



Hydrophobic interaction and solvatochromic shift of benzene in water

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Abstract

Monte Carlo simulations of one and two benzene molecules in water have been performed to analyze the hydrophobic hydration and hydrophobic interaction effects. Also, Monte Carlo structures have been used in the quantum mechanical calculations of the red shift of the $B_{2u}(\pi - \pi^*)$ band of benzene in water and the role of hydrophobicity analyzed. It has been found, on average, that the water molecule closest to benzene has one of the O–H bonds tangential to the benzene plane; the water-induced effect essentially doubles the benzene–benzene interaction and hydrophobicity has a small, but non-negligible, effect on the red shift of the first absorption band of benzene in water. © 1997 Published by Elsevier Science B.V.

1. Introduction

In recent years there has been an increasing interest in the description of solvent effects in molecular properties [1–4]. The theoretical description of the solute–solvent interaction and its influence on solute properties is of central concern in theoretical physical chemistry. This is, however, a complex problem. The nature of the intermolecular interaction involved influences differently the different molecular properties. The solute–solvent interaction is usually treated on the basis of electrostatic, induction and dispersion forces [3,4]. Specific interactions, such as the hydrogen bond, are treated with special attention. In the case of nonpolar solutes in water the so-called hydrophobic interaction appears [5]. This interaction is of interest in a variety of processes and is of special concern in biophysical systems. Important examples are the formation of micelles and biological mem-

branes [5,6]. There has been an increased interest in understanding the origin of the hydrophobic interaction [7] and some Monte Carlo/molecular dynamics simulations have addressed this point [8–13]. However, its influence on solvatochromism has been nearly ignored. As in several recent studies of solvent effects, we approach this issue from the viewpoint of computer simulation [14,15]. We analyze the benzene molecule in water. The hydrophobic effects of this system are of special interest from both experimental [16–19] and theoretical [20–22] points of view due to the interaction of the conjugated π system.

Using a Monte Carlo simulation we consider first the hydrophobic hydration, i.e. the relative molecular orientation of the solvent water near the solute benzene molecule. Next we consider the hydrophobic interaction, i.e. the solvent-induced interaction between two benzene molecules. Finally, the structures

obtained from the MC simulation are used in super-molecular quantum mechanical calculations of the first absorption band of benzene in water.

2. Monte Carlo simulation

The Monte Carlo (MC) simulations are performed using standard procedures for the Metropolis sampling technique [23] in the NVT ensemble and periodic boundary condition in a cubic box [24,25]. Two separate simulations are made. First one and next two molecules of benzene are surrounded by 343 water molecules. The volume of the cubic box is determined by the experimental density of the liquid water, $\rho = 0.9966 \text{ g/cm}^3$, and the temperature used is $T = 298 \text{ K}$. All molecules are rigid in the equilibrium structure: benzene has a D_{6h} structure with $r_{CC} = 1.40 \text{ \AA}$, $r_{CH} = 1.088 \text{ \AA}$ and $\Theta = 120^\circ$, and water has a C_{2v} structure with $r_{OH} = 1.00 \text{ \AA}$ and $\Theta_{HOH} = 109.47^\circ$. The molecular interaction is described by the sum of Lennard-Jones and Coulomb potentials:

$$U_{ab} = \sum_i^{\text{on } a} \sum_j^{\text{on } b} \left\{ 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j e^2}{(4\pi\epsilon_0) r_{ij}} \right\}, \quad (1)$$

where \sum^a is the sum over the atoms of molecule a , \sum^b is the sum over the atoms of molecule b , r_{ij} is the distance between atoms i and j , $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$, $\sigma_{ij} = \sqrt{\sigma_i \sigma_j}$ and σ_i , ϵ_i and q_i are the parameters of atom i . A spherical cut-off at center of mass separations of $r_c = 10.92 \text{ \AA}$ is used in the calculation of the pairwise potential. The potential parameters used for benzene [26] and water [27] were developed by Jorgensen and co-workers.

The initial configuration is generated randomly, considering the position and the orientation of each molecule. One MC step is completed after selecting all N molecules sequentially (i.e. in order of molecular index) and trying to translate it in all the Cartesian directions and rotate it around a randomly chosen axis. The sequential selection of molecules cuts down on the amount of random number generation

and is an equally valid method of generating the correctly weighted configurations [24,28]. Note that in our notation, one MC step generates N configurations. The maximum allowed displacement of the molecules is self adjusted after 50 MC steps to give an acceptance rate of new configurations around 50%. The maximum rotation angle is fixed during the simulation in $\delta\Theta = \pm 15^\circ$. The full simulation involves a thermalization stage of about 5000 MC steps followed by an averaging stage of 48000 MC steps.

3. Results

3.1. Hydrophobic hydration

Hydrophobic hydration usually refers to the interaction of a single nonpolar solute with the water solvent. As the enthalpic contribution to the solvation is negative it is the entropic contribution that makes the free energy of solvation positive. This decrease in entropy prompts an interest in the hydrogen bond network that characterizes the water system close to the solute molecule.

We first analyze the results of the MC simulation of one benzene molecule surrounded by 343 water molecules. Fig. 1a shows the radial pair distribution functions (RDF) of the carbon atoms of the solute benzene and the oxygens and hydrogens of the sol-

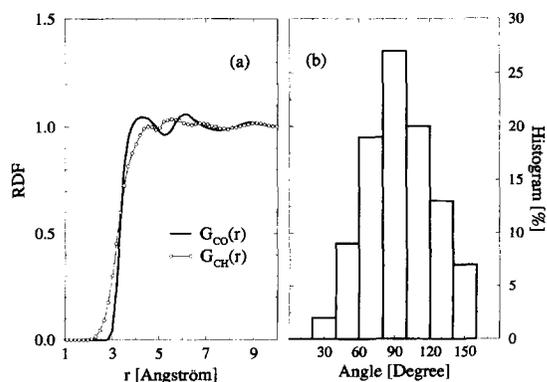


Fig. 1. Radial pair distribution function of benzene in water (a). G_{CO} and G_{CH} give the RDF of the carbon atoms of benzene and the oxygen and hydrogen atoms of water, respectively. (b) The histogram of the angle formed by the vector perpendicular to the benzene plane and one of the O–H bonds of water.

vent water. The two maxima at about 4.4 \AA is illustrative of the hydrophobic hydration of benzene in water, indicating that the distances of the nearby O and H atoms of water are nearly equidistant to the C atoms of the benzene molecule. Fig. 1b shows the histogram of angles between the vector normal to the benzene surface and the vector in the direction of the O–H bond. This has a maximum at 90° . We can thus conclude that, on average, the water molecules closest to benzene have one of the O–H bonds tangential to the surface of the solute. This is similar to the results obtained in other simulations of a nonpolar solute in water, in particular, the MD studies of methane in water by Guillot et al. [11]. This is indicative of the ordering of water around benzene so as to preserve their hydrogen bond structure.

Fig. 2 uses one MC structure to illustrate the relative orientation of the water molecule with respect to benzene. In Fig. 2a only benzene and the nearest water molecule (water#1) are shown. This structure is different from the experimental structure of the benzene–water dimer [16–18]. In this cluster the water molecule is isolated and not bound to any other water molecule. This water is then able to bind with benzene. A stable configuration is found where the water internally rotates about the sixfold axis of benzene with both hydrogen atoms pointing toward the π cloud and a center-of-mass-to-center-of-mass distance of about 3.32 \AA [16–18]. The estimated binding energy is small being slightly less than 1.8 kcal/mol . Clearly from this structural point of view the cluster has a different behavior from the liquid. This difference has its ground in water–water hydrogen bonds. This behavior can be seen in Fig. 2b which shows the second water molecule (water#2) of the same MC structure as in Fig. 2a. Water#1 has position and orientation relative to the benzene similar to that suggested in the experimental structure of

the benzene–water–water trimer [19]. The experiments of Garrett and Zwier [16] show that for $\text{C}_6\text{H}_6-(\text{H}_2\text{O})_n$ clusters with $n \leq 5$ all the water molecules are on the same side of benzene. However, for $n \geq 6$ there are marked changes in the water cluster structure. The results of our simulation give a hydration number of 18; i.e. integration of the first peak of the RDF G_{CO} gives the first solvation shell as composed by 18 water molecules surrounding the solute benzene.

3.2. Hydrophobic interaction

Hydrophobic interaction is referred to as the interaction of two nonpolar molecules in water. The actual analysis of the hydrophobic interaction of benzene in water requires consideration of the change in the benzene–benzene interaction in water as compared to the same interaction in free space. The thermodynamic argument is that as $\Delta H < 0$ a decrease in the entropy is necessary to obtain a positive ΔG . Thus the nonpolar molecules orient themselves closely packed so that they become immiscible. The reduction of the surface area of the solute in contact with water signifies a reduction in the number of broken hydrogen bonds that are necessary to accommodate the solute. The hydrophobic interaction is thus responsible for the limited solubility of nonpolar compounds in water [7]. This suggests that the interaction between two nonpolar molecules increases when put in water. This gives a solvent-induced benzene–benzene interaction [29].

To analyze this hydrophobic interaction between benzene in water we consider now the results obtained in our MC simulation of two benzene molecules surrounded by 343 water molecules. We start the simulation with the two benzene molecules separated by 3.2 \AA . During a long simulation (16.5×10^6 configurations), even though the benzenes are free to translate and rotate, their separation only varies between 3.8 and 7.6 \AA . We believe that the benzenes are confined in the first minimum of the potential and the thermal energy is not enough to make them cross the potential barrier. Fig. 3a shows the RDF of the carbon atoms of the two separate benzene molecules. As there are only two molecules involved in this RDF the results are better displayed

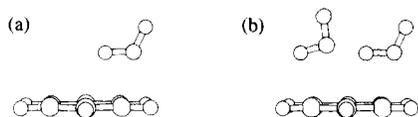


Fig. 2. One MC structure illustrating the relative orientation of the water molecule with respect to benzene. In (a) the nearest water molecule has one of the O–H bonds tangential to the benzene plane. In (b) the second water molecule is shown for the same MC structure.

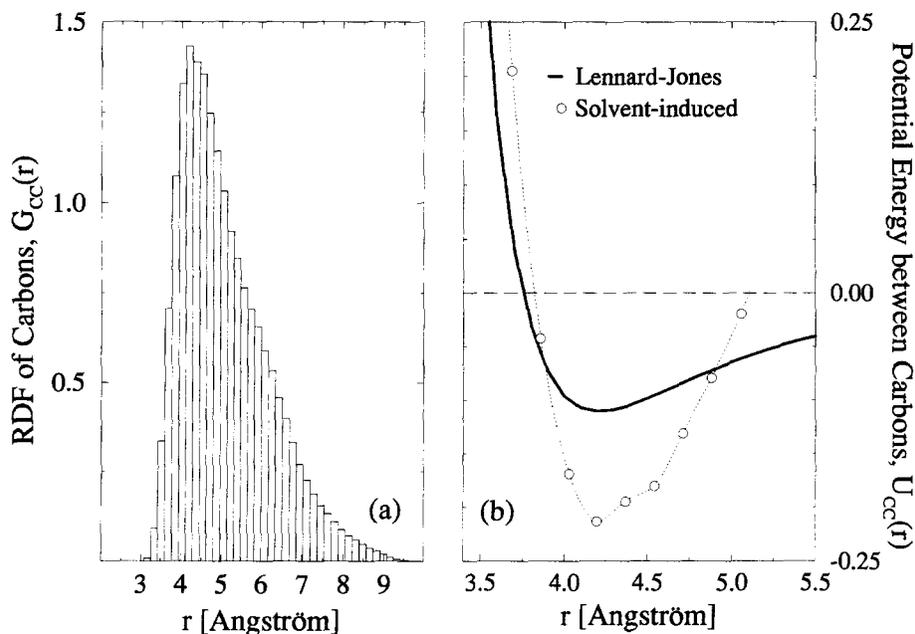


Fig. 3. The solvent-induced benzene–benzene interaction as obtained by the radial distribution function. Fig. 3a shows the histogram of C–C distances and Fig. 3b compares the C–C interaction in free space and in water (see text).

as a histogram. This histogram shows that the two benzene molecules do not move apart but remain within a maximum at about $r_{CC} = 4.2$ Å. The center-of-mass distance of the two benzenes has its maximum around 4.9 Å.

When two nonpolar molecules are dissolved in water with unconstrained positions they interact through a mean force that is solvent-induced. The potential of the mean force between the two molecules is defined as the work required to bring these two molecules from infinite separation to a distance r in water. In a constant-volume ensemble, as used here, this is the Helmholtz free energy. The magnitude of the potential dictates the probability of finding these two molecules a certain distance r apart. This distance distribution is obtained by the radial pairwise distribution function G_{CC} and the potential of the mean force is given by [10,12,29]

$$U_{CC}(r) = -kT \ln(G_{CC}(r)). \quad (2)$$

Therefore, from the calculated RDF $G_{CC}(r)$ it is possible to obtain directly the solvent-induced interaction. The calculation of the RDF between two solute molecules in solution is a hard task as the

calculation involves only two molecules and gives a poor statistic. In general, to obtain the correct behavior of the RDF for large r , some sort of preferential sampling in the simulations is required [13,30,31]. As we are only interested in the contact, or first, minimum of the potential, we have not made any sort of preferential sampling but used instead a relatively long simulation (16.5×10^6 configurations). This procedure guarantees a good statistic in the investigation of the first minimum (only) of the potential.

Fig. 3b gives this first minimum of the potential of the mean force obtained using Eq. (2) and the RDF of Fig. 3a. In fact we show the potential of the carbon–carbon interaction. Fig. 3b also shows for comparison the interaction in the absence of water. The solvent-induced effect essentially doubles the benzene–benzene interaction.

3.3. Solvatochromic shift

To calculate the first absorption band of benzene in water we use the structures generated by the MC simulation. However, two general assumptions are

made before the quantum mechanical (QM) calculation of these supermolecules can be performed. First we must judiciously reduce the number of solvent molecules to be included in the supermolecular calculations. Clearly, it is not possible to perform a QM calculation of nearly 350 molecules. This reduction can be done with the use of the RDF. Fig. 1 shows that the $G_{\text{CO}}(r)$ has three peaks with maxima at 4.4, 6.1 and 8.8 Å. The integration of each peak gives the number of solvent molecules that make up the solvation shells. The first solvation shell (up to 5.3 Å) has 18 water molecules. In a previous report [32] we have shown that this number stabilizes the solvatochromic shift so that the inclusion of only the first solvation shell seems appropriate. Second, as the solvatochromic shift is obtained here as an average (thermodynamic average) over the excitation energies ΔE_i of different MC structures i ,

$$\langle \Delta E \rangle_l = \frac{1}{l} \sum_i \Delta E_i, \quad (3)$$

we must also reduce the total number l of MC structures used. Again, it is not practical to perform QM calculations on every structure generated by the simulation after one MC step (nearly 50000). This reduction can be done with the use of the time (or step) correlation function and/or the related statistical inefficiency analysis [24]. In our previous report [33] we discuss the calculation of the statistical inefficiency as a good way of estimating the number of MC steps necessary to statistically uncorrelate structures. For the case of benzene in water we find ~ 800 MC steps. Thus thermodynamic averages obtained with 48000 MC structures give the same results as averages obtained with only 60 MC structures separated by 800 MC steps.

Hence QM calculations of the $B_{2u}(\pi - \pi^*)$ band of benzene in water use supermolecules of 1 or 2 C_6H_6 surrounded by the 18 first water neighbors and the calculated transition energy is averaged over 60 different QM calculations performed in these different MC structures. Finally, all the QM calculations reported here are made at the semi-empirical INDO/CIS level using the ZINDO program [34].

The numerical results of the calculations using one or two benzene molecules as solute give a red shift of 122 and 158 cm^{-1} , respectively, as com-

pared to the gas phase, both in good agreement with the experimental result of 140 cm^{-1} [35]. The result obtained using only the two benzene molecules after stripping all surrounding water molecules but using the same MC structures (without the solvent water molecules) results in a red shift of 65 cm^{-1} . This red shift obtained for the dimer has therefore two contributions: one is the structural effect due to the solvent water and the other is part of the red shift known to exist in the benzene dimer.

For the discrete model with supermolecular calculations we find that the red shift of the $B_{2u}(\pi - \pi^*)$ band of benzene in water is well reproduced whether we use only one solute C_6H_6 molecule or two solute C_6H_6 molecules interacting with one another. The results, however, show a small difference of about 40 cm^{-1} . Though small, this number is larger than the statistical error ($\sigma(\langle \Delta E \rangle) = 25 \text{ cm}^{-1}$) involved in Eq. (3); namely

$$\sigma(\langle \Delta E \rangle) = \sqrt{\frac{1}{l} (\langle \Delta E^2 \rangle - \langle \Delta E \rangle^2)}. \quad (4)$$

4. Summary

A Monte Carlo simulation of benzene in water has been performed to obtain the solvent-induced interaction between benzene molecules due to hydrophobicity. Analysis of the adjacent solvent water molecules was made using the radial distribution function. The results show some ordering of the water molecules for preserving their network of hydrogen bonds. The hydrophobic interaction is obtained from the solute–solute radial distribution function. It is found that the solvent-induced interaction nearly doubles the benzene–benzene interaction.

The structures generated by the MC simulation are judiciously used as supermolecules for the quantum mechanical calculation of the solvatochromic shift of the first $\pi - \pi^*$ absorption band of benzene. The calculated results are in good agreement with experiment. The calculations performed here using one or two benzene molecules differ by less than 40 cm^{-1} in the red shift for the first absorption band of benzene in water.

Acknowledgements

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