The Thermodynamics of Hydration of Phenols

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The solubilities and enthalpies of solution in water of 2-cresol and 4-cresol at 25 °C and the solubility of 4-t-butylphenol in water at four temperatures have been measured. The thermodynamic parameters for solution of the three phenols are combined with the parameters for sublimation to give information on the transfer of the phenols from the gas phase to aqueous solution. The free energies of hydration of seven substituted phenols are linearly related to the Hammett σ-parameters for the substituents. Either electron accepting or donating substituents in phenol make the enthalpy of hydration more negative. The greater the dipole moment of the phenol the stronger is the attractive solute–solvent interaction. The increment to the entropy of ionization of phenol produced by alkyl substitution results from partial compensation of larger increments to the entropies of hydration of both the phenoxide anion and the neutral phenol.

A STUDY of the apparent molal volumes and viscosity B coefficients of 4-substituted phenols in methanol led to the conclusion that the solute–solvent interaction between a phenol and solvent methanol was greater the larger the dipole moment of the phenol.[1] Measurements of the thermodynamics of hydration of phenol, 4-bromophenol, 4-formylphenol, and 4-nitrophenol has also confirmed this conclusion for aqueous solutions.[2] The enthalpies and free energies of hydration were more negative the stronger the electron-withdrawing power of the 4-substituent in the phenol. Considerations of the effect of solute–solvent interactions on the thermodynamics of ionization of phenols in hydroxylic solvents must take into account the significant effects for the neutral phenols. However the influence on the solvation of the phenoxide anions is the predominant contributing factor to the increment in the entropy of ionization which results on introducing a substituent into phenol. The measurements of the thermodynamics of hydration are here extended to include three phenols which are weaker acids than phenol itself in water.

EXPERIMENTAL

The purification of the phenols and methanol was as described before.[3,4]

Enthalpies of solution of 2-cresol and 4-cresol in water were measured with an LKB 8721-1 calorimeter. The thermostat temperature was stable to ±0·002 °C at 25 ± 0·05 °C. The solubilities of the two cresols were determined by shaking an excess of solid with water at 25 ± 0·1 °C for 24 h, filtering the saturated solution at thermostat temperature, and after appropriate dilution analysing it spectrophotometrically. A Unicam SP 500 spectrometer was used and linear calibration graphs of optical density at the absorption maxima of the neutral phenols against concentration confirmed the applicability of the Beer–Lambert Law. 4-t-Butylphenol was too sparingly soluble in water for reliable calorimetric measurement of its heat of solution and therefore the solubility of this phenol was determined at four temperatures. Each solubility was determined five times and the maximum spread of values for a given phenol and temperature was ±2% of the average value.

RESULTS

Free energies of solution of the three phenols were calculated from the solubilities C_s (Table 1) *via* equation (1) in which the activity coefficients of the neutral phenols in

$$\Delta G^\circ = -RT \ln C_s \qquad (1)$$

the saturated solutions have been taken as unity. For 2-cresol and 4-cresol the entropies of solution were deduced from the free energies and the calorimetrically determined enthalpies (Table 1). The solubilities of 4-t-butylphenol in water at four temperatures are given in Table 2. A graph of $\log_{10}C_s$ against the reciprocal of the absolute temperature was linear and, in accord with the Gibbs–Helmholtz equation, enabled calculation of the enthalpy and hence the entropy of solution (Table 1).

TABLE 1

Thermodynamic parameters * for the solution of three phenols (solid) in water at 25 °C

Phenol	Solubility (molal)	ΔG° kcal mol^{-1}	ΔH° kcal mol^{-1}	ΔS° cal K^{-1} mol^{-1}
4-Cresol	0·201	0·949	3·38	8·22
4-t-Butylphenol	0·00443	3·21	4·89	5·63
2-Cresol	0·310	0·694	3·65	9·91

* Throughout this paper 1 calorie = 4·184 J.

TABLE 2

The solubility of 4-t-butylphenol in water at four temperatures

Temperature (°C)	25	30	35	40
Solubility (10^{-3} molality)	4·43	5·08	5·79	6·54

DISCUSSION

The values for the solubilities of 2-cresol and 4-cresol in water at 25 °C are consistent with earlier determinations for $T > 40$ °C.[5]

Comparative information on the interactions between a series of substituted phenols and solvent water cannot be obtained by consideration of the thermodynamics of solution (Table 1) because of the contributions dependent on the thermodynamic properties of the solid phenols. The latter are eliminated by combination of the solution

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[1] C. H. Rochester and B. Rossall, *Trans. Faraday Soc.*, 1969, **65**, 992.

[2] G. H. Parsons, C. H. Rochester, and C. E. C. Wood, *J. Chem. Soc. (B)*, 1971, 533.

[3] C. H. Rochester and B. Rossall, *J. Chem. Soc. (B)*, 1967, 743.

[4] C. H. Rochester, *Trans. Faraday Soc.*, 1966, **62**, 355.

[5] N. V. Sidgwick, W. J. Spurrell, and T. E. Davies, *J. Chem. Soc.*, 1915, **107**, 1202.

data with the corresponding thermodynamic parameters for the sublimation of the cresols [6] and 4-t-butylphenol.[7] Hence the free energies, enthalpies, and entropies of hydration of the three phenols are given in Table 3 and may be discussed in conjunction with the corresponding data for phenol, 4-bromophenol, 4-formylphenol, and 4-nitrophenol.[2]

TABLE 3

Thermodynamic parameters for the sublimation [6,7] and hydration of three phenols at 25 °C

Phenol	ΔG_{sub} kcal mol^{-1}	ΔH_{sub} kcal mol^{-1}	ΔS_{sub} cal K^{-1} mol^{-1}
4-Cresol	5·19	17·67	41·86
4-t-Butylphenol	7·24	20·14	43·3
2-Cresol	4·67	18·17	45·28
	ΔG_{hyd} kcal mol^{-1}	ΔH_{hyd} kcal mol^{-1}	ΔS_{hyd} cal K^{-1} mol^{-1}
4-Cresol	−4·24	−14·29	−33·64
4-t-Butylphenol	−4·03	−15·25	−37·67
2-Cresol	−3·98	−14·52	−35·37

The free energies of hydration of the seven phenols show a trend in the sense that ΔG_{hyd} is more negative the greater the electron-withdrawing power of the substituent in the phenol ring. Thus a plot (Figure 1) of ΔG_{hyd} against the Hammett σ-parameters [8] for the substituents emphasizes this trend. The free energies of hydration conform to a linear free-energy relationship of the form of the Hammett equation which for 4-substituted phenols may be written as equation (2). For

$$\Delta G_{hyd}\ (\text{kcal mol}^{-1}) = -3{\cdot}50\sigma - 4{\cdot}72 \qquad (2)$$

alkyl substituted phenols the free energies of hydration are less negative than the value for phenol in accord with the negative σ-parameters for alkyl substituents. This contrasts with the behaviour of the enthalpies of hydration which are more negative for the alkyl phenols than for phenol itself. Thus 4-substitution of either electron-accepting or electron-donating groups into phenol make the enthalpy of hydration more negative. Since any 4-substituent increases the dipole moment of phenol [9,10] this is consistent with the suggestion [1,2] that the solute–solvent interaction between a phenol and water is stronger the greater the dipole moment of the phenol. The phenol–water interaction energy may be qualitatively associated with the forces which exist between the dipole of the phenol and the dipoles of the surrounding water molecules. The number of water molecules adjacent to the phenol molecule and therefore directly interacting will depend on the surface area of contact between the phenol and solvent. Assuming that the solute occupies a roughly spherical cavity the area will be approximately proportional to $V^{\frac{2}{3}}$ where V is the molal volume of the solute in water. Figure 2 shows that the enthalpies of hydration vary with a combination of dipole moment [9,10] and molal volume in the expected direction. Molal volumes were taken as those calculated previously (109·2 cm^3 mol^{-1} for 4-cresol) for phenols in a hypothetical non-hydrogen bonded liquid state.[1] Figure 2 is entirely empirical and is based on qualitative arguments. However the predicted trend in ΔH_{hyd} with varying phenol dipole moment and molal volume is consistent with the experimental results and suggests that the arguments are at least plausible. There is no simple correlation between the enthalpies and entropies of hydration although for the alkyl phenols (and 4-bromophenol [2]) substitution makes both ΔH_{hyd} and ΔS_{hyd} more negative in accord with a stronger and more ordering solute–solvent interaction. However for the substituents which exhibit a mesomeric effect (CHO, NO_2) the entropy of hydration is comparatively insensitive to substitution and the increment to ΔG_{hyd} predominantly results from the change in ΔH_{hyd}.[2]

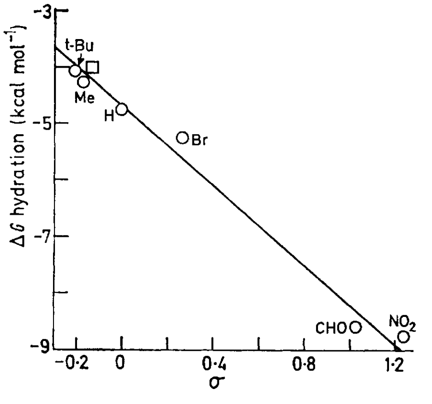

FIGURE 1 Correlation of the free energies of hydration of substituted phenols with the Hammett σ-parameters for the substituents: ○, 4-substituted phenols; □, 2-cresol

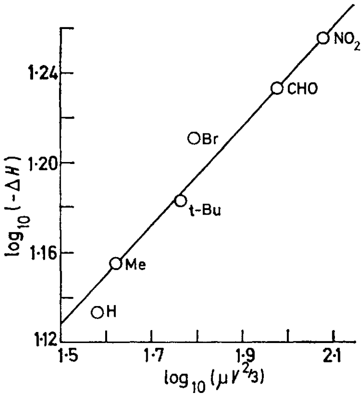

FIGURE 2 Empirical graph illustrating the variation of the heat of hydration of 4-substituted phenols with a combination of the dipole moments and molal volumes of the phenols

The sum of the entropies of hydration and ionization in water of a phenol equals the sum of the entropy of ionization of the phenol in the gas phase and the entropies of hydration of the proton and the phenoxide anion.[2]

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Because the entropies of ionization of phenols in the gas phase are probably similar [11] the comparison of the values of this sum for different phenols will largely reflect the effect of substituents on the entropy of hydration of the phenoxide anions. The figures for 2-cresol (—63·5 cal K^{-1} mol^{-1}) and 4-cresol (—62·2 cal K^{-1} mol^{-1}) compare with that for phenol (—56·9 cal K^{-1} mol^{-1}) in the manner expected if the solvation of a phenol anion is greater the greater is the charge density on the phenoxide oxygen atom. The increment (—1·5 cal K^{-1} mol^{-1}) to the entropy of ionization of phenol on 4-methyl substitution arises through partial compensation of the change in entropy of hydration of the phenoxide anion (—5·3 cal K^{-1} mol^{-1}) by the change in the entropy of hydration of the neutral phenol (—3·8 cal K^{-1} mol^{-1}). Thus the assumption that increments in entropy of ionization arise entirely from solvation changes involving the anions rather than the neutral phenols is not applicable. A similar conclusion follows for 2-cresol for which the results are similar. This conclusion could not be tested for 4-t-butylphenol because, unlike the cresols,[12,13] the enthalpy of ionization of this phenol in water is not known.

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