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Clathrate formation in the $Bu_4NCl–NH_4Cl–H_2O$ system

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Two new possible clatrate compounds have been found in the system $Bu_4NCl–NH_4Cl–H_2O$: $Bu_4NCl·37.7NH_4Cl$ and $Bu_4NCl·24H_2O$.

Recent studies[1] of the system $Bu_4NF–NH_4F–H_2O$ revealed that ammonium fluoride together with water molecules can participate in formation of clathrate frameworks, producing solid substitution solutions based on clathrate hydrates of composition $Bu_4NF·28.7H_2O$ and $Bu_4NF·32.3H_2O$. It should be noted that substitution (the ion pair NH_4^+ and F^- substitutes for two water molecules[2]) can be considerable and amount to ~70%. However, complete substitution is not possible in this case since in water frameworks the pentagon is the most common kind of polyhedral facet while an ion pair can obviously build a figure with an even number of vertices. The use of anhydrous tetrabutylammonium fluoride for use for the study of the binary system $NH_4F–Bu_4NF$ is complicated by the fact that concentration of its solutions (to ~80% and higher) results in its irreversible decomposition. It is not easy to observe anhydrous fluoride ammonium and tetrabutylammonium (TBA) compounds in a ternary system, even if they do exist there, because the range of their likely crystallization is overlapped by solid solutions penetrating deep into the systems. Therefore, in an attempt to obtain a compound of this kind we had to use a system where solid solutions do not form, *e.g.*, the system $Bu_4NBr–NH_4Br–H_2O$ at 0 °C studied earlier,[3] where in addition to clathrate hydrates we found the compound $Bu_4NBr·19NH_4Br$, the composition of which provides indirect evidence for its clathrate nature. This is an interesting fact since clathrates with similar kind of hosts had never been found before. We studied a system with chloride anion, which is located between F^- and Br^-. For this purpose we examined the solubility isotherm at 8 °C of the system $Bu_4NCl–NH_4Cl–H_2O$.

Tetrabutylammonium chloride synthesis was carried out by neutralization of TBA hydroxide with hydrochloric acid. The resulting product was recrystallized three times in the form of a clathrate hydrate. The three-component system was studied by Schreinemaker's technique, *i.e.* by analysis of the liquid phase and moist residue after equilibrium was established. The time taken for establishment of equilibrium (with mechanical stirring) varied from 2 h to 2 days (for concentrated

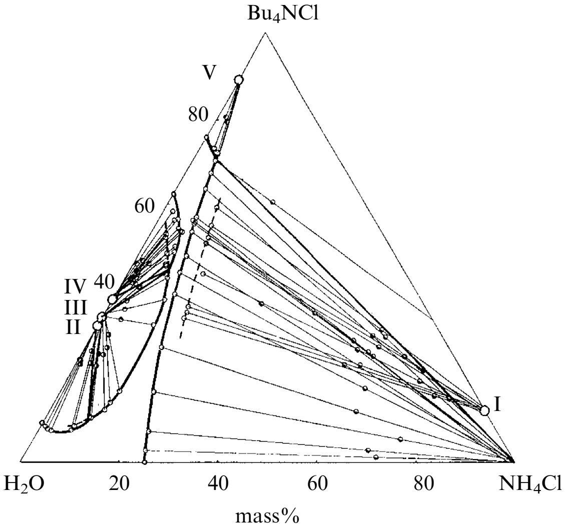

Figure 1 Solubility isotherm (8 °C) in the system Bu$_4$NCl–NH$_4$Cl–H$_2$O. ○, liquid phase; ◐, moist residual. I — Bu$_4$NCl·(37.66±0.65) NH$_4$Cl, II — Bu$_4$NCl·(32.21±0.28) H$_2$O, III — Bu$_4$NCl·(29.40±0.29) H$_2$O, IV — Bu$_4$NCl·(24.11±0.16) H$_2$O, V — Bu$_4$NCl·2H$_2$O.

solutions). The total amount of chloride anion was determined by titration with Hg(NO$_3$)$_2$ (15 mM); diphenyl carbazone was used as indicator. TBA ion was titrated with sodium tetraphenylborate (2 mM), using an ion selective indicator electrode.[4]

The results are presented in Figure 1. It is obvious from the figure that in this case, as in the case of the bromide system, a compound forms between TBA and ammonium chlorides. The compound is metastable over the whole crystallization field. The solubility curves of ammonium chloride and the above compound differ appreciably. Calculation of the compound composition, following a program that takes account of the intersection of Schreinemaker's rays with each other,[5] showed the compound to be binary (deviation along the axis $x = 0.26$ mass%). On this basis we calculated the composition of the compound Bu$_4$NCl (37.66 ± 0.65)NH$_4$Cl from intersection of Schreinemaker's rays and the axis of the binary system NH$_4$Cl–Bu$_4$NCl, using a program[6] that takes into consideration the statistical weight of each ray. The composition of the compound under study differs from that of the bromide system. However, the stoichiometry of the compound in this system also suggests that the compound is of clathrate nature. This is not improbable since the ionic pair NH$_4^+$ and X$^-$ (X = halogen), similar to a water molecule, is of tetrahedral coordination. As for water, we know, for instance,[7] that small deviations from tetrahedral angle and along the H-bond result in a variety of clathrate structures. However, as noted above, in water clathrate frameworks the facets of the polyhedra are usually pentagons and deviations from the tetrahedral angles are large (since, as indicated above, facets should have an even number of vertices), and formation of structures like these in terms of energy (although less probable) is not excluded altogether. Thus, there are water frameworks the cavities of which are cubic octahedrons with square and hexagonal facets,[8] and they can also be built of NH$_4$X molecules.

Thus, we have shown that formation of compounds of ammonium halides (although metastable) with the corresponding TBA halides (most likely to be of clathrate nature) where ammonium halides act as hosts is possible. However, the crystallization field of the compounds involved is completely overlapped by that of NH$_4$X, *i.e.* they are metastable with respect to NH$_4$X over the whole range studied.

When studying hydrate formation in this system we have found one more polyhydrate with composition

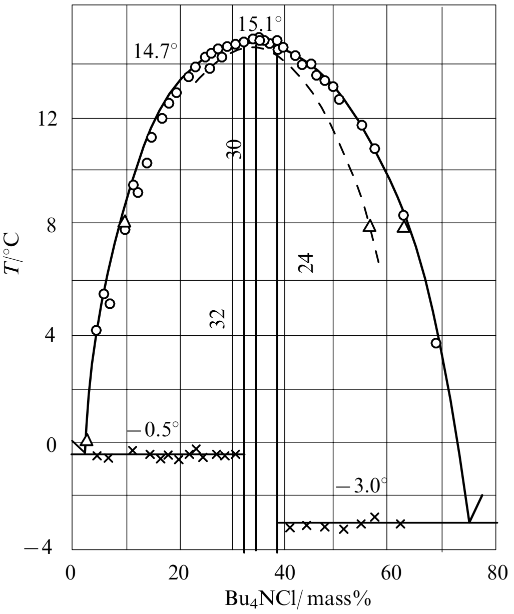

Figure 2 Phase diagram of the binary system Bu$_4$NCl–H$_2$O in the crystallization field of clathrate hydrates. Integral values of the hydrate numbers are presented along the axes. ○, points obtained for fusibility; △, points obtained for solubility; - - -, melting of metastable phases.

Bu$_4$NCl·24.1H$_2$O, unknown previously, in addition to two hydrates of composition Bu$_4$NCl·32.1H$_2$O and Bu$_4$NCl·29.8H$_2$O observed earlier.[9] Therefore, the diagram of the binary system chloride TBA–melting water[9] is now as shown in Figure 2. The similar melting points of the hydrates 1 : 24 (15.1 °C) and 1 : 30 (15.1 °C) hinder determination of their melting type. It is obvious that one of them (perhaps both) melts congruently. The fact that this compound had not been observed before might be explained by the differentiating action of the third component that affects the rate of formation of one or another compound. As for the metastable phase, its conversion (after it has been formed) to a stable one sometimes takes several days or even months.[10] The effect of the third component is shown markedly by the example of the system Bu$_4$NBr–H$_2$O–S (S is the third component),[3] where, depending on S and temperature, one or other of the four hydrates forming in the binary system Bu$_4$NBr–H$_2$O can be observed.[11] In this work ammonium chloride was used as the third component, whereas in the system mentioned earlier acetic acid and butylamine were used. This resulted in discovery of a polyhydrate that had not previously been observed in the this system (a hydrate of the same composition was observed in the system Bu$_4$NBr–H$_2$O[11]). We have obtained crystals of this compound, determined their composition (Bu$_4$NCl·24.22H$_2$O) which is in good agreement with that obtained by Schreinemaker's technique (see Figure 1), their density (1.039±0.002 g cm^{-3}) and melting points (15.1 °C). The most readily crystallizing hydrate in this system is that of composition 1 : 30. We managed to obtain it repeatedly even in the concentration range where it is metastable, both from hydrates 1 : 32 and 1 : 24.

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