[5] The strong complexing powers of hydroxamates for iron(III)[6] have been used in the design of pharmaceuticals for the amelioration of iron overload in patients,[7] and, conversely, for the treatment of anaemia.[8] In recent years their use has been considered in relation to the control of aluminium(III) levels in the body,[9] though they cannot compete effectively with human serum albumin for aluminium. In all these applications the solvation of the ligands and their complexes is important, in water, in non-aqueous and mixed aqueous media, and in micelles, microemulsions, and other "organised media." We recently reported solubilities of several aluminium(III) and iron(III) complexes of pyrone (1) and pyridinone (2) ligands in methanol-water mixtures, showing how preferential solvation depended on ligand nature.[11] We now describe our results of a similar investigation of solvation of some hydroxamate complexes. They are particularly suitable for selective solvation studies of this type,[12] since they are sparingly soluble[1,2] and of high stability.[13]

In the present paper we deal with three ligands, acethydroxamate, benzhydroxamate, and the 4-methyl derivative of the latter (3, with R = Me, C_6H_5 and 4-MeC_6H_4,

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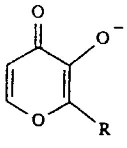
respectively). This group of ligands gives a useful range of hydrophilic/lipophilic properties of the respective complexes. We have studied complexes both of iron and of aluminium, and have used methanol and *t*-butylalcohol as co-solvents in binary aqueous solvent mixture series.

EXPERIMENTAL

The complexes were prepared by established methods;[2-4] products were checked by microanalysis and spectroscopy (n.m.r.; electronic-spectra). Alcohol-water mixtures were made up by volume before mixing (40% methanol was made up by mixing 40 cm^3 methanol and 60 cm^3 water), using deionised water and either dry methanol (refluxed with magnesium and iodine, then distilled) or pure *t*-butyl-alcohol. Solubilities were measured using the techniques and methods described earlier.[14] Concentrations of aluminium complexes were measured by atomic absorption (Perkin-Elmer 1100B); concentrations of iron complexes were determined spectroscopically. The visible absorption spectra of the iron tris-ligand complexes showed peaks at 413 nm ($\varepsilon = 1360$), 437 nm ($\varepsilon = 5040$), and 476 nm ($\varepsilon = 5200$) for the ligands 3 with R = Me, C_6H_5, and 4-MeC_6H_4, respectively.



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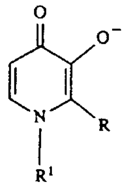

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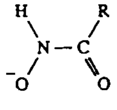

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RESULTS

Solubilities are reported in Table 1. This table also contains transfer chemical potentials, in all cases from aqueous solution, calculated from these measured solubilities. In view of the relatively low solubilities and the uncharged nature of the complexes, we have assumed that for each complex the ratio of its activity coefficient in a given alcohol-water mixture to that in water is unity. Transfer chemical potential trends are depicted in Figures 1 to 5. These figures are all drawn to the same vertical scale to facilitate intercomparison.

DISCUSSION

Trends for pairs of aluminium and iron complexes are shown in Figure 1. In the cases illustrated, and in other cases where direct aluminium *vs* iron comparison is possible, the respective complexes of the two elements show very similar solvation trends, generally the same within experimental uncertainty. This is hardly surprising in the light of the identical nature of the periphery and the very small difference in

Table 1 Measured solubilities (soly, in ppm or mol dm^{-3}) and derived transfer chemical potentials (Δ, in kJ mol^{-1}, from water, on the molar scale) for tris(hydroxamato)metal(III) complexes, at 298.2K.

Metal (III)	Substituent R in 3							
		Vol % MeOH	0	20	40	60	80	100
Al	$R = C_6H_5$	ppm	33	73	198	630	1110	1430
		Δ		−2.1	−4.4	−7.3	−8.7	−9.3
	$R = 4MeC_6H_4$	ppm	7	14	29	72	255	360
		Δ		−1.8	−3.5	−5.8	−8.9	−9.8
Fe	$R = CH_3$	soly	1.01	0.95	0.66	0.49	0.30	0.197
		Δ		+0.2	+1.1	+1.8	+3.0	+4.1
	$R = C_6H_5$	10^4soly	0.40	0.65	1.95	11.6	18.5	23.7
		Δ		−1.2	−3.9	−8.3	−9.5	−10.2
		Vol% *t*-BuOH	0	20	40	60	80	90
Al	$R = 4MeC_6H_4$	ppm	7	23	130	420	780	1050
		Δ		−3.0	−4.9	−10.1	−11.8	−12.4
Fe	$R = CH_3$	soly	1.01	0.84	0.28	0.090	0.017	0.0048
		Δ		+0.5	+3.2	+6.0	+10.1	+13.3
	$R = C_6H_5$	10^4 soly	0.40	0.84	3.9	6.7	12.2	13.1
		Δ		−3.0	−6.8	−8.1	−9.6	−9.8
	$R = 4MeC_6H_4$	10^4 soly	0.29	0.76	4.0	8.3	13.7	16.2
		Δ		−2.4	−6.5	−8.3	−9.5	−9.9

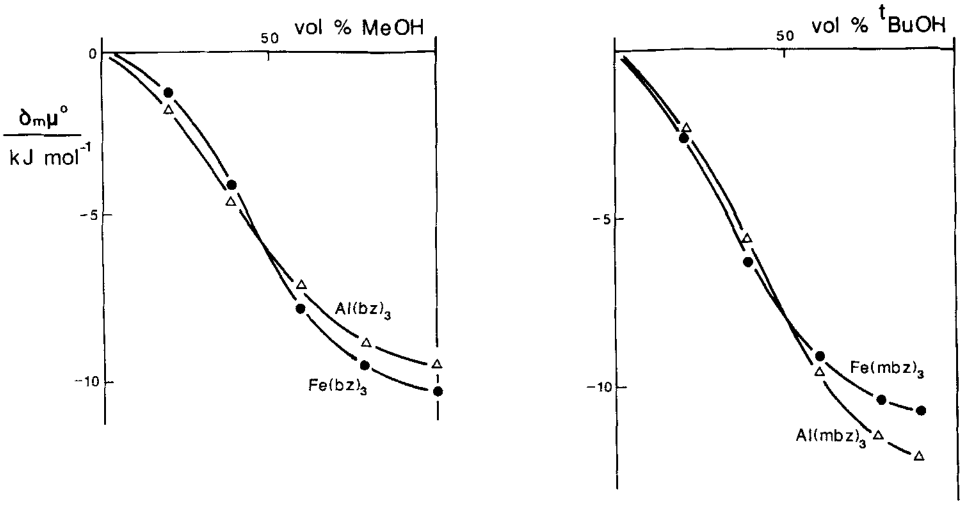

Figure 1 Transfer chemical potentials for the aluminium and iron(III) complexes of (a) benzhydroxamate(bz) and (b) 4-methylbenzhydroxamate(mbz) from water into methanol-water and *t*-butylalcohol-water mixtures respectively (298.2K; molar scale—for Figures 1-4).

size (ionic radii 0.67 and 0.69Å for Al^{3+} and Fe^{3+} respectively).[15] Similarly small aluminium complex *vs* iron complex solvation differences have previously been reported for pyrone and pyridinone complexes;[7] different solvation trends are only observed for significantly larger complexes,[16] *e.g.*, of In^{3+} (ionic radius 0.93Å).[15]

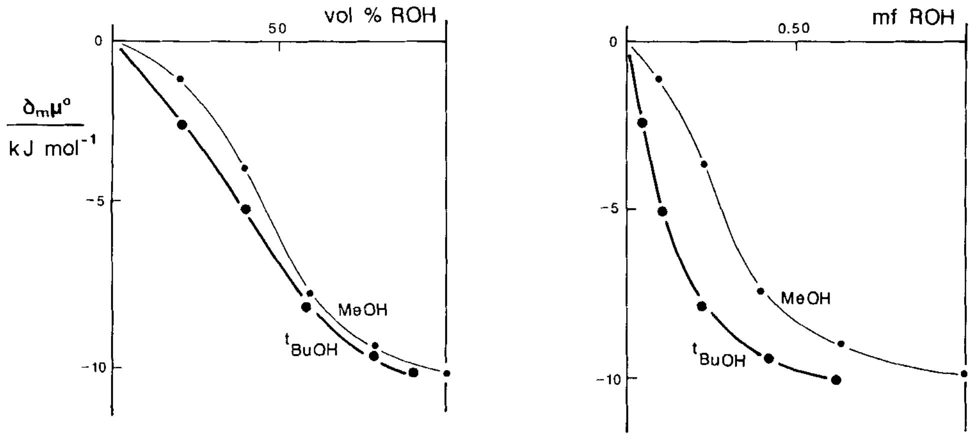

Figure 2 Comparisons of transfer chemical potentials for tris(benzhydroxamato)iron(III) to methanol-water and to *t*-butyl alcohol-water mixtures on (a) volume percentage and (b) mole fraction solvent composition scales.

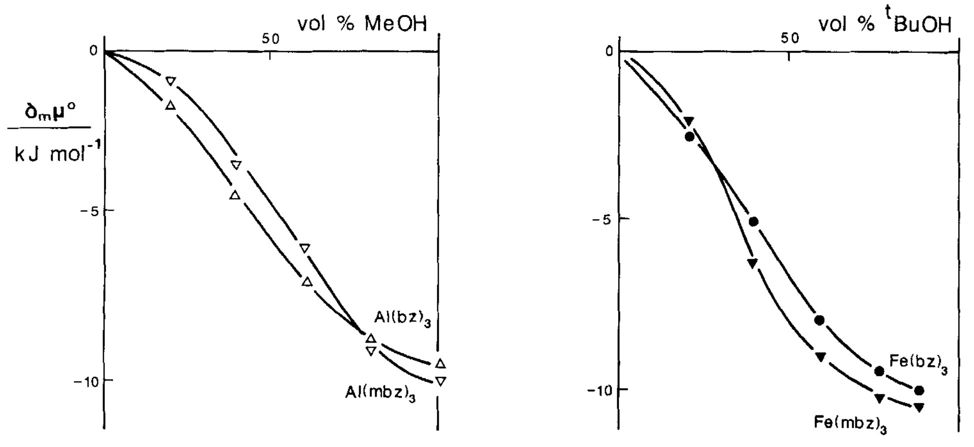

Figure 3 Effects of methyl substitution on transfer chemical potential trends for tris(benzhydroxamato) complexes of (a) aluminium and (b) iron(III) to methanol-water and *t*-butylalcohol-water mixtures respectively.

Figure 2 compares the effects of methanol and *t*-butylalcohol as co-solvents, plotted on the volume and mole fraction scales in (a) and (b), for the typical example of tris(benzhydroxamato)iron(III). It is interesting that transfer chemicals to alcohol-rich media are so similar. Figure 2(b) however shows that stabilisation of the complex by *t*-butylalcohol becomes important at lower mole fractions of alcohol than in the case of methanol. This is normal behaviour.

Figure 3 shows the very small effects of methyl substitution in the benzhydroxamate ligands, both for aluminium and for iron, and both for methanol and for *t*-butylalcohol as co-solvent. By way of contrast, Figure 4 shows the very large differences between acethydroxamate and benzhydroxamate complexes. The small acethydroxamate

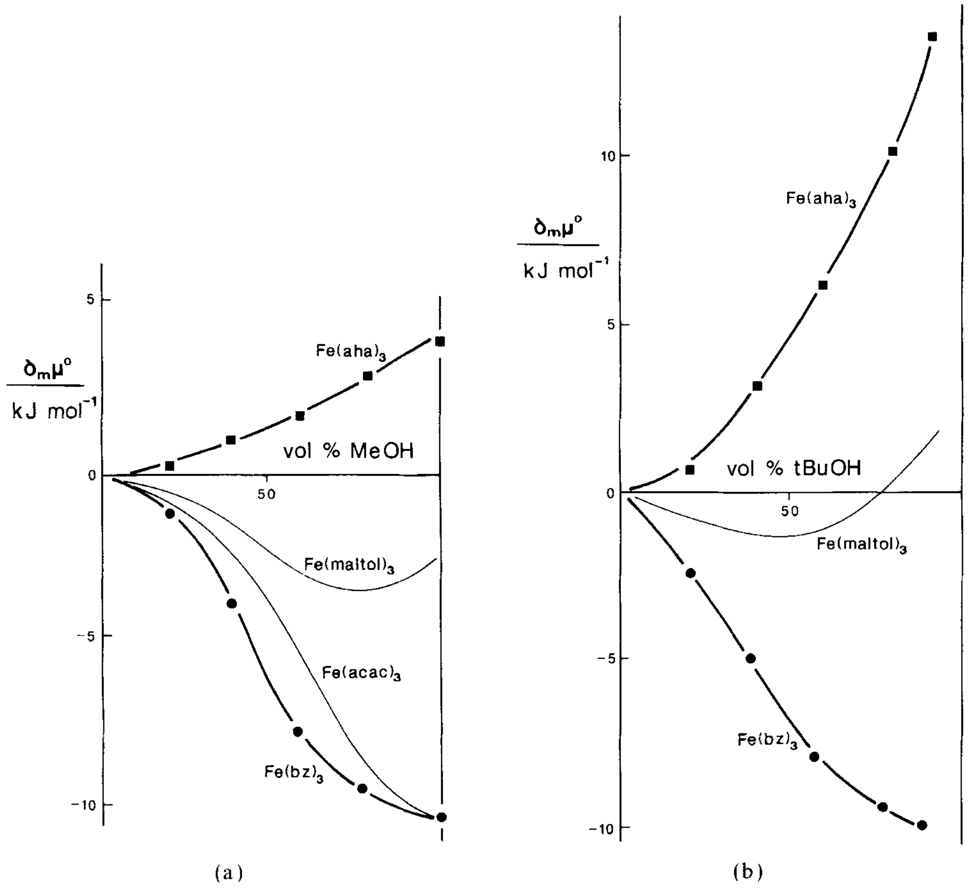

Figure 4 Comparison of transfer chemical trends for tris(benzhydroxamato)iron(III) with those for other iron(III) complexes, to (a) methanol-water and (b) *t*-butylalcohol-water mixtures. Ligands: aha = acethydroxamate (3, R = Me); maltol = 3-hydroxy-2-methyl-4-pyrone; acac = 2,4-pentanedione; bz = benzydroxamate (3, R = Ph).

complex shows marked preferential solvation by water in both series of alcohol-water mixtures. This may be attributed to strong favourable hydration of the —NHO^- portion of each coordinated acethydroxamate ligand. When the methyl group in these ligands is replaced by phenyl or 4-MeC_6H_4, then the lipophilic properties of the aromatic moieties dominate and the complexes are preferentially solvated by the alcohols in mixed solvent media. The trends for tris(maltolato)iron(III) have been included in both Figure 4(a) and Figure 4(b) for comparison with tris(benzhydroxamato)iron(III). In the case of the maltol complex, fairly closely balanced hydrophilic and lipophilic areas result in particularly favourable solvation in mixed solvents, where hydration of hydrophilic areas and solvation by alcohol at the lipophilic areas produce a maximum in the solubility, a minimum in chemical potential. Such a situation is not common, but has been reported for a number of inorganic (*e.g.*, $Fe(CN)_2(bipy)_2$)[17] and organic (*e.g.*, Succinic acid;[18] sulfacetamide[19]) compounds. The dominance of the lipophilic component of the benzhydroxamate complex means

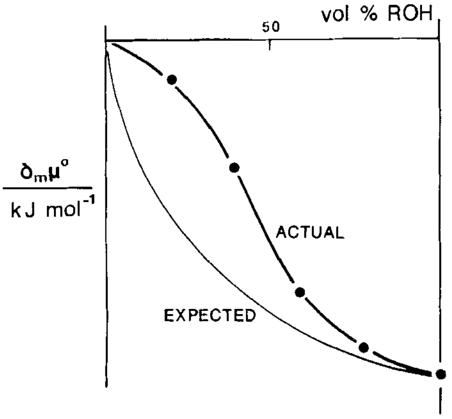

Figure 5 Comparison of a typical transfer chemical potential trend for a tris(hydroxamato)metal(III) complex to alcohol-water mixtures with that expected for simple preferential solvation by the alcohol component.

that there is no chemical potential minimum corresponding to particularly favourable overall solvation in mixed solvent media. The solubility and transfer chemical potential trends merely reflect increasingly favourable solvation by the alcohol component as its proportion increases. In this the benzhydroxamate complex behaves analogously to such hydrophobic complexes as tris(pentanedionato)iron(III), $Fe(acac)_3$ (included in Figure 4(a)), and tris(1,10-phenanthroline)iron(II), $Fe(phen)_3^{2+}$,[12] and indeed such species as Ph_4As^+ and Ph_4B^-.[20] However, the preferential solvation pattern for the benzhydroxamate complex, and also for $Fe(acac)_3$ and $Fe(phen)_3^{2+}$, is not entirely straightforward. Figure 5 compares the flattened-S curve observed for these complexes with the smooth curve that might be expected. The divergences at relatively low mole fractions of alcohol may well arise, as has been suggested earlier,[21] from a contribution from solvent structural effects. Increasingly favourable intra- or inter-solvent interactions at low alcohol contents—alcohols in small amounts are generally accepted to increase water structure[22]—may mean that solvent-solute interactions are significantly reduced. Solubility would be less enhanced than expected by the addition of small amounts of alcohol, which would give divergence in the direction shown in Figure 5, in other words explain the S-shape of the lower curves in Figure 4. These small divergences from expected trends do not disturb the overall pattern of preferential solvation and its dependence on the hydrophilic/lipophilic character of the peripheries of this group of complexes.

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