STRUCTURAL AND PHYSICO-CHEMICAL STUDIES OF IONIC CLATHRATE HYDRATES OF TETRABUTYL–AND TETRAISOAMYLAMMONIUM SALTS

Andrey Manakov1, Tatyana Rodionova, Irina Terekhova, Vladislav Komarov, Alexander Burdin, Artem Sizikov
Nikolaev Institute of Inorganic Chemistry SB RAS
3, Acad. Lavrentieva ave., Novosibirsk, 630090, RUSSIA

ABSTRACT
This contribution presents short review of resent results of structural and physico-chemical studies of ionic clathrate hydrates of tetrabutylammonium fluoride, chloride, bromide, as well as of linear, cross-linked tetrabutylammonium and tetraisoamylammonium polyacrylates and some double hydrates of these compounds with methane.

Keywords: ionic clathrate hydrate, tetrabutylammonium salt, tetraisoamylammonium salt, structure, enthalpy of fusion

NOMENCLATURE
CS - I – cubic structure I
SCS - I – superstructure of CS - I
CRPac – cross-linked polyacrylate anion
D cavity – pentagonal dodecahedron (512)
HS - I – hexagonal structure I
Pac – polyacrylate anion
P cavity - pentakaidecahedron (51263)
T cavity – tritaekadecahedron (51563)
TBA – tetrabutylammonium cation
TiAA – tetraisoamylammonium cation
TS - I – tetragonal structure I
ΔHf – enthalpy of fusion

INTRODUCTION
In the crystal structures of ionic clathrate hydrates of TBA and TiAA halides water molecules and halide anions form a polyhedral hydrogen bonded water-anion framework. In the ionic clathrate hydrates of tetraalkylammonium salts with carboxylate anions carboxyl group is included in water framework through its oxygen atoms to form an edge of a polyhedron whereas hydrophobic part of the anion occupies a cavity of the water framework. Butyl and isoamyl groups of the cations are arranged in polyhedral cavities of this water-anion host lattice; nitrogen atom of cations replaces water molecule situated in vertex common of four neighboring cavities. Host lattices of ionic clathrate hydrates are structurally related to those of gas hydrates and can be described as combination of face-sharing D, T, and P polyhedra. Hydrocarbon groups of the cations are located in the T and P cavities, D cavities are empty [1, 2] (in some cases part of D-cages can be filled with “guest” water molecules [3-7]). The structures that are most common of ionic clathrate hydrates structures are tetragonal structure-I (TS-I), hexagonal structure-I (HS-I), superstructure of cubic structure-I (SCS-I) with unit cell stoichiometry 4P16T10D172H2O, 2P2T3D40H2O, 48T16D368H2O, respectively.

It is well known that participation of auxiliary guest component in hydrate formation in many cases results in formation of double hydrate with a higher decomposition temperature [8]. This method was used for increasing the decomposition temperature of hydrogen hydrate with use of auxiliary guest component tetrahydrofuran[9,10]. Practical use of auxiliary guest components faces some additional requirements. Auxiliary component must not be lost during formation – decomposition of the hydrate, it must be produced in industrial scale, it must be relatively...

1 Corresponding author: Phone: +7 383 316 5346 Fax +7 383 330 9489 E-mail: manakov@niic.nsc.ru
inexpensive, etc. Tetraalkylammonium salts are prospective for use as auxiliary guest component because they at least partially meet the above challenge and can serve as promoters of gas hydrate formation process. At present, ionic clathrate hydrates of TBA and TiAA salts are the subject of extensive research stimulated by diverse possible applications. TBABr polyhydrates were suggested as cold storage and transportation material [11,12]. Crystal structures of ionic clathrate hydrates contain vacant voids suitable for inclusion of molecules of appropriate sizes, thus revealing potential for storage, transportation and separation of gases. It has been found that double polyhydrates H₂-TBAF [13, 14], H₂-TBACl [15], and H₂-TBABr [14, 16-18] are formed, which have better thermal stability (provided equal pressure) than hydrogen hydrate [19,20] or double hydrate H₂-THF [9, 16]. It was demonstrated recently that clathrate hydrate of TBA borohydride represents a hybrid hydrogen storage material (H₂ is produced not only on decomposition of the clathrate hydrate but also through hydrolysis of the borohydride ion) [21]. Ionic clathrate hydrates TBABF [22], TBABr [18, 22-24] are able to form double hydrates with CO₂. It was found quite recently that ionic clathrate hydrates of TBACl, TBANO₃, and (C₃H₇)₄PBr also form double hydrates with CO₂, which decompose at higher temperatures (for a given pressure) than pure CO₂ hydrate [25]. It was demonstrated that double hydrates are formed by TBABr with such gases as methane [18, 26-28], nitrogen [18, 24, 27], and hydrogen sulfide [27, 29], as well as by TBACl with methane and nitrogen [15]. Additionally, hydrates of TBABr appeared to be suitable for separation of gas mixtures [24, 26, 27, 29, 30]. Single crystal X-Ray structure analysis of hydrate of TiAABr with krypton and methane confirmed that the gas molecules are located in the D cavities; these hydrates are characterized with high thermal stability [31]. Development of methods of practical use of tetraalkylammonium salts requires information on their structures and thermodynamic properties. However, at present these points are studied rather poorly. Another interesting point is formation of double hydrates of tetraalkylammonium salts with gases in which gas molecules partially occupy large cavities. It is necessary to increase gas content in these hydrates. Unfortunately, no data concerning formation of such hydrates is available. Thereby, the studies of the composition and properties of double hydrates of tetraalkylammonium salts with different gases is a topical task.

Development of gas hydrate technologies applicable for gas storage and separation of gas mixtures is not possible without fast and energy-sparing industrial-scale synthesis of these compounds that, consequently, require creation of large interface between liquid water and a gas. At present energy-consuming procedures of water and/or gas dispersion are used to accelerate reaction of hydrate formation. A possible way to solve this problem is to use clathrate hydrates that do not change the aggregate state as they decompose. The authors of the work [32] suggest to use hydrate formation within slightly cross-linked sodium polyacrylate particles swelled in tetrahydrofuran – H₂O solution for storage of H₂ gas. Decomposition of clathrate hydrates in such medium does not cause the change of aggregative state of the system. Another way that is discussed in this work consists in using water swellable clathrate forming polymeric materials. These materials are slightly cross-linked TBA and TiAA polyacrylates (carboxylic cationites). The formation of polyhydrates in swollen grains of cross-linked TBA and TiAA polyacrylates with low degree of cross-linking was first revealed in [33]. Invariable aggregative state of these compounds in the course of hydrate formation and decomposition makes studies of these compounds very interesting. In this report we present the short review of our recent structural and physic-chemical studies of ionic clathrate hydrates of TBA and TiAA salts.

**EXPERIMENTAL SECTION**

The aqueous solutions of TBAF, TBACl, and TBABr were obtained by neutralizing the TBAOH solution with corresponding acid and following recrystallization of polyhydrates from aqueous solutions. For preparation of cation-exchange resins in TBA and TiAA forms the carboxylic cation-exchange resins in the H-form were neutralized with a 3-fold stoichiometric excess of 0.1N aqueous solutions of TBAOH and TiAAOH, washed with distilled water and after that were centrifuged at the same conditions. Aqueous solution of TiAAOH was synthesized from TiA iodide by reaction with Ag₂O in water suspension and purified through the recrystallization of a clathrate hydrate. Polyacrylic acid with average molecular mass of 1800 daltons (Aldrich) without further purification and tetraisoamylammonium

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**Note:** The text contains some abbreviations and chemical formulas that might require additional context or knowledge to fully understand. For instance, TBABr refers to tetraethylammonium bromide, TBAOH is tetraethylammonium hydroxide, and so on. The abbreviations and formulas are common in the field of chemical engineering and materials science, particularly in the study of gas hydrates and related storage technologies.
hydroxide solution were used to prepare TBA and TiAA salt of the linear (unlinked) polymeric anion. Methane gas with a purity not less than 99.9% and distilled water were used in experiments. The content of TBA (TiAA) cations was measured by potentiometric titration with a sodium tetraphenylborate solution using an ion-selective electrode. Samples of the double hydrates of TBA salts with methane were prepared in reaction of powdered crystals of TBA salts with compressed methane in autoclave. The synthesis was continued for 2-3 weeks to complete the reaction.

Single crystals of ionic clathrate hydrates of TBAF, TBACl, TBABr and TBApac with different hydrate numbers were prepared by cooling and holding of aqueous solutions with different concentrations in the home-made air thermostat for a span varying from a few hours to a few days. These crystals were used for measurement of enthalpies of fusion and X-ray diffraction experiments. The crystals were separated from the solutions and quickly dried between two sheets of filtering paper up to air-dry state. All procedures were conducted in the air thermostat at the temperature of the crystal growth. A portion of the crystals was further placed into flask for analytical determination of the hydrate composition, the other portion was used for calorimetric and X-ray experiments.

A differential scanning calorimeter DSC-111 (Setaram) was used for determination of enthalpies of fusion. The samples of hydrates were sealed up in 0.1 ml steel pans for calorimetric studies of enthalpies of fusion. 5-8 measurements were carried out for each of the hydrates. Samples weight varied from 0.03 to 0.09 g. Measurements were carried out at heating rate of 0.5°C/min. The observed heats of fusion were normalized by electric calibration provided by the manufacturer. Single-crystal diffraction experiments were conducted at 150±1 K on a Bruker X8 APEX CCD diffractometer with MoKα radiation [34]. X-Ray powder diffraction studies were performed at –20°C on a Bruker D8 Advance diffractometer (CuKα radiation, λ = 1.5418 Å) equipped with Anton Paar refrigerating device. Phase diagrams were investigated by DTA at high pressure; high-pressure equipment has been described in [35]. Pressure was measured with precise gauge (0.25% error). Temperature was measured with a Chromel-Alumel thermocouple with precision of 0.2°C. The release of gas from the studied samples was monitored as a function of temperature by collecting the gas into a calibrated burette placed into a concentrated aqueous NaCl solution [36].

RESULTS AND DISCUSSION

Calorimetric studies of TBAF, TBACl, and TBABr ionic clathrate hydrates.

Our results of determination of the compositions and enthalpies of fusion of TBAF, TBACl, TBABr ionic clathrate hydrates are listed together with the data available from the literature in Table 1.

<table>
<thead>
<tr>
<th>Hydrate number, (m.p., °C)</th>
<th>ΔHf, kJ/mol hydrate (kJ/mol H2O)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBAF hydrates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30.22 (25.0)</td>
<td>197.16 (6.52)</td>
<td>[38]</td>
</tr>
<tr>
<td>30.0 (28.3)</td>
<td>184±4</td>
<td>[39]</td>
</tr>
<tr>
<td>32.4, (27.2)</td>
<td>203.0±2.3 (6.26)</td>
<td>[40]</td>
</tr>
<tr>
<td>28.9</td>
<td>174.3±3.1 (6.03)</td>
<td></td>
</tr>
<tr>
<td>TBACl hydrates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.2, (15.0)</td>
<td>179.1±4.9 (5.56)</td>
<td>[41]</td>
</tr>
<tr>
<td>29.7, (15.1)</td>
<td>156.9±2.1 (5.28)</td>
<td>[41]</td>
</tr>
<tr>
<td>30.0 (15.0)</td>
<td>156±4 (5.2)</td>
<td>[39,42]</td>
</tr>
<tr>
<td>30.0 (15.2)</td>
<td>164.1 (5.47)</td>
<td>[43]</td>
</tr>
<tr>
<td>30.0</td>
<td>173.6 (5.79)</td>
<td>[25]</td>
</tr>
<tr>
<td>24.8, (14.9)</td>
<td>127.9±3.6 (5.16)</td>
<td>[41]</td>
</tr>
<tr>
<td>TBABr hydrates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38.0 (9.9)</td>
<td>200.98±5.32 (5.29)</td>
<td>[12]</td>
</tr>
<tr>
<td>38.1, (9.7)</td>
<td>219.4±4.9 (5.76)</td>
<td>[this work]</td>
</tr>
<tr>
<td>32.5, (12.0)</td>
<td>177.2±3.5 (5.45)</td>
<td>[this work]</td>
</tr>
<tr>
<td>26 (12.0)</td>
<td>152.76±6.74 (5.88)</td>
<td>[12]</td>
</tr>
<tr>
<td>26</td>
<td>151.9 (5.84)</td>
<td>[24]</td>
</tr>
<tr>
<td>26.46 (12.0)</td>
<td>150.7±3.1 (5.71)</td>
<td>[this work]</td>
</tr>
<tr>
<td>24.04 (12.3)</td>
<td>136.2±3.1 (5.68)</td>
<td>[this work]</td>
</tr>
</tbody>
</table>

Table 1. The stoichiometry, melting points, and the enthalpies of fusion of the TBAF, TBACl and TBABr polyhydrates.

Crystal structures

The crystal structure of TBAF 29.7H2O ionic clathrate hydrate. The study of TBAF – H2O [37] phase diagram revealed formation of two hydrates: TBAF32.4H2O (TS-I, [5]) and TBAF28.6H2O. We have determined crystal structure of TBAF28.6H2O hydrate [6]. Idealized water framework is isostructural with CS-I of gas hydrates but with eight-fold unit cell (SCS-I, I-43d, a=24.375(3) Å). Positions of fluoride-anions
Clons and oons are included in the studied in our laboratory by DTA and TBACl binary system and the solubility isotherm (8 hydrates. The crystal structures of TBACl ionic clathrate water framework 28.7. number 29.7 is greater than predicted by idealized (Fig.1b) water molecules with the filling degree 79.5 % in D "pressed in" cavities which are partially f...The arrangement of TBA cation of "guest" water molecule (O11) in distorted D cavity. Figure 1. The arrangement of TBA cation of TBAF within 4T cavity; (b) the inclusion of chloride anion of TBACl: (a) with displacement of one hydrogen bonded water molecule of host framework (oxygen atom O2 is substituted by Cl2), and (b) with displacement of two water molecules (pair O11-O12 is substituted by Cl1). are not localized. Nitrogen atom of the cation occupies the common vertex formed by four face-sharing T polyhedra forming combined 4T cavity (Fig.1a); hydrocarbon chains fill compartments of this cavity. Inclusion of the cation results in “pressed in” of some framework water molecules in D-cavities which are partially filled by “guest” water molecules with the filling degree 79.5 % (Fig.1b). With this in mind the calculated hydrate number 29.7 is greater than predicted by idealized water framework 28.7.

The crystal structures of TBACl ionic clathrate hydrates. T.X phase diagram of the TBACl – H2O binary system and the solubility isotherm (8°C) of TBACl – NH4Cl – H2O ternary system have been studied in our laboratory by DTA and Schreinemakers’ method, respectively [44]. It was shown that three ionic clathrate hydrates TBAClnH2O (n=32.2, 29.4, 24.1) form in this system. We carried out the X-ray diffraction experiments for four single crystals with the stoichiometry TBACl-nH2O (n=32.7(s1); n=30.4 (s2); n=30.1(s3); n=27.4(s4)). It was shown that all of them belong to space group P43/m corresponding to idealized host water framework TS-I, the unit cell dimenions, Å: \( a=23.571(11), c=12.4361(6); a=23.5818(12), c=12.4148(7); a=23.5281(15), c=12.4918(7); a=23.4881(44), c=12.5289(21), \) respectively. All structures resemble the structure of ionic clathrate hydrate TBAF32.8H2O [5]. TBA cations are located in four-compartment cavities of two types: 4T and 3TP (Fig.2). Chloride ions are included in the hydrate framework, two inclusion modes being found (Fig.3): (1) substitution of one water molecule of the host framework; (2) substitution of two hydrogen-bonded water molecules. Due to distortion of the host framework induced by inclusion of TBA cations, some of D-cavities have three “pressed in” vertices and residual electron density peaks within the cavities. This electron density was refined as oxygen atoms of included guest water molecule.

The comparison of pairwise \( R_{int}(i, j) \) statistics indicates that the intensity data arrays can be divided in two groups: \( s1, s2 \) and \( s3, s4 \). The most distinct differences between the groups \( s1, s2 \) and \( s3, s4 \) are manifested in details of the structural models (site occupation factors, positions and values of residual electron density peaks) obtained on structure solution. The major dissimilarities appear in occupation factors of chloride-ion positions and atomic displacement parameters of oxygen atoms of the host framework. Significant differences are also observed in positions of residual electron density peaks. Two of them are inside the T-voids involved in formation of the 4T cavities, and another two are inside the D-voids adjacent to these T-cavities. The last four electron density peaks are considerably separated from the host framework atoms and, apparently, indicate the inclusion of TBA cations in combined cavities involving D-voids. Correct structural model describing disordering in these crystals is, most likely, quite complicated and we have not succeeded yet in elaborating it. The data obtained suggest the formation of two phases of ionic clathrate hydrates of tetrabutylammonium chloride, both having TS-I but differing in...
Figure 4. Powder diffraction patterns of TBACl·nH₂O in 2θ range 5 to 25°.

stoichiometry. The total of the data obtained on the compositions of the hydrates indicates that the stoichiometry of crystals s₁, s₂ is, most likely, close to TBACl·32Н₂O, while for s₃, s₄ - to TBACl·30Н₂O. The occurrence of only two different hydrates in four experiments suggests the absence of continuous solid-state solubility in the studied concentration range.

In order to confirm the existence of hydrates with stoichiometry close to TBACl·32Н₂O, TBACl·30Н₂O, TBACl·24Н₂O and unit cell similar to that of TS-I, X-ray powder diffraction study of three samples of hydrate phases has been carried out. The chemical analysis of the composition of the representative probes taken from the samples revealed hydrate numbers n=32.2, 29.7, 24.8 (TBACl·nH₂O). In all three cases the diffraction patterns obtained are quite similar (Fig.4). We calculated positions of diffraction peaks expected for a TS-I hydrate possessing the highest symmetry P₄2/m known for this type of hydrates. All reflections observed in this range can be interpreted in the framework of TS-I structural model with P₄2/m symmetry. These results support the hypothesis about the presence of several hydrates having different compositions but the same TS-I unit cell.

The crystal structure of TBABr ionic clathrate hydrates. There are different data on the number of ionic clathrate hydrates and their stoichiometry in TBABr – H₂O binary system [12,39,45,46]. Our data on examination of T,X phase diagram of the TBABr – H₂O system and of solubility isotherms of TBABr – third component – H₂O systems indicated the occurrence of four ionic clathrate hydrates: TBABr·nH₂O (n=36, 32, 26, 24) [46]. With regard to structural characteristics the only

structure of orthorhombic TBABr·38H₂O is known at present [47]. We carried out a single crystal X-ray structure analysis of hydrate TBABr·24H₂O. The structure was solved by the direct method. The structure of host water framework is TS-I, space group is P-4 with unit cell dimensions a=23.492(3)Å, c=38.021(8)Å, structural hydrate number is 24.8±25.7. Two manners of inclusion of TBA cations were revealed: (1) arrangement of one TBA cation in four compartment 3TP cavity, and (2) insertion of two TBA cations in eight-compartment 4D4T cavity (Fig.5). Probably, the latter peculiarity is responsible for existence of several hydrates of TS-I in the same system and was not known until now. In addition, a previously unknown way of hydrophilic inclusion of Br⁻ in the host water framework is found. Br⁻ is coordinated by four water molecules so that it is situated on the top of a square pyramid (Fig.6). An occurrence of superstructure (triple c parameter) is apparently caused by minimization of distortions of hydrogen bond network of water anion host framework arising from formation of eight-compartment cavities.

Phase diagrams, structural and calorimetric studies of the polyhydrates of linear and cross-linked TBA and TiAA polyacrylates

We studied phase diagrams of the binary systems water – cross-linked TiAAACPac (0.5-3% crosslinking) [48], water – TBACRPac (1% cross-linking). The phase diagrams studies were also
Table 2. Properties of the hydrates of linear and cross-linked tetraisoamylammonium polyacrylates with different degrees of cross-linking \( \alpha \) (\( \alpha = 0 \) – 3\%). \( n \) – hydrate number (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, taken from Ref. [48]). m.p. – melting point.

<table>
<thead>
<tr>
<th>( n, ) (m.p., °C), ( \alpha )</th>
<th>( \Delta H_f ) kJ/mol hydrate (kJ/mol H(_2)O)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexagonal, ( P-6m2 ), ( a=12.15 ), ( c=12.58 ) Å (100 K) ( a=12.26 ), ( c=12.71 ) Å (276 K) [50]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40.8 (18.4), ( \alpha=0% )</td>
<td>218.8 ± 4.5 (5.36)</td>
<td>[54]</td>
</tr>
<tr>
<td>Hexagonal, ( a=12.25 ), ( c=12.72 ) Å (276 K) [49]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37.7 (15.5), ( \alpha=0.5% )</td>
<td>193.0 ± 2.3 (5.12)</td>
<td>[54]</td>
</tr>
<tr>
<td>37.6 (14.6), ( \alpha=1.0% )</td>
<td>189.1 ± 2.3 (5.03)</td>
<td>[54]</td>
</tr>
<tr>
<td>33.5 (13.7), ( \alpha=2.0% )</td>
<td>158.8 ± 2.3 (4.74)</td>
<td>[54]</td>
</tr>
<tr>
<td>29.7 (13.0), ( \alpha=3.0% )</td>
<td>123.9 ± 6.2 (4.17)</td>
<td>[54]</td>
</tr>
</tbody>
</table>

Table 3. Properties of the hydrates of linear and cross-linked tetrabutylammonium polyacrylates with cross-linking \( \alpha = 1\% \). \( n \) – hydrate number (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). m.p. – melting point.

<table>
<thead>
<tr>
<th>( n, ) (m.p., °C), ( \alpha )</th>
<th>( \Delta H_f ) kJ/mol hydrate (kJ/mol H(_2)O)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>monoclinic, ( 2/m ), ( a=23.456 ) Å, ( b=12.327 ) Å ( c=23.454 ) Å, ( \beta = 90.04^\circ ) (150 K), ( a=23.60 ) Å, ( c=12.40 ) Å (248 K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33.23± 0.27 ( (13.2), \alpha=0% )</td>
<td>157.1 ± 2.7 (4.74)</td>
<td>this work</td>
</tr>
<tr>
<td>tetragonal, ( a=23.471 ) Å, ( c=12.328 ) Å (150 K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31.62± 0.31 ( (15.0), \alpha=0% )</td>
<td>156.8 ± 2.3 (4.74)</td>
<td>this work</td>
</tr>
<tr>
<td>tetragonal, ( a=23.436 ) Å, ( c=12.330 ) Å (150 K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30.04± 0.31 ( (15.0), \alpha=0% )</td>
<td>156.8 ± 2.3 (4.74)</td>
<td>this work</td>
</tr>
<tr>
<td>tetragonal, ( a=23.425 ) Å, ( c=12.364 ) Å (150 K) ( a=23.58 ) Å, ( c=12.41 ) Å (248 K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28.43± 0.09 ( (17.5), \alpha=0% )</td>
<td>130.8 ± 6.8 (4.60)</td>
<td>this work</td>
</tr>
<tr>
<td>tetragonal, ( a=23.56 ) Å, ( c=12.37 ) Å (248 K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>29.9 ( (8.5), \alpha=1% )</td>
<td>128.9 ± 3.0 (4,31)</td>
<td>this work</td>
</tr>
<tr>
<td>tetragonal, ( a=23.61 ) Å, ( c=12.40 ) Å (248 K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26.5 ( (8.5), \alpha=1% )</td>
<td>119.2 ± 4.2 (4.50)</td>
<td>this work</td>
</tr>
</tbody>
</table>

Figure 7. Phase diagrams of the binary systems: (a) water – cross-linked TBACRPac (cross-linking 1\%) and (b) water – cross-linked TiAACRPac (cross-linking 1\%) in the region of clathrate hydrate formation.

Carried out with salts of linear polymers. Obtained information concerning compositions, melting temperatures, structures and enthalpies of fusion is summarized in Tables 2, 3. The graphical representation of phase diagrams is given in the Fig. 7.

The results of X-ray powder diffraction studies of 1, 2 and 3\% cross-linked TiAACRPac hydrates [49] and those of cross-linked (1\% cross-linking) TBACRPac revealed the existence of a crystalline hydrate phase in frozen swollen grains of the studied resins. It was shown that all TiAA hydrates are hexagonal with the unit cell parameters (Table 2) corresponding well to HS-I. Polyhydrates of cross-linked TBACRPac are tetragonal with the unit cell parameters (Table 3) that suit well to TS-1. Both structures are characteristic of many clathrate hydrates of TBA and TiAA salts [1]. The hydrate crystallites inside the grains are relatively large, up to 0.01 mm\(^3\); each grain contains 100-200 crystallites.

It is not possible to obtain single crystals of hydrates of cross-linked polymeric carboxylates hence precise determination of their crystal structure is also impossible. Therefore, a hydrate with linear polyacrylates of TBA and TiAA were attempted as a first model approximation. The validity of this approach was demonstrated by the comparison of powder X-ray diffraction patterns of the samples of the polyhydrates with linear polymers with those of cross-linked TiAA and TBA polymers that revealed the identity of the crystal structures (Fig. 8, 9, Tables 2, 3).

Phase diagram of the binary system water – tetraisoamylammonium polyacrylate (un-cross-linked) was determined using DTA method. 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.
Figure 8. Powder diffraction patterns of the polyhydrates of linear (f) and cross-linked (1%, 2%, 3%) TiAACRPac (a-d), recorded at 310°C and those (e) recorded at room temperature (20°C); c,d – 3% degree of cross-linking when using teflon (c) and lavsan (d) coating films.

Figure 9. Powder diffraction patterns of the polyhydrates of linear (lower pattern) and cross-linked (1%) TBA polyacrylates (upper pattern), recorded at -25°C.

and analyzed (six independent determinations) to give the composition TiAAPac-(40.8±0.5)H₂O (Table 2). The single crystal X-ray analysis of the hydrate of this compound [50] confirms its clathrate nature. The hydrate crystal was hexagonal; the unit cell dimensions refined using all data were a = 12.150(1), c = 12.580(1) Å (at 100 K). In the crystal structure, the water molecules form a 3-D hydrogen-bonded host framework which is distorted variant of HS-I. The

Figure 10. (a) the layer of face-sharing 15-hedral (P) polyhedra at the z~0 level and one of combined 4-sectioned cavities (P₂T₂, outlined with bold lines). (b) The layer of face-sharing 12-hedral (D) polyhedra at the z~0.5 level.

space group is P-6m2. The large P polyhedra are located in a layer at the z~0 level sharing their hexagonal faces (each P polyhedron has three hexagonal faces) and producing a honeycomb system (Fig.10a). 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~0.5, is filled with D polyhedra sharing their pentagonal faces (Fig.10b). All the large cavities are occupied by the hydrophobic alkyl groups of TiAA cation which is included in 2P₂T four-compartment cavity. Similar inclusion mode was observed in previously reported clathrate hydrates with this cation[51,52] and is consistent with the ability of the isoamyl fragment to fit only in a large cavity but not in a small one. The cations are situated in layers at z~0 level (Fig.10a). The crystal, therefore, has a pseudo-layered organization with respect to the location of guest. According to our structural model the chains of polyacrylate anion can only be located within the layer of D-polyhedra at z~0.5 (see Fig.10b). The location of the chains is impossible to find directly from the experiment due to a great number of possible positions that produces a multi-fold disorder from the viewpoint of crystallography.

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 [3,7,51]. 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. 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. 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 (HS-I hydrates contain 1 cation per unit cell). 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. Fig. 10b) and so the accommodation of the polyanion is very favorable in terms of entropy. The described above inclusion of the polyion 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 3D-intersection as evident from Fig. 10b. The accommodation would be more difficult within a channel structure as one reported for TBAPac [53]. 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. In order to characterize the hydrate phases crystallized in the system water – TBAPac single-crystal X-ray diffraction studies were performed for four polyhydrates formed in the system according to phase diagrams studies and analytical determination of the compositions of the hydrates. Unit cell parameters of all crystals studied are similar and vary in the ranges (a=b=23.42±0.48Å, c=12.33±0.37Å), the angles are close to 90° (Table 3). It was found in the course of the statistical analysis of hklF – data that the crystals of three studied polyhydrates have Laue class 4/m, the values of R_int indices vary from 0.024 to 0.062, the symmetry of the diffraction picture for the crystal of fourth hydrate is lower and is characterized with Laue class 2/m (R_int=0.057). The structural models obtained show that the studied hydrates have the crystalline water frameworks related to the TS-1. Because of the significant disordering in the guest and partially in the host subsystems the structure cannot be described in detail. It can be said, however, that the cations of the polymeric guest are included in the combined 3TP и 4T cavities in the structure. Besides, the presence of the electronic density in all symmetrically independent D cavities of the framework can be associated with the accommodation of the polyacrylate anion inside the cavities. The calorimetric studies of the polyhydrates of TBA and TiAA polyacrylates The heats of fusion were measured for the clathrate hydrates comprising linear and cross-linked TBACRPac (cross-linking degree 1%) and TiACRPac (cross-linking degree 0.5-3%) [54]. 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 linear TBA and TiAA polyacrylates have been reported by Nakayama [55]. The results of the calorimetric measurements are presented in Table 2.3. It is seen from the calorimetric data that cross-links in polymeric anion cause the decrease in the fusion enthalpies of the polyhydrates with cross-linked polymeric guests in comparison with those of the polyhydrates with linear polymers. For the polyhydrates of TiAA cross-linked polyacrylates it was shown [54] 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. Double ionic clathrate hydrates with gases TBABr – methane – water system. We studied decomposition curves of double TBABr - methane hydrate formed by aqueous solutions of TBABr with 1:38 (31.7 mass.%) and 1:81.5 (18 mass.%) TBABr to H_2O molar ratio and excess of gaseous
Figure 11. Decomposition curves of HS-I hydrate 
TBABr·3H₂O, double hydrate TBABr·3H₂O+CH₄ and hydrate phases formed by aqueous solution of TBABr (1:81.5 TBABr:H₂O molar ratio) with methane.

Double hydrates with cross-linked polyacrylates. The P,T curves of hydrate decomposition in the systems TBACRPac (0.5% cross-linking) – H₂O and TiAACRPac (2% cross-linking) – H₂O, along with the decomposition curves of these hydrates under a pressure of hydrogen, are presented in Fig.12. The melting curves for the hydrates of pure ion-exchange resins contain fractures (P = 46 MPa for TiAACRPac hydrate and P = 65 MPa for TBACRPac hydrate), which probably suggest the formation of new hydrate phases at these pressures. A considerable increase in hydrate decomposition temperatures is observed in both cases upon imposition of hydrogen pressure over the entire pressure range. Furthermore, no characteristic fractures on the curves were observed; the scatter of experimental points is within the experimental error. A similar picture is typical of the formation of double hydrates, i.e. the structures of TBACRPac and TiAACRPac hydrates contain vacant cavities; filling of the latter with hydrogen molecules increases their decomposition temperatures. It should also be noted that the specimens had the form of solid granules both before and after the experiment.

The experiments discussed above has shown that (1) reaction of methane with 18 mass.% solution of TBABr results in mixture of double hydrate and gas hydrate of pure methane, (2) cross-linked TiAACRPac and TBACRPac can form the double hydrate. Some experimental data which were obtained in these experiments are shown in Fig.11. 1:38 TBABr solution corresponds to stoichiometric ratio TBABr and water which was expected for double hydrate with the HS-I. On the basis of this information we attribute DTA effects corresponding to this solution to decomposition of double hydrate (Fig.11). In the case of 1:81.5 solution the situation was more complex (Fig.11). In addition to DTA effects corresponding to decomposition of double hydrate, 2 groups of DTA effects occur. Low-temperature group of weak effects at temperature close to 0°C correspond to melting of aqueous eutectic. Positions of the second group of DTA effects coincide with decomposition curve of methane hydrate. This hydrate was undoubtedly formed by aqueous eutectic and excess of methane gas. Temperature of methane hydrate decomposition in this case was not changed because aqueous eutectic in the TBABr·H₂O system represent itself almost pure water [40].

Figure 12. Effect of pressure on the decomposition points for (a) TBACRPac hydrate (0.5%): without hydrogen (A); under pressure of hydrogen (B); (b) TiAACRPac hydrate (2%): without hydrogen addition (A); under pressure of hydrogen (B).
Table 4. Volumes of gas emitted at 1-st and 2-d steps of decomposition of the samples of double hydrates with methane. 1) double hydrate was formed by 18 mass.% solution of TBABr (1 : 81.5 TBABr :water molar ratio); 2) double hydrate was formed by cross-linked polyacrilat of TBA, 80% substitution of H+ to TBA+ cations; 78 mass.% content of water.

<table>
<thead>
<tr>
<th>experiment</th>
<th>( \Sigma V )</th>
<th>( V_1 )</th>
<th>( V_2 )</th>
</tr>
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<tbody>
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<td>81.4</td>
<td>22.2</td>
</tr>
<tr>
<td>2</td>
<td>103.2</td>
<td>81.7</td>
<td>21.5</td>
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<tr>
<td>4</td>
<td>34.5</td>
<td>22.1</td>
<td>12.4</td>
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</tbody>
</table>

Figure 13. Typical curves of gas emission. For comments see the text.

Concluding remarks
The most interesting and unexpected result of this work is formation of several ionic clathrate hydrates with the same water framework (TS-1), almost indistinguishable parameters of the unit cell but significantly different compositions. Hydrates of this type occurred in the systems water - TBABr, TBACl and TBPac. We speculate that formation of these hydrates is result of the compromise between the tendencies to the closest filling of crystal structure with atoms and molecules, to formation of phases with highest entropy, and to form hydrate framework with undistorted hydrogen bonds. In the case of hydrate
formation in the diluted (in comparison with the hydrate compositions) solutions of TBACl and TBABr the hydrates with the smallest distortion of hydrate framework form. In these hydrates occupation degree of small D-cavities with guest component is zero or minimal. Crystallization of ionic clathrate hydrates from solutions with higher guest concentration results in the formation of hydrates with high content of occupied 3DT and 4T4D cavities and smaller hydrate numbers. In this case more dense packing of the hydrate framework is caused by partial occupation of small D-cavities with alkyl radicals of TBA cation. Formation of the hydrates with dense packing of crystal structure requires distortion of hydrate framework, e.g. in these frameworks coordination of some anions with water molecules is pyramidal instead of tetragonal. We believe that entropy of these hydrates is higher in comparison with the hydrates with larger hydrate numbers. The factors considered above result in systematic decrease of specific enthalpy of hydrate fusion with decrease of hydrate number of the respective ionic clathrate hydrates (Table 1). We suppose that the formation of several TS-I hydrates by cross-linked TBA polycylrates is caused by the same peculiarities of the crystal structures. Further work is necessary to prove this idea. Some other peculiarities of the studied hydrates should be mentioned. First of all the formation of several hydrates in one system with the same structural type but significantly different compositions is possible only for TBA salts. No examples of this type are known for TiAA hydrates. Most probably, the size of butyl group allows it to occupy small D-cavity with minimal distortion of the hydrate framework that is not possible for isoamyl group. The second interesting observation is that hydrates of this type form in the systems with the anion distorting hydrate framework (Cl, Br but not F) or even destroying it (cross-linked polycycylrates). Probably, weakening of hydrogen bonds in hydrate framework makes possible structural modernization of this framework without change of the type of this framework. Finally, the results concerning formation of double hydrates of TBABr and cross-linked polycylrates of TBA with methane show that substitution of TBA cation with methane is unlikely. In all cases the samples obtained after reaction of the row samples with methane contained not only double hydrate, but also gas hydrate of pure methane. We speculate that the formation of two types of gas hydrates is more favorable energetically in comparison with formation of double hydrates with partial occupation of large cavities with methane.

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REFERENCES


[34] Bruker AXS Inc. 2004: APEX2 (Version 1.08), SAINT (Version 7.03), SADABS (Version 2.11). Madison, Wisconsin, USA


