Relation between Local Structure and Thermodynamic Properties in Aqueous Fluids

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Using the conventional statistical-mechanical theory of concentration fluctuations, we examine the nature of local molecular structure in water and aqueous solutions. In particular, we evaluate Δ_H, the excess number of water-molecule protons in the region surrounding (but exterior to) a fixed water molecule. By comparing the temperature dependence of Δ_H with its analogs for alcohols and liquid methane, the anomalous nature of liquid water is affirmed. In the case of a few aqueous solutions for which both isothermal compressibilities and partial molar volumes at infinite dilution are available, the initial composition dependence of Δ_H has been obtained. The sign and magnitude of this solute effect on local water-molecule order constitutes a new way to classify these solutes as "structure formers" or "structure breakers."

I. Introduction

The invention and development of powerful theoretical techniques in recent years has produced significant progress in understanding the liquid state,[1,2] but it is fair to say that this progress has been confined largely to "simple fluids," that is, substances such as the noble gases whose constituent particles are actually (or nearly) spherical. Of incomparably greater importance in physical chemistry though are liquids composed of polyatomic molecules whose noncentral interactions produce characteristic chemical distinctions.

Foremost among the polyatomic liquids of course is water. There is ample experimental evidence that water is an anomalous substance both in pure form and as a solvent.[3] In the quest for a satisfactory quantitative description of the enormous range of chemical and biological reactions that occur in aqueous media, it surely will be necessary to devise a deductive theory first that predicts the anomalous behavior of water itself from fundamental principles.

The goal in this paper, however, is not the development of a first-principles theory of liquid water and aqueous solutions. Instead, our more modest aim is to produce a quantitative measure of hydrogen-bond order in aqueous fluids. As is the case with all other techniques that have been applied to this problem, whether spectroscopic, thermodynamic, or kinetic, the result is far less than a complete characterization of molecular order. However, we believe that addition of yet another measure of structure in water, and one which is independent of others currently available, will hasten the construction of the desperately needed fundamental statistical-mechanical theory of water.

The next section provides our line of reasoning for pure water. We show that experimental density and isothermal compressibility data, supplemented by some elementary knowledge of molecular structure, lead to a numerical measure, Δ_H, of local hydrogen-bond order in the liquid. Specifically, Δ_H equals the average proton excess in the proximity of (but exterior to) a

fixed water molecule. Both pressure and temperature effects on Δ_H are exhibited.

The third section broadens our analysis to include other hydrogenic liquids. To provide suitable contrasts for water, both methane (essentially a "simple fluid") and the aliphatic alcohols are examined. Even allowing for hydrogen bonding, water behaves anomalously.

Aqueous solutions are the object of attention in the fourth section. Partial molar volume measurements, along with isothermal compressibilities, for varying composition permits computation of the solute effect on Δ_H. The sign and magnitude of this effect comprises a convenient criterion for dividing substances into "structure-making" and "structure-breaking."[4]

The final discussion section provides a few comments on our method and tentative interpretation of our computations. Also we stress in that section the need for broader and more accurate solution data.

II. Pure Water

The key relation in our consideration of pure water is the rigorous fluctuation–compressibility theorem[5] which links the isothermal compressibility κ_T with the fluid's pair correlation function $g^{(2)}(r)$

$$kT\kappa_T = c^{-1} + \int [g^{(2)}(r) - 1]d\mathbf{r} \qquad (1)$$

Here k is the Boltzmann constant, T is the absolute temperature, c is the number density, and $g^{(2)}(r)$ must be regarded as the infinite-system limit function with asymptote unity so that the integral can span all space.

(1) H. L. Frisch and J. L. Lebowitz, "The Equilibrium Theory of Classical Fluids," W. A. Benjamin, Inc., New York, N. Y., 1964.

(2) S. A. Rice and P. Gray, "The Statistical Mechanics of Simple Liquids," Interscience Publishers, New York, N. Y., 1965.

(3) J. L. Kavanau, "Water and Solute-Water Interactions," Holden-Day, Inc., San Francisco, Calif., 1964.

(4) H. S. Frank and W.-Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957).

(5) T. L. Hill, "Statistical Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p 236.

For simple fluids consisting of spherically symmetric molecules it is natural to reckon the "position" of any given molecule as coincident with its geometric center, *i.e.*, its centroid. In fact, though, the fluctuation–compressibility theorem (1) is invariant to a shift of "position" of molecules relative to their centroids, for $g^{(2)}(r)$ is then modified merely by double convolution with a unit-integral kernel, and this operation leaves the integral in the right member of eq 1 unchanged.[6]

A similar observation is valid in the case of water. We thus have the option of supposing that the position of any given water molecule is precisely the position of its oxygen nucleus. With this convention, eq 1 for water may be written

$$kT\kappa_T = c^{-1} + \int [g_{OO}^{(2)}(r) - 1]d\mathbf{r} \qquad (2)$$

to stress the specific use of the pair correlation function for oxygen nuclei. A point of conceptual interest in eq 2 is that it has the outward appearance of a fluctuation–compressibility relation for an assembly of oxygen atoms; the protons play merely the passive (but extremely important!) role of providing the correct potential function for the set of oxygens as they move about.

One also has the freedom to take the reverse point of view, namely that the protons are the "important" particles upon which to focus attention, with the oxygens merely present to produce the correct potential function for those protons as they move about. The relation entirely analogous to eq 2 that applies to this alternative point of view is

$$kT\kappa_T = (2c)^{-1} + \int [g_{HH}^{(2)}(r) - 1]d\mathbf{r} \qquad (3)$$

We use here an obvious notation for the pair correlation function for the protons, and it has been recognized that their number density is twice that of the oxygens.

A further transformation is possible that stems from the view of liquid water as an electrolyte, albeit an extremely weak one. Thus water may be regarded as a stoichiometric mixture of doubly charged anions (the oxygens) and singly charged cations (the protons), and since this electrolyte has a nonvanishing conductivity, it is subject to microscopic electroneutrality conditions. In terms of $g_{OO}^{(2)}$, $g_{HH}^{(2)}$, and the cross-correlation function $g_{OH}^{(2)}$, these conditions are[7]

$$1 = c \int [g_{OH}^{(2)}(r) - g_{OO}^{(2)}(r)]d\mathbf{r} \qquad (4)$$

$$1 = 2c \int [g_{OH}^{(2)}(r) - g_{HH}^{(2)}(r)]d\mathbf{r} \qquad (5)$$

The first of these two conditions affirms that the net average charge in the vicinity of any oxygen anion is precisely equal in magnitude but opposite in sign to the anion's charge. The second, eq 5, provides the equivalent statement for average charge surrounding any proton.

Equation 4 may next be used to eliminate $g_{OO}^{(2)}$ from eq 2. The result is the same as one obtains by using eq 5 to eliminate $g_{HH}^{(2)}$ from eq 3

$$kT\kappa_T = \int [g_{OH}^{(2)}(r) - 1]d\mathbf{r} \qquad (6)$$

It is this last form of the fluctuation–compressibility relation that is most useful in assessing intermolecular structure in water.
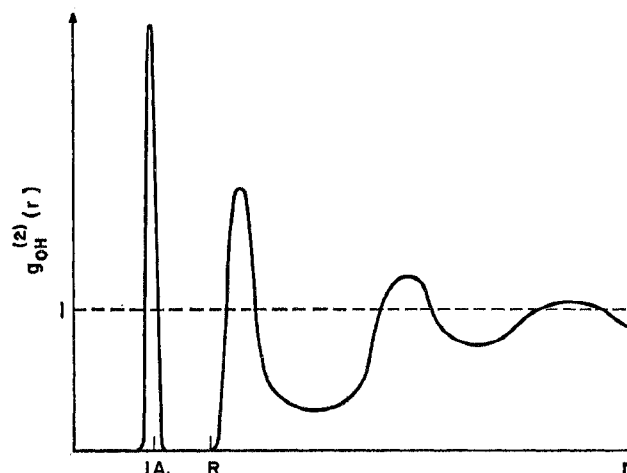

Figure 1. Schematic diagram of the cross-correlation function $g_{OH}^{(2)}(r)$ for liquid water. The sharp peak around 1 Å is the contribution of the intramolecular O–H covalent bonds. The distance R is a lower bound to all intermolecular O$\cdots$H pair distances, the smallest group of which represent direct hydrogen bonds between pairs of water molecules. $g_{OH}^{(2)}(r)$ for sufficiently large r approaches the limit unity.

Figure 1 provides a schematic plot of the cross-correlation function $g_{OH}^{(2)}$. As a distance r increases from zero, $g_{OH}^{(2)}$ at first is zero, but in the neighborhood of 1 Å, this function will have a high and narrow peak corresponding to the intramolecular covalent O–H bond distance. Although thermal motion and inherent positional indeterminacy of quantum-mechanical origin conspire to give this first peak a natural width, it should nevertheless be virtually isolated. The remaining oxygen–hydrogen distances will equal or exceed the distance of closest approach in hydrogen bonding. From the distances measured in ice (2.76 Å between neighboring oxygen atoms)[8] we conclude that

$$R = 1.75 \text{ Å} \qquad (7)$$

(6) The integrand of course does change under this process.

(7) Local electroneutrality conditions of this sort are basic in standard electrochemical theory. They provide for instance a means of determining one of the integration constants in the Debye–Hückel theory of ion atmospheres; see, for instance, R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth and Co. Ltd., London, 1955, p 78.

(8) Reference 3, p 1.

is a suitable greatest lower bond on intermolecular O$\cdots$H distances. Figure 1 indicates the position R will be well to the large-r side of the isolated intramolecular peak.

We now split the integral in eq 6 into two parts

$$kT\kappa_T = 4\pi \int_0^R [g_{OH}^{(2)}(r) - 1]r^2 dr$$

$$+ 4\pi \int_R^\infty [g_{OH}^{(2)}(r) - 1]r^2 dr \quad (8)$$

Were it not for the intramolecular isolated peak in the range $0 \le r \le R$, the integrand of the first integral in (8) would be simply -1, and the integral would be trivial to perform. However, the intramolecular peak provides an additional contribution to the integral which, for precisely two protons per water molecule,[9] is easily seen to yield

$$4\pi \int_0^R [g_{OH}^{(2)}(r) - 1]r^2 dr = -(4\pi R^3/3) + (1/c) \quad (9)$$

This reduction allows eq 8 to be rewritten thus

$$kT\kappa_T = -(4\pi R^3/3) + (1/c)$$

$$+ 4\pi \int_R^\infty [g_{OH}^{(2)}(r) - 1]r^2 dr \quad (10)$$

The average proton density at radial distance r from any oxygen atom is by definition $2cg_{OH}^{(2)}(r)$. Therefore, the quantity

$$\Delta_H = 2c \int_R^\infty [g_{OH}^{(2)}(r) - 1] \times 4\pi r^2 dr \quad (11)$$

equals the local average excess number of protons outside a radius-R sphere surrounding an oxygen atom in water, compared to the overall proton density $2c$. By multiplying eq 10 through by $2c$ and transposing terms, we obtain an expression for the microscopic quantity Δ_H in terms of macroscopic observables

$$\Delta_H = 2kTc\kappa_T - 2 + (8\pi R^3 c/3) \quad (12)$$

If the protons outside the R sphere were completely disordered, and thus uniformly distributed with density $2c$, the quantity Δ_H would vanish identically. Of course, the protons are not uniformly distributed in this exterior region as a result of the various forces operative. Principal among these is hydrogen bonding, and the first peak for $r > R$ in Figure 1 represents protons directly hydrogen bonded to the central oxygen. Presuming some suitable choice of maximum permissible distance for definition of hydrogen bonding, one could obtain the number of hydrogen bonds in liquid water directly from a curve such as Figure 1. Successive peaks and valleys of $g_{OH}^{(2)}(r)$ beyond $r = R$ contain contributions of longer and longer chains of hydrogen
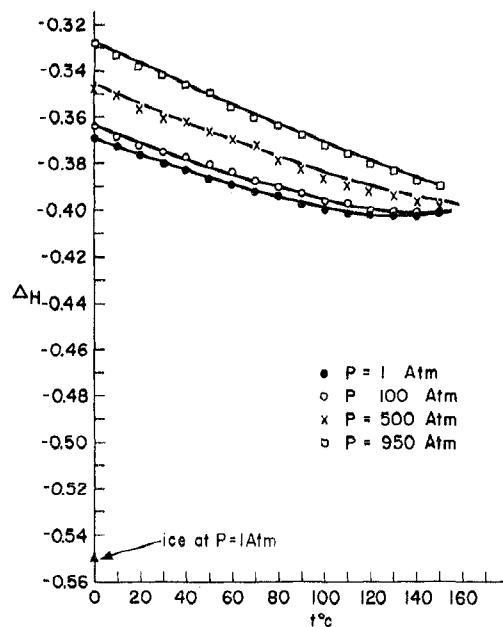

Figure 2. Local proton excess Δ_H for liquid water at various pressures, in the temperature range 0–150°. The value for ice at 1 atm and 0° has been included for comparison and differs very little from the value for ice at absolute zero. Above 100°, the $P = 1$ curve uses c and κ_T values extrapolated from higher pressures.

bonds. It is thus clear that Δ_H provides an overall measure of local hydrogen-bond order in water.

With the specific choice for R shown in eq 7, Δ_H has been evaluated from eq 12 for pure water. Figure 2 presents Δ_H in the temperature range 0–150° for several pressures. The required density and compressibility data for the calculations were obtained from the measurements of Kell and Whalley.[10] For comparison, Δ_H has also been computed for ice at 0° and 1 atm,[11] using the compressibility reported by Jona and Scherrer.[12] The fact that the "excess" Δ_H turns out to be negative merely indicates a local deficit of protons outside the R sphere in the temperature range considered.

A more extended temperature range for Δ_H is shown in Figure 3 (0–360°), but all confined to 325 atm. The necessary density and compressibility data were taken from Dorsey's compilation.[13] The obvious point of interest is the fact that the negative Δ_H for low temperature passes through a minimum and then increases to relatively large positive values. We defer comment on this phenomenon until the final discussion section.

(9) We disregard now the very small fraction ($\cong 10^{-7}$) of dissociated molecules.

(10) G. S. Kell and E. Whalley, *Phil. Trans. Roy. Soc. London*, **285**, 565 (1965).

(11) For ice it is necessary to interpret the correlation functions in their translationally and orientationally averaged sense. Otherwise the fluctuation–compressibility theorem takes a more elaborate form involving the solid's elastic constants; see F. H. Stillinger, Jr., *Phys. Rev.*, **142**, 237 (1966).

(12) F. Jona and P. Scherrer, *Helv. Phys. Acta*, **25**, 35 (1952).

(13) N. E. Dorsey, "Properties of Ordinary Water-Substance," Reinhold Publishing Corp., New York, N. Y., 1940.
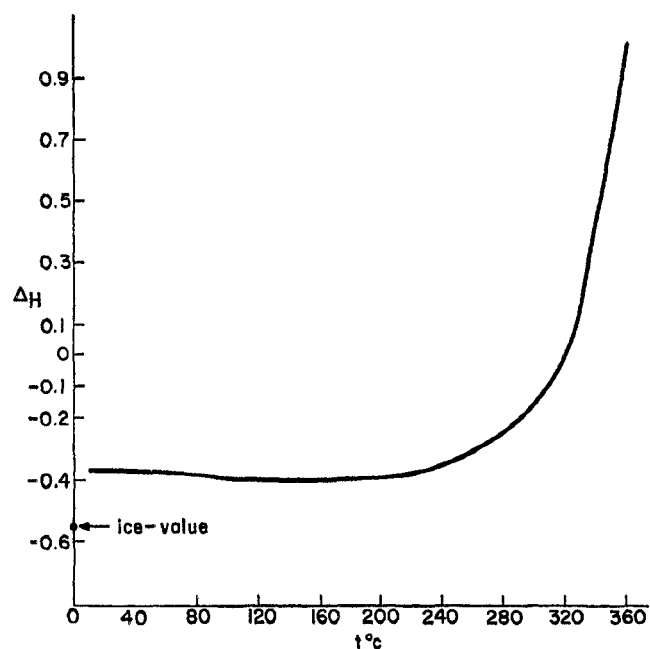
Figure 3. Variation of Δ_H for water with temperature up to about the critical temperature. The pressure is fixed at 325 atm.

III. Comparison with Other Pure Fluids

Unless equivalent structural information is available for other substances, the Δ_H values just exhibited for pure water are difficult to appreciate or interpret. For that reason we now extend our procedure to cover other liquids. Most commentary is reserved for the final section.

A. Methane. As a first example we consider methane, principally because it should typify the behavior of nonhydrogen-bonded fluids of compact molecules. The two obvious forms of the fluctuation–compressibility theorem, analogous to previous eq 2 and 3 for water, are

$$kT\kappa_T = c^{-1} + \int [g_{CC}^{(2)}(r) - 1]dr \qquad (13)$$

and

$$kT\kappa_T = (4c)^{-1} + \int [g_{HH}^{(2)}(r) - 1]dr \qquad (14)$$

Liquid methane under ordinary circumstances exhibits no detectable ionization, but still one formally has local electroneutrality conditions connecting the carbon–carbon and proton–proton correlation functions $g_{CC}^{(2)}$ and $g_{HH}^{(2)}$ to the carbon–proton cross-correlation function $g_{CH}^{(2)}$ [14]

$$1 = c \int [g_{CH}^{(2)}(r) - g_{CC}^{(2)}(r)]dr \qquad (15)$$

$$1 = 4c \int [g_{CH}^{(2)}(r) - g_{HH}^{(2)}(r)]dr \qquad (16)$$

These last relations may be used to convert either eq 13 or eq 14 to the analog of eq 6 for water

$$kT\kappa_T = \int [g_{CH}^{(2)}(r) - 1]dr \qquad (17)$$

The cross-correlation function $g_{CH}^{(2)}$ for liquid methane should behave qualitatively in very much the same way as shown in Figure 1 for its water analog. The major quantitative differences are that the isolated intramolecular peak should correspond to four protons (vs. two in water) and should occur at about 1.095 Å;[15] also the fact that the lattice spacing in solid methane is 4.16 Å[16] means that virtually no intermolecular C···H pairs can occur below a greatest lower bound of

$$R = 3.06 \text{ Å} \qquad (18)$$

In the same manner as before, we split the radial integration in eq 17 into two ranges, 0 to R and R to ∞. Then the former may be carried out explicitly, and the latter interpreted as a local proton excess for methane. We again denote this excess by Δ_H. One finally obtains the expression

$$\Delta_H = 4kTc\kappa_T - 4 + (16\pi R^3 c/3) \qquad (19)$$

where for methane

$$\Delta_H = 4c \int_R^\infty [g_{CH}^{(2)}(r) - 1] \times 4\pi r^2 dr \qquad (20)$$

Figure 4 displays the methane Δ_H, evaluated in the liquid phase at the vapor pressure, from 100–160°K.[17]
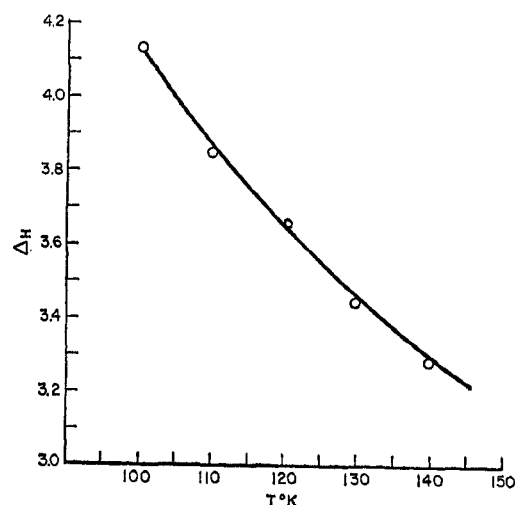

Figure 4. Local proton excess Δ_H for liquid methane in coexistence with its vapor.

(14) In deriving these relations, methane is formally regarded as a mixture of quadruply charged anions (the carbon atoms) and singly charged cations (the hydrogens).

(15) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 226.

(16) H. W. Schamp, Jr., E. A. Mason, A. C. B. Richardson, and A. Altman, *Phys. Fluids,* 1, 329 (1958).

(17) For comparison, note that methane's triplet-point temperature is 90.6°K, and its critical temperature is 190.16°K.

The requisite density and compressibility data were taken from the recent paper by Grigor and Steele.[18] The results are in marked contrast to those for water; they are large and positive and seem to decline in magnitude smoothly as T increases.

B. Alcohols. The alcohols constitute an interesting class of liquids in the present context because, like water, they are strongly associated by hydrogen bonding. Nevertheless, their physical, chemical, and biological properties are sufficiently different from those of water to lead one to expect rather different local structure.

One conceptual complication now intrudes. The alcohols contain protons not only as part of the hydroxyl groups, but also in the alkyl groups as well. However, under ordinary conditions the exchange rate between these two classes of protons will be negligible, so they may be regarded as distinguishable. Since the hydroxyl protons are the ones directly involved in the structure-forming hydrogen bonding, they are the only ones we shall consider. The alkyl-group protons will be disregarded.

Derivation of the alcohol Δ_H follows the same pattern as before. In the case of monohydroxy alcohols, with one oxygen atom and one relevant proton per molecule, the local excess of these relevant hydroxyl protons outside a fixed oxygen-centered R sphere is found to be

$$\Delta_H = kTc\kappa_T - 1 + (4\pi R^3 c/3) \tag{21}$$

where the correlation-function definition of the local excess is

$$\Delta_H = c \int_R^{\infty} \left[g_{OH}^{(2)}(r) - 1 \right] \times 4\pi r^2 dr \tag{22}$$

There is evidence that alcohols are able to form slightly shorter hydrogen bonds than water. A study[19] of the methanol crystal shows for example that nearest-neighbor hydrogen-bonded oxygen atoms are separated by only 2.66 Å, or about 0.10 Å less than in water. Furthermore, the first peak of the radical distribution functions measured for liquid methanol and ethanol[20] indicates that this shrinkage relative to water applies also after melting. However, it is also known that the covalent O–H bond length at least for methanol is somewhat smaller than for water.[21] Therefore, we feel justified in using the same R value for alcohols that was shown in eq 7 for water.

Figure 5 shows Δ_H for methanol and ethanol at 1 atm in the temperature range 0–60°.[22] Regrettably, simultaneous density and compressibility data for the higher alcohols are available only at 0°,[23] so these substances are represented only by single points on the graph. The notable features are that Δ_H is negative just as for water (but unlike methane), but in contrast to water the slopes of at least the two curves shown are positive. In the limit of very long aliphatic chain length for the homologous series of normal alcohols, eq 21 indicates
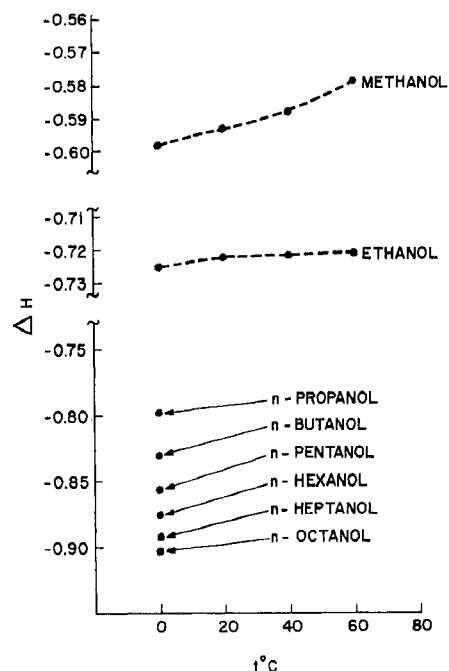

Figure 5. Δ_H values for some normal aliphatic alcohols. The pressure is 1 atm.

that Δ_H should formally converge to the temperature-independent constant -1.

IV. Binary Aqueous Solutions

The variations of Δ_H for pure water with changing temperature and pressure reflect the way that these externally controlled parameters affect local molecular structure. Another sort of perturbation that is available to the experimenter is addition of solutes to the water. In view of the large current interest in this solute effect on water structure, especially with regard to the so-called "hydrophobic bond,"[24,25] we now show that Δ_H can also serve as a useful probe for structure in aqueous solutions.

We restrict attention solely to binary aqueous solutions. The general Kirkwood–Buff solution theory[26] provides the necessary starting point in the form of an expression for the integral of the water–water pair correlation function. If we let subscript 1 refer to

(18) A. F. Grigor and W. A. Steele, *J. Chem. Phys.*, **48**, 1032 (1968).

(19) K. J. Tauer and W. N. Lipscomb, *Acta Cryst.*, **5**, 606 (1952).

(20) D. L. Wertz and R. K. Kruh, *J. Chem. Phys.*, **47**, 388 (1967).

(21) G. Herzberg, "Molecular Spectra and Molecular Structure," D. Van Nostrand, Inc., New York, N. Y., 1945, p 498.

(22) Compressibilities were taken from "Handbook of Chemistry and Physics," 47th ed, The Chemical Rubber Co., Cleveland, Ohio, 1966, p F-10; densities were obtained from "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1928, p 27.

(23) W. P. McKinney, G. F. Skinner, and L. A. K. Staveley, *J. Chem. Soc.*, 2415 (1959).

(24) W. Kauzmann, *Advan. Protein Chem.*, **14**, 1 (1959).

(25) G. Némethy, *Angew. Chem.*, **6**, 195 (1967).

(26) J. G. Kirkwood and F. P. Buff, *J. Chem. Phys.*, **19**, 774 (1951).

water and 2 to the solute, the analysis in ref 26 leads to the identity

$$\int [g_{00}^{(2)}(r) - 1]dr$$

$$= \frac{kT(\partial\mu_2/\partial N_2)_{T,V,N_1}}{Vc_1^2\{(\partial\mu_1/\partial N_1)_{T,V,N_2}(\partial\mu_2/\partial N_2)_{T,V,N_1}} - \frac{1}{c_1}$$

$$- (\partial\mu_1/\partial N_2)_{T,V,N_1}(\partial\mu_2/\partial N_1)_{T,V,N_2}\}$$ (23)

Here V is the system volume, and N_1 and N_2 are the numbers of water and solute molecules in V, respectively, and the chemical potentials are equal to μ_1 and μ_2. Also in eq 23 we have exercised the option as before to utilize the oxygen nuclei as "positions" of the water molecules.

The electroneutrality condition shown in eq 4 is still valid (with c_1 in place of c), so eq 23 may be rewritten in terms of the cross-correlation function,[27]

$$c_1 \int [g_{OH}^{(2)}(r) - 1]dr$$

$$= \frac{kT(\partial\mu_2/\partial N_2)_{T,V,N_1}}{Vc_1\{(\partial\mu_1/\partial N_1)_{T,V,N_2}(\partial\mu_2/\partial N_2)_{T,V,N_1}}$$

$$- (\partial\mu_1/\partial N_2)_{T,V,N_1}(\partial\mu_2/\partial N_1)_{T,V,N_2}\}$$ (24)

The constant-volume partial derivatives in this last relation may be eliminated in favor of the experimentally more direct constant-pressure derivatives via the formula $(\alpha, \beta = 1, 2; \gamma \neq \beta)$

$$\left(\frac{\partial\mu_\alpha}{\partial N_\beta}\right)_{T,V,N_\gamma} = \left(\frac{\partial\mu_\alpha}{\partial N_\beta}\right)_{T,p,N_\gamma} + \frac{\bar{v}_\alpha\bar{v}_\beta}{\kappa_T V}$$ (25)

Here we have introduced the partial molecular volumes

$$\bar{v}_\beta = \left(\frac{\partial V}{\partial N_\beta}\right)_{T,p,N_\gamma}$$ (26)

and the constant-composition isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N_1,N_2}$$ (27)

Also, the Gibbs–Duhem equation permits elimination of cross derivatives in eq 24. One thus obtains

$$c_1 \int [g_{OH}^{(2)}(r) - 1]dr$$

$$= \frac{(kT\kappa_T/c_1)[(\partial\mu_2/\partial N_2)_{T,p,N_1} + (\bar{v}_2^2/\kappa_T V)]}{\{(\partial\mu_1/\partial N_1)_{T,p,N_2}[\bar{v}_2^2 + (c_1\bar{v}_1\bar{v}_2/c_2)]}$$

$$+ (\partial\mu_2/\partial N_2)_{T,p,N_1}[\bar{v}_1^2 + (c_2\bar{v}_1\bar{v}_2/c_1)]\}}$$ (28)

Further considerable simplification results from use of

the formula

$$\left(\frac{\partial\mu_1}{\partial N_1}\right)_{T,p,N_2} = \left(\frac{N_2}{N_1}\right)^2\left(\frac{\partial\mu_2}{\partial N_2}\right)_{T,p,N_1}$$ (29)

whence

$$c_1 \int [g_{OH}^{(2)}(r) - 1]dr = kTc_1\left\{\kappa_T + \frac{\bar{v}_2^2}{V(\partial\mu_2/\partial N_2)_{T,p,N_1}}\right\}$$ (30)

The left member of eq 30 next may be treated in exactly the same way as for pure water. The generalized expression for the local proton excess thereupon becomes

$$\Delta_H = 2kTc_1\left\{\kappa_T + \frac{\bar{v}_2^2}{V(\partial\mu_2/\partial N_2)_{T,p,N_1}}\right\} - 2 + \frac{8\pi R^3 c_1}{3}$$ (31)

In the limit of infinite solute dilution, the divergence of the partial derivative $(\partial\mu_2/\partial N_2)$ allows one to recover eq 12 for pure water.

Our main interest in eq 31 is evaluation of the initial trend of Δ_H as a small amount of solute is added to pure water. If we use superscript zero to denote pure water, then in the dilute solution regime we may write

$$\Delta_H = \Delta_H^{(0)} + \Delta_H' c_2 + \ldots$$ (32)

also one has

$$c_1 = c_1^{(0)} - c_1^{(0)}\bar{v}_2^{(0)}c_2 + \ldots$$

$$\kappa_T = \kappa_T^{(0)} + Ac_2 + \ldots$$ (33)

The succeeding terms not explicitly shown in eq 32 and 33 will be proportional to c_2^2 for nonelectrolytes, and to $c_2^{3/2}$ for electrolytes. In order to obtain an expression for the desired coefficient Δ_H' from eq 31, it necessary only to use in addition the low-concentration form of the chemical potential derivative

$$\left(\frac{\partial\mu_2}{\partial N_2}\right)_{T,p,N_1} \approx \frac{kT}{c_2 V}$$ (34)

Hence we obtain

$$\Delta_H' = 2kTc_1^{(0)}A + \bar{v}_2^{(0)}c_1^{(0)}$$

$$\times [2\bar{v}_2^{(0)} - (8\pi R^3/3) - 2kT\kappa_T^{(0)}]$$ (35)

$$= 2kTc_1^{(0)}A + \bar{v}_2^{(0)}(2c_1^{(0)}\bar{v}_2^{(0)} - \Delta_H^{(0)} - 2)$$

The coefficient A for initial composition dependence of solution compressibility has been listed by Harned

(27) The solute molecules might contain hydrogens, but we take the point of view (analogous to that for the alcohols) that the water protons can be distinguished. The correlation function $g_{OH}^{(2)}(r)$ refers only to water protons.

and Owen for a few simple electrolytes.[28] For others, A may be obtained in principal from pressure dependence of $\bar{v}_2^{(0)}$, for if we denote

$$\varphi_K^{(0)} = \left(\frac{\partial \bar{v}_2^{(0)}}{\partial p}\right)_{T,N_1,N_2} \tag{36}$$

then it is easy to show that

$$A = \varphi_K^{(0)} - \kappa_T^{(0)} \bar{v}_2^{(0)} \tag{37}$$

Table I presents Δ_H' results for several salts at 25°. The required $\bar{v}_2^{(0)}$ values for the inorganic salts are listed in ref 28 [Table (8-5-1), p 361]. For the alkyl-ammonium salts $\bar{v}_2^{(0)}$ measurements were taken from Verrall and Conway[29] for the chlorides, from Wen and Saito for the bromides,[30] and from Conway, Verrall, and Desnoyers for the iodides.[31] The direct A values for lithium, sodium, and potassium chlorides are located by footnote 28. For the other inorganic salts, eq 37 was used to compute A from $\varphi_K^{(0)}$'s listed by Owen and Brinkley,[32] and $\bar{v}_2^{(0)}$'s in ref 28. The isothermal quantities $\varphi_K^{(0)}$ appear not to be available for the alkylammonium salts, so in their place the corresponding adiabatic quantities[33]

$$\varphi_{K,ad}^{(0)} = \left(\frac{\partial \bar{v}_2^{(0)}}{\partial p}\right)_{S,N_1,N_2} \tag{38}$$

were used; this replacement is justified first because our experience shows that the contribution of the A term to Δ_H' is relatively small for organic salts, and second

Table I: Coefficient of Initial Solute Dependence for Local Proton Defect in Aqueous Solutions of Various Electrolytes at 25°

Salt	Δ_H'
LiCl	−15.3
NaCl	−21.8
KCl	31.9
NaBr	14.3
KBr	96.0
CsBr	247
LiI	121
KI	239
Na$_2$CO$_3$	−50.3
K$_2$CrO$_4$	82.6
Na$_2$SO$_4$	−79.3
K$_2$SO$_4$	34.7
(CH$_3$)NH$_3$Cl	367
(CH$_3$)$_2$NH$_2$Cl	747
(CH$_3$)$_3$NHCl	1,240
(CH$_3$)$_4$NCl	1,800
(CH$_3$)$_4$NBr	2,090
(C$_2$H$_5$)$_4$NBr	5,140
(n-C$_3$H$_7$)$_4$NBr	9,970
(n-C$_4$H$_9$)$_4$NBr	16,000
(CH$_3$)$_4$NI	2,550
(C$_2$H$_5$)$_4$NI	5,790
(n-C$_3$H$_7$)$_4$NI	10,900
(n-C$_4$H$_9$)$_4$NI	17,000

because isothermal and adiabatic aqueous compressibilities differ by so little.[34]

Consistent with the procedure in section III, we have disregarded the alkyl group hydrogens in the substituted ammonium salts, and have allowed only the water-molecule hydrogens to be counted in Δ_H'.

V. Discussion

(1) Of the pure liquids examined by our Δ_H technique, water alone exhibits a minimum as temperature is varied. This apparently anomalous behavior immediately brings to mind the analogous behavior of water's molar volume, which among liquids uniquely has a minimum. This latter fact is often mentioned in connection with discussions of the extent of hydrogen-bond order in liquid water at various temperatures, and we feel that the Δ_H behavior is no less relevant in this regard. As temperature is lowered through 0°, the water molar volume curve extrapolated into the supercooled region approaches the molar volume of ice, and this single fact by itself would seem to indicate that the local order in water is literally icelike (i.e., pieces of the ice I lattice). However, we see from Figures 2 and 3 that the opposite is true for the independent quantity Δ_H. It seems most likely, therefore, that the structural order forming as liquid water is cooled is bulky, like ice I, but has rather different structure. The most reasonable assumption is that this structure is a random network composed of polygons of varying numbers of sides and conformations, with significant bridging, free chain ends, and innumerable random polyhedra. These various structures would be present in concentrations varying with temperature and pressure.

(2) As a result of steric hindrance by the alkyl chains and the fact that their hydroxyl groups can participate in only two hydrogen bonds at most, the range of possible structures in the alcohols is far narrower than in water. Very probably chains of various lengths predominate. Rise in temperature simply would reduce the mean chain length, and Δ_H rises monotonically to reflect this simple degradation. By contrast, the nonmonotonic Δ_H in liquid water presumably results partly from similar reduction in total amount of hydrogen bonding, but of at least equal importance is temperature-induced shift in *type* of order. It is not hard to imagine that Δ_H for water results from a delicate interplay among the geometrically distinct ways of linking together groups of water

(28) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, p 378.

(29) R. E. Verrall and B. E. Conway, *J. Phys. Chem.*, **70**, 3961 (1966).

(30) W.-Y. Wen and S. Saito, *ibid.*, **68**, 2639 (1964).

(31) B. E. Conway, R. E. Verrall, and J. E. Desnoyers, *Trans. Faraday Soc.*, **62**, 1 (1966).

(32) B. B. Owen and S. R. Brinkley, Jr., *Chem. Rev.*, **29**, 461 (1941).

(33) B. E. Conway and R. E. Verrall, *J. Phys. Chem.*, **70**, 3952 (1966).

(34) Reference 28, p 386.

molecules by hydrogen bonding, with some of these structures giving positive Δ_H contributions and other negative Δ_H contributions.

(3) That the water Δ_H and apparently those for the alcohols as well become large and positive near the critical point is relatively easy to understand. At this high temperature (374° for water), the fluid is far less dense than the ordinary liquid and may be well viewed merely as a somewhat compressed gas. The very strong attraction between water molecules then acts to produce an average increase in molecular density, surrounding a given molecule, that exceeds the low macroscopic density in the fluid. This shell of attracted neighbors (each with two protons) provides a strong positive contribution to Δ_H.

(4) On the basis of the very sketchy evidence we have so far been able to accumulate, negative Δ_H's seem to be characteristic of hydrogen-bonded molecular arrangements, i.e., molecules strongly and closely bound to a *small* number of nearest neighbors to produce a rather open overall structure. Methane with positive Δ_H must be representative of liquids with higher numbers of nearest neighbors and tighter overall packing. Indeed, if we assume that methane molecules are arranged as rigid spheres, with diameter a, we may use the scaled-particle theory of the rigid-sphere equation of state[35] to convert eq 19 to

$$\Delta_H = 4\left[\frac{(1-y)^4}{(1+2y)^2} - 1 + \frac{4\pi cR^3}{3}\right] \quad (39)$$

$$y = \frac{\pi ca^3}{6}$$

by introduction of an explicit form for the isothermal compressibility. For liquid methane $y \cong 1$ if a is chosen to be the crystal nearest-neighbor distance. The first term in the right member of eq 39 then is virtually zero and Δ_H is dominated strongly by the last term. The decrease of the positive methane Δ_H as temperature increases along the vapor pressure curve is therefore almost exclusively due to reduction in c in that last term by thermal expansion.

(5) Figures 2 and 3 show that in the temperature range for which the salt effects in Table I apply (25°), Δ_H decreases with increasing temperature for pure water. Those salts with negative Δ_H', therefore, may tentatively be considered as perturbing water in the same way as increasing temperature, and those with positive Δ_H' as equivalent to temperature reduction. Thus the former class may be called "structure breakers," and the latter class "structure formers," though these identifications should always be augmented by the understanding that solute structural

shifts are certainly more subtle and variegated than just the single temperature-shift type. Nevertheless, the strong effect exhibited in Table I toward more positive Δ_H's among the substituted ammonium salts, as the size and number of alkyl groups increase, is in full accord with the ideas underlying the hydrophobic bond concept for hydrocarbon substituents in aqueous media.[24,25] Aside from the possibly anomalous character of Li+, it can also seen from Table I that increase in size of spherical inorganic ions tends to produce an increase in Δ_H, that is, more overall structure.

(6) Unfortunately, we are prevented from studying the solute effect on water of dissociating protonic acids (such as HCl) or hydroxides (such as NaOH). The reason is simply that they would introduce a new effect which would obscure comparison with the other solutes, namely, a change in stoichiometry of the oxygen–hydrogen framework. By suitable combination of Δ_H results on several precisely measured systems with common ions, it may eventually be possible to isolate and evaluate this framework composition effect.

(7) Finally, we must remark on the desirability of measuring those thermodynamic properties for a wide variety of liquids that would permit a comprehensive extension of the few Δ_H computations presented here. As examples of pure substances, special interest attaches to HF, HCN, and NH₃ liquids, and we urge their densities and isothermal compressibilities be precisely and simultaneously determined over a wide range of temperatures and pressures. Liquid carboxylic acids, which seem to have a marked propensity for ring formation as dimers, would also be interesting. So far as solutions are concerned, it would first be advisable to study the effect of simple dissolved gases (e.g., Xe, N₂, CO, CH₄) by making the required κ_T and $\bar{v}_2$ measurements in dilute solution and then to compare those results with the behavior of more complicated substances like butane, urea, sucrose, and dimethyl sulfoxide. Furthermore, extension of the considerations in section IV to order c_2^2 for hydrocarbon solutions should provide additional information on the mechanism of hydrophobic bonding analogous to that provided by other solution data recently analyzed in great detail by Kozak, Knight, and Kauzmann.[36]

(35) H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.*, **31**, 369 (1959).
(36) J. J. Kozak, W. S. Knight, and W. Kauzmann, *ibid.*, **48**, 678 (1968).