

On the Intactness of Hydrogen Bonds around Nonpolar Solutes Dissolved in Water

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Angell developed a simple two-state model of hydrogen bonds with the aim to describe some properties of pure water. Muller extended the two-state model description to treat the unusual thermodynamics of hydrophobic hydration. We show here that, to correctly reproduce a qualitative feature of the temperature dependence of the hydration heat capacity change of nonpolar solutes by means of the two-state Muller's model, the hydrogen bonds in the hydration shell have to be more broken than those in bulk water. This contrasts with the suggestion in the literature that more hydrogen bonds form around a nonpolar solute in water.

Introduction

The extent of hydrogen bond formation among water molecules in the hydration shell of nonpolar solutes¹ is a matter of continuous debate since 1945, when Frank and Evans² proposed the so-called iceberg model to rationalize the unusual thermodynamics of hydrophobic hydration. No definitive conclusion has been reached, even though in the last several years a transparent scenario has been emerging, and it contrasts with the iceberg model.^{1,3} In particular, at the end of the eighties, Muller⁴ devised a two-state model for hydrogen bonds distinguishing the hydration shell from the bulk water. Such a model, notwithstanding its simplicity, is gaining attention and credibility.⁵ Muller showed that application of the model leads to the following conclusion: the hydrogen bonds in the hydration shell of nonpolar solutes are enthalpically stronger but *more* broken than those in bulk water. Lee and Graziano⁶ inserted the Muller's model in the context of a general theory of hydration,^{7,8} and found that only the Muller's scenario is compatible with experimental data for alkanes. The validity of this scenario has been verified also for the hydration shell of noble gases,⁹ and *n*-alcohols.¹⁰

In a recent article, however, Silverstein, Haymet, and Dill¹¹ (SHD), by using the Muller's model with different parameters for the bulk water, reached the opposite conclusion: the hydrogen bonds in the hydration shell of nonpolar solutes are *less* broken than those in bulk water. It is striking that the application of the same model to similar experimental data could lead to contrasting conclusions. However, the procedure adopted by SHD led to an unphysical temperature dependence of the calculated heat capacity change upon hydration.

The aim of the present study is to see if a general conclusion can be made on the number of hydrogen bonds in the hydration shell compared to that in the bulk in the two-state Muller's model. We find that it is indeed possible to prove that *the hydrogen bonds in the hydration shell have to be more broken than those in bulk water* in order for the model to reproduce a

qualitative feature of the temperature dependence of the hydration heat capacity change.

Temperature Dependence of the Experimental Heat Capacity Change upon Hydration

Edsall¹² was the first, in 1935, to point out that ΔC_p° is large positive for the hydration of nonpolar solutes at room temperature. Since then the large positive ΔC_p° is considered a hallmark of hydrophobic hydration.¹³ The temperature dependence of ΔC_p° for the hydration of noble gases and hydrocarbons has also been determined over the years in several laboratories. See the data of Crovetto and colleagues,¹⁴ and of Krause and Benson for noble gases;¹⁵ those of Wood and co-workers for argon;¹⁶ all the calorimetric measurements by Gill and co-workers for aliphatic hydrocarbons;¹⁷ and the calorimetric measurements by Makhataдзе and Privalov for aromatic hydrocarbons.¹⁸ A common feature is that the hydration heat capacity change shows a continuous and monotonic decrease with temperature for all nonpolar solutes over the temperature range 0–100 °C.

Experimental ΔC_p° values for Ar over the range 0–100 °C, determined in different laboratories,^{14–16,19,20} are collected in Table 1. We chose argon as an example because several reliable experimental determinations of ΔC_p° exist for this solute. Since there is practically no numerical correction for the hydration heat capacity change to pass from the conventional standard to the Ben-Naim standard,²¹ we quote directly the values reported in the original articles and indicate them with the usual superscript open circle. Even though the determinations have been done at different pressures, the pressure dependence of the heat capacity, estimated from the volumetric data,²² is less than the experimental error, so the comparison is justified. The good qualitative and quantitative agreement among the different sets of experimental values unequivocally shows that ΔC_p° decreases monotonically over the range 0–100 °C.

Finally, a group additivity analysis of experimental data for several organic solutes²³ showed that ΔC_p° for nonpolar moieties is a large positive quantity that decreases more or less linearly with temperature over the range 5–125 °C.

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TABLE 1. Hydration Heat Capacity Change for Argon, As Determined in Different Laboratories

<i>T</i> (°C)	ΔC_p° (cal K ⁻¹ mol ⁻¹)				
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
0	58.1	67.4	47.6	51.9	54.3
25	53.3	56.5	45.2	46.8	46.1
50	48.5	48.1	43.0	42.5	40.4
75	43.7	41.5	41.1	38.7	36.1
100	39.0	36.1	39.2	35.4	32.7

^a From Table 3 and Figure 5 of ref 14; Crovetto and colleagues performed solubility measurements over the temperature range 20–280 °C, at a total pressure of about 22 atm; the number at 0 °C is not truly experimental, but estimated on the basis of the linear temperature dependence of the ΔC_p° values at higher temperatures; this procedure is further justified by the analysis of solubility data over an extended temperature range performed by Fernandez-Prini and Crovetto.²⁰

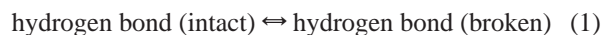
^b From eq 5 of ref 20, using the parameter values reported for argon.

^c From eq 5 of ref 16; Wood and co-workers performed direct calorimetric measurements over a very large temperature range, at a total pressure of about 172 atm. ^d From Table 3 of ref 19; Abraham and Matteoli analyzed experimental data from different laboratories and obtained these values by a fitting procedure. ^e From Table 11 of ref 15; Krause and Benson performed precise solubility measurements over the range 0–60 °C, and analyzed their data and data from other sources to cover a larger temperature range, using a procedure termed Mark II.

The Two-State Muller's Model

Even though liquid water has a continuum of energy levels,²⁴ spectroscopic measurements, showing isosbestic points in both IR and Raman spectra as a function of temperature,^{25–27} suggested the possibility to consider only two hydrogen bonding states. In addition, results obtained from computer simulations of different models of water^{5,11} supported the idea that hydrogen bonds in liquid water can be described by a two-state model.

On the basis of these observations Angell²⁸ developed a simple two-state model for the hydrogen bonds of liquid water, which was later extended by Muller.⁴ In this model two hydrogen bonding states are in equilibrium between each other:



with the equilibrium constant K_b (the subscript refers to the bulk water), which is given by:

$$K_b = f_b/(1 - f_b) = \exp[(-\Delta H_b^\circ/RT) + (\Delta S_b^\circ/R)] \quad (2)$$

where f_b is the fraction of broken hydrogen bonds; ΔH_b° and ΔS_b° are the enthalpy and entropy differences between the two states, assumed to be temperature independent; and R and T are the gas constant and the absolute temperature, respectively. Such two-state equilibrium gives rise to the following heat capacity contribution per each hydrogen atom in the system:

$$C_{p,b} = f_b \cdot (1 - f_b) \cdot (\Delta H_b^\circ)^2 / RT^2 \quad (3)$$

Equations 2 and 3 can be solved for ΔH_b° and ΔS_b° if the values of f_b and $C_{p,b}$ are known at least at one temperature. A robust determination of the bulk parameters is a fundamental step in rendering the model reliable and useful.

Angell²⁸ determined ΔH_b° and ΔS_b° by best-fitting the “configurational” heat capacity of water as a function of temperature. The “configurational” heat capacity of water is not an experimental quantity, but it was calculated theoretically by Eisenberg and Kauzmann,²⁹ subtracting the contributions due to molecular translations, rotations, and vibrations from the experimental heat capacity of bulk water in the whole liquid

range (i.e., the “configurational” heat capacity should contain only the contributions due to the hydrogen bonding network). In this manner, Angell obtained $\Delta H_b^\circ = 1.9$ kcal mol⁻¹ and $\Delta S_b^\circ/R = 2.4$. Muller⁴ determined another set of values for the bulk water parameters using a different procedure. However, SHD¹¹ have shown that the Angell's bulk parameters are consistent also with the f_b values determined by means of a careful analysis of Raman spectra by Hare and Sorensen.²⁷ We had used the Muller's parameters in previous articles,^{6,9,10} but in the present work we switch to the Angell's values in view of the analysis by SHD.

To treat the thermodynamics of hydrophobic hydration, Muller assumed that the two-state equilibrium of eq 1 is valid also for the water molecules constituting the hydration shell of nonpolar solutes. Correspondingly one has

$$K_{hs} = f_{hs}/(1 - f_{hs}) = \exp[(-\Delta H_{hs}^\circ/RT) + (\Delta S_{hs}^\circ/R)] \quad (4)$$

and

$$C_{p,hs} = f_{hs} \cdot (1 - f_{hs}) \cdot (\Delta H_{hs}^\circ)^2 / RT^2 \quad (5)$$

where the subscript *hs* stands for the hydration shell; ΔH_{hs}° and ΔS_{hs}° are the enthalpy and entropy differences between the two states in the hydration shell, assumed to be temperature independent. It should be noted that eqs 4 and 5 cannot be solved for ΔH_{hs}° and ΔS_{hs}° because f_{hs} and $C_{p,hs}$ are unknown.

However, the hydration heat capacity change, ΔC_p° , is an experimental quantity that has been carefully measured for several nonpolar solutes.^{14–18} Muller⁴ assumed that ΔC_p° is all due to the difference in the hydrogen bonding states between the hydration shell and the bulk water (i.e., to the reorganization of hydrogen bonds) and wrote:

$$\Delta C_p^\circ = \Delta C_p^h = n^h (C_{p,hs} - C_{p,b}) \quad (6)$$

where n^h is the number of hydrogen bonds in the hydration shell. The Muller's assumption is strongly supported by several means.^{13,30,31} Since n^h is considered independent of temperature,⁴ the temperature derivative of ΔC_p^h is given by:

$$(\Delta C_p^h)' = n^h [(C_{p,hs})' - (C_{p,b})'] \quad (7)$$

where $C_p' = \partial C_p / \partial T$. Since ΔH_b° and ΔS_b° are temperature independent, differentiation of eq 3 with respect to temperature gives:

$$(C_{p,b})' = [(1 - 2f_b)\Delta H_b^\circ - 2RT] \cdot (C_{p,b}) / RT^2 \quad (8)$$

and a corresponding expression is obtained for $(C_{p,hs})'$.

General Results

Two features have emerged from the experimental measurements of nonpolar solutes: (a) ΔC_p° is a large positive quantity over the range 0–100 °C and (b) ΔC_p° decreases in a continuous and monotonic manner over the range 0–100 °C. The latter feature is the main focus of the present investigation. We computed the dimensionless functions $\Delta c_p = (\Delta C_p^h / n^h \cdot R)$ and $T \cdot \Delta c_p' = T \cdot (\partial \Delta C_p / \partial T)$ for a range of ΔH_{hs}° and ΔS_{hs}° values, using the ΔH_b° and ΔS_b° parameters given by Angell. Contour lines of the two functions have been plotted by using as coordinates $\Delta \Delta H = \Delta H_{hs}^\circ - \Delta H_b^\circ$ and $T \cdot \Delta \Delta S = T \cdot (\Delta S_{hs}^\circ - \Delta S_b^\circ)$ at a fixed temperature. The plots of Δc_p at 0 and 20 °C are shown in Figure 1; those of $T \cdot \Delta c_p'$ at the same temperatures are shown in Figure 2. The investigated ranges are $0 \leq \Delta \Delta H$

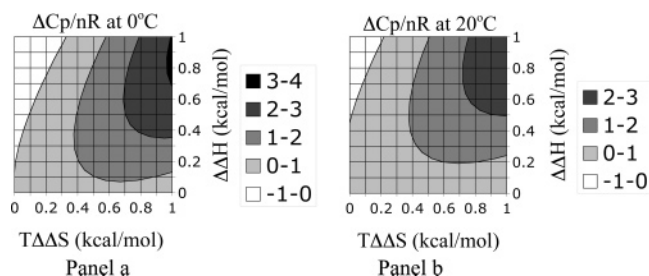


Figure 1. Contour lines of the dimensionless function $\Delta C_p = (\Delta C_p^h/n^h \cdot R)$ calculated over the ranges $0 \leq \Delta\Delta H \leq 1$ kcal mol⁻¹ and $0 \leq T \cdot \Delta\Delta S \leq 1$ kcal mol⁻¹ at 0 (panel a) and 20 °C (panel b).

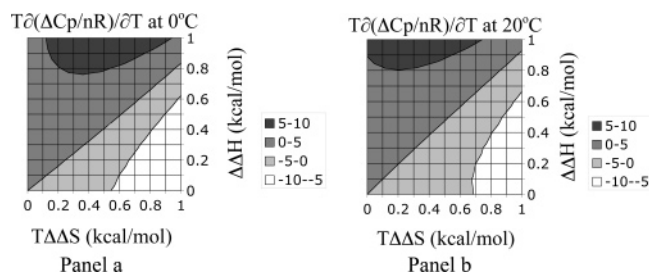


Figure 2. Contour lines of the dimensionless function $T \cdot \Delta C_p' = T \cdot (\partial \Delta C_p^h / \partial T)$ calculated over the ranges $0 \leq \Delta\Delta H \leq 1$ kcal mol⁻¹ and $0 \leq T \cdot \Delta\Delta S \leq 1$ kcal mol⁻¹ at 0 (panel a) and 20 °C (panel b).

≤ 1 kcal mol⁻¹ and $0 \leq T \cdot \Delta\Delta S \leq 1$ kcal mol⁻¹, since previous analyses have shown that $\Delta H_{hs}^\circ > \Delta H_b^\circ$ and $\Delta S_{hs}^\circ > \Delta S_b^\circ$ for noble gases and aliphatic hydrocarbons.^{4,6,9}

These coordinates have the following merits. In a 2-dimensional plot with $T \cdot \Delta\Delta S$ as the x -axis and $\Delta\Delta H$ as the y -axis, (a) $\Delta f = f_{hs} - f_b$ is zero along the diagonal line, since $\Delta\Delta G = \Delta\Delta H - T \cdot \Delta\Delta S = 0$ on this line; (b) Δf is negative in the area above the diagonal where $\Delta\Delta G > 0$; and (c) Δf is positive in the area below the diagonal where $\Delta\Delta G < 0$. In other words, (a) the area above the diagonal corresponds to the situation in which the hydrogen bonds in the hydration shell are *less* broken than those in the bulk; (b) the area below the diagonal corresponds to the situation in which the hydrogen bonds in the hydration shell are *more* broken than those in the bulk.

When $T = 0$ and 20 °C the plots of $T \cdot \Delta C_p'$ as a function of $T \cdot \Delta\Delta S$ and $\Delta\Delta H$ show that the $\Delta C_p' = 0$ contour line is near but below the diagonal (see Figure 2). Since to have $\Delta C_p' < 0$, as required by the experimental data, $T \cdot \Delta\Delta S$ and $\Delta\Delta H$ have to be in the area below the $\Delta C_p' = 0$ contour line, and since this line is itself below the diagonal, Δf has to be positive at 0 and 20 °C. This is a general result that holds for a relatively large range of ΔH_{hs}° and ΔS_{hs}° values.

It should be noted that, if this conclusion is correct at 20 °C, it has to be correct also at higher temperatures. Indeed, at $T_1 = 20$ °C, $\Delta f > 0$ implies $\Delta\Delta H < T_1 \cdot \Delta\Delta S$; clearly, at any $T_2 > T_1$, one still has $\Delta\Delta H < T_2 \cdot \Delta\Delta S$ because both $\Delta\Delta H$ and $\Delta\Delta S$ are positive quantities and assumed to be independent of temperature. The latter is a fundamental feature of the Muller's model,⁴ retained by us^{6,9,10} as well as by SHD.¹¹ Therefore, to have $\Delta C_p' < 0$ within the Muller's model with use of Angell's bulk water parameters, $\Delta f = f_{hs} - f_b$ has to be positive and so the hydrogen bonds in the hydration shell have to be more broken than those in the bulk at all temperatures between 0 and 100 °C.

Relationship with the SHD Work

SHD¹¹ best-fitted the experimental ΔC_p° for noble gases over a large temperature range, using the Muller's model with the

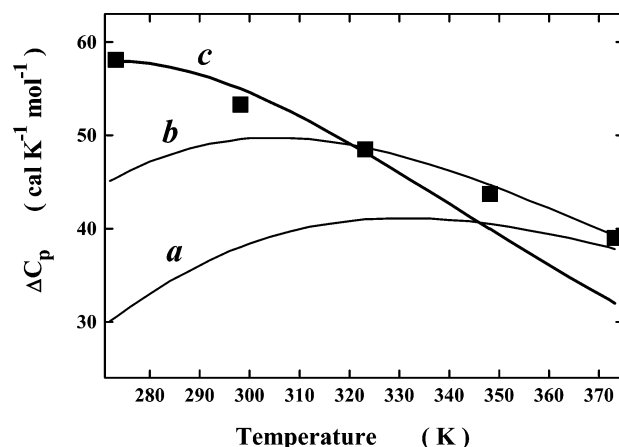


Figure 3. The ΔC_p^h functions calculated for argon ($n^h = 20$, as selected by SHD) with the Muller's model (Angell's bulk parameters: $\Delta H_b^\circ = 1.9$ kcal mol⁻¹ and $\Delta S_b^\circ/R = 2.4$) with $\Delta H_{hs}^\circ = 2.4$ kcal mol⁻¹ and $\Delta S_{hs}^\circ/R = 3.0$ (curve a), $\Delta H_{hs}^\circ = 2.4$ kcal mol⁻¹ and $\Delta S_{hs}^\circ/R = 3.2$ (curve b), and $\Delta H_{hs}^\circ = 2.33$ kcal mol⁻¹ and $\Delta S_{hs}^\circ/R = 3.37$ (curve c). The solid squares are the experimental ΔC_p° data by Crovetto and colleagues.¹⁴

Angell's bulk parameters, and obtained estimates for the hydration shell parameters. Specifically, they fitted ΔC_p° data over the range 50–280 °C derived from the solubility measurements of Crovetto and colleagues.¹⁴ SHD found that, for all noble gases, $\Delta H_{hs}^\circ = 2.4$ kcal mol⁻¹, while $\Delta S_{hs}^\circ/R$ passes from 3.2 for Ne and Ar, to 3.3 for Kr, and to 3.4 for Xe.

Further attention was focused on argon to show that the experimental ΔC_p° data can also be reproduced with hydration shell parameters calculated by using a constraint derived from computer simulations of the Mercedes-Benz model of water.^{5,32,33} According to the SHD analysis of the computer simulation data, at the temperature T_S where the hydration entropy change is zero, the fraction of broken hydrogen bonds in the bulk is equal to that in the hydration shell, $f_b = f_{hs}$. Applying this condition observed in the Mercedes-Benz model to the real water, with $T_S = 450$ K = 177 °C, they found that the optimum ΔH_{hs}° value did not change but that the optimum $\Delta S_{hs}^\circ/R$ was now 3.0, which is slightly but significantly smaller than the optimum value when this condition is not applied.

The ΔC_p^h functions calculated with $\Delta H_{hs}^\circ = 2.4$ kcal mol⁻¹ and $\Delta S_{hs}^\circ/R = 3.0$ (curve a) and 3.2 (curve b) are shown in Figure 3, along with the experimental ΔC_p° values for argon by Crovetto and colleagues.¹⁴ This figure corresponds to Figure 4 of the SHD article, except for the inclusion of experimental values at low temperatures. It can be seen that the calculated ΔC_p^h function for Ar shows a maximum at around 330 K when $\Delta S_{hs}^\circ/R = 3.0$ and around 305 K when $\Delta S_{hs}^\circ/R = 3.2$. This temperature dependence is qualitatively different from that of the available experimental ΔC_p° data (see Table 1). For example, the hydration heat capacity change at room temperature decreases with temperature, but these calculations predict that ΔC_p^h will increase with temperature. One can also note that the agreement with the experimental data is poorer when the ΔS_{hs}° value is lower.

Figure 4 shows the calculated fraction of broken hydrogen bonds in the hydration shell, f_{hs} , using $\Delta H_{hs}^\circ = 2.4$ kcal mol⁻¹ and $\Delta S_{hs}^\circ/R = 3.0$ (curve a) or 3.2 (curve b), along with f_b for comparison. When $\Delta S_{hs}^\circ/R = 3.0$, the condition $f_{hs} < f_b$ holds over the whole temperature range of 0–100 °C (see curve a in Figure 4). This is a direct result of the imposed condition that $f_{hs} = f_b$ at $T_S = 450$ K. When $\Delta S_{hs}^\circ/R = 3.2$, f_{hs} is equal to f_b at 45 °C and the condition $f_{hs} < f_b$ holds below this temperature.

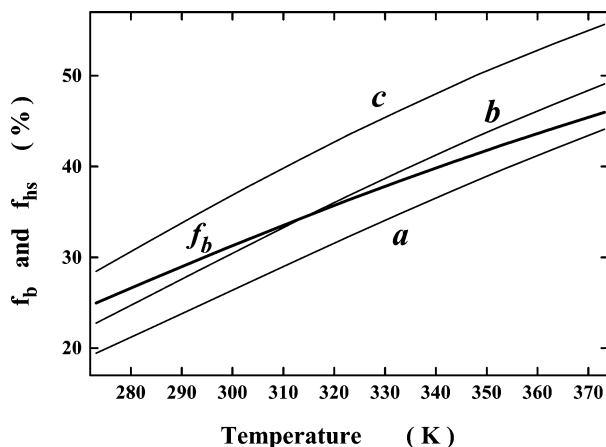


Figure 4. Trend of the fraction of broken hydrogen bonds in the hydration shell, f_{hs} , as a function of temperature calculated by using $\Delta H_{hs}^\circ = 2.4$ kcal mol $^{-1}$ and $\Delta S_{hs}^\circ/R = 3.0$ (curve a), $\Delta H_{hs}^\circ = 2.4$ kcal mol $^{-1}$ and $\Delta S_{hs}^\circ/R = 3.2$ (curve b), and $\Delta H_{hs}^\circ = 2.33$ kcal mol $^{-1}$ and $\Delta S_{hs}^\circ/R = 3.37$ (curve c). The trend of the fraction of broken hydrogen bonds in the bulk, f_b , calculated with use of the Angell's bulk parameters is also shown (thicker line).

Above 45 °C, where the corresponding ΔC_p^h function agrees with the experimental ΔC_p° values (see curve b in Figure 3), f_{hs} is greater than f_b .

The Muller's model, due to its great simplicity and to the assumption that the model parameters are temperature independent (i.e., for water a defocusing of the isosteric points has been observed over broad temperature ranges), does not accurately reproduce experimental ΔC_p° data over a large temperature range. By using the Angell's parameters for bulk water and $n^h = 20$, as used by SHD,¹¹ a best fitting ΔC_p^h function is obtained when $\Delta H_{hs}^\circ = 2.33$ kcal mol $^{-1}$ and $\Delta S_{hs}^\circ/R = 3.37$ (curve c in Figure 3). From 0 °C up to 50 °C the experimental ΔC_p° values are well reproduced by the calculated ΔC_p^h function. On further increasing the temperature, the latter decreases too rapidly, but it is not far away from the experimental values. The qualitative agreement can be considered satisfactory. With these hydration shell parameters, f_{hs} become equal to f_b below 0 °C so that $f_{hs} > f_b$ over the whole range 0–100 °C, as shown by curve c in Figure 4.

Therefore, in line with the original observation by Muller,⁴ two conditions must hold to reproduce the temperature dependence of ΔC_p° in a qualitatively correct manner: (a) the hydrogen bonds in the hydration shell of nonpolar solutes have to be enthalpically stronger than those in bulk water, $\Delta H_{hs}^\circ > \Delta H_b^\circ$; (b) their rupture must give rise to a larger entropy increase with respect to that occurring in bulk water, $\Delta S_{hs}^\circ > \Delta S_b^\circ$, so that $f_{hs} > f_b$ over the whole range 0–100 °C (see Figures 3 and 4).

Discussion

We have shown that for the two-state Muller's model to produce ΔC_p^h that decreases with temperature, the hydrogen bonds in the hydration shell have to be *more* broken than those in bulk water. This is a general conclusion, almost like a mathematical theorem, that holds over a relatively large range of parameters and at all temperatures between 0 and 100 °C.

This result contrasts with SHD,¹¹ who used the same Muller's model but with different parameters to reach the opposite conclusion that the hydrogen bonds are less broken in the hydration shell than in the bulk. Since the parameters they used produce $f_{hs} < f_b$, they necessarily produce ΔC_p^h that does not decrease with temperature at all temperatures, according to our

theorem above. Indeed, the two ΔC_p^h functions calculated by SHD for argon show a maximum at about 30 and 60 °C, respectively. This is of course in contrast with the available experimental data (see Table 1 and Figure 3) which show that ΔC_p° monotonically decreases with temperature.

SHD were led to their sets of parameters for two different reasons. First, SHD used only the ΔC_p° values from 50 to 280 °C for the best-fit and neglected data at lower temperatures, which tended to produce a biased outcome. However, one is most interested in the ΔC_p° values in the temperature range of 0–100 °C, and not the superheated water well over 100 °C, for the investigation of the hydrophobic hydration. The experimental ΔC_p° data are also most reliable over 0–60 °C. (See, for instance, the work by Krause and Benson,¹⁵ whose precision is unsurpassed, to the best of our knowledge.)

Second, their favored parameter set was obtained after imposing the condition that $f_{hs} = f_b$ at $T_s = 450$ K = 177 °C. Within Muller's model, this produces the parameter set that necessarily produces $f_{hs} < f_b$ at all temperatures below 177 °C. SHD considered that their results lend support to the "iceberg" model and wrote:¹¹ "For liquid water below $T = 177$ °C (for example under pressure), hydrogen bonds in the first shell around argon, a simple nonpolar solute, are less broken than hydrogen bonds in pure water. Above $T = 177$ °C, hydrogen bonds are predicted to be more broken around a solute than in pure water." However, this depends directly on the soundness of the assumption that $f_{hs} = f_b$ at T_s . This condition was observed in the computer simulation data by using the two-dimensional Mercedes-Benz model of water, but there is no evidence that indicates that the same condition will apply for real water. On the contrary, Figure 3 shows that the imposition of this condition causes the ΔC_p^h function to deviate more from the experimental ΔC_p° values in the 0–100 °C temperature range.

On the other hand, we note that all the parameter values considered correspond to the $\Delta\Delta H$ and $T\Delta\Delta S$ values that lie close to the line in Figure 2 at which $\partial\Delta C_p/\partial T$ is zero and which lies close to the diagonal line on which $f_{hs} = f_b$. This means that the number of hydrogen bonds in the hydration shell is not too different from that in the bulk. The sign of $\partial\Delta C_p/\partial T$ and $f_{hs} - f_b$ depends sensitively on small differences in the parameter values. This again demonstrates the observation we made earlier⁶ that Muller's model and probably all similar mixture models of water are sensitive to the parameter values because any effect is multiplied by the number of hydration shell water molecules. Conversely, it also means that even a relatively qualitative piece of data, such as the temperature dependence of the heat capacity, can help determine very precise values of the model parameters. Therefore, it is advisable to use as much experimental data as possible in choosing the proper parameter sets and not rely too much on purely theoretical calculations because these calculations rarely provide numbers with sufficient accuracy.

The present conclusion is rather robust against different parameter sets used in the Muller's model. For example, the same conclusion was reached from the analysis of the hydration thermodynamics of alkanes,⁶ noble gases,⁹ and *n*-alcohols,¹⁰ using a different set of parameters, the Muller's parameters, for bulk water (see the Appendix).

The conclusion that the hydrogen bonds are about the same in number, or more broken, in the hydration shell than in the bulk clashes with the conventional "iceberg" model² of nonpolar molecule hydration. The conclusion was reached for the Muller's model and it is fair to wonder if it will hold in real water systems. Gallagher and Sharp,³⁴ for example, recently concluded, after analyzing the results of Monte Carlo simulations, that there

are more hydrogen bonds in the hydration shell than in the bulk. However, this conclusion depended on a tricky counting procedure that they adopted. They also did not consider the temperature dependence of ΔC_p° , something that is very difficult to compute theoretically with any degree of confidence.

Many other studies are consistent with the notion that hydrogen bonds are more broken, or at least not much less broken, in the hydration shell than in the bulk, e.g., (a) the results of computer simulations performed by Laidig and Daggett,³⁵ and by Mancera,³⁶ who made use of detailed models of liquid water, (b) the results from neutron scattering and X-ray absorption spectroscopy measurements by Finney's group,^{37,38} and (c) the idea emerging from the theoretical approach by Lum, Chandler, and Weeks that hydrogen bonds are slightly perturbed by the presence of a small nonpolar solute molecule and simply go around it.³⁹

In conclusion, by using the Muller's model, we have shown that the hydrogen bonds in the hydration shell of nonpolar solutes have to be *more broken, not more intact*, than those in bulk water to reproduce in a qualitatively correct manner the temperature dependence of the hydration heat capacity change.

Appendix: Sensitivity to the Bulk Water Parameters

Since $(\partial \Delta C_p^\circ / \partial T)$ is negative for the hydration of noble gases, aliphatic and aromatic hydrocarbons over the temperature range 0–100 °C,^{14–20} eqs 7 and 8 imply that:

$$\{[(1 - 2f)\Delta H^\circ - 2RT] \cdot C_p\}_{hs} < \{[(1 - 2f)\Delta H^\circ - 2RT] \cdot C_p\}_b \quad (A1)$$

where the subscripts *hs* and *b* indicate the hydration shell and the bulk water properties, respectively. ΔC_p° is invariably positive for the hydration of all nonpolar solutes and so, within the Muller's model and according to eq 6, $C_{p,hs} > C_{p,b}$. Therefore, eq A1 can be transformed to:

$$[(1 - 2f)\Delta H^\circ - 2RT]_{hs} < [(1 - 2f)\Delta H^\circ - 2RT]_b \quad (A2)$$

over the temperature range where $[(1 - 2f)\Delta H^\circ - 2RT]_b$ is positive. Using the Muller's bulk parameters,⁴ $\Delta H_b^\circ = 2.34$ kcal mol⁻¹ and $\Delta S_b^\circ/R = 2.6$, the temperature dependence of f_b is such that $[(1 - 2f)\Delta H^\circ - 2RT]_b$ is positive over the range 0–39 °C. Since $\Delta H_{hs}^\circ > \Delta H_b^\circ$ in all the investigated cases,^{4,6,9,10} this means that:

$$(1 - 2f_{hs}) < (1 - 2f_b) \quad (A3)$$

or $f_{hs} > f_b$ over the range 0–39 °C. This analytical result and the numerical calculations for *n*-alkanes,⁶ noble gases⁹ and *n*-alcohols¹⁰ demonstrate that the hydrogen bonds in the hydration shell have to be more broken than those in the bulk.

Unfortunately, if the Angell's bulk parameters are used, the f_b values are such that the quantity $[(1 - 2f)\Delta H^\circ - 2RT]_b$ is negative also at 0 °C; this circumstance renders it practically impossible to obtain an analytical solution of the problem, if Angell's parameters are used.

References and Notes

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