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Diisoamyldibutylammonium Bromide Clathrate Hydrates

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Abstract — In the system i-Am_2Bu_2NBr–H_2O, along with the known compound i-$Am_2Bu_2NBr \cdot 38H_2O$, three new clathrate hydrates were revealed: i-$Am_2Bu_2NBr \cdot 32H_2O$, i-$Am_2Bu_2NBr \cdot 26H_2O$, and i-$Am_2Bu_2NBr \cdot 24H_2O$. Crystals of all the hydrates were isolated, and their compositions and melting points were determined.

The system i-Am_2Bu_2NBr–H_2O was studied previously, and a single 1 : 38 (salt : water) hydrate was revealed, congruently melting at 21.5°C [1]. Subsequently, clathrate hydrates of quaternary ammonium salts became subjects of active studies [2, 3]; it was found that, as a rule, the number of hydrates formed in any system is at least two, often three or four, and in some cases even up to ten (with tetrabutylammonium carboxylates [4, 5]). The compositions of the hydrates are often close, and these substances were considered previously as compounds of variable composition [6, 7]. However, thorough examination using various methods showed that the different stoichiometry is due to formation in the system of several discrete compounds of definite stoichiometries and different structures, rather than to formation of solid solutions of guest molecules in the host lattice. Therefore, the conclusion that only a single hydrate is formed in the i-Am_2Bu_2NBr–H_2O system seemed doubtful. On the one hand, this system can be an exception from the general trends [2, 3], but, on the other hand, data in [1] could be insufficient for revealing other hydrates. Therefore, we studied in this work the i-Am_2Bu_2NBr–H_2O system in more detail.

The system was studied by several methods. The melting diagram was studied by DTA, and at least three polyhydrates were revealed. They are manifested by two clearly defined peritectic lines and a maximum in the liquidus curve for the congruently melting compound. However, it is rather difficult to determine accurately the compositions and even the number of these compounds from the melting diagram. Therefore, we used the Schreinemakers method furnishing more accurate and reliable information for ternary systems. For this purpose, we studied the system i-Am_2Bu_2NBr–NH_4Br–H_2O at 16°C (Fig. 1; see table). We revealed three clathrate hydrates: 1 : 38, 1 : 32, 1 : 26, and 1 : 24. Each compound has its one

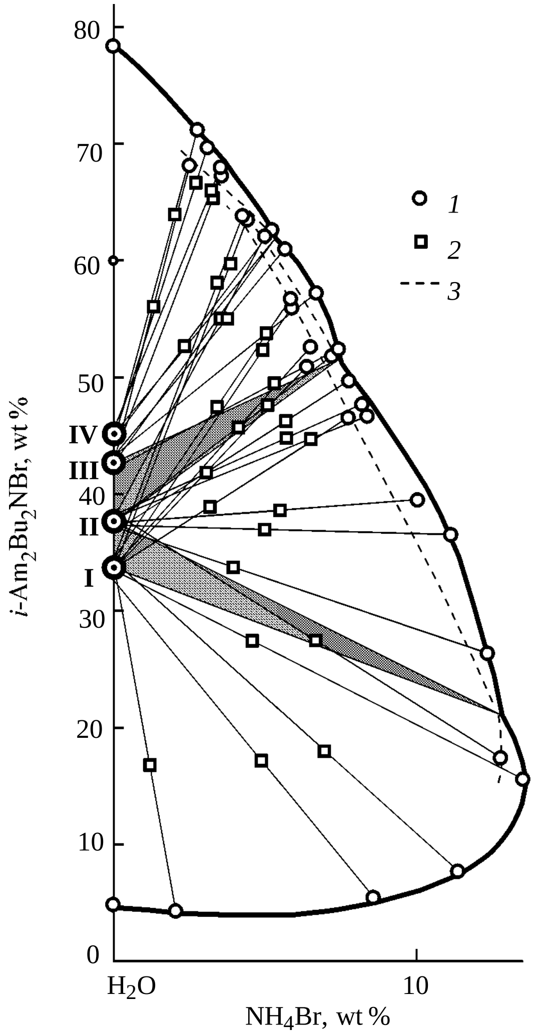

Fig. 1. Solubility isotherm (16°C) in the system i-Am_2Bu_2NBr–NH_4Br–H_2O in the range of crystallization of clathrate hydrates: (*1*) liquid phase, (*2*) wet residue, (*3*) solubility of phases in the metastable region, (**I**) i-$Am_2Bu_2NBr \cdot 38H_2O$, (**II**) i-$Am_2Bu_2NBr \cdot 32H_2O$, (**III**) i-$Am_2Bu_2NBr \cdot 26H_2O$, and (**IV**) i-$Am_2Bu_2NBr \cdot 24H_2O$. The three-phase regions are denoted by gray filling.

Solubility isotherm (16°C) in the system i-Am$_2$Bu$_2$NBr–NH$_4$Br–H$_2$O

Liquid phase, wt %		"Residue," wt %		Solid phase
i-Am$_2$Bu$_2$NBr	NH$_4$Br	i-Am$_2$Bu$_2$NBr	NH$_4$Br	
4.92	–	–	–	1:38
4.38	2.07	16.82	1.21	
5.53	8.59	17.21	4.90	
7.77	11.38	18.05	6.98	
15.65	13.53	27.48	4.59	
46.58[a]	7.76[a]	38.94	3.19	
50.93[a]	6.39[a]	41.90	3.08	
52.63[a]	6.51[a]	45.74	4.14	
55.98[a]	5.89[a]	52.36	4.95	
56.76[a]	5.86[a]	47.49	3.43	
63.53[a]	4.43[a]	59.72	3.87	
63.84[a]	4.27[a]	58.10	3.44	
17.48[a]	12.79[a]	27.49	6.69	1:32
26.42[a]	12.36	33.76	3.97	
36.57	11.15	37.00	5.01	
39.54	10.05	38.65	5.52	
46.71	8.39	44.76	6.53	
47.75	8.22	44.83	5.72	
49.74	7.78	46.28	5.71	
51.85[a]	7.22[a]	47.66	5.10	
62.11[a]	5.01[a]	55.04	3.55	
52.45	7.44	49.53	5.33	1:26
57.26	6.71	53.80	5.06	
61.01	5.67	55.03	3.77	
68.15[a]	2.52[a]	56.07	1.33	
62.65	5.24	52.70	2.35	1:24
67.27	3.58	65.37	3.30	
67.99	3.55	66.02	3.24	
69.70	3.11	66.65	2.73	
71.22	2.78	63.95	2.03	
78.40	–	–	–	

[a] Solubility of the hydrates in the metastable region.

stable crystallization field. For almost all fields, we were able to extend the solubility lines to the metastable regions, which allowed their better resolution.

The compositions of all the compounds were calculated according to [8] from the interception points of the Schreinemakers paths with the i-Am$_2$Bu$_2$NBr–H$_2$O side. They are as follows (H$_2$O : salt): 38.36 ± 0.27 (number of paths $n = 11$), 32.28 ± 0.23 ($n = 9$), 26.11 ± 0.30 ($n = 4$), and 24.19 ± 0.23 ($n = 5$).

The crystals of all polyhydrates were isolated from solutions with the compositions corresponding to the fields of their stability. Their hydrate numbers determined analytically (38.20, 32.25, 25.89, and 23.84, respectively) are consistent with the results obtained by the Schreinemakers method. The 1 : 38 hydrate crystallizes in the form of characteristic feathers, and the 1 : 32 hydrate, as tetragonal prisms. Crystals of the 1 : 26 and 1 : 24 hydrates were too fine to determine their habit (most probably, the crystals were isometric), but they clearly differed from those of the 1 : 38 and 1 : 32 hydrates. Crystals of the 1 : 38 and 1 : 32 hydrates readily grew from dilute binary solutions at room temperature (15–21°C). The 1 : 24

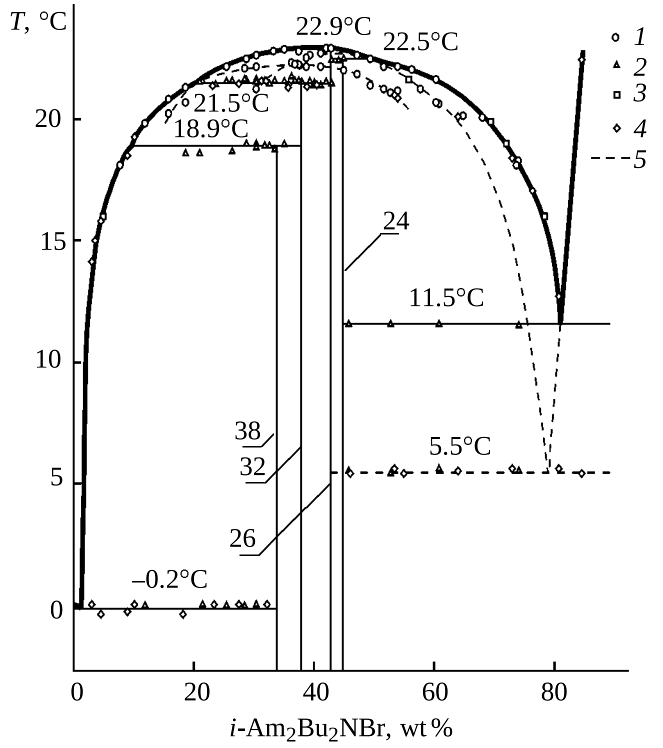

Fig. 2. Phase diagram of the binary system *i*-$Am_2Bu_2 \cdot NBr–H_2O$ in the region of crystallization of clathrate hydrates: (*1, 2*) points obtained in this work for the liquidus and solidus lines, respectively; (*3*) points obtained from the solubility data; (*4*) data of [1]; and (*5*) melting in the metastable region.

hydrate was obtained from concentrated solutions at 12–20°C. The 1 : 26 hydrate was isolated from the ternary system *i*-$Am_2Bu_2NBr–NH_4Br–H_2O$ at 16°C at the composition corresponding to the field of its stability (50–52% *i*-Am_2Bu_2NBr, 4–5% NH_4Br). Its melting point was determined visually in a capillary. The value obtained, ~22.9°C, is consistent with the melting diagram. The other compounds melt incongruently (i.e., in a range of temperatures), but, at least, the onset of melting of each hydrate is consistent with the peritectic lines in the melting diagram.

The whole set of data furnished by study of the ternary system, DTA, and preparative studies allowed us to construct the melting diagram shown in Fig. 2. Four polyhydrates crystallize in the system. Three of them melt incongruently: 1 : 38 (mp 18.9°C), 1 : 32 (mp 21.5°C), and 1 : 24 (mp 22.5°C), and one, congruently (1 : 26, mp 22.9°C). The liquidus lines of almost all the polyhydrates were extended to the metastable regions, which allowed their better resolution. Some points (Fig. 2) were obtained by the solubility method; as seen, they agree within the measurement error with the DTA data. In some cases, the equilibrium solid phase was isolated and analyzed; its composition corresponded to the liquidus line of the same hydrate in the phase diagram. As seen from Fig. 2, data obtained in [1] fall on one or another liquidus line obtained in this work. The relatively flat maximum at 21.5°C assigned in [1] to the 1 : 38 hydrate is more probably the peritectic line of the 1 : 32 hydrate. In an experiment on melting in a capillary of isolated crystals of the 1 : 32 hydrate, the onset of melting was obaerved at 21.5°C, and the end of melting, at about 22.9°C. For the 1 : 24 hydrate, the experimentally determined melting range was 22.5–22.9°C. From the side of concentrated solutions, we detected two eutectics: at 11.5°C (between the stable 1 : 24 hydrate and either the salt or a hydrate with a low hydrate number) and at 5.5°C in the metastable region (between the 1 : 26 hydrate and the salt). Thus, the detection of only one hydrate in [1] may be due the fact that the amount of *i*-Am_2Bu_2NBr available at that time was insufficient to study the system in more detail.

We have already mentioned that quaternary ammonium salts typically form several hydrates, which is due to the capability of water to form a number of structures of close energy; under varied conditions, the guest molecules preferably stabilize different host structures with fully occupied large voids, rather than gradually fill voids in the unchanged host structure; as shown in [9], the host structures formed in clathrates become thermodynamically unstable in the absence of guest molecules.

EXPERIMENTAL

Diisoamyldibutylammonium bromide was prepared in two stages.

(1) Isoamyldibutylamine was prepared from dibutylamine and isoamyl bromide in the presence of a copper catalyst. An equimolar mixture of reactants was placed in an ampule containing acetonitrile as solvent, sealed, and heated at 80–100°C for 35 h. The product was purified by distillation.

(2) The resulting tertiary amine was treated with isoamyl bromide in acetonitrile (Menshutkin reaction). The mixture was heated in a sealed ampule on a boiling water bath for 92 h. After distilling off the solvent, the product was recrystallized from ethyl acetate and three times from water in the form of a clathrate hydrate. The purified product was concentrated and dried in a desiccator over P_2O_5. The main substance content, 99.8 ± 0.2 wt %, was determined by potentiometric titration of the salt with a sodium tetraphenylborate solution using an ion-selective electrode [10].

The melting diagram was studied by DTA. The temperature reproducibility was ±0.05°C; the phase transition temperatures were determined with a ±0.2°C accuracy. The sample heating rate was 0.2 deg min^{-1}.

The ternary system was studied by the Schreinemakers method involving analysis of the liquid phase and wet residue after equilibration. The equilibrium was attained (with mechanical stirring) within a time from 3 h to 2 days (for concentrated solutions). The total content of bromide ions was determined by titration with a ~0.03 N $Hg(NO_3)_2$ solution, with diphenylcarbazone as indicator. Diisoamyldibutylammonium cation was determined as described above.

The crystals were isolated at 10–20°C by squeezing between filter paper sheets, and their composition and melting point (visually in a thin-walled capillary) were determined.

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