CLATHRATE FORMATION IN WATER–TETRAALKYL AMMONIUM IODIDE SYSTEMS AT HIGH PRESSURE

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ABSTRACT. The phase diagrams of aqueous binary systems with $PrBu_3NI(I)$, $Bu_4NI(II)$, $i-AmBu_3NI(III)$ and $i-Am_4NI(IV)$ were studied at atmospheric and high pressures by DTA method. In systems $III-H_2O$ and $IV-H_2O$ at atmospheric pressure we observed polyhydrates melting incongruently at 7.1 and 14.7°, correspondingly. In systems $I-H_2O$ and $II-H_2O$ hydrates form at higher pressure only, there are $PrBu_3NI$ $(15-25)H_2O$ at $P \geq 0.13$ kbar, Bu_4NI $(25-35)H_2O$ at $P \geq 0.4$ kbar. In water systems with II-IV at pressure 1.2, 1.4 and 0.26 kbar correspondingly polyhydrates with smaller hydrate number form. Formation of hydrates in solution in the $II-H_2O$ system does not occur at pressure greater than 7 kbar. The summarized P, T, X-phase diagram is discussed.

1. INTRODUCTION

The analysis of the thermal stability of clathrate polyhydrates in the tetrabutylammonium (Bu_4N) halogenide series has led us to believe that Bu_4NI clathrate hydrate must melt at positive temperatures /1/. This hydrate does not reveal itself, because the Bu_4NI crystal structure is stronger than that of other halogenides. This and a low hydration ability of the iodide ion are responsible for the low Bu_4NI solubility. In other words, the crystallization field of the salt itself overlaps that part of the phase diagram in which the crystallization field of the polyhydrate might be expected. A similar comparison /2/ of the thermal stability of the polyhydrates of $PrBu_3N$, $i-AmBu_3N$ and $i-Am_4N$ halogenides has also revealed that the greater the cation ability to stabilize the water framework the weaker the dependence of polyhydrate thermal stability upon the anion nature: $i-Am_4N$ fluoride, chloride, bromide hydrates have practically the same melting points and there is no reason to believe that the melting point of iodide hydrate (hydrates) would differ greatly, if it could melt congruently.

All this has caused us to believe that peralkylammonium iodides either form hydrates at the atmospheric pressure and they should be searched for more thoroughly, or, even if they are metastable, this metastabi-

lity is not great and the conditions can be met under which they can become stable.

For the hydrate formers (cations) considered that typical polyhydrate structures are pressure stabilized structures /3/. Ice is known to be destabilized by pressure up to 2 kbar, so under pressure its crystallization field decreases allowing place for the crystallization field of polyhydrates. The pressure effect up to 2-5 kbar on the crystallization field of salts must be weaker than in the case of hydrates and ice. Therefore, using pressure we meant to obtain stable hydrates of the iodides concerned.

2. REAGENTS AND EXPERIMENTAL

The synthesis and purification of peralkylammonium iodides are described in /4/. The minimum content of the basic substance in the salts was not less than 99.5%. The analysis of the salts was carried out by potentiometric titration of tetraphenyl borate with a cation-selective indicator electrode /5/. The P,T-curves were determined by DTA technique in high pressure cells described in /2,6/. In the $PrBu_3NI-H_2O$ system thin wall pressure-transmitting teflon ampoules with a capacity of 0.12 ml were filled with the solution of the appropriate composition at 35^oC (see the phase diagram, fig.1). In the rest of the systems the homogeneous solution with the appropriate composition cannot be obtained under the conditions convenient for carrying out work, that is why the ampoule was filled with the paste prepared of water and fine salt powder.

Exfoliation under pressure was studied using glass fiber light conductor introduced into the high pressure region as described in /6/.

3. RESULTS

Phase diagrams of the systems under consideration at   atmospheric pressure based on data /4,7/ taking into account the results obtained in the present work are given in figure 1. Incongruently melting hydrates $i-AmBu_3NI\cdot(30\pm5)H_2O$ (7.1^oC) and $i-Am_4BI\cdot(36\pm3)H_2O$ (14.7^oC*) form in the last two systems. In the $PrBu_3NI-H_2O$ system the retrograde salt solubility in the temperature range $0-8^oC$ and the existence of the low critical solvation temperature (LCST) /6/, are indicative of the conditions close to those necessary for clathrate formation. It is noteworthy that this is the only water-salt system with a closed exfoliation region we know, its temperature range being one of the smallest (LCST = 58.8^oC; UCST = 68.4^oC). The Bu_4NI-H_2O system is monotectic.

Figure 2 shows a fragment of the P,T-diagram of the $PrBu_3NI-H_2O$ system. If crystallization is carried out at   atmospheric pressure, curve 3 corresponding to the incongruent melting (with the decomposition into salt and solution) of the $PrBu_3NI\cdot mH_2O$ hydrate versus pressure is obtained.

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* The hydrate has been obtained. At 0^oC ρ = 1.0099 g/cm^3. It is orthorhombic. Fmmm, a=12.1(1), b=21.6(2), c=49.9(5). According to data /7/ it melts incongruently at 13.3^oC.
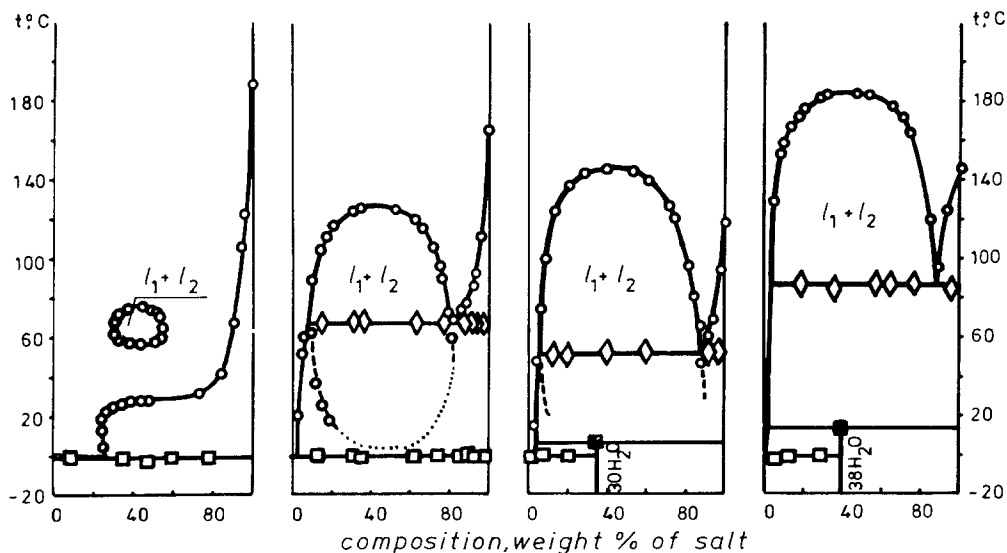
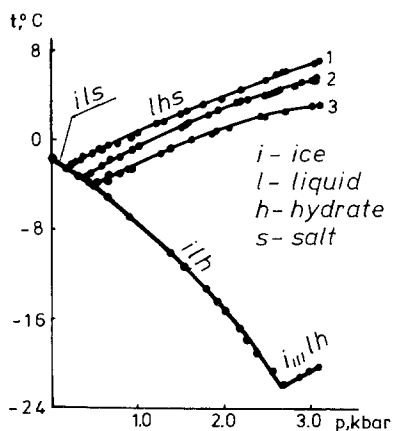Figure 1. Phase diagrams of the tetraalkyl ammonium iodide – water systems at atmospheric pressure.

Figure 2. Fragment of P,T–phase diagram of the $PrBu_3NI-H_2O$ system.

The value of m found to be 15–25 was determined considering the presence or absence of heat melting effects of water eutectics. To determine the hydrate composition accurately by constructing Tamman's triangle was not possible, because it was difficult to make clathrate formation reaction go to completion.

Thus, with this type of reaction, clathrate formation begins at 0.5 kbar. However, if the samples were exposed to pressure of 1.5–2.4 kbar for 1-2 hours at $-15\div-20^{\circ}C$, the warming curves showed effects at temperatures described by curves 1 and 2. More stable hydrates (with the compo-

sition within the same limits) or polyamorphous modifications are likely
to form under these conditions. The most stable of them (curve 1) has a
stable crystallization field already at P ≥ 0.13 kbar.

    Interesting is the behaviour of the exfoliation region (fig.3). As
follows from the supposition that LCST results from the destruction of
clathratelike structures in the liquid phase /4/, first it increases
with pressure up to $63.2^{\circ}C$ at 0.36 kbar, then it decreases to $42.4^{\circ}C$ at
2.45 kbar. UCST monotonously increases up to $130^{\circ}C$ at 2.45 kbar. The com-
position of LCST changes so that it becomes richer in water.

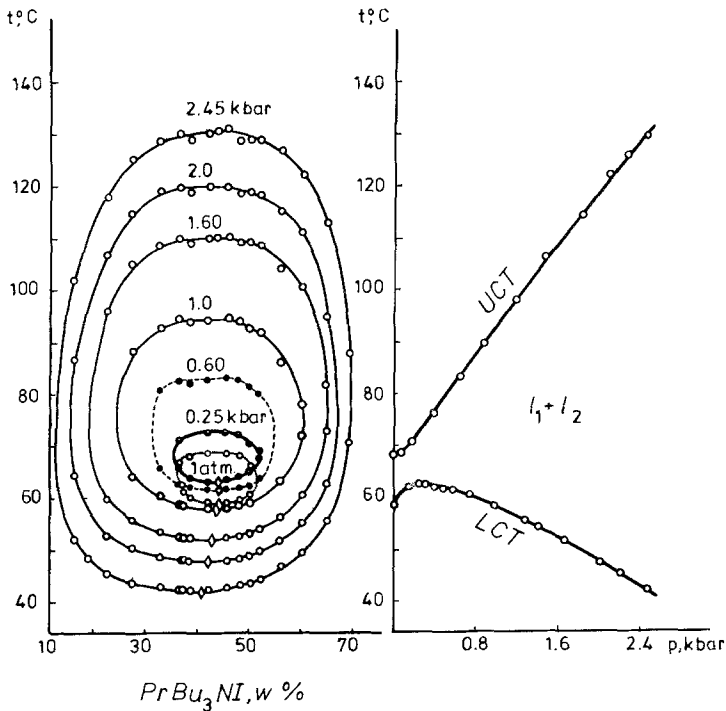Figure 3.   The exfoliation in the $PrBu_3NI-H_2O$ system under pressure.

    The Bu_4NI-H_2O system in which no hydrates have been discovered at
atmospheric pressure has been studied at pressures up to 9 kbar. At
P = 0.4 kbar (fig.4) hydrate h_1 forms whose composition 1:(25-35) was
determined as in the previous case. At P = 1.2 kbar one more hydrate h_2
with a smaller hydrate number forms which is evident due to the appear-
ance of water eutectics, when pressure exceeds the transition pressure.
At P = 7 kbar, which is not shown in the figure, no clathrate formation
occurs in the system, at least, from the solution.

    The $i-AmBu_3NI-H_2O$ system is shown in figure 4. In this system two
hydrates form as in the previous case. One of them with the composition
1:(25-35) is stable both at high and at   atmospheric pressure at tem-
peratures up to $+7.1^{\circ}C$ at which it melts incongruently to give salt and
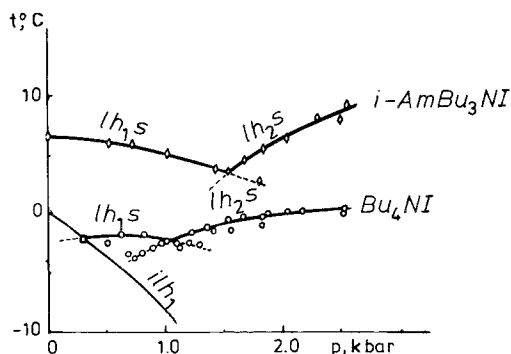
Figure 4. Fragment of the P,T-phase diagrams of the Bu_4NI-H_2O and $i-AmBu_3NI-H_2O$ systems.

solution (fig.1). The formation of the hydrate requires some supercooling. This seems to be the reason why we have not found it earlier while studying the $i-AmBu_3NI-H_2O$ system /4/. With increasing pressure the hydrate incongruent melting point decreases slightly (see fig.4). At P $\geq$ 1.4 kbar the second hydrate with a smaller hydrate number forms. This hydrate has a positive value of dt/dP. It should be noted that the analogous picture (but for the congruent melting of hydrates) was also observed in the $i-AmBu_3NBr-H_2O$ system /8/. This shows that the formation of the salt during the clathrate decomposition into a separate phase and its behaviour at high pressure do not determine the behaviour of the system under pressure. The latter mainly depends on the structure and the specific volume of clathrate phases determined by the structure.

In the $i-Am_4NI-H_2O$ system (fig.5) clathrate formation is rapid and occurs at   atmospheric pressure /7,8/. For this reaction dt/dP =4.5 $^{\circ}$C/kbar (1 atm). At 0.26 kbar one more hydrate (h_2) forms with a smaller hydrate number, which is shown by the appearance of the melting effects of water eutectics in the samples in which the salt content slightly exceeds that in the low pressure hydrate. We have managed to identify not only the incongruent melting lines of the hydrates, but also the monovariant equilibrium $h_1+h_2 = L$ line. The heat effect of this transition is negligible and it is approximately 100-200 times weaker than that of incongruent melting. The attempt to obtain the equilibrium $h_2+h_1 = S$ line by DTA technique was a failure. In figure 5 it is schematically depicted by a dashed line in the region allowed by the Schreinemakers rule /9/.

4. DISCUSSION

On the basis of the results obtained clathrate formation evolution in the water—iodides binary systems can be represented by the summarized P,T,X-diagram, whose P,T-projection and a number of characteristic isobaric sections are shown in figure 6.

First we will describe the case where at   atmospheric or close to atmospheric pressure (P_1 in fig.6) the hydrate is metastable with
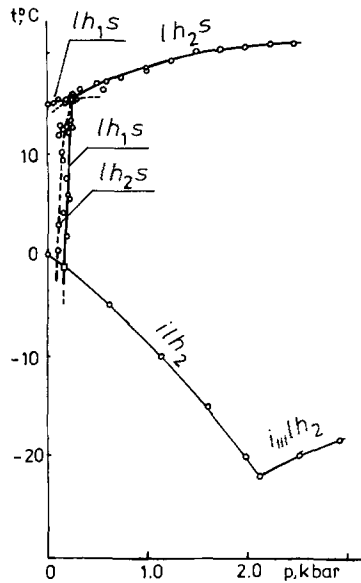
Figure 5.   P,T-phase diagram of the   i-Am$_4$NI-H$_2$O system.

respect to both crystal salt and ice when the composition of mixtures
is similar to that of clathrates, but the difference in the energy state
of these phases is not great. Since with increasing pressure the melting
point of ice Ih decreases, and the melting point of some clathrate poly-
hydrates generally increases /3/ (sometimes it can decrease but much
more slowly than that of ice Ih)at certain pressures the hydrate becomes
more stable than ice (P$_2$, fig.6). Further pressure increase results in
the hydrate h$_1$ crystallization field overlapping the limits of that of
ice and salt (P$_4$, fig.6) via nonvariant state at P$_3$*. Hydrate h$_1$ has
upper and low stability limits drawing nearer under pressure (P$_5$* and P$_6$)
and at P$_7$* it ceases to exist. Hydrate h$_2$ that appeared at comparative-
ly low pressures (curve 7 on the P,T-projection) at this pressure begins
to coexist with a liquid phase until it reaches the nonvariant state at
P$_9$, where ice, stabilizing more rapidly under pressure (according to the
scheme ice VI) depresses the crystallization field of hydrate h$_2$.
      All types of diagrams in figure 6 have been obtained at the atmosphe-
ric pressure with iodides whose cations possess different ability to sta-
bilize water-anion framework. The PrBu$_3$NI-H$_2$O system at the atmospheric
pressure with the hydrate whose melting is depicted by curve 3 in fi-
gure 2 can be attributed to the type at P$_1$ shown in figure 6. The cation
of this salt (of all the salts considered) has the least ability to form
clathrates. However, when with a stable hydrate (see fig.2, curve 1)
this system just as Bu$_4$NI-H$_2$O belongs to the type shown in figure 6 at
P$_2$. The i-AmBu$_3$NI-H$_2$O and i-Am$_4$NI-H$_2$O systems belong to the type at P$_4$.
      The probability of discovering the nonvariant state depicted by the
isobar at P$_3$ in figure 6 at the atmospheric pressure is insignificant
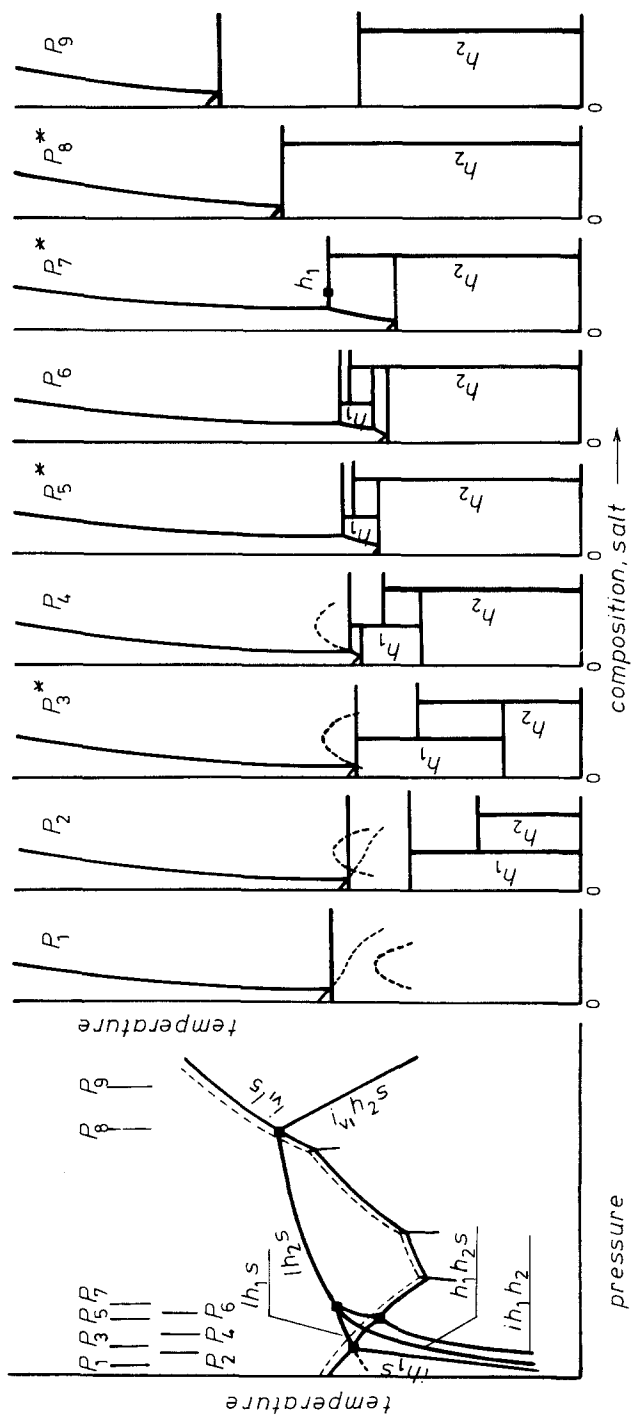both because of a small probability of the appearance of such type of a

Figure 6.   The summarized P,T,X-phase diagram of the tetraalkyl ammonium iodide – water system.

diagram at   atmospheric pressure and considerable difficulties in the
interpretation of the experimental data if they are obtained at one pres-
sure only.

The P_{10} type of isobar via P_9 is discovered in the Bu_4NI-H_2O system
at $P > 7$ kbar.

ACKNOWLEDGMENT

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