Clathrate Hydrates of Long-chain Tetrabutylammonium Carboxylates

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The dependence of melting points of polyhydrate formation in the systems $Bu_4NH(CH_2)_nCO_2–H_2O$ on the value of n (n = 6,7,9 and 10) has been determined, and they were unexpectedly found to increase at $n > 7$.

The study of a series of water binary systems with tetrabutylammonium (TBA) carboxylates (from formate to capronate)[1] revealed that the addition of a CH_2 group to the anion hydrocarbon chain significantly affects clathrate formation. The dependence of the stability of the compounds on the anion hydrocarbon chain (n) could be logically explained by the structure of the clathrates and the additional stabilization of the framework at the expense of the filling of the available vacant cavities (see below). It was interesting to study the behaviour of anions with longer hydrocarbon chains. Japanese researchers[2] studied binary systems with TBA carboxylates with n varying from 0 to 10 and demonstrated that low stability clathrate hydrates can form over the whole range of n values. However, in each of the systems only one hydrate was found and, as we mentioned above, it was only by accident that this particular hydrate was found out of the many hydrates (usually metastable ones) forming in every system. That is why in this case it is difficult to find any regularity. We investigated the systems where n values were 6, 7, 9 and 10 and discovered a very interesting phenomenon: the hydrate melting point rises sharply at $n = 10$.

The synthesis of TBA carboxylates was carried out by the reaction of neutralization of TBA hydroxide with the corresponding acid. The products obtained were recrystallized three times, yielding clathrate hydrates. The crystals of the hydrates were melted at room temperature and the solutions were concentrated in a desiccator over P_2O_5; the analysis for the main product content was carried out by potentiometric titration of the salt with sodium tetraphenylborate with the help of a TBA-selective electrode,[3] and for water content, by the Fisher's technique. In all the cases the total amount of salt and water did not exceed 99.4–100%. The phase diagrams were constructed on the basis of the thermal and differential-thermal (heating curves) analysis data.[4] The reproducibility near the maximum of the liquidus curve was ±0.02. The heating rate at thermographic investigation is 0.25–0.5 K min^{-1}. The heating curves of the samples previously cooled to $-30\,°C$ almost constantly showed several endothermic effects which corresponded to the melting of different (usually metastable) hydrates. Repeated cooling-heating processes (5–8 times) eliminated these effects. One of the effects corresponding to the melting of the most stable hydrate persisted at the highest temperature (it did not always appear during the first recording).

Figure 1 shows the phase diagrams of the binary water systems of TBA carboxylates whose anion hydrocarbon chain length n was equal to 6, 7, 9 and 10. We do not present all the data on the melting of the metastable hydrates so as not to burden the figures with unnecessary details. The data on the composition and the melting points of the most stable clathrates[†] in each of the hydrate system are cited in Table 1. The composition of the metastable hydrates vary from 26 to 39 at $n = 6$, from 26 to 34 at $n = 7$, from 26 to 31 at $n = 9$ and from 21 to 30 at $n = 10$. The melting points of the most stable hydrates first drop from 2.8 °C at $n = 6$ to 1.8 °C at

Table 1 Hydrate numbers and melting points of the most stable hydrates.

| Anion of TBA salt	n	m.p./ °C
$C_6H_{13}CO_2$	30.3	2.80
$C_7H_{15}CO_2$	30.8	1.80
$C_9H_{19}CO_2$	28.1	5.85
$C_{10}H_{21}CO_2$	19.0	20.5

$n = 7$, then begin to increase, and there is a sharp rise at $n = 10$. In the system with TBA undecanate ($n = 10$) crystals of two metastable hydrates[‡] were obtained. Their composition and melting points were determined by the preparative technique. Their hydrate numbers are: $h_1 = 26.7$ (m.p. =
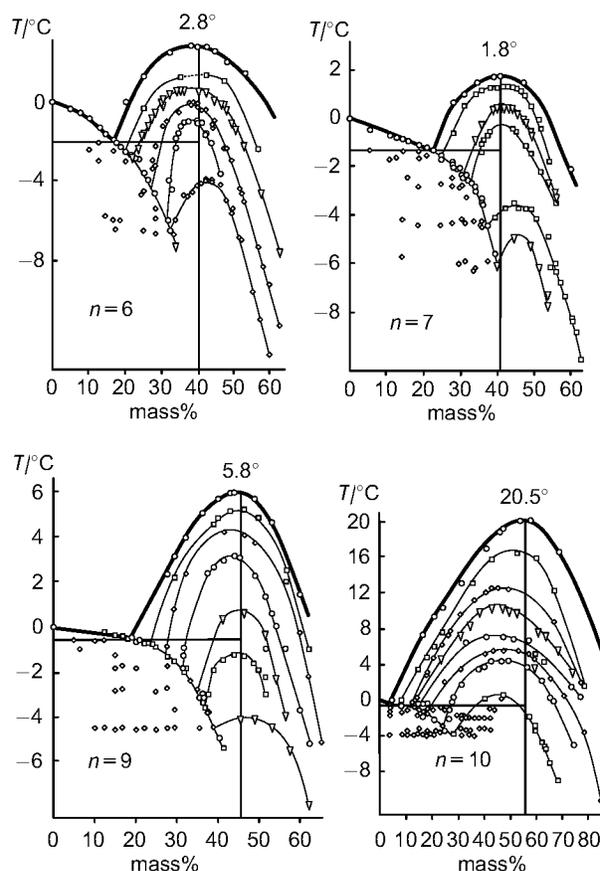
Figure 1 Phase diagrams of the $Bu_4NH(CH_2)_nCO_2–H_2O$ systems, where $n = 6$, 7, 9 and 10. Not to burden the figures we present the experimental data on the solidus only from the rich water side and do not draw the corresponding lines. Thick lines, melting of the most stable hydrates; thin lines, melting of metastable hydrates and of ice in the metastable field; figures over the melting curves, the melting points of the most stable hydrates.

[†] It follows from thermodynamics[5] that in systems with the same phase composition the highest melting phase is the most thermodynamically stable (if the liquid phase at melting is one and the same). If there are many phases of different composition, all compounds, fully situated in the crystallization field of some compound, are metastable to the latter.


[‡] It was not the aim of this work to obtain all the hydrates because this is a separate and quite a complicated (although, as experience suggests,[1] a tractable) task.
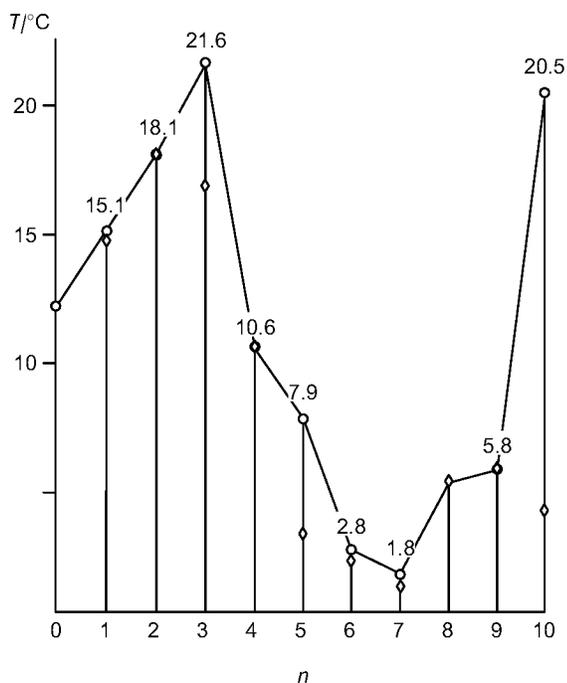
Figure 2 The dependence of the melting points of the most stable hydrates on the size of the anion hydrocarbon part (n). $\bigcirc$, our data, $\diamondsuit$, data from ref. 2.

Figure 3 The arrangement of carboxylate anions with $n = 3$ (1) and 4 (2) in the D-cavity.

12.4 °C) and $h_2 = 29.1$ (m.p. = 10.5 °C). The variety of compounds in the system might be due to several reasons. First, water can build a number of frameworks close in energy content. Therefore, the same guest can stabilize different framework structures under different conditions.[6] Second, the hydrophobic and hydrophilic parts of the anion can include in the framework in different ways which results in different clathrate numbers within one and the same water-anion framework. Besides, such complex guest molecules can undergo conformational changes, yielding hydrates of the same composition but of different stability within one and the same framework. All of these factors seem to be typical of TBA carboxylates and give rise to a great number of compounds.

Figure 2 shows the dependence of the melting temperature of the stable hydrates of TBA carboxylates on the length of the anion hydrocarbon chain for each of the systems (from $n = 0$ to $n = 10$). The figure shows that the stability of the hydrates first increases from formate ($n = 0$) to TBA butyrate ($n = 3$), then decreases to TBA caprylate ($n = 7$) after which it begins to increase once again and sharply rises at $n = 10$. Further, we will try to explain this in terms of the structure of the clathrates of TBA carboxylates. Formate includes in a hydrophilic way (i.e. it forms H-bonds with the adjacent water molecules) and forms a somewhat shorter polyhedron edge (2.3 Å) as compared with that of the idealized framework (2.8 Å).[7] That is why formate hydrate melts at much lower temperatures (11.8 °C) than the corresponding TBA hydroxide hydrate (27.4 °C)[8] in which the anion hydrophilic inclusion does not cause any additional distortion of the framework. The inclusion of the acetate methyl group in the vacant dodecahedral cavity D (hydrophobic inclusion) results in additional stabilization of the hydrate and an increase in its melting point. In TBA propionate and butyrate ($n = 2$ and 3) the anion hydrophobic part better corresponds to the dimension of the D-cavity (see Figure 3[§]), and the
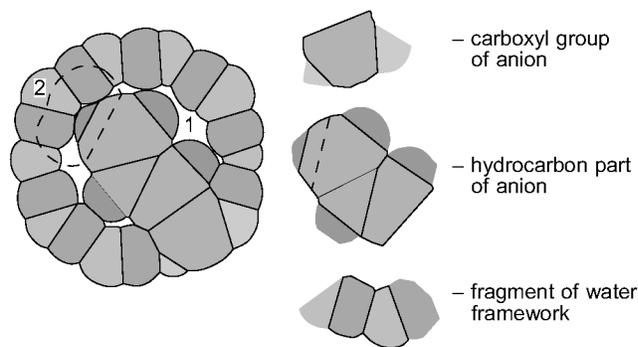
melting points of the hydrates are even higher (18.1 and 21.6 °C, respectively). The increase in the size of the anion hydrocarbon part causes the distortion of the D-cavity. In addition, at $n = 3$ the anion acquires the ability to stabilize the large cavities, which results in a different hydrate number within one and the same framework. The small cavities become vacant, and the hydrate stability decreases even if the complementarity of the anion and the large cavities is good (as is the case with valerate). On further increase of n the large cavities also become too small for these anions, and the hydrate melting point decreases to 1.8 °C at $n = 7$. An unexpected rise in the stability of the compounds with $n > 7$ suggests the formation of some other (possibly, not polyhedral) structures. Most likely, similar structures are also typical of the hydrates of polycarboxylates[9] and polyacrylates.[10] However, obtaining these hydrates and the study of their structure seem to be an even more complicated task.

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