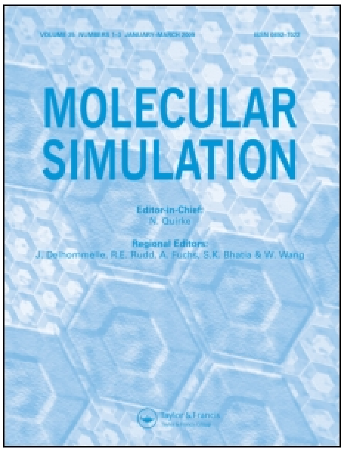

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ON THE STABILITY OF CLATHRATE HYDRATES ENCAGING POLAR GUEST MOLECULES: CONTRAST IN THE HYDROGEN BONDS OF METHYLAMINE AND METHANOL HYDRATES

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The stability of clathrate hydrates encaging highly polar guests has been investigated in order to explain the experimental observation that some amines form clathrate hydrates but alcohols act as inhibitor to hydrate formation. We choose methylamine and methanol as guest species and examine the stable structure, at which the total potential energy has a minimum value. At the local minima of those two hydrates, the potential energies of water-water and guest-water, and their hydrogen bonded networks are compared. It is found that methanol does not retain the host lattice structure, while the host-network structure is kept in the presence of methylamine. It is shown that the difference in the magnitude of the partial charge on the hydrogen atom between the hydroxyl and amino groups plays a much more significant role on the stability of both clathrate hydrates than the difference in molecular geometry. This is supported from the result of a methylamine-like model that has the same partial charges on the atoms in the hydrophilic site as methanol.

KEY WORDS: Clathrate hydrates, amines, alcohols, potential energy local minimum structure, hydrogen bond network

1 INTRODUCTION

Clathrate hydrates are essentially crystalline solids which consist of host water molecules located at the lattice sites and guest molecules occupying almost spherical cavities in the host lattice. Each host water, which is the main component of any hydrate, is connected by hydrogen bonds to four neighbors, in a similar way to ice. In general, each guest molecule encaged in the host lattice interacts with the water molecules through dispersion forces. The guest molecules do not interact through strong attractive forces, which may form hydrogen bonds between the guest and the host. It is also recognized that some of the cavities, but not all, need to be occupied by guests [1, 2]. Two types of crystalline, structures are known, which are referred to as structure I and structure II. These are conveniently called "true clathrates", which are distinguished from "semi-clathrate hydrates". Semi-clathrate hydrates have different hydrogen bond networks from true clathrate hydrates. In semi-clathrate hydrates, the guest molecules replace a number of water molecules in the host network structure. The present study is concerned only with "true clathrates", which we hereafter simply call clathrate hydrates.

Clathrate hydrates have attracted attention from an industrial point of view, since it was found that they were formed in and plugged natural gas pipelines. Also, there are huge amounts of methane and propane hydrate, which may provide a source for natural gas. The use of clathrate hydrates in the storage of carbon dioxide may be one of their most promising future applications. Scientifically, some anomalous properties of these substances are interesting. Fundamentally, clathrate hydrates resemble ice in their structure. However, they have much lower thermal conductivities than that of ice; and, unlike crystalline solids, the temperature dependence of their thermal conductivity is glass-like. An investigation of their formation mechanisms and melting processes is also intriguing.

The thermodynamic stability of clathrate hydrates has long been explained by the van der Waals and Platteeuw (vdWP) theory [3]. Recently, a generalization of the original vdWP theory has been proposed [4]. This enables us to evaluate the free energy of formation solely in terms of the intermolecular interactions. It is also free from some of the fundamental assumptions imposed on the original vdWP theory. Computer simulation has been used to study both the static and dynamic properties of clathrate hydrates from the microscopic point of view [5–9]. Some simulation studies focused on the effect of various guest molecules on the stability of the clathrate hydrates. In one case, the thermal expansion of structure I ethylene oxide hydrate was measured by X-ray powder diffraction, and then compared with the simulated results [7].

Both amine and alcohol molecules consist of hydrophobic and hydrophilic parts; the latter is the amino or the hydroxyl group. According to Franks [10], amines and alcohols are classified as "typical hydrophobic" solutes when dissolved in water. It is known that amines are clathrate-forming species. Although some amines form semi-clathrate hydrates, ethylamine, for example, is accommodated into the cage to form a structure I clathrate [1]. On the other hand, alcohols, like salts, generally act as inhibitor to clathrate formation. So far, no account has been given of different behavior of amines and alcohols in hydrates. The purpose of the present study is to clarify why some amines can be the guest species in a stable clathrate but alcohols cannot.

It is impossible at present to evaluate the thermodynamic stability of hydrates which encage non-spherical guest molecules by the generalized vdWP theory. We will make an alternative evaluation of the hydrate stability. In "true hydrates", the following two conditions must be fulfilled: (1) all the water molecules must have their four neighbors firmly hydrogen bonded; (2) guest molecules must not take part in the hydrogen bond network. An investigation of the stability of the clathrate hydrates can be done by stepwise analyses. That is to say, the first step is devoted to examining whether or not a clathrate of each guest species satisfies the clathrate-forming conditions at the potential energy local minimum. At the second stage, thermal motions are taken into account. It is expected that there is a large difference in the stability between amine and alcohol hydrates as conjectured from the clear distinction in the hydrate forming ability of the two. If true, the above question concerning the stability is rather easily answered at the first stage, by simply examining the structure at which the total potential energy takes its minimum value. Unless the structure of the local energy minimum satisfies the conditions for a 'true clathrate hydrate', the thermally excited hydrate cannot exist. Thus, we expect to be able to clearly estimate the stability or the instability of clathrate hydrates, by analyzing the local energy minimum structure.

In this paper, we present the first stage results for amine and alcohol clathrates.

To analyze the structure of the clathrate hydrates at the local minima, the total potential energy was divided into the potential energy of the host lattice, and that of the guest; and the hydrogen bonded networks encaging amines and alcohols were compared.

2 METHOD AND MODELS

Local energy minimum structures were obtained by the steepest descent method under periodic boundary conditions. Methylamine and methanol were chosen as guest molecules since these are the simplest amine and alcohol. We adopted structure I for methylamine and methanol clathrate hydrates, because the type of hydrate structure (either type I or II) depends largely on the size of the guest molecules. The diameters of methylamine and methanol obviously belong to a group of guest molecules which form structure I clathrate hydrates. Methane was adopted as a help gas in order to examine its contribution to the stability.

2.1 *Potential Model*

In the present study, the intermolecular interaction are described by sum of the simple intermolecular pair potential functions. The potential function, ϕ, for any pair is given by

$$\phi = \sum_{i,j} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{Z_i Z_j e^2}{r_{ij}}, \tag{1}$$

where t and j denote interaction sites, and the sum is taken over all the site-site pairs. The TIP4P water model [11] was used for describing the water-water interaction, since it is well known that this model can successfully reproduce both the static and dynamic properties of pure water. We used the OPLS parameters for the methanol model [12] and the parameters used by Weiner *et al.*, with some modifications, for the methylamine [13, 14]. The parameters for the like-site pair are listed in Table 1. The so-called Lorentz-Berthelot rule was adopted for the parameters between the unlike-sites.

The original potential functions were tapered by multiplying by a switching function, in order to avoid discontinuity at the cut-off distance from the central molecule. The functional form of the switching function is given elsewhere [15].

To ascertain the physical origin of the difference in the stability between amine and alcohol clathrate hydrates, an artificial molecule was also examined. This model mimics the methylamine in *molecular structure*, but the magnitude of the *charges* on nitrogen and hydrogen atoms in the hydrophilic group are respectively set equal to those on oxygen and hydrogen of methanol molecule. The parameters for this model are also listed in table 1.

2.2 *System*

46 water molecules are confined in a basic cubic box that corresponds to the unit cell of structure I (the cell constant L is 12.03 Å), in a way in which the oxygen atoms of the water molecules are placed on the lattice sites. The initial host structure

Table 1 Parameters for the water and guest molecules.

	site	σ(Å)	ϵ(*kJ/mol*)	*Z*
H_2O	O	3.154	0.6487	0
	M	0	0	−1.04
	H	0	0	0.52
CH_3NH_2	CH_3	3.861	0.7577	0.21
	N	3.475	0.3347	−0.79
	H	0	0	0.29
CH_3OH	CH_3	3.775	0.866	0.265
	O	3.070	0.711	−0.70
	H	0	0	0.435
Methylamine-like model	CH_3	3.861	0.7577	−0.17
	N	3.475	0.3347	−0.70
	H	0	0	0.435
CH_4	CH_4	3.758	1.2355	0

has a proton-disordered form, which is generated according to the ice rule, with a constraint of zero net dipole moment of the unit cell. All of the six larger cages in the unit cell are occupied by guest molecules, and the two smaller cages are either empty or occupied by help gas molecules. The centers of mass for the six guests are located at the centers of the cages, and the orientation of the six guests is assigned randomly. We generate twenty different sets of these orientations as our initial configurations. The potential cut-off radius, r_c, is 8.655 Å.

2.3 *Potential Energy Local Minima*

The steepest descent method is applied to hydrates in order to obtain the local potential energy minimum configurations from some initial structures, by solving the following partial differential equation:

$$dr_i/dt = -\partial\Phi/\partial r_i, \tag{2}$$

where Φ denotes the total potential energy function of the system and r stands for the six coordinates of each molecule: three center of mass coordinates and three Euler angles to specify the molecular orientation. Since the calculation of the gradient of the potential, with respect to the Euler angles, costs more CPU time than calculating torque, we use the relation between the derivatives of the potential energy, with respect to the Euler angles, and the torque acting on each molecule in the molecule-fixed framework [16],

$$\begin{aligned} -\partial\Phi/\partial\theta &= N_x\cos\psi - N_y\sin\psi \\ -\partial\Phi/\partial\phi &= N_x\sin\phi\sin\psi + N_y\sin\phi\cos\psi + N_z\cos\theta \\ -\partial\Phi/\partial\psi &= N_z \end{aligned} \tag{3}$$

where θ, ϕ, and ψ are the Euler angles and N is the torque on each molecule.

The initial orientation of the guest molecules is randomly assigned using random numbers. It is, however, reported that the rotational motion of even non-polar guests is not completely free, due to the oblate shape of the cages [17, 18]. Moreover, strong interaction is expected between the methylamine or methanol guests and the host water molecules. Therefore, some orientations may be unlikely to or never occur in real hydrates. If those energetically unfavorable orientations are assigned, the host-network structure may easily collapse. To avoid such breakdown, we obtain the local minimum structure by the following three step calculation:

(i) quench the initial structure of an empty hydrate to the corresponding potential minimum structure;
(ii) put the guest molecules into the cages with random orientations and solve Equation (2) for only the guest molecules interacting with the fixed host water molecules, which are obtained in (i);
(iii) solve Equation (2) for all molecules in the system obtained in (ii).

The first step gives the most stable initial host-network structure (note that this structure is metastable, since no guest exists in any of the cages). The second step removes any energetically "uncomfortable" orientations of the guest molecules in the fixed host-network. Finally, the local minimum structure is obtained in the third step.

3 RESULTS AND DISCUSSION

3.1 *Potential energies at the local minima*

The potential energies for methylamine and methanol clathrate hydrate at the local minima, as averaged over the twenty systems, are listed in Table 2. The stability of the clathrate hydrate can be investigated by examining the hydrogen bonds of the host-network structure. In order to account for the origin of the stability of these two hydrates, the total potential energy of the system, U_{total}, is divided into two: the contributions made from water-water interaction, U_h, and that made from the sum of guest-water and guest-guest interactions, U_g. In addition, the host-network energy for the empty hydrate, U_h^*, is listed in Table 2, as obtained in the first step calculation. The potential energy U_h for the methylamine hydrate is lower than the methanol hydrate by 1.80 kJ/mol. The energy difference between the occupied and empty hydrates, $\Delta U_h = U_h - U_h^*$, is 0.25 and 2.05 kJ/mol for the methy-

Table 2 Potential energies for the local energy minimum structures. All units are in kJ/mol. h and g stand for the host and guest, respectively. U_{total}, U_h, and U_g are the potential energies fot the system, the host-host, and the guest contribution; the values are for a mole of the whole, water, and guest molecules, respectively. An asterisk indicates the energy just before the third step calculation; $\Delta U_g = U_g - U^*_g$. All the values are the average over the twenty systems.

	Methylamine	*Methanol*
U_{total}	−51.62	−53.37
U^*_h	−54.83	−54.83
U_h	−54.58	−52.78
U_g	−28.93	−57.90
ΔU_g	−3.683	−26.81

lamine and methanol guests, respectively. These results indicate that the methylamine hydrate has a more stable host-network at the local energy minimum in the configuration space than the methanol hydrate. The accommodation of methanol leads the host-network to an energetically less stable state, compared with methylamine.

We pay attention to the difference in U_g between the methylamine and methanol system: U_g (methanol) $-$ U_g (methylamine) $= -29.0$ kJ/mol. This conspicuous difference in U_g contains two factors: (1) the guest-host and guest-guest interactions when the host network structure is fixed to the empty hydrate structure; (2) the potential energy change in the guest-host and the guest-guest interactions, when the total potential energy is at its minimum, allowing all the host and guest molecules to relax. The former, which is obtained in the second step, is estimated from U_g^*-that is, the potential energy of guest in the host-network structure fixed to the empty hydrate. The latter is evaluated in terms of the change of U_g in the third step calculation: $\Delta U_g = U_g - U_g^*$. This difference arises from the deformation of the cage structure, which also affects the difference in the host-host interaction, ΔU_h. U_g^* for methanol clathrate is lower than that for methylamine clathrate by 6 kJ/mol. This indicates that methanol interacts with water molecules more strongly than methylamine, due to the nature of the methanol molecule. A much larger value of ΔU_g for methanol hydrate is obtained: the ratio of methanol to methylamine amounts to more than 7. This result suggests that the stronger interaction for methanol at the local minimum structure is mainly due to the difference in the host-network structure. This conjecture is consistent with the ΔU_h result.

3.2 *Hydrogen bonded network analysis*

The local energy minimum structures for methylamine and methanol clathrates are investigated by examining, firstly, whether or not they are composed of only water molecules connected with four neighbors by hydrogen bonds and, secondly, whether or not there is any hydrogen bond with a guest molecule. It is found that the host lattice structure encaging methanol is considerably different from that encaging methylamine. In the present study, we regard an arbitrarily chosen pair of molecules as a hydrogen bonded pair if the potential energy of the pair u_{ij} is lower than a threshold value, u_{HB}. This definition, dependent only on the pair potential energy, has often been used to describe hydrogen bonded network systems. No appreciable differences were found, compared with other definitions such as those based on the mutual geometry of pairs of molecules.

The distributions of the number of hydrogen bonds of individual water molecules are given in Figure 1. Here we choose the $u_{HB} = -16$ kJ/mol (we will adopt this choice unless otherwise mentioned). For the methylamine systems, almost all the water molecules have four hydrogen bonds, although 0.33% of the water molecules are hydrogen bonded with three neighbors. On the other hand, for the methanol systems, 13.7% of the water molecules do not have four hydrogen bonds. Among the 46 water molecules in the unit cell, the average number of water molecules which are hydrogen bonded with three and two neighbors are 5.1 and 1.0, respectively. Even water molecules having only one hydrogen bond with other water molecules are found in the methanol hydrate. Thus we conclude that the host-network structure for the methanol systems, at the local energy minimum, is clearly different from that of a "true clathrate hydrate"; whereas that the hydrate I structure is

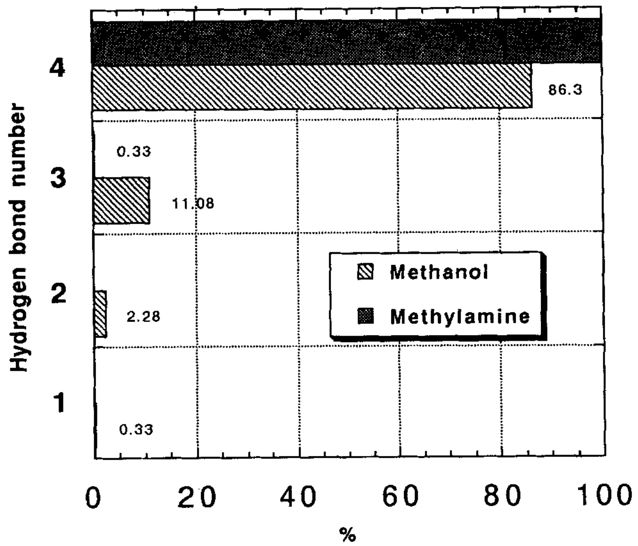

Figure 1 Comparisons of the distribution in the number of hydrogen bonds for each water molecule in the host structure I lattice encaging methylamine and methanol guests. The two distributions are the average over the twenty systems, and are depicted with the different pixel patterns shown in the figure. The hydrogen bond energy criterion is −16 kJ/mol.

almost always kept in the case of methylamine hydrate.

It is also confirmed that our conclusion is independent of the particular energetic criterion chosen. Here we present some results where the $u_{HB} = -14\,\mathrm{kJ/mol}$. Although the percentage of deficient hydrogen bonded water decreases in the methanol hydrate, imperfect host network structures are always obtained for all of the twenty initial configurations. For the methylamine systems, no defect in the hydrogen bonded network of the host is found in any of the initial configurations. One can see that any water molecule that is hydrogen bonded with only three neighbors under a stringent criterion of −16 kJ/mol turns to a fully hydrogen bonded molecule when a looser criterion is adopted.

The hydrogen bonds between the host and guest are examined by the same method as used in the host-network analysis. Figure 2 shows the distribution of the guest-host hydrogen bond numbers per guest molecule for the methylamine and methanol clathrates. It can be seen that no guest methylamine forms a hydrogen bond with its neighboring host water molecules at the local energy minimum structure, no matter which initial configuration of guest molecules is chosen. In contrast, the guest methanol has a strong tendency to form hydrogen bonds with the water molecules: over 70% of the methanol molecules are connected by a hydrogen bond with at least one of the host water molecules. Thus, a comparison of the number of hydrogen bonds between the guest and host indicates that the attractive interaction between water and methanol is much stronger than that of methylamine-strong enough to break the hydrogen bonds in the host network.

We also examine the effect of using a "help gas" to stabilize the host network.

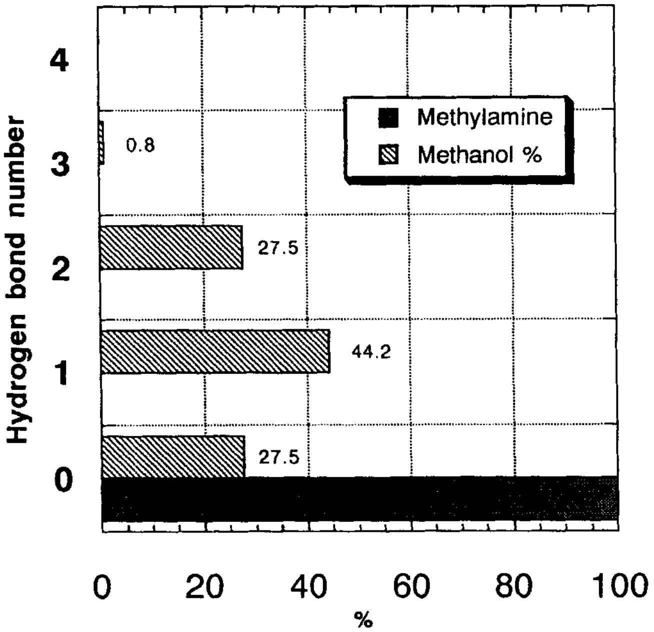

Figure 2 Comparisons of the distribution of the number of hydrogen bonds for each guest methylamine and methanol encaged in the structure I hydrates. The energy criterion is the same as that in Figure 1.

We pick up three initial configurations, in which some hydrogen bonds in the host network are broken upon the inclusion of methylamine guests. It is found by the hydrogen bond network analysis that all the water molecules have four hydrogen bonded neighbors in any case of inclusion of the help gas in the smaller cages, although the difference in the potential energy of the host water between two hydrates with and without help gas is, at most, −0.011 kJ/mol. However, in spite of the introduction of help gases, no methanol clathrate keeps an unbroken host network at the local energy minimum.

Examples of the local energy minimum structure of the methylamine and methanol systems are illustrated in Figure 3. The methylamine host network keeps almost perfect structure I polyhedral cages, while the cages in the methanol clathrate hydrate are distorted and the host network is partly broken. In particular, some of the hydrogen bonds between water and methanol molecules are formed, in place of hydrogen bonds between water molecules. When this happens, the hydrogen bonds connect oxygen (water) with hydrogen (methanol), or hydrogen (water) with oxygen (methanol). Thus, we conclude that the methanol guest does not form a clathrate hydrate at the local energy minimum structure. Namely, methanol hydrates will never be produced, even though the hydrate is not thermally excited, while the methylamine guest satisfies the clathrate forming conditions at the local minimum structure.

Next, we consider what makes the significant difference in the stability of amine and alcohol hydrates. Methanol and methylamine have two different aspects that

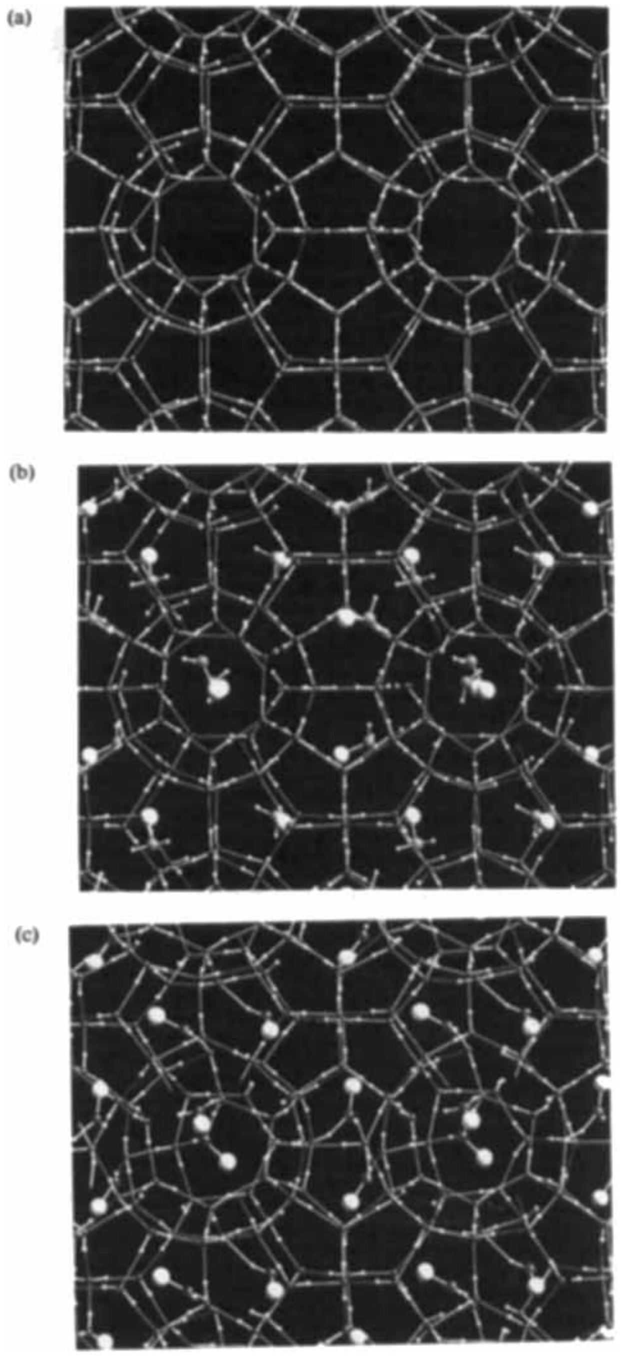

Figure 3 Examples of the local energy minimum structures of the (a) empty, (b) methylamine and (c) methanol clathrate hydrate. The hydrogen bonds between water molecules and between guest and water molecules are colored yellow and purple, respectively. (See colour plates)

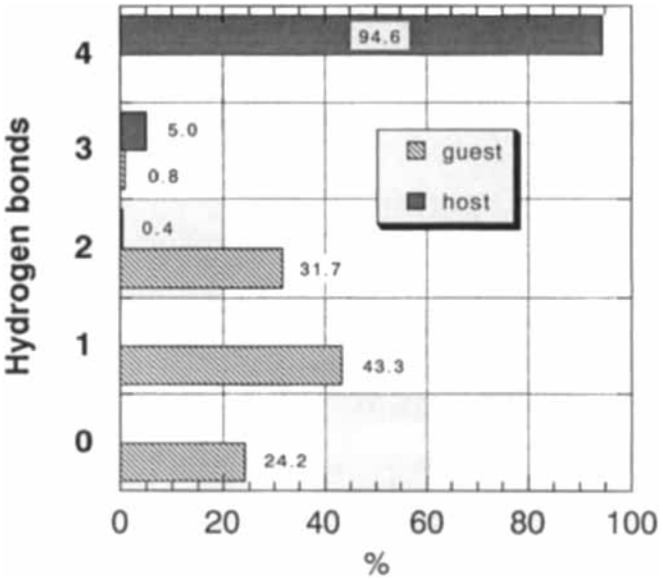

Figure 4 Distributions of the number of hydrogen bonds for each host water molecule and for the guest methylamine-like model at the potential energy local minimum structure. The distributions are the average over the twenty systems and depicted with the different pixel patterns shown in the figure. The energy criterion is the same as that in Figure 1.

may affect the stability of the clathrate hydrate: the molecular structure, and the partial charges on the hydroxyl and the amino group. It is found that the stable host network structure is not compatible with the strong attractive guest-host interaction, which is described by the Coulombic interaction between a hydrophilic group and water. As an additional test, we adopt a "methylamine-like model", whose geometrical and LJ parameters are identical to those of methylamine, but the magnitude of the partial charges on the hydrogen and the nitrogen atom are identical to those on the hydrogen and oxygen atom of methanol. The local energy minimum structures are obtained for twenty initial configurations by the same procedure as used previously. The distribution of the number of hydrogen bonds for the host network and for the guest are shown in Figure 4. The shapes of these distributions are obviously similar to those of methanol, and not to methylamine. The host network structure is not seriously deformed compared with those in the methanol hydrate, but far from the normal state such as in methylamine clathrate hydrates. The number of hydrogen bonds between the guest and host molecules is almost the same as that for the methanol guest. Thus the methylamine-like model, like methanol, does not satisfy the clathrate forming conditions at the potential energy local minimum.

We, therefore, conclude that the difference in the attractive guest-host interaction (i.e. between the hydrophilic group and water) plays a dominant role in the stability of the hydrate. That is, the magnitude of the partial charge on the hydrogen atom for methanol is nearly the same as that on the oxygen atom. This yields the strong guest-host attractive interaction, which breaks the hydrogen bonds between the host water molecules. In the case of methylamine, however, the magnitude of the partial charge on the hydrogen atom is approximately half of that on the nitrogen atom, and thus the attractive interaction is relatively weak and does not inhibit formation of the clathrate hydrate structure–at least at the local energy minimum structure.

4 CONCLUSION

In order to account for the experimental observation that amines can be introduced as guest molecules in clathrate hydrates, and that alcohols cannot, we analyzed host network structure I hydrates encaging methylamine and methanol at the local potential energy minimum structure. For the methanol clathrate, the potential energy of the host lattice is very high compared with that for the methylamine clathrate. Also, the guest-host interaction is much stronger in the case of methanol. Moreover, it is found that methanol does not satisfy the clathrate-forming conditions. The host network is partly broken and guest-host hydrogen bonds are formed. Methylamine, on the other hand, maintains the host lattice structure of clathrate hydrate I. Although the molecular structures of the methylamine and methanol guests may slightly affect the stability of the host lattice as an excluded volume effect, the partial charge on the hydrogen atom in the amino and the hydroxyl group dominates as to whether the clathrate encaging the guest species can be formed or not.

For amine hydrates, further investigation is needed in order to examine their stability under thermal excitation caused by molecular motions. Then we can thoroughly understand the physical origins of the stability or instability of amine and alcohol clathrate hydrates.

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