Enthalpies of Solution of 2,2′-Bipyridyl, 1,10-Phenanthroline, and 1,10-Phenanthroline Monohydrate

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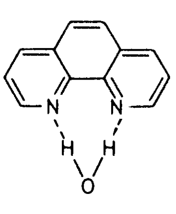
Enthalpies of solution are reported for 1,10-phenanthroline and its monohydrate in water and in benzene, and for 2,2′-bipyridyl in water and in series of methanol–water and t-butyl alcohol–water mixtures.

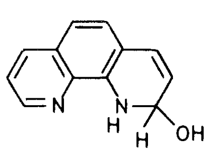
QUALITATIVE information on solubilities of various isomers of bipyridyl [1] and of phenanthroline [2] has been available for many years. More recently, quantitative solubility measurements have been reported for 2,2′-bipyridyl (bipy) in water [3] and in various alcohol–water mixtures,[4] and for 1,10-phenanthroline (phen) in water and in some methanol–water mixtures.[5] However there seems to be a dearth of information on enthalpies of solution of compounds of this type. Enthalpies of solution of bipy [3] and of 1,10-phenanthroline monohydrate, phenH_2O,[5] in water have been reported, but these values were derived from the temperature dependence of solubilities rather than by direct calorimetry. Since phenH_2O is the solid phase in equilibrium with saturated aqueous solutions of phen,[6] the enthalpy of solution of anhydrous phen in water cannot be obtained in this van't Hoff manner.

There is also a little information on related enthalpies, specifically on the enthalpy of dissociation of water from phenH_2O [7] and the enthalpy of addition of water to phen in benzene solution.[8]

We are interested in enthalpies of solution of diaza-aromatic compounds of the bipy and phen type for two reasons. The first is for the derivation of enthalpies of transfer, for use in dissecting solvent effects on enthalpies of activation of reactions involving such ligands into initial state and transition state contributions.[9] The second is in connection with the question as to whether the so-called 1,10-phenanthroline monohydrate is indeed a ' true ' hydrate with the water molecule hydrogen-bonded to the two nitrogen atoms (1),[10] or whether it is a ' covalent hydrate ' as shown in (2).[11]



(1)



(2)

We have therefore determined, by direct calorimetry, enthalpies of solution of bipy in water, in aqueous methanol, and in aqueous t-butyl alcohol, and of phen and its hydrate in water and in benzene. The measurements in benzene permit us to connect our investigation with that in benzene cited above,[8] which connection gives us an additional check on consistency.

EXPERIMENTAL

2,2′-Bipyridyl (B.D.H.) was recrystallised from aqueous ethanol. Anhydrous 1,10-phenanthroline was prepared from the monohydrate (Aldrich) by heating at 380 K over phosphorus pentaoxide *in vacuo*.[12]

Calorimetric measurements were carried out in an assembly, previously described,[13] based on an LKB 8700 calorimeter vessel. The performance of this apparatus was checked periodically against the enthalpy of solution of potassium chloride in water.[14] All calorimetry was performed at 298 K.

RESULTS

Our determinations of enthalpies of solution of bipy, phen, and phenH_2O in water and in benzene are reported in the Table. Enthalpies of solution of bipy in aqueous methanol and in aqueous t-butyl alcohol are presented graphically in Figure 1. Uncertainties in solution enthalpies in water and in water-rich solvent mixtures are rather larger than norm-

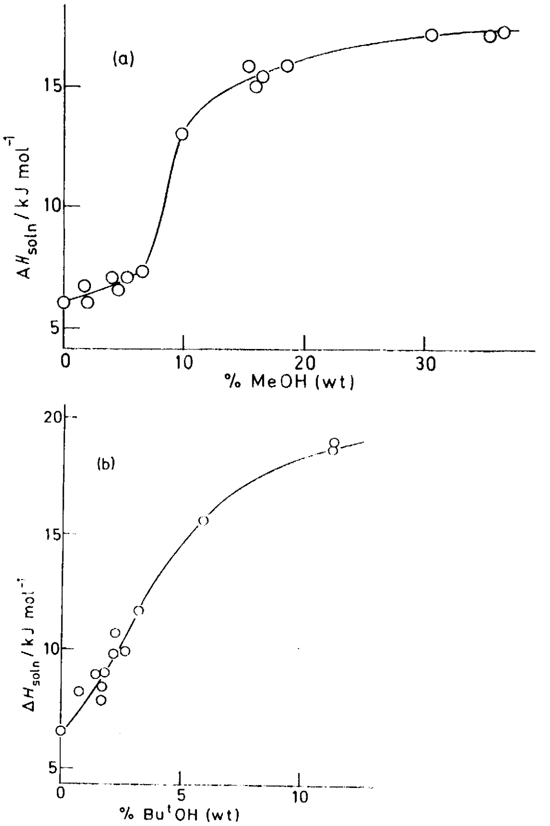


FIGURE 1 Enthalpies of solution of 2,2′-bipyridyl in (a) aqueous methanol and (b) aqueous t-butyl alcohol

ally expected. This is due to the use of unusually small samples and the relative slowness of dissolution, both factors consequent on the very limited solubilities of these compounds in these solvent media.

DISCUSSION

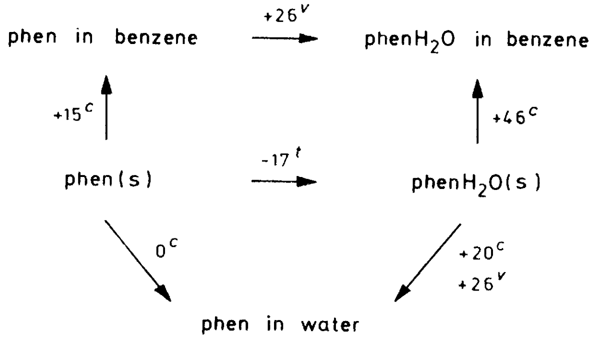
There is tolerable agreement between van't Hoff estimates and direct calorimetric determinations where such comparison is possible, that is for bipy and for phenH_2O in water. In fact the reported van't Hoff estimate for the enthalpy of solution of bipy in water had been subjected to an ill defined correction, so may be closer to the calorimetric value than appears at first sight.[3]

Enthalpies of solution (ΔH_{soln}) at 298.2 K

Compound	Solvent	ΔH_{soln}/kJ mol^{-1}
bipy	Water	$+6.3 \pm 0.7$ [a]
phen	Water	$+0.3 \pm 1.0$
	Benzene	$+14.7 \pm 0.1$
phenH_2O	Water	$+20.0 \pm 1.5$ [b]
	Benzene	$+46.7 \pm 0.15$

[a] *Cf.* −1 kJ mol^{-1} from temperature-dependence of solubilities (ref. 3). [b] *Cf.* +26 kJ mol^{-1} from temperature-dependence of solubilities (ref. 5).

Enthalpy of solution and related data for phen and for phenH_2O are collected together in the Scheme. The value of −17 kJ mol^{-1} for the conversion of anhydrous phen into the monohydrate was calculated from the published value of −61 kJ mol^{-1} for addition of water (gas phase) to solid phen, derived from the temperature variation of the vapour pressure over phenH_2O,[7] and 44 kJ mol^{-1} for the enthalpy of vaporisation of water at 298.2 K.[15] Hess's law summation of enthalpies round the various cycles of the Scheme gives values which approximate to zero. Perfect summation to zero is hardly to be expected, in view of the (small) uncertainties in the calorimetric values and the (less small) doubts in van't Hoff derivations of enthalpies; it is impossible to avoid including at least one van't Hoff value in any cycle extracted from this Scheme. Our results confirm the vapour pressure studies on phenH_2O and support the conclusion there that the phenanthroline–water bonding was 'quite strong.' Comparison of the 20 kJ mol^{-1} difference between the solution enthalpies of phen and phenH_2O with differences reported for other organic molecules and their respective hydrates, which range from 6 to 26 kJ mol^{-1} (per water molecule) for tartaric acid, caffeine, orcinol, raffinose, and lactose,[16] shows that the phen — phenH_2O difference is within the normal range. We cannot therefore use our result to help distinguish between structures (1) and (2) for phenH_2O. It is unfortunate that it appears so far to have proved impossible to establish the position of the oxygen atom in phenH_2O by *X*-ray crystallographic methods.



SCHEME Enthalpies are quoted in kJ mol^{-1}; ^{c} calorimetric; ^{v} van't Hoff; ^{t} see text

It is interesting to compare the enthalpies of solution of 1,10-phenanthroline (anhydrous) and of 2,2′-bipyridyl with that for pyridine. The values are 0 and +6 kJ mol^{-1} for the first two, while a value of −1 kJ can be estimated for two moles of solid pyridine from the known enthalpy of fusion of pyridine[17] and the known enthalpy of solution of liquid pyridine.[18]

Figure 2 shows the variation in enthalpies, Gibbs free energies, and entropies of transfer of bipyridyl with solvent composition for water-rich methanol–water mixtures. The observed trend in solubilities is the resultant of opposing trends in enthalpies and entropies, with the latter term dominating. The plots in Figure 2 do not show marked points of inflection or extrema, indicating that solvent structural changes in methanol–water mixtures do not find a dramatic reflection in the solution thermodynamic parameters for bipy.

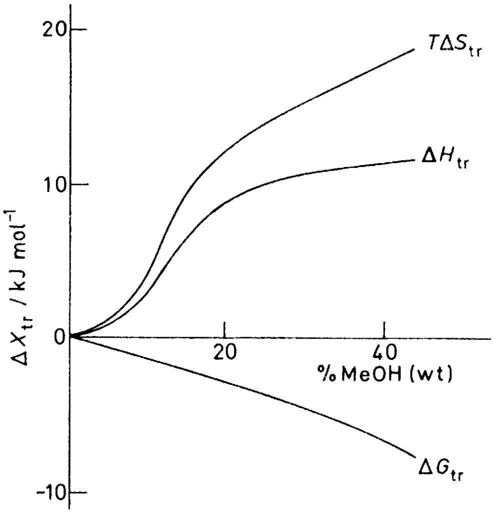


FIGURE 2 Transfer enthalpies (ΔH_{tr}), Gibbs free energies (ΔG_{tr}), and temperature-entropy products ($T\Delta S_{tr}$) for 2,2′-bipyridyl from water into aqueous methanol, at 298 K

The enthalpies of transfer of bipy from water into aqueous methanol reported here have, with parallel information of transfer enthalpies for the Ni^{2+} cation, enabled us to dissect solvent effects on the activation enthalpy[19] for the Eigen–Wilkins formation reaction for $Ni(bipy)^{2+}$ into initial state and transition state contribution.[20] It turns out that the solvation changes around the Ni^{2+} cation are considerably more important than those around the bipy in determining reactivity trends, at least in the water-rich methanol–water mixtures investigated here.

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