

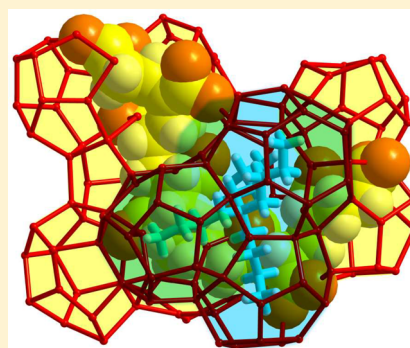
# Physicochemical and Structural Studies of Clathrate Hydrates of Tetrabutylammonium Polyacrylates

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## S Supporting Information

**ABSTRACT:** In this work, physicochemical and structural studies have been carried out for semiclathrate hydrates of linear (un-cross-linked) and cross-linked tetrabutylammonium polyacrylates with different degrees of cross-linking of the polymeric guest molecules ( $n = 0.5, 1, 2, 3\%$ ) and different degrees of substitution of proton ions of carboxylic groups in poly(acrylic acid) for TBA cations ( $x = 1, 0.8, 0.6$ ). The changes in the hydrates' stability and composition depending on the outlined parameters were examined in the course of phase diagram studies of the binary systems water–tetrabutylammonium polyacrylates using differential thermal analysis method and calorimetric measurements of fusion enthalpies of the hydrates. Phase diagram studies of the binary system water–linear tetrabutylammonium polyacrylate revealed the formation of four hydrates. Based on the data of chemical analysis of hydrate crystals the compositions of all hydrates have been determined. Single-crystal X-ray diffraction studies revealed a tetragonal structure, space group  $4/m$ , and unit cell parameters are close for different hydrates and lie in the ranges  $a = 23.4289\text{--}23.4713\text{ \AA}$  and  $c = 12.3280\text{--}12.3651\text{ \AA}$  (150 K). The structure can be related to tetragonal structure I typical for the clathrate hydrates of tetraalkylammonium salts with monomeric anions. Powder X-ray diffraction analyses confirmed the identity of the above crystal structure to that of the hydrates with cross-linked tetrabutylammonium polyacrylates. The behavior of TBA polyacrylate hydrates under the pressure of methane was studied and quantitative assessment of the gas content in the hydrates was made using volumetric analysis method.



## ■ INTRODUCTION

In the semiclathrate hydrates (or ionic clathrate hydrates<sup>1</sup>) of tetrabutylammonium (TBA) and tetraisoamylammonium (TiAA) salts that constitute the most studied group of semiclathrate hydrates of tetraalkylammonium salts, the host lattices are structurally related to those of gas hydrates and can be described as a combination of face-sharing D, dodecahedral ( $S^{12}$ ), T, tetradecahedral ( $S^{12}6^2$ ), and P, pentadecahedral ( $S^{12}6^3$ ) water polyhedra.<sup>1</sup> In the polyhydrates of tetraalkylammonium salts with simple anions such as halides, sulfate, formate, etc. (a term “polyhydrate” underlines the large hydration numbers peculiar to the ionic clathrate hydrates of tetraalkylammonium salts which can have the values 20–40<sup>1,2</sup>), water molecules together with the anions form a crystalline host framework linked by hydrogen bonds (hydrophilic inclusion of the anion). Hydrocarbon chains of the cation fill the compartments of the combined water polyhedra, formed by fusing four tetrahedrally arranged large cavities of the water framework (2T·2P, 3T·1P, 4T, depending on the structure), with displacing a water molecule common for the cavities by the central nitrogen atom of the cation (hydrophobic inclusion of the cation).<sup>1,2</sup> Small D-cavities are empty<sup>1,2</sup> or in some cases can be partially filled with “guest” water molecules.<sup>3</sup> In ionic clathrate hydrates of tetraalkylammonium salts with complex carboxylate anions hydrophobic–hydrophilic inclusion of the

anion occurs: the carboxyl group is included in water framework in a hydrophilic way to form an edge of a polyhedron, whereas the hydrophobic part of the anion occupies the cavity of water framework.<sup>4–7</sup> The most common ionic clathrate hydrate structures are tetragonal structure-I (TS-I), hexagonal structure-I (HS-I), cubic structure-I (CS-I) with ideal unit cell stoichiometry  $4P\cdot6T\cdot10D\cdot172H_2O$ ,  $2P\cdot2T\cdot3D\cdot40H_2O$ , and  $6T\cdot2D\cdot46H_2O$ , respectively.<sup>1</sup>

Because of the availability in the structures of vacant D-cavities, which can be occupied by gas molecules of a diameter less than 5.2 Å ( $O_2$ ,  $N_2$ ,  $CO_2$ ,  $CH_4$ ,  $C_2H_4$ ,  $H_2S$ , etc.),<sup>1</sup> at present gas hydrate formation with tetraalkylammonium salts used as auxiliary guest component is the subject of extensive research in terms of application of the hydrates for gas storage and separation.<sup>8–12</sup>

It is well-known that participation of auxiliary guest component in many cases results in the stabilization of gas hydrate structures.<sup>13</sup> This method was applied to reduce the equilibrium pressure of hydrogen hydrate,<sup>10,14,15</sup> which is 200 MPa at a temperature of 273 K.<sup>16</sup> According to the studies Florusse et al.<sup>14</sup> and later studies of Hashimoto et al.,<sup>10</sup> the use

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of tetrahydrofuran (THF), occupying large cavities in CS-II structure of gas hydrates,<sup>13</sup> reduces the equilibrium pressure of double hydrogen hydrate which is 5 MPa at 279.6 K<sup>14</sup> and 0.10 MPa at 277.8 K.<sup>10</sup> THF was also used as the auxiliary guest component for stabilization of nitrogen and methane hydrates.<sup>17</sup> According to the data,<sup>17</sup> the decomposition temperature of the double methane and THF hydrate is 292 K at a pressure of 2 MPa which is 15 K higher than the decomposition temperature of pure methane hydrate at the same pressure.

Semiclathrate hydrates of tetraalkylammonium salts are stable at room temperatures and atmospheric pressure<sup>2</sup> and the use of them as auxiliary guest component leads to even greater stabilization of gas hydrates.<sup>8–12,18</sup> As shown in ref 10, taking tetrabutylammonium bromide (TBABr) as the second guest component caused an increase in decomposition temperature of double hydrogen hydrate which is 285.4 K at a pressure of 0.13 MPa. The decomposition temperature of double TBABr and methane hydrate is ~291 K at atmospheric pressure.<sup>12</sup> The availability of the gas molecules in small D-cavities of the clathrate hydrate framework was strongly confirmed by the studies of TiAABr-CH<sub>4</sub>, THF-H<sub>2</sub>, and TBABr-H<sub>2</sub> double hydrates using single-crystal X-Ray structural analysis, Raman spectroscopy,<sup>1</sup> <sup>1</sup>H MAS NMR spectroscopy, and gas evolution analyses.<sup>18–20</sup> According to volumetric analyses data,<sup>19,21</sup> hydrogen occupancy degree of small D-cavities in the semiclathrate hydrate of TBABr of HS-I structure with unit cell stoichiometry 6D·4T·4P·76H<sub>2</sub>O synthesized at a pressure of 13.8 MPa and a temperature of 279.5 K is 0.36.<sup>19</sup> In the TBABr and methane double hydrate of this structure, methane occupancy degree of D-cavities is 0.5–0.6.<sup>21</sup>

It should be noted that, as distinguished from tetrahydrofuran, tetraalkylammonium salts are not volatile and therefore the gas that evolved on decomposition of the double hydrate will not be contaminated by this auxiliary guest component.

A practical limitation in using the gas hydrate technologies for gas storage and separation of gas mixtures may be the slow kinetics of clathrate formation observed for the bulk systems,<sup>20</sup> and so creation of a large interface between liquid water and gas is required. The energy-consuming procedures of water and/or gas dispersion were used to accelerate reaction of gas hydrate formation.<sup>20,22</sup> In the work,<sup>23</sup> the method was demonstrated that considerably improved the kinetics and reusability for gas clathrates by using an ultra-low-density emulsion-templated polymerized high internal phase emulsion (polyHIPE) material as a support for the dispersed clathrate hydrate phase. Significant kinetics enhancements were observed for H<sub>2</sub> hydrates with THF and TBABr and also for CH<sub>4</sub> hydrates by using the polyHIPE support with respect to very little gas uptake in the bulk systems.<sup>18,23</sup> The limitation of the method is the lower gas capacity of the materials in the comparison with this in the bulk possibly due to insufficient wettability of the hydrophobic support. The possibility was also investigated of using particulate hydrophilic water-swelling polymer networks as supports for improving the kinetics and recyclability of H<sub>2</sub> enclathration within clathrate hydrates.<sup>24</sup> It was shown that the use of slightly cross-linked poly(acrylic acid) sodium salt (PSA) as a support improved considerably H<sub>2</sub> enclathration kinetics and capacity in THF–H<sub>2</sub>O clathrate hydrate with respect to bulk solutions.

Another way that is discussed in this work consists in using water-swelling clathrate-forming polymeric materials as supports for gas storage. These materials are carboxylic

cationites of polyacrylate type, slightly cross-linked tetrabutylammonium and tetraisoamylammonium polyacrylates (TBA- and TiAAPac), which can be described by the general formula (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NCOOR<sub>n</sub> or (i-C<sub>5</sub>H<sub>11</sub>)<sub>4</sub>NCOOR<sub>n</sub>, R<sub>n</sub> is the polymeric cross-linked polyacrylate anion with the degree of cross-linking  $n = 0, 5, 1, 2, 3\%$  using divinylbenzene or divinyl sulfide as the cross-linking agents. The formation of the hydrate phase melting at positive temperature in swollen grains of slightly cross-linked TBA and TiAA polyacrylates (which can contain up to 78 wt % of water) was first revealed in ref 25. Invariable aggregative state of carboxylic cationite materials in the course of clathrate hydrate formation and decomposition processes makes the studies of the hydrate structures and thermodynamic properties very interesting from the viewpoint of the applications of the mentioned materials for gas storage.

In the ref 26 the results of our studies on the clathrate hydrate formation in swollen grains of carboxylic cationites in TiAA form (with the degree of cross-linking of polymeric molecules varying from 0 to 3%) were reported that included data on the structural, phase equilibria, and calorimetric studies of the hydrates formed. The total of the data obtained made it possible to suggest the model describing both the overall and local structure of the hydrates of TiAA polyacrylates with cross-links in the polymeric anion. The hydrate phase formed in the grain consists of a number of crystallites.<sup>27</sup> The crystal structure, independent of the degree of cross-linking, was found to be a variation of HS-I structure characteristic of the semiclathrate hydrates of tetraalkylammonium salts with monomeric anions.<sup>1</sup> The presence in the structure of unoccupied D-cavities capable of including small gas molecules was strongly confirmed by DTA studies under the pressure of hydrogen.<sup>26</sup>

Proceeding with our physicochemical and structural studies on the clathrate hydrate formation in the systems water–linear and cross-linked tetraalkylammonium polyacrylates, the clathrate hydrate formation with linear and cross-linked tetrabutylammonium polyacrylates ( $n = 0.5, 1, 2, 3\%$ ) has been studied for the first time. In order to investigate the clathrate hydrate formation with cross-linked TBA polyacrylates ( $n = 1\%$ ) depending on the mole fraction of TBA cations ( $x$ ) in the total amount of (TBA + H) cations in the polymeric molecule, the phase diagrams have been studied using differential thermal analyses (DTA) method of the binary systems H<sub>2</sub>O – [ $x$ (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N + (1 –  $x$ )H]COOR<sub>n</sub> ( $x = 1, 0.8, 0.6$ ). To estimate quantitatively the stability of the hydrates depending on the mentioned parameters, calorimetric studies have been conducted and the fusion enthalpies of the hydrates have been measured. In order to support the clathrate nature of the studied compounds, structural studies of the hydrates with linear and cross-linked TBA polyacrylates have been carried out. With the intent of examination of the availability of cavity space in the structures for the gas molecules in this work, the behavior of TBA polyacrylate hydrates under a pressure of methane has been studied for the first time and the quantitative assessment of the gas content in the hydrates depending on the mole fraction of TBA cations in the polymeric salt has been made using volumetric analysis method.

## ■ EXPERIMENTAL SECTION

**Reagents.** The carboxylic cation-exchange resins (cationites) in the H-form (0.5, 1, 2, and 3% of cross-linking by divinylbenzene as the cross-linking agent) were first treated with 0.1 M solutions of HCl and NaOH, and washed with

Table 1. Physicochemical and Structural Properties of the Polyhydrates of Tetrabutylammonium Polyacrylates

hydrate composition <sup>a</sup>	decomp temp, °C	$\Delta H_{\text{fusion}}$ , kJ/(mol of H <sub>2</sub> O) (kJ/(mol of hydrate))	crystal system, space group, unit cell dimensions (Å)
(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NCOOR <sub>1</sub> ·30.0H <sub>2</sub> O <sup>b</sup> ( <i>n</i> = 1%) <i>x</i> = 1	+8.5	4.31 ± 0.10 (128.9 ± 3.0)	tetragonal, <i>P4/m</i> , <i>a</i> = 23.598(25), <i>c</i> = 12.392(2) (248 K)
(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NCOOR <sub>1</sub> ·30.0H <sub>2</sub> O <sup>b</sup> ( <i>n</i> = 1%), metastable	+5.0	3.74 ± 0.16 (112.2 ± 4.8)	—
(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NCOOR <sub>1</sub> ·26.3H <sub>2</sub> O <sup>b</sup> ( <i>n</i> = 1%) <i>x</i> = 1	+8.5	4.50 ± 0.16 (118.4 ± 4.2)	tetragonal, <i>a</i> = 23.61, <i>c</i> = 12.40 (248 K)
[(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N]COOR <sub>1</sub> ·26.5H <sub>2</sub> O <sup>b</sup> ( <i>n</i> = 1%), <i>x</i> = 0.8	+8.0	4.34 ± 0.16 (115.0 ± 4.2)	tetragonal, <i>P4/m</i> , <i>a</i> = 23.590(30), <i>c</i> = 12.398(2) (248 K)
[(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N]COOR <sub>1</sub> ·26.5H <sub>2</sub> O <sup>b</sup> ( <i>n</i> = 1%) <i>x</i> = 0.8, metastable	+5.0	3.86 ± 0.20 (102.3 ± 5.3)	—
[(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N]COOR <sub>1</sub> ·25.0H <sub>2</sub> O <sup>b</sup> ( <i>n</i> = 1%) <i>x</i> = 0.6	+6.2	3.93 ± 0.12 (98.2 ± 3.0)	tetragonal, <i>P4/m</i> , <i>a</i> = 23.595(30), <i>c</i> = 12.400(2) (248 K)
[(-CH <sub>2</sub> CHCOO(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N-)]·(32.87 ± 0.20)H <sub>2</sub> O] <sub>m<sup>c</sup></sub> ( <i>n</i> = 0)	+13.2	4.74 ± 0.08 (155.8 ± 2.7)	tetragonal, <i>4/m</i> , <i>a</i> = 23.4591(18), <i>c</i> = 12.3280(6) (150 K) <i>a</i> = 23.592(28), <i>c</i> = 12.398(2) (248 K)
[(-CH <sub>2</sub> CHCOO(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N-)]·(31.62 ± 0.31)H <sub>2</sub> O] <sub>m<sup>c</sup></sub> ( <i>n</i> = 0)	+15.0	—	tetragonal, <i>4/m</i> , <i>a</i> = 23.4713(19), <i>c</i> = 12.3281(10) (150 K)
[(-CH <sub>2</sub> CHCOO(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N-)]·(30.04 ± 0.31)H <sub>2</sub> O] <sub>m<sup>c</sup></sub> ( <i>n</i> = 0)	+15.0	—	tetragonal, <i>4/m</i> , <i>a</i> = 23.4356(8), <i>c</i> = 12.3303(5) (150 K)
[(-CH <sub>2</sub> CHCOO(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N-)]·(28.43 ± 0.09)H <sub>2</sub> O] <sub>m<sup>c</sup></sub> ( <i>n</i> = 0)	+17.5	4.60 ± 0.24 (130.8 ± 6.8)	tetragonal, <i>4/m</i> , <i>a</i> = 23.4289(16) <i>c</i> = 12.3651(8) (150 K) <i>a</i> = 23.551(45), <i>c</i> = 12.438(4) (248 K)
(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NCOOR <sub>3</sub> ·27.3H <sub>2</sub> O <sup>b</sup> ( <i>n</i> = 3)	+6.0	3.68 ± 0.24 (100.5 ± 7.0)	—
(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NCOOR <sub>3</sub> ·23.8H <sub>2</sub> O <sup>b</sup> ( <i>n</i> = 3)	+6.0	—	—

<sup>a</sup>For the polyhydrates of linear and cross-linked polyacrylates, the hydration number given is the number of water molecules per the elementary group [(-CH<sub>2</sub>CHCOO(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N-)]. <sup>b</sup>Phase diagram studies. The composition of the metastable hydrate phase was assumed to be consistent with that of the stable hydrate. <sup>c</sup>Chemical analysis of the isolated crystals (6–10 definitions).

ethanol and then with a large amount of distilled water to remove ethanol. The tetrabutylammonium form of the studied resins was prepared under static conditions by neutralizing the polymeric acid with a 3-fold stoichiometric excess of aqueous 0.1N solution of (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NOH. The mixed [*x*(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N + (1 - *x*)H]COOR<sub>*n*</sub> forms of the resin with *n* = 1% (*x* = 1, 0.8, 0.6) were prepared in the same manner by neutralizing the polymeric acid with calculated amount of 0.1N solution of (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NOH. After the neutralization reaction was completed, the grains of the resins were centrifuged for 10 min in a hermetic vessel at a rate of 2300 rpm (400g) and washed with distilled water until the washing water became neutral, and after that were centrifuged at the same conditions. The ability of cationites conditioned according to the above procedure to swell was examined by the measured mass loss upon drying using NaOH (solid) as the dehydration agent, the residual water content (1–2 wt %) was determined on drying a portion of cationite over P<sub>2</sub>O<sub>5</sub>. For carboxylic cationite with *n* = 1% the maximum values of water content in the swollen samples of cationite with different mole fraction of TBA cations in the polyacrylate chains were determined to be 77.4 wt % H<sub>2</sub>O (*x* ≈ 1); 78.0 wt % H<sub>2</sub>O (*x* = 0.8); 74.9 wt % (*x* = 0.6). The cationite ion exchange capacity with respect to TBA cations, provided proton ions of the carboxylic groups have been fully substituted for TBA cations, is close to 3.02 mg equiv of TBA per 1 g of dry resin in TBA form. This value is 95% of the theoretical one (3.17 mg equiv of TBA per 1 g of dry resin in this form) due to the cross-linkages in the polymer guest subsystem.

Tetrabutylammonium hydroxide (10% aqueous solution, “Chemapol”) of “pure” grade was purified through the recrystallization in the form of a clathrate hydrate.

Poly(acrylic acid) (Pac) with average molecular mass of 1800 Da (Aldrich) without further purification and tetrabutylammonium hydroxide solution were used to prepare tetrabutylammonium salt of linear (un-cross-linked) polymer.

Methane gas with a purity not less than 99.99% and distilled water were used in the experiments.

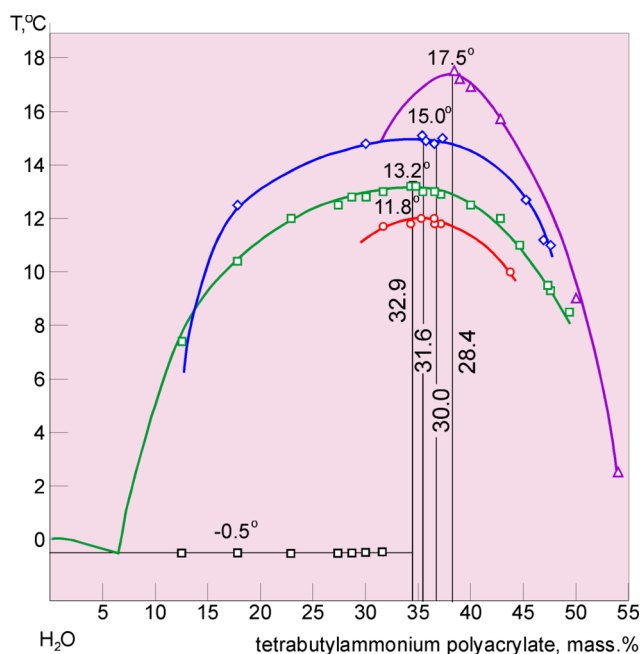
The concentration of TBAPac in the solution was determined by potentiometric titration of a sample with 5 × 10<sup>-3</sup> M aqueous solution of sodium tetraphenylborate using cation-selective electrode.

**Preparation of the Samples for DTA, Calorimetric, and X-ray Studies.** The samples for DTA studies of binary systems water–cross-linked tetrabutylammonium polyacrylates were prepared by a weighing technique. In this procedure, a quartz ampule was loaded with weighed portion of a dried resin (with residual water content 1–2 wt %) and then a calculated amount of water was added to prepare the sample of given composition. The samples were equilibrated in the hermetically closed ampules for 24 h for the grains to swell and then were recorded. In order to study the phase diagram of water–linear TBA polyacrylate system the solutions with different concentrations of the salt were used.

The samples for calorimetric studies of the hydrates of cross-linked TBA were prepared using the above procedure. For this purpose, a weighed portion of a dried resin and a certain amount of water, corresponding to the amount of water in the hydrate (the data of phase diagram studies, Table 1), were placed in an ampule made of quartz and allowed to stand for 24 h in tightly closed ampoules for the grains to swell. After that, the conditioned samples were transferred into stainless steel ampules used for the measurements.

The crystals of the semiclathrate hydrates of linear TBA polyacrylates with different compositions used for calorimetric and X-ray diffraction experiments were grown in a homemade air thermostat from aqueous solutions of the salt in the concentration and temperature stability regions of the hydrates defined by phase diagram studies (Figure 1). The crystals were separated from the supernatant fluid at the temperature of the crystal growth and squeezed quickly between two sheets of filter paper to remove residual amount of fluid. After that, a





**Figure 1.** Phase diagram of the binary system water–linear (uncross-linked) tetrabutylammonium polyacrylate in the region of the clathrate hydrate formation.

portion of crystals was taken for chemical analysis, and the other portion was simultaneously used for calorimetric and X-ray experiments.

For the calorimetric studies, the samples of the hydrate crystals of 40–50 mg were enclosed in steel ampoules which were used for measurements. The absence of residual supernatant fluid in the samples was confirmed by the absence of the corresponding signal on the DSC curve in the course of measurements.

For the single-crystal X-ray diffraction study, a crystal picked from under the supernatant fluid was instantly frozen to 150 K and studied at this temperature. The polycrystalline samples of the hydrates of tetrabutylammonium polyacrylates for powder X-ray diffraction studies were prepared by careful graining the crystalline phase in a chamber kept at a temperature below 0 °C. Powdered crystalline silicon (5–10 wt %) was added as an internal standard. The powderlike samples were placed on a standard holder and placed into low-temperature X-ray diffraction cell.

For volumetric analyses, a weighed portion of the sample of cross-linked TBA polyacrylate hydrate phase (~500 mg) was placed in a container of volume 1 mL and conditioned in autoclave under a pressure of methane of ~8 MPa and a temperature of ~2 °C for 2–3 weeks.

**Methods.** In order to determine the phase diagrams of the systems water–tetrabutylammonium polyacrylate, differential thermal analysis (DTA) method was used to record the temperatures of phase transformations. The setup utilized was equipped with chromel–alumel thermocouples and was calibrated with a mercury thermometer. The samples (30–40 mg) were placed in special quartz ampoules. The systems were studied in the temperature range from –30° to +30 °C at the heating rate of 1°/min. Phase transition temperatures were determined with an accuracy of 0.2 °C.

The compositions of the incongruently melting hydrates of cross-linked polyacrylates were determined by the Tamman

triangle method using the relative values of the heat effects for the hydrate decomposition process with the maximum value being in line with the hydrate composition.<sup>28</sup> The compositions of the hydrates could also be judged from the decrease of the heat effects of decomposition of eutectic mixtures (near 0 °C) approaching the concentrations, corresponding to the compositions of the hydrates. It was assumed on the calculation that the hydration number for the clathrate hydrates of cross-linked polyacrylates in the mixed (TBA + H) form that protonated carboxyl group in the polymer chain was hydrated with 4.8 water molecules according to our data obtained in the studies of the hydration of protonated form of carboxyl cationite (cross-linked polyacrylate) with 3% degree of cross-linking. The data were in agreement with the results of the studies<sup>29</sup> showing that the hydration numbers for protonated forms of carboxyl cationites with low and average degree of cross-linking fall in the range 4–5.

The compositions of the clathrate hydrates of linear TBAPac were determined by chemical analysis of isolated crystals (Table 1).

The calorimetric measurements were conducted using a differential scanning calorimeter DSC 111 from Setaram in the temperature range from –100 to +50 °C, at the heating rate of 0.5 °C/min. For the hydrates of cross-linked TBA polyacrylates and of linear TBA polyacrylate with composition 1:32.9, the average values for the enthalpy of fusion were calculated from 6 to 10 measurements; the standard deviation was below 3%. For the hydrate of linear TBA polyacrylate with the composition 1:28.4, the enthalpy of fusion was calculated from five measurements, and the standard deviation was ~5%. It should be noted that neither DTA nor the DSC thermograms of the samples with linear and cross-linked polyacrylates,<sup>26</sup> which corresponded to exact hydrate compositions, revealed any other thermal events but the melting of the hydrates in the studied temperature range. When the amount of water in a sample exceeded the water content in the expected hydrate, an additional effect at ~0 °C was observed on the DTA and DSC thermograms, the effect arising from the water–hydrate eutectics.

The temperatures of hydrate dissociation as a function of pressure were measured by DTA conducted under high pressures. The pressure was determined with the standard deviation of 0.5% and the temperatures were measured with an accuracy of 0.3 °C. The experimental apparatus used was described in detail elsewhere.<sup>30</sup> The samples of the hydrate phase of carboxylic cation-exchange resins in TBA form were loaded into DTA container with a volume of 0.05 mL. The container was hermetically closed and connected with a 6–8 mL stainless steel flask equipped with a movable piston and a back valve. After that, the flask was filled with the methane gas at pressures up to 2 MPa. The assembled cell was placed into the zone of high hydrostatic pressure produced by compression of a silicon oil–hexane mixture. The pressure was transmitted into the cell by means of the piston movement. The temperatures of phase transitions were recorded in the course of heating the DTA cell at the moment of maximum temperature difference between a reference thermocouple and a sample thermocouple inserted into the container with a sample.<sup>26</sup>

In the course of volumetric measurements of methane gas content in the hydrates, the release of methane from the studied samples was monitored as a function of temperature by

collecting the gas into a calibrated buret placed into a concentrated aqueous NaCl solution.<sup>31</sup>

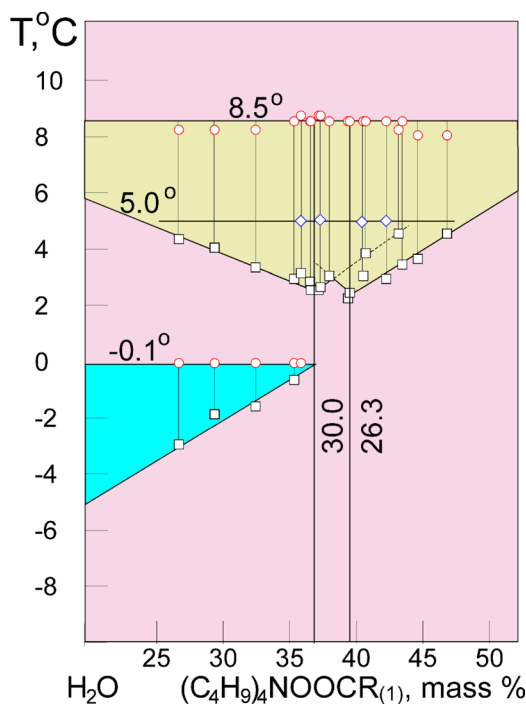
X-ray powder diffraction studies were performed at the temperature of 248 K on a Bruker D8 Advance diffractometer (Cu K $\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$ ) equipped with Anton Paar refrigerating device. The powder diffraction patterns were recorded in  $2\theta$  scan mode in the range of  $1\text{--}50^\circ$  with steps of  $0.02^\circ$  on  $2\theta$ . In the single-crystal X-ray diffraction experiments of the hydrates of linear TBA polyacrylates, the diffraction data were collected on a Bruker X8APEX CCD diffractometer with a graphite-monochromatized Mo K $\alpha$  radiation using  $\phi$  scans.<sup>32</sup> The structure was solved by direct methods and refined by full-matrix least-squares method against  $|F|^2$  using SHELXTL programs package.<sup>33</sup>

## RESULTS AND DISCUSSION

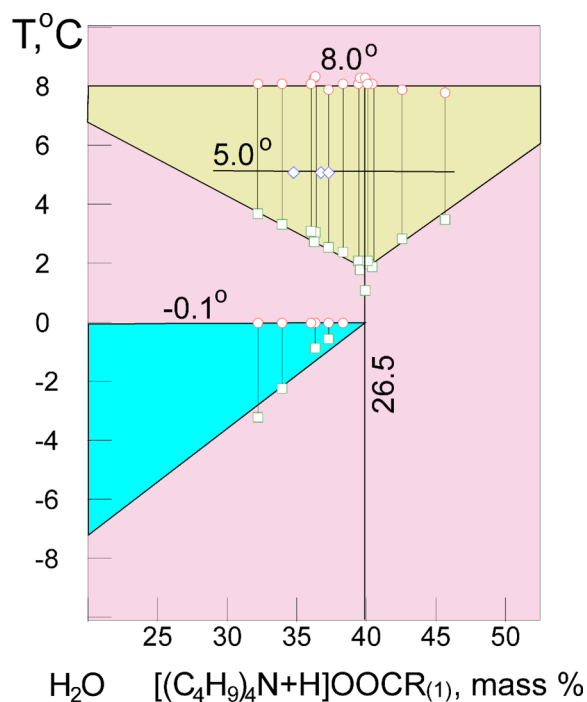
**Phase Diagram Studies.** The phase diagram studies of the binary systems water–TBA polyacrylates using DTA technique made it possible to define the concentration and temperature stability regions of the hydrates formed. On the basis of the data of phase diagram studies of the system with linear TBA polyacrylate (Figure 1), the crystals of all hydrates were grown and the compositions of the compounds were determined by chemical analysis of isolated crystals.

It should be noted that the phase diagram studies of the binary water systems with water-soluble TBA salts having monomeric anions, reported previously,<sup>2,7</sup> revealed the formation of congruently melting semiclathrate hydrates, as in the case of water-soluble TBA polyacrylate studied in this work.

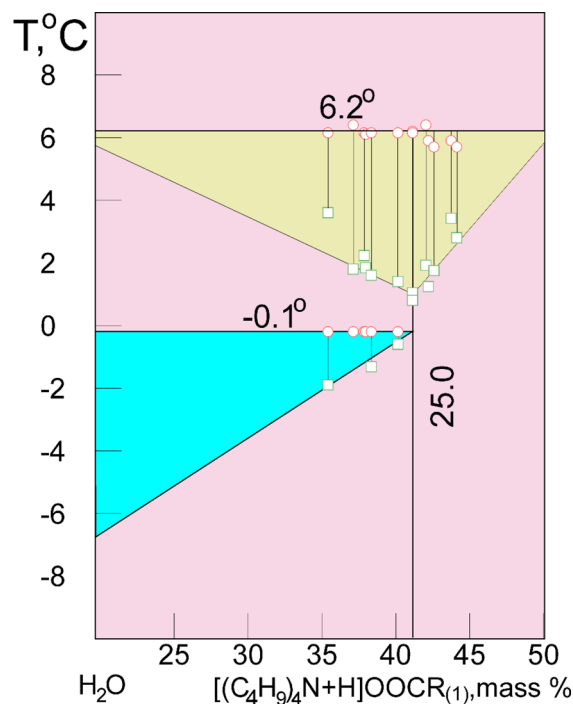
Since cross-linked TBA polyacrylates are water-insoluble, the hydrates formed in the binary water systems (Figures 2–5) decompose incongruently at a constant temperature.



**Figure 2.** Phase diagram of the binary system  $\text{H}_2\text{O}-(\text{C}_4\text{H}_9)_4\text{NCOOR}_1$  ( $n = 1\%$ ) in the region of the clathrate hydrate formation. Decomposition of metastable hydrate phase ( $5^\circ\text{C}$ ) is denoted with a straight line.

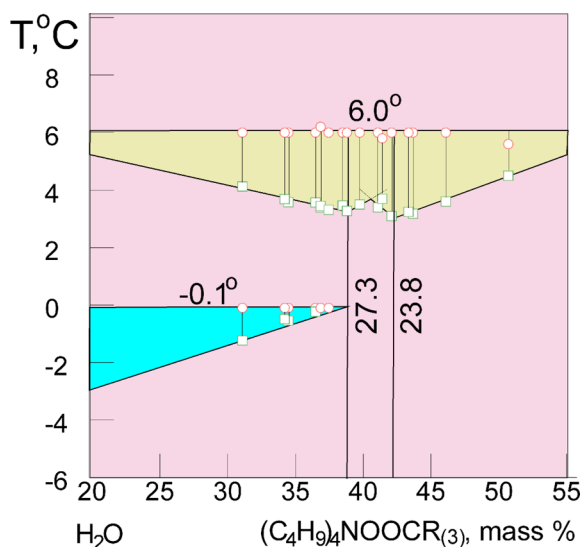


**Figure 3.** Phase diagram of the binary system  $\text{H}_2\text{O}-[(\text{C}_4\text{H}_9)_4\text{N} + \text{H}]\text{COOR}_1$  ( $n = 1\%$ ,  $x = 0.8$ ) in the region of clathrate hydrate formation. Decomposition of metastable hydrate phase ( $5^\circ\text{C}$ ) is denoted with a straight line.



**Figure 4.** Phase diagram of the binary system  $\text{H}_2\text{O}-[(\text{C}_4\text{H}_9)_4\text{N} + \text{H}]\text{COOR}_1$  ( $n = 1\%$ ,  $x = 0.6$ ) in the region of clathrate hydrate formation.

The compositions of the hydrates, melting incongruently, were estimated by “Tamman triangle” method using the relative values of the heat effects for the hydrate decomposition process, which could be determined as a ratio of area of corresponding thermal effects in DTA curves to a sample weight (relative values of the hydrate decomposition heat effects are denoted by



**Figure 5.** Phase diagram of the binary system  $\text{H}_2\text{O}-(\text{C}_4\text{H}_9)_4\text{NCOOR}_n$  ( $n = 3\%$ ) in the region of the clathrate hydrate formation

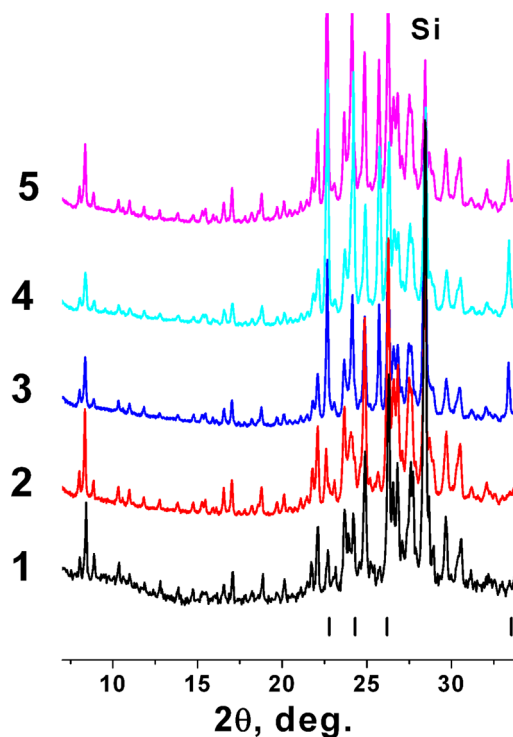
lines in upper shadow regions in Figures 2–5). The upper shadow regions represent the changes in relative values of hydrate decomposition heat effects dependent on the composition of the sample in the binary system. The maximum value will correspond exactly to the hydrate composition.<sup>28</sup> The lower shadow regions in Figures 2–5 represent the decrease in the decomposition heat effects of water–hydrate eutectics mixtures (near 0 °C) approaching the concentrations, corresponding to the compositions of the hydrates. It should be noted that DTA thermograms of the samples with linear and cross-linked polyacrylates, that corresponded to exact hydrate compositions, did not reveal any other thermal events but only the melting of the hydrates in the studied temperature range. When the amount of water in a sample exceeded the water content in the expected hydrate, an additional effect at ~0 °C was observed on the DTA thermograms, the effect arising from the water–hydrate eutectics.

The results of phase diagram studies are summarized in Table 1 along with structural and calorimetric data.

It is seen from phase diagram data that decomposition temperatures of the hydrates decrease with the increase in cross-linking degree and with the decrease in mole fraction of TBA cations in the polymeric molecules. The compositions of the hydrates were found to be close to those characteristic of the clathrate hydrates of tetraalkylammonium salts with monomeric anions having the polyhedral water framework.<sup>1</sup> It was found in the course of phase diagram studies that metastable hydrate phases crystallize readily in the systems on rapid cooling of the initial samples (Figures 1–3). The formation of metastable semiclathrate hydrates was observed also in earlier studies of the binary water systems with TBA salts having monomeric anions.<sup>2,7</sup> In the system water–linear (uncross-linked) TBA polyacrylate, the formation of the metastable hydrate with melting temperature of 11.8 °C and composition  $\text{TBA Pac} \cdot 31.9\text{H}_2\text{O}$  (preparative analysis data, single definition) was revealed (Figure 1). Apparently, analogous hydrate phase with the hydration number  $30 \pm 1$  and melting temperature of 11.2 °C was discovered by Nakayama<sup>34</sup> in studies of this system using DSC method under the same conditions.

To determine if the hydrates were stable hydrates, in some cases long hold times were required at the particular temperature conditions (for two weeks, as in the case of the hydrates of cross-linked TBA polyacrylate with mole fraction of TBA cation  $x = 0.8$  and 0.6).

**Structural Studies.** The determination of the crystal structure would be extremely difficult to complete for the hydrates of cross-linked polymeric carboxylates as the obtaining of single crystals of the hydrates is impossible. Therefore, a hydrate with linear tetrabutylammonium polyacrylate as in the case of the polyhydrate with linear tetraisoamylammonium polyacrylate reported previously<sup>35</sup> was attempted as a first model approximation. The validity of this approach was clearly demonstrated by the comparison of powder X-ray diffraction patterns of the samples of the hydrates with linear and cross-linked TBA polymers that revealed the identity of the crystal structures (Figure 6; see also Supporting Information, Tables S1–S3).<sup>36</sup> This point will be discussed below in more detail.



**Figure 6.** Powder diffraction patterns (248 K) of the hydrates of linear polyacrylates of TBA (1,2) and the hydrates of cross-linked TBA polyacrylates with degree of cross-linking  $n = 1\%$  (3–5). 1,  $\text{TBA Pac} \cdot 28.43\text{H}_2\text{O}$ ; 2,  $\text{TBA Pac} \cdot 32.87\text{H}_2\text{O}$ ; 3,  $(\text{C}_4\text{H}_9)_4\text{NCOOR}_n \cdot 30.0\text{H}_2\text{O}$  ( $x = 1$ ); 4,  $(\text{C}_4\text{H}_9)_4\text{NCOOR}_n \cdot 26.5\text{H}_2\text{O}$  ( $x = 0.8$ ); 5,  $(\text{C}_4\text{H}_9)_4\text{NCOOR}_n \cdot 25.0\text{H}_2\text{O}$  ( $x = 0.6$ ). Si, (111) reflection of silicon which was used as internal standard. Sticks correspond to the positions expected for ice Ih reflections.

In order to characterize the hydrate phases crystallized in the system water – tetrabutylammonium polyacrylate single-crystal X-ray diffraction studies were performed for four semiclathrate hydrates formed in the system according to phase diagram and analytical studies (Figure 1, Table 1).

Because of significant disordering in the guest and partially in the host subsystems, we failed to solve the structure in detail at present. However, important structural peculiarities have been revealed. Unit cell parameters of all crystals studied are close and vary in the ranges  $a \approx b = 23.4289\text{--}23.4713\text{Å}$ ,  $c =$

12.3280–12.3651 Å (150 K), and the angles are close to 90° (Table 1). It was found in the course of the statistical analysis of *hklf* data that crystals of all studied hydrates have Laue class 4/*m*. The structural models obtained using SHELX software<sup>33</sup> show that studied hydrates have the crystalline water frameworks related to TS-I characteristic of semicathrate hydrates of tetrabutylammonium salts with monomeric anions.<sup>1</sup> The TBA cations of the polymeric guest are included in the combined T<sub>3</sub>P and T<sub>4</sub> cavities in the structure. These complex cavities are typical for TS-I structure of semicathrate hydrates of TBA salts with monomeric anions and were discovered earlier by Jeffrey et al. in the tetragonal structures of semicathrate hydrates of tetrabutylammonium fluoride and tetrabutylammonium benzoate<sup>1,4</sup> and also in the structure of tetrabutylammonium valerate hydrate reported recently.<sup>6</sup>

It can be assumed that the incorporation of the carboxylate groups of the polymeric anion in the structure of the hydrate of TBA polyacrylate occurs as a hydrophilic inclusion, as it was observed in the structures of semicathrate hydrates of tetrabutylammonium benzoate, tetraisoamylammonium propionate, and tetrabutylammonium valerate<sup>4–7</sup> and was also considered for the structure of the hydrate of TiAA polyacrylate.<sup>26,35</sup> In this mode of inclusion, the two O atoms of the carboxylate group replace two adjacent O atoms in the water polyhedron. Based on the presence of the electronic density in all symmetrically independent D-cavities of the framework, revealed in the course of structural studies, it may be assumed that the hydrophobic part of polyacrylate anion is accommodated inside small D-polyhedra in the structure. As may be suggested for the studied hydrates having TS-I structure, in this type of inclusion the hydrophobic part of the polyacrylate anion penetrates through associated D-cavities that are present in TS-I structure as the blocks constituted by five face-shared D-polyhedra<sup>1</sup> (two blocks per elementary unit cell). It should be noted that location of hydrophobic part of propionate ion in the D-cavity of the water framework (propionate ion is a monomeric unit of polyacrylate anion) was observed in the structure of the semicathrate hydrate of tetraisoamylammonium propionate.<sup>5</sup> The accommodation of the hydrophobic part of polyacrylate anion inside the layers of D-polyhedra was considered for the hydrate of tetraisoamylammonium polyacrylate of HS-I structural type.<sup>26,35</sup>

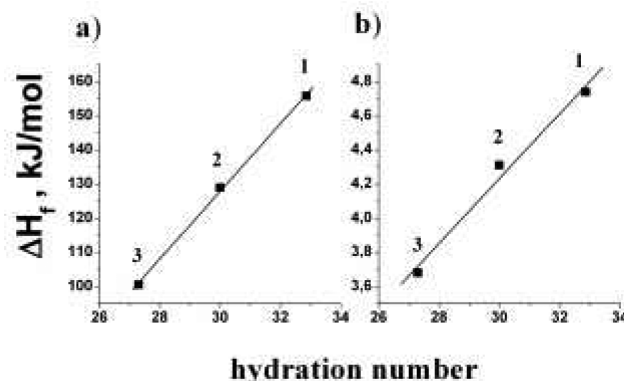
X-ray powder diffraction studies of cross-linked TBA polyacrylate hydrates with  $n = 1\%$  and  $\alpha \cong 1$ ,  $\alpha = 0.8$ , and  $\alpha = 0.6$  confirm the existence of a crystalline hydrate phase in swollen grains of studied carboxylic cationites in the temperature ranges, determined by DTA studies. As is seen from Figure 6, powder X-ray diffraction patterns are very similar that reveals the isostructurality of studied hydrates. To investigate the influence of cross-linking degree on the structure of the hydrates of cross-linked TBA polyacrylates, X-ray powder diffraction studies were performed also of the samples of the carboxylic cationites in the TBA form with degree of cross-linkages 0.5% and 2% (Table S1 in the Supporting Information). Analysis of the patterns of the hydrates with different mole fraction of TBA cations in the polymeric chain and different degree of cross-linking has shown that all patterns may be interpreted assuming the formation of the hydrates with tetragonal crystal system and close unit cell parameters that suit well to TS-I typical for many clathrate hydrates of tetrabutylammonium salts with monomeric anions<sup>1</sup> (Table 1, and Supporting Information, Tables S2 and S3). It should be noted that the hydrate of tetrabutylammonium propionate that

is a monomeric unit of tetrabutylammonium polyacrylate guest molecule  $[-CH_2CHCOO(C_4H_9)_4N-]$  having the hydration number 31.6 and melting temperature of 16.8 °C also crystallizes in TS-I structure with unit cell parameters  $a = 23.7$  Å and  $c = 12.5$  Å (263 K).<sup>6</sup>

X-ray diffraction experiments performed for the metastable hydrate phase made it possible to suggest TS-I for this hydrate with many structural defects present (powder diffraction patterns are similar to those of the stable hydrate phase, presented in Figure 6, though the reflections are broadened).

**Calorimetric Studies.** In order to evaluate quantitatively the destabilization of the hydrate framework caused by cross-links in the polymeric guest subsystem and by deficiency in TBA cations in the polymeric guest molecule, the heats of fusion were measured for stable and some metastable hydrates formed in the systems studied. The results are given in Table 1. It should be noted that some data on fusion enthalpies of the hydrates with linear TBA and TiAA polyacrylates have been reported by Nakayama.<sup>34</sup> According to the data,<sup>34</sup> the fusion enthalpy of the hydrate with linear TBA polyacrylate with hydration number  $30 \pm 1$  and melting temperature of 11.2 °C is 4.60 kJ/(mol of H<sub>2</sub>O). The value is comparable to the values of fusion enthalpies measured in this work for the hydrates of linear TBA polyacrylates TBAPac-32.87H<sub>2</sub>O (13.2 °C) and TBAPac-28.43H<sub>2</sub>O (17.5 °C) which are 4.74 kJ/(mol of H<sub>2</sub>O) and 4.60 kJ/(mol of H<sub>2</sub>O), respectively (Table 1).

It was shown in DSC studies that fusion enthalpies of studied hydrates as well as their decomposition temperatures decrease with increase in cross-linkage degree and with decrease in mole fraction of TBA cations in the polymeric guest molecule. It becomes evident from Figure 7 that as in the case of the



**Figure 7.** Fusion enthalpies of the polyhydrates of cross-linked TBA polyacrylates with the different degree of cross-linking relative to (a) mole of hydrate and (b) mole of water vs the hydration number. 1, TBAPac-32.9H<sub>2</sub>O,  $n = 0$ ; 2,  $(C_4H_9)_4NCOOR_1 \cdot 30.0H_2O$ ,  $n = 1$ ; 3,  $(C_4H_9)_4NCOOR_3 \cdot 27.3H_2O$ ,  $n = 3$ .

hydrates of cross-linked TiAA polyacrylates, discussed earlier,<sup>26</sup> the fusion enthalpies of the hydrates of cross-linked TBA polyacrylates with different degree of cross-linking are linear functions of the hydration number. (In the presence of several hydrates in the system, the comparison was made of fusion enthalpies of the hydrates with maximum value of the hydration number.)

It follows from the data obtained that the removal of one water molecule from the hydrate framework that belongs to TS-I type of structure decreases on average the fusion enthalpy by 9.7 kJ/(mol of hydrate) (Figure 7). For comparison, for the



hydrates of cross-linked TiAA polyacrylates related to HS-I type this value was determined to be 8.4 kJ/(mol of hydrate).<sup>26</sup>

The analysis of the experimental data made it possible to summarize the properties of the semicathrate hydrates of TBA polyacrylates. It may be suggested that similar to the hydrates of cross-linked tetraisoamylammonium polyacrylates the crystalline hydrate phase formed in swollen grains of cross-linked TBA polyacrylates (carboxylic cationites in TBA form) consists of a number of crystallites the formation of which requires some ordering of adjacent chains in a microregion inside the cationite grain.<sup>27</sup> Taking into account the isostructurality of the hydrates with cross-linked and linear polyacrylates, the motif of such ordering is likely to copy the corresponding structural motif of the hydrate with linear polyacrylate.<sup>26</sup>

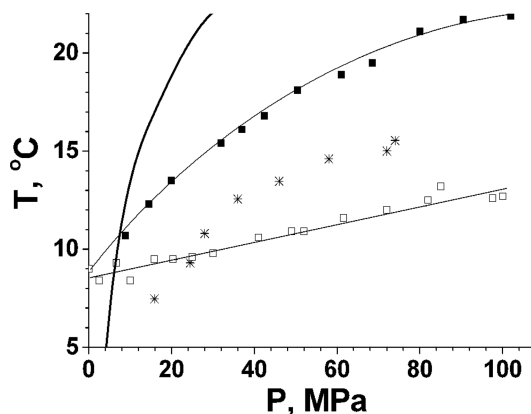
The cross-links, "chemical knots" and caused by them "physical knots" in the polymeric guest molecules (the formation of those may result from electrostatic interaction of the polar groups in the adjacent chains or from their mechanical entanglement<sup>37</sup>), are incorporated in these crystallites. According to the estimations of the size of hydrate crystallites formed in swollen grains of carboxylic cationites in TiAA form,<sup>27</sup> a typical size of crystallites is over 1000 Å. This value exceeds the distance between cross-links in polyacrylate chain ( $\sim 250$  Å for  $n = 1\%$ ) and counts in favour of incorporation of cross-links in the structure. Since the hydration number is reduced with the increase of cross-linking degree (as follows from phase diagram studies), the conclusion can be made that incorporation of cross-links cause the displacement of the water molecules from the hydrate framework. Created defects destabilize the structure decreasing the fusion enthalpies and decomposition temperatures of the hydrates. The same dependences were observed earlier for the semicathrate hydrates of cross-linked TiAA polyacrylates.<sup>26</sup>

For the hydrates of cross-linked TBA polyacrylates with nonstoichiometric content of TBA cations in the polymeric guest molecule, destabilization of the structure with the decrease in mole fraction ( $x$ ) of TBA cations can be associated with the deficiency in TBA cations occupying large combined  $T_4$  and  $T_3P$  cavities in the TS-I structure.

It can be said, however, that the structural defects caused by cross-links in the polymeric guest molecules or by deficiency in TBA cations (on incomplete substitution of the proton ions of the carboxylic groups for TBA cations) do not alter the structural type (TS-I) and unit cell parameters of the hydrates (Table 1).

**Double Hydrates of Cross-Linked TBA Polyacrylates and Methane.** According to our structural results and earlier structural studies on the polyhydrates of TiAA carboxylates,<sup>4,35</sup> some of the D-cavities in the structures may be vacant from the main guest. The availability of vacant cavity space in the structure of TBA polyacrylate hydrates for other molecules, especially for gas molecules, is of significant interest. In order to examine this availability, the behavior of TBA polyacrylate hydrates with different mole fraction of TBA cations in the polymeric guest molecule was investigated under the pressure of methane.

In the Figure 8 the  $P$ – $T$  decomposition curve for the double hydrate of cross-linked TBA polyacrylate ( $x = 1$ , full substitution of proton ions of carboxylic groups with TBA cations) and methane is presented along with the  $P$ – $T$  decomposition curve for the hydrate of TBA polyacrylate with the composition  $(C_4H_9)_4NCOOR_1 \cdot 30.0H_2O$  (Figure 2). Extrapolation of experimental points of the latter curve to the



**Figure 8.** Pressure–temperature decomposition curve for the hydrate  $(C_4H_9)_4NCOOR_1 \cdot 30.0H_2O$  ( $x = 1$ ) (open squares) and that of the double hydrate with methane (solid squares). Some typical thermal effects that could be assigned to the decomposition of the double hydrate  $(C_4H_9)_4NCOOR_{(1)} \cdot 25.0H_2O$  with methane (obtained for the sample with  $x = 0.6$ ) are presented as asterisks. The lines are given as the guide for eyes. Pressure–temperature decomposition curve for methane hydrate  $CH_4 \cdot 6H_2O$  is represented by the solid line.

atmospheric pressure gives the hydrate decomposition temperature corresponding to that of stable hydrate phase determined in DTA studies at atmospheric pressure (8.5 °C).

It is seen from Figure 8 that the hydrate decomposition temperature increases by  $\sim 9$  °C under the pressure of methane of 50 MPa and by  $\sim 13$  °C under the pressure of 100 MPa. The obtained results indicating the additional stabilization of the hydrate structure by methane molecules gave strong evidence of the presence in the hydrate structure of vacant cavities, capable of including gas molecules.

The limited time of holding of the samples in the DTA device used at the particular conditions of pressure and temperature did not allow to study  $P$ – $T$  decomposition curves of stable hydrates for TBA polyacrylates with mole fraction of TBA cations in the polymeric chain ( $x$ ) equal to 0.8 and 0.6 as well as corresponding curves of double hydrates of these TBA polyacrylates with methane. It was demonstrated that decomposition temperatures of metastable hydrate phases formed in the course of the experiments under a pressure of methane were in line with those in the absence of gas. Hence, the conclusion was made that metastable hydrate structures have not stabilized with gas molecules. It was revealed, however, that in some cases on standing the frozen samples under a pressure of methane we succeeded in recording thermal effects that could be assigned to decomposition of the double hydrate (asterisks in Figure 8).

For detailed research of hydrate formation with the cross-linked TBA polyacrylates under a pressure of methane and quantitative assessment of gas content, the samples of the double hydrates were synthesized at a pressure of methane of 8 MPa and a temperature of 2 °C within 2–3 weeks, and after that the volume of the gas evolved on heating of the samples was measured. Based on the data obtained, the compositions of the double hydrate phases were calculated. The results are given in Table 2.

Two types of the samples of carboxylic cationites differentiating in water content were used in the synthesis of double hydrates: (1) the samples with the water content corresponding exactly to that in the hydrate; (2) the samples with maximum



Table 2. Compositions of the Hydrate Phases with Methane Based on Volumetric Analyses Data

N	composn of hydrate phase, deg of cross-linking ( $n$ ), mole fraction of TBA cation ( $x$ )	$\sum V_{CH_4}$ , mL/g of hydrate phase	$V_1$	$V_2$	composn of hydrate phases with methane
1	$(C_4H_9)_4NCOOR_{(1)} \cdot 50.2H_2O$ , (swollen state), $n = 1\%$ , $x = 1$	45.3	30.7	14.6	$(C_4H_9)_4NCOOR_{(1)} \cdot 30.0H_2O \cdot 0.78CH_4 + 1.65(CH_4 \cdot 6H_2O)$
2	$(C_4H_9)_4NCOOR_{(1)} \cdot 30.0H_2O$ (hydrate composition), $n = 1\%$ , $x = 1$	17.8	8.7	9.1	$(C_4H_9)_4NCOOR_{(1)} \cdot 30.0H_2O \cdot 0.37CH_4 + 0.36(CH_4 \cdot 6H_2O)$
3	$[(C_4H_9)_4N + H]COOR_{(1)} \cdot 52.2H_2O$ , (swollen state), $n = 1\%$ , $x = 0.8$	56.3	40.6	15.7	$(C_4H_9)_4NCOOR_{(1)} \cdot 26.5H_2O \cdot 1.05CH_4 + 2.18(CH_4 \cdot 6H_2O)$
4	$(C_4H_9)_4NCOOR_{(1)} \cdot 26.5H_2O$ , (hydrate composition), $n = 1\%$ , $x = 0.8$	23.0	8.9	14.1	$(C_4H_9)_4NCOOR_{(1)} \cdot 26.5H_2O \cdot 0.57CH_4 + 0.26(CH_4 \cdot 6H_2O)$
5	$[(C_4H_9)_4N + H]COOR_{(1)} \cdot 55.0H_2O$ , (swollen state), $n = 1\%$ , $x = 0.6$	57.5	43.0	14.5	$(C_4H_9)_4NCOOR_{(1)} \cdot 25.0H_2O \cdot 0.92CH_4 + 1.66(CH_4 \cdot 6H_2O)$
6	$(C_4H_9)_4NCOOR_{(1)} \cdot 25.0H_2O$ , (hydrate composition), $n = 1\%$ , $x = 0.6$	27.9	13.8	14.1	$(C_4H_9)_4NCOOR_{(1)} \cdot 25.0H_2O \cdot 0.63CH_4 + 0.32(CH_4 \cdot 6H_2O)$

water content in the swollen grains. The typical gas emission curve is presented in Figure 9.

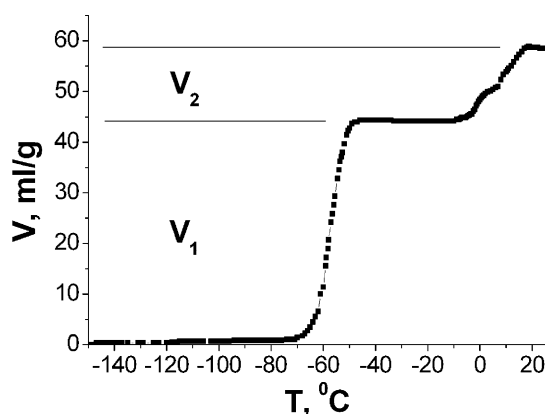


Figure 9. Typical gas emission curve recorded in the experiment with the sample obtained by saturation of the hydrate phase  $[(C_4H_9)_4N + H]COOR_{(1)} \cdot 55.0H_2O$  ( $n = 1\%$ ,  $x = 1$ ) with methane (sample 5 in the Table 2). Marks  $V_1$  and  $V_2$  correspond to steps of gas emission shown in the Table 2.

As shown in Figure 9, gas evolution process occurs in two stages within two temperature intervals: from  $-80$  to  $-60$  °C and from  $0$  to  $15$  °C. X-ray powder diffraction studies of the quenched samples (Figure 10) showed that the first stage of gas emission corresponds to decomposition of methane hydrate of CS-I structural type. The second stage could be referred to decomposition of the double hydrate with methane of TS-I structure (see also Supporting Information, Table S4).

It was assumed when calculating the compositions of the double hydrate phases that (1) the composition of methane hydrate of CS-I structure agreed with the ideal stoichiometry  $CH_4 \cdot 6H_2O$ ; (2) all TBA cations present in the guest molecule were involved in the double hydrate formation; and (3) the ratio of mole quantities of water to those of the cation in the double hydrate was equal to that in the hydrate formed in the absence of methane.

As follows from the data obtained that though methane hydrate is present in all studied samples its content in water-rich samples of carboxylic cationite (swollen cationite grains) is systematically higher. Methane content in double hydrates formed in swollen cationite grains is also higher in comparison with that in double hydrates formed in the samples of cationite with water content corresponding exactly to the hydrate composition (Table 2).

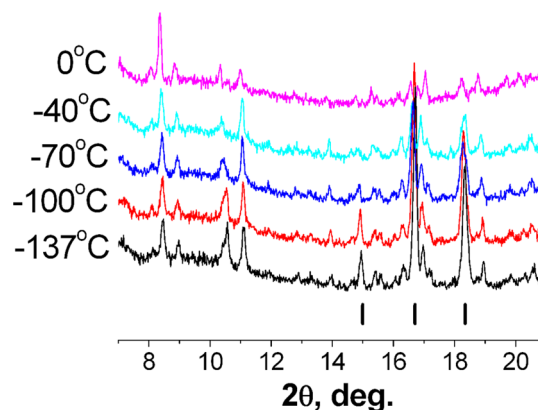


Figure 10. Typical low-angle part of powder X-ray diffraction patterns of samples of the double hydrates of cross-linked tetrabutylammonium polyacrylate with methane at different temperatures. Reflections corresponding to CS-I hydrate are marked by sticks. Other reflections correspond to TS-I hydrate. Reflections of CS-I hydrate disappear at temperatures above  $-70$  °C. The patterns were recorded for the sample  $[(C_4H_9)_4N + H]COOR_{(1)} \cdot 52.2H_2O$  ( $x = 0.8$ ) saturated with methane (sample 3 in Table 2).

It follows from the comparison of calculated compositions with the expected composition  $(C_4H_9)_4NCOOR_n \cdot 2CH_4 \cdot MH_2O$ , provided all small D-cavities in the hydrate of TS-I structure are fully occupied with methane molecules, that for the studied hydrates occupancy degree of D-cavities varies within the intervals  $0.39$ – $0.52$  and  $0.18$ – $0.32$  depending on the mole fraction of TBA cation in the polymeric guest molecule and water content in the sample (Table 2).

It should be noted that the occupancy degree of all D-cavities in the structure of double hydrate formed by the hydrate of tetraisoamylammonium bromide  $(TiAA_4NBr \cdot 38H_2O)$  and methane in the presence of polyHIPE support is  $0.55$ .<sup>18</sup>

Gas evolution analyses and X-ray powder diffraction studies of the quenched samples of double hydrates have demonstrated the complexity of the hydrate formation processes in the cationite grains. It was revealed that at given values of pressure and temperature ( $8$  MPa,  $2$  °C) in all studied samples the formation of methane hydrate along with the formation of double hydrate with methane occurs. The higher water content in cationite grains is favorable for the formation of methane hydrate as well as for the formation of double hydrate.

In order to estimate the rate of the gas uptake by the hydrate phase formed in swollen cationite grains, the volume of methane absorbed as a function of time was studied under a pressure of methane of  $8$  MPa and a temperature of  $2$  °C. Two

types of samples of cationite varying in mole fraction of TBA cations in the polymeric chain were used: (1) the sample of cationite with stoichiometric content ( $x = 1$ ) and (2) with nonstoichiometric content of TBA cations ( $x = 0.8$ ) in the polymeric chain.

It was shown in the course of the studies that in the first 300 min the volume of methane absorbed by the hydrate phase formed in swollen grains of cationite of the first type comes to 81% of total amount of methane that could be enclathrated in the sample according to gas evolution analyses (Table 2, sample 1). For the hydrate phase formed in swollen grains of cationite of the second type, the volume of gas absorbed in this time interval is considerably lower and comes to 29% of total amount of methane that could be enclathrated in the sample (Table 2, sample 3). In both cases further decrease in the rate of gas absorption was observed.

Based on the results of gas uptake, the conclusion was made that methane enclathration kinetics in the hydrate phase formed in swollen grains of carboxylic cationite with stoichiometric content of TBA cations ( $x = 1$ ) in the polymeric chain is comparable with the kinetics of methane uptake in TiAABr semiclathrate hydrate and also with methane enclathration kinetics in water when emulsion templated polymerized high internal phase emulsion (polyHIPE) material was used as a support.<sup>18,23</sup>

## CONCLUSIONS

The results of structural studies indicate that the semiclathrate hydrates of linear and cross-linked TBA polyacrylates with different mole fractions of TBA cations in the polymeric guest are crystalline and isostructural; the crystal structure they form can be related to tetragonal structure I (TS-I) characteristic of the clathrate hydrates of tetraalkylammonium salts with monomeric anions.<sup>1</sup>

As evident from the phase diagram studies, the thermal stability of the hydrates of TBA polyacrylates is defined (1) by the degree of cross-linking and (2) by the mole fraction of TBA cations in the polymeric guest and goes down with the increase in the degree of cross-linking and with the decrease in the mole fraction of TBA cations in the polymeric guest. The hydrate number also decreases in the series. The determination by the DSC method of fusion enthalpies for the hydrates of TBA polyacrylates makes it possible to evaluate quantitatively the destabilization of the hydrate framework depending on the mentioned parameters.

The availability of the vacant D-cavity space in the structure of stable hydrates of cross-linked TBA polyacrylates ( $n = 1\%$ ,  $x = 1$ ) for gas molecules was strongly confirmed on studying  $P$ – $T$  hydrate decomposition curves in the absence of gas and under the pressure of methane.

The gas evolution experiments have demonstrated the complexity of the hydrate formation processes in the cationite grains. It was shown that in cationite grains with different water content conditioned under a pressure of methane of 8 MPa and a temperature of 2 °C within 2–3 weeks the formation of methane hydrate along with the formation of double hydrate with cross-linked TBA polyacrylate and methane occurred.

The analysis of the results of methane uptake by the sample of the hydrate phase formed in swollen grains of carboxylic cationite with stoichiometric content of TBA cations ( $x = 1$ ) in the polymeric chain (8 MPa, 2 °C) made it possible to conclude that methane enclathration kinetics in the hydrate phase formed in swollen grains of the carboxylic cationite is

comparable with the kinetics of methane uptake in TiAABr semiclathrate hydrate and also with methane enclathration kinetics in water hydrate when emulsion-templated polymerized high internal phase emulsion (polyHIPE) material was used as a support.<sup>18,23</sup>

## ASSOCIATED CONTENT

### Supporting Information

Observed and calculated positions of reflections in powder diffraction patterns for the hydrates of cross-linked TBA polyacrylates with the cross-linking degree  $n = 0.5\%$  and  $2\%$  (Table S1). Observed and calculated values of interfacial distances for the structures of hydrates of linear TBA polyacrylates (Table S2) and cross-linked TBA polyacrylates (Table S3). Observed and calculated values of interfacial distances for the structures of double hydrates of cross-linked TBA polyacrylates with methane (Table S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

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## ABBREVIATIONS

TS-I - tetragonal structure I; HS-I - hexagonal structure I; CS-I - cubic structure I of gas hydrates; TBAPac TiAAPac - un-cross-linked tetrabutylammonium and tetraisoamylammonium polyacrylates;  $(C_4H_9)_4NCOOR_n$  ( $i-C_5H_{11}$ ) $_4NCOOR_n$  - cross-linked tetrabutylammonium and tetraisoamylammonium polyacrylates (carboxyl cationites in TBA and TiAA form);  $R_n$  - cross-linked polyacrylate anion;  $n$  - degree of cross-linking;  $[x(C_4H_9)_4N + (1 - x)H]COOR_n$  - the mixed form of cross-linked polyacrylates;  $x$  - mole fraction of TBA cations relative to the total amount of the cations in the polymeric salt

## REFERENCES

- (1) Jeffrey, G. A. Hydrate Inclusion Compounds. *Comprehensive Supramolecular Chemistry*; Pergamon Press: Oxford, UK, 1996; Vol. 6.
- (2) Dyadin, Yu. A.; Udachin, K. A. Clathrate Polyhydrates of Peralkylonium Salts and Their Analogs. *J. Struct. Chem.* **1987**, *28*, 394–432.
- (3) Komarov, V. Yu.; Rodionova, T. V.; Terekhova, I. S.; Kuratieva, N. V. The Cubic Superstructure–I of Tetrabutylammonium Fluoride  $(C_4H_9)_4NF \cdot 29.7H_2O$  Clathrate Hydrate. *J. Inclusion Phenom.* **2007**, *59*, 11–15.
- (4) Bonamico, M.; Jeffrey, G. A.; McMullan, R. K. Polyhedral Clathrate Hydrate. III. Structure of the Tetra-*n*-Butyl Ammonium Benzoate Hydrate. *J. Chem. Phys.* **1962**, *37*, 2219–2231.
- (5) Suwinska, K.; Lipkowski, J.; Dyadin, Yu. A.; Komarov, V. Yu.; Terekhova, I. S.; Rodionova, T. V.; Manakov, A. Yu. Clathrate Formation in Water–Tetraisoamylammonium Propionate System: X-ray Structural Analysis of the Clathrate Hydrate ( $i-C_5H_{11}$ ) $_4NC_2H_5CO_2 \cdot 36H_2O$ . *J. Inclusion Phenom.* **2006**, *56*, 331–335.

- (6) Rodionova, T. V.; Komarov, V.Yu.; Lipkowski, J.; Kuratieva, N. V. The Structure of the Ionic Clathrate Hydrate of Tetrabutylammonium Valerate ( $C_4H_9$ )<sub>4</sub>NC<sub>4</sub>H<sub>9</sub>CO<sub>2</sub>·39.8H<sub>2</sub>O. *New J. Chem.* **2010**, *34*, 432–438.
- (7) Dyadin, Yu. A.; Gaponenko, L. A.; Aladko, L. S.; Bogatyryova, S. V. Clathrate Hydrates of Tetrabutylammonium Carboxylates and Dicarboxylates. *J. Inclusion Phenom.* **1984**, *2*, 259–266.
- (8) Sakamoto, J.; Hashimoto, S.; Tsuda, T.; Sugahara, T.; Inoue, Y.; Ohgaki, K. Thermodynamic and Raman Spectroscopic Studies on Hydrogen + Tetra-n-Butylammonium Fluoride Semi-clathrate Hydrates. *Chem. Eng. Sci.* **2008**, *63*, 5789–5794.
- (9) Chapoy, A.; Anderson, R.; Tohidi, B. Low-Pressure Molecular Hydrogen Storage in Semi-Clathrate Hydrates of Quaternary Ammonium Compounds. *J. Am. Chem. Soc.* **2007**, *129*, 746–747.
- (10) Hashimoto, S.; Murayama, S.; Sugahara, T.; Sato, H.; Ohgaki, K. Thermodynamic and Raman Spectroscopic Studies on H<sub>2</sub> + Tetrahydrofuran + Water and H<sub>2</sub> + Tetra-n-Butylammonium Bromide + Water Mixtures Containing Gas Hydrates. *Chem. Eng. Sci.* **2006**, *61*, 7884–7888.
- (11) Hashimoto, S.; Sugahara, T.; Moritoki, M.; Sato, H.; Ohgaki, K. Thermodynamic Stability of Hydrogen + Tetra-n-Butylammonium Bromide Mixed Gas Hydrate in Nonstoichiometric Aqueous Solutions. *Chem. Eng. Sci.* **2008**, *63*, 1092–1097.
- (12) Arjmandi, M.; Chapoy, A.; Tohidi, B. Equilibrium Data of Hydrogen, Methane, Nitrogen, Carbon Dioxide, and Natural Gas in Semi-Clathrate Hydrates of Tetrabutylammonium Bromide. *J. Chem. Eng. Data* **2007**, *52*, 2153–2158.
- (13) Dyadin, Yu. A.; Bondaryuk, I. V.; Zhurko, F. V. Clathrate Hydrates at High Pressures. *Inclusion Compounds*; Oxford University Press: Oxford, UK, 1991; Vol. 6.
- (14) Florusse, L. J.; Peters, C. J.; Schoonman, J.; Hester, K. C.; Koh, C. A.; Dec, S. F.; Marsh, K. N.; Sloan, E. D. Stable Low-Pressure Hydrogen Clusters Stored in a Binary Clathrate Hydrate. *Science* **2004**, *306*, 469–471.
- (15) Lee, H.; Lee, J.; Kim, D. Y.; Park, J.; Seo, Yu.; Zeng, H.; Moudrakovski, I. L.; Ratcliffe, C. I.; Ripmeester, J. A. Tuning clathrate hydrates for hydrogen storage. *Nature* **2005**, *434*, 743–744.
- (16) Dyadin, Yu. A.; Larionov, E. G.; Manakov, A. Yu.; Zhurko, F. V.; Aladko, E. Ya.; Mikina, T. V.; Komarov, V.Yu. Clathrate Hydrates of Hydrogen and Neon. *Mendeleev Commun.* **1999**, 209–210.
- (17) Seo, Y.-T.; Kang, S.-P.; Lee, H. Experimental Determination and Thermodynamic Modeling of Methane and Nitrogen Hydrates in the Presence of THF, Propylene Oxide 1,4-Dioxane and Acetone. *Fluid Phase Equilibria* **2001**, *189*, 99–110.
- (18) Wang, W.; Carter, B. O.; Bray, C. L.; Steiner, A.; Bacs, J.; Jones, J. T. A.; Cropper, C.; Khimyak, Y. Z.; Adams, D. J.; Cooper, A. I. Reversible Methane Storage in a Polymer-Supported Semi-Clathrate Hydrate at Ambient Temperature and Pressure. *Chem. Mater.* **2009**, *21*, 3810–3815.
- (19) Strobel, T. A.; Koh, C. A.; Sloan, E. D. Hydrogen Storage Properties of Clathrate Hydrates Materials. *Fluid Phase Equilib.* **2007**, *261*, 382–389.
- (20) Strobel, T. A.; Taylor, C. J.; Hester, K. C.; Dec, S. F.; Koh, C. A.; Miller, K. T.; Sloan, E. D., Jr. Molecular Hydrogen Storage in Binary THF-H<sub>2</sub> Clathrate Hydrates. *J. Phys. Chem. B* **2006**, *110*, 17121–17125.
- (21) Manakov, A.; Rodionova, T.; Terekhova, I.; Komarov, V.; Burdin, A.; Sizikov, A. Structural and Physico-Chemical Studies of Ionic Clathrate Hydrates of Tetrabutyl- and Tetraisoamylammonium Salts. *Proceedings of the 7th International Conference on Gas Hydrates*, Edinburgh, Scotland, United Kingdom, 2011.
- (22) Anderson, R.; Chapoy, A.; Tohidi, B. Phase Relations and Clathrate Hydrate Formation in the System H<sub>2</sub> – THF – H<sub>2</sub>O. *Langmuir* **2007**, *23*, 3440–3444.
- (23) Su, F.; Bray, C. L.; Tan, B.; Cooper, A. I. Rapid and Reversible Hydrogen Storage in Clathrate Hydrates Using Emulsion-Templated Polymers. *Adv. Mater.* **2008**, *20*, 2663–2666.
- (24) Su, F.; Bray, C. L.; Carter, B. O.; Overend, J.; Cropper, C.; Iggo, J. A.; Khimyak, Y. Z.; Fogg, A. M.; Cooper, A. I. Reversible Hydrogen Storage in Hydrogel Clathrate Hydrates. *Adv. Mater.* **2009**, *21*, 2382–2386.
- (25) Bogatyryov, V. L.; Dyadin, Yu. A.; Pirozhkov, A. V.; Maksakova, G. A.; Zemskova, S. M.; Moroz, N. K.; Zhurko, F. V.; Skobeleva, V. I.; Villevald, G. V. Klatratnye Poligidraty Polimerov (Clathrate Polyhydrates of Polymers). *Izv. Akad. Nauk SSSR, Ser. Khim. Nauk* **1986**, *9*, 2152 (in Russian).
- (26) Terekhova, I. S.; Manakov, A.Yu.; Soldatov, D. V.; Suwinska, K.; Skiba, S. S.; Stenin, Yu.G.; Villevald, G. V.; Karpova, T. D. The Calorimetric and X-Ray Studies of Clathrate Hydrates of Tetraisoamylammonium Polyacrylates. *J. Phys. Chem. B* **2009**, *113*, 5760–5768.
- (27) Terekhova, I. S.; Manakov, A.Yu.; Feklistov, V. V.; Dyadin, Yu. A.; Komarov, V.Yu.; Naumov, D.Yu. X-Ray Powder Diffraction Studies of Polyhydrates of Cross-Linked Tetraisoamylammonium Polyacrylates. *J. Inclusion Phenom.* **2005**, *52*, 207–211.
- (28) Anosov, V. Ya.; Ozerova, M. I.; Fialkov, Yu. Ya. *Osnovy Fisiko-Khimicheskogo Analiza (Fundamentals of Physico-Chemical Analysis)*; Nauka: Moscow, 1976.
- (29) Helfferich, F. *Ionenaustauscher (Ionites)*; Verlag Chemie GmbH: Weinheim, Germany, 1959.
- (30) Dyadin, Yu. A.; Larionov, E. G.; Mirinskij, D. S.; Mikina, T. V.; Aladko, E. Ya.; Starostina, L. I. Phase Diagram of the Xe-H<sub>2</sub>O System up to 19 Kbar. *J. Inclusion Phenom.* **1997**, *28*, 271–285.
- (31) Ogienko, A. G.; Kurnosov, A. V.; Manakov, A.Yu.; Larionov, E. G.; Ancharov, A. I.; Sheromov, M. A.; Nesterov, A. N. High Pressure Gas Hydrates. Composition, Thermal Expansion and Self-Preservation. *J. Phys. Chem. B* **2006**, *110*, 2840–2846.
- (32) Bruker AXS Inc. 2004: APEX2 (Version 1.08), SAINT (Version 7.03), SADABS (Version 2.11), Madison, WI.
- (33) Sheldrick, G. M. A Short History of SHELX. *Acta Crystallogr.* **2008**, *A64*, 112–122.
- (34) Nakayama, H. Hydrates of Organic Compounds. XIII. The Conformation of the Formation of Clathrate-Like Hydrates of Tetrabutylammonium and Tetraisoamylammonium Polyacrylates. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2319–2326.
- (35) Soldatov, D. V.; Suwinska, K.; Terekhova, I. S.; Manakov, A.Yu. Structural Investigation of Hydrate Compounds of Tetraisoamylammonium Form of Polyacrylate Ion Exchange Resins. *J. Struct. Chem.* **2008**, *49*, 712–718.
- (36) It should be noted that ice Ih reflections in the powder diffraction patterns of the samples of polyhydrates of cross-linked polymeric molecules (Figure 6) could be associated with the presence of water phase in the intergranular space.
- (37) Shataeva, L. K.; Kuznetsova, N. N.; El'kin, G. E. *Karboxyl'nye Kationity v Biologii (The Use of Carboxylic Cation-Exchange Resins in Biology)*; Nauka: Leningrad, 1979.