Journal of Non-Crystalline Solids 407 (2015) 431–440

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Deuteron magnetic resonance and dielectric studies of guest reorientation and water dynamics in six clathrate hydrates containing ring-type guests

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ARTICLE INFO

Article history:
Received 29 April 2014
Received in revised form 25 August 2014
Accepted 30 August 2014
Available online 18 September 2014

Keywords:
Nuclear magnetic resonance;
Clathrate hydrates;
Hydrogen bonds

ABSTRACT

Using deuteron nuclear magnetic resonance and high-resolution dielectric spectroscopy the guest dynamics of tetrahydropyran, cyclopentane, trimethylene oxide, 1,3-dioxolane, and 1,4-dioxane clathrate hydrates is studied. By investigating lattice-deuterated as well as guest-deuterated crystals, the anisotropic guest reorientation is scrutinized and compared with previous results for tetrahydrofuran clathrate hydrate. The reorientational energy barriers depend linearly on the size of the guest molecules except for the clathrate hydrate of cyclopentane, a molecule which exhibits a dipole moment of the order of 0.01 D. The ether oxygens of the other guests can induce Bjerrum L defects on the hydrate lattice. Their concentration is examined for ammonia-doped tetrahydrofuran clathrate hydrate. Covering a wide range of NH_3 concentrations x, a minimal overall Bjerrum defect concentration is observed that leads to a maximum mobility on the hydrate lattice at $x \approx 0.03\%$. To examine guest-induced Bjerrum L defects further, the translational motion on the undoped hydrate lattices is studied using stimulated-echo spectroscopy: The proton dynamics of CP clathrate hydrate is virtually identical to that of hexagonal ice and the water motion of THP clathrate hydrate closely matches that of the tetrahydrofuran compound.

1. Introduction

Clathrate hydrates represent a unique combination of two different kinds of molecules: host water molecules which crystallize into a lattice framework containing voids and guest molecules which are incorporated into these voids and which help to stabilize the framework structures not the least by virtue of their guest–host interactions [1,2]. While for ether-type guests an influence of hydrogen bonds as a possible contributor to these interactions was mentioned long ago [3,4], only recently was their impact explicitly studied more thoroughly using computer simulations. It was found that short-lived hydrogen bonds with a mean lifetime on the ps time scale at 200 K form between hydrate host and polar guests [5–7]. Computations suggest that the hydrogen bonds are particularly strong for alcohol guests [8] and they do not appear for nonpolar guest molecules [9]. Direct experimental observation of guest–host hydrogen bonding events is challenging, and efforts were directed at observing the impact of this hydrogen bonding on the dynamics and structure of the lattice water molecules by single-crystal X-ray diffraction and infrared spectroscopy [6,10,11].

Clathrate hydrate properties like guest dynamics and decomposition temperatures were often related to the guest-to-cage-size ratio [1,12]. Recently, it was emphasized that the stability of clathrate hydrates does also depend on whether the guest molecules contain oxygen which typically lowers the melting point of the clathrate hydrate [11]. This finding indicates that in addition to van der Waals type interactions polar characteristics such as hydrogen bonding propensity also bear importance for hydrate decomposition. Guest free clathrate hydrates have not been produced in the laboratory so far and were studied only using computer simulations [13].

Fig. 1(b) presents melting points, T_m, of several structure II clathrate hydrates containing cyclic guest molecules like those depicted in Fig. 1(a). With increasing guest size (as measured by their calculated van der Waals radius [14]) the clathrate hydrate stability typically tends to increase. This can lead to rather high melting points, e.g., for the nonpolar guest molecules cyclobutane (C_4H_8; $T_m \geq 14$ °C [11]) or cyclopentane (CP: C_5H_{10}; $T_m \approx 7.2$ °C [15]). Further included in Fig. 1(b) are the clathrate hydrates of trimethylene oxide (TMO: C_3H_6O [16]), 1,3-dioxolane (DXL: $C_3H_6O_2$ [16]), tetrahydrofuran (THF: C_4H_8O [2]), 1,4-dioxane (DXN: $C_4H_8O_2$ [16]), and tetrahydropyran (THP: $C_5H_{10}O$ [17]).

A promising experimental approach, directed at studying the nature of the guest–host interactions, is to analyze the dynamic properties of a series of structure II clathrate hydrates that contain cyclic guest

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http://dx.doi.org/10.1016/j.jnoncrysol.2014.08.059
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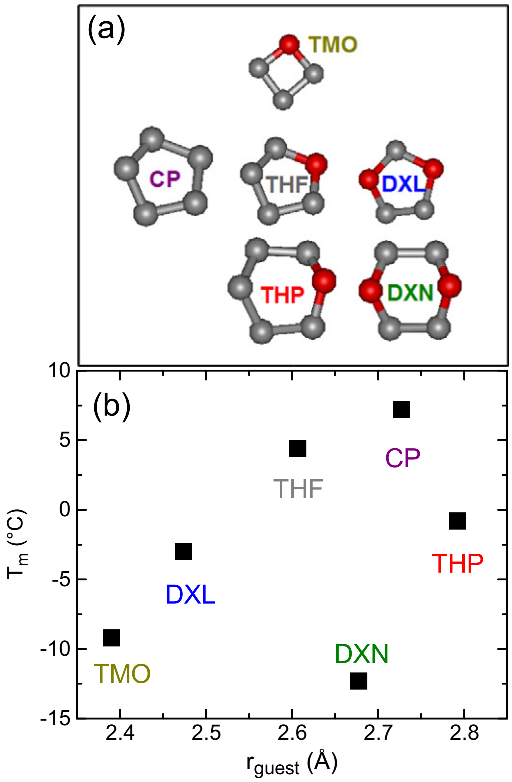

Fig. 1. (a) Schematic representation of the ring-type guest molecules that are in the focus of the present work. Red spheres represent oxygen atoms and gray spheres represent CH_2 groups. (b) The melting points, T_m, of the clathrate hydrates made from H_2O (references are given in the text) are plotted against the guest molecule radius, r_{guest}, as calculated according to the procedure described in [14]. The given melting points refer to protonated clathrate hydrates. The melting points of clathrate hydrates made from D_2O are typically 3–4 °C larger, similar to the situation in hexagonal D_2O ice, see Table 2.4 of [25].

molecules for which parameters like the molecular diameter and the electrical dipole moment vary.

Rather large effective gas phase dipole moments [18] are exhibited by TMO (1.94 D), THF (1.63 D), THP (1.63 D), and DXL (1.47 D) and the values in the solid state are usually similar. However, the dipole moment of CP is very small (~0.01 D, see below) and DXN presents a special case: In its clathrate cage DXN exists in the non-dipolar chair configuration but was reported to induce an effective dipole moment of about 0.2 D on the water molecules forming the embedding hydrate cage [19]. Furthermore, in the structure II clathrate, the boat form of THP is favored so that the "van der Waals contact" to the cage forming water molecules is maximized which reduces the dipole moment somewhat to below the value given above [20].

The purpose of the present article is twofold. On the one hand, we report deuteron NMR results of several clathrate hydrates [21]. This technique provides a single-particle dynamical probe but, as far as we know, was never applied to some of the currently studied systems. Several of them were, however, already studied using ^{1}H NMR and/or dielectric spectroscopy as will be compiled below. The second goal is to compare these results with data for clathrate hydrates which were studied before see, e.g., [1,6,12,22,23]. The collection of clathrate hydrates containing the ring-type molecules shown in Fig. 1(a) all crystallize in the cubic structure II [16,24] and they all populate the *larger* of their cage species. This situation allows for a systematic comparative analysis of these systems with respect to parameters like guest molecule radius, molecular dipole moment, guest mobility, and guest-lattice distance.

Ether type guests can create proton defects on the hydrate lattice and the consequent enhancement of the guest-affected lattice dynamics will be studied using stimulated-echo spectroscopy. With the goal to explore the dynamics of the ice-like defects further, we investigated THF clathrate hydrate. In simulation studies THF was reported to induce guest–host hydrogen bonding and to inject Bjerrum L defects into the water lattice [5,7]. Here, we doped THF clathrate hydrate with ammonia concentrations up to about 1% (the latter corresponding to a 1:0.17:17 composition of the THF:NH_3:H_2O mixture). If NH_3 replaces a water molecule on the hydrate lattice, Bjerrum D defects are created. These doping related defects can then interact with the L defects induced by the ether oxygen of the guests.

2. Experimental details

Selectively guest- or lattice-deuterated samples of THP and CP clathrate hydrates were crystallized from solution. Deuterated water of 99% purity (from Sigma Aldrich) as well as de-ionized and bidistilled protonated water were used. CP-d_6 was isotope labeled, distilled 3 times, and cleaned using a 4 Å molecular sieve. THP-d_4 was 98% isotope labeled at the four deuteron sites closest to the oxygen. THP·16.9 D_2O and THP-d_4·16.9 H_2O solutions were filled into NMR glass tubes or dielectric cells. Because THP is not very soluble in water [26], the mixture was emulsified through shaking before the crystallization procedure began. Upon cooling the solution turns from opaque to transparent around 0 °C, i.e., a phase separation seems to vanish immediately before freezing. The frozen THP clathrate hydrates were stored for at least one day at −18 °C, well below their melting point, $T_m = -0.8$ °C [26].

CP·16.9 D_2O and CP-d_6·16.9 H_2O clathrate hydrates were crystallized prior to inserting them as powder samples into the NMR tube or the dielectric cell. CP is not miscible with water and therefore a crystallization procedure similar to the one described by Jacobs et al. was adopted [12]. It involves keeping the solution at +4 °C for several days with shaking and dipping of the sample into liquid nitrogen about three times a day until the sample is fully crystallized. The crystallization of CP clathrate hydrate was thoroughly investigated [27, 28] and the melting point of CP·16.9 H_2O is reported to be $T_m = +7.2$ °C [15].

TMO·16.9 D_2O, DXL·16.9 D_2O, and DXN·16.9 D_2O were prepared by mixing 98% pure deuterated water with protonated guest substances in appropriate proportions. Guest deuterated samples of DXL-d_2·16.9 H_2O and DXN-d_8·16.9 H_2O were prepared using de-ionized and bidistilled water. DXL-d_2 was isotope labeled to about 99% isotopic purity at the carbon atom located between its two oxygen atoms. 99% isotopically pure DXN-d_8 was purchased from Sigma Aldrich. The DXN, DXL, and TMO clathrate hydrate samples were slowly crystallized in a sealed NMR tube or a dielectric cell and also kept at −18 °C for at least one day. For phase diagrams of H_2O/DXL and of H_2O/DXN see [29]. For all measurements the crystallized samples were inserted into a precooled cryostat. The ^{2}H NMR measurements were performed using a home-built spectrometer at a Larmor frequency of $\omega = 2\pi\nu_L = 2\pi \times 55.55$ MHz and π-pulses were typically 5.5 μs long.

Using X-ray diffraction we checked the crystal structure of our clathrate hydrate samples and quantified the ice contamination. These experiments showed that slowly crystallized samples contain less ice impurities than samples quenched in liquid nitrogen. For CP·16.9 D_2O and THP·16.9 D_2O the ice content in our slowly crystallized NMR samples was about 50 wt.%. The other samples were found to contain the following contaminations: <4 wt.% of ice for TMO·16.9 D_2O, <20 wt.% for DXL·16.9 D_2O, and <50 wt.% for DXN·16.9 D_2O. In all our NMR measurements we are able to discriminate the dynamics of ice from that of the clathrate hydrates, because either the time scales of lattice versus guest dynamics or the spin–lattice relaxation times of the different phases differ vastly. We determined the lattice constants, *a*, for several clathrate hydrates and confirmed that they depend linearly [1,20] on the diameter of the guest. We found that *a* ranges from 17.05 Å for the TMO to 17.22 Å