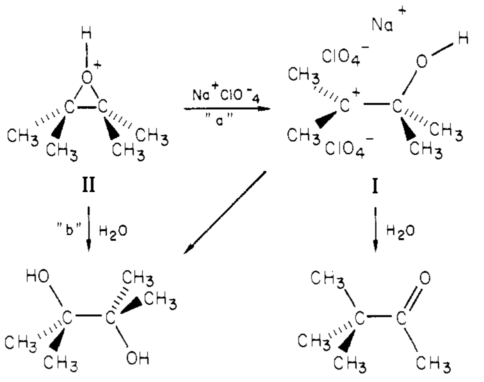
the latter by attack by water. The perchlorate counterions which account for the second-order dependence with salt would easily be pushed aside during the bond rotation and migration step.

A comprehensive mechanistic description of the reaction of TMEO unites the results found in dilute buffer solutions with those found in high-salt media.[9] The protonated epoxide, II, plays a pivotal role in this mechanism in that it can be transformed to products by two paths. One path (path a) is the spontaneous ring opening to a carbonium ion; the other (path b) is an S_N2-like process involving a water molecule. A change in mechanism from path b to path a is observable in solutions with high salt content. Greater transition-state stabilization due to ionic aggregation may make path a more favorable than path b. It is also possible that the acidity dependence of path a may be greater than that for path b.[25] In either case, an effect of this nature observable in water is striking. It is analogous to the effects found in acetic acid and in aqueous acetone solvolysis studies where the ion-pair mechanistic schemes were first developed. Most studies in aqueous media, however, have not been designed to exceed the "limiting laws" for solution behavior, and thus have not uncovered unusual effects of salts as has been done here. Even with the knowledge that salt effects of this type could be observed the choice of the substrate is probably a critical factor in revealing them. Tetramethylethylene oxide is very unusual in that its modes of reaction lie so near the mechanistic demarcation between S_N1 and S_N2 processes.



The phenomenon of mechanistic switching as explored here is very interesting and is under active investigation with a number of epoxides. Whether the epoxide ring itself imparts intrinsic sensitivity to the reaction environment or whether the extent of substitution engenders such sensitivity are questions currently being addressed.

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(24) A consequence of the existence of I could be its collapse with perchlorate ion to produce a covalent ester. The stability of this ester is anticipated to be very low owing to the leaving-group characteristics of perchlorate ion and because the ester would be tertiary. Even methyl perchlorate has very limited stability in aqueous solution: D. N. Kevill and G. M. L. Lin, *Tetrahedron Lett.*, 949–952 (1978). The NMR spectra of our reaction solutions do not show any resonances in addition to pinacolone and pinacol. If such an ester is formed, it must be below the detectable level.

(25) We are indebted to the referees for directing our attention to the possibility that a differential acidity dependence may be the origin of the mechanistic switch.

Relationship between the Gas-Phase Entropies of Molecules and Their Entropies of Solvation in Water and 1-Octanol

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Abstract: The entropies of solvation of ammonia, methane, and water in water are almost identical, yet their enthalpies of solvation are quite different. This suggests that, despite differences in the solute–solvent interactions, all molecules, including water, lose the same fraction of their entropy upon going from the gas phase into water and that changes in the entropy of water contribute little to the entropy of solvation. An equation containing no adjustable parameters is derived from these assumptions and found to reproduce the entropies of solvation of the hydrocarbons, alcohols, aromatic compounds, primary amines, and inert gases in water. These ideas are successfully extended to the water/1-octanol partition coefficients of the hydrocarbons. Our ideas are in conflict with prevailing ideas of the origin of entropies of solvation in water. Reasons for their validity and success are discussed.

Introduction and Results

Solutions and solute–solvent interactions play an important role in chemistry. One aspect of this subject that has received much attention is the so-called "hydrophobic interaction". The hydrophobic interaction refers to the low solubilities of nonpolar molecules (e.g., hydrocarbons) in water and to the tendency of molecules containing both highly water soluble groups and nonpolar groups to form micelles when dissolved in water.

Most discussions of the origins of the hydrophobic interaction are in terms of the "structured-water" hypothesis of Frank and Evans.[1] The low solubility of nonpolar groups in water is due to a negative entropy of solvation which overcomes a favorable enthalpy of solvation. The structured-water hypothesis rationalizes these facts by saying that water in the vicinity of nonpolar solutes is more structured than bulk water. The nature of this structured water is not specified, but it is assumed that it has more hydrogen bonds per water molecule than the bulk water and that these additional hydrogen bonds restrict the mobility of the water molecules, resulting in a lower entropy for such water molecules.[2,3] The additional hydrogen bonds are believed to account for the favorable enthalpy of solvation.

The structure of water and how solutes affect it have been the subject of a variety of experimental studies. Most of the experimental results have been interpreted as showing that nonpolar solutes increase the number of hydrogen bonds,[4,5] but some studies have been interpreted as showing that nonpolar solutes decrease the number of hydrogen bonds.[6,7]

We were led to reexamine the idea that hydrogen bonds and changes in the structure of water made the dominant contributions to the entropies of solvation by some seemingly anomalous data. As Table I shows, adding a methyl group to a compound makes it, at best, slightly less soluble in water and often makes it slightly

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(1) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

(2) F. Franks and D. S. Reid in "Water, a Comprehensive Treatise", Vol. 2, F. Franks, Ed., Plenum Press, New York, 1973, Chapter 5.

(3) G. Nemethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3382, 3401 (1962).

(4) T. S. Sarma and J. C. Ahluwalia, *Chem. Soc. Rev.*, **2**, 203 (1973).

(5) E. Wicke, *Angew. Chem., Int. Ed. Engl.*, **5**, 106 (1966).

(6) H. H. Ruterjans and H. A. Scheraga, *J. Chem. Phys.*, **45**, 3296 (1966).

(7) B. Z. Gorbanov et al., *Zh. Strukt. Khim.*, **16**, 816 (1975).

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Table I. A comparison of the Free Energies of Solvation[a] of Various Compounds and Their Methylated Analogues in Water at 25 °C

parent compd	$\Delta G_{\mathrm{solvation}}$, kcal/mol	methyl-substituted compd	$\Delta G_{\mathrm{solvation}}$, kcal/mol
methane	1.99[b]	ethane	1.83[b]
ammonia	−4.37[c]	methylamine	−4.56[d]
water	−6.38[e]	methanol	−5.14[f]
benzene	−0.89[g]	toluene	−0.91[g]

[a] For the process of taking the molecule from the gas phase to a water solution whose concentration (mol/L) is the same as the gas-phase concentration. [b] D. B. Wetlaufer, S. K. Malik, L. Stoller, and R. L. Coffin, *J. Am. Chem. Soc.*, **86**, 510 (1964). [c] R. G. Bates and G. D. Pinching, *J. Res. Natl. Bur. Stand.*, **42**, 419 (1949). [d] A. O. Christie and D. J. Crisp, *J. Appl. Chem.*, 17, 11 (1967). [e] Reference 19. [f] J. A. V. Butler, D. W. Thomson, and W. H. Mclennon, *J. Chem. Soc.*, 674 (1933). [g] R. D. Wauchope and R. Hague, *Can. J. Chem.*, 50, 133 (1972).

Table II. Gas-Phase Entropies and Entropies and Enthalpies of Solvation in Water at 25 °C

molecule	$S°$ gas phase,[a] eu	$-\Delta S_{\mathrm{solvation}}$, eu	$\Delta H_{\mathrm{solvation}}$, kcal/mol
ammonia	46.0	14.2[b]	−8.54[c]
methane	44.5	13.1[b](15.0[e])	−1.95[d](−2.50[e])
water	45.1	14.1[a]	−10.48[a]

[a] D. R. Stull, E. F. Westrum, and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, 1969. [b] Entropies calculated using the equation $\Delta S = (\Delta H - \Delta G)T$. Free energies of solvation taken from Table I. [c] F. M. Jones, III, and E. M. Arnet, *Prog. Phys. Org. Chem.*, **11**, 263 (1974). Entropies adjusted for the process/atm gas phase (1/24.5 mol/L) to a 1/24.5 mol/L solution. [d] Enthalpy of vaporization taken from reference *a* above is assumed to be the same as the enthalpy of solvation. See the text for a discussion of this assumption. [e] Obtained from a plot of $\Delta G_{\mathrm{solvation}}$ vs. T. $\Delta G_{\mathrm{solvation}}$ taken from reference given in footnote *b*, Table I.

Table III. A Comparison of the Calculated and Experimental Entropies of Solvation of Hydrocarbons in Water at 25 °C

compd	exptl[a] $-\Delta S_{\mathrm{solvation}}$	exptl[b] $-\Delta S_{\mathrm{solvation}}$	calcd[c] $-\Delta S_{\mathrm{solvation}}$
methane	13.1	15.0	13.9
ethane	17.9	17.8	18.7
propane	24.0	21.6	23.1
butane	25.1	26.2	27.5
isobutane	24.6	23.2	25.8

[a] Calculated from $\Delta S = (\Delta H - \Delta G)/T$, assuming that $\Delta H_{\mathrm{solvation}} \equiv \Delta H_{\mathrm{vaporization}}$. See text for a discussion of this assumption. $\Delta H_{\mathrm{vaporization}}$ taken from Table II, footnote *a*. $\Delta G_{\mathrm{solvation}}$ taken from Table I, footnote *b*. [b] Calculated from the change in the $\Delta G_{\mathrm{solvation}}$ with temperature. The $\Delta G_{\mathrm{solvation}}$ obtained from footnote *b*, Table I. [c] Equation 1 in text.

Table IV. Comparison of the Calculated and Experimental Entropies of Solvation of Some Alcohols, Amines, Aromatics, and Inert Gases in Water at 25 °C

	$-\Delta S_{\mathrm{calcd}}$	$-\Delta S_{\mathrm{exptl}}$
	Alcohols[a,b]	
methanol	20.0	19.0
ethanol	24.4	25.4
propanol	29.1	29.8
butanol	33.3	32.5
	Amines[a,c]	
ammonia	13.8	14.2
methylamine	20.0	20.6
ethylamine	24.8	27.8
propylamine	29.1	29.2
butylamine	33.3	32.0
diethylamine	32.2	36.7
triethylamine	38.9	45.1
	Aromatics[a,d]	
benzene	23.0	22.6
toluene	28.6	26.2
ethylbenzene	33.0	29.6
	Inert Gases[e,f]	
neon	16.1	12.9
argon	17.0	16.2
krypton	18.0	18.2
xenon	18.6	18.0

[a] The calculated entropies of solvation were obtained using eq 1 and standard gas-phase entropies taken from D. R. Stull, E. F. Westrum, and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, 1969. [b] The experimental entropies of solvation were obtained using $\Delta S = (\Delta H - \Delta G)/T$. The free energies of solvation calculated from the data of D. J. T. Hill and D. M. Alexander, *Aust. J. Chem.*, **22**, 347 (1969). Enthalpies of solvation taken from C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, **73**, 1572 (1969). [c] The experimental entropies of solvation were taken from F. M. Jones, III, and E. M. Arnet, *Prog. Phys. Org. Chem.*, **11**, 263 (1974). Entropies given in the above reference are for the process 1 atm gas phase to 1 M solution and were adjusted so that they correspond to the process 1 atm gas phase (1/24.5 mol L^{-1}) to a 1/24.5 mol L^{-1} solution. [d] Experimental entropies of solvation were determined using the equation $\Delta S = (\Delta H - \Delta G)/T$. Enthalpies of solvation taken from S. J. Gill, N. F. Nichols, and I. Wadso, *J. Chem. Thermodyn.*, 8, 445 (1967). Free energies of solvation determined from data in R. D. Wauchope and R. Hague, *Can. J. Chem.*, 50, 133 (1972). [e] The calculated entropies of solvation were obtained using eq 1 in text and entropies in ref 19. [f] The experimental entropies of solvation were obtained using $\Delta S = (\Delta H - \Delta G)/T$. Enthalpies of solvation taken from D. M. Alexander, *J. Phys. Chem.*, **63**, 994 (1964). Free energies of solvation determined from the data of S. Valentiner, *Z. Phys.*, **42**, 253 (1927).

more soluble in water. Yet methane is very insoluble in water. Why does removing one of methane's four hydrogens and converting it into a methyl group completely change its solubility behavior?

One obvious difference between methane and a methyl group is that the methane is a molecule while methyl groups are only a part of a molecule. When one takes a molecule from the gas phase and places it in a liquid, its free volume is reduced and the amplitude of the molecule's translational and rotational motions becomes restricted because of close and continual contact with neighboring solvent molecules. This loss of freedom results in a reduction in the entropy. A methyl group is not an independent molecule and its motions, relative to the remainder of the molecule, are highly restricted. This means that, compared to methane, a methyl group does not have much entropy to lose when it is transferred from the gas phase to the liquid phase.

Assuming that these ideas are correct, what fraction of total entropy of solvation is due to a loss of gas-phase entropy by the solute? Table II compares the entropy loss on transferring ammonia, methane, and water from the gas phase to water. The enthalpies of solvation in Table II show that the water–solute interactions of ammonia, methane, and water are quite different, but Table II also shows that their entropies of solvation in water are almost identical. This could be a coincidence, but an alternative explanation suggests itself.

Ammonia, methane, and water are quite different chemically, but their gas-phase entropies are almost identical.[8] Perhaps the reason these three molecules with quite different water–solute interactions have the same entropy of solution is that the entropy of solvation is almost entirely due to the restrictive effects of the liquid discussed above and that these effects are insensitive to differences in the water–solute interactions. If this explanation is correct, then perhaps all molecules lose the same fraction of their entropies upon going into water and changes in the entropy of water itself contribute little to the entropy of solvation.

If one assumes that changes in the entropy of water contribute nothing to the entropy of solvation and that all molecules, including

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(8) D. R. Stull, E. F. Westrum, and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, 1969.

water, lose the same fraction of their entropy when transferred from the gas phase to water, then eq 1 can be obtained (Appendix 1) without using any adjustable parameters.

$$\Delta S_{\text{solvation}} = -0.46(S° - 14.3) \tag{1}$$

$\Delta S_{\text{solvation}}$ is the entropy of solvation of the solute in water at 25 °C and $S°$ is the third-law ideal-gas entropy of the solute at 25 °C and 1 atm.

As Table III shows, the entropies of solvation of the hydrocarbons calculated using eq 1 are in as good agreement with two different estimates of the experimental entropies of solvation as the two estimates are with each other. Thus, it appears that eq 1 reproduces the entropies of solvation of the hydrocarbons to within the accuracy of the available experimental data. Table IV compares the calculated and experimental entropies of solvation of some alcohols, amines, aromatics, and inert gases. The agreement between the calculated and experimental entropies of solvation of the alcohols is quite good. The agreement between the calculated and experimental entropies of solvation of the aromatics is also good. The agreement between the calculated and experimental entropies of solvation of the primary amines is excellent. The agreement for the secondary and tertiary amines is not as good. The secondary and tertiary amines are more basic than the primary amines. We believe that this greater basicity causes effects associated with the acid–base reaction of these amines with water to contribute significantly to the observed entropies of solvation. Equation 1 cannot be expected to account for effects associated with chemical reactions, such as acid–base reactions. Despite this limitation, eq 1 is still a useful approximation of the entropies of solvation of secondary and tertiary amines.

Except for neon, the agreement between the calculated and experimental entropies of solvation of the inert gases in water is good. The claimed experimental error in the enthalpy of solvation of neon, upon which the experimental entropy of solvation is based, is ±30%. Thus, we believe that experimental error is the cause of the difference between the calculated and experimental entropies of solvation of neon.

It is of interest to know if this idea can be extended to solvents other than water. Reliable entropies of solvation from the gas phase into solvents other than water are not readily available.[9] Data on the partition coefficients of solutes between water and 1-octanol are readily available but the entropies of this process have not been determined. However, where the enthalpies of solvation of the hydrocarbons in water have been measured (see ref 2 for a compilation of $\Delta H_{\text{solution}}$), they are the same or almost the same as the heats of vaporization of the hydrocarbons (i.e., the enthalpy of solvation of the hydrocarbons in water and in the liquid hydrocarbon are the same to within the experimental error). Since 1-octanol is in many ways intermediate between a hydrocarbon and water, it is reasonable to assume that the enthalpy of solvation of a hydrocarbon in 1-octanol is the same as it is in water and in the liquid hydrocarbon. If this is true, then virtually all of the free energy of transferring a hydrocarbon from water to 1-octanol is due to differences in the entropies of solvation in the two liquids.

1-Octanol loses 17% of its entropy upon going from the gas phase to liquid 1-octanol.[10] If the entropies of solvation in 1-octanol have the same functional form as the entropies of solvation in water (i.e., all molecules lose the same fraction of their entropy upon being solvated by 1-octanol as 1-octanol does upon being solvated by 1-octanol), then the entropies of transferring a solute from 1-octanol to water will be 63% of the entropy of solvation of the compound in water (0.63 = (0.46 − 0.17)/0.46). Thus, the free energies of transfer from water to 1-octanol, assuming, for the reasons given above, that the enthalpy of transfer is zero, will be

$$\Delta G_{\text{1-octanol/water}} = -0.63T(\Delta S_{\text{gas/water}}) \tag{2}$$

where $\Delta S_{\text{gas/water}}$ is the entropy of solvation of the compound in water and $\Delta G_{\text{1-octanol/water}}$ is the free energy of transferring the compound from 1-octanol to water.

Table V. Comparison of Calculated and Experimental Free Energies (kcal/mol) of Transferring a Hydrocarbon from 1-Octanol to Water at 25 °C

compd	$\Delta G_{\text{approx-1}}$	$^a\Delta G_{\text{approx-2}}{}^b$	$\Delta G_{\text{exptl}}{}^c$
methane	2.46	2.82	2.54
ethane	3.37	3.38	3.53
propane	4.51	4.10	4.28
butane	4.72	4.96	5.00

[a] $\Delta G_{\text{approx-1}} = T0.63\Delta S_{\text{water}}$. $\Delta S_{\text{water-1}}$ is the entropy of solvation of the hydrocarbon in water obtained assuming that the heat of vaporization of the compound and its enthalpy of solvation in water are the same. See the text for a discussion of this approximation. Free energies of solvation calculated from the data of Table I, footnote *b*. [b] $\Delta G_{\text{aporox-2}} = T0.63\Delta S_{\text{water-2}}$. $\Delta S_{\text{water-2}}$ is the entropy of solvation of the compound in water obtained from the temperature dependence of the free energies of solvation and assuming that the enthalpies and entropies of solvation are unaffected by changes in temperature. Free energies of solvation calculated from data of Table I, footnote *b*. [c] R. D. Cramer, III, *J. Am. Chem. Soc.*, 99, 5408 (1977).

As Table V shows, eq 2 reproduces the free energies of transferring a hydrocarbon from 1-octanol to water. This implies that the origin of the entropies of solvation is the same in both solvents.

Discussion

We have shown that the entropies of solvation of a wide variety of nonelectrolytes in water can be reproduced by an equation derived assuming (1) that all molecules, whether or not they form hydrogen bonds, lose the same fraction of their gas-phase entropy when they go from the gas phase into water and (2) that changes in the entropy of water contribute nothing to the entropies of solvation.

Others have proposed that loss of entropy by the solute contributes to the entropy of solvation[12-14] and have criticized the structured water hypothesis.[15-17] We are, however, the first to show that loss of entropy by the solute could account for all of the entropy of solvation.[18]

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(9) Entropies of solvation can in principle be derived from the changes in the free energy with temperature using the Gibbs–Helmholtz equation. However, some anomalous entropies and enthalpies of solvation have been obtained in this manner. For example, it was found that whatever change occurred in either the entropy or enthalpy of methane with temperature change in the opposite direction occurred with ethane. Another example is the finding that both the entropy and enthalpy of solvation of helium in cyclohexane are *positive*. G. M. Badner (*J. Chem. Educ.*, **57**, 117 (1980)) has shown that from changes in the solubility with temperature one obtains the differential molar enthalpies and entropies of solvation *at saturation* and that these quanities are often uncorrelated with the integral molar enthalpies and entropies of solvation *at infinite dilution* that one obtains from dilute solution calorimetric studies. Since it is the entropies at infinite solution that eq 1 attempts to reproduce, this explains why many of the derived entropies of solvation seem anomalous.

(10) The ideal gas entropy of 1-octanol at 6.33 mol/L (the density of 1-octanol at room temperature) is 114.1 eu. The entropy of liquid 1-octanol is 94.4 eu. These quantities are derived from the standard entropies in Stull et al. (ref 8), densities in ref 19.

(11) A. Ben-Naim, "Water and Aqueous Solutions", Plenum Press, New York, 1974, p 170.

(12) R. H. Aranow and L. Witten, *J. Phys. Chem.*, **64**, 1643 (1960).

(13) O. W. Howarth, *J. Chem. Soc., Faraday Trans. 1*, **71**, 2303 (1975).

(14) M. Osinga, *J. Am. Chem. Soc.*, **101**, 1621 (1979).

(15) M. Yaacobi and A. Ben-Naim, *J. Phys. Chem.*, **78**, 175 (1974).

(16) A. Holtzer and M. F. Emerson, *J. Phys. Chem.*, **73**, 26 (1969).

(17) R. D. Cramer, III, *J. Am. Chem. Soc.*, **99**, 5408 (1977).

(18) Howarth (*J. Chem. Soc., Faraday Trans. 1*, **71**, 2303 (1975)) proposed, on the basis of NMR T_1 studies, that the 10–19-eu excess in the entropies of solvation of hydrophobic groups in water compared to their entropies of solvation in other solvents was due to the unique ability of water to restrict the motion of such molecules and that structuring effects contributed little. We differ from this conclusion only to the extent that it implies that only in water are the motions restricted (relative to the gas phase). Despite our agreement with Howarth's conclusion, we believe that his analysis of the T_1 data is faulty. The T_1 data enables one to determine the rotational correlation time. The correlation times measure the *rate* at which the solute and water diffuse from one configuration to another. Since thermodynamic properties are unaffected by the rate at which configurations interchange (assuming that the rates are high enough that the system is at equilibrium), T_1 measurements cannot be used to determine entropies or other thermodynamic properties.

Table VI. The Fraction of the Entropy Lost by Hydrogen-Bonded and Non-Hydrogen-Bonded Particles When Transferred from the Ideal Gas to a Condensed-Phase Configuration[a]

$(R^\circ - R)$	H-bonded water	non-H-bonded water	methane
0.25	0.73	0.69	0.71
0.20	0.68	0.65	0.66
0.15	0.64	0.59	0.60

[a] The calculations summarized in this table are described in Appendix 3.

Since eq 1 was derived directly from these assumptions and contains no adjustable parameters, its success implies that these assumptions are valid. However, because these assumptions are in conflict with the prevailing beliefs we will show that they can be derived from fundamental laws and experimental data.

Statistical mechanics says that to determine the entropy one needs to know two things: the spacing between energy levels and the number of different configurations in the system. (A configuration is a group of molecules that are oriented in some defined way relative to each other. In a liquid, unlike a solid, there are many different configurations.) We define S_{config} to be the entropy of molecules when in the typical configuration, as calculated from the spacing of the energy levels in that configuration, and we define S_{mix} to be the entropy of mixing term due to the presence of the large number of configurations in a liquid. Since these two terms account for the entire entropy of a system, to show that changes in the entropy of water contribute little to the entropies of solvation we must show that S_{config} and S_{mix} of water are the same in solutions as in pure water.

Since the number of hydrogen bonds per water molecule in a solution differs from the number in pure water, we implicitly assumed that the number of hydrogen bonds has little effect on S_{config} of water in liquid water. The idea that the number of hydrogen bonds has little effect on the entropy of water molecules in liquid water seems to contradict the well-established fact that, when two gas-phase water molecules form a hydrogen bond, the entropy of the resulting gas-phase dimer is lower than the sum of entropies of two independent gas-phase water molecules. This loss of entropy occurs because, when the gas-phase dimer is formed, the two molecules cease to move independently and as a result three single molecule translational and three single molecule rotational degrees of freedom are replaced by six dimer vibrational degrees of freedom. The entropy of the dimer vibrational degrees of freedom will be substantially less than the entropy of the single molecule translational and rotational degrees of freedom they replace no matter what forces are holding the dimer together. For example, the entropy loss on forming a van der Waals dimer is 80% of the entropy loss on forming a hydrogen-bond dimer (conditions: gas phase, 1 atm, 25 °C, and potential-energy functions in Table VI).

For a gas-phase dimer to be at equilibrium, the force between the two molecules making up the dimer must be zero.

$$F_{\text{dimer interaction}} = 0 \tag{3}$$

In a condensed phase, where there are many interacting molecules, the criterion for a configuration to be at equilibrium[24] is

$$F_{\text{total interaction}} = \sum_i^{\text{nni}} F(i) + \sum_j^{\text{nnni}} F(j) = 0 \tag{4}$$

where nni stands for nearest-neighbor interactions and nnni stands for non-nearest-neighbor interactions.

Since the interactions between non-nearest-neighbors are attractive

$$\sum_j^{\text{nnni}} F(j) < 0 \tag{5}$$

When eq 4 and 5 are combined, one obtains

$$\sum_j^{\text{nni}} F(i) = -\sum_j^{\text{nnni}} F(j) > 0 \tag{6}$$

Thus, in a condensed phase, the attractive non-nearest-neighbor interactions cause the nearest-neighbor interactions to be repulsive.

The existence of repulsive interactions between nearest neighbors is well known in solids where it is consistently found that the intermolecular contact distances are smaller than the distance at the minimum in the isolated dimer intermolecular potential.[22] This effect is also seen in ice, where the O–O distance[23] is 0.22 Å smaller than the O–O distance at the minimum in the water dimer potential.[23] The only significant difference between a liquid and a solid in regard to the repulsive interactions between immediate neighbors is that in a solid the structure is static. In a liquid, the thermal agitation and movement cause the structure[5,24] and immediate neighbors to change about every 10^{-10}–10^{-11} s.

The repulsive interactions between nearest neighbors greatly reduce the effect the attractive portion of the intermolecular potential has on the entropy of molecules in a liquid. In the gas-phase dimer the molecules oscillate between the attractive and repulsive portions of the potential. The existence of the repulsive interactions at equilibrium[24] between nearest neighbors in a liquid means that the molecules in a liquid vibrate between the repulsive potentials of the molecules on either side of it. The repulsive interactions keep the amplitude of the oscillations so small that the molecules never get far enough apart to encounter the attractive side of the potential. Thus, the nature of the attractive portion at the potential has little effect on the entropy of a molecule in a liquid. The calculations in Table VI confirm these qualitative arguments.

Table VI compares the fraction of the gas-phase entropy lost by three different types of particles upon going from the ideal-gas phase to the middle of a face-centered cubic box. The particle in the middle of the box has repulsive interactions with the particles in the center of each face. (The calculations are described in Appendix 3 and it must be read to learn exactly how the calculations were carried out.) In this model each molecule has six nearest neighbors while in ice each molecule has four nearest neighbors. To account for this difference the force constants calculated using this model were reduced by $^1/_3$ before calculating the vibrational frequencies. The second column of Table VI gives the entropy loss of a hydrogen-bonded water particle. Our model gives realistic estimates of the entropy lost by a water molecule upon going from the gas phase into a condensed-phase configuration as shown by the good agreement between the calculated entropy loss factor of 0.68 when $(R^\circ - R) = 0.20$ Å with the experimental entropy loss factor of 0.67 for ice (corrected for hydrogen disorder), where $(R^\circ - R) = 0.22$ Å[23].

Column 3 of Table VI gives the entropy loss factor of a "non-hydrogen-bonded" water particle. Despite the fact the attractive interactions of our "non-hydrogen-bonded" water

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(19) "Handbook of Chemistry and Physics", R. C. Weast, Ed., Chemical Rubber Publishing Co., Cleveland, 1977.

(20) O. Weres and S. A. Rice, *J. Am. Chem. Soc.*, **94**, 8983 (1972).

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(22) (a) F. A. Momany, L. M. Carruthers, R. F. McGuire, and H. A. Scheraga, *J. Phys. Chem.*, **78**, 1595 (1974); (b) N. H. Allinger, M. A. Miller, F. A. VanCatledge, and J. A. Hirsch, *J. Am. Chem. Soc.*, **89**, 4345 (1967).

(23) Ice O–O distance at 2.76 Å from J. L. Kavanau, "Water and Solute Water Interactions", Holden-Day, London, 1969. Water O–O distance from A. H. Narten and H. A. Levy, *J. Chem. Phys.*, **55**, 2263 (1971). The minimum in the O–O dimer potential is taken from the ab initio CI data of O. Matsuoka, E. Clementi, and M. Yoshimine, *J. Chem. Phys.*, **64**, 1351 (1976), for the configuration closest to that found in ice.

(24) For a configuration of molecules in a liquid to be in equilibrium the attractive forces between nonneighboring molecules must be counterbalanced by the repulsive forces between immediate neighbors. Thus, configurations where there are attractive interactions between a molecule and one or more of its immediate neighbors are nonequilibrium configurations and higher in energy than an equilibrium configuration would be. As a result of their higher energy, such nonequilibrium configurations will occur too infrequently to significantly affect the thermodynamic properties, although their presence is important to rate processes such as diffusion.

(25) T. L. Hill, "Introduction to Statistical Thermodynamics", Addison-Wesley, Reading, Mass., 1960, p 179.

(26) H. A. Bent, "The Second Law", Oxford University Press, London, 1965, p 179.

(27) A. Ben-Naim, *J. Phys. Chem.*, **82**, 792 (1978).

(28) C. Tosi, D. Wertz, E. Clementi, and H. Scheraga, to be published.

particle differ from those of water by 50% (a difference in the attractive interactions four times greater than the 13% decrease in the enthalpy that occurs when ice melts), the fraction of the entropy lost by the hydrogen-bonded and "non-hydrogen-bonded" particles differ at most by only 5%.

Table VI shows that the entropy lost by a water molecule when it goes from the ideal-gas phase into a condensed-phase configuration is essentially the same whether it is completely hydrogen bonded in that configuration or non-hydrogen-bonded in that configuration. Thus the entropy of a water molecule when in a configuration in water (which is what we defined to be S_{config} of water) is essentially the same no matter how many hydrogen bonds there are. As a result, S_{config} of water will not be significantly affected by any changes in the number of hydrogen bonds that occur when solute molecules are placed in liquid water. Thus Table VI shows that S_{config} of water is the same in a solution as it is in pure water.

Since, as shown by Table VI, S_{config} of water in a condensed phase is the same no matter how many hydrogen bonds the water molecules have, it means that the other contributor to the entropy, S_{mix} (the entropy of mixing due to the number of configurations), must be responsible for the entire entropy of fusion of ice. This fact was recognized by Weres and Rice,[20] who calculated that the number of different configurations in liquid water and the number of different ways these configurations can be oriented accounts for 6.2 eu of the entropy of liquid water. The number of different orientations in ice (often called the disorder parameter) contributes 0.8 eu to the entropy of ice.[21] Thus, S_{mix} is calculated to be 5.4 eu or 0.1 eu greater than the experimental entropy of fusion of water.

The nearest-neighbor O–O distance in water is 0.05 Å greater than in ice.[23] This might be interpreted as evidence that the nearest-neighbor repulsive interactions are weaker in water than in ice. Table VI shows that the entropies of the hydrogen-bonded and non-hydrogen-bonded molecules are almost identical not only when $(R^\circ - R) = 0.2$ Å, as it does in ice, but also when $(R^\circ - R) = 0.15$ or 0.25 Å. We believe, in any case, that the increased nearest-neighbor O–O distance in water is caused by distorted hydrogen bonds and a greater number of nearest neighbors. It is probable that the nearest-neighbor interaction is slightly more repulsive in water than in ice. The density of water is 10% greater than the density of ice. This means that the number of attractive non-nearest-neighbor interactions is also about 10% greater. A larger non-nearest-neighbor attractive interaction results in a larger nearest-neighbor repulsive interaction.

Let us now examine the contribution of S_{mix} of water (in other words, the number of configurations) to the entropies of solvation. It has been found from NMR relaxation time measurements that the rotational correlation time of water molecules around a nonpolar solute is about a factor of 2 greater than in pure water.[4,5] The rotational correlation time is inversely proportional to the average rate at which a configuration is replaced by a new configuration. If we assume that the rate at which a configuration is replaced is equal to the number of configurations in the system times the average rate at which any two particular configurations interconvert, then the observed factor of 2 increase in the rotational correlation time implies that there has been a factor of 2 decrease in the number of configurations. A factor of 2 decrease per solute molecule in the number of configurations in a solution will cause a 1.4-eu decrease in S_{mix}. A 1.4-eu decrease in the entropy is barely 10% of the entropy of solvation of methane in water. Thus, the relaxation-time measurements imply, as does the success of eq 1, that changes in S_{mix} contribute little to the entropy of solvation.

The above analysis probably overstates the decrease in the number of configurations because it implicitly assumes that the rate for interconverting any two configurations is the same in solution and in pure water. The activation energy for configurational conversion occurs because in going from one configuration to another interactions in the old configuration must be broken before the interactions in the new configuration can be formed. It is generally believed that there are more water–water hydrogen bonds in solutions than in pure water.[2,3] If this is true, then the average activation energy for configurational conversion should be greater in solution than in pure water. Thus, if there are more hydrogen bonds in the solution, the observed increase in rotational correlation times is consistent with the same or even slightly more water configurations in the solution than in pure water.

Since both S_{config} and S_{mix} of water are about the same in the solution as in pure water, it means that changes in the entropy of water contribute little to the entropy of solvation. Thus, the entropies of solvation in water are due to changes in the entropy of the solute. This fact and the data in Tables III–V, which show that the entropies of solvation in water of a wide variety of solutes are equal to a fixed fraction of the gas-phase entropy of the solute, mean that the validity of our first assumption has been shown. Namely, all molecules, whether or not they form hydrogen bonds, do lose the same fraction of their entropy upon going from the gas phase into water.

The validity of assuming that all molecules lose the same fraction of their entropy upon going from the gas phase into water is also shown by the fact that in water the S_{config} of methane, a solute that does not form hydrogen bonds, is the same as S_{config} of water. This is shown by column 4 of Table VI, which gives the fraction of its entropy that a methane-like particle loses when it goes from the gas phase into configurations with different nearest-neighbor repulsive interactions. The strengths of the water–water and water–solute repulsive interactions in water are almost identical.[24] Table VI shows that when the repulsive interactions of the water and methane-like particles are the same they lose virtually identical amounts of entropy—as is required if our assumption is valid.

Let us now consider the question of whether S_{mix} of a solute in water is the same as the S_{mix} of water in water. This question was implicitly answered when we concluded that the S_{mix} of water in solutions was almost the same as the S_{mix} in pure water. This is because the configurations in a solution contain both water and solute molecules. Thus the conclusion that the NMR relaxation time measurements implied that the S_{mix} per molecule was the same in the solution as it was in pure water applied to both the water and the solute molecules.

Our discussion of how the repulsive nearest-neighbor interactions affect the entropy of molecules in a liquid has for the sake of simplicity considered only the translational degrees of freedom. It is clear that the repulsive interactions between nearest neighbors also restrict the amplitude of the external rotational degrees of freedom and convert them into librations. The situation with respect to the internal vibrational degrees of freedom is more complex. If the amplitude of the internal vibrational degrees of freedom are small compared to the amplitude of the librations of the external degrees of freedom allowed by the repulsive nearest-neighbor interactions, then these vibrations will be little affected by the nearest-neighbor interactions. Vibrations of this type are found in the fingerprint and higher frequency regions of the IR and contribute little to the entropy of the molecule.

If the amplitude of the internal vibrational degree of freedom is large compared with the amplitude of the oscillations allowed by the repulsive nearest-neighbor interactions, then the amplitude of these vibrations will be restricted in the same way that the amplitude of the librations of the external degrees of freedom are restricted. Vibrations of this type are found in the far IR and do contribute significantly to the entropy of a molecule in the gas phase. Thus, when a molecule with this type of degree of freedom, typically a torsional mode, goes from the gas phase into the liquid, the entropy contributed by this internal vibration will be reduced.

While it is clear that going from the gas phase into the liquid will cause a molecule to lose entropy from its internal degrees of freedom, it is not clear, given the wide variation in the amplitude of vibrations, that the fraction of the entropy lost will necessarily be the same for the internal as for the external degrees of freedom. The internal degrees of freedom contribute a larger fraction of the entropy in a large molecule than in a small one. If the entropy loss factor for the internal and external degrees of freedom differed significantly, the result would be a larger percentage deviation between the experimental entropies of solvation and those calculated using eq 1 for the large molecules than for the small ones. We see no evidence of this in Tables III and IV but this could be because the molecules we have examined are all fairly small and the internal degrees of freedom contribute relatively little to their gas-phase entropies. For example, the internal degrees of freedom of butane, the largest molecule in Table III, contribute only 15% of the gas-phase entropy. Thus the entropy loss factors might differ but we are unable to see it in the molecules studied here.

Conclusion

In this paper, we examined the consequences and validity of assuming (1) that all molecules lose the same fraction of their entropy upon going from the gas phase into water and (2) that changes in the entropy of water contribute little to the entropies of solvation in water. A corollary of the first assumption is that the number of hydrogen bonds or even their presence or absence has little effect on the entropy of molecules (including water) in liquid water.

Statistical mechanics says that the entropy of a molecule depends on only two things: the number of different configurations in the system and its vibrational frequencies in these configurations. NMR relaxation time measurements indicate that changes in the number of configurations contribute little to the entropy of solvation. We also showed that the librational frequencies of the external degrees of freedom of a molecule in water are almost identical whether or not the molecule forms hydrogen bonds. These facts mean that changes in the entropy of water contribute little to the entropy of solvation of molecules in water and that almost all of the entropies of solvation of molecules in water are due to a loss of entropy by the solute molecule when it goes from the gas phase into water.

In this paper we have considered only nonelectrolytes, partially because we felt that it was unlikely that the assumptions used in deriving eq 1 would be valid for ionic solutes. However, a referee pointed out that the estimated gas to liquid entropy of solvation for $K^+ + Cl^-$ is about the same as for 2Ar—which is what would occur if our ideas applied to ions as well as nonelectrolytes.

We extended these ideas to 1-octanol and found that we were able to reproduce the water/1-octanol partition coefficient of the saturated hydrocarbons. We would have liked to explore the applicability of these ideas to solvents other than water but we have used in this paper all the reliable experimental entropies of solvation that we know about. Dilute solution entropies of solvation are not widely available and virtually all of what is available are derived from changes in solubility with temperature. We consider the entropies derived in this way, as opposed to entropies based on calorimetrically determined enthalpies of solvation, to be unreliable. (See footnote 9 for the reasons why we consider derived entropies of solvation to be unreliable.) We hope that this paper stimulates dilute solution calorimetric research so that the applicability of our ideas to nonaqueous solutions can be tested.

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Appendix 1. Derivation of an Equation Relating the Gas-Phase Entropy and the Entropy of Solvation

As is discussed in the text, the data in Table II might mean that all molecules lose the same fraction of their entropy upon going from the gas phase into water and that changes in the entropy of the water contribute little to the entropy of solvation. Water is a molecule whose entropy in both the gas and liquid phases is accurately known. Using water as our test solute has the advantage over other possible choices because we can be sure that the entropy of liquid water is not changed by this solute and so a loss of entropy by the solute is the only contributor to the entropy of solvation.

The gas-phase entropy of water when its concentration is identical with the liquid phase concentration is 30.8 eu. The entropy of liquid water is 16.7 eu.[19] Thus, water loses 46% of its entropy when it goes from the gas phase into water. If one assumes that all molecules lose 46% of their entropy when they go into water from the gas phase and that changes in the entropy of water contribute nothing to the entropy of solvation, then

$$\Delta S_{\text{solvation}} = -0.46S \tag{1.1}$$

where S is the gas-phase entropy of the solute at a concentration of 55.5 mol/L. This equation is fine if one is interested in solutions whose concentration is 55.5 mol/L. However, real solutions do not have solute concentrations of 55.5 mol/L. We can extend the use of this entropy loss factor to concentrations other than 55.5 mol/L by breaking the process of forming a dilute solution into three steps.

In the first step, the solute is treated as an ideal gas and compressed from 1 atm to 55.5 mol/L. This results in a 14.3-eu entropy loss. In the second step, the solute is transferred to a hypothetical 55.5 mol/L solution which has the intermolecular interactions of a dilute solution. If our assumptions are correct, then in this step the molecule loses 46% of the remaining entropy. In the third step, we dilute this hypothetical solution so that the concentration of the solute becomes the same as its concentration in the gas phase. This dilution results in a 14.3-eu increase in the entropy of configurational mixing.[26] Thus, for a solution whose concentration is the same as that of an ideal gas at 1 atm and 25 °C (1/24.5 mol/L), the entropy of solvation predicted by our assumptions is

$$\Delta S_{\text{solvation}} = -14.3 - 0.46(S^\circ - 14.3) + 14.3 \tag{1.2}$$

where S° is the gas-phase entropy of the solute at 25 °C and 1 atm.

An examination of the standard statistical-mechanical formulas used to calculate the translational[25] and configurational mixing[26] entropies shows that for a *dilute* solution the entropy lost in the first step and the entropy gain in the third step will always cancel—if the concentration (mol/L) of the gas and solution are identical. Thus, for these conditions the equation derived from our assumptions is

$$\Delta S_{\text{solvation}} = -0.46(S^\circ - 14.3) \tag{1.3}$$

where S° is the standard, 1 atm, gas-phase entropy of the solute.

The fact that the translational entropy loss and entropy of configurational mixing gain cancel if the concentrations of the solute in the gas and the solution are identical deserves more comment. In the past, entropies of solvation have most often been given for the process of taking the solute at 1 atm in the gas phase and placing it in a hypothetical solution that contained only solute (i.e., mole fraction equals one) but with the intermolecular interactions of a dilute solution.[2,3] This is the same as using only the first two steps of our cycle. The motivation for using this cycle was to avoid making the increase in the configurational mixing entropy on dilution (i.e., cratic entropy) part of the entropy of solvation. This two-step cycle does avoid making the increase in the entropy of configuration mixing on dilution part of the entropy of solvation but it achieves this goal at the expense of making the equally large translational entropy loss of the first step part of the entropy of solvation. Since the entropy loss in the first step is not the result of solute–solvent interactions, it is just as extraneous as the increase in the entropy of configurational mixing on dilution. For dilute solutions our cycle avoids making either the translational or increase in the entropy of configurational mixing on dilution part of the entropy of solvation because under these conditions the two terms cancel each other. This conclusion was also arrived at by Ben-Naim[27] using arguments based on the chemical potential discussed in Appendix 2.

Appendix 2. Thermodynamics of Transfer

Some of the calculations and discussions of the thermodynamics of water solutions assume that the chemical potential of a single spherical monatomic molecule in condensed phase can be written as[11]

$$\mu_{\text{liquid}} = kT \ln \left(\frac{\Lambda^3 N}{V} \right) kT \ln e^{-u/kT} \tag{2.1}$$

where u is the mean interaction energy of the solute with the other molecules of the system. This quantity differs for each phase and solute–solvent combination.

$$\Lambda = h/(2mkT)^{1/2} \tag{2.2}$$

The partition function that gives this chemical potential is

$$Q_{\text{liquid}} = \frac{1}{N!}\left(\frac{V}{\Lambda^3}e^{-u/kT}\right)^N \tag{2.3}$$

The entropy of molecule obtained from this partition function using standard statistical-mechanical formulas is

$$S_{\text{liquid}} = Nk \ln\left(\frac{\Lambda^3 Ne^{5/2}}{V}\right) \tag{2.4}$$

The entropy of vaporization is calculated from eq 2.4 and the entropy at an ideal gas (N/V the same in both phases for the reasons given in Appendix 1) is

$$\Delta S_{\text{calcd}} = (S_{\text{liquid}} - S_{\text{gas}}) = Nk \ln\left(\frac{\Lambda^3 Ne^{5/2}}{V}\right) - Nk \ln\left(\frac{\Lambda^3 Ne^{5/2}}{V}\right)$$

$$\Delta S_{\text{calcd}} = 0 \tag{2.5}$$

The zero entropy of vaporization calculated using eq 2.3 is in conflict with the well-known experimental fact that molecules do lose entropy when they go from the gas phase into their own liquid phase. Thus eq 2.3 and the chemical potential derived from it (eq 2.1) are invalid and any conclusions or calculations based on eq 2.1 must be considered questionable.

One conclusion derived from eq 2.1 is that the experimental entropy of solvation (solute concentration the same in both phases) is identical with the entropy of the process of transferring a molecule from a fixed position in the gas phase to a fixed position in the liquid phase.[11] Since the entropy of a fixed molecule is the same no matter what phase it is in, this is the same as saying that the entropy of molecules does not change when going from the gas phase into a liquid. This claim is clearly in conflict with the conclusions of this paper. This claim is also in conflict with the experimental fact that, when molecules go from the gas phase into their own liquid phase, they, not the molecules already in the liquid phase, lose entropy.

Appendix 3. Calculation of the Entropy Loss Factors in Table VI

Table VI gives the fraction of the ideal gas entropy lost by three different types of particles when they go from the gas phase into the middle of a cube which has particles in the middle of each face. The central particle has repulsive interactions with each of the particles in the faces of the cube. The entropies of the central particles were determined by treating them as harmonic oscillators. The vibrational frequencies were calculated from the second derivatives of the potential energy functions described below by using standard formulas. In this model, each molecule has six immediate neighbors while in ice each molecule has four neighbors. So that the calculated entropy loss could be compared with the experimental entropy loss for ice, the second derivatives were multiplied by $^2/_3$. The mass of the particles was 20 g/mol. The entropy of the gas phase particles was calculated by treating them as monoatomic particles and assuming their concentration was 1 molecule per 3.0 Å^3. The experimental entropy loss factor for ice of 0.67 quoted in the main text was calculated for the process of taking water at a concentration of 1 molecule per 3.0 Å^3 in the gas phase and transferring it into ice that has no hydrogen disorder. Table VI gives the fraction of the entropy lost by each of the spherical particles at various ($R° - R$) values, where R is the distance, in angstroms, from the central particle to the particles around it. $R°$ is the distance at which the particles have their minimum potential energy. The values of $R°$ for each type of particle are given below. The values ($R° - R$) given in column 1 of Table VI are for the hydrogen-bonded water molecule at different R values. The entropy loss factors for the other particles were calculated under the condition that their repulsive interactions were the same as those for the water particle. The corresponding ($R° - R$) values for these cases are 0.363, 0.302, and 0.237 Å, respectively, for the non-hydrogen-bonded water and 0.336, 0.277, and 0.212 Å, respectively, for the methane particle.

The potential energy function, $E_{\text{H-bond}}$, used for the hydrogen-bonded particle is:

$$E_{\text{H-bond}} = \epsilon[(R°/R)^8 - 2.0(R°/R)^4] \tag{3.1}$$

where $\epsilon = 5.6$ kcal/mol and $R° = 3.0$ Å. A 4–8 potential was used instead of the 10–12 potential often used to represent a hydrogen bond because the 4–8 potential gave the best fit to the ab initio water–water interaction energies of O. Matsuoka et al.[13] An $E_{\text{min}} = -5.6$ was used because the water dimer in this reference that had a configuration that most closely resembled the configuration found in ice had an $E_{\text{min}} = -5.63$.

The potential energy function, $E_{\text{non-H-bond}}$, used for the non-hydrogen-bonded particle is:

$$E_{\text{non-H-bond}} = \epsilon[(R°/R)^8 - 2.0(R°/R)^4] \tag{3.2}$$

where $\epsilon = -2.8$ kcal/mol and $R° = 3.0$ Å. A 4–8 potential was chosen because this potential best fits the ab initio energies of all the configurations of Matusoka et al.[13] When ice melts the enthalpy decreases by 13%. The $E_{\text{min}} = -2.8$ kcal/mol is 50% of the E_{min} of the hydrogen-bonded particle. A much smaller E_{min} was chosen for the calculations of the non-hydrogen-bonded particles to emphasize the fact that the increase in entropy that occurs when ice melts is not due to a decrease in the number of strength of the hydrogen bonds.

The potential energy function, E_{methane}, used for the methane-like particle is:

$$E_{\text{methane}} = \epsilon[(R°/R)^{14} - 2.33(R°/R)^6] \tag{3.3}$$

where $\epsilon = -1.1$ kcal/mol and $R° = 3.8$ Å. The value for $R°$ was fixed at 3.8 Å because this is where the minimum in the Hartree–Fock ab initio water–methane potential energies[29] occurs. The configuration where this occurs is one where the water molecule approached the methane molecule with its dipole along the line defined by a methane C–H bond and with the water hydrogens pointed away from the methane. All of the available water–methane ab initio calculations have been done at the Hartree–Fock level and do not include configuration interactions. Since it is the configuration interactions that account for attractive van der Waals interactions, the Hartree–Fock calculations show, as expected, only nominal attractive water–methane interactions. Thus, the strength of the attractive van der Waals interactions had to be estimated. The strength of the attractive van der Waals interactions increases as the number of electrons increases and as the polarizability of the electrons in the interacting molecules increases. Water and methane have the same number of electrons and as indicated by the refractive indexes of hydrocarbons and water their polarizabilities are similar. This implies that the attractive water–van der Waals interactions are very close to the −1.1 kcal/mol contribution to the interaction energies of the water dimer made by configuration interactions.[13] An attractive van der Waals interaction of −1.1 kcal/mol for water–methane interactions is also consistant with the fact that the heat of vaporization of hydrocarbons and their enthalpies of solvation in water are almost identical and with the fact that the heat of vaporization of methane is about one-fifth that of water. One-fifth of the minimum in the water–water potential (−5.6 kcal/mol) is also about −1.1 kcal/mol.