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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · MAY 2009

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Calorimetric and X-ray Studies of Clathrate Hydrates of Tetraisoamylammonium Polyacrylates

Irina S. Terekhova,^{*,†} Andrey Yu. Manakov,[†] Dmitriy V. Soldatov,[‡] Kinga Suwinska,[§] Sergey S. Skiba,[†] Yuri G. Stenin,[†] Galina V. Villevald,[†] Tamara D. Karpova,[†] and Alexander S. Yunoshev^{||}

Nikolaev Institute of Inorganic Chemistry, M.A. Lavrentyev Institute of Hydrodynamics, Siberian Division of RAS, Novosibirsk, Russia, Department of Chemistry, University of Guelph, Guelph, Ontario, Canada, and Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw

Received: October 31, 2008; Revised Manuscript Received: February 27, 2009

The structure of clathrate hydrates with tetraisoamylammonium polyacrylate salt incorporated as guest has been studied in this work. Also, quantitative studies on the stability changes of the clathrate hydrates with different degrees of cross-linking of the guest polymer (varied from 0 to 3%) have been conducted. A single crystal X-ray diffraction study of a crystal of the hydrate with linear (uncross-linked) tetraisoamylammonium polyacrylate as guest reveals a hexagonal structure (space group $P6m2$, $a = 12.15 \text{ \AA}$, $c = 12.58 \text{ \AA}$ at 100 K) with 39 host framework water molecules per one guest monomeric unit. Powder X-ray diffraction analyses confirm the identity of the above crystal structure of the hydrate with linear guest polymer and the crystal structure of the hydrates with cross-linked guest (hexagonal, $a = 12.25 \text{ \AA}$, $c = 12.72 \text{ \AA}$ at 276 K). In order to quantitatively determine the stability differences of the hydrates with the included guests having various degrees of cross-linking of the anionic chain, a series of differential scanning calorimetry measurements of the fusion enthalpy of the hydrate samples has been carried out. On the basis of the results obtained, a structural model describing the decrease in the stability of the clathrate hydrates with tetraisoamylammonium polyacrylate guest as a function of the degree of cross-linking of the guest polymer has been suggested.

Introduction

As was first shown¹ and then summarized² clathrate hydrates can form at positive temperatures in swollen grains of certain types of cation exchange resins (cationites), cross-linked tetrabutylammonium (TBA) and tetraisoamylammonium (TiAA) polyacrylates with low degree of cross-linking.

The cationites of this work are described by the general formulas $(C_4H_9)_4NCOORn$ and $(i-C_5H_{11})_4NCOORn$, where Rn is the polymeric cross-linked polyacrylate anion and n is the percentage of the cross-linked groups in particular polyacrylate chains relative to the total number of the acrylate monomeric units in the chains. The cationites used had divinylbenzene and divinylsulfide groups as the cross-links with n of 0.5, 1, 2 and 3%. The repeating monomeric unit of the polymeric chain is shown in Figure 1.

The studied materials are of interest due to several reasons.

The accumulation of detailed chemical, physicochemical, and structural data concerning the synthetic carboxylic polyelectrolytes of the mentioned type, the studies of their interaction with solvents and especially with water is of great significance since they are widely used for solving the medical and biological problems.³ The special interest in studies of clathrate hydrate formation in water systems with carboxylic polyelectrolytes is in modeling the hydration processes involving biopolymers.⁴ Some structural studies of hydrated proteins, made at cryogenic

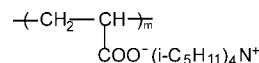


Figure 1. Elementary repeating unit of the polymeric chain of tetraisoamylammonium polyacrylate.

and ordinary temperatures, revealed the formation of highly ordered water clathrate-like networks around the hydrophobic parts of biopolymeric molecules.^{5,6}

The clathrate hydrates of the carboxylic polyelectrolytes may be also considered as reservoirs with molecular-size cavities for the storage and separation of gases. The crystal structures of the clathrate hydrates are known to possess empty dodecahedral cavities⁷ that can accommodate small molecules of a gas (e.g., Ar, Xe, CH₄, H₂) playing the role of an auxiliary guest and additionally stabilizing the clathrate structure. Because of this feature currently the potential use of clathrate hydrates in general for the above purposes is extensively studied.^{8–11} In the context of the problem of hydrogen storage the clathrate hydrogen hydrates are investigated,^{10–16} and the hydrogen content in some hydrogen hydrates was estimated. The hydrogen content in double tetrahydrofuran (THF)-H₂ hydrate was found to be 4 wt % at pressures of 5 MPa and temperature 279.6 K¹² in comparison with pure hydrogen hydrate containing 5.3 wt % of hydrogen stable at high pressures of 220 MPa and temperature 249 K.¹⁴

The clathrate hydrates of tetraalkylammonium salts that are stable at room temperatures and atmospheric pressure seem to be more suitable for hydrogen storage. The melting temperature of H₂-(C₄H₉)₄NF double clathrate hydrate was found to be 302 K at atmospheric pressure.¹⁵ In addition the standard volumetric analyses of H₂-(C₄H₉)₄NBr hydrates at 1 MPa and 283 K gave

* To whom correspondence should be addressed. Phone: (7-383) 316 5346. Fax: (7-383) 330 94 89. E-mail: clat@che.nsk.su.

[†] Nikolaev Institute of Inorganic Chemistry, Siberian Division of RAS.

[‡] University of Guelph.

[§] Polish Academy of Sciences.

^{||} M.A. Lavrentyev Institute of Hydrodynamics, Siberian Division of RAS.

TABLE 1: Properties of the Hydrates of Tetraisoamylammonium Polyacrylates with Different Degrees of Cross-Linking ($n = 0 - 3\%$) and Tetraisoamylammonium Propionate

Hydrate composition ^a , degree of cross-linking (n)	dec. temp., °C	crystal system, space group, unit cell dimensions	ΔH fusion ^b	
			kJ/(mol of hydrate)	kJ/(mol of H ₂ O)
(i-C ₅ H ₁₁) ₄ N COOR \times 40.8H ₂ O ($n = 0$)	+18.4	hexagonal, $P-6m2$, $a = 12.15$, $c = 12.58$ Å (100 K), $a = 12.26$, $c = 12.71$ Å (276 K)	218.8 \pm 4.5	5.36 \pm 0.11
(i-C ₅ H ₁₁) ₄ N COOR _{0.5} \times 37.7H ₂ O ($n = 0.5$)	+15.5 ref 17	Hexagonal, $a = 12.25$, $c = 12.72$ Å (276 K) ref 21	193.0 \pm 2.3	5.12 \pm 0.06
(i-C ₅ H ₁₁) ₄ N COOR ₁ \times 37.6H ₂ O ($n = 1$)	+14.6 ref 17		189.1 \pm 2.3	5.03 \pm 0.06
(i-C ₅ H ₁₁) ₄ N COOR ₂ \times 33.5H ₂ O ($n = 2$)	+13.7 ref 17		158.8 \pm 2.3	4.74 \pm 0.07
(i-C ₅ H ₁₁) ₄ N COOR ₃ \times 29.7H ₂ O ($n = 3$)	+13.0 ref 17 and 18		123.9 \pm 6.2	4.17 \pm 0.21
(i-C ₅ H ₁₁) ₄ N COOC ₂ H ₅ \times 36.0H ₂ O	+27.4 ref 20	Orthorhombic, $Cmc2_1$, $a = 21.281$, $b = 12.010$, $c = 24.768$ Å (150 K) ref 20	268.2 \pm 5.8	7.45 \pm 0.16

^a For the hydrates of the polymeric salts the hydration number given is the number of water molecules per the elementary unit of the polymeric chain. ^b The data of this work.

the value of hydrogen ~ 8 times higher than that for H₂-THF hydrates at the same pressure.¹⁶

The availability of vacant cavities in the hydrates of carboxylic cationites in TBA and TiAA form is possible and they could well be used for gas storage and separation. One of serious problems in the context of the application of gas hydrates materials to the hydrogen storage is the change in the aggregative state of the clathrate (solid) during the reaction of its dissociation (the products are liquid + gas). The reason is the change dramatically decreases the area of interphase contact after the clathrate dissociates making the reverse reaction of its regeneration (for example, in order to “recharge” a hydrate battery) impossible. The very attractive peculiarity of carboxylic cationite materials here is unchangeability of their aggregative state where the clathrate formation and dissociation processes take place inside the swollen polymeric grain.

The above considerations stimulated our detailed structural and physicochemical studies on the titled systems as reported in this work.

Previous physicochemical and structural studies on carboxylic cationite hydrates in tetraisoamylammonium form revealed the following details. As a result of the determination of phase diagrams for the binary systems H₂O–(i-C₅H₁₁)₄NCOOR_{*n*} ($n = 0.5, 1, 2$, and 3%) by DTA method,¹⁷ the compositions of the hydrates (the hydration number in this case is the number of water molecules per elementary unit of the cationite macromolecule) as well as the temperature and concentration ranges of their stability were found. An independent determination of composition of the TiAA polyacrylate hydrate ($n = 3\%$) conducted in the system H₂O–(i-C₅H₁₁)₄NCOOR₃–C₂H₅OH (isotherm at 0 °C) by Schreinemakers’ method of wet residues yielded a very close result.¹⁸ It is clear from Table 1 that as the degree of cross-linking increases, the thermal stability of the hydrates decreases and their hydration number decreases as well. Also it becomes evident from the data obtained that the TiAA polyacrylates form hydrates with the compositions being very similar to the compositions of monomeric tetraalkylammonium salt hydrates having polyhedral clathrate frameworks.⁷ The clathration ability of monomeric tetrabutylammonium and tetraisoamylammonium carboxylates, as well as of other carboxylates, has been well studied.^{19,20} Because the elementary unit of the tetraisoamylammonium polyacrylate studied in this work is similar in composition to monomeric tetraisoamylammonium acrylate and

propionate (Figure 1) and the compositions of the corresponding hydrates are close, it was possible to expect a clathrate nature of the hydrates of this work, where the polymeric molecule acts as a guest.

More recent powder X-ray diffraction studies of the tetraisoamylammonium cross-linked polyacrylate hydrates with $n = 1, 2$ and 3% confirmed the existence of a crystalline hydrate phase in the swollen grains of the studied resins at 3 ± 1 °C.²¹ It was shown that for the various degrees of cross-linking the hydrate crystallizes in hexagonal system with the unit cell parameters of $a = 12.25$ Å and $c = 12.72$ Å (Table 1) corresponding well to the basic ideal Hexagonal Structure I of clathrate hydrates (HS-I) characteristic of many clathrate hydrates of tetraisoamylammonium salts.^{7,20} The hydrate crystallites inside the grains are relatively large up to 0.01 mm.²¹ Therefore, all the experimental data collected previously suggested hydrate formation between water and tetraisoamylammonium cross-linked polyacrylates with the hydrates, although having various thermal stability as a function of the degree of cross-linking of the guest polymeric molecule, but all exhibiting the same crystal structure corresponding to the Hexagonal Structure I of clathrate hydrates.

In this work, we present new experimental data on the fusion enthalpies of the clathrate hydrates forming in the binary systems water–tetraisoamylammonium polyacrylate for a series of polyacrylate polymers with the degree of cross-linking varying from 0 to 3%. Also, the results of a single-crystal X-ray diffraction study of the hydrate with linear polyacrylate ($n = 0\%$) are reported. On the basis of these new results and previously obtained data on the structural type of the hydrates with cross-linked polyacrylate,²¹ a structural model has been developed that explains the experimental observations for the studied here and other similar systems.

Experimental Section

Reagents. The carboxylic cation-exchange resins in the H-form were first treated with 0.5 M solutions of HCl and NaOH, washed with ethanol and then with a large amount of distilled water to remove ethanol. The tetraisoamylammonium forms of the studied resins were prepared under static conditions by neutralizing the polymeric acids with a 3-fold stoichiometric excess of aqueous 0.1N (i-C₅H₁₁)₄NOH. 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 (400 g), washed with distilled water until the washing water became neutral, and after that were centrifuged at the same conditions. The ability of resins conditioned according to the above procedure to swell was examined by the measured mass loss upon drying followed by the determination of the residual humidity content by the Karl Fischer method. The maximum water contents depended on the degree of cross-linking: 71.69% H₂O ($n = 0.5\%$), 67.60% H₂O ($n = 1\%$), 60.40% H₂O ($n = 2\%$), 53.43% H₂O ($n = 3\%$). The ion exchange capacity for tetraisoamylammonium cation of the cationites studied is close to 2.65 mg equivalent TiAA per 1 g of dry resin (TiAA form, $n = 0.5$ to 2%) or 2.62 mg equivalent TiAA per 1 g of dry resin (TiAA form, $n = 3\%$). Because of the low degree of cross-linking, the capacity values are 96–97% of the theoretical value 2.72 mg equivalent TiAA per 1 g of dry resin in the tetraisoamylammonium form.

Tetraisoamylammonium hydroxide (aqueous solution) was synthesized from tetraisoamylammonium iodide by ion-exchange reaction with Ag₂O in the presence of water. The resulting tetraisoamylammonium hydroxide solution was separated from the precipitate and purified through the recrystallization in the form of a clathrate hydrate.

Polyacrylic acid with average molecular mass of 1800 daltons (Aldrich) without further purification and tetraisoamylammonium hydroxide solution were used to prepare tetraisoamylammonium salt of the linear (uncross-linked) polymer.

Preparation of the Samples for X-ray and Calorimetric Studies. The crystals of the hydrate of tetraisoamylammonium polyacrylate were prepared by cooling (from room temperature to 4 °C) a solution containing tetraisoamylammonium hydroxide (0.8 g of ~15% aqueous solution) and poly(acrylic acid) (0.09 g). The crystals grew as colorless, not well-defined prisms. The total amount of TiAA polyacrylate and water in the bulk samples, as determined by chemical analysis, was 99.3%.

For the single crystal X-ray diffraction study, a crystal picked from under the supernatant fluid was instantly frozen to 100 K and studied at this temperature. The crystals of the hydrate of tetraisoamylammonium propionate were prepared as described elsewhere.²⁰

The polycrystalline samples of the hydrate of tetraisoamylammonium polyacrylate for powder X-ray diffraction studies were prepared by carefully graining the crystals in a chamber kept at a temperature below 0 °C. Powdered crystalline silicon (5 to 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 the calorimetric studies (the measurement of the enthalpy of fusion), the hydrate crystals of tetraisoamylammonium propionate or polyacrylate were separated from the corresponding supernatant fluids and dried by filtering paper. The samples of 40–50 mg were enclosed in an aluminum ampule, which was 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. In the case of cross-linked TiAA polyacrylates, the samples for calorimetric studies were prepared by a weighing technique. For this purpose, a portion of air-dried resin grains (residual water content 7–10 wt %) and a certain amount of water, corresponding to the amount of water in the hydrate (Table 1), were placed in an ampule made of quartz. The samples were kept 24 h in tightly closed ampules for the grains to swell; then the sample of the hydrate formed was transferred into the aluminum ampule used for the measurements.

Methods. The water content in the studied samples was determined by Karl Fischer method. In order to determine the water content in the grains of cation-exchange resin, the reverse titration by the Karl Fischer reagent was used. For this purpose, a weighed sample (30–40 mg) was stirred for 5–7 min with excess of the Karl Fischer reagent. The unreacted reagent was then titrated with ethanol or pyridine containing a small amount of water (0.2–0.3 wt %). The concentration of TiAA in the solution was determined by potentiometric titration with sodium tetraphenylborate solution (5×10^{-3} M) using a cation-selective electrode.

In order to determine the phase diagrams of the systems water–tetraisoamylammonium polyacrylate, the DTA (differential thermal analysis) 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 ampules. The systems were studied in the temperature range from –30 to +30 °C at the heating rate 1°/min. and the accuracy of the determination of the phase transition temperatures was ± 0.2 °C.

The samples for the DTA studies were prepared as follows. In order to determine the phase diagram with linear TiAA polyacrylate as a second component, a series of its water solutions with desired concentrations was used. In order to determine phase diagrams with cross-linked TiAA polyacrylate,¹⁷ the samples were prepared by the weighing technique. In this procedure, a quartz ampule was loaded with air-dried resin (residual water content of 7 to 10 wt %) and then a calculated amount of water was added to have a desired resulting composition of the mixture. The samples were equilibrated in the hermetically closed ampule for one day and then were recorded. The composition of the compounds in the systems was determined by the Tamman triangle method.

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°/min. For the hydrates of TiAA polyacrylates with $n = 0, 0.5, 1$, and 2%, the average values for the enthalpy of fusion were calculated from 6 to 10 measurements; the standard deviation was below ~2%. For the hydrate of TiAA polyacrylate with $n = 3\%$ the enthalpy of fusion was calculated from three measurements, and the standard deviation was ~5%. The enthalpy of fusion for the hydrate of monomeric guest, TiAA propionate, was also calculated from three measurements, and the standard deviation was close to 2% (Table 1). It should be noted that neither DTA¹⁷ nor the DSC thermograms of the samples with cross-linked polyacrylates that 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. This expected appearance of eutectic melting effects was observed both for soluble and cross-linked polymeric guests.

The temperatures of hydrate dissociation as a function of pressure were measured by DTA conducted under high pressures. The experimental apparatus used was described in details elsewhere.²² The samples of carboxylic cation-exchange resins in the TiAA form were loaded into a DTA container with a volume of 0.05 mL. The container was hermetically closed in a 6–8 mL stainless steel flask equipped with a movable piston and a back valve. After that, the flask was filled with the

hydrogen 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 the maximal difference of temperatures between a reference thermocouple and the sample thermocouple inserted into the container with sample.

X-ray powder diffraction studies were performed at the temperature of +3 °C on a Bruker D8 Advance diffractometer ($\text{CuK}\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$) equipped with Anton Paar refrigerating device. The powder diffraction patterns were recorded in 2θ scan mode in the range of 1–50 deg with steps of 0.02 deg on 2θ .

Single-crystal X-ray diffraction experiment was conducted at 100 K on a Nonius Kappa CCD diffractometer with monochromatic $\text{MoK}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). The experimental data for unit cell measurement and structure solution were collected in the θ -range of 3.2–23.2° (h,k,l-range: –13/13, –11/11, –13/13; completeness >99%). Unit cell was hexagonal, the dimensions refined using all the data were $a = 12.150(1)$, $c = 12.580(1) \text{ \AA}$, $V = 1608.3(2) \text{ \AA}^3$, calculated density 1.107 g/cm³, assuming the gross formula $\text{C}_{23}\text{H}_{125}\text{NO}_{41}$ ($\text{C}_{20}\text{H}_{44}\text{N}$, $\text{C}_3\text{H}_5\text{O}_2$, $39\text{H}_2\text{O}$) and $Z = 1$. Total of 3092 data were measured, 944 unique ($R_{\text{int}} = 0.015$). An empirical absorption correction utilized the SADABS routine. The structure solution was conducted by direct methods followed by full-matrix least-squares refinement on F^2 using SIR97 and SHELX software.^{23,24} Observed systematic absences indicated several possible space groups. All were tested and some were ruled out as leading to chemically unreasonable solutions. The best solution was obtained in the space group $P6_3/m2$ (no. 187). The oxygen atoms of the clathrate hydrate framework appeared unambiguously, were stable, and displayed realistic thermal parameters in the course of all solution/refinement procedures. With the eight O-atoms of the framework, the solution was stable with $R = 0.236$ (47 parameters and 0 restraints). A series of residual maxima located in the large cavities (with max = 2.6 e/\AA^3) could not be directly assigned to the atoms of the tetraisoamylammonium cation that locates in a general position and therefore has to be highly disordered in this highly symmetric structure. The cation was introduced manually with a series of restraints imposed on the first and second neighbor distances and the thermal parameters, and the structure was refined. At this stage, the R value dropped down to 0.135 for 894 intense data ($I > 2\sigma_I$), 540 restraints and 197 parameters (refinement on F^2). The residual extrema (max = 0.88 e/\AA^3 ; min = -0.41 e/\AA^3) concentrated in small cavities, the only residual space where the polyacrylate anionic chains could be located (as all large cavities are occupied with TiAA cations). The exact geometry of this accommodation could not be found; a qualitative description on possible arrangements of the polymer in the structure is given in the next section. Full crystallographic information on the structure studied is provided in Supporting Information.

Results and Discussion

Structure and Composition of Hydrates. The determination of the crystal structure would be extremely difficult to accomplish for the hydrates of cross-linked polymeric carboxylates as the obtaining of single crystals of the hydrates is impossible. Therefore, a hydrate with linear polyacrylate (tetraisoamylammonium form) was attempted as a first model approximation.

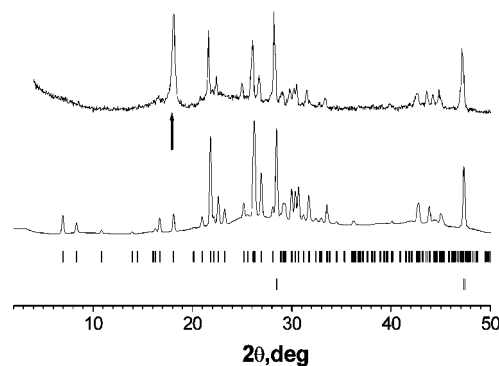


Figure 2. Powder diffraction patterns of studied hydrates ($\text{Cu K}\alpha$, $\lambda = 1.5418 \text{ \AA}$) at 276 K. Upper pattern: hydrate of cross-linked tetraisoamylammonium polyacrylate with $n = 3\%$. The sample was protected with a Teflon film; the peak pointed by arrow arises from the film. Lower pattern: hydrate of linear tetraisoamylammonium polyacrylate. Expected positions of reflections for the hydrate (upper row) and silican used as an internal standard (lower row) are shown by bars.

The validity of this approach is clearly demonstrated by the comparison of powder X-ray diffraction patterns of the samples with cross-linked and linear polymers (Figure 2). It is evident that the hydrates have basically the same crystal structure. All the lines on the powder pattern of the hydrate comprising linear polymer correspond to the crystal structure derived from the single crystal X-ray diffraction analysis described below. The unit cell is hexagonal, space group $P6_3/m2$, and unit cell parameters $a = 12.26$, $c = 12.71 \text{ \AA}$ (276 K). This basic structure corresponds to idealized Hexagonal Structure I (HS-I) of clathrate hydrates (in particular, this structure was found for trimethylamine hydrate⁷) whose unit cell comprises 40 molecules of water. The powder pattern of the hydrate with cross-linked polymer is very similar with unit cell parameters $a = 12.25 \text{ \AA}$ and $c = 12.72 \text{ \AA}$ (276 K)²¹ (Figure 2, Table 1). Some differences in the intensity of peaks observed at low angles are caused by a protected film used in earlier experiments for samples with cross-linked polymer. Therefore, the powder diffraction results suggest the hydrates with cross-linked and uncross-linked linear polyacrylates are isostructural and the latter was studied in more detail.

The phase diagram of the binary system water–tetraisoamylammonium polyacrylate (uncross-linked) was determined using DTA method (Figure 3). Only one compound forms in the studied concentration range with the melting point of +18.4 °C. The compound was isolated as a crystalline product and analyzed (six independent determinations) to give the composition $(\text{i-C}_5\text{H}_{11})_4\text{NOOCR} \cdot (40.8 \pm 0.5)\text{H}_2\text{O}$.

The single crystal X-ray analysis of the hydrate of uncross-linked tetraisoamylammonium polyacrylate conducted in this work confirms clathrate nature of the hydrate compounds studied in this work. The hydrate crystal was hexagonal; the unit cell dimensions refined using all data were $a = 12.150(1)$, $c = 12.580(1) \text{ \AA}$, $V = 1608.3(2) \text{ \AA}^3$ (at 100 K). In the crystal structure, the water molecules form a 3D hydrogen-bonded host framework that was recognized as HS-I.⁷ The ideal HS-I has the symmetry of $P6_3/mmm$ space group and the stoichiometry $2\text{P} \cdot 2\text{T} \cdot 3\text{D} \cdot 40\text{H}_2\text{O}$, where P, T, and D refer to 15-, 14- and 12-hedral cavities, respectively (P and T cavities are large cavities, while D is a small cavity). Real structures display lower symmetries mostly due to some distortions caused by hydrophobic inclusion of guest and differ in water content due to hydrophilic inclusion of guest species (that can replace a water molecule from the hydrate framework). Previously reported

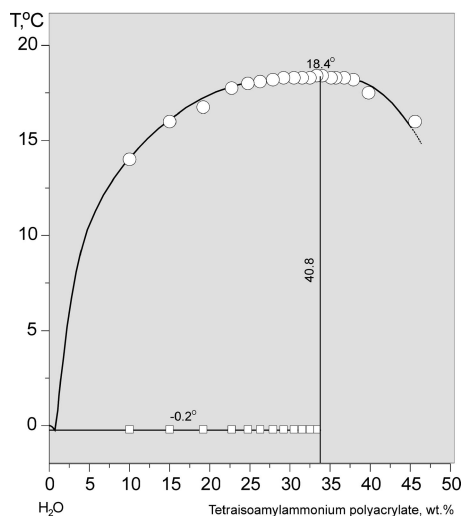


Figure 3. Phase diagram of the binary system water–tetraisoamylammonium polyacrylate (uncross-linked) in the concentration region of the existence of the 1:40.8 hydrate.

structures of HS-I type include a hydrate of tetraisoamylammonium fluoride, $N(i-C_5H_{11})_4^+ \cdot F^- \cdot 38H_2O$ (orthorhombic, *Pbmm*),²⁵ hydrate of tetraisoamylammonium propionate, $N(C_5H_{11})_4^+ \cdot (C_2H_5COO)^- \cdot 36H_2O$ (orthorhombic, *Cmc2₁*),²⁰ as well as orthorhombic hydrates of tetraisoamylammonium chloride, chromate, and tungstate²⁶ and monoclinic hydrates of tetraisoamylammonium benzoate and di-*n*-butyl-di-isoamylammonium fluoride²⁷ (unit cells only).

In the structure of this work, the ideal HS-I symmetry is reduced to that of *P6₃/m2* space group. The positions of oxygen atoms of the hydrate framework are listed in Table 2 and the H-bond connectivity is explained in Figure 4 (for full crystallographic information see Supporting Information available). The H-bond distances and polyhedral angles are listed in Table 3. The O–O distances vary from 2.6 to 3.1 Å, while the O–O–O angles vary from 99 to 113° (ideal 108°) and from 116 to 126° (ideal 120°) for pentagonal and hexagonal faces, respectively.

The large P polyhedra are located in a layer at the $z \sim 0$ level sharing their hexagonal faces (each P polyhedron has three hexagonal faces) and producing a honeycomb system (Figure 5, top). Each hole is filled with two T polyhedra on both sides of the layer; the T cavities stack on top of each other producing columns along the *c* axis. The next layer, at $z \sim 0.5$, is filled with D polyhedra sharing their pentagonal faces (Figure 5, bottom).

All the large cavities are occupied by the hydrophobic alkyl groups of tetraisoamylammonium cation. As a rule, the inclusion of a tetraalkylammonium cation in clathrate hydrate structures occurs by replacing one of framework water molecules with the nitrogen atom (hydrophilic inclusion) and inserting the alkyl chains in four adjacent cavities (hydrophobic inclusion).⁷ In the structural model of this work, tetraisoamylammonium cation is included this way in P₂T₂ four-compartment cavity (Figure 6). Similar inclusion mode was observed in previously reported clathrate hydrates with this cation^{20,25} and is consistent with the ability of the isoamyl fragment to fit only in a large cavity but not in a small one (the length of isoamyl group in the TiAA cation *l* of ~ 7.04 Å is compatible with the maximal inside diameters *d* of P- and T-cavities equaled to 7.0 and 6.4 Å, respectively, but exceeds significantly the maximal inside diameter of small D-cavity of 5.2 Å). The nitrogen atom of the cation replaces the atom O8 of the hydrate framework, while

the other atoms of the cation all occupy general positions and so may fill a greater number of symmetrically equivalent positions due to the high symmetry of the crystal. Presumably, these factors make a significant contribution to the overall stability of the hydrate crystal favoring its entropy component. One of the many equivalent positions of the cation in the P₂T₂ cavity is shown in Figure 6. The cations concentrate in layers at $z \sim 0$ level filling all large cavities available in the structure. The crystal therefore has a pseudolayered organization with respect to the location of guest.

According to the structural model used, the chains of polyacrylate anion can only be located within the layer of D-polyhedra at $z \sim 0.5$ (see Figure 5, bottom). The location of the chains is impossible to find directly from the experiment due to a great number of possible (symmetrically equivalent) positions that produces a multifold disorder from the viewpoint of crystallography. Considering the structure of the clathrate framework and the guest polyacrylate anion (Figure 1), the following features of the guest polymer accommodation can be expected.

There is no doubt that the incorporation of the carboxylate groups of the polymeric chain occurs as a hydrophilic inclusion, as it was observed for tetraalkylammonium salts of monomeric carboxylates.^{20,28} In other words, the two O atoms of the carboxylate group replace two adjacent O atoms in the polyhedron. At the same time, the incorporation of the main hydrocarbon chain of the polymer in the layer of undistorted D-polyhedra is not feasible because the D polyhedra do not have “windows” of sufficient size. One could assume that the local microenvironment around the chain is distorted in such a way that the D-polyhedra form a channel. The formation of such channels requires energetically unfavorable distortion of the hydrate framework. It should be noted that the incorporation of carboxylate groups (and probably hydroxyl groups) facilitates such a distortion.⁷ The parameters of the polyacrylate main chain should be similar to those of polyethylene for which the translational period of 2.54 Å is expected.²⁹ Taking the shortest dimension of the hydrate unit cell, 12.15 Å, at least five polyacrylate monomers should fit in a single unit cell through which the polymeric chain would run, producing a negative charge far greater than it is necessary to balance the 1+ charge of the cation. Therefore, there is excessive space for the accommodation of the polyanion, most unit cells do not host the polymer at all, and the concentration of local distortions induced by the anion inclusion is relatively low. In addition, there are several ways of how the chain may enter and exit the unit cell (cf. Figure 5, bottom) and so the accommodation of the polyanion is very favorable in terms of entropy.

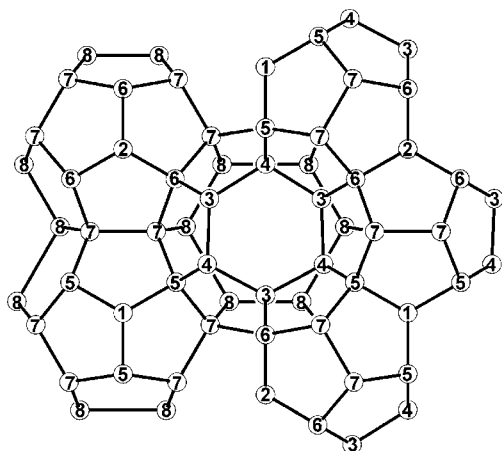
On the other hand, the described above inclusion of the polyanion should create high local concentrations of negative charge in the structure which would be very unfavorable in terms of enthalpy. Partially the loss is compensated by the entropy term. However, the transfer of a proton from the host hydrate framework to carboxylate group is very probable here. The residual hydroxyl anions may be located near the positively charged nitrogen atoms of the cation.

In conclusion, it should be noted that the observed layered organization of the structure explains the possibility of inclusion in the crystal of cross-linked polyacrylate. The availability of excessive space within the D-layer and high freedom for the polymeric chain accommodation facilitate the inclusion. The chain can change direction at every D₃-intersection as evident from Figure 5, bottom. The accommodation would be more

TABLE 2: Positioning of Oxygen Atoms in the Hydrate Framework (Asymmetric Unit)

atom	x/a	y/b	z/c	$U_{eq}, \text{\AA}^2$	Wyckoff position	multiplicity of the position	occupancy
O1	1/3	2/3	-0.3902(4)	0.029(1)	<i>h</i>	2	1/6
O2	2/3	1/3	-0.3970(7)	0.063(2)	<i>i</i>	2	1/6
O3	0.2623(5)	0.1311(2)	-1/2	0.045(2)	<i>k</i>	3	1/4
O4	0.1356(3)	0.2712(7)	-1/2	0.054(2)	<i>k</i>	3	1/4
O5	0.2085(2)	0.4171(4)	-0.3178(3)	0.046(1)	<i>n</i>	6	1/2
O6	0.4225(4)	0.2113(2)	-0.3209(3)	0.052(1)	<i>n</i>	6	1/2
O7	0.3819(3)	0.3848(3)	-0.1990(3)	0.065(1)	<i>o</i>	12	1
O8	0.289(2)	0.271(1)	0	0.184(8)	<i>l</i>	6	5/12 ^a

^a The position is shared with the N-atom of tetraisoamylammonium cation (N1, $x/a = 0.2675(1)$, $y/b = 0.2488(1)$, $z/c = 0$, $U_{eq} = 0.063(3) \text{\AA}^2$, occupancy = 1/12).

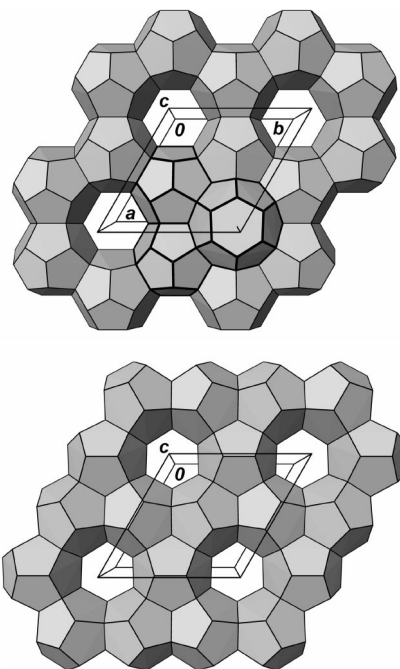
**Figure 4.** Connectivity of oxygen atoms in the hydrate framework and key to interatomic distances.**TABLE 3: Polyhedral Interatomic Distances (O–O, \AA) and Angles (O–O–O, deg.) in the Hydrate Framework (See Figure 4 for Numeration Scheme)**

1–1	2.77(1)	1–1–5	109.1(1)	2–6–3	106.6(2)
1–5	2.779(5)	5–1–5	109.8(1)	2–6–7	109.2(2)
2–2	2.60(2)	2–2–6	110.3(2)	3–6–7	110.0(2)
2–6	2.740(5)	6–2–6	108.6(2)	7–6–7	111.8(2)
3–4	2.809(4)	4–3–4	123.6(3)	5–7–6	103.9(2)
3–6	2.815(5)	4–3–6	106.46(8)	5–7–7	108.1(1)
4–5	2.756(6)	6–3–6	106.2(2)	5–7–8	113.5(4)
5–7	2.765(4)	3–4–3	116.4(3)	6–7–7	106.5(1)
6–7	2.844(4)	3–4–5	107.02(6)	6–7–8	107.2(3)
7–7	2.835(6)	5–4–5	112.6(3)	7–7–8	116.7(2)
7–8	2.813(6)	1–5–4	104.6(2)	7–8–7	125.9(4)
8–8	3.09(3)	1–5–7	107.0(1)	7–8–8	99.2(4), 106.7(3)
		4–5–7	112.4(1)	8–8–8	120.0
		7–5–7	112.7(2)		

difficult within a channel structure as one reported for tetra-*n*-butylammonium polyacrylate.³⁰

According to the above results, most D-cavities in the hydrates are vacant from the main guest. This available cavity space may be utilized for accommodating an auxiliary guest. It is quite possible that some of the D-cavities are occupied with water molecules as reported previously.³¹ The availability of this space for other molecules, especially for gas molecules, is of significant interest for these hydrates.¹⁵ In order to examine this possibility, the behavior of the TiAA polyacrylate hydrate was investigated under high pressure of a gas.

Figure 7 shows the dependences of the melting temperature for the hydrate TiAA polyacrylate with $n = 2\%$ as a function of pressure in the presence and absence of the hydrogen gas. In the presence of hydrogen, the melting temperature is significantly higher indicating additional stabilization of the hydrate

**Figure 5.** Polyhedral organization of the hydrate framework studied. Top: the layer of face-sharing 15-hedral (P) polyhedra at the $z \sim 0$ level; one combined four-compartment cavity, P_2T_2 , is outlined with bold lines. Bottom: the layer of face-sharing 12-hedral (D) polyhedra at the $z \sim 0.5$ level.

framework by a second guest (a very common phenomenon for all mixed hydrates³²), that is the inclusion of hydrogen molecules in the vacant D-cavities of the structure. This experimental result provides a solid evidence of the vacant D-cavities present in the structure and supports the structural model discussed here. Also, these data point out the potential of the hydrates studied as materials for gas storage or separation. In earlier studies,² similar studies were conducted for a hydrate of tetrabutylammonium polyacrylate with $n = 3\%$ under pressure of CO_2 and N_2O gases up to 1 MPa.

Influence of Cross-Linking on the Hydrates Stability. In order to quantitatively evaluate the destabilization of the hydrate framework by cross-links of the guest polymeric anion, the heats of fusion were measured for the clathrate hydrates comprising tetraisoamylammonium polyacrylates with varying degree of cross-linking from 0 to 3%. It should be noted that no data on clathrate formation thermodynamics for any tetraalkylammonium salts with cross-linked polymeric anions could be found in the literature, while only some data on fusion enthalpies of the hydrates with tetraalkylammonium salts with monomeric (fluoride and chloride) and linear polyacrylate anions have been reported by Nakayama.^{33–35}

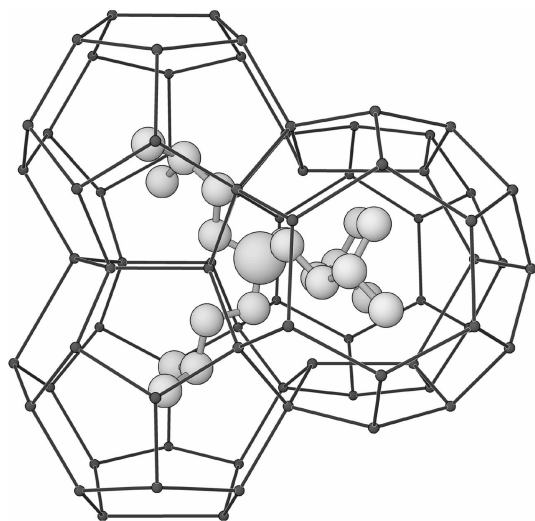


Figure 6. The accommodation of tetraisoamylammonium cation inside the combined four-compartment (P_2T_2) cavity. For clarity, only one of several symmetrically equivalent positions of the cation is shown.

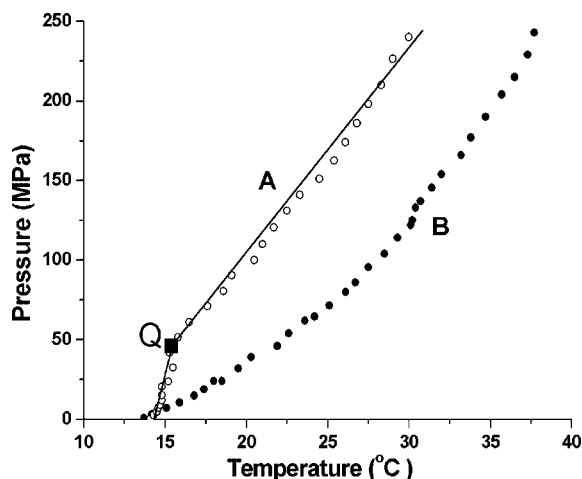


Figure 7. The dependencies of the dissociation (melting) temperature of the hydrate of tetraisoamylammonium polyacrylate ($n = 2\%$) on pressure. **A**, in the absence of hydrogen (purely hydrostatic pressure). **B**, under the pressure of hydrogen gas.

The results of the calorimetric measurements are presented in Table 1 and in Figure 8. The fusion enthalpy of the hydrate of TiAA propionate, $(i-C_5H_{11})_4N\ OOCC_2H_5 \cdot 36.0H_2O$, is shown for comparison in Figure 8a. The lower values of fusion enthalpy for the hydrates with polyacrylate are in agreement with the energetically unfavorable distortion of the clathrate hydrate framework necessary for the formation of polymer-accommodating channels, as discussed in the previous section.

The fusion enthalpy of the hydrate with linear (uncross-linked) polyacrylate, $(i-C_5H_{11})_4N\ COOR \cdot 40.82H_2O$, equaled to 218.80 kJ/(mol of hydrate) or 5.36 kJ/(mol of water) agrees well with the value of 5.45 kJ/(mol of water) reported by Nakayama (DSC studies of aqueous solutions of TiAA polyacrylate).³⁵ This value is $\sim 10\%$ lower of the fusion enthalpy of pure ice (6.01 kJ/mol at $0\ ^\circ C$).³⁶ This 10% difference is a quantitative estimation of the destabilization energy of the hydrate framework. It becomes evident from Figure 8 that both the fusion enthalpy and composition of the hydrates of TiAA polyacrylate are linear functions of the degree of cross-linking of the guest polymeric anion included in the hydrate framework. The removal of one water molecule from the hydrate framework decreases on

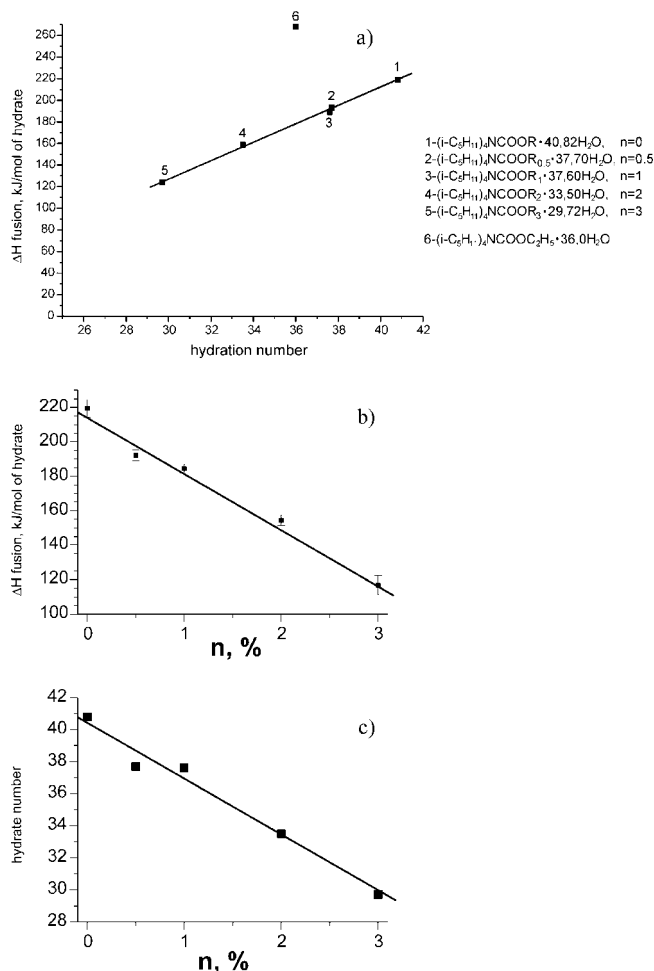


Figure 8. Fusion enthalpy of hydrates as a function of changes in the guest anion. (a) Fusion enthalpy vs hydration number (see anions used are given on the insert; the fusion enthalpy of the hydrate of TiAA propionate is added for comparison). (b) Fusion enthalpy vs the degree of cross-linking (n). (c) Hydrate number vs the degree of cross-linking.

average the fusion enthalpy by 8.4 kJ/(mol of hydrate) (Figure 8a) that destabilizes the framework as a whole.

The analysis of all experimental data reported or mentioned here leads to the following general picture of the structural peculiarities in the hydrates of TiAA cross-linked polyacrylate. The formation of hydrate crystallites inside the grains of the cationite requires some ordering of adjacent chains in a microregion of the grain. The motif of this ordering is likely to copy the structural motif of the hydrate studied and described in the previous section, as the hydrates with linear and cross-linked polyacrylates are isostructural.

The cross-links, “chemical knots” and caused by them “physical knots” in the polymeric molecules (the formation of those results from electrostatic interaction of polar groups in the adjacent chains or from their mechanical entanglement³), are incorporated in these crystallites. The incorporation of cross-links should take place as a typical size of crystallite of $>1000\ \text{\AA}$ ²¹ exceeds the distance between cross-links in the same chain (300 to 45 \AA for different n). The incorporated cross-links create defects in the ideal crystal structure reducing the hydrate number and decreasing fusion enthalpy of the hydrates. As the introduction of 1% cross-links in the polyanion results in the hydrate number reduction by 3.7, one defect occupies a volume corresponding to 370 water molecules in the crystallite, that is, taking cations into account as well, 6 to 8 unit cells of the crystal

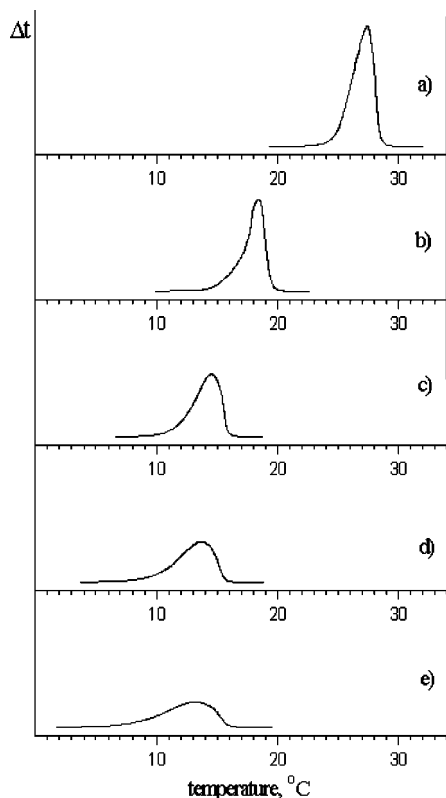


Figure 9. DSC curves showing melting of the hydrate phase (end up): (a) with TiAA propionate (monomeric anion); (b) with TiAA polyacrylate (linear polymer); (c,d,e) with TiAA polyacrylates with $n = 1, 2, 3\%$, respectively.

structure. Noteworthy, the extrapolation of fusion enthalpy for the hydrates with cross-linked polyacrylate yields a zero fusion enthalpy for the hydrate with $n \sim 6.5\%$, the value being in good agreement with previous studies³⁷ that signify the inability of polycarboxylates in the form of TiAA with this degree of cross-linking to form clathrate hydrates. An alternative hypothesis, the concentration of cross-links on intercrystallite boundaries, appears less probable, as in this situation the hydrate number and fusion enthalpy did not depend noticeably on the degree of cross-linking. The defects practically do not alter the unit cell parameters of the hydrate structure and, therefore, the defects are presumably localized in the regular structure as some sort of voids that occur in the regions of location of the “chemical knots” and “physical knots” in the polymeric guest.

While comparing the shape of the DSC curves for hydrates with carboxylic cationites, one can see the width of the melting endotherm consistently growing with the degree of cross-linking (Figure 9). Although the peak is asymmetric, with the onset extended to lower temperature the asymmetry does not depend on cross-linking (the ratio of right and left areas from the maximum retains approximately constant at 65:35 for all the samples).

The observed widening of the peaks can be interpreted assuming that the number of cross-links (or, more likely any characteristic value proportional to the number of cross-links; at present we cannot determine this characteristic value and will discuss the number of cross-links) incorporated in a given crystallite follows the binomial distribution.³⁸ This assumption is very likely to be appropriate due to the analogy between the initial postulates leading to the binomial law³⁸ and the probability of having a given number of cross-links in the crystallite. In both of these cases, there are a fixed number of available

positions and a certain number of suitable filling fragments (for polyacrylate: links in the polymeric chain and interchain cross-links, respectively). The probability of the fragment to fill a position is equal for all the positions available; this is true for polyacrylates having a low degree of cross-linking when the probability to have more than one cross-link in the same position is negligible. With such a statistical distribution of cross-links, the number of cross-links in a given crystallite will be proportional to the average degree of cross-linking with the width of the peak at half-maximum for the binomial distribution $\sigma = (Npq)^{1/2}$.³⁸ For the system under consideration, N is the number of potential spots for cross-linking, or the number of monomers per a volume unit of cationite grain. The N value can be estimated from the unit cell volume for the hydrate²⁰ taking into account that each unit cell contains on average one monomer. The p value, the probability to find a cross-link on the polymeric molecule, is defined by the degree of cross-linking. The Np product is the average concentration of cross-linking groups. The q value is equal to $1 - p$. The ratio of widths of the DSC peaks at half-maximum for the hydrates containing polymers with $n = 1, 2$, and 3% calculated from the above formula is 1:1.41:1.71. This calculated ratio is in reasonable agreement with the ratio found in the experiments of this study: 1:1.38:1.92. Another consequence of the model proposed is the reverse proportion between the melting point of a crystallite and the concentration of cross-links, that is the widening of a DSC peak for higher degrees of cross-linking is caused by a higher dispersion of the number of cross-links per a volume unit of the cationite grain. Therefore, the observed widening of the experimental peaks is reasonable and supports the incorporation of cross-links in the volume of the crystallites.

Conclusions

New results obtained in this work and their comparison with data reported previously²¹ indicate that the hydrates of the linear and cross-linked TiAA polyacrylates with low degree of cross-linking (1, 2, 3%) are crystalline and isostructural; the crystal structure they form is a variation of HS-I characteristic of hydrates of monomeric tetraalkylammonium salts.⁷

As evident from the phase diagrams of the corresponding binary systems, the thermal stability of the hydrates of TiAA polyacrylates is defined by the degree of cross-linking in the polymeric anion decreasing as the degree of cross-linking increases (0, 0.5, 1, 2, 3%), while the hydrate number also decreases in the series (data of this work and ref 12).

The determination by the DSC method of fusion enthalpies for the hydrates of TiAA polyacrylates ($n = 0$ to 3%) makes it possible to evaluate quantitatively the destabilization of the hydrate framework. The fusion enthalpy is shown to be a linear function of the degree of cross-linking (availability of cross-linkages, “chemical knots” in the polymeric chains initiates also the formation of “physical knots”³³) and, correspondingly, of the hydrate number. The removal of a single water molecule from the framework decreases the fusion enthalpy by 8.4 kJ/(mol of hydrate) that is the increase of the degree of cross-linking destabilizes the hydrate as a whole.

The total of data obtained makes it possible to suggest a model describing both the overall and local structure of the hydrates of TiAA polyacrylates with cross-links in the polymeric anion. Taking into account the isostructurality of the hydrates with cross-linked and linear polyacrylates, the formation of hydrate crystallites most likely follows some ordering of adjacent chains in a microregion inside the cationite grain. The motif of such ordering is likely to copy the corresponding structural motif

of the hydrate with linear polyacrylate. The cross-links become incorporated in the crystallites forming defects in the crystal structure; the defects cause the decrease of the hydration number, fusion enthalpy, and the width of the melting DSC peaks experimentally observed for the resulting hydrates. The comparison of a typical size of crystallite (>1000 Å) and the distance between cross-links in the same chain (300 to 45 Å for different n) counts in favor of incorporation of cross-links in the hydrate crystallites.

Acknowledgment. The study was supported by the Integral project No. 62 of the Siberian Branch of the Russian Academy of Sciences. The structural studies were carried out within cooperation agreement between the Institute of Inorganic Chemistry, Siberian Division, Russian Academy of Sciences, and the Institute of Physical Chemistry, Polish Academy of Sciences.

Supporting Information Available: Full crystallographic information on the linear tetraisoamylammonium polyacrylate polyhydrate. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JP809622N