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ARTICLES

Stabilization Energies and Rotational Motions in Clathrate Hydrate of Benzene Studied by Molecular Dynamics Simulations

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Molecular dynamics simulations have been carried out on benzene in aqueous solution and clathrate hydrate (structure II cages) in order to compare the stability of the systems and rotational motions of benzene between 227 and 390 K. The total potential energy is 3−7 kJ mol^{-1} lower in the clathrate hydrate than that in the aqueous phase as a result of the formation of more stable hydrogen bonds in the rigid host frameworks. The rotational relaxation times of benzene molecules in both liquid water and clathrate hydrate cages increase with decreasing temperature. At corresponding low temperatures, however, the relaxation time of benzene in the clathrate hydrate is a few times *shorter* than that in the liquid water, as found recently by NMR experiment. Thus, the anomaly in the relaxation time of benzene experimentally observed can be interpreted as a transition of environment due to the formation of clathrate hydrate in the low-temperature regime.

I. Introduction

Recently dynamic high-resolution NMR spectroscopic studies have discovered that a jump exists in the rotational mobility of benzene-d_6 at around −20 °C and that the line width of the ^{2}H signal of benzene-d_6 remains narrow even at −50 °C as an indication of the presence of fast guest dynamics.[1,2,3] The anomalous increase in the mobility in the low-temperature phase has been interpreted by assuming a rotational speeding up of the guest molecule caused by the formation of a more or less ordered or symmetric clathrate hydrate. The high mobility has been ascribed to the narrow ^{1}H and ^{2}H for benzene in the clathrate hydrate (type II). An alternative interpretation based on the phase separation was discarded because the benzene solubility in water increases with decreasing temperature and because the phenomenon was repeatedly observed without agitation. Nevertheless, the alternative interpretation has been taken by Ripmeester and Ding.[4] The latter interpretation is associated with their observation of a broad ^{2}H NMR signal for benzene-d_6 trapped in the large cages of the structure II benzene-d_6/xenon double hydrate. They regarded the broadness of the solid-state NMR signal as being intrinsic and ascribed it to the low local symmetry of the structure II large cage by neglecting the broadening due to the low resolution. This motivates the present molecular dynamics (MD) simulation study, which can inform us of the intrinsic line shape or the dynamic time scale. Here we want to elucidate: (1) that a jump

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in the rotational mobility of benzene is induced by the clathrate hydrate formation, and (2) that the rotational anisotropy of benzene in both aqueous solution and clathrate hydrate is even smaller than that in pure liquid.[5,6]

Low solubility of hydrocarbons and noble gases in water has long been accounted for in terms of hydrophobic hydration; the decrease in the hydration entropy term dominates over the decrease in the hydration enthalpy.[7] The solubility of an aliphatic hydrocarbon decreases when the alkyl chain has larger size and molecular weight. On the other hand, the reverse holds for the solubility of spherical molecules such as noble gases; the solubility of xenon is much higher than that of neon. This could be accounted for by the stronger interaction mainly due to the large polarizability of xenon compared with that of neon and by a difference in reorganization of water structure in the vicinity of a solute. Benzene occupies a unique position among nonpolar substances. It has a relatively high solubility, and the solubility increases with decreasing temperature. The high solubility enables us to explore purely hydrophobic effect in laboratory experiments such as recent dynamic NMR studies.[1,2,3]

Clathrate hydrate consists of guest molecules and host water molecules, which form hydrogen-bonded polyhedra owing to planar pentagonal and hexagonal rings.[8,9] Two kinds of clathrate hydrate structures have been well-known, which are referred to as *structure I* and *structure II* (*structure H* has recently been found.[10]) The clathrate hydrate is stable owning to interactions between guests and host water molecules. It is this interaction, though weak, that plays a crucial role in the stability of clathrate hydrates. However, only three types of cages for structures I and II are available to accommodate guest species. Those cages are pentagonal dodecahedron, tetrakaidekahedron, and hexakaidekahedron. In order for each type of cage to be firmly hydrogen-bonded, only small fluctuation is allowed in its size. On approaching the limiting cage size to accommodate a guest species, a cage distortion becomes dominant over the guest−water interaction.

Benzene is accommodated only in a large cage of structure II (hexakaidekahedron), while a smaller cage (pentagonal dodecahedron) is left unoccupied by a benzene molecule. The benzene molecule is large enough, and the surrounding cage is expected to be somewhat distorted. Even if this distortion is not energetically unfavorable, the vibrational free energy of host water becomes higher in the presence of large guest molecules than in a clathrate hydrate encaging a small guest. This is because the host vibrational mode frequencies are modulated to the high-frequency side owing to the host−guest interaction.[11−13] Thus, an introduction of a sort of small guest molecule, called a help gas, is required to compensate this unfavorable distortion in a clathrate hydrate containing a large guest. This is indeed the case in the benzene hydrate. Whenever the benzene hydrate is formed under normal conditions, some of the smaller cages are filled simultaneously with help gas molecules.

As mentioned above, NMR spin−lattice relaxation times have recently been measured over a wide range of temperature in order to obtain reorientational relaxation time of benzene molecule in aqueous environment.[1] The relaxation time increases with decreasing temperature down to −20 °C. Upon further cooling, the NMR rotational correlation time becomes three times shorter than that in the aqueous solution. This was accounted for in terms of the formation of a clathrate hydrate structure in the supercooled region without help gas. However, more direct evidence for the formation of clathrate hydrate structure around a benzene molecule is needed.

It is necessary to calculate the free energy of clathrate formation when discussing the stability of benzene hydrate. It is, however, hard to apply the method we proposed previously to thermodynamic stability of benzene hydrate relative to supercooled water[11−13] because no reliable method to evaluate the chemical potential difference between empty hydrate and supercooled water has been established.

Several MD simulation studies on clathrate hydrates have been reported in connection with the thermodynamic stability. Current emphasis has been placed on the difference in the thermal conductivity between ice and clathrate hydrate and on its anomalous temperature dependence[14−17] and on the large thermal expansivity.[18,19] Thus, MD simulation is a powerful tool and can provide an alternative way to investigate a connection between hydrated structure and reorientational relaxation time.

In the present study, several MD simulations are performed in order to examine whether the reorientational relaxation time is much smaller in the less fluctuating clathrate hydrate cage than in the collapsible aqueous solution. It is impossible at the present stage, where computational resources are limited, to realize a nucleation process to crystalline clathrate hydrate structure starting from liquid water and randomly dispersed benzene molecules. Instead, we will examine reorientational relaxation times for benzene in both the clathrate hydrate and the liquid water and compare them to those obtained from experiment. The reorientational time can be a probe to affirm that a benzene hydrate could be made in a deeply supercooled water without any help gas.

The present paper is organized as follows: The intermolecular interactions, cell structure, and the method of MD simulations are briefly described in Section II. Results obtained from MD simulations are presented and are compared with those from experiments in Section III. Our finding is summarized in Section IV.

II. Model and Methods

a. Intermolecular Interactions. The stability of benzene clathrate hydrates and rotational motions of guest benzene are evaluated with intermolecular potentials currently available. In the present study, all interactions are assumed to be pairwise-additive. The water−water intermolecular interaction is described by the TIP4P potential.[20] This potential has been used most frequently in the study of water and is believed to be the most reliable within the framework of pair potential, at least in reproducing thermodynamic and structural properties of pure water. The TIP4P model consists of four interaction sites: a positive charge q_H on the hydrogen atom, a negative charge $(-2q_H)$ on the bisector of two OH bonds, and a Lennard-Jones interaction between oxygen atoms.

The benzene−water and benzene−benzene intermolecular potential functions were obtained from Hartree−Fock level SCF calculation. In this potential benzene has 12 sites located at atom positions.[21] These potential functions are given by

$$\phi(r) = \sum_{i,j} A_{ij}\frac{1}{r_{ij}} + B_{ij}\frac{1}{r_{ij}^4} + C_{ij}\frac{1}{r_{ij}^6} + D_{ij}\frac{1}{r_{ij}^9} + E_{ij}\frac{1}{r_{ij}^{12}}$$

where r_{ij} is the distance between site i and j and the coefficients A_{ij}, B_{ij}, C_{ij}, D_{ij}, and E_{ij} of the potential function are given in ref 21. In several MD simulations, we also examine the effect of help gas on the stability. Methane is chosen as a help gas species. In our model calculation, methane molecules occupy all the smaller cages while the larger cages are filled with

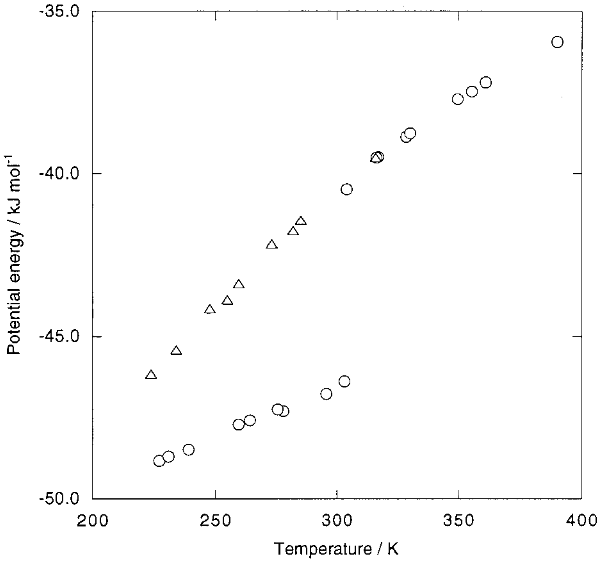

Figure 1. Potential energy for clathrate hydrate and aqueous solution for benzene at various temperatures. MD simulations are started from either clathrate hydrate (open circles) or aqueous solution (triangles). In high-temperature region, clathrate hydrate structure may collapse.

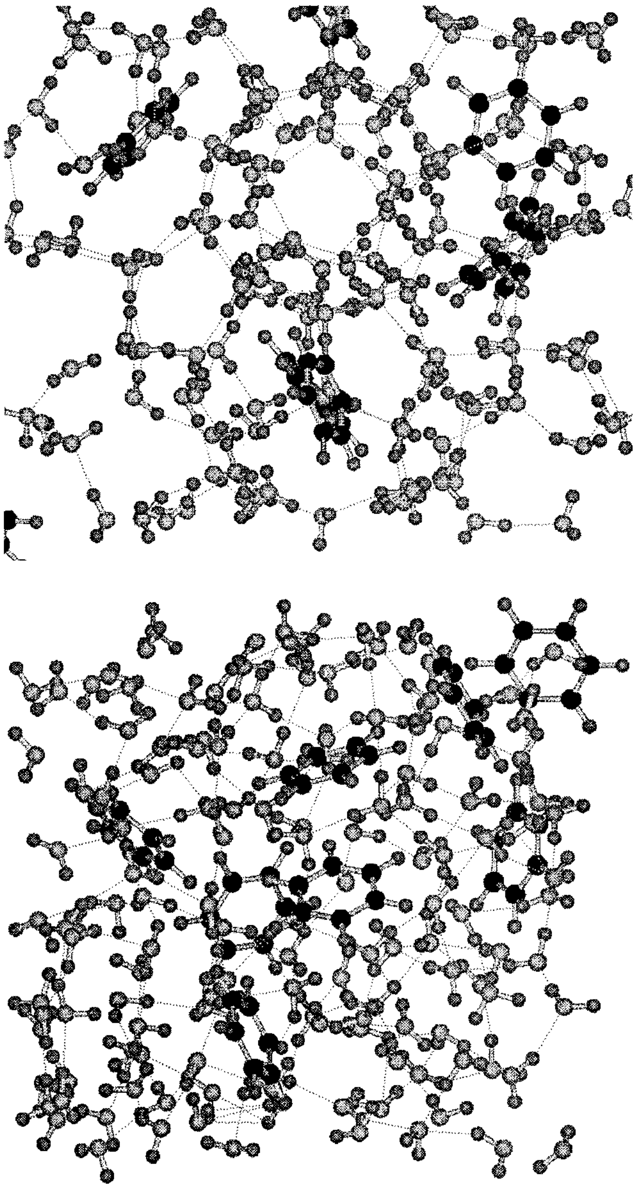

Figure 2. Snapshot of instantaneous structures obtained from MD simulations at temperature 303 K (a, top) and 308 K (b, bottom).

benzene molecules. A methane molecule is approximated to a spherical particle interacting via Lennard-Jones potential whose size and energy parameters are 3.73 Å and 1.25 kJ mol^{-1}.[22] The interaction potentials for all pairs of molecules are truncated smoothly at 8.655 Å.[11]

b. Structure of the Unit Cell. In this study, we use the type II structure of clathrate hydrate. The unit cell of type II structure is cubic and lattice constants are $a = b = c = 17.31$ Å, which are fixed throughout this study. The structure is of proton-disordered form and has zero net dipole moment. There are 8 larger and 16 smaller cages in the unit cell of type II structure. Only larger cages are occupied by benzene molecules. A unit cell of the structure II contains 136 water molecules. The simulation cell is composed of a single unit cell. In examining the effect of help gas, all smaller cages are filled with methane molecules.

c. Molecular Dynamics Simulation. MD simulations are performed with a fixed volume at several temperatures with a constant-temperature method to examine the rotational motions of benzene molecules. The numbers of water and benzene molecules are 136 and 8, respectively. The temperatures, T, are set to 18 values from 227 to 390 K for the clathrate hydrate and 9 values from 224 to 316 K for aqueous solution. The time step Δt for the integrations of motion is 5.0×10^{-16} s. The number of time steps is 100 000 for calculation of potential energy and rotational relaxation times in each MD simulation after temperature control of 100 000 and equilibration period of 600 000 time steps.

III. Results and Discussion

First of all, we show that the benzene hydrate is energetically more stable than the aqueous solution at low temperatures. In Figure 1 are plotted the total potential energies for both the clathrate hydrates and the aqueous solutions of benzene as a function of temperature. The total potential energy includes all the interactions, water−water, water−benzene, and benzene−benzene. The potential energies for the both phases monotonically increase as temperature is raised. The potential energy difference between clathrate hydrate and aqueous solution is about 3−7 kJ mol^{-1} in the low-temperature regime, which is large enough to distinguish the two phases. The difference becomes larger with increasing temperature. This arises from an anharmonic energy, whose temperature dependence is more significant in the liquid state than in the crystalline state. When the clathrate hydrate is heated, its potential energy has a sudden jump at around 308 K as an indication of the lattice collapse. Above this temperature, the potential energy of the clathrate hydrate lies on the line of the aqueous solution.

Snapshot pictures may be useful for examining how benzene molecules are solvated or aggregated in the clathrate hydrate and the aqueous solution. A snapshot of the clathrate hydrate at 303 K given in Figure 2 a illustrates that individual benzene molecules are encapsulated by polyhedra. In contrast, a snapshot at 308 K in Figure 2b clearly shows that benzene and water molecules are randomly distributed without regular polyhedra, which indicates a phase separation is unlikely to occur.

Although the potential energy of the whole system increases upon the lattice collapse as shown above, the potential energy of the guest benzene might have a different tendency from the total potential energy. Indeed, the potential energy of benzene

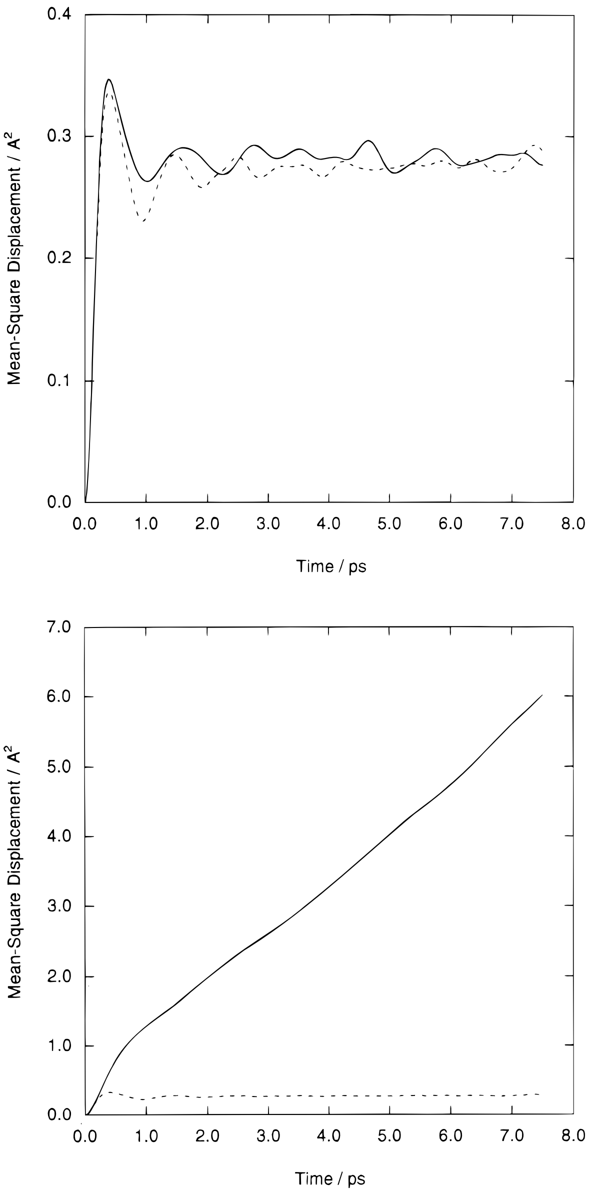

Figure 3. Mean-square displacement for benzene at 303 K (a, top) and 308 K (b, bottom). Solid line, without help gas; dashed line, with help gas.

in clathrate hydrate at 303 K (-52.41 kJ mol^{-1}) is higher than that in aqueous solution at 308 K (-54.05 kJ mol^{-1}). In the clathrate hydrate, the guest molecule is trapped in the approximately spherical cage. Even if the cage is occupied, some vacant space is left inside the cage. Therefore, a benzene molecule interacts more strongly with water molecules in an aqueous environment than in clathrate hydrate, which results in slower rotational relaxation in aqueous solution.

Let us inspect dynamical aspects of the two phases. Oscillatory character of mean-square displacement (MSD) at 303 K presents a striking contrast to a linearly sloped MSD at 308 K as shown in parts a and b of Figure 3, respectively. Although no translational diffusion for benzene is observed at 303 K, the self-diffusion coefficient is 1.2×10^{-5} cm^2 s^{-1} at 308 K, which is in good agreement with experiment.[3] The mean vibrational amplitudes of water in the solid phase (square root of plateau values for MSD) are 0.34, 0.37, and 0.41 Å at 223, 273, and 303 K, respectively, with an average intermolecular (O−O) separation of 2.8 Å. Usually, melting occurs when Lindemann's parameter, which is defined as the mean vibrational amplitude divided by the average intermolecular distance, exceeds approximately 0.1.[23] The relative mean vibrational amplitude of the clathrate hydrate just below the lattice collapse temperature in our simulation is 0.15, which is slightly larger than Lindemann's criterion. This can be attributed to the nature of the perfect crystalline clathrate hydrate and to the fixed volume in our simulation. It is known that a perfect crystal without a surface can be superheated substantially above its thermodynamic melting temperature.[24] In our simulation, the lattice collapse corresponds to the mechanical instability of the crystalline structure.

TABLE 1: Rotational Relaxation Times for Benzene

from clathrate hydrate			from aqueous solution			experimental data	
temp (K)	$\tau_{2R\perp}$ (ps)	$\tau_{2R\parallel}$ (ps)	temp (K)	$\tau_{2R\perp}$ (ps)	$\tau_{2R\parallel}$ (ps)	temp (K)	τ_{2R} (ps)
223	0.994	0.991	223	5.11	4.48	223	4.26
233	0.888	0.830	233	3.02	3.00	235	3.55
243	0.838	0.872	243	2.93	3.75	243	2.78
253	0.774	0.792	253	2.62	2.78	251	2.45
263	1.02	1.02	263	2.78	3.02		7.96[a]
273	0.785	0.731	273	1.88	1.97	253	2.43
283	0.796	0.766	283	2.00	1.94		7.30[a]
293	0.768	0.747	293	1.69	1.64	273	3.58[a]
303	0.784	0.766	303	1.35	1.24	303	1.88[a]
308	1.29	1.44				333	1.25[a]
313	1.33	1.29				353	1.03[a]
318	1.14	1.32				373	0.878[a]
323	1.22	1.18					
333	0.987	1.02					
343	1.06	1.03					
353	1.02	1.16					
363	0.958	0.977					
373	0.914	0.943					

[a] In the clathrate hydrate.

A time correlation function, $\theta(t)$, associated with rotation of the unit vector **u** is given by

$$\phi(t) = \langle P_2(\cos\theta(t))\rangle = {}^1/_2\langle 3\cos^2\theta(t) - 1\rangle$$

where $\cos\theta(t)$ is defined as

$$\cos\theta(t) = \mathbf{u}(t)\cdot\mathbf{u}(0)$$

The measured rotational correlation time τ_{2R} is evaluated by integrating the time correlation function as

$$\tau_{2R} = \int_0^\infty \langle P_2(\theta(t))\rangle \, dt$$

For the case of symmetric top molecule such as benzene, there are two kinds of correlation times associated with the rotations *of* and *around* the 6-fold rotational axis. The former and the latter are called molecular tumbling (⊥) and spinning (||) and the rotational correlation times are denoted by $\tau_{2R\perp}$ and $\tau_{2R\parallel}$, respectively. The rotational anisotropy can be expressed in terms of the ratio

$$\chi = \tau_{2R\perp}/\tau_{2R\parallel}$$

This quantity reflects to what extent molecular rotations deviate from the spherical one. The rotational correlation times calculated from MD simulation are compared with those determined by NMR measurement in Table 1. Before discussing these, we note that in the case of ^{2}H spin−lattice relaxation times, the unit vector **u** in eq 3 is defined by the C−D bond

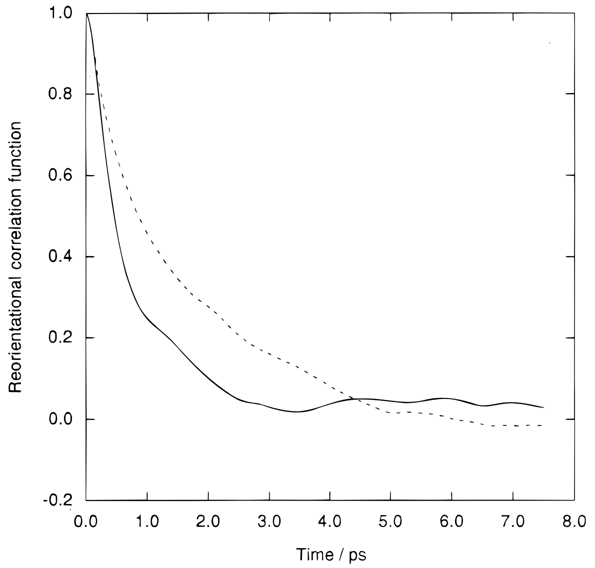

Figure 4. Reorientational correlation function for benzene at 303 K (solid line) and 308 K (dashed line).

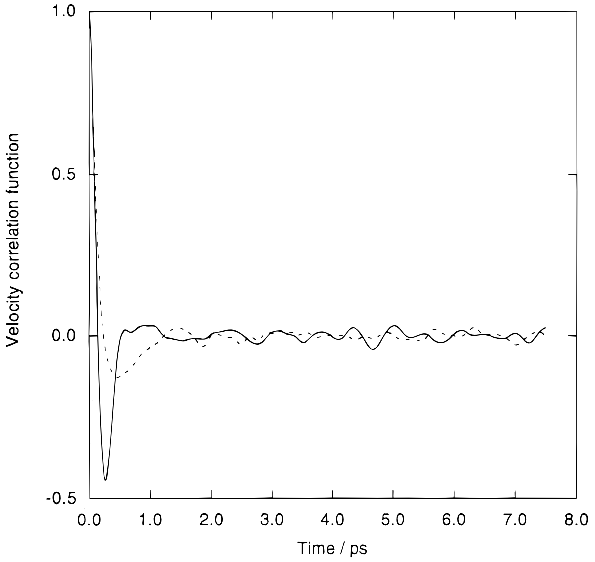

Figure 5. Velocity autocorrelation function for benzene at 303 K (solid line) and 308 K (dashed line).

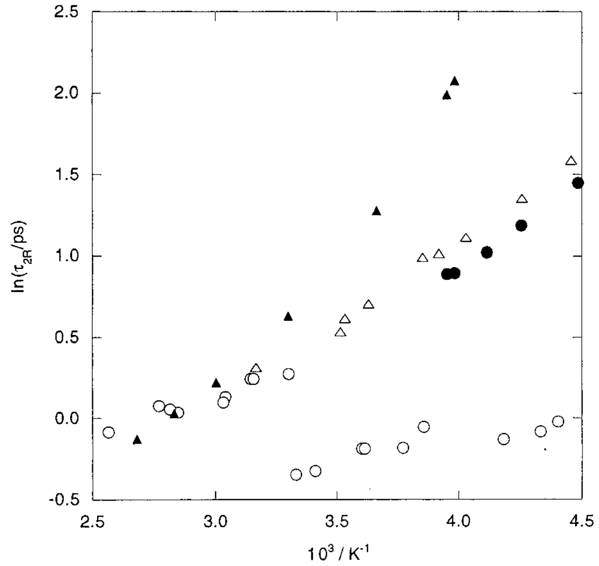

Figure 6. Arrhenius plot of rotational relaxation times, τ_{2R}, for benzene in clathrate hydrate or aqueous solution (open circles, clathrate hydrate; open triangles, aqueous solution; filled triangles and circles, experimental).

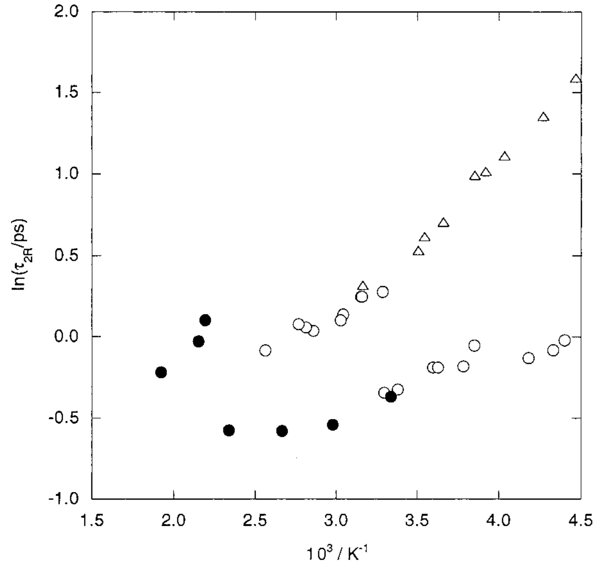

Figure 7. Arrhenius plot of rotational relaxation times, τ_{2R}, for benzene in clathrate hydrate (open circles and triangles, without help gas; filled circles, with help gas).

vector in the molecular plane of benzene-d_6. Both $\tau_{2R\perp}$ and $\tau_{2R\parallel}$ contribute to the correlation time τ_{2R} determined experimentally.

Typical time-correlation functions for benzene in the drastically different states are shown in Figure 4, where the temperatures are nearly the same but water mobilities are different. Noticeably, the correlation function for the liquid state exhibits, on the contrary, slower decay (larger friction coefficient) compared with that of the clathrate state. As to the translational motions of benzene, a more sharp oscillation is seen in the clathrate hydrate than in liquid state as shown in Figure 5.

The relaxation times at various temperatures in the different phases are summarized in Table 1, and the Arrhenius plots are also given in Figure 6. The relaxation time becomes longer with declining temperature in both the clathrate hydrate and aqueous solution. A discontinuity in the temperature dependence of relaxation time is found at around 300 K, which is the same location as the sudden change appears in the potential energy (see Figure 1). Thus, the discontinuity of the relaxation time is associated with a marked change in structure from the clathrate to the aqueous solution. In our simulation, the rotational correlation times τ_{2R} decrease by a factor of 2. The jump is observed around 250 K in laboratory experiment and the difference in the relaxation time between solution and clathrate is smaller in MD simulation than the observed one: three times longer in the liquid water than in the clathrate.[1] Although the observed relaxation time itself is somewhat different from the calculated one, the potential energy (Figure 1) and the relaxation time (Figure 6) plots clearly show the anomalous temperature dependence of the rotational relaxation time arises from the formation of the benzene clathrate hydrate. The transition temperature in the MD simulation lies between 303 and 308 K, while the experimental value lies around 250 K. This difference can be accounted for by considering that we adopt a fixed volume condition and that a perfect crystalline form is simulated in MD study. Apart from the transition temperature, the jump in the relaxation time upon melting is successfully simulated in good agreement with experiment.[1]

Is the present MD simulation supporting the experimental observation of a sharp signal for benzene-d_6 in both the clathrate hydrate and aqueous solution? This is an important question in the sense that the anomalous jump in the rotational mobility of benzene has been interpreted in two manners as mentioned in the Introduction. As can be seen in Table 1, the benzene rotations are almost isotropic in the clathrate hydrate as in the aqueous solution. In the neat benzene liquid, the anisotropy factor, χ, is reported to be about 2 in both experiment[5] and simulation.[6] Thus, the cage symmetry in the clathrate hydrate is fairly high on average. The motional narrowing due to the high rotational mobility as well as high cage symmetry is responsible for the sharp ^{2}H signal observed for benzene-d_6 in the clathrate hydrate.

Finally, we show the effect of help gas molecules on the dynamics of guest molecules and the collapse of the host framework.[25] We performed MD simulations for benzene clathrate hydrate in which all the smaller cages are occupied with methane molecules and examined how the rotational relaxation time of benzene is affected by the cage occupation. As seen in Figure 7, the occupation of the help gas in the small cages results in a drastic increase in the melting temperature of the lattice collapse; the shift is as large as 150 K. This large shift indicates that the help gas plays a crucial role in stabilizing the benzene hydrate. In fact, it is experimentally observed that the benzene solution must be cooled to a very low temperature such as 250 K so that it may be transformed into the clathrate hydrate. The rotational correlation time of benzene itself is dependent on temperature but insensitive to the cage occupation by the help gas. Thus in the clathrate hydrate, the rapid relaxation is controlled locally by the large cage polyhedron.

IV. Conclusions

MD simulations have been carried out in order to investigate rotational motions of benzene in aqueous solutions and also those confined in cages of clathrate hydrates. It is reasonable to conclude in the following observations that the experimentally observed anomaly in the rotational correlation time arises from a transition of environment: the formation of clathrate hydrate in low-temperature regime.

(1) The potential energy of the clathrate hydrate exhibits a sudden jump by about 7 kJ mol^{-1} at a certain temperature, above which the rigid lattice framework is transformed into an aqueous solution.

(2) The potential energy of benzene in the clathrate is higher than that in the aqueous solution. This implies that the guest benzene molecule is not bound to the surrounding water molecules and its rotation is less hindered in the clathrate hydrate than in the aqueous solution.

(3) The rotational correlation time changes by factor of 2 at the same temperature where the potential energy jumps.

(4) The present structural and dynamical analyses based on the MD simulation show that the molecular field felt by the guest benzene is not inhomogeneous but rather spherical as observed by the recent solution NMR experiment.

(5) The help gas changes the transition temperature as expected from theoretical consideration. However, it does not affect the magnitude of the rotational correlation at the same temperature.

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(25) In the present MD simulation, the lattice structure remains intact without any help gas even at 303 K. This does not mean the true melting point exists around 303 K. This temperature corresponds to the limit of mechanical stability as shown by Lutsko.[24] However, this does not rule out the benzene clathrate hydrate without help gas at deeply supercooled state because its stability increase with declining temperature.