

Solubilities of 1,10-Phenanthroline and Substituted Derivatives in Water and in Aqueous Methanol

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The solubilities of 1,10-phenanthroline in water over the temperature range 298.2–323.2 K and in water-methanol mixtures at 298.2 K, and the solubilities of some substituted derivatives of 1,10-phenanthroline in water at 298.2 K, are reported.

The solubility of the important and widely used ligand 2,2'-bipyridyl in aqueous solution has been established over the temperature range 273.2–333.2 K by Bennetto and Letcher (7). Data on the solubility of the closely related, and equally important, ligand 1,10-phenanthroline and of substituted 1,10-phenanthrolines are sparse. In this paper we report the solubility of 1,10-phenanthroline in water over the temperature range 298.2–323.2 K, the solubility of 3,4,7,8-tetramethyl-1,10-phenanthroline (3,4,7,8-Me₄phen) in water at 298.2 K and at 323.2 K, the solubility of 4,7-dimethyl- and 5-nitro-1,10-phenanthrolines (4,7-Me₂phen and 5-NO₂phen) in water at 298.2 K, and the solubility of 1,10-phenanthroline in aqueous methanol, containing up to 25% by volume of methanol, at 298.2 K.

Experimental Section

The phenanthrolines were obtained from commercial sources and were purified by recrystallization from aqueous ethanol. Their purity was assessed by ultraviolet spectroscopy and by NMR methods. NMR clearly showed, for instance, how such recrystallization reduces the small amount of 3- and 8-methyl impurities in commercial 4,7-Me₂phen to negligible levels. However, these spectroscopic techniques may not always show up the presence of small quantities of related phenanthrolines present as impurities (and of course elemental analysis is powerless to indicate the presence of isomers). We have therefore also assessed the purity of our phenanthrolines by a kinetic method, based on aquation of their iron(II) complexes. This kinetic assessment simply involved monitoring aquation kinetics over 4 or 5 half-lives. Differences in rate constants for different substituted phenanthroline complexes are large, so that a very small percentage of a foreign phenanthroline complex will show up in significant deviations from linearity of the normally very good logarithm of absorbance vs. time plots.

An excess of the phenanthroline was equilibrated with the solvent in a stirred and thermostated vessel. Aliquots of the solution were withdrawn at intervals (and maintained at 298.2 K) for analysis until repeated spectrophotometric determinations indicated that equilibrium had been attained. Optical densities were measured, where necessary after appropriate dilution, in 10-mm silica cells in a Unicam SP800A recording spectrophotometer, at the wavelengths of maximum absorption detailed in Table III. The optical density scale of the spectrophotometer was checked against potassium chromate solution. The molar extinction coefficients of the phenanthrolines were determined from solutions containing known concentrations—these concentrations were checked via conversion into iron(II) complexes of known extinction coefficients.

Results

The solubility of 1,10-phenanthroline in water is reported in Table I. From the observed variation of solubility with tem-

Table I. Concentrations of 1,10-Phenanthroline in Saturated Aqueous Solutions as a Function of Temperature

T/K	[phen]/mol dm ⁻³	T/K	[phen]/mol dm ⁻³
298.2	0.0149 ^a	313.2	0.0255
304.0	0.0185	318.6	0.0288
308.0	0.0209	323.2	0.0341

^a Compare value of 0.0161 mol dm⁻³ in ref 3.

Table II. Concentrations of 1,10-Phenanthroline in Saturated Methanol-Water Solutions, and Gibbs Free Energies of Transfer (ΔG_{tr}) of 1,10-Phenanthroline from Water into the Solvent Mixtures, at 298.2 K

% MeOH (v/v)	[phen]/mol dm ⁻³	ΔG_{tr} /kJ mol ⁻¹
5.0	0.0173	-0.4
10.0	0.0207	-0.8
15.0	0.0247	-1.3
20.0	0.0280	-1.6
25.0	0.0339	-2.0

Table III. Concentrations of Saturated Aqueous Solutions of 1,10-Phenanthroline and of Related Compounds at 298.2 K

	$\lambda_{max}/$ nm	ϵ	[Compound], mol dm ⁻³	Molecular volume \times 10 ⁴ , m ³ mol ⁻¹
phen	265	29 510	0.0149	1.374
5-NO ₂ phen	267	28 410	0.000121 ^a	1.549
4,7-Me ₂ phen	266	37 490	0.000107	1.656
3,4,7,8-Me ₄ phen	278	41 590	0.0000064	1.938
4,7-Ph ₂ phen			<10 ⁻⁶	2.590
5-Br(phen)			0.00099 ^b	1.549
bpy			0.038, ^c 0.041 ^d	1.244

^a Compare value of 0.000 119 in ref 3. ^b Reference 3. ^c Reference 1. ^d Reference 2.

perature a value of -2.6 kJ mol⁻¹ can be deduced for the corresponding enthalpy of solution. The standard deviation of this enthalpy is 0.02 kJ mol⁻¹; the probable error, including systematic as well as random uncertainties, must be considerably larger, perhaps about 10 times larger, than this. This enthalpy of solution for 1,10-phenanthroline is similar to that reported for 2,2'-bipyridyl, -4.2 kJ mol⁻¹ (7). The solubility of 1,10-phenanthroline at temperatures around ambient is rather lower than that of 2,2'-bipyridyl. At 298.2 K, a saturated aqueous solution of 1,10-phenanthroline is 0.015 mol dm⁻³ (Table I); a saturated aqueous solution of 2,2'-bipyridyl is 0.038 mol dm⁻³ (7) or 0.041 mol dm⁻³ (2).

The solubility of 1,10-phenanthroline increases as the proportion of methanol increases in binary aqueous methanol solvent mixtures (Table II). This is the expected trend, in that compounds of this type are generally much more soluble in alcohols than in water. Thus, for example, a saturated solution of 1,10-phenanthroline in ethanol is 2.78 mol dm⁻³ (4). Gibbs free energies of transfer (molarity scale) of 1,10-phenanthroline from aqueous solution into aqueous methanol mixtures at 298.2 K are included in Table II.

Solubilities of phenanthroline derivatives at 298.2 K are listed in Table III. These solubilities do not correlate with the hydrophilic or hydrophobic natures of the substituents nor with their

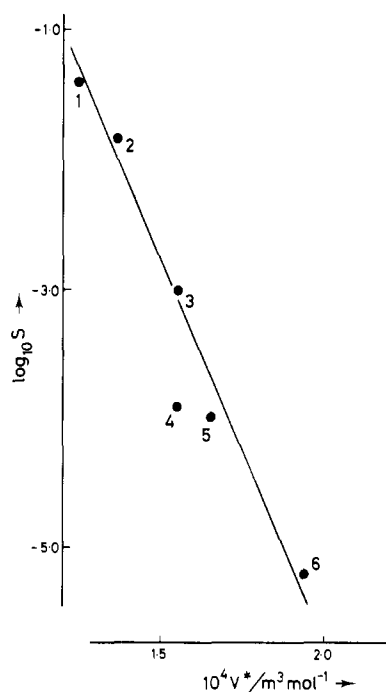


Figure 1. Relation between the logarithms of solubilities (S) of 1,10-phenanthroline and related compounds and their molecular volumes (V^*): 1, bpy; 2, phen; 3, 5-Br(phen); 4, 5-NO₂phen; 5, 4,7-Me₂phen; 6, 3,4,7,8-Me₄phen.

electron releasing or withdrawing effects. Rather they depend on the size of the molecule (3), with solubility decreasing with increasing size. Indeed a plot of logarithm of solubility against molecular volume is linear for all the phenanthrolines and 2,2'-bipyridyl (Figure 1).

The concentration of a saturated aqueous solution of 3,4,7,8-tetramethyl-1,10-phenanthroline at 323.2 K is 3.9×10^{-5} mol dm⁻³. From this and the solubility at 298.2 K (Table III), an estimate of about -2.6 kJ mol⁻¹ can be made for its enthalpy of solution. This value is very similar to those established for 1,10-phenanthroline itself and for 2,2'-bipyridyl. The very different solubilities of these compounds therefore must reflect markedly different entropies of solution.

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The Apparent Molal Volume and Adiabatic Compressibility of Some Organic Solutes in Water at 25 °C

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The apparent molal volumes and adiabatic compressibilities of aqueous solutions of some ureas, thioureas, acetamide, thioacetamide, dioxane, sugars, and succinic acid have been determined at 25 °C from precise density and sound measurements. The sugars have large negative values for the infinite dilution partial molal adiabatic compressibilities, $\bar{K}_s^\circ \sim -16.2 (\pm 3.3) \times 10^{-4}$ cm³ mol⁻¹ bar⁻¹ (of the same order of magnitude as amino acids) suggesting that these molecules are highly hydrated. Positive values of $\bar{K}_s^\circ \sim 7.0 (\pm 2.6) \times 10^{-4}$ cm³ mol⁻¹ bar⁻¹ are observed for dioxane, acetamide, thioacetamide, tetramethylurea, and succinic acid suggesting very little hydration for these molecules in water. For urea, 1,3-dimethylurea, and thiourea $\bar{K}_s^\circ \sim -1.9 (\pm 1.5) \times 10^{-4}$ cm³ mol⁻¹ bar⁻¹ suggesting these molecules are slightly hydrated. The degree of hydration increases with the number of functional groups which can hydrogen bond with water molecules. The substitution of sulfur for oxygen causes a decrease in hydration.

Introduction

An understanding of solute-water interaction of organic solutes having >C=O and >NH₂ functional groups is of paramount

importance in problems concerning helix-random coil transitions (6) and conformational stability of polypeptides (13). Many experiments (1-5, 7, 8, 10-12, 14-18, 23-29, 35, 36, 38, 39, 41-44) on the physicochemical properties of ureas, amides, and sugars indicate that the interactions with water molecules occur through hydrogen bonding with >NH, >C=O, and -OH groups. The stability of >C=O...HOH, >NH...OH₂ and H₂O...HOH hydrogen bonds has also been suggested by ab initio molecular orbital calculations for water-water dimers and amide-water systems (21). To better understand the hydration of ureas, thiourea, acetamide, thioacetamide, dioxane, succinic acid, and sugars we have determined the apparent molal volumes and apparent molal adiabatic compressibilities for some of these solutes in water at 25 °C.

Experimental Section

Materials. Urea, 1,3-dimethylurea, 1,1,3,3-tetramethylurea, and D-ribose (Eastman), 1,4-dioxane and acetamide (Fisher reagent grade), dextrose, sucrose, thiourea, and thioacetamide (Baker analyzed), and succinic acid (Aldrich) were used without further purification. All solutions were prepared by weight with Millipore Super Q ion-exchanged water. Tetramethylurea solutions were made by weight dilutions of the stock solution. All weights were vacuum corrected.