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The Structure of Dilute Clusters of Methane and Water by ab Initio Quantum Mechanical Calculations

Eli Ruckenstein,*[,†] Ivan L. Shulgin,[†] and Jeffrey L. Tilson[‡]

Department of Chemical Engineering and Center for Computational Research,
State University of New York at Buffalo, Amherst, New York 14260

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Ab initio quantum mechanical methods have been used to examine clusters formed of molecules of methane and water. The clusters contained one molecule of one component (methane or water) and several (10, 8, 6, 4, and 1) molecules of the other component. The Møller−Plesset perturbation theory (MP2 method) was used in the calculations. The cluster geometries were obtained via optimization and the interaction energies between the nearest neighbors were calculated for the geometries obtained in the first step. It is shown that the interaction energies and intermolecular distances between the molecules of methane and water are quite different in the clusters $CH_4\cdots(H_2O)_{10}$ and $H_2O\cdots(CH_4)_{10}$. They are also different from those in the water/methane dimer. The structure of the cluster $CH_4\cdots(H_2O)_{10}$ is highly affected by the hydrogen bonding among the water molecules, and the methane molecule is located inside a cage formed of water molecules. In contrast, the molecules of methane and water are randomly distributed in the cluster $H_2O\cdots(CH_4)_{10}$. The average methane/water intermolecular distance in the cluster $CH_4\cdots(H_2O)_{10}$ provided by the quantum mechanical calculations is in agreement with the experimental and simulation results regarding the position of the first maximum in the radial distribution function $g_{oc} = g_{oc}(r_{oc})$ in dilute mixtures of methane in water, where r_{oc} is the distance between the C atom of methane and the O atom of water. It is shown that the water molecules in the vicinity of a central methane molecule can be subdivided into two groups, A and B. Molecules of type A are touching nearest neighbors of the central methane molecule. They are located on a sphere with a radius corresponding to the first maximum in the radial distribution function $g_{oc} = g_{oc}(r_{oc})$ and are tangentially oriented toward the central methane molecule. The layer of A water molecules is somewhat denser than bulk water. The molecules of type B are also located in the first hydration layer of a central methane molecule (up to a distance given by the position of the first minimum of the radial distribution function $g_{oc} = g_{oc}(r_{oc})$), but are not touching nearest neighbors. They are distributed more randomly than the molecules of type A, because they are less affected by the hydrophobic core of the solute.

1. Introduction

The interactions in mixtures of nonpolar substances, such as noble gases and hydrocarbons, with water constitute the simplest manifestation of the hydrophobic effect. A large number of publications (many thousands) have been devoted to this topic and information about the hydrophobic effect was summarized in books and recent reviews.[1−7] The hydrophobic effect is germane to chemistry (gas solubility in water, phase separation, and self-assembling in aqueous mixtures), biology (protein folding and micellization), and even geology (undersea deposits of methane hydrates). Two manifestations of the hydrophobic effect can be considered: the interaction of one molecule of a nonpolar solute with the surrounding water molecules (hydrophobic hydration) and the interactions of nonpolar molecules among themselves in a water environment (hydrophobic interactions).[1−7] While Kauzmann was the first to introduce the notion of hydrophobic interactions in the 1950s,[8,9] some fundamentals of hydrophobic hydration were established earlier in the 1930s and 1940s in the publications of Butler and those of Uhlig and Eley.[10−13] In their papers, they tried to explain the poor solubilities of nonpolar molecules in water (as a rule they are smaller by 1−3 orders of magnitude than those in organic substances) by dividing the dissolution process into two steps: (1) the creation of a "cavity" in the bulk water and (2) the insertion of the nonpolar molecule into the cavity. This scheme became classic and was used to explain the behavior of various thermodynamic functions that characterize the dissolution of nonpolar substances in water under ambient conditions: the free energy change ΔG^d is positive (unfavorable), the enthalpic change ΔH^d is negative (favorable), the entropic change ΔS^d is negative (unfavorable with a larger absolute value of $T\Delta S^d$ than ΔH^d), and the change in the isobaric heat capacity $\Delta c_p{}^d$ is large and positive.[14] Reliable values of these thermodynamic functions are now available for numerous substances.[14−16] Frank and Evans[17] provided an additional insight in the understanding of the hydrophobic hydration by suggesting that during the second step the layers of water around the solute molecule become more ordered. The formation of the more ordered structures (icebergs) around a molecule of a nonpolar solute was in their opinion the cause of the great loss of entropy in the process of dissolution. This idea dominated the field for several decades and more detailed theories were

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* Corresponding author. E-mail: feaeliru@acsu.buffalo.edu. Fax: (716) 645-3822. Phone: (716) 645-2911/ext. 2214.

[†] Department of Chemical Engineering.

[‡] Center for Computational Research.

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developed to provide quantitative explanations for the behavior of the above thermodynamic functions and for the temperature and pressure dependencies of the solubility in water.[1−7] The concept of iceberg led to the conclusion that the decrease in entropy caused by the organization of the water molecules is responsible for the low solubility of hydrocarbons in water. In reality, the change in entropy due to ordering is compensated by the change in enthalpy caused by the interactions between the hydrocarbon molecule and water.[18−22] Shinoda[18,19]concluded that the formation of a cavity constitutes the main effect, while Ruckenstein [20−22] has shown, on the basis of a simple thermodynamic approach, that while the formation of a cavity provides the largest contribution, the "iceberg" formation also plays a role.

A different interpretation of the hydrophobic effect was suggested by Lucas and Lee.[23−24] They suggested that the poor solubility of nonpolar compounds in water is due to an excluded volume effect, which is amplified, in the case of liquid water, by the small size of the water molecules, and that the entire hydrophobic effect is a result of their small size. The combination of this idea[25−28] with Muller's two-state water structure[29] provided reasonable results regarding the hydrophobic hydration. The more recent application[30−32] of information theory to the treatment of the hydrophobic effect was used to explain[5] (a) the temperature dependence of the hydrophobic hydration, (b) the water/hydrogen isotope effect, etc.

During the last 2 decades, the availability of powerful computers and the wide use of modern experimental methods, especially X-ray and neutron scattering, allowed one to obtain valuable information about the nanostructure of mixtures containing hydrophobic solutes. Moreover, one can observe a certain redirection in the research of the hydrophobic effect. While in the past the main goal was to obtain reliable data concerning the thermodynamics of the hydrophobic hydration and to interpret them using different models, the goal now is to obtain information about the nanostructure of water around a hydrophobic solute and to find out how this nanostructure differs structurally and energetically from that of bulk water. While the existence of several layers of water molecules around a hydrophobic solute which are affected by the solute is beyond doubt (it was demonstrated experimentally[33−35]), the characteristics of this "perturbed" water are not yet well-known. Several questions arise regarding them and the difference from bulk water: (1) how many water molecules are involved or how many water molecules are affected by the presence of a hydrophobic solute? (2) is its structure more ordered than that of bulk water? (3) what is the local density of this "perturbed" water? and so on.

It is clear that these questions can be answered if information about the local structure and intermolecular interactions in the layers of the "perturbed" water can be obtained.

An important step in understanding the local structure around a nonpolar solute in water was made by Jorgensen et al.[36] Using Monte Carlo simulations based on an intermolecular potential, which contained Lennard-Jones and Coulomb contributions, they determined the number of water molecules in the first hydration layer (located between the first maximum and the first minimum of the radial distribution function) around a nonpolar solute in water. This number (20.3 for methane, 23 for ethane, etc.) was surprisingly large compared with the coordination numbers in cold water and ice (4.4 and 4, respectively). These results provided evidence that major changes occur in the water structure around a nonpolar solute and that the perturbed structure is similar to that of the water−methane clathrates,[37] which involve 20−24 water molecules that form a clathrate cage around a methane molecule. The conclusions of Jorgensen et al.[36] were verified both experimentally[34,35] (ref 35 provided a value of 16 for the number of water molecules in the first hydration layer) and by molecular simulations.[38−40] Similar results regarding the number of water molecules in the first hydration layer were obtained for infinitely dilute aqueous solutions of noble gases,[38,41] oxygen,[42] etc. As expected the number of water molecules in the first hydration layer depends on the size of the nonpolar solute: this number is about 20 for methane, 17 for oxygen, 19 for argon, 22 for krypton, 23 for xenon, 23 for ethane, 27 for *n*-propane, and 30 for *n*-butane.[36,38−42]

The local density of water around a nonpolar solute was found to be somewhat larger than the bulk density under ambient conditions,[42−43] but lower[42] for $T > 311$ K and approaching[42] the bulk density of water at sufficiently high temperatures. Another important characteristic of the aforementioned "perturbed" water is the number of hydrogen bonds (H-bonds) per water molecule. Molecular dynamics[40] and Monte Carlo[44] simulations indicated that the number of H-bonds per water molecule in the first hydration layer was slightly smaller than that in bulk water. It was found that the number of water molecules in the first hydration layer that possess four H-bonds was slightly lower and those with 1, 2, and 3 H-bonds slightly larger when compared to bulk water. However, as noted by Meng and Kollman[45] the water molecules in the first hydration layer have the same average number of H-bonds as the bulk water molecules. These results appear to favor the opinion[4] that "water does not undergo a major structural change in the presence of an apolar solute but maintains its original structure by accommodating the apolar solute in its original hydrogen bond network. The unique property of water is that it can dissolve an apolar solute of limited size without sacrificing a significant number of hydrogen bonds".[4] There is good agreement between the X-ray, neutron scattering and molecular simulations regarding the radial distribution functions *g* in dilute mixtures of nonpolar species and water. In the particular case of methane,[34−36,39−40,44−46] the position of the first maximum in the dependence $g_{oc} = g_{oc}(r_{oc})$, where r_{oc} is the distance between a C atom of methane and an O atom of water, was found to be at about 3.5−3.7 Å. The first minimum was found at 5.1−5.7 Å and the second maximum[39] at about 6.3 Å. Neutron diffraction scattering[34,41] indicated that the second maximum was very shallow. This means that one or at most two adjoining layers of water are affected by the presence of a nonpolar solute (methane). The water molecules in these adjoining layers have peculiar properties, the nearest to the nonpolar molecule being tangentially oriented toward its surface,[34] due to the "hydrophobic wall" (or hard core) effect of the solute. Their H-bonds are slightly shorter,[44] and the average number of their nearest neighbors slightly smaller than in bulk water.[44,46−47]

Another approach to investigate the hydrophobic effect is the ab initio quantum mechanical technique.[48,49] It is based on first principles (the Schrödinger equation), and this constitutes its main advantage compared to molecular dynamics and Monte Carlo approaches, which are based on classical potentials. At the present time, the ab initio quantum mechanical methods have limitations connected to the complexity and size of the molecular clusters considered.[48,50,51] Nevertheless, these methods have been often used to accurately predict the structure and energy of a system of two molecules (dimers),[50−52] such as the system methane/water.[49,53−57] However, the structure and energy of a dimer are different from those in a condensed phase. Let us consider pure water as an example. The water dimer was investigated using various quantum mechanical ab initio methods, and reliable information about its structure and interaction energy is available.[50] They are different from those in condensed mixtures, where the effect of the nearest neighbors is an important factor. For pure water, it was clearly demonstrated[58] how the equilibrium intermolecular distance depends on the number of water molecules involved in the ab initio calculations. As already emphasized,[49] for the methane/water mixture, “the system of final interest is not $CH_4 \cdots H_2O$ ..., but $CH_4 \cdots (H_2O)_n$”.[49] Sandler and co-workers have used quantum mechanical ab initio calculations for a group of several molecules to simulate the condensed mixtures and calculated the intermolecular interaction energies between a solute and the solvent molecules.[59−61] They employed the Hartree−Fock self-consistent field approximation[50,51] to calculate the intermolecular interaction energies for aqueous solutions of alcohols. The obtained energies were used to calculate the Wilson and UNIQUAC parameters and then to (successfully) predict the activity coefficients. Recently,[62] we used a quantum mechanical ab initio method [the Møller−Plesset perturbation theory[50,51] (MP2 method)] to compute the intermolecular energies for the $CF_4 + CCl_4$ dimer and used the results to (accurately) predict the solubility of solid CCl_4 in supercritical CF_4.

The Møller−Plesset perturbation theory will be employed in this paper to investigate the mixture methane/water. We selected this mixture because it is an ideal candidate for investigating the hydrophobic hydration. The mixture methane/water has also importance in understanding the structure and intermolecular interactions of the methane hydrates, though the specifics of these hydrates will not be addressed in this paper. These hydrates constitute[63] a major potential fuel reserve.

The main goal of the present paper is to obtain information about the intermolecular interactions and distances between several molecules of water (10, 8, 6, 4, and 1) and a single molecule of methane and vice versa using quantum mechanical ab initio methods. In addition, the interactions between the nearest neighbors water molecules in the vicinity of the hydrophobic solute will be calculated and compared to those of the bulk water phase.

The paper is organized as follows: in the next section, the quantum mechanical ab initio method employed will be presented. This will be followed by the results obtained for dilute mixtures of methane and water. Further, these results will be compared with the available information obtained experimentally and by simulations. Finally, they will be used to examine the hydrophobic hydration and shed light on the structure and other features of the water molecules in the vicinity of a hydrophobic solute.

2. Methodology of Calculations

It would be ideal to use for these calculations molecular clusters containing a single molecule of a solute and many (dozens or even hundreds of molecules) of a solvent. Unfortunately, at the present time, the ab initio methods based on the Møller−Plesset perturbation theory have computational limitations regarding the size of the cluster.[64] Therefore, we will have to compromise between a “dilute solution” and a relatively small number of solvent molecules. The largest investigated molecular clusters will contain a single molecule of methane (water) surrounded by 10 molecules of water (methane). To verify whether this cluster (1:10) is sufficiently large to capture the essential physics of the interactions, the same procedure will be carried out with smaller clusters (1:8, 1:6, 1:4, and 1:1) and with a larger one (1:11), and the trends will be analyzed. For the $CH_4 \cdots H_2O$ pair the dispersion interactions are vitally important[49] (this statement is valid for all mixtures involving weak interactions[50,65]). Therefore, the second-order Møller−Plesset perturbation theory, which partially accounts for dispersion interactions, constitutes a suitable though not ideal approximation. The cluster geometries will be obtained by optimizing each of them with respect to all coordinates, using the MP2 method with a compact 6-31G basis set. This basis set makes tractable the numerous geometry optimizations required in this work. The convergence to an energy minimum was confirmed by calculating the vibrational frequencies. There is another important feature concerning the quantum mechanical ab initio calculations for clusters containing several molecules, namely, the effect of the initial configuration. Indeed, the equilibrium structure of a weakly interacting cluster, for example, 1:10, can be affected by the initial guess of the configuration which can lead to a local minimum. To minimize the errors associated with the initial guesses, we carried out the minimization for every cluster composition several times (at least eight times) starting from different initial configurations.

TABLE 1: Bond Lengths in Methane and Water Molecules in the Optimized Clusters

component	bond length [Å] exptl[67−68]	bond length [Å] calcd
water (r_{OH})	0.9571	0.986
methane (r_{CH})	1.089	1.096

After generating optimized clusters, the intermolecular interaction energies between pair molecules α and β ($E^{int}_{\alpha\beta}$) in the cluster were calculated using the supermolecular approach[59,60,66]

$$E^{int}_{\alpha\beta} = E_{\alpha\beta}\{\alpha\beta\} - E_{\alpha}\{\alpha\beta\} - E_{\beta}\{\alpha\beta\} \tag{1}$$

where $E_{\alpha\beta}\{\alpha\beta\}$ is the total energy of an αβ pair with the {αβ} basis set, and $E_{\alpha}\{\alpha\beta\}$ and $E_{\beta}\{\alpha\beta\}$ are the energies of α and β molecules with the {αβ} basis set, respectively, calculated by the ghost atoms method.[64] This method partially accounts for the basis set superposition error (BSSE). The energies ($E_{\alpha\beta}\{\alpha\beta\}$, $E_{\alpha}\{\alpha\beta\}$, and $E_{\beta}\{\alpha\beta\}$) were computed with a much better basis set than that employed for the cluster geometry optimization. Specifically all MP2 pair energies were calculated with the triple-ζ 6-311++G(3d,2p) basis set. This basis set includes polarization and diffuse functions. All of the ab initio computations were performed using the Gaussian 94 program on the IBM SP at the Center for Computational Research (CCR), at the University at Buffalo.

3. Results of the ab Initio Computations

3.1. The Dilute Mixture of Methane in Water. The calculated bond lengths in methane and water molecules of the optimized clusters (1:10) are listed in Table 1 together with data from literature. The arithmetic average distance and interaction energy between a methane molecule and the nearest touching water molecules in the cluster $CH_4 \cdots (H_2O)_n$ are listed in Table 2.

One of the typical minimized clusters 1 (methane):10 (waters) is presented in Figure 1a,b. They show that the methane molecule is enclosed in a cavity formed by water molecules. The two spheres centered on a methane molecule, with radii of 3.6 and 5.35 Å, correspond to the first maximum and the first minimum in the radial distribution function $g_{oc} = g_{oc}(r_{oc})$ in dilute mixtures of methane in water. It is worth noting that

TABLE 2: Arithmetic Average Distance and Interaction Energy[a] between a Methane Molecule and Touching nearest Neighbors Water Molecules (Type A Water Molecules) in the Clusters $CH_4 \cdots (H_2O)_n$

cluster $CH_4 \cdots (H_2O)_n$	r_{CO} [Å]	$E^{int}_{CH_4-H_2O}$ [KJ/mol]	data from literature
$n = 1$ (dimer)	3.69	−1.06	(1) r_{CO} =3.5 Å (exptl value[34] of the position of the first peak in the radial distribution function $g_{oc} = g_{oc}(r_{oc})$ in dilute methane−water mixtures)
$n = 4$	3.73	−1.02	(2) r_{CO} = 4.0 Å (in solid methane hydrate[69])
$n = 6$	3.77	−0.93	(3) (a)r_{CO} =3.6 Å, (b) r_{CO} =3.73 Å (the position of the first peak in the radial distribution function $g_{oc} = g_{oc}(r_{oc})$ in dilute methane−water mixtures found by (a) Monte Carlo[44] and (b) by molecular dynamics[70] simulations)
$n = 8$	3.80	−0.79	
$n = 10$	3.74	−0.75	

[a] The interaction energies were calculated between a central methane molecule and all the water molecules located not further than 4.1 Å from the central methane molecule (type A water molecules) as arithmetic averages. The values listed for the distances are also arithmetic averages.

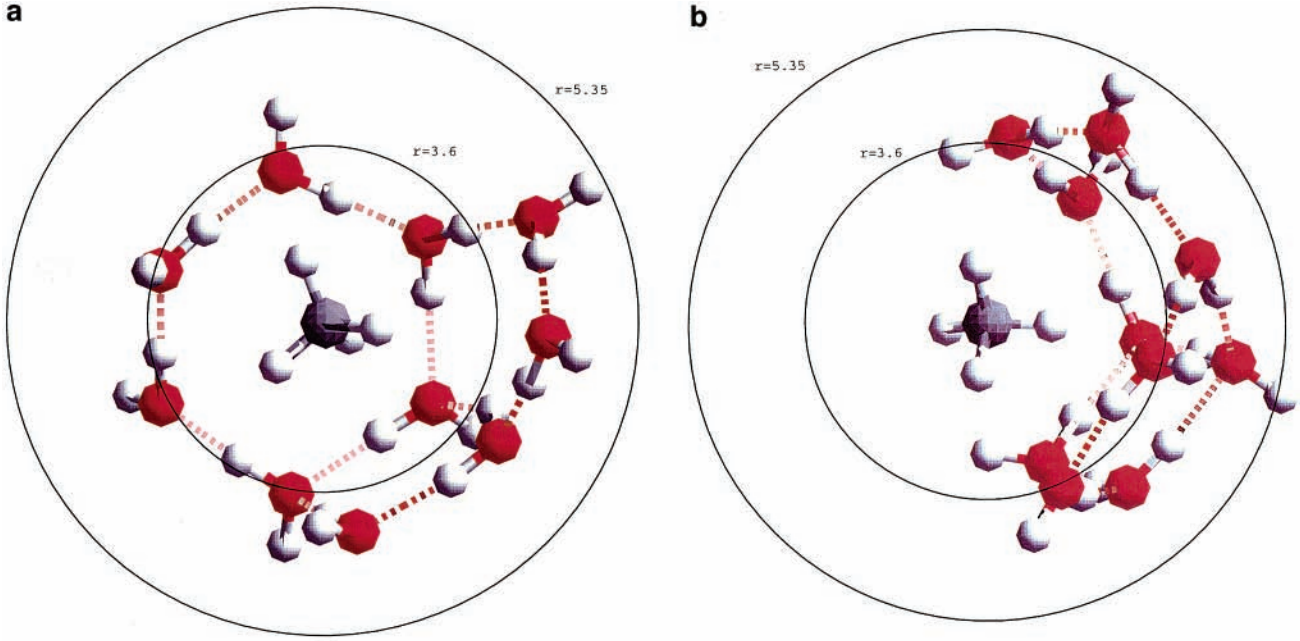

Figure 1. Optimized methane (1):water (10) cluster. (a) The front view. (b) The view from the right. The two circles in Figure 1 correspond to the first maximum (3.6 Å) and first minimum (5.35 Å) of the radial distribution function $g_{oc} = g_{oc}(r_{oc})$.

Jorgensen et al.[36] used the distance of 5.35 Å in their Monte Carlo simulations as a cutoff distance for the definition of the number of water molecules in the first hydration layer around a methane molecule in water. One can see from Figure 1a,b that the water molecules between the spheres with radii 3.6 and 5.35 Å include not only touching nearest neighbors but also water molecules from a second sublayer which are non touching nearest neighbors. Consequently, the space between the first maximum and first minimum in the radial distribution function $g_{oc} = g_{oc}(r_{oc})$ around a central molecule of methane is filled with water molecules of type A (or first sublayer), which are touching nearest neighbors, and water molecules of type B (or second sublayer), which are nontouching nearest neighbors of the methane molecule. The water molecules of types A and B are quite different because their distances from the central methane molecule, their orientations toward it, the number of H-bonds per water molecule, the energy of interaction with the central molecule, etc. (see also Discussion), are different.

TABLE 3: Orientation of the Average Water Molecules in the First and Second Sublayers Surrounding the Methane Molecule

layer	the average distance between the carbon atom of methane and the oxygen and hydrogen atoms of the water molecules in the cluster $CH_4 \cdots (H_2O)_{10}$ [Å]		
	r_{OC}	$r_{CH(1)}$	$r_{CH(2)}$
$r_{OC} \leq 4.1$ Å (type A)	3.704	3.769	3.771
4.1 Å $< r_{OC} \leq 5.6$ Å (type B)	4.570	4.339	5.138

TABLE 4: The Average Intermolecular Distances between nearest Water Molecules in the Vicinity of a Methane Molecule

pair of water molecules	r_{OO} [Å]	data from literature[71,72]
both are of type A	2.69	r_{OO} =2.84 Å in liquid water at 4 °C and r_{OO} =2.759 Å in ice at 223 K
one is of type A and the other of type B	2.73	

The distances between the C atom of methane and O and H atoms of the water molecules of type A (C−O and C−H) are almost equal to each other (see Table 3) and are tangentially oriented toward the surface of the methane molecule, as was also found experimentally.[34] However, the B water molecules have a different orientation (see Table 3). Another important characteristic of the water molecules in the vicinity of a hydrophobic molecule, besides their interaction with the latter, is the interactions between themselves. The intermolecular distances between the water molecules in the vicinity of a methane molecule are listed in Table 4. Following the suggestion of ref 40 we define the water molecules which are located not

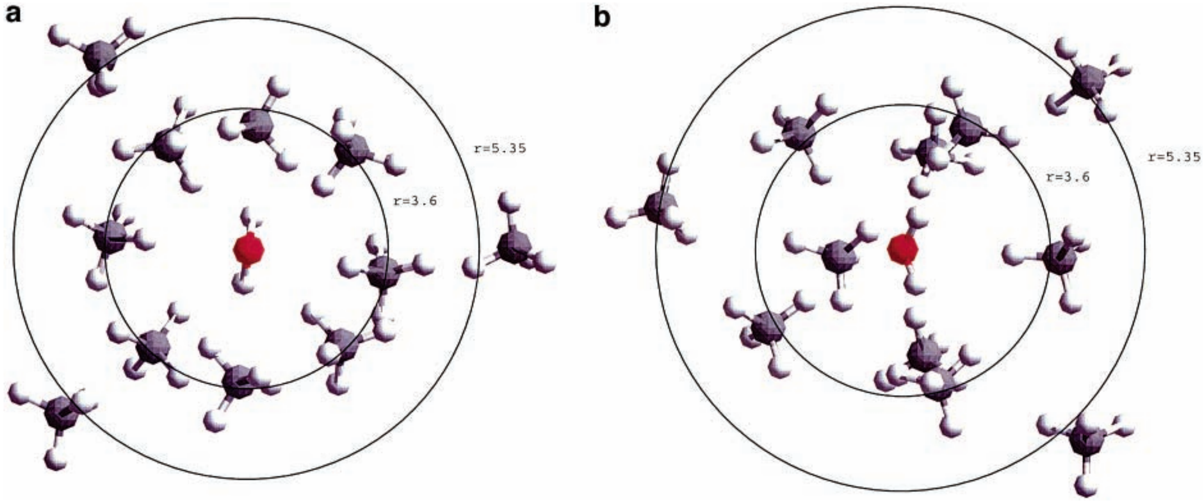

Figure 2. Optimized water (1):methane(10) cluster. (a) The front view. (b) The view from the right. The two circles in Figure 2 correspond to the first maximum (3.6 Å) and first minimum (5.35 Å) of the radial distribution function $g_{oc} = g_{oc}(r_{oc})$.

TABLE 5: The Average Distance and Interaction Energy between a Water Molecule and nearest Methane Molecules in the Clusters $H_2O\cdots(CH_4)_n$

cluster $H_2O\cdots(CH_4)_n$	r_{OC} [Å]	$E^{int}_{CH_4-H_2O}$ [KJ/mol]
$n = 8$	3.70	−1.79
$n = 10$	3.69	−1.83

further than 3.5 Å from a central water molecule as its nearest neighbors. For comparison, the same parameters for pure water are also listed in Table 4.

3.2. The Dilute Mixture of Water in Methane. When one molecule of water is surrounded by methane molecules, the molecule of water behaves like a regular nonpolar molecule (see Figure 2, where one of the typical minimized clusters 1 (water):10 (methane) is presented). The average intermolecular distance and interaction energy between a water molecule and the nearest neighbors methane molecules in the clusters $H_2O\cdots(CH_4)_{10}$ are listed in Table 5.

4. Discussion

4.1. Comparison between Two Clusters: $CH_4\cdots(H_2O)_n$ and $H_2O\cdots(CH_4)_n$. The results listed in Tables 2 and 5 show that the interaction energies between a water and a methane molecule in the two clusters $CH_4\cdots(H_2O)_n$ and $H_2O\cdots(CH_4)_n$ are very different not only one from another but also from that in the $H_2O\cdots CH_4$ dimer. While the intermolecular distances r_{oc} are not very different from one another and from the intermolecular distance r_{oc} in the methane/water dimer, the interaction energies between methane and water depend on the cluster type. It reflects the fact that the two kinds of clusters represent two different physical systems. Indeed, the two extreme cases at mole fractions $x_1 \rightarrow 0$ and $x_2 \rightarrow 0$ are very different. When one molecule of methane is located in water, the molecules of water are subjected to hydrogen bonding which will affect the interaction between H_2O and CH_4.[73] When one molecule of water is located in CH_4, the water molecule is no longer subjected to hydrogen bonding, but the interactions with the other methane molecules interfere with the interaction between H_2O and CH_4.

The single molecule of methane is located inside a cage formed by water molecules which are bound through hydrogen bonds (Figure 1). In contrast, in the second case (a single water molecule and 10 molecules of methane, Figure 2), the molecules of methane do not form a cage around a water molecule, but simply surround it. This generates a difference between the water/methane intermolecular interaction energies in the two cases and clearly indicates that the intermolecular interaction energy between the molecules of water and methane depends on the composition, which must be taken into account when calculating phase equilibria. However, usually, the models based on lattice theories ignore this dependence and use the pair intermolecular energy in the condensed mixtures as a composition independent quantity.

4.2. Molecules of Water in the Vicinity of a Methane Molecule. First, one should clearly emphasize the difference between (1) the number of water molecules in the first hydration layer around a methane molecule and (2) the coordination number of a methane molecule in an infinitely dilute aqueous solution. Jorgensen et al.[36] defined the number of water molecules in the first hydration layer around a methane molecule as the water molecules located between the spheres with radii 3.6 and 5.35 Å. Hence, Jorgensen's first hydration layer contains both A and B species. However, the coordination number in a liquid is usually defined[74] as the number of nearest touching neighbors and corresponds to A type molecules.

Let us consider two spheres with radii 3.6 and 5.35 Å in pure liquid water. Under ambient conditions and assuming the density equal to that of bulk water one can easily compute that there are 6.5 water molecules inside the first sphere and 24.5 water molecules inside the second, and hence, that there are 18 water molecules between the two spheres. If this number is compared to that of Jorgensen et al.[36] (20.3), one can conclude that the water layer around a central methane molecule is slightly denser than the bulk water. Our calculations regarding the intermolecular distance between neighboring water molecules in the vicinity of a central methane molecule (Table 4) is in agreement with this observation. It is not possible to calculate accurately the number of water molecules of types A and B because the number of water molecules considered in the calculations (10) is smaller than their number between two spheres of radii 3.6 and 5.35 Å in pure liquid water. However, a simple evaluation can be made by taking into account that a central molecule of methane replaces 6.5 molecules of water inside the first sphere. Because each of these molecules of water has 4.4 nearest neighbors in pure water, by subtracting the nearest neighbors that are present among them, one obtains that the methane molecule has 15−16 water molecules of type A. Our computa-

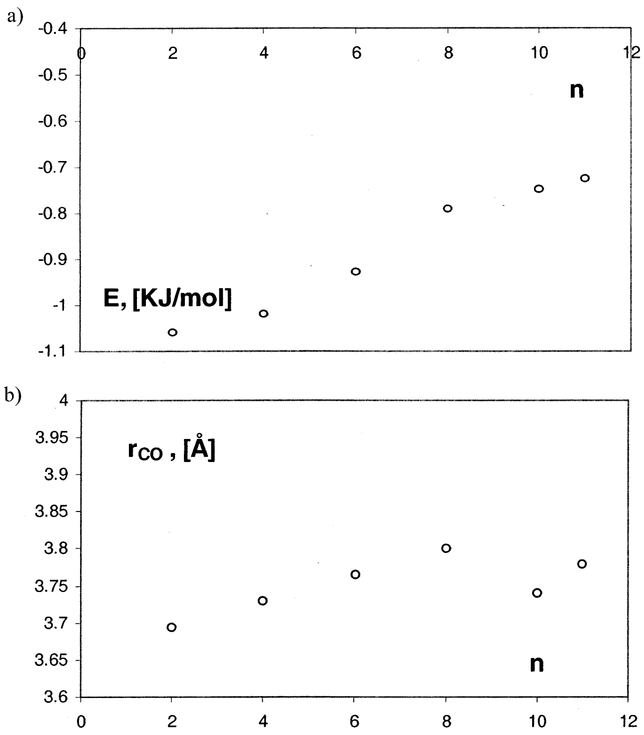

Figure 3. The dependence of the interaction energy (a) and average distance (b) between a methane molecule and water molecules of type A in the clusters $CH_4\cdots(H_2O)_n$ on the number of water molecules in the cluster *n*.

tions (Table 4) showed that the A water molecules have hydrogen bonds slightly shorter between them, than with the water molecules of type B. These results are in agreement with the Monte Carlo simulations.[44] Table 3 provides information about the orientation of the water molecules in the vicinity of a central methane molecule. One can see that the water molecules in the first sublayer (type A) are oriented almost tangentially toward to methane molecule; this peculiar orientation was also found experimentally.[34] However, the water molecules in the second sublayer (type B) are oriented more randomly. We agree with the previous authors[40,44] that the tangential orientation is due to the "hydrophobic wall" effect. Consequently, the water molecules of type A are quite different not only from the "bulk" water molecules, but also from the water molecules of type B. If one returns to the Frank and Evans[17] "iceberg", one can state that the iceberg is not uniform, but contains at least two types of water molecules. A simplified model of water like the Mercedes-Benz (MB) model[75] probably can be used to simulate the first sublayer of water (type A molecules) around the central methane molecule.

4.3. Cluster Size. The critical problem is how many water molecules should be used to accurately represent the hydration layers around nonpolar molecules. As already mentioned, it would be ideal to use in such calculations molecular clusters containing a single molecule of solute and hundreds of solvent molecules. Unfortunately, the ab initio methods based on MP2 are computationally expensive and this limits the size of clusters that can be attempted.[64] To fully understand whether the cluster 1:10 is sufficiently large to capture the essential physics of the interactions, we carried out additional calculations for clusters containing a single molecule of methane surrounded by 11 molecules of water (1:11). A comparison of the average distance and interaction energy between a methane molecule and the water molecules of type A in the cluster $CH_4\cdots(H_2O)_{11}$ with those for smaller clusters (see Table 2) is presented in Figure 3. This figure shows that the arithmetic average distance and interaction energy between a methane molecule and the nearest water molecules (type A) is almost the same in the clusters $CH_4\cdots(H_2O)_{10}$ and $CH_4\cdots(H_2O)_{11}$. One can, therefore, conclude that the cluster $CH_4\cdots(H_2O)_{10}$ is large enough for a correct estimation of the average distance and interaction energy between a methane molecule and the A water molecules in dilute solutions of methane in water. A more detailed analysis of the clusters $CH_4\cdots(H_2O)_{11}$ leads to the same conclusions regarding the water molecules in the vicinity of a central methane molecule for the clusters $CH_4\cdots(H_2O)_{10}$ (see section 4. 2). However, the clusters ($CH_4\cdots(H_2O)_{10}$ and $CH_4\cdots(H_2O)_{11}$) are not large enough to accurately represent the characteristics of the B water molecules and of the water molecules in the second, third, and so on, hydration layers.

4.4. Influence of Temperature. As is well-known, the ab initio quantum mechanical methods provide results valid at 0 K and zero pressure. While the interactions depend on temperature and pressure,[76,77] this dependence is expected to be weak up to normal conditions. Indeed, it was shown[76,77] that for pure water the length of the hydrogen bond changed by at most four parts per thousand when the temperature varied by 100 K.

5. Conclusion

In this paper, the Møller−Plesset perturbation theory was applied to clusters formed by one molecule of methane and several molecules of water, or one molecule of water and several molecules of methane. The goal was to determine the intermolecular distances and interaction energies between a water molecule and a methane molecule in the clusters $CH_4\cdots(H_2O)_n$ and $H_2O\cdots(CH_4)_n$ and to compare the obtained results with available experimental data.

It was found that the intermolecular distances and interaction energies between a water molecule and a methane molecule are quite different in the clusters $CH_4\cdots(H_2O)_{10}$ and $H_2O\cdots(CH_4)_{10}$. The average intermolecular distance between a central methane molecule and the touching nearest neighbor water molecules is in agreement with the experimental value regarding the position of the first minimum in the radial distribution function $g_{oc} = g_{oc}(r_{oc})$. It was shown that the water molecules in the vicinity ($r_{oc} \leq 5.35$ Å) of a central methane molecule can be subdivided into two groups. A first group of water molecules (type A) in the immediate vicinity ($r_{oc} < 4.1$ Å) of the central methane molecule, which are touching nearest neighbors and a second group of water molecules (type B) in the second sublayer (4.1 Å $< r_{oc} \leq 5.6$ Å). The molecules of type A are tangentially oriented toward the central methane molecule and have shorter hydrogen bonds; the central methane molecule interacts with the water molecules (type A) through the so-called "hydrophobic wall" effect.

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References and Notes

(1) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, 2nd ed.; Wiley: New York, 1980.
(2) Ben-Naim, A. *Hydrophobic Interactions*; Plenum: New York, 1980.
(3) Dill, K. A. *Biochemistry* **1990**, *29*, 7133.
(4) Blokzijl, W.; Engberts, J. B. F. N. *Angew. Chem., Int. Ed.* **1993**, *32*, 1545.
(5) Hummer, G.; Garde, S.; Garcia, A. E.; Pratt, L. R. *Chem. Phys.* **2000**, *258*, 349.
(6) Schmid, R. *Monatsh. Chem.* **2001**, *132*, 1295.
(7) Ludwig, R. *Angew. Chem. Int. Ed.* **2001**, *40*, 1809.

(8) Kauzmann, W. Denaturation of Proteins and Enzymes. In *The Mechanism of Enzyme Action*; McElroy, W. D., Glass, B., Eds.; Johns Hopkins Press: Baltimore, 1954; p 71.

(9) Kauzmann, W. *Adv. Protein Chem*. **1959**, *14*, 1.

(10) Butler, J. A. V. *Trans. Faraday Soc.* **1937**, *33*, 229.

(11) Uhlig, H. H. *J. Phys. Chem.* **1937**, *41*, 1215.

(12) Eley, D. D. *Trans. Faraday Soc*. **1939**, *35*, 1281.

(13) Eley, D. D. *Trans. Faraday Soc.* **1944**, *40*, 184.

(14) Abraham, M. H. *J. Am. Chem. Soc.* **1982**, *104*, 2085.

(15) Abraham, M. H. *J. Chem. Soc., Faraday Trans. 1*, **1984**, *80*, 153.

(16) Abraham, M. H.; Matteoli, E. *J. Chem. Soc., Faraday Trans. 1*, **1988**, *84*, 1985.

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

(18) Shinoda, K. *Principles of Solution and Solubility*; M. Decker: New York, 1977.

(19) Shinoda, K. *J. Phys. Chem.* **1977**, *81*, 1300.

(20) Ruckenstein, E. A Simple Interpretation of Hydrophobic Interactions and Critical Concentrations in Micellar Solutions. In *Progress in Microemulsions*; Martelucci, S., Chester, A. H., Eds.; Plenum Press: New York, 1989; p 31.

(21) Ruckenstein, E. *Colloids Surf.* **1992**, *65*, 95.

(22) Ruckenstein, E. *J. Dispersion Sci. Technol.* **1998**, *19*, 329.

(23) Lucas, M. J. *J. Phys. Chem.* **1976**, *80*, 359.

(24) Lee, B. *Biopolymers* **1985**, *24*, 813.

(25) Lee, B.; Graziano, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 5163.

(26) Graziano, G. *J. Phys. Soc. Jpn.* **2000**, *69*, 3720.

(27) Graziano, G. *J. Phys. Chem. B* **2000**, *104*, 9249.

(28) Graziano, G.; Lee, B. *J. Phys. Chem. B* **2001**, *105*, 10367.

(29) Muller, N. *J. Solution Chem.* **1988**, *17*, 661.

(30) Hummer, G.; Garde, S.; Garcia, A. E.; Pohorille, A.; Pratt, L. R. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 8951.

(31) Hummer, G.; Garde, S.; Garcia, A. E.; Paulaitis, M. E.; Pratt, L. R. *J. Phys. Chem. B* **1998**, *102*, 10469.

(32) Garde, S.; Hummer, G.; Garcia, A. E.; Paulaitis, M. E.; Pratt, L. R. *Phys. Rev. Lett.* **1996**, *77*, 4966.

(33) Haselmeier, R.; Holz, M.; Marbach, W.; Weingartner, H. *J. Phys. Chem.* **1995**, *99*, 2243.

(34) De Jong, P. H. K.; Wilson, J. E.; Neilson, G. W.; Buckingham, A. D. *Mol. Phys.* **1997**, *91*, 99.

(35) Koh, C. A.; Wisbey, R. P.; Wu, X. P.; Westacott, R. E.; Soper, A. K. *J. Chem. Phys.* **2000**, *113*, 6390.

(36) Jorgensen, W. L.; Gao, J.; Ravimohan, C. *J. Phys. Chem.* **1985**, *89*, 3470.

(37) Glew, D. N. *J. Phys. Chem.* **1962**, *66*, 605.

(38) Lue, L.; Blankschtein, D. *J. Phys. Chem.* **1992**, *96*, 8582.

(39) Guillot, B.; Guissani, Y. *J. Chem. Phys*. **1993**, *99*, 8075.

(40) Chau, P. L.; Forester, T. R.; Smith, W. *Mol. Phys.* **1996**, *89*, 1033.

(41) Broadbent, R. D.; Neilson, G. W. *J. Chem. Phys.* **1994**, *100*, 7543.

(42) Fois, E.; Gamba, A.; Redaelli, C. *J. Chem. Phys*. **1999**, *110*, 1025.

(43) Matubayasi, N.; Levy, R. M. *J. Phys. Chem.* **1996** *100*, 2681.

(44) Chau, P. L.; Mancera, R. L. *Mol. Phys.* **1999**, *96*, 109.

(45) Meng, E. C.; Kollman, P. A. *J. Phys. Chem.* **1996**, *100*, 11460.

(46) Mancera, R. L.; Buckingham, A. D.; Skipper, N. T. *J. Chem. Soc., Faraday Trans*. **1997**, *93*, 2263.

(47) Ikeguchi, M.; Shimizu, S.; Nakamura, S.; Shimizu, K. *J. Phys. Chem. B* **1998**, *102*, 5891.

(48) Clementi, E. *Computational Aspects for Large Chemical Systems*; Springer-Verlag: Berlin, 1980.

(49) Bolis, G.; Clementi, E.; Scheraga, H. A.; Tosi, C.; Wertz, D. H. *J. Am. Chem. Soc.* **1983**, *105*, 355−360.

(50) Levine, I. N. *Quantum Chemistry*, 4th ed.; Prentice Hall: Englewood Cliffs, NJ,

(51) Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry. Introduction to Advanced Electronic Structure Theory*; Dover Publication: New York, 1996.

(52) Frisch, M. J.; Delbene, J. E.; Binkley, J. S.; Schaefer, H. F. *J. Chem. Phys*. **1986**, *84*, 2279.

(53) Owicki, J. C.; H. A. Scheraga, H. A. *J. Am. Chem. Soc.* **1977**, *99*, 7413.

(54) Swaminathan, S.; Harrison, S. W.; Beveridge, D. L. *J. Am. Chem. Soc*. **1978**, *100*, 5705.

(55) Novoa, J. J.; Tarron, B.; Whangbo, M.-H.; Williams, J. M. *J. Chem. Phys.* **1991**, *95*, 5179.

(56) Szczesniak, M. M.; Chalasinski, G.; Cybulski, S. M.; Cieplak, P. *J. Chem. Phys.* **1991**, *95*, 5179.

(57) Cao, Z. T.; Tester, J. W.; Trout, B. L. *J. Chem. Phys.* **2001**, *115*, 2550.

(58) Liu, K.; Cruzan, J. D.; Saykally, R. J. *Science* **1996**, *271*, 929.

(59) Sum, A. K.; Sandler, S. I. *Ind. Eng. Chem. Res.* **1999**, *38*, 2849.

(60) Sum, A. K.; Sandler, S. I. *Fluid Phase Equilib.* **1999**, *160*, 375.

(61) Lin, S. T.; Sandler, S. I. *AIChE J.* **1999**, *45*, 2606.

(62) Ruckenstein, E.; Shulgin, I. *Ind. Eng. Chem. Res.* **2001**, *40*, 2544.

(63) Appenzeller, T. *Science* **1991**, *252*, 1790.

(64) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian94*, revision C.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(65) Woon, D. E. *Chem. Phys. Lett*. **1993**, *204*, 29.

(66) Chalasinski, G.; Gutowski, M. *Chem. Rev.* **1988**, *88*, 943.

(67) Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press: New York, 1969.

(68) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, *2*, 2, S1.

(69) McMullen, R. K.; Jeffrey, G. A. *J. Chem. Phys*. **1965**, *42*, 2725.

(70) Skipper, N. T. *Chem. Phys. Lett.* **1993**, *207*, 424.

(71) Page, R. H.; Frey, J. G.; Shen, Y. R.; Lee, Y. T. *Chem. Phys. Lett.* **1984**, *106*, 373.

(72) Huisken, F.; Kaloudis, M.; Kulcke, A.; Voelkel, D. *Infrared Phys. Technol*. **1995**, *36*, 171.

(73) Ruckenstein, E.; Shulgin, I. *Ind. Eng. Chem. Res.* **1999**, *38*, 4092.

(74) Prausnitz, J. M.; Lichtenhaler, R. N.; Gomes de Azevedo, E. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1986.

(75) Silverstein, K. A. T.; Dill, K. A.; Haymet, A. D. *J. Fluid Phase Equilib.* **1998**, *151*, 83.

(76) Dougherty, R. C. *J. Chem. Phys*. **1998**, *109*, 7372.

(77) Dougherty, R. C.; Howard, L. N. *J. Chem. Phys*. **1998**, *109*, 7379.