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Hydrate Formation in the System Tetraethylammonium Bromide–Water

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Abstract—Hydrate formation in the binary system tetraethylammonium bromide–water was studied by differential thermal analysis. Three stable solid phases were detected, as well as two hydrates melting in metastable regions.

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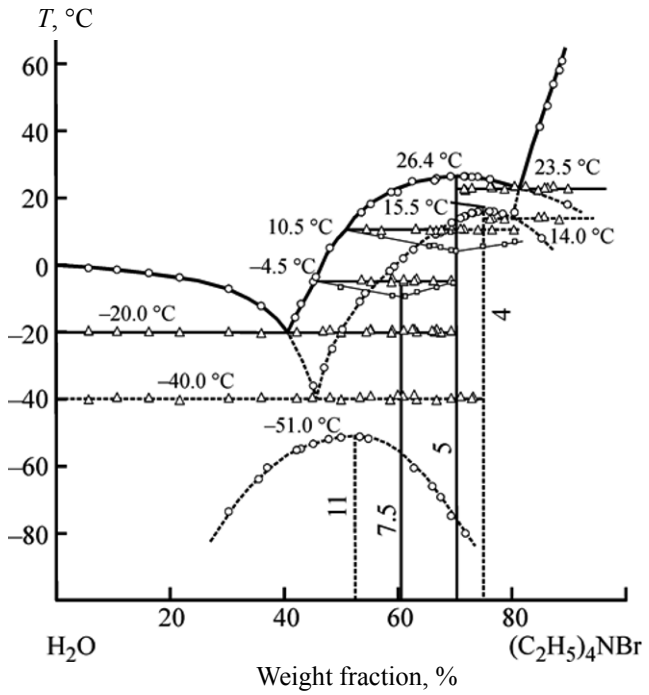
It was believed [1] that quaternary ammonium salts form clathrate hydrates if the alkyl groups therein are butyl or isopentyl, for their size and shape fit best the cavities of clathrate frameworks. However, hydrates of salts with smaller cations, such as Me_4N^+, Et_4N^+, and Pr_4N^+, were also reported [2–4], and some of these had clathrate structures but with different hydration numbers and frameworks. It should be noted that of detailed systematic studies were performed of binary and ternary systems containing tertetrabutyl- and tetra(isopentyl)ammonium salts with different anions [5, 6], which revealed the effect of the anion size and shape on the clathrate formation. By contrast, only scanty data are available for cations with smaller hydrocarbon radicals; these data include either preparation of particular compounds and their IR spectra [7, 8] or determination of their structure [4, 9–11]. Binary phase diagrams were studied only for a few compounds [2, 3], though just such studies provide comprehensive information on the number and composition of compounds and their stability ranges. For example, Mootz and Seidel [2] examined the system tetramethylammonium hydroxide–water and detected eight crystalline phases with hydration numbers of 2 to 10. Compounds with hydration numbers of 11, 5, and 2.75 were found in the system tetraethylammonium fluoride–water [3]. The recent study on the system tetraethylammonium chloride–water [12] revealed at least five crystalline phases in addition to two previously known 1:1 [13, 14] and 1:4 compounds [10].

The goal of the present work was to study hydrate formation in the system tetraethylammonium bromide–water over a wide temperature range with a view to detect as many compounds formed therein as possible and determine their stability ranges.

Figure shows the melting diagram for the system tetraethylammonium bromide–water according to the data of differential thermal analysis. There are three stable solid phases: two solid phase modifications with a composition of 1:5 (salt:water), which melt at 26.4 and 10.5°C, and a 1:7.5 compound incongruently melting at –4.5°C. In addition, two hydrates (1:4, mp 15.5°C, and 1:11, mp –51°C) were found; their crystallization curves completely fall into the metastable regions. The compositions of the congruently melting compounds (1:4, 1:5, and 1:11) were determined from the maxima on the liquidus curve. In addition, the most stable 1:5 compound was isolated in the crystallization region, and its hydration number was evaluated at 5.05, which is very consistent with that determined from the maximum on the liquidus curve. Drawing of the Tamman triangle (see figure) suggests that the maximal heat effect at –4.5°C should be observed at a composition of ~61 wt % which corresponds to the 1:7.5 hydrate. The effects at 10.5°C originate from the solid–solid phase transition of 1:5 hydrate (see the Tamman triangle in figure). Solid-phase transitions for hydrates with analogous compositions were also observed in other systems (Et_4NF [3], Et_4NCl [12]). The liquidus curve for the 1:5 hydrate extends to the metastable region. A stable



Phase diagram of the system $Et_4NBr–H_2O$. Circles denote liquidus curves, triangles denote solidus curves, dashed lines correspond to melting in metastable region, and squares denote Tamman lines; figures along the composition lines are hydration numbers.

eutectic of the 1:5 hydrate with a less hydrated compound (or salt) was found in the high concentration region. Eutectics of the 1:4 hydrate were observed in both dilute and concentrated solutions. The formation of lower hydrates (e.g., 1:1, as those found for tetraethylammonium fluoride [7] and chloride [13, 14]) at higher salt concentration cannot be ruled out, but the corresponding region was not studied.

Metastable phases appeared in almost all cases (either all together or separately) in addition to stable phases in each DTA run. Presumably, the transition from a metastable state to stable takes some time which sometimes appreciably exceeds the recording time of the heating curve, so that melting effects of both hydrates could be detected by DTA. Repeated melting–cooling cycles made it possible to eliminate metastable phases and to obtain only stable compounds. The formation of several metastable phases in a system is a fairly frequent case, especially in those systems where water is one of the components [15, 16]. The reason is that water molecules linked through flexible (by both angle and length) hydrogen bonds are capable of forming a number of structures (frameworks) with similar energies, which are stabilized by insertion of other molecules (tetraethylammonium bromide). Although some frameworks do not attain a thermodynamically stable state, they approach it and appear as metastable hydrates.

Thus at least five crystalline phases were detected in the system tetraethylammonium bromide–water. Taking into account known data for the other systems, some conclusions concerning crystalline structure of the hydrates formed can be drawn. The structure of tetraethylammonium chloride tetrahydrate was studied in [10]. It may be represented as anionic host lattice composed by $(H_2O)_4Cl^-$ tetrahedra whose vertices are linked through hydrogen bonds, generating two open linear channel systems. These channels accommodate ordered tetraethylammonium cations. It may be presumed that tetraethylammonium bromide tetrahydrate has analogous crystalline structure; in this case, the same cation (Et_4N^+) would be embedded in channels formed by H-bonded water molecules. The lower melting point of the 1:4 hydrate formed by tetraethylammonium bromide may be rationalized by stronger destabilizing effect of bromide anion whose size (3.4 Å) differs from the size of water molecule (2.8 Å) to a greater extent as compared to chloride ion (3.1 Å). Structures of higher hydrates (1:5, 1:7.5) were reported for tetramethylammonium hydroxide [2]. However, tetraethylammonium cation is larger than tetramethylammonium, so that it cannot be housed in the corresponding frameworks. Most probably, a different framework is formed, either that possessing large polyhedral cavities and their combinations, or channel-like, or layered. The structure of tetraethylammonium fluoride undecahydrate was studied in [3]. Here, water molecules and fluoride ions form a three-dimensional framework consisting of channels and cavities. The channels are occupied by tetraethylammonium cations, the narrower parts of the channels accommodating one cation, and the wider parts, two cations. The 4^25^8 cavities found previously for $(iso\text{-}C_5H_{11})_4PBr\cdot 32H_2O$ [17] and $Me_4NOH\cdot 7.5H_2O$ (β-phase) [2] remain unoccupied. A similar structure may be assumed for analogous hydrate of tetraethylammonium bromide.

EXPERIMENTAL

Tetraethylammonium bromide of pure grade was recrystallized thrice from ethanol and was dried in a desiccator over P_2O_5. The concentration of the main substance was estimated at 99.8±0.2 wt % by potentiometric titration with a solution of sodium tetraphenylborate using a ion-selective electrode [18].

The melting diagram was studied by differential thermal analysis on a custom-made setup. The required compositions were prepared by weighing from tetraethylammonium bromide and water, and the concentrations were determined as indicated above. A mixture with a definite composition and a reference liquid (silicone oil) were placed in ~0.1-ml tightly capped polyethylene ampules, and hot junctions of chromel–copel thermocouples were immersed therein. The cold junctions were placed in a Dewar flask charged with melting ice. The ampules containing a sample and reference were symmetrically mounted in sockets of a cylindrical thermoblock wrapped with a heating wire. The thermoblock containing the ampules was placed in a Dewar over liquid nitrogen. The temperature was controlled with the aid of a PIT-3 automatic controller ensuring both maintaining a constant temperature and linear temperature rise at a required rate. The thermocouples immersed in the sample and reference were connected so that to obtain a differential thermocouple. The output signals were the potentials of the thermocouple immersed in the sample and differential thermocouple, which were recorded in parallel using an automatic recorder. The signal from the differential thermocouple was amplified using an F-136 photoamplifier. The phase transition temperatures were determined from the maxima on the differential curves, and the potential of the working thermocouple was recalculated to temperature using a known calibration curve. The thermocouple was calibrated with the aid of an MIT-8 multichannel precision temperature meter and a resistance thermometer. The validity of the measurements was checked intermittently by the melting point of water.

The composition of peritectically melting compounds was determined by constructing the Tamman triangle [19]. The differential peak area for the corresponding phase transition was measured (it is proportional to the heat effect). Such experiments were carried out with equal amounts of samples.

The accuracy in the temperature measurement was ±0.1°C, and the accuracy in the determination of phase transition temperatures was ±0.2°C. Samples were heated at a rate of 0.5 to 1 deg/min and were cooled with liquid nitrogen at a rate of 10–15 deg/min; cooling curves were not recorded.

Crystals were isolated preparatively in a cold chamber at ~5°C by squeezing between filter paper sheets, and their composition was determined.

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