

## Composition of the clathrate polyhydrate of a carboxyl cationite in the tetraisoamylammonium form

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It is shown that a clathrate polyhydrate of constant composition is formed at 0 °C in the three-component system: cross-linked carboxylic cationite in tetraisoamylammonium form–water–ethanol in the range of ethanol concentration from 0 to 22 mass%.

Tetrabutylammonium (TBA) and tetraisoamylammonium (TiAA) salts with simple anions (such as halides, sulfate, formate, *etc.*) form clathrate polyhydrates with water under specific conditions. In these polyhydrates, water molecules, together with the anions, form a crystalline framework linked by hydrogen bonds (hydrophilic inclusion of the anion), while the hydrocarbon radicals of the cation are incorporated into the so-called 'large' cavities of the framework (hydrophobic inclusion), hence stabilising it. The carboxylate anion is incorporated in a hydrophilic way through its two oxygen atoms to form an edge of the polyhedron, while the hydrocarbon part of the anion (if any) is positioned in vacant dodecahedral (D) 'small' cavities, the number of which in such structures is usually no less than the number of formula units of the salt. This results in additional stabilisation of the framework as long as the dimensions of the hydrophobic part of the anion do not exceed those of the D-cavity.<sup>1</sup> The stability of polyhydrates of monomeric TBA carboxylates has been shown to depend on the length of the hydrophobic part of the anion.<sup>1,2</sup> In accordance with the above, the maximum stability corresponds to polyhydrates of TBA butyrate, which has the best spatial conformity to the D-cavity (the mp of TBA butyrate hydrate is 21.6 °C). Further lengthening of the hydrophobic part of the anion causes the polyhydrate melting point to decrease because of destabilisation of the water framework by the anion (the mp of TBA caprylate hydrate is 1.8 °C). However, when the length of the hydrophobic part of the anion increases to  $n = 10$ , the melting point of polyhydrates increases strongly once again (20 °C), which was explained<sup>2</sup> by the formation of new, possibly non-polyhedral structures. On the other hand, the polyhydrates of linear polyacrylates with a degree of polymerisation of acrylic acid  $n = 2100$ ,<sup>3</sup> and especially those of cross-linked polyacrylates in TBA and TiAA forms are rather stable.<sup>†</sup> For example, the decomposition temperature of the polyhydrate with the composition  $(i-C_5H_{11})_4NCOOR \cdot 25H_2O$ <sup>‡</sup> [where  $(i-C_5H_{11})_4NCOOR$  is a cross-linked carboxyl cationite in the TiAA-form] determined by studying the binary system  $(i-C_5H_{11})_4NCOOR \cdot H_2O$  is +13.0 °C.<sup>4</sup> One of the reasons for the special interest in hydrate formation with ion-exchange resins is that three-dimensional polymers are disordered phases, whereas the hydrate framework should be crystalline; however, building a polyhydrate long-range ordered structure with a guest of this type is difficult due to the imperfection of such structures because of cross-linkages in the polymeric guest molecules. This raises the question: what is the nature of a polymer hydrate phase, and in particular, does this phase have a variable composition typical of ionites or it is a compound of constant composition characteristic of polyhydrates of monomeric peralkylammonium salts? In this respect, studying the composition of polymer polyhydrates over the widest range of equilibrium conditions is of interest.

<sup>†</sup> The cross-linked polyacrylate used in this study is a carboxylic cationite synthesised from acrylic acid and divinyl sulfide (3% of sulfide cross-linkage). Its polyanion elementary unit is analogous in elemental composition to that of propionate and acrylate ions.

<sup>‡</sup> The composition was estimated preliminary by constructing a Tamman triangle.<sup>4</sup>

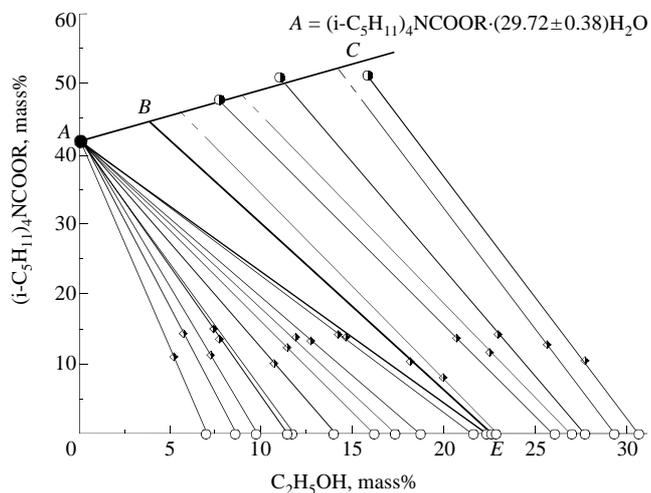
Even for monomeric clathrate-forming tetraalkylammonium salts, the determination of polyhydrate composition is very difficult because several hydrates of very similar composition usually exist in tetraalkylammonium salt–water systems. These hydrates can be mistaken for a phase of variable composition if the resolution of the technique for composition determination is insufficient. For example, three hydrates of different structures exist in the system  $(i-C_5H_{11})_4NF \cdot H_2O$  in the water concentration range from 96.4 to 97.4 mol%.<sup>5</sup> A number of methods have been elaborated to increase the resolution in such systems. Combined application of these methods made it possible to determine the composition of polyhydrates reliably, *e.g.* the Schreinemakers method allows the determination of the composition of a hydrate without its isolation using subsequent mathematical treatment of the data obtained; this is followed by preparative analysis of the crystals isolated and by structural studies. Additional efforts are required for the determination of the composition of polymer polyhydrates with insoluble bottom phases and solid hydrate phases; this problem is now being stated for the first time. For this purpose, the solubility isotherm of the three-component system  $(i-C_5H_{11})_4NCOOR \cdot H_2O \cdot C_2H_5OH$  was studied at 0 °C by the Schreinemakers method and it was shown for the first time that a polymer forms a polyhydrate of constant composition.

The carboxyl cationite in the H-form was preliminarily conditioned with 0.5 M solutions of HCl and NaOH, washed with ethanol and then washed with a great amount of distilled water to remove the ethanol. The ion-exchange capacity of the cationite relative to the  $Na^+$  cation was found to be

**Table 1** The solubility isotherm (0 °C) in the  $(i-C_5H_{11})_4NCOOR \cdot H_2O \cdot C_2H_5OH$  system.

Experiment no.	Initial composition, mass%		Equilibrium liquid phase, mass%
	$C_2H_5OH$	$(i-C_5H_{11})_4NCOOR$	$C_2H_5OH^a$
1	5.18	10.95	6.98
2	5.71	14.34	8.63
3	7.23	11.15	9.76
4	7.35	15.09	11.69
5	7.66	13.74	11.52
6	10.70	9.97	13.97
7	11.40	12.37	16.22
8	11.82	13.81	17.33
9	12.70	13.40	18.73
10	14.21	14.38	21.62
11	14.65	13.81	22.40
12	18.15	10.52	22.70
13	19.98	8.00	22.91
14 <sup>b</sup>	20.75	13.74	25.88
15	22.50	11.81	27.01
16 <sup>b</sup>	22.90	14.37	27.76
17	25.64	12.86	29.33
18 <sup>b</sup>	27.78	11.37	31.00

<sup>a</sup>Since the carboxylic cationite is practically insoluble in water, the liquid phase composition lies on the  $x$  axis. <sup>b</sup>For composition nos. 14, 16 and 18, preparative analyses of the hydrate-liquid phase was performed. According to the results, the content of  $C_2H_5OH$  in the samples (mass%) is 8.66%, 11.40% and 15.31%, respectively; the water content in the samples is 43.80%, 37.61% and 34.40%, respectively.



**Figure 1** The solubility isotherm (0 °C) in the three-component system  $(i-C_5H_{11})_4NCOOR-H_2O-C_2H_5OH$ . Conventional symbols:  $\blacklozenge$ , initial composition;  $\circ$ , equilibrium liquid phase;  $\bullet$ , hydrate phase;  $\odot$ , hydrate-solvate phase; *B*, hydrate-solvate phase in the equilibrium with the hydrate (A) and eutonic solution (*E*); *BC*, hydrate-solvate phase of variable composition.

13.0 mg equiv.<sup>-1</sup> of Na<sup>+</sup> per 1 g of dry cationite in the H-form. The swelling capacity of the cationite in the H-form was determined to be 5 water molecules per each ionogenic group.

The TiAA form of the carboxyl cationite (complete replacement of cationite carboxyl protons for TiAA cations) was synthesised under static conditions by neutralisation of the polymeric acid with a three-fold stoichiometric excess of a 0.1 M solution of  $(i-C_5H_{11})_4NOH$ . After the neutralisation was completed, the samples of the cationite 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 air-dried.

The water content in the cationite was determined by the Fisher method (reverse titration). For this purpose, a weighed sample of an ion-exchange resin (30–40 mg) was stirred for 5–7 min with excess Fisher's reagent. The unreacted reagent was then titrated with ethanol or pyridine containing small quantities of water (0.2–0.3 mass%).

In studies of the three-component system, the initial three-component mixture was prepared by the weighing technique. Weighed samples of an air-dried cationite containing a known amount of water and a water-ethanol mixture of a certain composition were placed in a tube. The equilibrium was established by stirring the mixture for 24 h at the temperature of melting ice. After the equilibrium had been established, the liquid phase was withdrawn and analysed for water content by the Fisher method.

The Schreinemakers rays were drawn through the points corresponding to the initial composition of the three-component mixture and the equilibrium composition of the liquid phase.

Figure 1 and Table 1 present the results of the study of the solubility isotherm of the three-component system  $(i-C_5H_{11})_4NCOOR-H_2O-C_2H_5OH$  at 0 °C. Graphical construction of Schreinemakers rays indicates that a polyhydrate crystallises in the system in the  $C_2H_5OH$  concentration range from 0 to 22 mass%. The composition was also calculated using the programs that take into account the statistical weights of each Schreinemakers ray intersecting with the axis of the binary system cationite-water and their pair combinations when they intersect each other.<sup>6</sup> Calculation of hydrate composition using this program showed the compound to be binary within experimental error. The calculated composition is  $(i-C_5H_{11})_4NCOOR \cdot (29.72 \pm 0.38)H_2O$ . It is seen in Figure 1 that the hydrate phase is stable in equilibrium with the liquid phase containing up to 22 mass% of  $C_2H_5OH$ ; a further run of Schreinemakers rays shows the water content in the cationite granules to decrease because of  $C_2H_5OH$  sorption by the cationite and formation of hydrate-solvate phases. The compo-

sition of the hydrate-solvate phase was determined using a preparative technique. For this purpose, the cationite granules were isolated at 0 °C from the mother liquor and squeezed out between filter paper sheets and analysed both for water content by the Fisher method and for the overall content of water and ethanol determined by the loss of sample weight on drying in a vacuum oven at 50–60 °C. In a similar way, the polyhydrate composition in its crystallisation field was determined to be  $(i-C_5H_{11})_4NCOOR \cdot (30.87 \pm 0.46)H_2O$ .

According to ref. 7, an ionite placed in a mixed solvent can adsorb both its constituents on swelling. Ionites usually prefer the polar component of the solvent over the non-polar one. There should be no difference in this respect between ethanol and water whose dipole moments are similar,<sup>7</sup> and hence  $\lambda$  (the distribution coefficient of ethanol between the ionite phase and the solution) should be close to 1. However, it is evident from Figure 1 that at 0 °C the adsorption of ethanol by the cationite does not occur in the concentration range from 0–22 mass% ethanol. This fact correlates with the conclusion about the clathrate nature of the phase in question. Along with a similarity between ethanol and water as regards their polarity and ability to form H-bonds, which is sufficient for them to behave similarly in the adsorption on surfaces, a difference is observed due to the inability of ethanol molecules to create a three-dimensional network through H-bonds and their geometrical difference from water molecules.

Thus, the study of the solubility isotherm in the three-component system  $(i-C_5H_{11})_4NCOOR-H_2O-C_2H_5OH$  shows that the composition of the hydrate of the carboxyl cationite in the tetraisoamylammonium form,  $(i-C_5H_{11})_4NCOOR \cdot (29.7 \pm 0.4)H_2O$ , remains constant on varying the concentration of ethanol in the equilibrium liquid phase from 0 to 22 mass%. This is quite uncharacteristic of ionites but typical of TiAA salts. At higher concentrations of ethanol, its distribution between the liquid and ionite phases is usual for ionites. The observed anomaly of the ionite behaviour in the mixed solvent can easily be explained by assuming the clathrate nature of the polyhydrate.

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