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Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:
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To cite this Article Matsuo, Takasuke and Yamamuro, Osamu(1995) 'Phase transitions in some clathrate compounds[1]', Supramolecular Chemistry, 6: 1, 103 — 108

To link to this Article: DOI: 10.1080/10610279508032525

URL: http://dx.doi.org/10.1080/10610279508032525

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SUPRAMOLECULAR CHEMISTRY, Vol. 6, pp. 103–108
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Phase transitions in some clathrate compounds[1]

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(Received August 5, 1994)

Low temperature properties of clathrate compounds of hydroquinone and thiourea and of clathrate hydrates are discussed using experimental results from calorimetry, neutron scattering and nuclear resonance experiments. All of them undergo phase transitions of order-disorder type, involving orientational ordering of the guest molecules in the first two and ordering of both the guest and host molecules in the third. Even though the basic situation as to the motional freedom of the guest molecule in the cavity is the same in the three clathrate systems, the time scales of the reorientational motion range from 1 ps to more than hours even at a fixed temperature of 20 K. In the slowest case, the substance behaves as a glass. For clathrate hydrates, not only the host lattice determines the motion of the guest molecule, but the guest molecule controls ordering of the orientation of the water molecules in the host lattice.

INTRODUCTION

In a clathrate inclusion compound, the force binding the host molecules together is usually anisotropic, making it possible for them to build an open structure in which the guest molecules are accommodated. Hydrogen bonding is the most important interaction for the host lattice formation. Empty host lattices are obviously less stable than their neat crystalline counterparts. The clathrate compounds are eventually stabilized by host-guest interactions resulting from non-specific interactions between the guest molecule occupying the cavity and the host molecules forming the wall of the cavity. The host-host and host-guest interactions are thus the most important molecular interactions that stabilize a clathrate compound against decomposition. These are nearest neighbour interactions and thus stronger than those between more distant pairs of molecules.

Although the guest-guest interactions are weaker than the host-guest interactions, many clathrate compounds have properties that can only be explained by assuming the presence of significant guest-guest effects. In this report we deal with phase transitions in clathrate inclusion compounds as indications of guest-guest interactions.

The basic idea derives from a simple general notion of symmetry. We suppose that a clathrate compound formed by *polar* guest molecules crystallizes in a structure that is symmetric with respect to a plane perpendicular to an axis (call it the z-axis). We suppose further that the stable orientation of the guest molecule in the cavity is such that the polar axis of the molecule is parallel to the z-axis. It often happens that the mirror symmetry results from disorder of the orientation of the molecules, the mirror plane passing through the center of the cavity. The up-down symmetry pre-supposes that the cavity itself is symmetric in the same way. In this situation, the guest molecule is as likely to point up as point down. The orientational disorder could persist down to zero kelvin, if there were no agent to break the up-down symmetry. Obviously this violates the third law of thermodynamics. The third law is saved in reality thanks to the interaction between the guest molecules. In the disordered phase the probability of a guest molecule pointing up is equal to that of pointing down, but there is a certain dissimilarity between a pair of guest molecules being parallel and those being anti-parallel. The dissimilarity in energy makes one pair or the other more prevalent on the average. At a low enough temperature this leads to spontaneous ordering of the entire collection of the guest molecules. Since this occurs with no obvious preference of one orientation over the other, it is called spontaneous breaking of the symmetry. The ordered state has a different symmetry from the original phase. The whole process is a phase transition. A key ingredient for this to occur is the interaction between the guest molecules. Without this the up-down symmetry is preserved and no phase transition occurs. Roughly speaking, the difference

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in energy between parallel and antiparallel pairs determines the transition temperature. In actual cases, the broken symmetry may be more complicated than the mirror symmetry, involving loss of a three-fold axis or some of translation group elements. The ordering may also proceed in two or more steps.

It is important to recognize that there are two types of molecular motion. They are vibrational and reorientational motions. The time scales involved therein are different in the absolute values as well as in the temperature dependence. The vibrational motion, typically described as harmonic oscillation, are the usual molecular and lattice vibrations and have time scales of ps or less. Thermal equilibrium in this degree of freedom is attained equally rapidly. The reorientational motion of a molecule is a less frequent process, involving a stochastic element in which only some of the thermally activated molecules acquire enough energy to surpass the energy barrier hinddering the motion. The average time between two reorientational jumps may be as short as 1 ps and as long as hours or years depending on the activation energy and temperature. The average life time of the molecular orientation (relaxation time) depends strongly on the temperature. The temperature at which the relaxation time is equal to the time scale of a particular type of experiment is an important characteristic of the combined sample and experiment. For the calorimetric experiment, it is called the glass transition temperature. The time scale of calorimetric experiments is in the order of 100 s to 10000s and it can locate the temperature at which the molecular reorientation life time enters this range.

Low Temperature Adiabatic Calorimetry [1,2]

In heat capacity measurement with an adiabatic calorimeter, one places a sample in an abiabatically isolated environment, give an accurately measured amount of energy to the sample electrically, and measures the temperature rise resulting from the added energy. The ratio of the amount of energy to the temperature rise give the heat capacity of the sample. The vibrational motion of molecules discussed above contribute to the heat capacity, which, in harmonic approximation, may be represented by Debye, Einstein and other heat capacity functions. Reorientational motion may or may not carry a significant part of the internal energy of the sample. It contributes to the heat capacity when long-range or short-range order of the molecular orientation changes with temperature. This occurs when a crystal undergoes a phase transition. While the vibrational degree of freedom always contribute to the heat capacity, it is not clear whether an experimentally determined heat capacity of a substance at a certain temperature contains a reorientational component. But in one specific situation, i.e., at a glass transition Tg, one knows that the heat capacity contains a reorientational contribution at $T > Tg$ and it does not at $T < Tg$. The magnitude of the reorientational heat capacity is given by the difference of the two heat capacity values.

As an extension of the calorimetric experiment beyond its traditional role that it determines the energetic relation of one equilibrium state of a substance to another equilibrium state, an adiabatic calorimeter may be used to study the rate process of the molecular reorientation. In order to do this one cools the sample rapidly to Tg and place it in adiabatic isolation. The sample warms itself spontaneously as its orientational degrees of freedom approaches a new equilibrium. The rate of the equilibration is given by the spontaneous heating rate. The time scale involved in such measurement is 100s to 10000s as discussed above. This is dictated by the time constant of thermal conduction in the sample cell and sensitivity and stability of the thermometry and adiabatic control.

Hydroquinone Clathrate Compounds

These are the earliest clathrate compounds recognized as such[3,4]. They are still of interest to study in relation to the ordering and molecular interaction of the guest molecules. Vibrational motion of the guest molecules in the cavity was studied by heat capacity measurement in early calorimetric work[5]. Orientational ordering was also studied, providing the first examples of polar guest molecules becoming ordered at low temperature[6–8]. The host structure is rigid because of the rigidity of a hydroquinone molecule and the hydrogen bonds forming the cavity wall. It has been known that the hydroquinone clathrate structure is stable even if some of the cavities are empty[9]. This means that the structure sustains itself without being supported from within the cavity. This is another reason for which a clathrate crystal is of interest from the view point of molecular motion and phase transitions. When a small enough molecule is trapped in the cavity, it need not support the wall to prevent the collapse of the cavity, because the host structure is already stable by itself. The guest molecule sits in the cavity simply because its presence lowers the total energy. Therefore it is free to rotate in the cavity, with only a small variation of the potential energy due to the attractive part of the atom-atom potential. In an ordinary molecular crystal, molecules attract and repulse each other and the actual lattice packing is determined by the balance between these opposing interactions. As a result rotation of the molecule is accompanied by a large variation of the energy[10,11].

The barrier to rotation was calculated for hydrogen chloride in a hydroquinone host cavity in atom-atom approximation for which the parameters in the atom-atom potential were taken from [12]. The barrier height calculated was 90 Jmol^{-1}. This is two to three orders of magnitude smaller than a typical barrier height in an ordinary organic molecular crystals.

Molecular motion in such a low barrier crystal may be studied by a neutron scattering. Figure 1 shows spectra obtained on hydrogen chloride trapped in the deuterated hydroquinone host[13]. At the lowest temperature (2.3 K) a broad but definite peak occurred at 4.5 meV, corresponding to 36 cm^{-1}, with weaker peaks at 8.5 and 12 meV. As the temperature increased the peak broadened gradually and between 8.5 and 13.5 K changed into a wing of the elastic peak. The quasi-elastic peak thus emerging is exceptional in that it appeared at such low temperatures. The orientational life time calculated from the width of the quasi-elastic wing was about 1.7 ps at 22.0 K. This bears out our basic notion of the clathrate structure that the guest molecules move in cavities secured by the host wall.

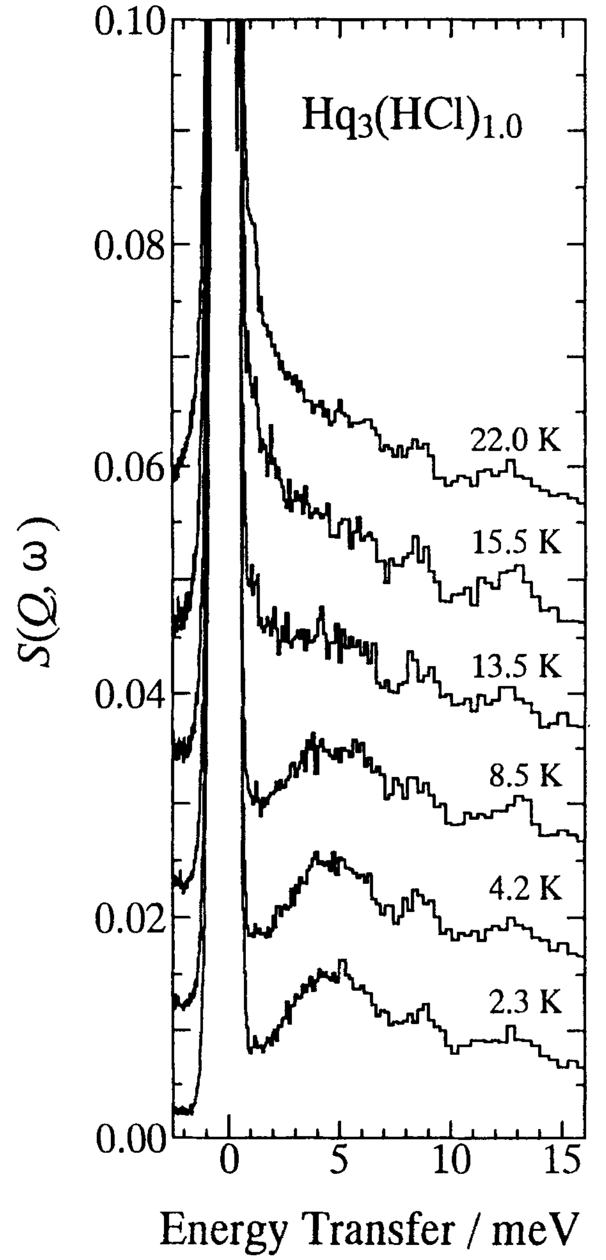

Figure 1 Neutron energy loss spectra of (d-hydroquinone)$_3$HCl [13].

The temperature 13 K is a special temperature for this compound. Figure 2 shows its heat capacity as a function of temperature[14]. The peak at 13 K is due to a phase transition. Above this temperature the guest molecules rotates and reorients randomly at an average rate of once in 1 ps. Below this temperature, the molecules are ordered and the rotational excitation becomes more coherent, giving rise to the inelastic neutron peak instead of the quasi-elastic wing of the central elastic peak. The entropy associated with the heat capacity peak was comparable with the gas constant *R*, supporting the basic idea that the anomalous heat capacity and the change of the neutron spectrum are both caused by a dynamic order-disorder transition in the collection of the guest molecules.

Hydrogen sulphide is another small molecule that can be trapped in the hydroquinone cavity. Quasi-elastic scattering was found also in its neutron spectrum[15]. For this compound a theoretical calculation showed that the ordering occurs only if the guest molecule is sufficiently polar[16–19].

Classical order-disorder changes have been found in hydroquinone clathrates of methanol and hydrogen cyanide[6–8]. Interestingly, the very polar guest molecule,

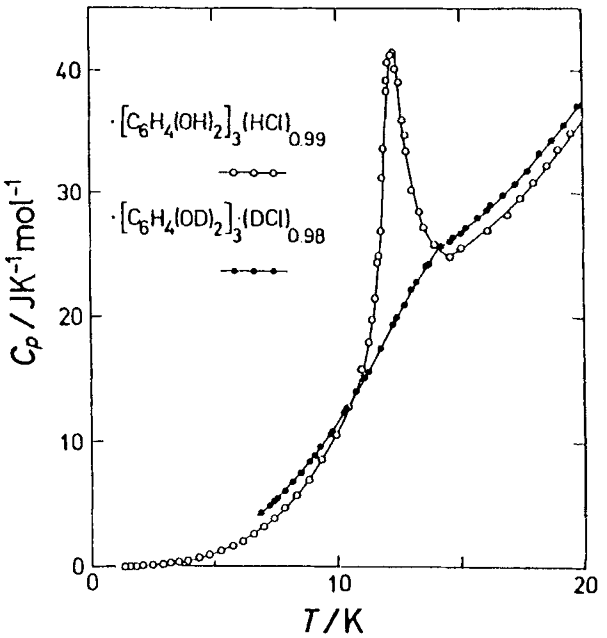

Figure 2 Low temperature heat capacities of hydroquinone clathrate compounds containing HCl and DCl[14].

CH_3CN, is orientationally ordered when it is incorporated in the hydroquinone host lattice at an ambient temperature[20].

Thiourea Channel Compounds

Cyclic and branched aliphatic hydrocarbons have been known to form addition compounds with thiourea[21] and their low temperature properties studied by calorimetry[22]. Structurally simpler molecules such as carbon tetrachloride also form channel type compounds with thiourea[23]. These are of interest because of the possibilities they offer for the study of the relation between the molecular interaction and phase transitions.

We studied low temperature thermal properties of thiourea inclusion compounds formed by CCl_4[24] and the brominated analogues and chlorinated ethanes[24]. Figure 3 shows the heat capacity of the thiourea $CBrCl_3$ inclusion compound. There are three temperatures of anomalous heat capacity of which two are easily seen and the third is more subtle. In figure 4 one sees an expanded part of the heat capacity curve embracing the two phase transitions at 84 K and 92 K. The 84 K anomaly is due to a first order transition where a latent heat effect is seen as a delta-function type of a peak. The 92 K anomaly is similarly evident but it is a higher order transition where the heat capacity remains finite and decreases suddenly to the high temperature value above the transition temperature. The structural aspect was studied by neutron diffraction. Interestingly the $CBrCl_3$ inclusion compound is isomorphous with the CCl_4 compound, indicating that Cl and Br are not distinct as to the sites they occupy in the crystal. They are also indistinguishable in the low temperature phases. This was suspected from the occurrence of a glass transition, which is the third point to be noticed in the heat capacity curve. In figure 5, one see an increase of the heat capacity at 19 K. This anomaly was accompanied by spontaneous heating of the sample when it was kept under adiabatic condition. This glassy behavior was not found in the analogous CCl_4 compound. It is thus probable that the glass transition is related to the exchange motion (or freezing thereof) of Cl and Br atoms belonging to the guest molecule.

Nuclear quadrupole resonance experiments gave clear evidence that the two halogen atoms are not fully ordered at the lowest temperature[26,27]. The chlorine resonance spectra were much broader for the $CBrCl_3$ compound than for the CCl_4 compound and the line width could be attributed to the exchange disorder. The NQR experiment showed that there are two sets of sites for the halogen atoms: one for which the carbon-halogen bond lies in the hexagonal basal plane and the other for which it makes an angle with the plane[28]. These gave different resonance frequencies. The intensities of the lines were the same for the chlorine compound, whereas they were 2:1 for the $CBrCl_3$ compound. Therefore, the bromine atom occupies either in-plane sites or out-of-plane sites exclusively but not both. The randomness related to the glassy state originates in this model from the choice of one

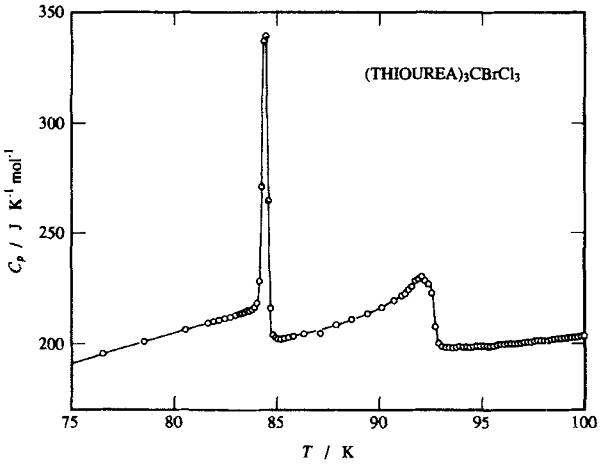

Figure 4 Heat capacity of the thiourea $CBrCl_3$ clathrate compound near the phase transition temperatures.

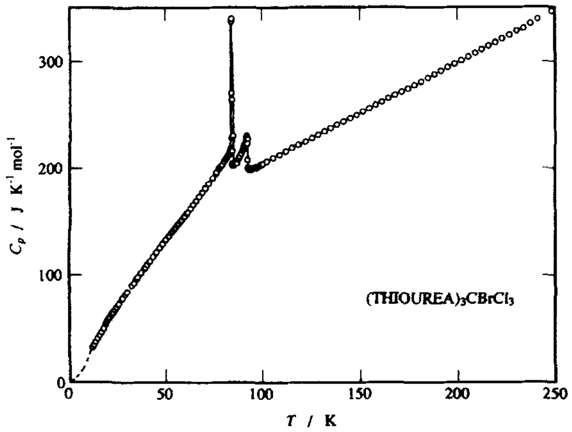

Figure 3 Heat capacity of the thiourea $CBrCl_3$ clathrate compound.

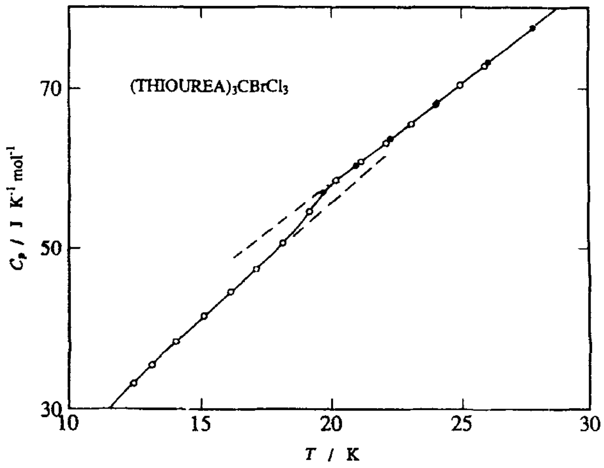

Figure 5 Heat capacity of the thiourea $CBrCl_3$ clathrate compound near the glass transition temperatures.

orientation out of two in-plane sites (or two out-of-plane stites) for the bromine atom. We do not know which, the in-plane or out-of-plane site, is the actual one. Disorder of the guest molecules was also found for adamantane in thiourea.[29]

For the neat crystal of $CBrCl_3$, the same randomness persists down to the lowest temperature in the same way as in the thiourea compound. However, the exchange between Br and Cl does not occur below $T_g = 90$ K[30]. Thus, the molecular motion is more strongly hindered in the neat crystal than in the adduct, supporting the basic idea that the molecular motion is relatively free in clathrate compounds because the guest molecule occupies a space secured by the host wall. But neither in the neat crystal nor in the adduct is the energy difference between a Cl-Br pair and Cl-Cl (or Br-Br) pairs large enough to be recognized between neighboring molecules.

Clathrate Hydrates

In clathrate hydrates another element comes in to consideration: disorder of hydrogen atoms in the hydrogen-bond framework of the host wall. The stability of the lattice was discussed for this system[31]. Extremely high mobility of small molecules in clathrate hydrates has been studied by NMR and dielectric measurement[32]. It has been pointed out that the guest molecules cannot be orientationally ordered because of the random electric field due to the orientational disorder of the water molecules[33]. The orientational disorder of the water molecules in ordinary ice (ice Ih) is removed at a phase transition which occurs at 72 K when the ice is doped with KOH in a very small quantity (0.01 mol kg^{-1})[34]. We found the same effect in clathrate hydrates. Figure 6 shows the heat capacity curves of acetone hydrates with and without addition of KOH[35,36]. The neat clathrate hydrate undergoes a glass transition at 90 K. This temperature demarks the boundary between the equilibrium and nonequilibrium states of the crystal with respect to the position of the hydrogen atoms in the host cavity wall. The doped sample underwent a phase transition at 46.6 K. The entropy change associated with the transition was 2.48 JK^{-1} $(H_2O\text{-mol})^{-1}$. The entropy value shows that the transition involves ordering of the host hydrogen atom, even though the guest molecules become ordered at the same time. But the latter contributes only 1/17 in term of the number of molecules. Although the main ingredient of the phase transition of the clathrate hydrate is the ordering of the positions of the protons in the host lattice, the transition temperature does depend on the guest species. In figure 7 the excess heat capacities of various clathrate hydrates doped with KOH are plotted. The transition temperature and the short range effect differ from one guest species to another. The short range order is quantified in Fig. 8 as the decrease of the configurational entropy calculated by integration of $\Delta Cp/T$. It was found that guest molecules with larger molecular size induce ordering of the host

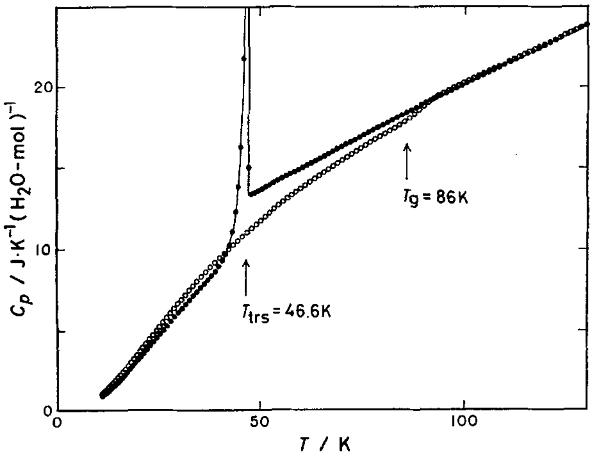

Figure 6 Heat capacity curves of acetone hydrates with and without 0.01 mol kg^{-1} of KOH added[35,36].

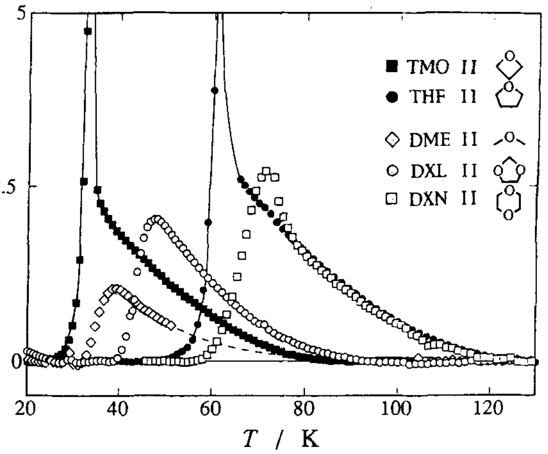

Figure 7 Excess heat capacities of clathrate hydrates containing polar guest molecules and doped with KOH.

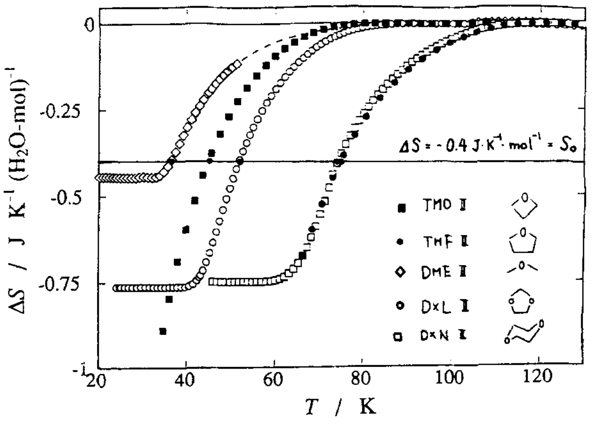

Figure 8 Excess entropies of clathrate hydrates containing polar guest molecules and doped with KOH, referred to the fully disordered state.

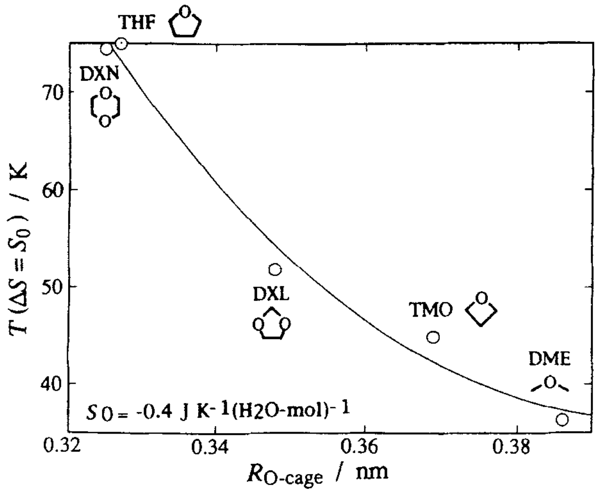

Figure 9 Temperatures at which the entropy decreases by 0.4 JK-1 mol-1 from the fully disordered state plotted against the distance between the oxygen atom of the guest molecule and the cavity wall. The correlation suggest that close approach of the oxygen atom to the wall facilitates local order of the protons in the wall.

lattice at higher temperatures. This is summarized in Figure 9 where the temperature at which the entropy decreases by 0.4 JK^{-1} $(H2O\text{-mol})^{-1}$ from the high temperature value is plotted against the distance between the oxygen atom of the guest molecule and the cavity wall[37]. The correlation presented in this plot suggests that the short range order in the cavity wall is promoted by close approach of the negatively charged oxygen atom of the guest molecule.

We have discussed low temperature properties of three clathrate systems. In hydroquinone and thiourea compounds, guest-guest interaction determines their behavior at low temperatures. For clathrate hydrates positional disorder of protons in the host structure plays the major role while the presence of the guest molecule critically controls their ordering. Even though the main goal of our study—identification of the microscopic origin of the molecular interaction responsible for phase transitions and glass transitions in the clathrate systems—is elusive, their study, employing newly available experimental techniques, has revealed hitherto unknown aspects of their properties, which we hope will be understood in the future in a greater generality.

ACKNOWLEDGEMENTS

The authors thank Professor H. Suga for his keen interest in the subjects discussed here and Dr. S. Takeda for his kind help and collaboration on the hydroquinone HCl clathrate compound. The experimental work on the hydroquinone clathrates, thiourea adducts and clathrate hydrates were performed with former graduate students of the authors, Dr. M. Ukekawa, Y. Mizutani, N. Kuratomi and T. Yonekura. The authors thank them for their patient cooperation. Finally T. Matsuo thanks Professor M. S. Conradi and Dr. N. L. Adolphi for their collaboration on the spectroscopic work on the thiourea systems.

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