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Temperature Effect on the Hydrophobic Hydration in Aqueous Solution of Nonpolar Molecule by Monte Carlo Calculation

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Monte Carlo calculations have been carried out for pure water and aqueous solution of Lennard-Jones particle at infinite dilution between 273.15 K and 353.15 K in order to examine temperature effect on the hydrophobic hydration. It is found that internal energy of mixing ΔU due to the introduction of the solute into water becomes less negative monotonously with increasing temperature. It is in good correspondence with the tendency obtained from solubility measurement, and represents that heat capacity of mixing ΔC_V is positive. Furthermore the dissolution proceeds no longer exothermically at 353.15 K, where water behaves as a normal solvent. Several structural and energetical distribution functions have been calculated for the deep understanding of these observations.

In a previous paper,[1] it was shown that the energetic stabilization and free energy increase due to the hydrophobic hydration in dilute aqueous solution of methane can be reproduced by Monte Carlo (MC) calculations adopting the ST-2 model[2] for water and Lennard-Jones (LJ) potential for methane. The MC calculation was later extended to other LJ solutes having larger sizes and the size effect in hydrophobic hydration has been clarified.[3] In principle, the energetic stabilization can be directly evaluated by calorimetry; however extremely low solubility of nonpolar solutes in water prevents the establishment of accurate and reliable value for the energy change from ordinary laboratory experiments. Thus, we are at present forced to rely on the information from the temperature dependence of solubility. The solubility of nonpolar gas into water decreases with increasing temperature, and this anomaly is not observed in other solute and solvent systems.[4] It must be related to the temperature dependence of the hydrophobic hydration.

Computer experiment may be more favourable in studying these phenomena of the hydrophobic hydration. Although many MC or MD (molecular dynamics) studies have been reported recently for aqueous solution of nonpolar solute,[5] no extensive calculation has been hitherto made on the temperature effect in hydrophobic hydration. We will present here MC results for aqueous methane solutions at 273.15, 333.15, and 353.15 K. Temperature effect on hydrophobic hydration will be discussed based upon these calculations together with the results in the previous calculation at 298.15 K.[1]

Model and Method of Computation

The model and method of computation used here are the same as those in preceding papers.[1,3] They are summarized briefly as follows.

Monte Carlo calculations have been carried out with the ordinary Metropolis method[6] in NVT-ensemble where N=64 (64 water molecules or 63 water molecules+one LJ particle whose potential parameters are those of methane), T=273.15, 333.15, and 353.15 K, and V=18.02, 18.32, and 18.54 cm^3 mol^{-1} at the above three temperatures, respectively. The volume of each system is determined from the molar volume of pure water at each temperature, no correction being made for the volume change due to the introduction of the solute. The total number of configurations generated is $(5-9)\times10^5$ for pure water and $(6-12)\times10^5$ for methane solutions.

Table 1. Internal energy and internal energy of mixing at each temperature for aqueous solution of methane. The standard state of the solute is assumed to be ideal gas

		T/K			
		273.15	298.15	333.15	353.15
U/kJ mol^{-1}	Pure	−38.5	−35.1	−31.7	−30.4
	Soln	−40.2	−36.1	−32.1	−29.1
ΔU/kJ mol^{-1}		−2.3	−1.5	−0.9	0.9

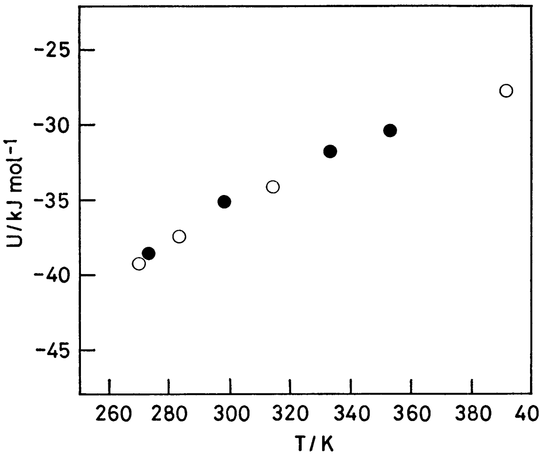

Fig. 1. Internal energies U of pure water as a function of temperature.
Closed circle: this work, open circle: Stillinger and Rahman.[2]

Results and Discussion

The convergence characteristics of the system to an equilibrium state are the most important problem in the MC calculation. This has been already discussed in detail elsewhere[3] and enough convergence has been also confirmed for the present systems.

Internal Energies. The internal energies U of

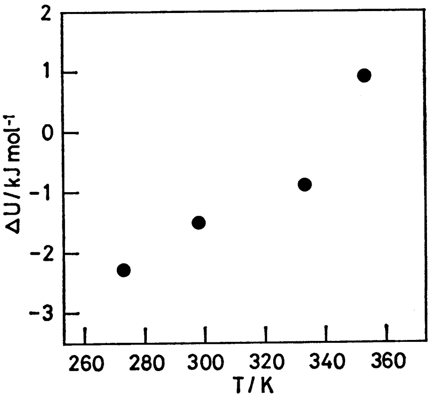

Fig. 2. Internal energies of mixing ΔU of aqueous solution of methane as a function of temperature. The standard state of the solute is assumed to be ideal gas.

both pure water and aqueous methane solution have been calculated as a function of temperature and the results are given in Table 1.

First the temperature dependence of U for pure water shown in Fig. 1 is examined. This kind of calculation has already been carried out with the MD method by Stillinger and Rahman[2] in a wide range of temperature, and their results are also given in the figure. The present calculations are concerned with a narrower temperature range in detail and the results are in good agreement with those obtained by Stillinger and Rahman.[2] Although U increases with increasing temperature as expected, the U *vs.* T curve is convex upward, which means that the heat capacity C_v decreases with increasing temperature. This result coincides with experimental observation.[7] The C_v value evaluated from the present result of the temperature gradient is $80\,\mathrm{J\,K^{-1}\,mol^{-1}}$ at 298.15 K. The agreement with the experimental value ($75\,\mathrm{J\,K^{-1}\,mol^{-1}}$)[7] is reasonable in view of the present status of computer experiment.

It must be noted here that the fluctuation of internal energies for pure water and the solution at 273.15 K is so large that the values are less reliable than those at higher temperatures. This uncertainty in the present calculation is unavoidable. It may be caused by the continuous phase transition from liquid state to ice in computer experiment owing to the restriction of initial phase condition. Then the thermodynamic properties and distribution functions at 273.15 K are limited only to the comparison with those at other temperatures. For this reason, we present here only the results of internal energy at 273.15 K, and do not discuss the distribution functions in detail.

In Table 1 are given the internal energies of mixing ΔU,

$$\Delta U = U_{\mathrm{soln}} - (x_{\mathrm{water}}U_{\mathrm{water}} + x_{\mathrm{solute}}U_{\mathrm{solute}}),$$

where the reference state of the solute is an ideal gas state and x refers to mole fraction. The ΔU *vs.* T relation is plotted in Fig. 2. Except at 353.15 K, the dissolution proceeds exothermically which is evidence for hydrophobic hydration.

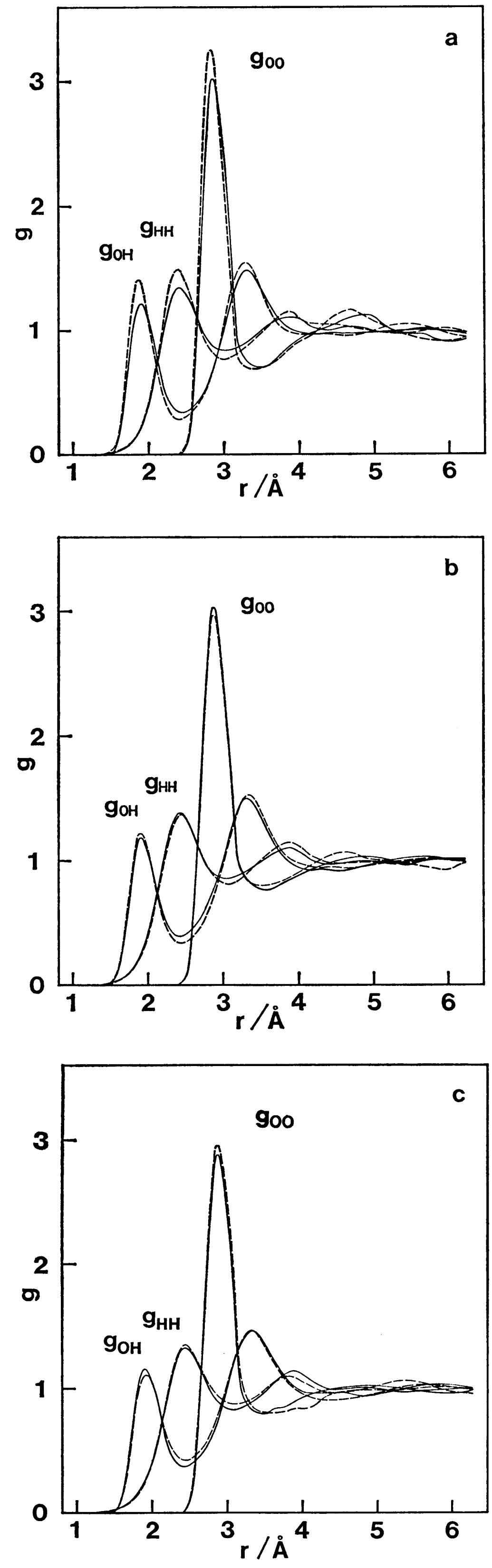

Fig. 3. Atom-atom pair correlation functions, g_{OO}, g_{OH}, and g_{HH} at (a) 298.15 K, (b) 333.15 K, (c) 353.15 K.
Solid line: pure water, broken line: aqueous solution of methane.

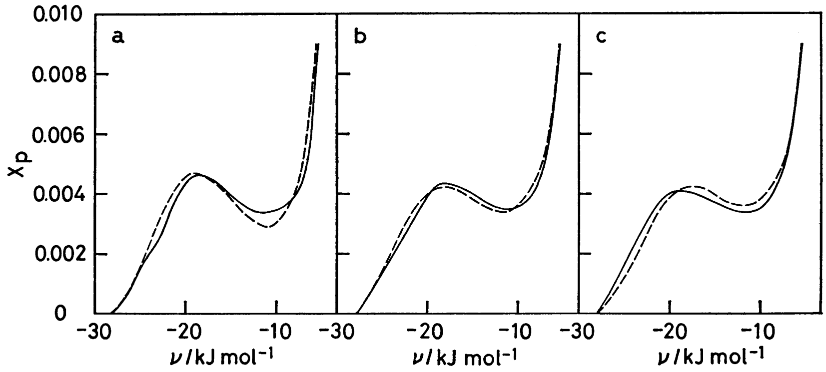

Fig. 4. Pair interaction distribution function x_p at (a) 298.15 K, (b) 333.15 K, and (c) 353.15 K.
Solid line: pure water, broken line: aqueous solution of methane.

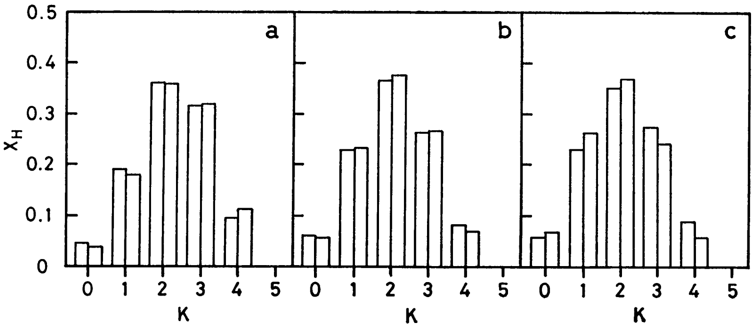

Fig. 5. Hydrogen bonding number distribution function x_H for $\nu_H = -16$ kJ mol^{-1} at (a) 298.15 K, (b) 333.15 K, and (c) 353.15 K.
Left: pure water, right: aqueous solution of methane.

The solubilities of nonpolar molecules in water decrease regularly as temperature increases; then the change in partial molar enthalpies $\Delta\bar{H}°$ associated with dissolution is negative and its absolute values become smaller as temperature increases.[4] The temperature dependence of ΔU obtained from the present MC calculations is in good accordance with that of $\Delta\bar{H}°$. From the positive slope of the internal energy of mixing it becomes clear that the heat capacity of mixing is positive.

Radial Distribution Functions. In order to explore the behaviour of ΔU which reflects hydrophobic hydration in aqueous solutions, we have calculated various distribution functions. In the first place, atom-atom radial distribution functions, g_{OO}, g_{OH}, and g_{HH} are presented and discussed in this subsection. Figure 3 shows the three rdf's as a function of temperature. Among these rdf's, g_{OH} is very important in discussing the structuration of water near the solute because higher positional correlation between oxygen and hydrogen atoms corresponds to stronger hydrogen bonding and is evidence for structuration of water molecules around a nonpolar solute. As is clearly seen in Fig. 3, the height of the first peak of g_{OH} for aqueous solution of methane is much larger than that for pure water only at 298.15 K. At 333.15 K, the correlation is still higher in the case of aqueous solution, though the difference becomes smaller. However, the reverse of this order is observed at 353.15 K, where the correlation is smaller for the aqueous solution. This suggests that water behaves as a normal solvent at this temperature.

Other Distribution Functions. The results of radial distribution functions presented above show a good correspondence with the internal energy of mixing ΔU for the solution at each temperature. It is now interesting to examine the temperature dependence of other distribution functions, such as hydrogen bonding number distribution function (HBNDF) and pair interaction distribution function (PIDF). The former function represents fractions of water molecules which make hydrogen bondings with other K water molecules and the latter function represents fraction of molecular pair which interacts with each other by ν kJ mol^{-1}. The detailed definitions are given elsewhere.[3,8] The results for PIDF are shown in Fig. 4, whereas those for HBNDF are plotted in Fig.5.

We first discuss the PIDF results. It is seen from Fig. 4 that the peak at about -20 kJ mol^{-1} indicates the hydrogen bonding. With the increase in temperature, the peak of PIDF gradually shifts to higher energy direction both for pure water and aqueous solution. The value of ν at the peak for aqueous solution is lower than that for pure water at 298.15 K and 333.15 K. This is the region where the structuration of water due to nonpolar solute takes place significantly. On the contrary, the peak for aqueous solution shifts slightly to higher energy compared with that for pure water at 353.15 K. At this rather higher temperature, most of water molecules seem to behave as an ordinary molecular liquid, though a considerable number of hydrogen-bonded species are still retained.

The above picture can be further confirmed by the information from HBNDF which counts the number of hydrogen bonds in the system. Although we have calculated the distribution functions with different criteria for the hydrogen bonding strength, it is enough for the present purpose to give only the HBNDF at $\nu_H = -16$ kJ mol^{-1}. Figure 5 clearly shows that the number of water molecules with the hydrogen bonding number $K=3$ or 4 in pure water at 353.15 K is evidently larger than that in aqueous solution at the same temperature, indicating overall decrease in hydrogen bonding structure by the introduction of the solute molecule. On the other hand, the fractions of molecules with $K=3$ and especially $K=4$ for aqueous solution are larger than those in pure water at 298.15 K. The fractions for $K=1$, 2, and 3 in aqueous solution are slightly larger than those in pure water at 333.15 K.[9] These are also in the same situation with other distribution functions.

The mole fraction of the nonpolar solute in the present systems is as large as 0.015, which is much more concentrated than that in the gas solubility equilibrium of methane and related compounds in water. In spite of this different situation, one can depict a fairly consistent picture on the temperature effect on the hydrophobic hydration as below.

1) The value for internal energy of mixing ΔU is negative except at 353.15 K.

2) The heat capacity of mixing ΔC_v is positive at all temperatures.

3) Radial distribution function and other distribution functions show that the structuration of water due to apolar solute is significant at 298.15 K and 333.15 K. These are in good correspondence to those observed in solubility measurements of nonpolar molecule in water.

4) At 353.15 K, unique structural properties of water are lost and the introduction of nonpolar solute is energetically unfavourable.

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9) It must be noted that the negative ΔU value at 273.15 K is not due to the increase in the number of hydrogen bonds with larger interaction energy, but due to the enhancement of smaller dipole-dipole interactions. Thus energetical stabilization at 273.15 K is quite different from those at higher temperatures. However, the statistical error in the calculation for 273.15 K is so large that we cannot reach a final conclusion here.