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Metastable ionic cubic structure I clathrate hydrate formed with tetra-*n*-butylammonium bromide

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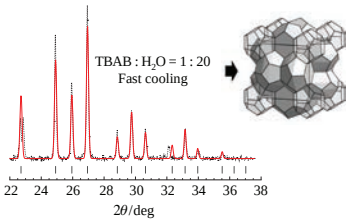
Ionic clathrate hydrates formed from aqueous solutions of tetra-*n*-butylammonium bromide in the course of rapid cooling (30 K min^{-1}) to –35 °C have been examined. An earlier unknown metastable hydrate of cubic structure I was obtained from the solutions with concentrations from 3.2 to 4.8 mol%.



Keywords: ionic clathrate hydrate, tetra-*n*-butylammonium bromide, cubic structure I, metastable state, powder X-ray diffraction.

As is well known, ionic clathrate hydrates of quaternary ammonium salts can be used for separating gas mixtures[1–5] and as cold accumulators.[6] The ionic clathrate hydrates of tetra-*n*-butylammonium bromide (TBAB) possess physicochemical characteristics (temperature and phase transition enthalpy) required for their use in air conditioning systems.[7] The most important thing here is to reduce the supercooling required for crystallization. The memory effect[8] or additives that accelerate nucleation can be used for this purpose.[9] A more complicated situation was observed in the separation of gas mixtures. TBAB is ineffective in separating methane–nitrogen mixtures,[10] while TBAB hydrates bind carbon dioxide with high selectivity.[1,11] Recently, Muromachi[2] noted that the efficiency of different hydrate phases in the binding of CO_2 could vary significantly. The formation of five hydrates in the TBAB–H_2O system is reliably known,[12–14] while the record number of hydrates has been found in the *tert*-butylamine–water system, namely 7 different hydrates at atmospheric pressure[15] and two more at high pressures.[16] It was also shown that the introduction of an additional component could lead to a change in the stability of hydrate phases,[17] and in the type of equilibrium itself.[18] The plenty of various structures with similar composition, as well as high-pressure phases, makes possible the manifestation of metastability.[19–21] Moreover, this phenomenon has been observed frequently in systems with hydrate formation.[22–24]

In this work, we studied formation of tetra-*n*-butylammonium bromide hydrates.[†] The X-ray diffraction data for TBAB hydrates single crystals (at atmospheric pressure) suggest the existence of an orthorhombic hydrate (TBAB · 38H_2O),[12] three tetragonal hydrates with different stoichiometry (hydrate numbers from 24.5 to 32.4) based on tetragonal structure I (TS-I),[13] and a low-water trigonal hydrate (TBAB · $2^1/_3H_2O$).[14] Unlike similar tri-*n*-butylsulfonium fluoride–water[26,27] and tetra-*n*-butylammonium fluoride–water[28] systems, the formation of a cubic TBAB hydrate was not detected previously. The aim of this study was to identify the crystallization of metastable phases during the rapid cooling of the system.

The selected solutions cover all fields of a state diagram where the formation of hydrate phases is possible (hydrate of hexagonal structure I + ice, tetragonal hydrates, and hydrates of tetragonal structure I + low-water hydrates). Figure 1 shows the diffraction patterns of frozen solutions. The samples prepared from 1 : 50 and 1 : 40 solutions exhibited a large number of diffraction peaks which can be matched with TS-I hydrate,[13] and no diffraction peaks due to ice were found. Note that orthorhombic 1 : 38 hydrates usually crystallize in a concentration range from 1 : 40 to 1 : 50 at slight supercooling and long exposure, which is consistent with the state diagram. The diffraction patterns of samples obtained from 1 : 30 and 1 : 20 solutions are undoubtedly similar in the strongest peaks, while the 1 : 30 sample has a significant number of additional small peaks. An experiment repeated with the 1 : 20 sample resulted in a similar diffraction pattern but with six additional diffraction peaks [Figure 2(*a*)]. The diffractogram of the 1 : 20 sample obtained in an experiment with stopped cooling was very

[†] TBAB (purity, >99%; Sigma-Aldrich) and deionized water (Milli-Q) were used. The phase composition of frozen aqueous solutions of TBAB was studied in a concentration range from 2 to 4.8 mol% (TBAB : H_2O molar ratios of 1 : 50, 1 : 40, 1 : 30, and 1 : 20) using a Bruker D8 Advance diffractometer (CuKα, 1.5418 Å) equipped with a TTK 450 Anton Paar low-temperature device. For a minimum deviation of the sample plane from a goniometer axis, the solution surface coincided with the upper edge of the sample holder. The solution was cooled at a rate of 30 K min^{-1} to –35 °C or the cooling was interrupted at –10 °C for 5 min and then continued at the above rate in order to obtain powder diffraction patterns of rapidly frozen samples that were not subjected to mechanical stress and did not stand for a long time after crystallization. The WINPLOTR software package was used for processing diffraction patterns.[25]

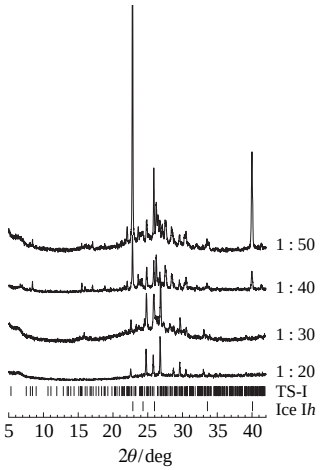


Figure 1 Powder diffraction patterns of frozen aqueous TBAB solutions at –35 °C (linear cooling at a rate of 30 K min^{-1}); the TBAB : H_2O molar ratios are specified. The reflections of TBAB hydrate of tetragonal structure I (TS-I) and ice I*h* are pointed as vertical bars.

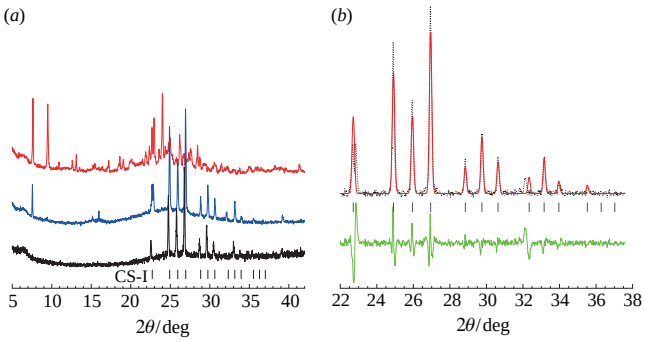


Figure 2 (*a*) Powder diffraction patterns (–35 °C) of a frozen aqueous solution of TBAB [4.8 mol% TBAB (1 : 20)] cooled at a constant rate of 30 K min^{-1} (lower curve is the first experiment, middle one is a repeat) and with a 5 min delay at –10 °C (top curve). (*b*) Results of the profile fitting of the powder diffraction pattern (*a*), middle curve. Dotted line corresponds to the experimental data, solid line is the fitted pattern, bottom line is the difference. The reflections of hydrate of cubic structure I (CS-I) are pointed as vertical bars.

complex and not similar to the powder diffraction patterns of other samples. It is most likely that the crystallization of a mixture of low-water content hydrates occurred. Based on these data, we concluded that a metastable hydrate or a mixture of hydrates crystallized upon the freezing of 1 : 20 and 1 : 30 (to a lesser extent) solutions, respectively. The powder diffraction pattern of a 1 : 20 sample contained the smallest number of diffraction peaks. It seemed to be likely a pure hydrate. In addition, the diffraction pattern was similar to the ones of hydrates of cubic structure I (CS-I). Indexing showed good agreement of the observed reflections with those expected for CS-I with a cell parameter of 12.38 Å [Figure 2(*b*), Table 1]. The TBAB hydrate of cubic structure I was not reported previously. According to Rodionova *et al.*,[13] a TBAB · 26H_2O hydrate should crystallize in the TBAB–water system in a concentration range from 3.2 (1 : 30) to 4.8 (1 : 20) mol%.

It is well known that tri-*n*-butylsulfonium fluoride forms a 20-aqueous CS-I hydrate with a unit cell parameter of 12.34 Å (the hydrate was obtained at +5 °C, and the measurement was carried out at –20 °C),[26,27] and tetra-*n*-butylammonium fluoride builds a hydrate of cubic superstructure I (24.37 Å; the crystal was grown at room temperature, and the diffraction pattern was taken at –123 °C) with a hydrate number of 29.7.[28] The unit cell parameter determined in this work is close to those found for related compounds. The presence/absence of a superstructure in our case cannot be established due to the weak reflections and the poor quality of powder diffraction patterns. The composition of the hydrate obtained seems close to the composition of a tetra-*n*-butylammonium fluoride hydrate.

Thus, we studied the crystallization of a solid phase from an aqueous solution of TBAB under rapid cooling. We have revealed that a metastable phase of TBAB hydrate with cubic structure I is formed in the TBAB–water system in a concentration range from 3.2 to 4.8 mol%. This process is affected by the rate (intensity) of cooling. As the formation of metastable phases can have an impact on the efficiency of gas separation processes using TBAB, it should be taken into account in the development of an appropriate technology.

Table 1 Experimental data for a 1 : 20 composition.

2θ / deg (obs.)	2θ / deg (calc.)	*d* / Å (calcd.)	*hkl*
22.69	22.71	3.915	310
24.91	24.91	3.574	222
25.94	25.95	3.434	320
26.94	26.95	3.309	321
28.86	28.85	3.095	400
29.76	29.75	3.003	410
30.64	30.64	2.918	330, 411
33.17	33.16	2.702	421
33.97	33.96	2.639	332
35.54	35.52	2.527	422

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