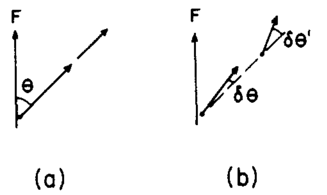

Figure 7. Model used in calculation of χ_{or}. (a) The dipoles are oriented in the direction of the unperturbed minimum. (b) Potential minimum in the presence of the internal field F.

properties to be used are those for the time-average configuration and thus apply only if the period of observation (ca. one cycle of the alternating field) is long compared to periods for libration and hindered rotation of a water molecule in its network. Judging by the frequencies in Table II, at 300 GHz this requirement is on the verge of not being satisfied.

The property to be analyzed is the dielectric constant at the beginning of the faster step, which is expressed by ϵ_∞ for the slower step and is measured at about 300 GHz. Values at various temperatures are listed in Table III. All are significantly greater than the value of $n^2 = 1.8$ expected for distortion polarization alone.

The gist of the mechanism to be proposed is that at frequencies at which the slower step is unable to follow, one can still have orientation polarization because the electric field perturbs eq 15 and produces a small change in the angle ϕ at which $V(\phi)$ is at a minimum. This in turn slightly polarizes the molecular population in the potential well. Debye has shown that when the unperturbed well is symmetric, such polarization is independent of the temperature.[34] In terms of eq 3, it contributes an additive term to the polarizability: $\chi = \chi_{distortion} + \chi_{or}$.

Table III lists values of χ_{or} calculated from ϵ_∞ via eq 3 by letting $g\mu^2/3kT = 0$ and $\chi_{distortion} = 1.5 \times 10^{-24}$, the value used by OK.[22] In Figure 7, let θ denote the angle between the internal field F and the dipole direction in the unperturbed minimum. Let $\delta\theta$ and $\delta\theta'$ denote respectively the deviations of μ and μ_{nwrk} from θ. The perturbed potential minimum then is located according to (21).

$$\delta\theta = -2a(1 - g/3) \qquad \delta\theta' = 2a(1 - 2g/3)$$
$$a = 2\mu F(\sin\theta)/W \tag{21}$$

The moment m induced in the central water molecule is $-\mu\delta\theta \sin\theta = 4\mu^2 F(\sin^2\theta)(1 - g/3)/W$. The mean induced moment $\langle m\rangle$ is then obtained by averaging m over all possible directions. The resulting polarizability is $\langle m\rangle/F$.

$$\chi_{or} = \langle \mathrm{m}\rangle/F = \int_0^\pi (m(\sin\theta)/2F)\,\mathrm{d}\theta$$
$$= 8\mu^2(1 - g/3)/3W \tag{22}$$

Application of the two-state model then gives (23). Because $1 - g_A/3 \simeq 0$, χ_{or} depends practically on state B. Equation 23 involves no new parameters.

$$\chi_{or} = \frac{8\mu^2}{3}\left[\frac{\alpha(1 - g_A/3)}{W_A} + \frac{(1 - \alpha)(1 - g_B/3)}{W_B}\right] \tag{23}$$

Values calculated from (23) are included in Table III. They are clearly of the correct magnitude; the averages for the columns based on ϵ_∞ and on eq 23 agree within the error limits. On the other hand, the values predicted from (23) show the greater temperature coefficient. On the whole, the agreement is good enough to warrant refinemént of the model to allow for the high spectral frequency.

Concluding Remarks. By defining the two states as water molecules with two different coordination numbers in a flexible network, some of the theoretical misgivings about the two-state model of water may have been overcome. If the two-state model is accepted, then the second, five-coordinated state is now as well characterized as the familiar four-coordinated state of Bernal and Fowler[22] has been for some time. In its proposed version, the two-state model also explains some of the apparent "schizophrenia" of water. While some properties (such as the oxygen-oxygen radial distribution function of Morgan and Warren[24a]) are dominated by features ascribable to the four-coordinated state, others (such as the dielectric relaxation spectrum) do not fit such a model at all, being dominated by the five-coordinated state. In its proposed version, the two-state model in no way forbids appropriate infrared spectral properties from reflecting quasi-continuous microscopic distributions and, thus, may defuse a controversy of long standing.[17a] Discreteness of state properties is expected only if the time scale of the experiment is long enough (probably at least 1 ps) to sample the time-average state of the network, and this is clearly not true at infrared frequencies. Finally, the mixing of four-coordinated and five-coordinated states results in a network with long-range disorder and thus satisfies an essential theoretical requirement for a liquid.

Registry No. H_2O, 7732-18-5.

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Thermodynamic Properties of Nonpolar Solutes in Water and the Structure of Hydrophobic Hydration Shells[1]

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Abstract: Experimental partial molar entropies and heat capacities in water for noble gases, nonpolar diatomic gases, and hydrocarbons were analyzed thermodynamically by delphic dissection to evaluate the contributions from solute-induced perturbations of the water network. These contributions, which are typically large, were then interpreted in terms of the familiar two-state model of liquid water. Changes in the fractions of the two states and of their relative enthalpies, per mole of solute, were thus evaluated. The numbers of water molecules that are nearest neighbors to the solute, and the manner in which the nearest neighbors are tied to the bulk water network, could be elucidated.

Liquids, like crystals, are conveniently classified into molecular and network categories. Water, with its hydrogen-bonded structure,[2,3] is a network liquid. Solvation of a nonelectrolyte solute in a network liquid consists of two parts. There is ordinary direct

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solvation, which involves precisely the same sort of physical interactions that operate in molecular solvents. And there is perturbation of the solvent network by the added solute, which is peculiar to network liquids.[4,5]

In a previous paper[6] the author presented a general thermodynamic approach for separating ordinary solvation from solute perturbation of the solvent network. To apply this approach to a specific network solvent, a model of network structure must be introduced. In this paper, the preceding two-state model of the water network[7] will be used to examine the partial molar free energy, entropy, and heat capacity of hydration of noble gases, diatomic gases, and hydrocarbons.[8] The analysis will yield fairly explicit descriptions of the solutes' perturbation of the water network.

First, a brief orientation as to the magnitude of network perturbation effects is in order. In practice, one can gain such orientation by noting how much the properties of aqueous solutions deviate from predictions based on correlation schemes established for molecular solvents. It turns out that the size of the deviations depends very much on the property being considered. Standard partial molar free energies apparently show no deviations at all. This is clear, for example, from the far-reaching linear free energy correlations of physical organic chemistry,[9] which make no qualitative distinction between network solvents (including water) and molecular solvents. The same model equations apply to both categories; solvent specificity enters only in the form of specific values for certain parameters.[10] For example, the reference process for the well-known Hammett ρ-σ equation is benzoic acid dissociation *in water*. Yet the set of substituent constants obtained in this way applies to standard free energy changes for several hundred reactions with equal validity in water, other protic solvents, and aprotic solvents.[11]

On the other hand, Frank and Evans[5] showed as early as 1945 that partial molar entropies of hydration do not fit into correlation schemes established for molecular solvents; they are more negative for hydration. And recent advances in dilute-solution calorimetry[12-14] have given accurate heat capacities of hydration which are not only greater but markedly greater than the corresponding values for molecular solvents.[8]

Thermodynamic Equations. The preceding aspects are consistent with the author's thermodynamic analysis,[6] which will now be reviewed. When a liquid is said to be a network liquid, this implies, thermodynamically, that there exists a set of variables $\{\alpha_1, \alpha_2, ..., \alpha_n\}$ such that, when values are assigned to these variables, the thermodynamic state of the network is defined. The nature and number of these variables depends on the chosen model. In the model adopted here, a single variable α (defined below) is sufficient. The following equations are therefore specialized for networks depending on a single variable.

Table I. Definitions and Thermodynamic Equations for Network Solvents

Definitions

isodelphic, a solution process in which the thermodynamic state of the solvent network is constant (α = constant)

lyodelphic, the net result of solute perturbation of the solvent network in a solution process

α, variable which defines the thermodynamic state of the solvent network

$y = \partial G/\partial\alpha$; at equilibrium (eq), $y = 0$

$h_x = (\partial^2 G/\partial\alpha^2)\cdot(\partial\alpha/\partial x)_y$

subscripts: 1 = solvent, 2 = solute

concentration units, such as m_2 and x_2, are independent of temperature

Delphic Equations

$(\partial G/\partial n_2)_y = (\partial G/\partial n_2)_\alpha + y(\partial\alpha/\partial n_2)_y$ (1)

$\bar{G}_2 = (\partial G/\partial n_2)_{\rm eq} = (\partial G/\partial n_2)_\alpha$ (2)

$-\bar{S}_2 = (\partial^2 G/\partial n_2\partial T)_{\rm eq} = (\partial^2 G/\partial n_2\partial T)_\alpha - (\partial^2 G/\partial\alpha^2)[(\partial\alpha/\partial n_2)\cdot(\partial\alpha/\partial T)]_{\rm eq}$ (3)

$-\bar{C}_{\rm p2}/T = (\partial^3 G/\partial n_2\partial T^2)_{\rm eq} = (\partial^3 G/\partial n_2\partial T^2)_\alpha + (\partial^3 G/\partial\alpha^3)[(\partial\alpha/\partial n_2)\cdot(\partial\alpha/\partial T)^2]_{\rm eq} - [(\partial h_T/\partial n_2)(\partial\alpha/\partial T) + (\partial h_T/\partial T)(\partial\alpha/\partial n_2) + (\partial h_{n_2}/\partial T)(\partial\alpha/\partial T)]_{\rm eq}$ (4)

Table II. Thermodynamic Equations for the Two-state Model of Water Network

$[{\rm B}]/[{\rm A}] = (1 - \alpha)/\alpha = K$ (5a)
$(1 - \alpha_0)/\alpha_0 = K_0$(pure water) (5b)
$\ln K = \ln K_0 - j_{21}m_2$ (6)
$\partial G_{\rm A,B} = -RT \ln K$ (7)
$\partial\delta G_{\rm A,B}/\partial m_2 = RTj_{21}$ (8)
$\partial\delta H_{\rm A,B}/\partial m_2 = -RT^2 (\partial j_{21}/\partial T)$ (9)
$\partial\alpha/\partial m_2 = \alpha(1 - \alpha)j_{21}$ (10)
$(\bar{G}_2{}^\circ)_{\rm eq} - (\bar{G}_2{}^\circ)_\alpha = 0$ (11)
$(\bar{S}_2{}^\circ)_{\rm eq} - (\bar{S}_2{}^\circ)_\alpha = -\alpha(1 - \alpha)m_1\delta H_{\rm A,B}j_{21}/T$ (12)
$(\bar{C}_{\rm p2})_{\rm eq} - (\bar{C}_{\rm p2})_\alpha = R\alpha(1 - \alpha)(1 - 2\alpha)m_1(\delta H_{\rm A,B}/RT)^2 - 2\alpha(1 - \alpha)m_1\delta H_{\rm A,B} (\partial j_{21}/\partial T)$ (13)
At 298 K, $\alpha_0 = 0.694$, $m_1 = 55.5$ molal, $\delta H_{\rm A,B} = 2510$ cal/mol (14)
$\partial\delta G_{\rm A,B}/\partial m_2 = -5.99(\Delta S^\circ{}_{\rm 2,W} - \Delta S^\circ{}_{\rm 2,M})$ (15)
$\partial\delta H_{\rm A,B}/\partial m_2 = 2.994(\Delta C^\circ{}_{\rm p2,W} + \Delta C^\circ{}_{\rm p2}({\rm vap})) - 4.921(\Delta S^\circ{}_{\rm 2,W} - \Delta S^\circ{}_{\rm 2,M})$ (16)

Like any intensive variable of state, the thermodynamic variable α expresses the average value for the liquid, the average being taken over microscopic fluctuations. When a solute is added, the average will probably change. If the change can somehow be measured, the molal increment $\partial\alpha/\partial m_2$ expresses the molal network perturbation by the specific solute.

In the author's thermodynamic analysis,[6] one compares a partial molar property measured at equilibrium with the corresponding partial molar property for a solution process in which the thermodynamic state of the solvent network remains constant. For solution processes at constant T and P, first let $G = G(n_1, n_2, \alpha, T, P)$. Let $y = (\partial G/\partial\alpha)_{n_1,n_2,T,P}$. Then change variables so that $G = G(n_1, n_2, y, T, P)$. The change from α to y is useful because at equilibrium, $y = 0$. Since y is a partial derivative of G with respect to the primary variable α, the change of variable is like that in a Legendre transformation,[15] a familiar operation in thermodynamics.[16] Equation 1 follows directly. The first term

$$\left(\frac{\partial G}{\partial n_2}\right)_{y,n_1,T,P} = \underbrace{\left(\frac{\partial G}{\partial n_2}\right)_{\alpha,n_1,T,P}}_{\text{isodelphic}} + \underbrace{y\left(\frac{\partial\alpha}{\partial n_2}\right)_{y,n_1,T,P}}_{\text{lyodelphic}} \qquad (1)$$

on the right in (1) expresses the partial molar change in G for a solution process in which the thermodynamic state of the solvent

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(1) Work supported in part by a grant from the National Science Foundation.

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Table III. Fit of Regular Solution Theory (Equations 17 and 18) and Isodelphic Free Energy Test at 298 K[a]

solute	$\Delta S°_{2,M}$ nonpolar[c]	$\Delta S°_{2,M}$ polar[c]	fit of $\Delta G°_{2,M}$[b] nonpolar[c]	fit of $\Delta G°_{2,M}$[b] polar[c]	fit of $\Delta G°_{2,W}$[d]
He	−10.2 ± 0.8 (16)	−10.4 ± 1.0 (7)	78 (16)	255 (8)	336
Ne	−10.7 ± 1.0 (16)	−10.8 ± 0.9 (8)	82 (16)	295 (8)	637
Ar	−13.0 ± 0.5 (16)	−13.3 ± 0.5 (6)	81 (16)	196 (7)	112
Kr	−13.6 ± 0.5 (15)	−14.0 ± 0.4 (5)			
Xe	−15.0 ± 0.5 (7)	−15.0 ± 0.4 (5)	85 (7)	273 (6)	66
H_2	−11.3 ± 0.3 (9)	−12.6 ± 0.2 (3)	78 (10)	124 (4)	171
O_2	−13.4 ± 0.6 (6)	−13.8 (2)			
N_2	−11.8 ± 1.0 (5)	−13.5 (2)	83 (10)	329 (4)	3
CO	−12.9 ± 0.4 (5)	−13.9 (2)			
CH_4	−14.4 ± 1.1 (10)	−14.6 (2)	99 (10)	194 (3)	229
C_2H_6	−16.1 ± 0.6 (6)	−16.2 (2)	75 (10)	216 (4)	511
all solutes: mean dev	0.7	0.6	82	242	296

[a] Data from ref 8. [b] Mean deviation from eq 18, in cal/mol. Solute, v_2, δ_2 (cal$^{1/2}$ cm$^{-3/2}$): He, *18*, 0.80; Ne, *31.4*, 4.01; Ar, *42.5*, 5.84; Xe, 68, *6.93*; H_2, 19.1, *2.66*; N_2, *35.5*, 5.01; CH_4, 52, *6.95*; C_2H_6, 70, *7.02*. References 23 and 24. Values in italics were adjusted by least squares. [c] Number in parentheses denotes number of solvents. [d] δ_w = 14.14 ± 0.2; absolute value of deviation, in cal/mol.

network remains constant. The second term, proportional to $\partial\alpha/\partial n_2$, expresses the effect of solute-perturbation of the solvent network.

At equilibrium (eq), $y = 0$ and $(\partial G/\partial n_2)_{eq,n_1,T,P} = \bar{G}_2$. Hence eq 1 shows that at equilibrium, $\bar{G}_2 = (\partial G/\partial n_2)_{\alpha,n_1,T,P}$; the term due to solute perturbation of the solvent network goes to 0.

Extension of this approach to second and third derivatives of the free energy gives equations for the partial molar entropy and heat capacity. These equations and related definitions are listed in Table I. In contrast to the partial molar free energy, the partial molar entropy and heat capacity at equilibrium retain terms involving $\partial\alpha/\partial n_2$. These properties are therefore sensitive to solute perturbation of the solvent network.

The equations in Table I are valid whenever the state of the solvent network depends on a single variable. Since they apply at *any* solute concentration, they apply also in the reference state for activity coefficients and in the standard state of unit activity. Accordingly, the *standard* partial molar free energy is also insensitive to solute perturbation of the solvent network, while the standard entropy and heat capacity are sensitive.

To facilitate discussion, the previously employed "delphic" terminology[17] will be used. If the thermodynamic state of the solvent network remains constant, the solution process is called *isodelphic.* Partial molar contributions due to solute-perturbation of the solvent network in a solution process are called *lyodelphic.* Dissection of a partial molar property into isodelphic and lyodelphic additive terms is called *delphic dissection.* In this terminology, at equilibrium $\bar{G}°_2$ is always purely isodelphic, while $\bar{S}°_2$ and $\bar{C}°_{p2}$ can be resolved into isodelphic and lyodelphic contributions.

Table II outlines the application of the two-state model of the water network[18] to the thermodynamic equations. More complete derivations have been given in ref 6. Excepting (22b), eq 20–23 in ref 6 apply without change. Equation 22b, i.e., the assumption that $\partial\delta H_{A,B}/\partial m_2 = 0$, is now dropped. Moreover, because of the change in model from sitewise equilibrium (per H bond) to statewise equilibrium (per molecule), factors of 2 in eq 24–26 are now omitted. Equation 25b is now corrected to include a negative sign,[6b] and the expression for $\bar{C}°_{p2}$ is revised accordingly.

The key equations of the two-state model are eq 5–10 in Table II. Substitution in (3) and (4) then leads to (12) and (13). Equations 11–13 are written so that the right-hand side expresses the lyodelphic term, i.e., the solute-perturbation of the water network. Assuming that the terms on the left can be evaluated (next section), the solute perturbation of the water network can be analyzed as follows. Equation 12 for the entropy, with (14) and (10), permits evaluation of j_{21}, the solute-network interaction constant, and of $\partial\alpha/\partial m_2$, the molal network perturbation. Equation 13 for the heat capacity, with (9), then permits evaluation of $\partial\delta H_{A,B}/\partial m_2$, the effect of the solute on the difference in molar enthalpy of the two network states. These properties will be useful for devising a model of the network perturbation.

Delphic Dissection. In evaluating the lyodelphic contributions to the entropy and heat capacity according to eq 12 and 13, the equilibrium values will be experimental results[8,13,14,19-21] and the isodelphic values will be predicted. The basis for prediction is as follows.

In water there are two kinds of solvation effects, direct solvent–solute interaction and solute perturbation of the water network, which are expressed respectively by the isodelphic and lyodelphic terms. The direct solvent–solute interaction involves the same physical mechanisms in water as in molecular solvents. The main difference is that the water molecules, being part of a network, are less orientable. However, according to the Oster–Kirkwood model for the dielectric constant,[22] the water network is quite flexible, and the orientational constraints may be unimportant. Suppose that a correlation model exists which predicts free energy, entropy, and heat capacity in molecular solvents. These functions are not independent; microscopically they come from the same potential function and energy levels. Thus, if it can be shown that the correlation model fits any one of the isodelphic functions in water, it will probably fit the others as well. Fortunately, the partial molar free energy is purely isodelphic and thus may be used to test the applicability of the correlation model to aqueous solutions.

In the following the regular solution model[23] will be used, because of its ease of application and wide acceptance. Let *g*, *M*, and *W* denote respectively gas phase, molecular solvent, and water. Let $\Delta S°_{2,M} = S°_2(M) - S°_2(g)$, $\Delta S°_{2,W} = S°_2(W) - S°_2(g)$, and similarly for heat capacity. The regular solution equations then are eq 17–19; δ is the solubility parameter, v is the molar volume, and vap denotes vaporization of the pure liquid.

$$\Delta S°_{2,M} = -\Delta S°_2(\text{vap}) \tag{17}$$

$$\Delta G°_{2,M} = -\Delta G°_2(\text{vap}) + v_2(\delta_2 - \delta_1)^2 \tag{18}$$

$$\Delta C°_{p2,M} = -\Delta C°_{p2}(\text{vap}) \tag{19}$$

A test of the regular solution model for a series of nonpolar solutes in molecular solvents and an isodelphic free energy test

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[17] A reader who knows the reputation of the Delphic Oracle may see some humor here.

[18] Following tradition, the word "state" is used in this paper with two different meanings, to denote either the thermodynamic "state" of the macroscopic solution or the microscopic "state" of the network environment surrounding a water molecule.

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Table IV. Delphic Dissection of Thermodynamic Data at 298 K[a]

solute	$\Delta S^\circ_{2,W}$	$\Delta C^\circ_{p2,W}$	$\Delta S^\circ_{2,M}$	$\Delta C^\circ_{p2,M}$	lyodelphic difference $S_{2,lyo}$	lyodelphic difference $C_{p2,lyo}$
He	−24.1	28.1	−10.2	8	−13.9	20
Ne	−26.3	35.5	−10.7	8	−15.6	28
Ar	−30.6	44.5	−13.1	8	−17.5	36
Kr	−32.3	50.2	−13.7	8	−18.6	42
Xe	−34.2	60.0	−15.0	8	−19.2	52
H_2	−25.4	34	−11.6	9	−13.8	25
N_2	−31.2	45.2	−12.2	9	−19.0	36
O_2	−31.0	45.9	−13.5	9	−17.5	37
CO	−30.7	46	−13.2	9	−17.5	37
CH_4	−31.7	52	−14.4	9	−17.3	43
C_2H_6	−36.1	68	−16.2	10	−19.9	58
C_3H_8	−38.9	79	−16.7	11	−22.2	68
n-C_4H_{10}	−41.6	93	−18.6	11	−23.0	82
n-C_6H_{14}	−48.2	117	−22.1	13	−26.1	104
c-C_6H_{12}	−45.1	98	−22.4	12	−22.7	86
C_2H_2	−26.1	36.8	−15.1	9	−11.0	28
C_2H_4	−31.9	56.5	−15.8	10	−16.1	46
C_6H_6	−36.8	66	−23.0	13	−13.8	53
MeC_6H_5	−40.8	78	−23.9	13	−16.9	65
EtC_6H_5	−44.6	90	−25.2	14	−19.4	76
n-PrC_6H_5	−48.4	108	−26.3	15	−22.1	93

[a] Units: cal/(mol·K). References 8, 13, 14, 19, 20.

Table V. Solute-Perturbation of the Water Network, 298 K

solute	j_{21}[a]	$\partial\alpha/\partial m_2$[b]	s[c]	s_{rp}[d]	$\partial\,\delta H_{A,B}/\partial m_2$[e]	$\Delta H_{A,nwrk}$[f]
He	0.140	0.0298	5.4	6.2 (14)[g]	128	−1310
Ne	0.158	0.0336	6.1	6.5 (6)	161	−1460
Ar	0.177	0.0376	6.8	7.2 (6)	194	−1580
Kr	0.188	0.0400	7.2	7.6 (5)	217	−1670
Xe	0.194	0.0412	7.5	8.2 (9)	250	−1850
H_2	0.140	0.0296	5.4	6.7 (21)	143	−1470
N_2	0.192	0.0408	7.4	7.3 (−1)	201	−1500
O_2	0.177	0.0376	6.8	7.2 (6)	197	−1600
CO	0.177	0.0376	6.8	7.3 (7)	197	−1600
CH_4	0.175	0.0372	6.7	7.6 (13)	214	−1770
C_2H_6	0.201	0.0427	7.7	8.6 (11)	272	−1960
C_3H_8	0.224	0.0477	8.6	9.4 (9)	313	−2020
n-C_4H_{10}	0.232	0.0493	8.9	10.0 (12)	359	−2230
n-C_6H_{14}	0.264	0.0561	10.1		440	−2400
c-C_6H_{12}	0.230	0.0487	8.8		369	−2320

[a] kg/mol; eq 12 and 14. [b] kg/mol; eq 10. [c] Equation 23. [d] Equation 24b. Collision diameters (Å) at 298 K, ref 30: He, 2.29; Ne, 2.69; Ar, 3.63; Kr, 4.11; Xe, 4.82; H_2, 2.97; N_2, 3.74; O_2, 3.60; O atom, 3.19; CO, 3.74; CH_4, 4.14; C_2H_6, 5.27; C_3H_8, 6.20; *n*-C_4H_{10}, 6.88; H_2O, 4.67. [e] Equation 16; cal kg mol^{-2}. [f] cal/mol; eq 29. [g] Number in parentheses denotes % difference between s and s_{rp}.

in water are given in Table III. It can be seen that $\Delta S^\circ_{2,M}$ is nearly independent of the solvent, with a precision of ca. 0.7 cal/(mol·K). There is little if any difference between nonpolar and polar molecular solvents. Equation 18 for $\Delta G^\circ_{2,M}$ fits better in nonpolar than in polar solvents. However, the mean error of fit of $\Delta G^\circ_{2,M}/T$ in polar solvents, 0.8 cal/(mol·K), is compatible with the variability of $\Delta S^\circ_{2,M}$. Extension to water evaluates δ_W as 14.1 ± 0.2 cal$^{1/2}$ cm$^{-3/2}$ and reproduces $\Delta G^\circ_{2,M}/T$ with a mean error of 1.0 unit.[23b] Interestingly, the value obtained for the δ_W parameter nearly agrees with Hansen's $(\delta^2_{\text{dispersion}} + \delta^2_{\text{polar}})^{1/2}$ for water,[24] without the parameter for hydrogen bonding.

Sufficient data are not available for testing eq 19 in molecular solvents, and this equation will be used without test. Data for $\Delta C_{p2}(\text{vap})$ will be taken from a review by Shaw,[25] or estimated with an accuracy of 1 cal/(mol·K) by methods described by Shaw[25] and Benson.[26]

The actual delphic dissection is summarized in Table IV. The key equations are (20) and (21). The errors of the lyodelphic

$$(S^\circ_2)_{eq} - (S^\circ_2)_\alpha = \Delta S^\circ_{2,W} - \Delta S^\circ_{2,M}(\text{av}) \qquad (20)$$

$$(C^\circ_{p2})_{eq} - (C^\circ_{p2})_\alpha = \Delta C^\circ_{p2,W} + \Delta C^\circ_{p2}(\text{vap}) \qquad (21)$$

entropies based on (20) are of the order of 1 cal/(mol·K), or 5–10%. The errors of the lyodelphic heat capacities based on (21) are 3–5 cal/(mol·K), or 5–15%.

Hydration Shell. Nearest Neighbor Model. The lyodelphic differences in Table IV will now be analyzed in terms of the equations listed in Table II for the two-state model of the water network. State A, with fraction α, is defined to be the state of relatively low energy, low entropy, and large volume. Network parameters at 298 K are given in (14).

The analysis is summarized in Table V. The interaction constants j_{12}, calculated by eq 12, lead directly (eq 10) to values of $\partial\alpha/\partial m_2$. Since these values are positive, the nonpolar solutes induce the formation of the low-energy, low-entropy water molecules belonging to state A. This is of course a well-known conclusion. Gurney[4] has described this shift in the water network as "structure making", and H. S. Frank[5] has described it as formation of four-coordinated "patches of ice". It should be noted, however, that Table V quantifies the effect.

In the author's view, the chief driving force for the shift toward state A is the 15–20% greater statewise volume associated with state A. The solution process in water differs from that in *molecular* solvents in one crucial respect. Solution in a molecular solvent is essentially *substitutional*,[27] that is, the solute essentially takes the place of a solvent molecule in the liquid lattice. In water, by contrast, a nonpolar molecule cannot substitute for a water molecule in the water network—it lacks the necessary hydrogen-bonding functions. Solution therefore must be regarded as interstitial, even though in most cases the solute molecules are *not* relatively small. Steric and spatial requirements of the solute molecule will be unusually important. The phenomenon of "solute-perturbation of the water network" from this point of view is just the rearrangement of network strands so as to create suitable cavities for the solute. Given two states of water molecules with quite different molecular densities in their surrounding networks, the state with the lower surrounding molecular density is clearly more appropriate for interstitial insertion of a solute and thus is preferred for being adjacent to the solute.

For example, in the model favored by the author, a water molecule has four hydrogen-bonded neighbors in state A and five in state B. It is evident at once that a molecule in state A can insert a solute molecule, or part of a solute molecule, into its nearest-neighbor shell to produce a configuration with a total of five nearest neighbors. On the other hand, the same solute molecule probably will not fit next to state B because configurations with a total of six nearest neighbors appear to be overcrowded. In order for the solute molecule to enter the nearest-neighbor shell in state B, one of the water molecules must be displaced. The central water molecule thus becomes four-hydrogen bonded and, by definition, enters state A.

These ideas find expression in the *nearest-neighbor model*, which will now be stated and tested. Let s denote the hydration number of the *solute*, defined as the number of nearest-neighbor water molecules. (Later we shall define a second number, the occupation number N, which includes non-nearest neighbor molecules in network strands inside the hydration shell.) The nearest-neighbor model assumes that the s nearest neighbors of the solute belong to state A, while the other water molecules remain at the same state fractions (α_0, $1 - \alpha_0$) as in the pure solvent. The resulting expression for α is (22). Differentiation (eq 23) then relates s to $\partial\alpha/\partial m_2$, which is known from delphic dissection. Values obtained for s according to (23) are given in Table V. The numbers are of a plausible magnitude.

$$m_1\alpha = m_2 s + (m_1 - m_2 s)\alpha_0 \qquad (22)$$

$$s = m_1\,(\partial\alpha/\partial m_2)/(1 - \alpha_0) \qquad (23)$$

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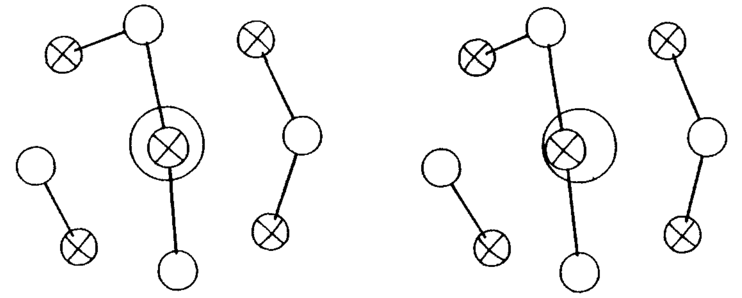

Figure 1. Stereographic view of part of a possible solvation shell. Only a portion of the hydrogen bonds in the solvation shell is shown. Large sphere, nonpolar solute, $\sigma = 3.2$ Å. Cross-hatched spheres, nearest-neighbor water molecules. Plain spheres, a group of next-nearest-neighbor water molecules located in the solvation shell and surrounding one of the nearest-neighbor molecules. O–O distances range from 2.9 Å for hydrogen bonds to 3.2–3.5 Å otherwise. The figure was prepared with C. K. Johnson's version of ORTEP adapted for the IBM-PC by B. Foxman.

Table VI. Solute-Perturbation of the Water Network by Unsaturated Hydrocarbons

solute	j_{21}[a]	$\partial\alpha/\partial m_2$[b]	s_{rp}[c]	s_d[d]	$\partial\delta H_{A,B}/\partial m_2$[e]
C_2H_2	0.111	0.0236	8.2	1.4 ± 0.2	138
C_2H_4	0.163	0.0346	8.3	0.6 ± 0.2	217
C_6H_6	0.140	0.0296	10.6	1.9 ± 0.2	227
MeC_6H_5	0.171	0.0363	11.3	1.7 ± 0.2	278
EtC_6H_5	0.196	0.0416			323
n-PrC_6H_5	0.223	0.0474			387

[a] kg/mol; eq 12 and 14. [b] kg/mol; eq 10. [c] Equation 24b. Collision diameters at 298 K (ref 30): C_2H_2, 4.81; C_2H_4, 4.93; C_6H_6, 7.45; MeC_6H_5, 8.11; O atom, 3.19; H_2O, 4.67. [d] Equation 27; $s = s_{rp}/1.09$. [e] Equation 16; cal kg mol^{-2}.

It is not possible to test the hydration numbers (s) by direct comparison with experiment because direct measurements are lacking. However, one can compare the results with values predicted by an independent theoretical approach. The approach used in the following is suggested by Stokes and Robinson's (SR) theory for estimating ionic hydration numbers.[28]

The pertinent assumption made by SR is that the density of water molecules in nearest-neighbor hydration shells agrees with Alder's model of random packing of spheres[29] and thus is 78% of that for closest packing. Let σ_{11} and σ_{12} respectively denote the water–water and water–solute encounter diameters. Treating the molecules as spheres, the hydration number then is proportional to the ratio of the volume of the nearest-neighbor shell to that of a water molecule, as in (24a). The parameter k depends on the type of packing. When $\sigma_{12} = \sigma_{11}$, $s = 12$ for closest packing, as is well-known. Thus $s = 0.78 \times 12 = 9.4$ for random packing (rp). Accordingly, $k_{rp} = 0.36$ and s_{rp} is given by (24b).

$$s = k[8 + 12\sigma_{12}/\sigma_{11} + 6(\sigma_{12}/\sigma_{11})^2] \qquad (24a)$$

$$s_{rp} = 2.88 + 4.32\sigma_{12}/\sigma_{11} + 2.16(\sigma_{12}/\sigma_{11})^2 \qquad (24b)$$

Before applying (24b) we note that s_{rp} depends on the *ratio* of σ_{12}/σ_{11}. The σ's should therefore be obtained by a consistent method. The author will use collision diameters based on gas viscosities at 298 K, for which adequate data exist.[30] Furthermore, because the solute–solvent attraction is largely due to London forces, one may assume that in the hydration shell the water oxygen atoms face the solute molecule. Hence σ_{12} is taken as $(1/2)(\sigma_{solute} + \sigma_{O\text{-atom}})$, where $\sigma_{O\text{-atom}}$ is derived from σ_{O-O} by allowing for the O–O covalent distance.

Results for s_{rp} based on (24b) are compared with the results for s based on (23) in Table V. For these nonpolar solutes, the two methods of predicting hydration numbers agree well. The mean discrepancy for 13 solutes is 9 ± 4%. One may reasonably attribute 9% to systematic error and 4% to random statistical error. Thus, in spite of their different theoretical frameworks, the two sets of hydration numbers could be equal.

Indeed, the consistency between s and s_{rp} for the non-hydrogen bonding solutes in Table V is so good that the greater discrepancies for Lewis bases in Table VI may be significant. These unsaturated hydrocarbons can act as hydrogen bond acceptors. For example, Ravishanker, Mehrotra, Mezei, and Beveridge (RMMB)[31] inferred from their computer simulation of a quantum system consisting of benzene in water that the C_6H_6 molecule accepts two hydrogen bonds, one on each face of the benzene hexagon. The nearest-neighbor number s of the benzene molecule in a stereographic view included in RMMB's paper[31] was counted by two unbiased viewers as 10 or 11, in agreement with the value of 10.6 obtained for s_{rp}. It therefore seems worthwhile to expand the model of eq 22 and 23 so as to include hydrogen bond donation to the solute.

Let $s = s_n + s_d$, where s_d is the number of water molecules acting as hydrogen bond donors. As before, all water molecules in the hydration shell are assumed to be four-hydrogen bonded and thus belong to state A. However, the s_d molecules which donate a hydrogen bond to the solute form only three hydrogen bonds to other water molecules. The s_d water molecules which are displaced then are required by the model to coordinate with water molecules *outside* the hydration shell, so that s_d(A) change to s_d(B). The resulting equations are eq 25–27. If one assumes that $s_{rp}/1.09$

$$s = s_n + s_d \qquad (25)$$

$$m_1\alpha = sm_2 + (m_1 - [s + s_d]m_2)\alpha_0 \qquad (26)$$

$$s = m_1 (\partial\alpha/\partial m_2)/(1 - \alpha_0) + s_d\alpha_0/(1 - \alpha_0) \qquad (27)$$

correctly represents s, the lyodelphic results for $\partial\alpha/\partial m_2$ can be used to deduce s_d. Results are shown in Table VI. The values are of a plausible magnitude. In particular, the value of 1.9 ± 0.2 obtained for benzene nearly agrees with RMMB's value[31] of 2.

In conclusion, it appears that the nearest-neighbor model is sufficient to account quantitatively for the negative lyodelphic contribution to the entropy of solution of nonpolar nonelectrolytes in water. In the terminology of H. S. Frank,[5] the "patches of ice" built up near the solute can be equated to the nearest-neighbor water molecules. The model does not prohibit perturbation of the water network beyond the nearest-neighbor shell—in physical reality, that is probably unavoidable, but it constrains the perturbation so that the ratio of [B]/[A] outside the nearest-neighbor shell remains practically constant.

Perturbation of Statewise Enthalpy. In addition to an uncommonly negative entropy of solution, nonpolar solutes in water display an uncommonly positive heat capacity of solution[32] —so much so as to cause surprise. As Table IV shows, the isodelphic contribution is fairly small, and most of the heat capacity is

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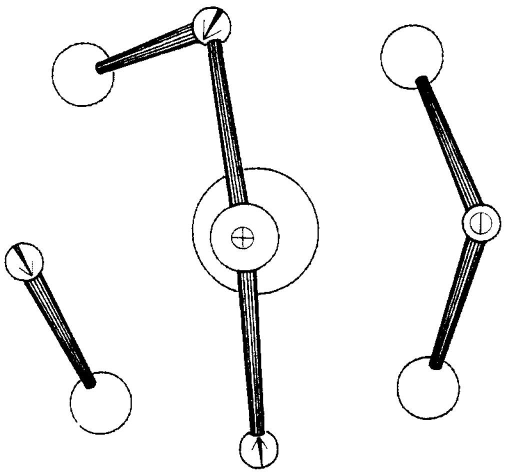

Figure 2. Same configuration as in Figure 1, showing directions (–, arrow) of water dipoles in the solvation shell near the forward molecule (+). Figure was prepared with C. K. Johnson's version of ORTEP adapted for the IBM-PC by B. Foxman.

lyodelphic. Thus, according to eq 16, there is a marked perturbation of $\delta H_{\mathrm{A,B}}$, the statewise enthalpy difference.

Values of $\partial\delta H_{\mathrm{A,B}}/\partial m_2$ are listed in Table V. These numbers represent average changes for the entire network, per mole of solute added to 1 kg of water. Conceptually, they express a change in the interaction of water molecules with their surrounding network owing to the addition of the solute. Emphatically, they do *not* include enthalpies of direct solvent-solute interaction—those are gathered up in the isodelphic terms. Rather, they express the enthalpic consequence of rearranging the strands of the water network so as to create a suitable cavity for the solute.

It is instructive, in first approximation, to examine the values in terms of the nearest-neighbor model. We shall assume, as before, that only the s water molecules which are nearest neighbors to the solute make a significant contribution. The molecules outside that shell are also perturbed, but we shall assume that their perturbations are relatively small and nearly cancel in $\delta H_{\mathrm{A,B}} = H_{\mathrm{B}} - H_{\mathrm{A}}$. Recalling that the s nearest neighbors exist in state A, let $\Delta H_{\mathrm{A,nwrk}}$ denote the molar enthalpy change defined in (28). $\Delta H_{\mathrm{A,nwrk}}$ then is related to $\partial\delta H_{\mathrm{A,B}}/\partial m_2$ according to (29).

$$\Delta H_{\mathrm{A,nwrk}} = H_{\mathrm{A}}(\text{nearest neighbor}) - H_{\mathrm{A}}(\text{bulk}) \qquad (28)$$

$$\Delta H_{\mathrm{A,}}\mathrm{n}_{\mathrm{wrk}} = -m_1\ (\partial\delta H_{\mathrm{A,B}}/\partial m_2)/s \qquad (29)$$

Results obtained on this basis are included in Table V. They are remarkable in two respects. First, the numbers are negative—the strands of the water network rearrange to accommodate the solute in such a way that the molar enthalpy due to interaction of the nearest-neighbor water molecules *with their surrounding network* decreases. Second, the magnitudes are large—so much so that one has cause to worry whether the delphic approach is valid. (In a previous paper[6] the author had even assumed, incorrectly, that $\partial\delta H_{\mathrm{A,B}}/\partial m_2 = 0$.) The following analysis will show, however, that values of this magnitude are quite possible.

For definiteness, consider the conceptual model of a solvation shell shown in stereographic view in Figure 1. (The large sphere is the solute, the others represent water molecules.) The model assumes that $s = 6$ and that the nearest neighbors (cross-hatched spheres) occupy octahedral sites. The relatively polarizable oxygen atoms are directed toward the solute molecule. Each nearest-neighbor water molecule by hypothesis forms two H-donor and two H-acceptor hydrogen bonds. The H-donor bonds are not shown in Figure 1; they face into the bulk liquid and represent normal network strands. The H-acceptor bonds face into the solvation shell, toward sites not already occupied by nearest neighbors. That limits their possible directions, and Figure 1 shows part of a likely, sterically possible, configuration. The H-acceptor bonds here go to water molecules located near the corners of an imaginary cube whose face-centers are occupied by the nearest neighbors. These water molecules (plain spheres in Figure 1) are next-nearest neighbors to the solute. Their maximum number is limited by the number of available "corners", and about half of them donate both of their two H-donor bonds to a nearest neighbor. (In Figure 1 the fraction is exactly $^1/_2$ because in the complete solvation shell, 8 "corner" water molecules donate 12 hydrogen bonds to 6 nearest neighbors.)

For $\Delta H_{\mathrm{A,nwrk}}$, the key facts in this model are as follows: (1) Each nearest-neighbor water molecule now has 6 water molecules relatively close-by—four that are hydrogen bonded and two that are not. Four of the close-by molecules are at or near corners (cf. the plain spheres in Figure 1). The other two are in bulk water. (2) As shown in Figure 2, the dipoles of the six near-by molecules are oriented so as to produce attractive dipole–dipole interactions. Thus, even though each nearest-neighbor water molecule forms only four hydrogen bonds, two non-hydrogen-bonded water molecules also exist nearby and cause a substantial reduction in $\Delta H_{\mathrm{A,nwrk}}$.

In constructing the common geometry of Figures 1 and 2, no attempt was made to optimize the dipole–dipole interaction energy. For the geometry shown, the dipole–dipole energy is –1.1 kcal.[33] By comparison, for Ne and Ar (whose s numbers and sizes the model nearly simulates), $\Delta H_{\mathrm{A,nwrk}} = -1.5$ kcal, of similar magnitude.

If one overlooks the distinction between nearest and next-nearest neighbors and simply adds up all the water molecules residing in the solvation shell, the total occupation number N thus obtained is considerably greater than s. Each of the s nearest neighbors has two hydrogen bonds directed into the solvation shell, but perhaps half of them end in a common water molecule. The total occupation number N therefore should be between $2s$ and $3s$. This prediction is consistent with results from computer simulations. Two examples will be cited. For benzene, according to Table VI, $s \simeq s_{\mathrm{rp}}/1.09 = 9.7$, while N, according to RMMB,[31] is 23. Hence $N/s \simeq 2.4$. For argon, $s = 6.8$ while N, according to Alagona and Tani,[34] is 17. Hence $N/s \simeq 2.5$.

In summary, because each nearest-neighbor water molecule forms four hydrogen bonds, geometrical constraints force an average of two, or nearly two, of the emanating network strands to pass through the hydration shell, with dipole orientations which give highly significant extra attractive interactions. The order of magnitude of the lyodelphic results in Table V can be nearly reproduced by a simple model. More exacting tests by computer simulation are being planned.

Strong evidence has been accumulating recently that the partial molar heat capacity of nonelectrolytes in dilute aqueous solution is an additive-constitutive property of molecular structure.[35] In terms of delphic dissection this implies, with high probability, that $\Delta H_{\mathrm{A,nwrk}}$ is also an additive-constitutive property. It therefore seems likely that a rational structural theory for hydration shells around nonelectrolyte molecules can be developed.

Acknowledgment. It is a pleasure to thank Prof. B. Foxman for discussions of hydrogen-bonded geometries and for producing the figures.

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