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Clathrate Formation in Tetraisopentylammonium Bromide–Water System

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Abstract — Three polyhydrates of tetraisopentylammonium bromide with 38, 32, and 26 water molecules and also the dihydrate were found in the *i*-Pent$_4$NBr–H$_2$O system.

The system tetraisopentylammonium bromide (*i*-Pent$_4$NBr)–water was previously studied by DTA [1]. A polyhydrate was revealed, melting at 30.5°C with decomposition into two liquid phases. Plate-like crystals of this hydrate were isolated, and their analysis gave the composition *i*-Pent$_4$NBr·(38.07 ± 0.16)H$_2$O. However, thorough studies made for tetraisopentylammonium fluoride [2] and chloride [3] showed the possibility of formation of three polyhydrates (1 : 38, 1 : 32, and 1 : 27) for both compounds. Therefore, there were all reasons to expect that *i*-Pent$_4$NBr forms more than one clathrate hydrate also. Furthermore, it is known [4, 5] that water can form a series of clathrate frameworks close in energy and often consisting of the same polyhedra. To gain a better insight into this problem, we performed a detailed study of the *i*-Pent$_4$NBr–H$_2$O system.

In the case of clathrate hydrates of quaternary ammonium salts, the fusibility curve mostly provides insufficient information on the number and composition of compounds formed; even more so for the system in hand characterized by the syntectic type of the curve. The Schreinemakers method [6] is more descriptive and reliable, allowing detection of all compounds formed in the system and exact determination of their composition. Therefore, in this work we used this method to study the ternary system *i*-Pent$_4$NBr–NH$_4$Br–H$_2$O at 15°C (see table and Fig. 1). In this system, we found the crystallization regions of three polyhydrates (1 : 38, 1 : 32, and 1 : 26) and dihydrate of tetraisopentylammonium bromide, anhydrous *i*-Pent$_4$NBr, and NH$_4$Br. We succeeded in separating the crystallization regions of the polyhydrates after we extended their solubility curve to the area where they are metastable. We determined the eutonic points between the 1 : 26 polyhydrate and dihydrate and also between the dihydrate and *i*-Pent$_4$NBr (see table). Determination of the eutonic point between *i*-Pent$_4$NBr and NH$_4$Br was facilitated by the fact that one of the solid phases (*i*-Pent$_4$NBr) appeared to be lighter than the equilibrium liquid phase, so that it floated, and the second solid phase (NH$_4$Br) remained under the solution. The hydrate numbers of the compounds were estimated as intersection points of Schreinemakers paths (*n*) with the *i*-Pent$_4$NBr–H$_2$O axis using a program described in [7]. As a result, we obtained the hydrate numbers 38.06 ± 0.35 (n = 4), 32.28 ± 0.21 (n = 11), 25.99 ± 0.21 (n = 6), and 1.91 ± 0.10 (n = 5).

Knowing the stability areas allowed isolation of all the compounds formed in the system. Their hydrate numbers and melting points are as follows: 38.26 ± 0.38 (number of runs m = 3, mp 28.3°C), 32.24 ± 0.25 (m = 5, mp 29.5°C), 26.02 ± 0.36 (m = 3, mp 30.3°C), and 1.95 ± 0.20 (m = 3). These data are well consistent with those obtained in studying the ternary system. Crystals of all the polyhydrates differ from each other. The compound 1 : 38 was isolated as plates or typical “feathers”; the hydrate 1 : 32, as tetragonal prisms; and the hydrate 1 : 26 crystallized as fine isometric crystals.

From the inflections in the liquidus, visual findings, and DTA data, we determined the melting points for all the compounds formed in the binary system *i*-Pent$_4$·NBr–H$_2$O, despite the fact that for polyhydrates the melting points are very close (Fig. 2).

The 1 : 38 and 1 : 32 compounds melt incongruently at 28.3 and 29.5°C, respectively. The 1 : 26 hydrate melts syntectically at 30.3°C. The dihydrate melts incongruently at 37.7°C. Compared to the results obtained in [1], thorough study of the system helped to find not one, but three polyhydrates; among them, as mentioned above, the hydrate 1 : 26 has the highest melting point. The liquidus of the 1 : 38 hydrate is somewhat distinguished: it is well consistent with the extension of the fusibility curve of the 1 : 32 hydrate towards the metastable region. It was observed that the 1 : 32 hydrate is readily realized in the metastable

Solubility isotherm (15°C) in the system i-Pent$_4$NBr–NH$_4$Br–H$_2$O

Liquid phase, wt%		Residue, wt%		Solid phase
i-Pent$_4$NBr	NH$_4$Br	i-Pent$_4$NBr	NH$_4$Br	
0.96	–	–	–	1:38
0.66	4.85	17.62	2.45	
0.54	7.70	17.69	3.98	
0.54	10.00	20.02	4.46	
0.55	15.25	12.46	10.08	
1.82[a]	6.36[a]	13.99	4.31	1:32
1.54[a]	10.75[a]	12.74	7.60	
1.58[a]	13.79[a]	17.24	8.09	
1.55	16.27	10.44	12.41	
1.50	16.70	4.50	15.25	
1.52	17.02	15.86	10.60	
1.64	17.52	16.34	10.89	
1.53	19.84	14.43	13.10	
2.42[a]	20.67[a]	17.23	12.35	
2.51[a]	21.27[a]	21.82	9.97	
4.55[a]	24.38[a]	17.25	15.62	
2.99[a]	17.40[a]	15.00	12.44	1:26
2.23	20.12	12.84	14.95	
0.75	22.30	25.03	9.85	
0.97	23.03	22.33	11.79	
2.37	24.45	20.05	14.40	
2.67	24.58	22.48	13.09	
3.93	25.19	50.89	10.31	1:26 + 1:2
3.86	25.31	55.36	10.45	1:2
1.91	29.65	43.69	15.76	
1.14	31.00	13.33	26.83	
1.01	33.79	58.03	12.61	
1.01	34.52	26.27	24.94	
1.22	35.47	21.54	27.80	1:2 + i-Pent$_4$NBr
0.87	36.59	15.96	31.02	i-Pent$_4$NBr
0.86	37.81	22.34	29.63	
0.82	39.61	20.02	31.90	
0.94	40.49	23.51 0.49	31.26 68.99	i-Pent$_4$NBr + NH$_4$Br
0.81	40.59	0.33	75.66	NH$_4$Br
0.59	40.71	0.29	70.87	
0.47	40.85	0.23	70.81	
–	41.10	–	–	

[a] Metastable phase.

region, and at room temperature (~20°C), we were able to obtain (in different weighing bottles) both the 1:32 hydrate and the 1:38 hydrate stable under these conditions.

It is interesting that a practically close region of phase separation is observed in the i-Pent$_4$NBr–H$_2$O system, which, in itself, is a rather rare phenomenon. Furthermore, the phase separation region is situated just over the clathrate hydrate crystallization areas, as in some other systems [8]. In such cases, one of possible reasons for the retrograde solubility of liquids is clathrate formation in the liquid phase [8]. The phase separation region was studied by the Alekseev's method [9] and also by the solubility method. As seen from Fig. 2, the results obtained by these methods are well consistent.

Finally, three polyhydrates and a dihydrate of tetraisopentylammonium bromide are formed in the system i-Pent$_4$NBr–H$_2$O. The 1:38 and 1:32 polyhydrates are typical of quaternary ammonium salts [5]. The 1:38 hydrates form rhombic structures, while 1:32 hydrates, tetragonal structures [5, 10]. The 1:26 hydrates are less abundant. For tetraisopentylammonium fluoride and chloride, the 1:27 hydrate was found, forming a tetragonal lattice with space group $I4_1/a$ (a = 16.89 Å, c = 17.11 Å) [2]. It is quite possible that the hydrate shell frameworks in 1:26 and 1:27 hydrates are quite similar, but it is not unlikely that these are two different clathrate structures.

The results obtained allow some conclusions about the effect of anions on clathrate formation in the series i-Pent$_4$NHlg–H$_2$O (Hlg = F, Cl, Br). All the three salts form the same number of polyhydrates, at least two of them having similar compositions (1:38 and 1:32) and structures. The relative stability of the hydrates slightly changes in the series. Comparison with similar series for tetrabutylammonium salts [3] shows that the effect of anions in the series i-Pent$_4$·NHlg–H$_2$O is considerably weaker, as demonstrated, for example, by data on the melting points. In the series i-Pent$_4$NHlg–H$_2$O, the melting points of hydrates change only slightly (32.4–34.6, 29.5–29.8, and 28.3–30.3°C for the fluoride, chloride, and bromide, respectively), while for tetrabutylammonium, the melting point decreases from 27.4 to 9.5°C on passing from the fluoride to the bromide. Presumably, this is due to the fact that bulkier tetraisopentylammonium cation exerts a stronger stabilizing effect on the cavities in the clathrate frameworks, so that the effect of anions is less pronounced on this background.

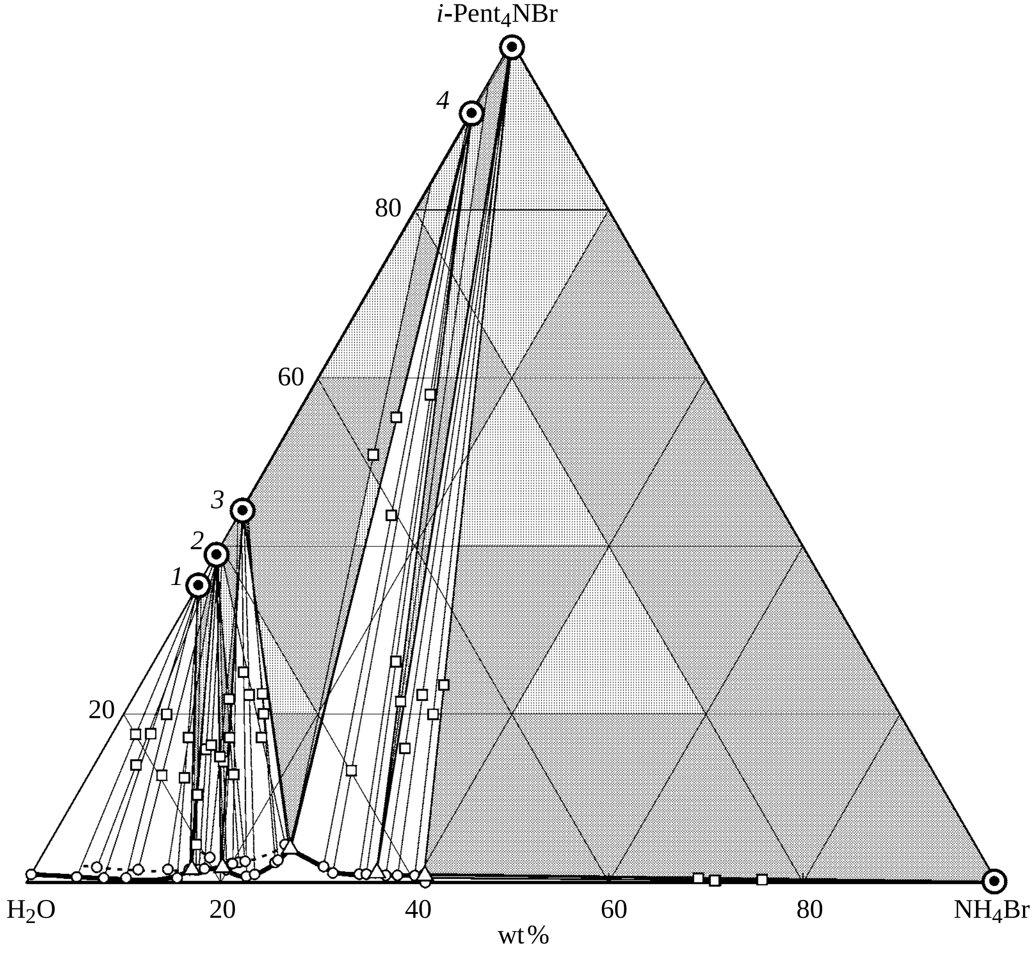

Fig. 1. Solubility isotherm (15°C) in the system *i*-$Pent_4NBr$–NH_4Br–H_2O (circles and squares refer to the liquid phase and wet residue, respectively. Dotted line shows the solubility of metastable phases). (*1*) *i*-$Pent_4NBr \cdot (38.06 \pm 0.35)H_2O$, (*2*) *i*-$Pent_4NBr \cdot (32.28 \pm 0.21)H_2O$, (*3*) *i*-$Pent_4NBr \cdot (25.99 \pm 0.21)H_2O$, and (*4*) *i*-$Pent_4NBr \cdot (1.91 \pm 0.10)H_2O$ (three-phase areas are cross-hatched; triangles refer to eutonic points).

EXPERIMENTAL

Tetraisopentylammonium bromide was synthesized by the Menshutkin's reaction [11]. Equivalent amounts of triisopentylamine and isopentyl bromide were refluxed for 28 h in acetonitrile. To prepare a clathrate hydrate, the product was recrystallized twice from ethyl acetate and then three times from water. Then the product was concentrated and dried in a desiccator over P_2O_5. The main substance content was determined by potentiometric titration with sodium tetraphenylborate [11] to be 99.8±0.2 wt%.

The fusibility curve was constructed using the DTA data from [1] and DTA and solubility data obtained in this work (these data are quite consistent). In solubility measurements, an oversaturated aqueous solution of a salt was kept for 4–7 h at various temperatures with stirring, and the salt concentration was determined as described above. In DTA experiments, the heating rate was 0.2 deg min^{-1} (the temperature was controlled to within 0.05°C). The phase separation region was studied by the solubility and Alekseev methods.

The ternary system was studied by the Schreinemakers method involving analysis of the liquid phase and wet residue after equilibration. The time required for establishment of the equilibrium (under mechanical stirring) was 4–6 h. The total bromide was determined by titration with ~0.03 N $Hg(NO_3)_2$ using diphenylcarbazone as an indicator. Tetraisopentylammonium was determined as described above.

Crystalline samples were isolated at 10–15°C by pressing between two sheets of filter paper. Then their

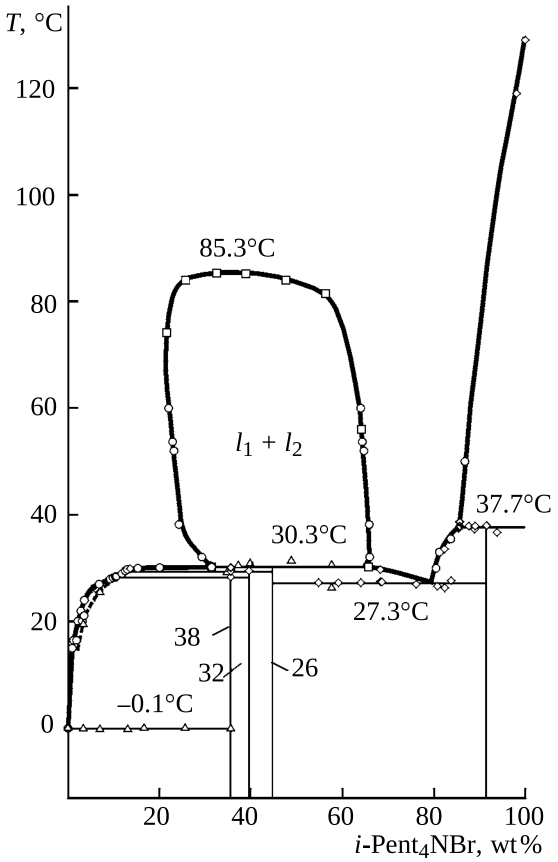

Fig. 2. Phase diagram of the system i-Pent$_4$NBr–H_2O. The numerals along the composition lines refer to the hydrate numbers; rhombs and triangles show DTA data obtained in this work and in [1]; circles and squares represent points obtained from the solubility data and by the Alekseev's method; and l_1 and l_2 are the liquids rich in water and organic phase, respectively.

elemental composition and melting point were determined (visually in a thin-wall capillary).

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