

# Solvation Thermodynamics of Water in Nonpolar Organic Solvents Indicate the Occurrence of Nontraditional Hydrogen Bonds

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Received: September 23, 2004; In Final Form: October 28, 2004

Experimental data for the solvation of water in nonpolar organic solvents indicate that the process is spontaneous under the Ben-Naim standard conditions, due to a large and negative enthalpy change. The process is analyzed by considering that the solvation Gibbs energy change is given by the sum of two opposing terms: the work to create a suitable cavity and the work to turn on the attractive solute–solvent interactions. Basic calculations point out unequivocally that, beyond the van der Waals contributions, additional favorable interactions occur between water and the surrounding solvent molecules. These additional favorable interactions should be nontraditional hydrogen bonds such as those between the delocalized  $\pi$ -electron cloud of the aromatic ring and the hydrogen atoms of water, and those between the CH groups of both aliphatics and aromatics and the oxygen atom of water.

## Introduction

Recently Henn and Kauzmann<sup>1</sup> collected practically all of the available and reliable experimental data on the solvation thermodynamics of water in nonpolar organic solvents. They reported the solvation enthalpy and entropy changes corrected for the Ben-Naim standard,<sup>2</sup>  $\Delta H^\circ$  and  $\Delta S^\circ$  (i.e., the superscript filled circle is used to denote the Ben-Naim standard), to construct a Barclay-Butler plot,<sup>3</sup>  $\Delta S^\circ$  versus  $\Delta H^\circ$  at room temperature, and to compare it with that obtained for pure liquids. From such comparison, Henn and Kauzmann<sup>1</sup> concluded that “solutions of water in several organic solvents, relevant to studies of proteins and micelles, appear *abnormal*.” The data points for water in nonpolar organic solvents show a definite tendency to lie above the Barclay-Butler line determined by Henn and Kauzmann for 53 pure liquids. This is reminiscent of the fact that all of the data points for aqueous solutions of nonpolar solutes fall well above the Barclay–Butler line. This finding prompted me to perform a further investigation with the hope to reach a better understanding of the origin of the abnormality.

From the collection of Henn and Kauzmann, I selected data for the solvation of water at 25 °C in *n*-hexane, *n*-octane, isooctane, carbon tetrachloride, benzene, toluene, and *m*-xylene.<sup>4,5</sup> The corresponding  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  values are reported in Table 1. In the latter also, the values of the molar fraction of water in the various solvents when the total pressure is 1 atm at 25 °C, and the corresponding mole-fraction based standard solvation Gibbs energy change,  $\Delta G^\circ$ , at 25 °C are listed. It should be noted that, by adopting the Ben-Naim standard, solvation refers to the transfer from a fixed position in the gas phase to a fixed position in the liquid phase and the translational degrees of freedom of the solute do not contribute to the standard thermodynamic quantities.<sup>1,2</sup> The mole-fraction based standard solvation Gibbs energy change (whose standard state is the extrapolated hypothetical unit mole fraction solution),

**TABLE 1: Experimental Values at 25 °C of Molar Fraction of Water Dissolved at Equilibrium at 1 atm of Total Pressure in the Various Solvents, and of the Mole-Fraction-Based Standard Gibbs Energy Change Are Listed in the Second and Third Columns<sup>a</sup>**

|                  | $x_2 \times 10^4$ | $\Delta G^\circ$ ,<br>kJ mol <sup>-1</sup> | $\Delta G^\circ$ ,<br>kJ mol <sup>-1</sup> | $\Delta H^\circ$ ,<br>kJ mol <sup>-1</sup> | $\Delta S^\circ$ ,<br>J K <sup>-1</sup> mol <sup>-1</sup> |
|------------------|-------------------|--|--|--|---|
| <i>n</i> -hexane | 6.0               | 9.8  | -3.2                                       | -11.5                                      | -27.8   |
| <i>n</i> -octane | 5.1               | 10.2                                       | -2.2                                       | -9.5                                       | -24.5   |
| isooctane        | 5.1               | 10.2                                       | -2.2                                       | -9.3                                       | -23.8   |
| CCl <sub>4</sub> | 8.6               | 8.9  | -4.8                                       | -16.4                                      | -38.9   |
| benzene          | 31.4              | 5.7  | -8.2                                       | -20.8                                      | -42.3   |
| toluene          | 27.8              | 6.0  | -7.5                                       | -19.4                                      | -39.9   |
| <i>m</i> -xylene | 24.6              | 6.3  | -6.8                                       | -20.3                                      | -45.3   |

<sup>a</sup> Ben-Naim standard Gibbs energy, enthalpy and entropy changes associated with the solvation at 25 °C of water in nonpolar organic solvents are reported in the remaining columns. Data are from refs 1, 4, and 5.

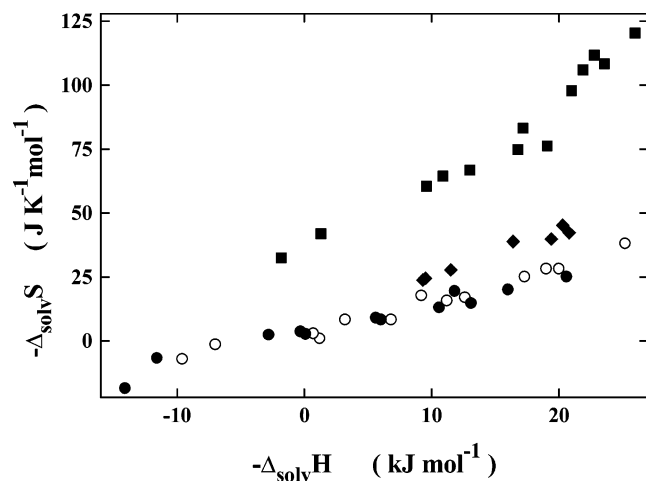
$\Delta G^\circ$  has to be corrected because the magnitude of the translational entropy of a mole of solute molecules depends on the available molar volume. The latter quantity is clearly different in the gas phase and in the liquid phase at the same temperature and pressure. The relationship to perform the correction is<sup>2</sup>

$$\Delta G^\circ = \Delta G^\circ - RT \ln(v_g/v_l) \quad (1)$$

where  $v_g = RT/p^\circ$  is the molar volume in the gas phase at  $p^\circ = 1$  atm and  $v_l$  is the molar volume of the liquid. Performing the correction, even though the  $\Delta G^\circ$  values for water in organic solvents are positive, the  $\Delta G^\circ$  ones are negative in all the considered liquids.

Inspection of Table 1 reveals that (a) the  $\Delta G^\circ$  magnitude is larger in aromatics than in aliphatics,  $\Delta G^\circ$  (in kJ mol<sup>-1</sup>) = -3.2 in *n*-hexane and -8.2 in benzene; (b)  $\Delta H^\circ$  is always a negative quantity whose magnitude is larger in aromatics,  $\Delta H^\circ$  (in kJ mol<sup>-1</sup>) = -11.5 in *n*-hexane and -20.8 in benzene; (c)  $\Delta S^\circ$  is a negative quantity in all solvents with a larger magnitude in aromatics,  $\Delta S^\circ$  (in J K<sup>-1</sup>mol<sup>-1</sup>) = -27.8 in *n*-hexane and -42.3

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**Figure 1.** Barclay–Butler plot for the solvation at 25 °C of (a) noble gases and aliphatic hydrocarbons in *n*-hexane (filled circles) and in benzene (open circles); (b) noble gases and aliphatic hydrocarbons in water (filled squares); (c) water in the seven nonpolar organic liquids considered in this study (filled diamonds). The data for water solvation are those listed in Table 1; all of the other data come from Tables 2 and 3 of ref 6.

in benzene. These values indicate that, under the Ben-Naim standard conditions, the solvation of water in nonpolar organic solvents is a spontaneous process because the favorable enthalpy change overwhelms the unfavorable entropy change. To gain perspective one has to consider that the solvation of water in water at 25 °C is characterized by  $\Delta H^\circ = -41.8 \text{ kJ mol}^{-1}$ ,  $\Delta S^\circ = -51.3 \text{ J K}^{-1} \text{ mol}^{-1}$ , and  $\Delta G^\circ = -26.5 \text{ kJ mol}^{-1}$ .

Figure 1 is the Barclay–Butler plot for the solvation, at 25 °C, of (a) water in the seven nonpolar liquids considered; (b) noble gases and aliphatic hydrocarbons in *n*-hexane and benzene;<sup>6</sup> (c) noble gases and aliphatic hydrocarbons in water.<sup>6</sup> It is evident that the points for water solvation in nonpolar liquids lie in the middle between those for the hydration of nonpolar compounds and those for the solvation of nonpolar compounds in *n*-hexane and benzene. This means that water solvation in nonpolar organic liquids is characterized by negative enthalpy and entropy changes larger in magnitude than those expected using as reference the solvation thermodynamics of noble gases and aliphatic hydrocarbons in the same liquids. In particular, the negative solvation enthalpy change of water in such solvents is strikingly large in magnitude in comparison to that, in the same solvents, of neon, argon, and methane, which have a number of electrons close to that of the water molecule. Indeed: (a) for neon  $\Delta H^\circ$  (in  $\text{kJ mol}^{-1}$ ) = 7.0 in *n*-hexane and 14.1 in benzene; (b) for argon  $\Delta H^\circ$  (in  $\text{kJ mol}^{-1}$ ) = -1.2 in *n*-hexane and 2.8 in benzene; (c) for methane  $\Delta H^\circ$  (in  $\text{kJ mol}^{-1}$ ) = -0.7 in *n*-hexane and 0.3 in benzene.<sup>6</sup>

Since the Barclay–Butler plot cannot give further understanding, I would like to provide a rationalization of these findings, using a general statistical mechanical theory of solvation,<sup>7–11</sup> that has provided considerable insight into the understanding of the hydrophobicity puzzle. According to this theory the solvation process is dissected in two consecutive steps: (a) creation of a cavity in the solvent suitable to host the solute molecule; (b) turning on the solute–solvent attractive interactions. Correspondingly the Ben-Naim standard Gibbs energy change is given by<sup>7–11</sup>

$$\Delta G^\circ = \Delta G_c + E_a \quad (2)$$

where  $\Delta G_c$  is the work of cavity creation and  $E_a$  is the energy associated with turning on the solute–solvent interactions.

The analysis points out that the excluded volume effect is the primary source of the unfavorable entropy change, whereas the direct water–nonpolar solvent attractive interactions are the primary source of the favorable enthalpy change. In particular, the attractive interaction energy between a water molecule and the surrounding molecules of hydrocarbons is markedly larger than expected on the basis of the customary values of Lennard–Jones parameters. This finding supports the existence of (a) weak hydrogen bonds between water and the aromatic ring,<sup>12,13</sup> and (b) nontraditional C–H···O hydrogen bonds between water and aliphatics.<sup>14</sup>

## Methods

The work of cavity creation is calculated with the formula provided by scaled particle theory,<sup>15,16</sup> SPT, assuming both the solute and solvent molecules to be spherical

$$\Delta G_c = RT[K_0 + K_1(\sigma_2/\sigma_1) + K_2(\sigma_2/\sigma_1)^2 + K_3(\sigma_2/\sigma_1)^3] \quad (3)$$

where  $K_0 = -\ln(1 - \xi)$ ;  $K_1 = u = 3\xi/(1 - \xi)$ ;  $K_2 = u(u + 2)/2$ ;  $K_3 = \xi P v_1/RT$ . In these relations,  $R$  is the gas constant;  $\xi$  is the volume packing density of pure solvent, which is defined as the ratio of the physical volume of a mole of solvent molecules over the molar volume of the solvent,  $v_1$  (i.e.,  $\xi = \pi \sigma_1^3 N_A v_1/6$ );  $\sigma_1$  and  $\sigma_2$  are the hard sphere diameters of the solvent and solute molecules, respectively; and  $P$  is the pressure. To perform calculations, the experimental values of the density at 25 °C of the various hydrocarbons are used,<sup>17</sup> and the pressure is fixed at 1 atm, as claimed by several authors.<sup>16,18</sup>

The cavity size is defined as the diameter of the spherical region from which any part of any solvent molecules is excluded. In this study it corresponds to the size of a water molecule. To select an effective diameter for a water molecule, it is important to recognize that there are two relevant sizes:<sup>19</sup> (a) the distance of closest approach between two hydrogen bonded water molecules,  $\sigma(\text{H}_2\text{O}) = 2.8 \text{ \AA}$ , on the basis of the location of the first peak in the oxygen–oxygen radial distribution function of liquid water;<sup>20</sup> (b) the distance of closest approach between two non-hydrogen bonded water molecules,<sup>19</sup> corresponding to the van der Waals diameter of an oxygen atom,  $\sigma(\text{H}_2\text{O}) = 3.2 \text{ \AA}$ . Calculations have been performed with both diameters in order to take into account the two different situations.

The SPT results are sensitive to the  $\sigma$  value selected for solvent molecule.<sup>21</sup> I selected the effective hard sphere diameters obtained by Wilhelm and Battino<sup>22</sup> for all the seven organic solvents considered in this work. These diameters are close to those obtained using the group contributions of Ben-Amotz and Willis.<sup>23</sup> It should also be noted that the  $\sigma$  values determined by Wilhelm and Battino from the analysis of gas solubility data in such liquids are able to reproduce the vaporization enthalpy at 25 °C of the same liquids with errors of a few percent when used in SPT-derived formulas for the vaporization enthalpy.<sup>24</sup> All of the  $\sigma$  values used are listed in the third column of Table 2.

The  $E_a$  term accounts for the attractive interactions of water molecules with surrounding nonpolar solvent molecules. The dispersion and dipole–induced dipole components of the interaction are estimated using a simple formula devised by Pierotti,<sup>16</sup> assuming that dispersion interactions are represented by the Lennard–Jones potential. The formula proposed by Pierotti is

$$E_a = -[(64/3)\xi\epsilon_{12}(\sigma_{12}/\sigma_1)^3] - [8\xi(\mu_2^2\alpha_1)/(\sigma_1\sigma_{12})^3] \quad (4)$$

**TABLE 2: Molar Volume, Hard Sphere Diameter, Volume Packing Density, Lennard-Jones Potential Parameter, and Polarizability of the Solvents Considered in This Work<sup>17,22a</sup>**

|                  | $v$ ,<br>cm <sup>3</sup> mol <sup>-1</sup> | $\sigma$ ,<br>Å | $\xi$ | $\epsilon/k$ ,<br>K | $\alpha$ ,<br>Å <sup>3</sup> | $\Delta_{\text{vap}}H$ ,<br>kJ mol <sup>-1</sup> | ced,<br>J cm <sup>-3</sup> | $\gamma$ ,<br>mN m <sup>-1</sup> |
|------------------|--|-----------------|-------|---------------------|------------------------------|--|----------------------------|----------------------------------|
| <i>n</i> -hexane | 131.62                                     | 5.92            | 0.497 | 517                 | 11.9                         | 31.56  | 221                        | 17.89                            |
| <i>n</i> -octane | 163.54                                     | 6.54            | 0.539 | 611                 | 15.9                         | 41.49  | 238                        | 21.14                            |
| isooctane        | 166.10                                     | 6.52            | 0.526 | 602                 | 15.4                         | 35.14  | 197                        |                                  |
| CCl <sub>4</sub> | 97.09                                      | 5.37            | 0.503 | 536                 | 11.2                         | 32.43  | 308                        | 26.43                            |
| benzene          | 89.41                                      | 5.26            | 0.513 | 531                 | 10.7                         | 33.83  | 351                        | 28.22                            |
| toluene          | 106.86                                     | 5.64            | 0.529 | 575                 | 12.3                         | 38.01  | 332                        | 27.93                            |
| <i>m</i> -xylene | 123.47                                     | 5.97            | 0.543 | 586                 | 14.2                         | 42.65  | 325                        | 28.47                            |

<sup>a</sup> For water I used:  $\sigma = 2.8$  Å and  $3.2$  Å,  $\epsilon/k = 85$  K,  $\alpha = 1.47$  Å<sup>3</sup> and  $\mu = 1.84$  D. In the last three columns are reported the values, at 25 °C, of the vaporization enthalpy change, the cohesive energy density,  $\text{ced} = (\Delta_{\text{vap}}H - RT)/v$ , and the surface tension of the various solvents.<sup>17</sup>

**TABLE 3: Values of the Solvation Gibbs Energy of Water in Organic Solvents  $\Delta G^\circ$ , of the Work of Cavity Creation  $\Delta G_c$ , of the Water-Organic Solvent Attractive Energy Calculated by Means of Pierotti's Formula  $E_a(\text{Pierotti})$ , and Obtained,  $E_a(\text{exp})$ , in Order to Perfectly Reproduce the Experimental  $\Delta G^\circ$ <sup>a</sup>**

|                  | $\Delta G^\circ$ ,<br>kJ mol <sup>-1</sup> | $\Delta G_c$ ,<br>kJ mol <sup>-1</sup> | $E_a(\text{Pierotti})$ ,<br>kJ mol <sup>-1</sup> | $E_a(\text{exp})$ ,<br>kJ mol <sup>-1</sup> | $\Delta S_x$ ,<br>J K <sup>-1</sup> mol <sup>-1</sup> |
|------------------|--|--|--|---|---|
| <i>n</i> -hexane | -3.2                                       | 9.3                                    | -7.9   | -12.5                                       | -31.2   |
|                  |  | 11.0                                   | -8.9   | -14.2                                       | -36.9   |
| <i>n</i> -octane | -2.2                                       | 10.0                                   | -8.4   | -12.2                                       | -33.5   |
|                  |  | 11.9                                   | -9.4   | -14.1                                       | -39.9   |
| isooctane        | -2.2                                       | 9.4                                    | -8.2   | -11.6                                       | -31.5   |
|                  |  | 11.2                                   | -9.2   | -13.4                                       | -37.6   |
| CCl <sub>4</sub> | -4.8                                       | 10.8                                   | -9.2   | -15.5                                       | -36.2   |
|                  |  | 12.9                                   | -10.4  | -17.6                                       | -43.3   |
| benzene          | -8.2                                       | 11.7                                   | -9.6   | -19.9                                       | -39.2   |
|                  |  | 14.0                                   | -10.9  | -22.2                                       | -47.0   |
| toluene          | -7.5                                       | 11.5                                   | -9.5   | -19.0                                       | -38.6   |
|                  |  | 13.8                                   | -10.7  | -21.3                                       | -46.3   |
| <i>m</i> -xylene | -6.8                                       | 11.5                                   | -9.2   | -18.3                                       | -38.6   |
|                  |  | 13.7                                   | -10.4  | -20.5                                       | -46.0   |

<sup>a</sup> Estimates of the excluded volume entropy contribution  $\Delta S_x = -\Delta G_c/T$  are listed in the last column. For each solvent, the values in the first line are calculated using  $\sigma(\text{H}_2\text{O}) = 2.8$  Å, whereas those in the second line are calculated using  $\sigma(\text{H}_2\text{O}) = 3.2$  Å.

where  $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ ;  $\epsilon_{12} = (\epsilon_1\epsilon_2)^{1/2}$ ,  $\epsilon_1$  and  $\epsilon_2$  are the Lennard-Jones potential parameters for the solvent and solute, respectively;  $\alpha_1$  is the polarizability of solvent molecules;  $\mu_2$  is the dipole moment of solute molecule (i.e., of water). This formula is readily derived from the statistical mechanical relation for the intermolecular energy, in the assumption that (a) the two types of interactions can be considered independent, spherically symmetric, and pairwise additive; (b) the radial distribution function of solvent molecules is equal to one outside the boundary of the solute molecule.<sup>16</sup> The values of the Lennard-Jones potential parameter and polarizability used in the calculations are listed in the fifth and sixth columns, respectively, of Table 2. Customary values for  $\epsilon/k$ , determined by Wilhelm and Battino,<sup>22</sup> were selected. Obviously, the formula devised by Pierotti cannot account for other types of attractive interactions, such as the possible weak nontraditional hydrogen bonds.

## Results

The SPT estimates of  $\Delta G_c$  in the various solvents are reported in the third column of Table 3. They are not very different among the various solvents: (a) for  $\sigma(\text{H}_2\text{O}) = 2.8$  Å,  $\Delta G_c$  (in kJ mol<sup>-1</sup>) = 9.3 in *n*-hexane and 11.7 in benzene; (b) for  $\sigma(\text{H}_2\text{O}) = 3.2$  Å,  $\Delta G_c$  (in kJ mol<sup>-1</sup>) = 11.0 in *n*-hexane and 14.0 in benzene. The estimates of  $E_a$  from the dispersion and

dipole-induced dipole interactions, as calculated by means of Pierotti's formula, are listed in the fourth column of Table 3. The pseudo-experimental values of  $E_a(\text{exp}) = \Delta G^\circ - \Delta G_c(\text{SPT})$ , which would perfectly reproduce the experimental  $\Delta G^\circ$  numbers, in the assumption that the SPT estimates of  $\Delta G_c$  are exact, are listed in the fifth column of Table 3. The important observation is that the  $E_a(\text{Pierotti})$  values are remarkably smaller in magnitude than the  $E_a(\text{exp})$  values. The difference  $E_a(\text{exp}) - E_a(\text{Pierotti})$  is significant for all solvents, and larger for aromatics (about -10 kJ mol<sup>-1</sup>) than for aliphatics (about -5 kJ mol<sup>-1</sup>). Since Pierotti's formula should satisfactorily account for the contribution of van der Waals interactions,<sup>6</sup> the observed difference has to be attributed to other types of interactions.

In the case of aromatics, this difference can readily be attributed to the weak hydrogen bonds that the hydrogen atoms of water form with the delocalized  $\pi$ -electron cloud of the aromatic ring.<sup>12,13</sup> In the case of aliphatics the difference could be due to the existence of nontraditional C-H...O hydrogen bonds that water molecules can form with aliphatic chains.<sup>14</sup> Actually, these nontraditional C-H...O hydrogen bonds may occur also with aromatic CH groups.<sup>25</sup> In this respect, one has to note that hydrogen atoms bonded to both aliphatic and aromatic carbon atoms carry positive partial charges of  $\approx 0.12$  e; without such partial charges it was not possible to reproduce simultaneously the energies and the packing geometries of hydrocarbon crystals.<sup>26</sup>

It has been noted that the use of SPT to determine  $\Delta G_c$  causes an underestimation of the magnitude of the work of cavity creation with respect to detailed computer simulations.<sup>27,28</sup> This means that also the magnitude of  $E_a$  to reproduce the experimental  $\Delta G^\circ$  values by means of the basic relationship  $\Delta G^\circ = \Delta G_c + E_a$  should be underestimated. Nevertheless, the  $E_a$  values calculated by means of Pierotti's formula are too small in magnitude, suggesting the existence of additional favorable interactions.

The values of the cohesive energy density, ced, and those of the surface tension of the various solvents considered are reported in the last two columns of Table 2. A comparison between these values and those of  $\Delta G^\circ$  for the water solvation indicates that there is no correlation, in contrast to the general claim by Kodaka<sup>29</sup> and Lazaridis.<sup>30</sup> Both ced and surface tension do not seem to play a role in determining the solubility of water in nonpolar organic solvents, as already pointed out for other cases.<sup>31</sup>

Also the negative  $\Delta S_x$  values should merit attention. It is difficult to imagine that the insertion of a water molecule in nonpolar organic solvents causes an increase of order or an enhancement of structure. The major part of the negative entropy change should be due to the excluded volume effect associated with cavity creation. According to statistical mechanics,<sup>32</sup>  $\Delta G_c$  represents the work to select the fraction of the total liquid configurations possessing a cavity of the desired diameter. Since this configuration selection reduces the number of configurations accessible to the liquid,  $\Delta G_c$  proves to be a purely entropy term related to the excluded volume effect caused by the presence of the cavity.<sup>32,33</sup>  $\Delta G_c = -T\Delta S_x$ . Solvent reorganization associated with configuration selection leads to an additional entropy change beyond that due to the excluded volume effect. It is readily shown that this reorganization entropy contribution is perfectly compensated for by a corresponding enthalpy term.<sup>32,33</sup>

Therefore, the excluded volume entropy contribution is related to the work of cavity creation by  $\Delta S_x = -\Delta G_c/T$ . The estimates of  $\Delta S_x$  in the various liquids are listed in the last column of



Table 3. It is evident that they are close to the experimental  $\Delta S^\circ$  values. This implies that the entropy contribution coming from the structural reorganization of solvent molecules is a small quantity. Similarly, the  $E_a(\text{exp})$  estimates are close to the experimental  $\Delta H^\circ$  values, implying that also the enthalpy contribution provided by the structural reorganization of solvent molecules upon the insertion of a water molecule is a small quantity. This finding is unexpected because the solvation of noble gases and aliphatic hydrocarbons in nonpolar organic liquids is characterized by a significant structural reorganization of solvent molecules.<sup>6,9</sup>

The finding that there is little structural reorganization should imply, for instance, that the inserted water molecule can form weak hydrogen bonds with some of the aromatic rings surrounding the cavity without the need of a structural reorganization of benzene molecules. This could be related to the fact that the coordination number of a benzene molecule in liquid benzene around room temperature is 12,<sup>34</sup> and so there is a significant probability that some of the rings have the right orientation to form weak hydrogen bonds with an inserted water molecule. This is particularly true by considering that a water molecule can form weak nontraditional hydrogen bonds with both the delocalized  $\pi$ -electron cloud of the ring using its hydrogen atoms, and the CH groups of the ring using its oxygen atom. Similar arguments can be provided in the case of the other nonpolar liquids.

## Discussion

The performed calculations indicate that the energetic interactions of water molecules with nonpolar liquids have to be stronger than predicted by considering only van der Waals contributions. This finding is expected in the case of aromatic hydrocarbons because the existence of weak hydrogen bonds between water and aromatic rings is well established. Both theoretical calculations and spectroscopic measurements indicate that, at very low temperature, benzene forms a weak hydrogen bonded complex with water, with both hydrogen atoms of water pointing toward the  $\pi$ -electron cloud of the ring;<sup>13</sup> the distance between the center of mass of the two moieties is  $\approx 3.35$  Å and the binding energy is  $\approx 8.4$  kJ mol<sup>-1</sup>. The existence of such weak hydrogen bonds is confirmed by rotational and vibrational spectroscopy measurements of water molecules dissolved in nonpolar liquids.<sup>35</sup> The perturbation of the vibrational modes of water is more pronounced in liquid benzene than in other nonpolar solvents and the spectra support the existence of weak hydrogen bonds between the water hydrogen atoms and the aromatic ring. However, the perturbation is not negligible also in carbon tetrachloride and alkanes, supporting the notion that the strength of energetic interactions is significant. Careful analysis of the spectra led to the conclusion that water exists as solitary molecules and does not form aggregates in nonpolar solvents, in contrast to the claim by Marmur.<sup>36</sup>

In addition, quantum chemical calculations have shown that<sup>37</sup> (a) the binding energy for the approach of one of the water protons toward the delocalized  $\pi$ -electron cloud of the benzene ring is  $\approx 8.8$  kJ mol<sup>-1</sup>; (b) the binding energy for the approach of the oxygen atom of water toward one of the CH groups of benzene is  $\approx 4.6$  kJ mol<sup>-1</sup>; (c) the binding energy for the approach of the oxygen atom of water toward one of the CH groups of methane is  $\approx 3.7$  kJ mol<sup>-1</sup>. Clearly, the magnitude of these nontraditional hydrogen bonds is the right one in order to account for the difference  $E_a(\text{exp}) - E_a(\text{Pierotti})$ .

It is worth noting that, 30 years ago, Goldman<sup>38</sup> calculated the solubility of water in benzene, carbon tetrachloride and

c-hexane by means of an approach similar to that adopted in the present article. Goldman used SPT to calculate the work of cavity creation and a formula similar to the Pierotti's one to calculate the interaction energy of water with nonpolar organic solvents. The fundamental point, apart some differences in the selected  $\sigma$  values, was the use for water of a very large  $\epsilon/k$  value, equal to 775 K, determined from the application of the Stockmayer potential to reproduce the second virial coefficient of water over a large temperature range.<sup>39</sup> Clearly, 775 K is almost an order of magnitude larger than the value used by me, 85 K, and renders the magnitude of  $E_a$  as large as required to satisfactorily fit the solubility data. This confirms that the interactions of water molecules with nonpolar solvents contain, beyond van der Waals contributions, additional contributions coming from weak nontraditional hydrogen bonds.

Recently, Amovilli and Floris<sup>40</sup> analyzed the experimental solubility data of water in a large set of liquid hydrocarbons by combining the polarizable continuum model and the mobile order theory. They concluded that it would be necessary to consider "nonclassical solute-polarized solvent interactions (i.e., attractive solute dipole-solvent quadrupole and charge-transfer interactions)" in order to reproduce the experimental data. In other words, the interaction energy of a water molecule with the surrounding hydrocarbon molecules is more negative (i.e., larger in magnitude) than expected on the basis of the customary values of the Lennard-Jones parameters used for water and hydrocarbons. This finding is in line with that emerged in the present investigation.

In conclusion, the occurrence of nontraditional hydrogen bonds in an isotropic liquid phase between an inserted water molecule and the surrounding aliphatic or aromatic molecules emerged from the analysis of the solvation thermodynamics of water in nonpolar organic solvents. Even though the occurrence of nontraditional hydrogen bonds is well documented in the crystal structures of both small molecules and large ones, such as proteins,<sup>14,41</sup> the present study points out their existence in more common systems such as liquids. It is necessary to consider the occurrence of nontraditional hydrogen bonds in order to account for the large negative solvation enthalpy of water in both aliphatics and aromatics.

**Acknowledgment.** Work supported by the grant COFIN-2002 from Italian Ministry for Instruction, University and Research (M.I.U.R., Rome).

## References and Notes

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