CLATHRATE FORMATION IN THE TETRAISOAMYLAMMONIUM PROPIONATE–WATER SYSTEM

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In this paper we examine clathrate formation in the tetraisoamylammonium propionate–water binary system. We have found formation of four polyhydrates, two of which are metastable over the whole temperature range studied. All polyhydrate crystals were isolated and their compositions and densities determined; for \((i-C_{11}H_{23})_4NC_3H_7COO \cdot 36.5H_2O\), unit cell parameters were additionally found. The results are compared with data for tetra-n-butylammonium carboxylate polyhydrates, and the structure of the title compounds is suggested. It is confirmed that the isoamyl radical stabilizes the tetradecahedral void of the clathrate hydrate framework better than the n-butyl radical.

Tetra-n-butylammonium (TBA) and tetraisoamylammonium (TiAA) cations are known to be the best stabilizing guest cations for clathrate framework voids in clathrate hydrates of tetraalkylammonium salts [1]. The effect of hydrophilic insertion of simple (halide) anions on clathrate formation was studied for both tetra-n-butylammonium [1, 2] and tetraisoamylammonium [1, 3] salts. However, in the case of carboxylate ions, which are inserted by the hydrophobic-hydrophilic mechanism, clathrate formation was studied only for some TBA salts [1, 4]. It was found that the carboxyl group of the anion is inserted into the framework hydrophilically, replacing two water molecules. The hydrophobic moiety, depending on its size, occupies either a vacant small dodecahedral (D) or a large tetradecahedral (T) or pentadecahedral (P) void. For tetraisoamylammonium carboxylates, no such data are available in the literature. In this paper we present the results of our investigation of clathrate formation in the TiAA propionate–water system and compare them with data for binary TBA carboxylate systems. The title system is also of interest to gain more profound insight into clathrate formation involving ionogenic polymers because TiAA propionate is a unit of carboxylic clathromionite synthesized from acrylic acid.

EXPERIMENTAL

Tetraisoamylammonium propionate was obtained from tetraisoamylammonium hydroxide by a neutralization reaction with propionic acid (bromothymol blue as an indicator).

Tetraisoamylammonium hydroxide was synthesized from tetraisoamylammonium iodide by an ion-exchange reaction with \(Ag_2O\). The resulting TiAA hydroxide solution was separated from the precipitate and then purified by recrystallization to clathrate hydrate.

The concentration of the tetraisoamylammonium cation in solution was measured by titration of the sodium tetrphenyl borate solution using a cation-selective electrode [5]. Thermal analysis was performed by the procedure and on the apparatus that are described in detail in [6]. The composition of products was determined by chemical analysis of isolated crystals. The density of hydrate crystals was found by the flotation method in the \(CCl_4 + C_{10}H_{22}\) mixture at 0°C.
RESULTS AND DISCUSSION

The phase diagram of the tetraisoamylammonium propionate–water system was studied in the region of clathrate formation by the DTA method. The results are presented in Fig. 1 and Table 1. In the diagram it is seen that two stable and two metastable compounds are formed in the system. Both stable polyhydrates seem to melt congruously; they have close melting temperatures (Table 2). The crystallization region is represented by a rather narrow concentration range for the 1:41 metastable hydrate (see Fig. 1) and by a wide concentration range for the incongruously melting 1:26 metastable hydrate in the field of existence of the 1:30.4 stable hydrate.

All polyhydrate crystals were isolated and analyzed and their melting points were determined. Crystal densities of stable hydrates were found; for 1:36.5 hydrate, unit cell parameters were additionally determined (see Table 2). The 1:36.5 crystals were readily isolated from \((i-C_3H_11)_4NC_2H_5COO\) solutions (20 wt. %) in the form of rhombic plates. The 1:30.4 crystals formed upon isothermal evaporation of this solution, with rhombic plates transformed into tetragonal prisms. During attempted preparation of 1:36.5 crystals from solutions with 15-20 wt. % of the salt, we occasionally observed co-crystallization of hydrates of both types, i.e., rhombic plates and tetragonal prisms. On seeding 1:30.4 crystals into the 40% tetraisoamylammonium propionate solution, crystals of only this hydrate formed.

The 1:26 metastable hydrate easily formed from solutions with 45-50 wt. % of the salt when the sample was quickly cooled to liquid nitrogen temperature. The presence of the 1:41 hydrate could only be established from data of three preparative determinations and by the narrow crystallization region in the range of existence of the 1:36.5 hydrate.

Regarding the structure of the compounds in question we can assume \((i-C_3H_11)_4NC_2H_5COO \cdot 36.5H_2O\) to be isostructural to \((C_4H_9)_4NC_2H_5COO \cdot 36.8H_2O\). For the latter, a complete X-ray structure investigation was carried out; it was shown that the structure is hexagonal and is a superstructure of a hexagonal gas hydrate structure of type I [1]. The 1:30.4 hydrate obviously crystallizes within tetragonal structure I (provided that two water molecules are replaced by the carboxylate ion from the framework, the calculated composition should be 1:31.4, as in the case of the corresponding tetrabutylammonium propionate hydrate). The 1:26 metastable hydrate is evidently an analog of the \((C_4H_9)_4NC_2H_5COO \cdot 26H_2O\) cubic hydrate [1]. The 1:41 hydrate possibly crystallizes within tetragonal structure I provided that the hydrophobic part of the anion occupies the T void rather than the D one as in the case of tetrabutylammonium carboxylate polyhydrates [1].

![Fig. 1. Phase diagram of the tetraisoamylammonium propionate–water binary system in the region of clathrate formation.](image-url)