# CLATHRATE FORMATION IN WATER-PERALKYLONIUM SALTS SYSTEMS

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ABSTRACT. We discuss composition, stoichiometry and stability (phase diagrams) of peralkylonium salts and analogues ($Alk_3XO$, where X=N,P,As) polyhydrates depending on the dimensions and the configuration of the hydrophobic part of a guest-molecule and its ability to interact in a hydrophilic way with the framework.

## 1. INTRODUCTION

Clathrate nature of peralkylonium salts polyhydrates, which have been discovered [1], is described in a series of Jeffrey's and McMullan's papers (beginning with paper [2]). They have been perfectly well summarized in articles [3,4]. In contrast to gas hydrates, in this case the cation is the guest situated in the framework cavities and separated from the host molecules by the distance not less than the sum of Van der Waals radii (hydrophobic inclusion ). A simple anion of a halogenide type displaces the water molecule in the framework, forming H-bonds together with the neighbouring molecules (hydrophilic inclusion ), causing the framework to become of water-anion type. The anion with a hydrophobic part (e.g., benzoate) includes in a hydrophilic way with the polar group, forming the framework knot or edge, the hydrocarbon part being situated in one of the framework cages. (Alkylamines include in a similar way, which made Jeffrey call their hydrates "semiclathrates" [4 ]). Of all the peralkylonium salts only well soluble butyl- and isoamylonium salts have been found [1,2 ] to form polyhydrates, and from Jeffrey's and coworkers' articles it follows that hydrates with tetragonal structure and composition 1:32 per cation are characteristic of the tetrabutylammonium (TBA) series (Table I), and hydrates 1:38 with orthorhombic symmetry formed on the basis of a hexagonal framework - of tetraisoamylammonium (TIAA) salts. However, polyhydrates of other structures have been found, which suggested the insufficiency of the preparation technique and the necessity to study phase diagrams. Here we will discuss some aspects of structure, based on Jeffrey's papers and supplemented by more recent facts, and some aspects of polyhydrate stoichiometry and stability (phase diagrams of hydrate former - water systems), depending on the molecule geometry and hydrophility.

## 2. BRIEF STRUCTURAL INFORMATION, STOICHIOMETRY AND THE NUMBER OF HYDRATES

In Table I we present some information on idealized frameworks, determined from the data on the known structures of gas, peralkylonium salts and tributylphosphine oxide hydrates. The hydrate number can be determined using the data of this Table and taking into account the nature of the guests concerned by Jeffrey's formula [3]

$$h = [V - (CZ + nZ)]/Z, \tag{1}$$

where $V$ is the number of water molecules in the idealized framework unit cell, $C$ is the anion charge, $Z$ is the number of the guest molecules in the cell, $n$ is the number of water molecules, forced out from the framework by a single anion.

TABLE I. Idealized water frameworks (based on [3,5,6])

| The cell type, spacial group | The number and the type of the cages* | Parameters, Å, density ($\rho$), g/cm$^3$ | Examples of hydrates | References |
|---|---|---|---|---|
| Cubic I (CS-I) Pm3n V**=46 | 2D 6T | a=12 $\rho$=0.791 | $H_2S \cdot 6H_2O$ cyclo-$C_3H_6 \cdot 7.8H_2O$ $Bu_3SF \cdot 20H_2O$ $Bu_4NF \cdot 28.6H_2O$ $Bu_4NC_3H_7CO_2 \cdot 31.5H_2O$ | 7 7 3,8 9 10 |
| Cubic II (CS-II) Fd3m  V=136 | 16D 8H | a=17.3 $\rho$=0.785 | $SF_6 \cdot 17H_2O$ | 7 |
| Hexagonal (HS) P6/mmm V=40 | 3D 2T 2P | a=12.4 c=12.5 $\rho$=0.718 | $Br_2 \cdot 10H_2O$ (?) i-$Am_4NF \cdot 38H_2O$ | 11 2,3 |
| Tetragonal I (TS-I) P4$_2$/mnm V=172 | 10D 16T 4P | a=23.5 c=12.3 $\rho$=0.756 | $Br_2 \cdot 8.6H_2O$ $Bu_4NF \cdot 32.8H_2O$ | 11,12 2,13 |
| Tetragonal II (TS-II) I4/mcm V=68 | 4d 8P | a=15.4 c=12.0 $\rho$=0.709 | i-$Am_4PBr \cdot 32H_2O$ | 5 |
| Orthorhombic (RS) Pbam V=148 | 14D 4T 4P 4H | a=23.5 b=19.9 c=12.1 $\rho$=0.782 | $Br_2 \cdot 12H_2O$ (?) $Bu_3PO \cdot 34.5H_2O$ | 11 6 |

*) In Jeffrey's terms [3] D,T,P,H are the cavities-polyhedra: pentagondodecahedron ($5^{12}$), 14-($5^{12}6^2$), 15-($5^{12}6^3$) and 16-hedra($5^{12}6^4$), respectively, d - decahedron ($4^25^8$, i.e. 2 square faces and 8 pentagonal faces).
**) V - the number of vertices.

Due to its tetrahedral coordination water can form a number of frameworks of similar energies, only some of them being known now (Table I). Of these structures the most stable are those whose size, shape and cage arrangement correspond to the guest molecule size and configuration best of all. The gas hydrates CS-I and CS-II series and TS and RS series for TBA and TIAA salts illustrate this. However, the difference in the big cages (T,P,H, see Table I) dimensions and their ability to "breathe" from structure to structure allows one and the same guest to form hydrates with different structures depending on the equilibrium conditions. The $Bu_4NBr-H_2O$ system can illustrate this (Table II, Fig. 6).

TABLE II. Some properties of tetraalkylonium salts and tributylphosphine oxide polyhydrates, whose phase diagrams have been studied[*].

| Hydrate | Melting point, (°C) and melting type | $\rho$, $\frac{g}{cm^3}$ | Cell type and diffr. class | Unit cells parameters, Å | Z | References |
|---|---|---|---|---|---|---|
| $Bu_4NF \cdot 28.6H_2O$ | 27.4k | 1.057 | Im3m | a=24.4 | 12 | 9 |
| $Bu_4NF \cdot 32.3H_2O$[**] | 27.2i | 1.035 | P4/m | a=23.5;c=12.3 | 5 | 2,9,13 |
| $Bu_4NCl \cdot 29.7H_2O$ | 15.0k | 1.034 | - | - | | 15 |
| $Bu_4NCl \cdot 32.1H_2O$ | 14.7i | 1.029 | P4/m | a=23.8;c=12.6 | 5 | 2,15 |
| $Bu_4NBr \cdot 24H_2O$ | 12.4k | 1.123 | C2/m | a=28.5;b=16.9 c=16.5;ß=125° | 6 | 15,16 |
| $Bu_4NBr \cdot 26H_2O$ | 12.2[***] | 1.094 | P4/mmm | a=23.9;c=50.8 | 24 | 15,16 |
| $Bu_4NBr \cdot 32H_2O$ | 11.6i | 1.082 | P4/m | a=33.4;c=12.7 | 10 | 15,16 |
| $Bu_4NBr \cdot 36H_2O$ | 9.5i | 1.028 | Pmmm | a=21.3;b=12.9 c=12.1 | 2 | 15,16 |
| $Bu_4NOH \cdot 28.3H_2O$ | 27.4k | 1.063 | Im3m | a=24.6 | 12 | 15 |
| $Bu_4NOH \cdot 32.3H_2O$ | 19.0i | 1.046 | P4/m | a=23.6;c=12.6 | 5 | 15 |
| $Bu_4NNO_3 \cdot 26H_2O$ | 5.4k | 1.051 | P4/mmm | a=23.3;c=13.2 | 6 | 17 |
| $Bu_4NNO_3 \cdot 31.8H_2O$ | 4.8m | 1.039 | P4/m | a=23.5;c=12.5 | 5 | 17 |
| $i-Am_4PBr \cdot 32H_2O$[**] | 30.0s | 1.069 | P$\bar{4}$ | a=15.4;c=12.0 | 2 | 5 |
| $i-Am_4NI \cdot 38H_2O$ | 14.7i | 1.099 | Fmmm | a=12.1;b=21.6 c=49.9 | 8 | 18 |
| $Bu_3PO \cdot 34.5H_2O$[**] | 7.1k | 0.968 | P2_12_12 | a=23.5;b=19.9 c=12.1 | 4 | 6 |

*) Analogous information on TBA carboxylate and dicarboxylate polyhydrates is presented in this issue, p. 259.
**) The structures are completely described [5,6,13].
***) The hydrate might have no stable crystallization range.
k - congruent melting, i - incongruent melting, m - metastable hydrate, s - melting into two liquid phases.

With the increase of the guest content in the equilibrium solution the increase of its quantity in the solid phase occurs, if at all, in a step-wise fashion due to the building of a new framework rather than at the expense of the increase of the cage's filling degree in the same framework.

Experimental results [9,11,14,16], obtained after article [3] had appeared, confirm the conclusion about hydrate structures stability only in the case, where the big (T,P,H) cavities are completely occupied. This all the more concerns the combined cavities. Thus, we can draw a conclusion of the clathrate frameworks lability (dynamic instability) rather than of their metastability in the absence of the guest.

## 3.   THE GUEST HYDROPHOBIC PART:DIMENSIONS AND CONFIGURATION EFFECT

The claims for the molecule hydrate former hydrophobic part dimensions and configuration are quite evident: they must fit the most advantageous framework structures, which can be built of water molecules together with an anion (or the guest-molecule hydrophilic part). The structure, containing D,T,P and H cavities are the most advantageous (Table I). The molecules hydrate formers involved occupy the combined (of all the simple mentioned) cavities, therefore it is important that the hydrocarbon radicals arrangement should be in accordance with that of the simple cavities in the structure.

In accordance with the hydrocarbon radicals arrangement in the T cavity (Fig.1) in the series of the systems $RBu_3NBr-H_2O$ [19,20] the change of polyhydrates stability is observed (Fig.2a). When R=Bu, as we have already mentioned, four polyhydrates form. If R=Pr, one hydrate with the least hydrate number 24 remains, its melting point being only $0.8^{\circ}C$ (whereas that of $Bu_4NBr \cdot 24H_2O$ is $12.4^{\circ}C$). If R=Am, the hydrate $AmBu_3NBr$ $38H_2O$ forms, whose melting point is $8.1^{\circ}C$ ($Bu_4NBr \cdot 36H_2O$ melts incongruently at $9.5^{\circ}C$). If R=Me,Et or Hex, clathrate formation in the temperature range concerned does not occur.

An analogous series of fluorides (Fig.3a) has been studied more recently [21]. The picture of hydrate stability dependence upon radical dimensions is analogous, though different hydrates form except for the
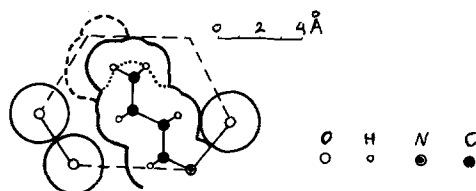


Figure 1. ... Propyl, —— butyl, --- amyl radicals in the T cavity. Section along the mirror plane, going across the main axis. Zigzag of the hydrocarbon chain (to be more clear it is of relative size) is in the Figure plane. Cavities T,P,H do not differ significantly in size (Table I) and the Figure shows the accordance between the dimensions of the "big" cavities and hydrocarbon radicals in general outline rather than in detail.
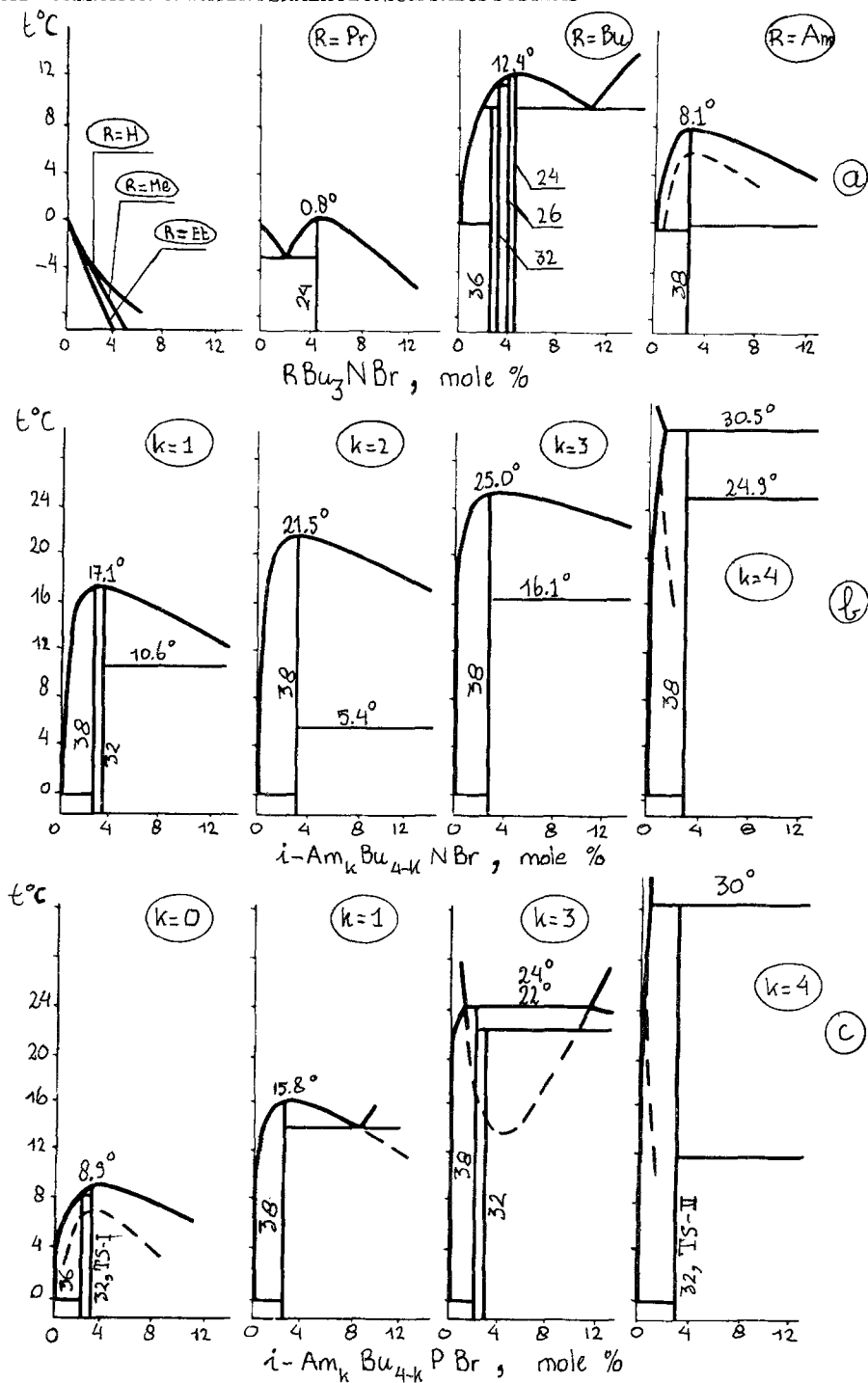
Figure 2. The effect of the dimensions and the configuration of tetraalkylonium bromides cations on clathrate formation. Series: a) $RBu_3NBr-H_2O$ [19,20]; b) $i-Am_kBu_{4-k}NBr-H_2O$ [20]; c) $i-Am_kBu_{4-k}PBr-H_2O$ [20].
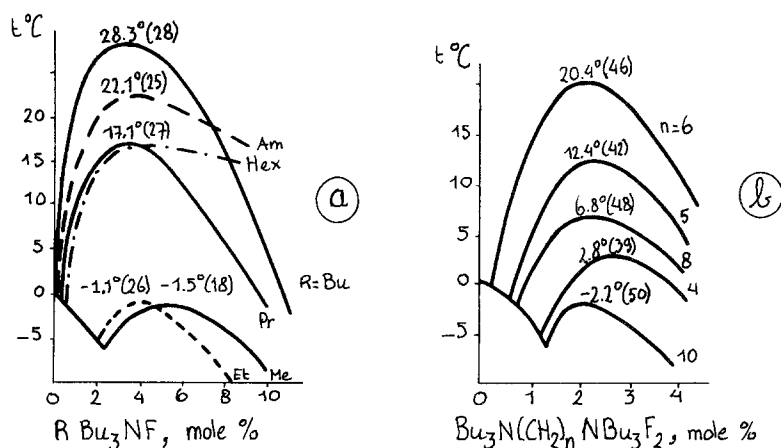
Figure 3. The effect of the cation geometry on clathrate formation in the series: a) $RBu_3NF-H_2O$ [21]; b) $Bu_3N(CH_2)_nNBu_3F_2-H_2O$ [27]. Melting point and hydrate numbers (in brackets) are given above the liquidus line.

hydrate $Bu_4NX \cdot 32H_2O^*$ (X=F,Br). It is clear that the anion plays its part here, its influence is also revealed in the case with X=F. When R=Me,Et, hydrate formation takes place.

Consecutive displacement in TBA bromide of the butyl radical by iso-amyl causes 4-5° increase in hydrate melting point (Fig. 2b, 7a). The hydrate structure changes from TS-I (1:32.4) to, probably, RS (1:38).

In the series of phosphonium systems $i-Am_kBu_{4-k}PBr-H_2O$ (Fig.2c, 7b) one can observe an analogous increase of hydrate stability with the increase of the isoamyl radical number in a cation, but besides hydrates TS-I (1:32.4) and RS (1:38), hydrates TS-II (1:32) appear in the case with $i-Am_4PBr \cdot 32H_2O$ [5] and, probably, with $i-Am_3BuPBr \cdot 32H_2O$. Judging by the cavities geometry, the most suitable radical for their stabilization would be expected to be neohexyl, but there are no data concerning this.

The simultaneous replacement of all the four radicals in $Bu_4NBr$ by Pr or Am results in the following: clathrate hydrates do not form, but in the case with $Alk_4NX$ (X=F,Cl,OH) (but not $Pr_4NX$ [21]) hydrates form, though with relatively low melting points [22-24]. Our data [22,23], which agree with [24] for X=F, are presented in Figure 4a,b,c (in [24] m.p.= =3.6°C, hydrate number is 39). If X=Cl, the data [24] (m.p.=-2.3°C) are more similar to those which we have obtained for the metastable hydrate.

In the series of trialkylphosphine oxides $RBu_2PO$ [26] a similar picture of the ability to form hydrates is observed. Hydrate $Bu_3PO \cdot 34H_2O$ is more stable (m.p.=7.1°C) (Several hydrates with similar melting points seem to form in the system. The structure of one of them viz. $Bu_3PO \cdot 34H_2O$, has been found [6]), hydrate $MeBu_2PO \cdot 18H_2O$ melts incongruently at -11.3°,

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*) The results of the phase diagram $Bu_4NF-H_2O$ study [9] (Table II), obtained by us simultaneously with [21],agree well as for the liquidus and congruently melting hydrate 1:28 (Fig.6). Hydrate TS-I 1:32, described in [2], whose structure is completely described [13] has not been found. Our data on this hydrate are given in Table II and in Figure 6.
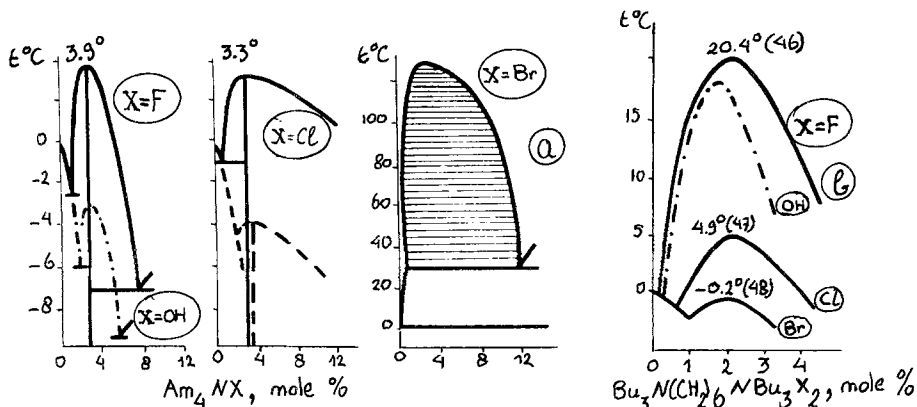
Figure 4. Clathrate formation in the systems: a) $Am_4NX-H_2O$ [22,23];
b) $Bu_3N(CH_2)_6NBu_3X_2-H_2O$ [27] (X=F,Cl,Br and OH). (In the system
$Am_4NBr-H_2O$ there is no clathrate formation).

hydrate $PrBu_2PO \cdot 18H_2O$ melts at 3.3°C [26].

In Figure 5b the diagrams of fusibility in the water-trialkylphos-
phine oxide systems with the gross formula $C_{12}H_{27}PO$ [26] are given. In
spite of the hydrophobic part volume of all the molecule isomers being
the same and practically equal ability to interact in a hydrophilic way,
clathrate formation is observed only in the case with $Bu_3PO$. We have found
triisoamylphosphine oxide clathrate hydrate to form at positive tempera-
tures and melt decomposing into two liquid phases.

Thus, the least possible change of the size (by $CH_2$-group) and the
configuration in $Alk_3PO$ molecules and $Alk_4Y^+$ (Y=N,P) cations results in
both noticeable quantitative (the melting point of hydrates of the same
structure changes), and qualitative changes in the clathrate formation
picture, which causes the change of the polyhydrate structure and their
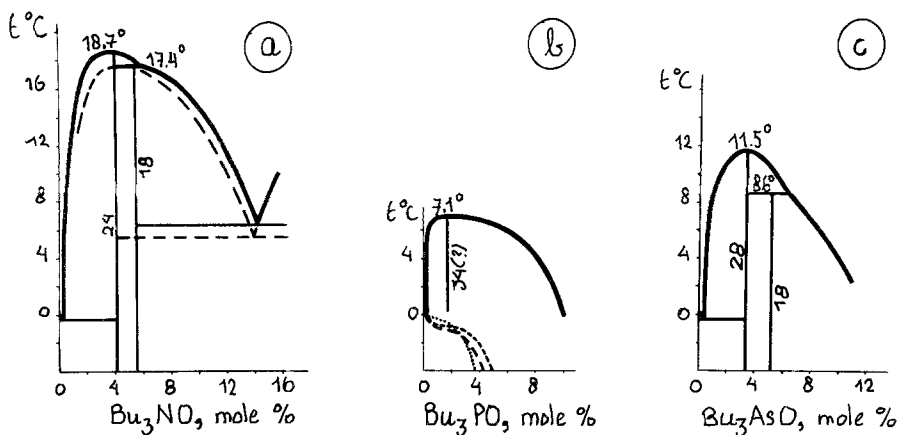number in the system. In some cases it depends on such clathrate former



Figure 5. Clathrate formation in the systems: a) $Bu_3NO-H_2O$ [28]; b) $Bu_3PO$
(--- $EtAm_2PO$, — — $HexPr_2PO$,.... $OctEt_2PO$)-$H_2O$ [26]; c) $Bu_3AsO-H_2O$ [28].

changes, whether clathrate formation occurs or not.

Since references [1,2] appeared, isoamyl and butyl have been known
to be the most suitable radicals for the formation of alkylonium salts
polyhydrates. The data of this section and reference [21] data allow us
to arrange alkyl radicals in the order of the decrease of stabilizing abi-
lity:

i-Am>Bu>Am>Pr>i-Pr,i-Bu>Et>Me>Hex,Hep,
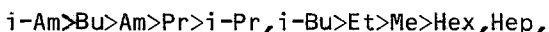
which is quite explicable in terms of stereochemistry (e.g., Fig. 1).

For diammonium cation salts a similar picture of the stability al-
teration of the forming hydrates, depending on the hydrocarbon chain
length, is observed [27] (Fig. 3b).


4.   HYDROPHILIC INCLUSION

The effect of the hydrophilic interaction during hydrate formation is not
so obvious as that of the molecule hydrophobic part dimensions and confi-
guration but without it the formation of hydrates with     big molecule
hydrate formers is hardly possible.

If the hydrophilic interaction effect is significant (in low molecu-
lar alkylamines [4] and peralkylonium salts [29]), every particular guest
builds "its own" structure. When, however, the hydrophobic interaction
prevails (in the molecules considered), hydrate formation, depending first
of all on the molecule's hydrophobic part size and configuration, becomes
less sensitive to the hydrophilic interaction changes.

In Figure 6 the TBA halogenides – water systems phase diagrams are
presented. This Figure (Table II) shows, that hydrates TS-I are common
for the whole series. The remaining hydrates are different. If nitrate
and hydroxide together with the first numbers of carboxylates and dicar-
boxylates series were added to the halogenides series, the clathrate for-
mation picture would be common in many respects, but more complex, than
that in [2,3]. Here are some regularities, we have managed to observe.

1. In the cases, where the anion does not differ greatly in its size
from the water molecule (especially, in the direction of increasing),
i.e. where the anion-water edge, formed during the hydrophobic inclu-
sion, does not differ significantly from that in pure water structure,
TBA salts form hydrates of CS-III(superstructure CS-I with doubled para-
meter [24]) with stoichiometry 1:28.7 per cation (if the anion has $c_{TBA}=$
=1, n=1, see p. 62). The authors of [8] have observed hydrates with such
structure for oxalate and wolframate, but they considered them to be me-
tastable. These hydrates have the highest melting point and, as a rule,
melt congruently.

2. As Jeffrey and McMullan have observed [1,2], hydrates TS-I with
the approximate composition 1:32 are characteristic of TBA salts. They
occur in all the systems studied (in some only as metastable). It is hyd-
rates of such structure that from the kinetic point of view seem to form
more easily. However, hydrates with this structure melt congruently only
in the systems with formate, acetate, malonate and succinate. In the rest
of the systems their neighbours are the hydrates with higher melting
points, which make them either incongruently melting, or completely meta-
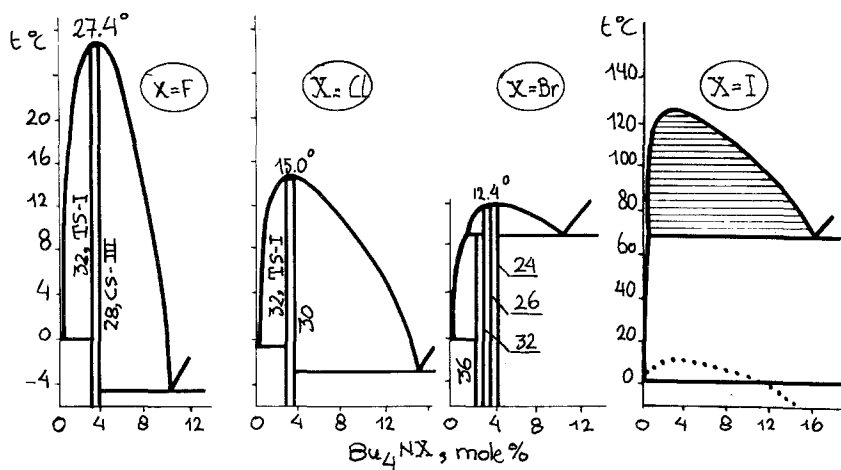stable. At any rate, the change of the anion affects the hydrates TS-I

Figure 6. Clathrate formation in the system $Bu_4NX-H_2O$ [15].

stability to a smaller degree, which accounts for their presence being displayed in some way or another in all the systems studied.

3. The less the anion differs from the water molecule in size and ability to form the H-bond, the more durable are the hydrates within one structure. This can be seen in Figure 7c, showing the melting points of the hydrates of peralkylonium salts halogenides depending on the anion radius. A similar picture (Fig. 4d, 7c) is observed in the systems $Bu_3N(CH_2)_6NBu_3X_2-H_2O$ (where X=F,Cl,Br,OH) [27]. From Figure 7c it follows, that the anion dependence is the stronger, the less the cation ability to stabilize clathrate structures and that the polyhydrates of all the iodides, except for $PrBu_3NI$, would have to melt at positive temperatures. Guided by this, we have discovered hydrates of all the iodides mentioned both at high and atmospheric pressure [18,30]. (Some time earlier H.Nakayama [24] pointed out that the hydrate $i-Am_4NI \cdot hH_2O$ (h was determined approximately) melted incongruently at $13.3°C$.

Thus, summing up this section, we can say the anion affects polyhydrate stability within one structure, the number of the hydrates forming in the system, their structures. In some cases it depends on the anion, whether clathrate formation occurs or not. This occurs in the case with tetraamylammonium and methyl- and ethyltributylammonium salts (see section 4), which do not form hydrates, if the anion is bromide, but which do, if the anion is fluoride, hydroxide or chloride.

In Figure 5 the phase diagrams of $Bu_3XO-H_2O$ (X=N,P,As) systems are presented. According to their structural data [6] these hydrates are referred to as semiclathrates in Jeffrey's terms [4]. In spite of the fact that molecules hydrate formers mentioned have big hydrocarbon radicals and clathrate formation with their participation depends on the whole on the hydrophobic interaction, the hydrophilic interaction plays its part, too. The polarity increase of the functional groups ($pK_a$ for oxides $(CH_3)_3XO$ equals to 4.5 [31], -0.5 [32] and 3.7 [31] for X=N,P and As, respectively) facilitates polyhydrate formation.

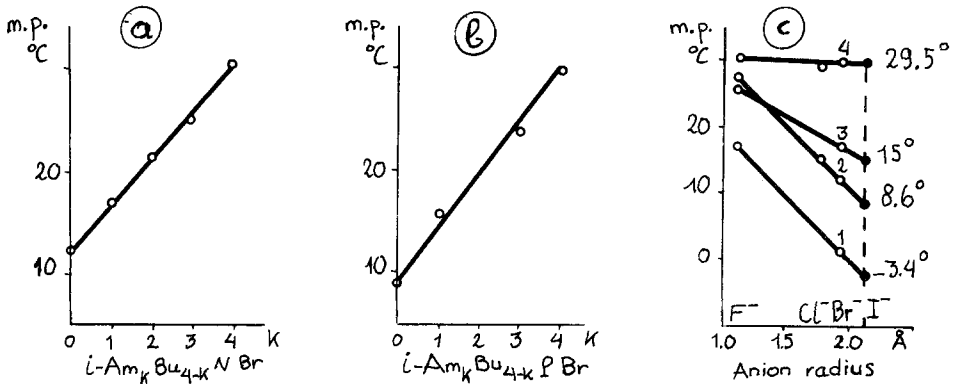Figure 7. Melting points of peralkylonium polyhydrates depending on ca-
tions dimensions: a) i-Am$_k$Bu$_{4-k}$NBr [20]; b) i-Am$_k$Bu$_{4-k}$PBr [20] and halo-
genide anions (c). 1) for PrBu$_3$NX [19,21]; 2) Bu$_4$NX (M·32H$_2$O, structure
TS-I) [15]; 3) i-AmBu$_3$NX [20,21]; 4) i-Am$_4$NX [2,20,28] (M·38H$_2$O, RS).

## 5.   HYDROPHOBIC-HYDROPHILIC INCLUSION   OF THE ANION

This aspect is discussed in more detail in the present issue [33], carbo-
xylate and dicarboxylate being taken as an example. An interesting pecu-
liarity of such inclusion  is that as the anion hydrophobic part grows,
it first occupies small cages with additional stabilization, and,while in
the case with carboxylates the inclusion  goes from formate immediately
to propionate or butyrate, depending on the structure (Fig. 4 in [33]),
in the case with dicarboxylates it occurs as a "throw out" on glutarate
and adipate, the former is due to the hydrophilic inclusion  restric-
tions. If the anion hydrophobic part can be situated only in the big ca-
ges, the stoichiometry within one framework structure changes in a step-
wise fashion and the melting point is lower (no additional stabilization
at the expense of filling the small cages takes place). If the anion di-
mensions are intermediate, it can be situated either only in the big or
only in the small cavities or can be distributed between them. All this
and the fact, that the big anions can include  in various conformations
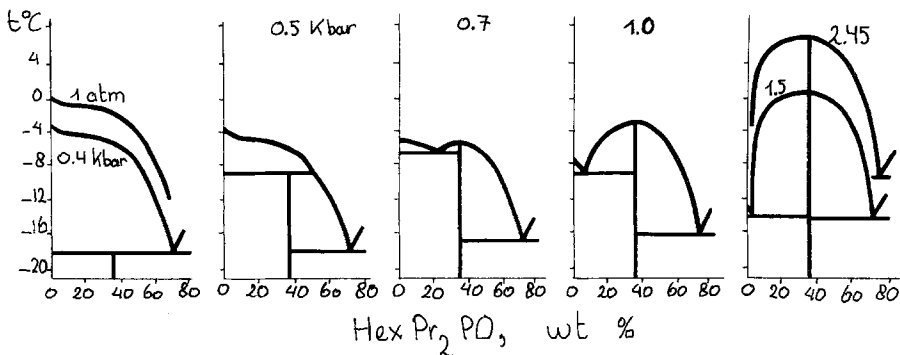


Figure 8. Pressure effect on the clathrate formation in the system
HexPr$_2$PO-H$_2$O [38].

and that water can form a number of almost isoenergetic frameworks, suggest many variants of the formation of similar in thermodynamic stability hydrates. Since less thermodynamically stable hydrates form more easily from the kinetic point of view, we manage to discover (and often to single out and study a whole number of metastable hydrates, which often have very similar hydrate numbers (Table I in [33])). It is appropriate here to compare the mentioned hydrates with protein hydrates, which may be of a similar nature [34]. The phenomena, mentioned here, may be partially the reason of the well known difficulty in obtaining protein crystalline hydrates, on the other hand, perhaps, the protein hydrates obtained are not the only hydrates and are not by all means stable thermodynamically under the synthesis conditions.


## 6.   PRESSURE EFFECT

Ice Ih is known to be destabilized by pressure, while the majority of clathrate hydrates melts (decomposes) at higher temperatures during the increase of pressure, and they are destabilized, if at all, by pressure (like hydrates CS-II) to a significantly lesser extent than ice Ih [35]. Thus, 1,4-dioxane hydrate CS-II, melting incongruently at P=1 atm., melts congruently in the pressure range 0.57-2.3 kbar [36,37]. In the system $Hex_2Pr_2PO-H_2O$, as we have already pointed out, no hydrate formation occurs at atmospheric pressure, but at $P \geqslant 0.4$ kbar hydrate $M \cdot 22H_2O$ forms, which melts congruently at 2.45 kbar (6.7°C) (Fig. 8) [38].

In tetraalkylammonium iodides – water systems the clathrate formation picture is complicated by the crystallization field being overlapped completely (as in the systems with $PrBu_3NI$, $Bu_4NI$) or to a significant degree ($i-AmBu_3NI$, $i-Am_4NI$) by the crystallization field of the salt itself [18,30]. The pressure increase causes clathrate hydrates stabilization and the going out of their recrystallization field into the stability range. Thus, hydrate $PrBu_3NI \cdot \sim 20H_2O$ has a stable existence range at $P \geqslant 0.13$ kbar, hydrate $Bu_4NI \cdot \sim 30H_2O^-$ – at $P \geqslant 0.4$ kbar, hydrates $i-AmBu_4NI \cdot \sim \sim 30H_2O$ and $i-Am_4NI(36 \pm 3)H_2O$ melt incongruently at atmospheric pressure at 7.1° and 14.7° respectively (Table II). At high pressures in the last three systems more dense hydrates with smaller hydrate numbers form. In the system $Bu_4NI-H_2O$ at $P>7$ kbar hydrate formation ceases. Thus, just as in the systems with gas hydrates [36], the optimum pressure for hydrate formation in the systems concerned is 1.5-3.5 kbar.

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