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Formation of $(C_xH_{2x+1})_4NBr\cdot nH_2O$ ($x = 1–3$) Hydrates

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Abstract—The phase diagram of the binary system tetramethylammonium bromide–water was studied by the differential thermal analysis. In the stable region two phases, ice and the salt itself, were detected, and in the metastable region, three tetramethylammonium bromide hydrates (bromide–water, 1 : 4, mp 68.8°C, 1 : 5, mp 36.0°C, 1 : 7.5, mp –19.5°C) were found. Formation of $(C_xH_{2x+1})_4NBr\cdot nH_2O$ ($x = 1–3$, $n = 4, 5, 7.5$) hydrates was revealed.

Keywords: tetrabutylammonium bromide, hydrates, DTA

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Phase diagram studies of a series of systems containing quaternary ammonium salts [1–7] and structural studies [1, 2, 8–10] showed that, in contrast to the previous belief, clathrate hydrates can be formed not only by butyl and isoamyl groups whose size and shape are best suited to the cavities of the clathrate frameworks [11]. It turned out that under certain conditions salts with smaller cations (Me_4N^+, Et_4N^+, Pr_4N^+) form hydrates some of which either have a clathrate polyhedral structure or belong to channel- or layered-type inclusion compounds. The largest number of compounds was revealed for tetramethylammonium hydroxide [1], of which five are clathrate hydrates, and two, channel-type compounds. In other systems from two to seven compounds were found. For some of them, crystal structures were determined. The most comprehensive and reliable data on the number, composition, and stability of the compounds formed in the systems considered are provided by their phase diagram studies, and this was specifically the research approach taken by us.

Here, we carried out a detailed study of the $Me_4NBr–H_2O$ system over a broad temperature range (from –100 to 80°C). Previously, tetraethylammonium- [6] and tetrapropylammonium–water systems [7] were studied with the bromide ion. Thus, using data for the Me_4NBr–water system it will be possible to determine how formation of hydrates in the tetraalkylammonium bromide–water systems is influenced by a Me_4N^+, Et_4N^+, Pr_4N^+ series cation.

Figure 1 presents the phase diagram of tetramethylammonium bromide–water system according to the differential thermal analysis data. In the stable region, only ice and Me_4NBr salt are formed. The lack of stable hydrates is evidently due to a high strength of the crystal structure of the salt proper, whose crystallization field overlaps with the possible stability regions of compounds. In the metastable region, three congruently melting hydrates with the salt–water ratios of 1 : 7.5 (mp –19.5°C), 1 : 5 (mp 36.0°C), and 1 : 4 (mp 68.8°C) were detected. The compositions of the compounds were determined from the maxima on the liquidus curves. Metastable phases appeared along with a stable phase in almost all recorded thermograms (either all at once or separately). Apparently, a transition from metastable to stable state takes a time that in some cases exceeds noticeably the time of recording the heating curve, so that melting could be measured for one or another hydrate by the DTA technique. The formation of several metastable phases in systems is a fairly common phenomenon, especially in systems with a water component [12, 13]. This is due to the fact that owing to flexible hydrogen bond (by both angle and length) the water molecules can

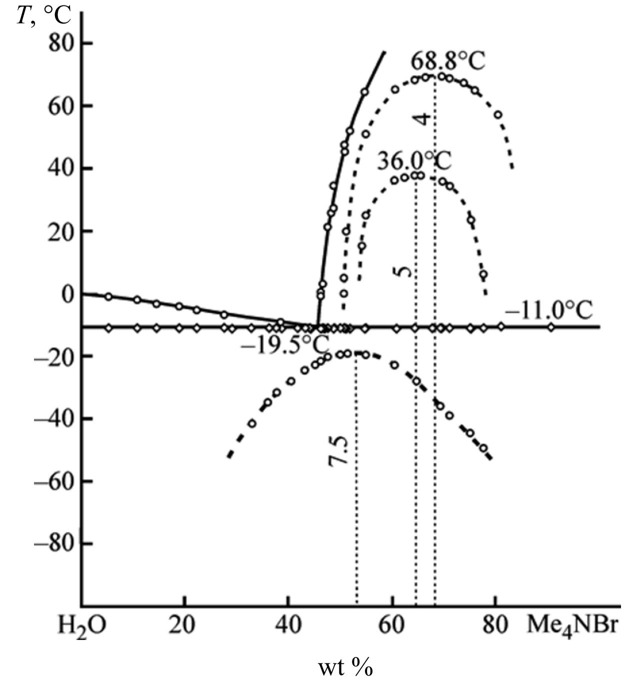

Fig. 1. Phase diagram of the $(CH_3)_4NBr–H_2O$ system. (Circles) Liquidus curves, (diamonds) solidus curves, and (dashed lines) metastable melting curves. Digits along the composition lines are hydration numbers.

form a number of structures close in energy. Some frameworks, though do not attain a thermodynamically stable state, nonetheless approach it and appear as metastable hydrates.

Studies of the $Me_4NBr–H_2O$ system added new data on the hydrate formation in the systems containing quaternary ammonium salts with a Me_4N^+, Et_4N^+, Pr_4N^+ series cation and the same bromide anion (Fig. 2). In each of the systems, 3–4 hydrates crystallizing in both the stable and metastable regions were found; among them, tetramethylammonium bromide hydrates are the most high-melting compounds. Further, the stability of the hydrates tends to decrease in the system with tetraethylammonium bromide and to even greater extent in those with tetrapropylammonium bromide. This trend holds for the compounds with identical compositions 1 : 4 and 1 : 5. However, the 1 : 7.5 hydrate formed in two systems, $Me_4NBr–H_2O$ and $Et_4NBr–H_2O$, exhibits a higher stability in the latter case. The reason apparently lies in the structures of the compounds formed in these systems. The structures of the 1 : 4 compounds were examined for tetramethylammonium hydroxide [1] and tetraethylammonium chloride [8]. In

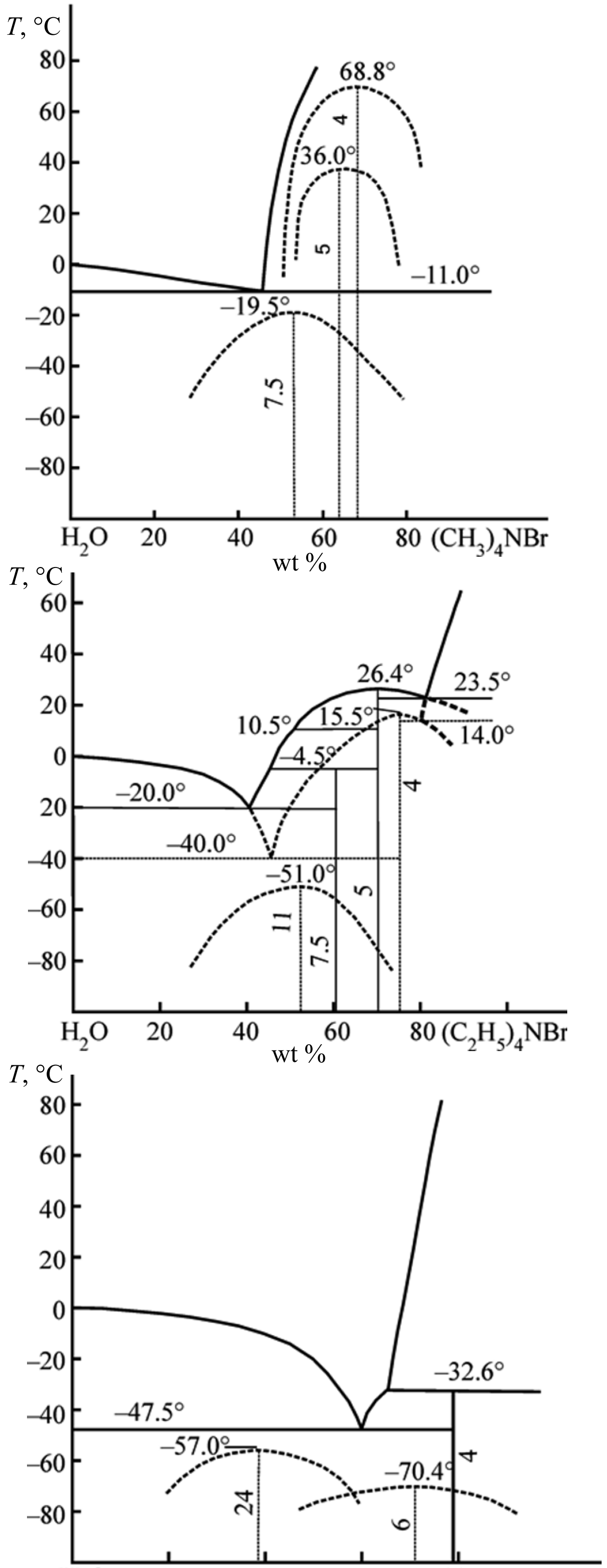

Fig. 2. Phase diagrams of the $(C_xH_{2x+1})_4NBr–H_2O$ (x = 1–3) systems. Dashed lines are metastable melting curves. Digits along the composition lines are hydration numbers.

both cases the hydrates have a water-anion channel framework into which cations are included, but their structures are different. Apparently, the Me_4N^+ cation better fits in size and shape the framework channels than does Et_4N^+, and especially Pr_4N^+, so its hydrates exhibit higher stability.

Hydrates with higher hydration numbers (1 : 5 and 1 : 7.5), found in the $Me_4NBr–H_2O$ and $Et_4NBr–H_2O$ systems, are known for tetramethylammonium hydroxide (mp 68 and 16°C, respectively); they have polyhedral frameworks [1]. Under the assumption that the Me_4NBr hydrates have the same structure, their lower stabilities (36°C and –19.5°C) may be attributed to a stronger destabilizing effect exerted by the bromide ion, whose size substantially differs from that of the water molecule: 3.4 against 2.8 Å. The tetraethylammonium cation, with its shape and size exceeding that of tetramethylammonium cation, cannot fit in the cavities of the frameworks considered. The tetraethylammonium hydrates, most likely, form some other type of framework (either that with large polyhedral cavities or a channel-type or a layer-type framework).

Figure 2 shows that not only the stability but also the composition and the number of hydrates vary depending on the anion. For all systems, the crystallization of a 1 : 4 hydrate is observed; 1 : 5 and 1 : 7.5 hydrates were additionally formed in the $Me_4NBr–H_2O$ and $Et_4NBr–H_2O$ systems. A 1 : 11 hydrate was revealed in the system with tetraethylammonium bromide, like in that with tetraethylammonium fluoride (mp –13.6°C) [2]. In the latter case, the examination of the hydrate structure showed that water and fluoride anions form a three-dimensional framework consisting of channels and cavities. The channels are filled with tetraethylammonium cations; one cation is included in the narrow part of the channel, and two cations, in the broad part. The cavities revealed earlier for $(i\text{-}C_5H_{11})_4PBr \cdot 32H_2O$ [14] and $(CH_3)_4NOH \cdot 7.5H_2O$ (β-phase) hydrates [1] remain vacant.

It can be assumed that tetraethylammonium bromide hydrate of identical composition has the same structure, and its lower melting point (–51°C) is most likely due to the destabilizing effect of the anion. In the $Pr_4NBr–H_2O$ system, 1 : 6 (like previously in the system with tetrapropylammonium hydroxide [5]) and 1 : 24 hydrates were detected. The 1 : 24 hydrate, known for tetrabutylammonium bromide (mp 12.4°C) [15], has a clathrate framework. Replacement of one of the butyl groups in the cation of tetrabutylammonium bromide by the propyl group leads to the formation of a hydrate of the same composition though with a lower melting point (0.8°C) because the propyl group fits worse the size of the clathrate framework cavities [16]. Based on the composition of tetrapropylammonium bromide hydrate (1 : 24), it can be presumed that it has the same type of the framework, but the stability of this compound is significantly lower (mp –57.0°C), since its cation has all the four propyl groups. Thus, under certain conditions quaternary ammonium salts with relatively small alkyl groups (in the present case, Pr_4N^+) may also form clathrate compounds with high hydration numbers, like in the case of butyl or isoamyl groups, though with much lower stability.

EXPERIMENTAL

Tetramethylammonium bromide of pure grade was thrice recrystallized from ethanol and dried in a desiccator over P_2O_5. The main substance content (99.8 ± 0.2 wt%) was determined by titration of bromide ion with ~0.03 N $Hg(NO_3)_2$ solution using diphenylcarbazone as indicator.

The phase diagram was studied by the differential thermal analysis on a setup described in [6]. The reproducibility of temperature measurement was ±0.1°C; the phase transition temperature was measured accurately to within 0.2°C. The heating rate for the samples was 0.5–1°C min^{-1}. The samples were cooled using liquid nitrogen at a rate of 10–15°C min^{-1}.

The compositions of the compounds formed in the systems was determined from the maxima on the liquidus curves.

REFERENCES

1. Mootz, D. and Seidel, R., *J. Inclus. Phenom.*, 1990, vol. 8, no. 2, p. 139.
2. Udachin, K.A. and Lipkowski, J., *Mendeleev Commun.*, 1996, no. 3, p. 92.
3. Aladko, L.S., *Russ. J. Gen. Chem.*, 2009, vol. 79, no. 8, p. 1613.
4. Aladko, L.S., *Russ. J. Inorg. Chem.*, 2011, vol. 56, no. 12, p. 2009.
5. Aladko, L.S., *Russ. J. Phys. Chem.*, 2011, vol. 85, no. 4, p. 716.
6. Aladko, L.S., *Russ. J. Gen. Chem.*, 2012, vol. 82, no. 12, p. 1913.

7. Aladko, L.S., *Russ. J. Phys. Chem.*, 2014, vol. 88, no. 2, p. 346.
8. Mak, T.C.W., Slot, H.J., and Beurskens, R.T., *J. Inclus. Phenom.*, 1986, vol. 4, no. 3, p. 295.
9. McMullan, R.K., Mak, T.C.W., and Jeffrey, G.A., *J. Chem. Phys.,* 1966, vol. 44, no. 6, p. 2338.
10. Lipkowski, J., Liboradzki, R., Udachin, K., and Dyadin, Yu., *J. Inclus. Phenom.*, 1992, vol. 13, no. 3, p. 295.
11. Jeffrey, G.A. and McMullan, R.K., *Progr. Inorg. Chem.*, 1967, vol. 8, no. 43, p. 43.
12. Dyadin, Yu.A., Gaponenko, L.A., Aladko, L.S., and Bogatyryova, S.V., *J. Inclus. Phenom.*, 1984, vol. 2, no. 3, p. 259.
13. Lipkowski, J., Suwinska, K., Rodionova, T.V., Udachin, K.A., and Dyadin, Yu.A., *J. Inclus. Phenom.*, 1994, vol. 17, no. 2, p. 137.
14. Dyadin, Yu.A, Yakovlev, I.I., Bondaryuk, I.V., Aladko, L.S., and Zelenina, L.S., *Dokl. Akad. Nauk SSSR,* 1972, vol. 203, no. 5, p. 1068.