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Jump in the Rotational Mobility of Benzene Induced by the Clathrate Hydrate Formation

Masaru Nakahara, Chihiro Wakai, and Nobuyuki Matubayasi

Combined with the capillary method, NMR spin-lattice relaxation time measurements were performed to obtain the reorientational relaxation time of benzene in water between -50 and 120°C . A clathrate hydrate of the smallest aromatic molecule was formed without high pressure or help gas. It is found that the guest benzene molecule reorients three times faster with a smaller friction in a clathrate hydrate (probably, type II) at a lower temperature than in a supercooled solution at a higher temperature. Correspondingly, the activation energy for the reorientation of the guest benzene molecule is found to be smaller in the clathrate hydrate.

Keywords: Water structure/ Binary aqueous solution/ Hydrophobic hydration/ Hydration cage/ NMR

Hydrophobic hydration, which is a very important phenomenon in biology, reflects the unique geometrical nature of water, which develops more at lower temperatures, in particular in a supercooled regime. The study of supercooled water is important for understanding the anomalous dynamic and static properties of ambient water [1]. Recently we have examined the rotational motions in hydrophobic hydration of benzene below the water freezing point in order to investigate the dynamical aspects of supercooled aqueous solutions and clathrate hydrates. Here we report this work [2].

Under some pressures and at relatively low temperatures (recall CO_2), clathrate hydrates may be prepared in laboratory, found in nature, and proposed to exist as the "snows" on planets. Thermodynamic, structural, and dynamical studies on clathrate hydrates have been accelerated by technical interest in the natural

gas pipeline blockage and potential fuel resources in perpetually frozen lands and deep-sea sedimentary deposits. The aliphatic hydrocarbons from methane to butane are included as guests in the cages of hydrogen-bonded polyhedral frameworks formed by host water molecules.

The clathrate hydrate structures are classified into types I, II, etc. In the type II structure, the smaller and the larger cages are formed by 12 pentagonal faces (5^12) and 12 pentagonal and 4 hexagonal faces ($5^{12}6^4$), respectively. The latter and the former are occupied by larger guests and smaller help gas molecules like H_2S , respectively. The upper limit of the larger cage radius is 3.3 \AA , which is slightly smaller than the effective radius of a benzene molecule (3.6 \AA).

The experimental difficulties such as low solubility of the hydrophobic solute, low measurement sensitivity, and solute disturbance of supercooling can be overcome by

INTERFACE SCIENCE —Solutions and Interfaces—

Scope of research

Structure and dynamics of a variety of ionic and nonionic solutions of physical, chemical, and biochemical interests are systematically studied by NMR under extreme conditions. Simple and complex solution systems are supercooled, overheated, and compressed to high pressures to shed light on microscopic factors which control rotational and translational motions of ions and molecules. Vibrational spectroscopic studies are carried out to elucidate structure and orientations of organic and water molecules in ultra-thin films. Crystallization of protein monolayers, advanced dispersion systems at liquid-liquid interfaces, and biomembranes are also investigated.



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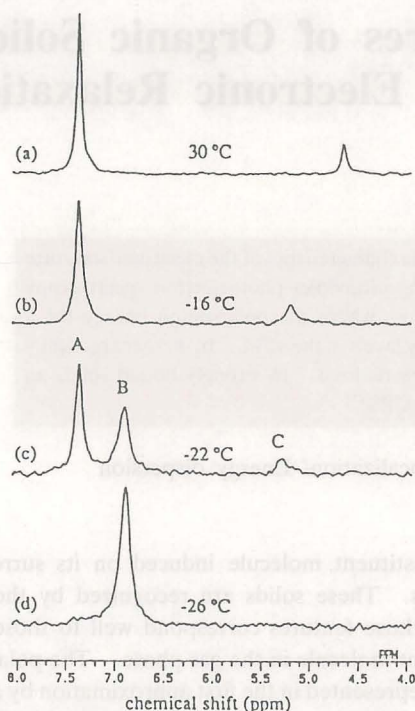


Figure 1. Temperature dependence of ^2H spectra of C_6D_6 (23 mM) in H_2O (HOD, 0.032%).

using bundled capillaries in a large sample tube for the high-resolution ^2H -NMR spin-lattice relaxation time measurement. By using the integrated capillary method, we could not only supercool the aqueous solution but also prepare a clathrate hydrate [2]. Figure 1 shows the ^2H spectra for solute benzene- d_6 and solvent water over a temperature range of -50 to 120°C . The dilute benzene solution can be supercooled down to about -20°C , as indicated by the presence of the sharp signal assigned to water (HOD, signal C in spectrum c); cf., spectra a, b, and c. The sharp water signal, which reflects the very rapid rotational dynamics of the solvent, shifts to a lower field. The temperature dependence of the water chemical shift is steeper at lower temperatures as already noticed. The down-field shift, indicative of stronger hydrogen bonds, continues in the supercooled regime. At about -20°C , however, the sharp water signal disappears as a result of the solvent freezing. At the same time, the solute benzene signal at 7.5 ppm begins to be taken over by a sharp new signal at a higher field; see signals A and B in spectrum c. The up-field shift would be due to the complete loss of weak hydrogen bonding interactions [3] between benzene and water molecules induced by the phase transition.

These spectral changes observed both on the host and guest sides indicate that a clathrate hydrate of benzene is formed at about -20°C , and that the benzene molecule encaged reorients very rapidly in the cavities, probably in the type II structure; this is expected from the fact that formation of a cyclohexane clathrate hydrate of type II with a help gas is reported [4]. The effective radius of a benzene molecule is estimated as 3.6 \AA , which is slightly larger than the upper-limit cage radius (3.3 \AA) in the type II structure. The clathrate formation can be regarded as

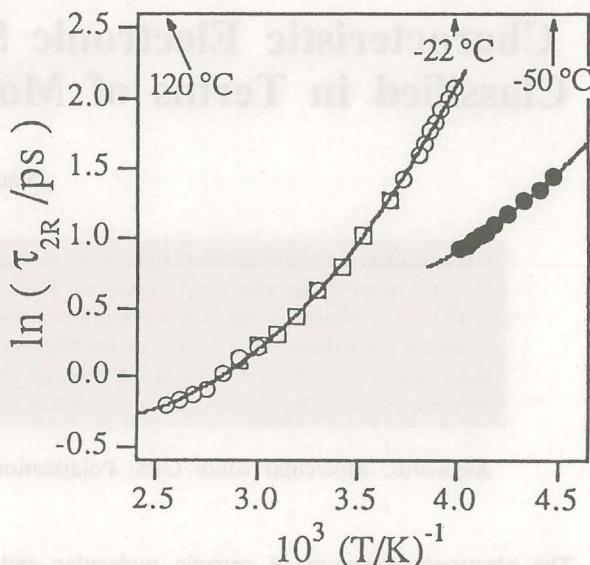


Figure 2. Arrhenius plots of the rotational correlation times τ_R for C_6D_6 in water. Open squares and circles are results obtained from a usual NMR tube of $\sim 4 \text{ mm}$ i.d. and capillaries of $0.2\text{--}0.3 \text{ mm}$ i.d., respectively; the agreement of the results between the large tube and capillaries shows that our capillary data at lower temperatures are not affected by capillary interfaces. The solid circles indicate τ_R for C_6D_6 in clathrate hydrates.

an indication of the hydrophobicity of the benzene molecule, though it is not so strong as lower aliphatic hydrocarbons which more easily yield a clathrate hydrate.

The experimental results are transformed into the rotational correlation times τ_R by the usual method [5, 6]. Figure 2 shows the logarithm of the rotational correlation time as a function of the inverse temperature ($1/T$). Noticeably, the rotational correlation time jumps within the transition temperature range, where the local environment of the solute changes from a vigorously fluctuating solution cage into a somewhat rigid clathrate cage. At -22°C , the τ_R value is 7.96 ps in the supercooled aqueous solution cage and 2.45 ps in the clathrate hydrate cage. Unexpectedly, the reorientational correlation decays 3.2 times faster in the clathrate cage than in the solution cage. Corresponding to the rotational mobility jump, the activation energy for the molecular rotation at -22°C drops from 22 kJ mol^{-1} in the solution to 7.6 kJ mol^{-1} in the clathrate hydrate.

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