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Incorporation of gas molecules into the frameworks of clathrate hydrates of ion-exchange resins in tetraalkylammonium form

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The decomposition temperatures of the hydrates of carboxylic cationites in tetraisoamylammonium (TiAA) and tetrabutylammonium (TBA) forms increase considerably in the presence of hydrogen (at 50 MPa, $\Delta T \approx 6.5$ °C for TiAA and 5.0 °C for TBA; at 150 MPa, $\Delta T \approx 8.1$ °C for TiAA and 6.2 °C for TBA).

Clathrate hydrates belong to the class of cellular clathrate compounds in which the host framework is formed by water molecules, while the guest molecules are incorporated into the framework cavities.[1] In case of guest molecules built with covalent bonds (N_2, CH_4, tetrahydrofuran and $CHCl_3$), guest–host interactions are of pure van der Waals nature, and the guest molecule is incorporated in the framework cavities in a hydrophobic way. However, numerous clathrate hydrates are known that are similar in the topology of the host frameworks and where tetrabutyl- and tetraisoamylammonium salts (TBA and TiAA, respectively) serve as the guests.[1] In case of clathrate hydrates of salts with simple anions, *e.g.*, halide ions, the anion is involved in the buildup of the host framework by bonding with adjacent framework water molecules by hydrogen bonds (hydrophilic incorporation of the anion), while the cation is incorporated hydrophobically into the combined four-section cavity of the water-anion framework that is formed upon merging of four big cavities.[1] As clathrate hydrates of tetraalkylammonium salts with carboxylate anions are formed, hydrophobic-hydrophilic incorporation of the anion occurs: the oxygen atoms of the carboxylate anion are incorporated hydrophilically into the framework, whereas the hydrocarbon part of the anion occupies the big or small cavity of the water framework.[2,3] In the structure of a clathrate hydrate of linear tetrabutylammonium polyacrylate, the polyanion chain is situated in the channels formed by the fusion of large cavities of a water clathrate framework.[4]

In the past few years, attention was focused on the use of clathrate hydrates, in particular the clathrate hydrates of tetraalkylammonium salts, for the storage and transportation of gases and for the separation of gas mixtures.[5–8] They can be used for this purpose provided that techniques for fast and energy-sparing industrial-scale synthesis of these compounds are created. A serious challenge is to create a large area of interface contact between liquid water and a gas, which is necessary for the heterogeneous formation of hydrates. A possible way to solve this problem is to use clathrate hydrates that do not change the aggregate state as they decompose. Compounds of this kind include clathrate hydrates that are formed in swollen granules of cross-linked TBA and TiAA polyacrylates with small cross-linking ratios (0.5–3%, divinylbenzene or divinyl sulfide), which correspond to carboxylic cationites – a kind of ion-exchange resins. The formation of clathrate hydrates in the swollen grains of carboxylic cationates in TBA and TiAA forms was shown previously,[9] the following results including the study of the pressure influence on the decomposition temperature of the polyhydrate of cross-linked TBA polyacrylate (3% of cross-linkages) under the pressures of CO_2 and N_2O gases up to 1 MPa were summarised.[10]

The study of the phase diagrams of H_2O–R'_4NCOOR_n binary systems (where R′ is butyl or isoamyl; R_nCOO^- is a polymeric cross-linked polyacrylate ion; and n is the cross-linking ratio equal to 0.5, 1 or 3%) allowed us to determine the compositions of the polyhydrates formed.[11] Depending on the cross-linking ratio, TiAA polyacrylates form the polyhydrates $(i\text{-}C_5H_{11})_4NCOOR_n\cdot(37.7\text{–}29.7)H_2O$, which are similar in stoichiometry to clathrate hydrates of monomeric tetraalkylammonium salts with a polyhedral clathrate framework.[1] Depending on the cross-linking ratio of the polymeric anion, the decomposition temperature of polyhydrates is 13.0–15.6 °C. Tetrabutylammonium polyacrylate ($n = 0.5\%$) forms the polyhydrate $Bu_4NCOOR_{0.5}\cdot 31.7H_2O$ with a decomposition temperature of 8.7 °C at 0.1 MPa. A study of samples of these hydrates by powder diffractometry at 3±1 °C confirmed the existence of a crystalline hydrate phase in swollen granules of the ion exchange resins.[12] It was also shown that, irrespective of the cross-linking ratio, TiAA polyacrylate polyhydrates are crystallised in the hexagonal syngony and the unit cell parameters are in good agreement with the idealised basic cell of hexagonal structure I of clathrate hydrates, which is typical of many clathrate hydrates formed by tetraisoamylammonium salts. TBA polyacrylate polyhydrates are crystallised in the tetragonal syngony and the unit cell corresponds to tetragonal structure I of clathrate hydrates, which is typical of clathrate hydrates of tetrabutylammonium salts.[1] Structural studies[1] showed that the hydrate frameworks of TiAA and TBA salts with monomeric ions having the structural types specified above contain small vacant cavities, which can incorporate gas molecules.[13] Since no detailed structural data on the hydrates of ion-exchange resins in tetraalkylammonium form have been published, it remained unknown whether their structures contained vacant cavities available for incorporation of gas molecules, that is, their potential for the storage of gases and separation of gas mixtures remained unclear. It is also important to decide whether the structures of these polyhydrates contain vacant cavities in view of gathering structural information for this class of clathrate hydrates.

If the structure of a clathrate hydrate contains vacant cavities, the filling of these cavities with additional guest molecules with appropriate size stabilises the structure. Hence, the decomposition temperature of the double hydrate increases in comparison with that of the original one.[14–16] In view of the above, we considered it interesting to study the behaviour of these hydrates under a pressure of gaseous hydrogen.

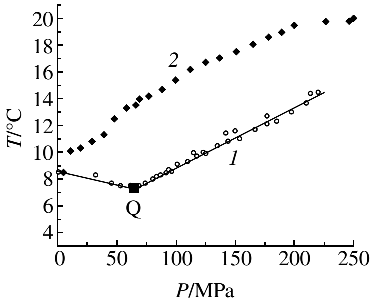

Figure 1 Effect of pressure on the decomposition points of tetrabutylammonium polyacrylate hydrate (n = 0.5%): (*1*) without hydrogen addition and (*2*) with hydrogen addition.

The test specimens were prepares as described below. A carboxylic cationite was preconditioned by cyclic acidic-alkaline treatment in 0.1 N NaOH and HCl solutions, washed with ethanol and then with a large amount of distilled water to remove ethanol. The TBA and TiAA forms of the carboxylic cationite were obtained under static conditions by the neutralisation of the polyacid with a three-fold excess of a 0.1 N solution of tetraisoamylammonium or tetrabutylammonium hydroxide. After the neutralisation was completed, the specimens were centrifuged, washed with distilled water and air dried (the residual content of water in the specimens determined by the Fischer method was 7–10 wt%). To prepare a specimen with a water content equal to that in the hydrate phase,[11] a calculated amounts of water was added to a weighed amount of air-dry cationite, and the specimens were kept for 24 h in a sealed tube to allow swelling.

The decomposition temperatures of hydrates were measured by differential thermal analysis (DTA) at hydrostatic pressures up to 250 MPa in a temperature range from –20 to +50 °C. The relative error of pressure determination was 0.5% and the temperatures were measured to within ±0.3 °C. The experimental set-up was described previously.[17] To record the decomposition temperatures of hydrates without extra hydrogen addition, a specimen of the swollen resin (0.03 g) was placed in a plastic tube with an inserted Chromel–Alumel thermocouple. After that, the remaining unoccupied space of the tube was filled with water (0.05 ml) through which pressure was applied to the sample. The decomposition temperatures of hydrates in ternary systems (under a pressure of gaseous hydrogen) were measured using a tailored cell with a liquid piston to which a tube with swollen resin (0.015 g) was attached. The cell inner compartment was filled with 2.5 ml of hydrogen; hydrostatic pressure was applied to the specimen through mercury contained in the cell outer compartment.

The *P–T* curves of hydrate decomposition in the cross-linked tetrabutylammonium polyacrylate (cross-linking ratio 0.5%)–H_2O and cross-linked tetraisoamylammonium polyacrylate (cross-linking ratio 2%)–H_2O systems along with the decomposition curves of these hydrates under a pressure of hydrogen, are presented in Figures 1 and 2. The melting curves for the hydrates of pure ion-exchange resins contain kinks (P = 46 MPa for TiAA polyacrylate hydrate and P = 65 MPa for TBA polyacrylate hydrate), which probably suggest the formation of new hydrate phases at these pressures, *i.e.*, these kinks are quadrupole points on the *P–T* projections of the corresponding phase diagrams. 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 kinks in the curves are observed; the scatter of experimental points is within the experimental error. A similar picture is typical of the formation of double hydrates;[14–16] *i.e.*, the structures of TBA and TiAA polyacrylate hydrates contain vacant cavities; filling of the latter with hydrogen molecules stabilises the hydrates and hence increases their decomposition temperatures. Note that the specimens had the form of solid granules both before and after the experiment.

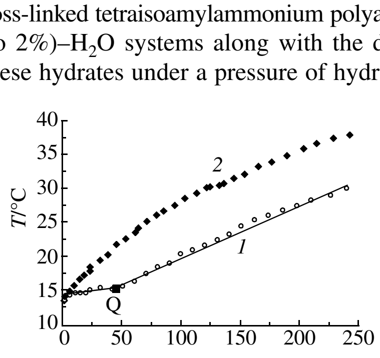

Figure 2 Effect of pressure on the decomposition points of tetraisoamylammonium polyacrylate hydrate (n = 2%): (*1*) without hydrogen addition and (*2*) with hydrogen addition.

We also performed an experiment to find the amount of gas contained in TBA polyacrylate hydrate. A weighed sample (1 g) of the swollen resin was placed in a high-pressure cell, and a hydrogen pressure of 12.5 MPa was created in the cell. The specimen was kept at –14 °C for a week in order to establish an equilibrium in the system and to form a hydrate. Prior to the withdrawal of the double hydrate from the high-pressure cell, the latter was frozen at liquid nitrogen temperature; experiments to determine the evolved gas volume were carried out using a quenched hydrate specimen. According to preliminary estimates, the resulting hydrogen concentration in the specimens was ~0.1 wt%, or about 10.5 ml of hydrogen per gram of the hydrate specimen.

Thus, the results suggest the principal possibility of using the hydrates of carboxylic cationites in tetraalkylammonium form for the storage of gases and for the separation of gas mixtures (*e.g.*, as stationary phases in chromatography).

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