

# Double clathrate hydrates of tetrabutylammonium fluoride + helium, neon, hydrogen and argon at high pressures

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**Abstract** Decomposition curves of double ionic clathrate hydrates of tetrabutylammonium fluoride with helium, neon, hydrogen and argon were studied at pressures up to 800 MPa. Formation of double hydrates with helium, neon and hydrogen does not lead to any significant increase of the temperatures of decomposition of these hydrates; at high temperatures the hydrates may decompose even at lower temperatures than the hydrate of pure tetraalkylammonium salt does. Decomposition temperatures of double hydrates with argon in all cases were 4–8 °C higher in comparison with the decomposition temperature of ionic clathrate hydrates of tetrabutylammonium fluoride. We suppose that this behavior is caused by simultaneous effect of three factors on hydrate decomposition temperature: (1) partial filling of the small cavities in the framework of the hydrate with water molecules, (2) weakness of the van der Waals interactions between the gas molecules and the host water molecules, and (3) dissolution of helium, hydrogen and neon in the solution of tetrabutylammonium salt causing a decrease of melting temperatures of the hydrates formed from these solutions.

**Keywords** Argon · Gas hydrate · Helium · High pressure · Hydrogen · Neon · Phase diagram · Tetrabutylammonium fluoride

## Introduction

In the crystal structure of ionic clathrate hydrates of tetraalkylammonium salts, water molecules and (most often) guest anions build up a polyhedral hydrogen-bonded framework; its polyhedral cavities are occupied by cations [1–5]. The most typical representatives of ionic clathrate hydrates are polyhydrates of the salts of alkylonium cations with monoatomic halide anions. Alkyl radicals occupy the «compartments» of combined cavities formed while the central atom of the tetrahedral cation extrudes the water molecule situated in the center of four contiguous water polyhedra. The most characteristic structural types of the ionic clathrate hydrates of tetraalkylammonium salts are superstructure of cubic structure I, tetragonal structure I and hexagonal structure I (CSS-I, TS-I and HS-I, respectively). The composition of the unit cell for these structures may be expressed as follows: CSS-I—48T\*16D\*384H<sub>2</sub>O (this means that a cell has 6 large cavities of T type and 2 small pentagondodecahedral cavities of D type, and 48 water molecules); TS-I—4P\*16T\*10D\*172H<sub>2</sub>O; HS-I—2P\*2T\*3D\*40H<sub>2</sub>O. The detailed data on ionic clathrate hydrate structures are presented in [1–5].

At present the only one way to increase decomposition temperature of a gas hydrate is admixing of additional guest to a main guest component that results in formation of double hydrate with a higher decomposition temperature [6]. As the example of the successful use of this method for increasing the decomposition temperature of the hydrogen hydrate the recent data can be cited [7, 8], where the addition of the help component (tetrahydrofuran) to hydrogen hydrate resulted in the significant increase of the decomposition temperature of formed double hydrate in comparison with hydrate of pure hydrogen. It is interesting to note that modification of the crystalline framework of

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the hydrates with the intent to increase their decomposition temperature at present seems unlikely to be realized because ammonium fluoride (that is the only known compound which could be dissolved noticeably in ice and hydrates) destabilizes ice-like frameworks [9]. The methods of storage (transportation) of the gases (presumably natural gas and hydrogen) in the form of gas hydrates as well as separation of gas mixtures with the use of gas hydrates are important from the viewpoint of the possible practical use (e.g. [10–12]). It requires “mild” temperature and pressure conditions of existence of hydrates. That causes a set of additional requirements. For example, the solution of the third component should be used many times (e.g., the third component must not be lost during the cyclic process formation—decomposition of the hydrate) or the presence of this compound in the gas mixture evolved in the course of hydrate decomposition must not prevent the use of the latter, the additional components must be produced in the industrial scale, must be relatively inexpensive, etc. The significant problem stayed is a low content of hydrogen (methane) in the hydrate that is provoked by filling of the significant part of cavities in the hydrate framework by the molecules of “help” component. One of the possible ways of solving this problem is production of a hydrate in which a help component fills only a little part of the hydrate cavities providing sufficiently high content of the main component in the hydrate and at the same time an acceptable decomposition temperature of the hydrate. Tetraalkylammonium salts are not volatile and form clathrate hydrates with high decomposition temperatures. These properties make topical investigation of the double clathrate hydrates of tetraalkylammonium salts with gases [13–19].

In the formation of ionic clathrate hydrates, the guest cations occupy only large cavities, while the small ones may be partially occupied with water molecules [20–22], nitrogen or oxygen molecules captured from the air [4] or, finally, they may be vacant. When the vacant small cavities in the structures of clathrate hydrates are filled with guest molecules having appropriate size (inert gases, methane, nitrogen, hydrogen sulphide etc.; they are called help-gas), double hydrates are formed; as a rule, their decomposition temperature is higher than that of the hydrates of pure components [6, 23–25]. This effect is most clearly pronounced at high pressures. For instance, at a pressure of 0.18 GPa, the hydrate of pure tetrahydrofuran melts at  $-5\text{ }^{\circ}\text{C}$ , the double hydrate of tetrahydrofuran with He melts at  $12\text{ }^{\circ}\text{C}$ , Ne— $21\text{ }^{\circ}\text{C}$ , Ar— $54\text{ }^{\circ}\text{C}$ , Kr— $62\text{ }^{\circ}\text{C}$ , Xe— $65\text{ }^{\circ}\text{C}$  [25]. A similar situation may also be expected for double hydrates of gases and tetraalkylammonium salts; however, it should be stressed that the above-considered filling of small cavities in the hydrates of tetraalkylammonium salts may bring essential complications into the picture of

hydrate formation. This idea determined our attention to the subject of the present investigation. Here we present our recent results on the double hydrates of a number of gases with tetrabutylammonium salts.

## Experimental

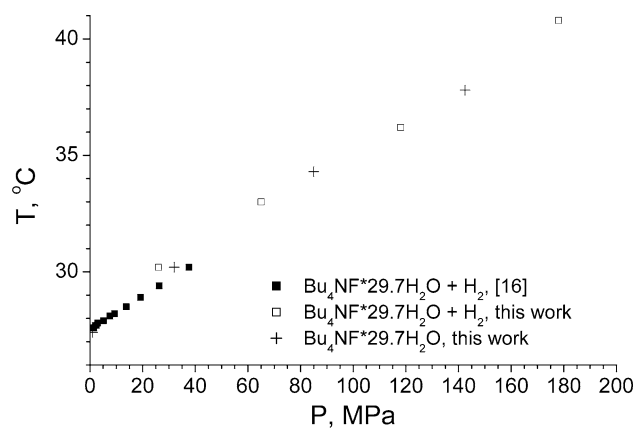
Hydrate decomposition temperatures in the system tetraalkylammonium salt–water–gas were measured by means of differential thermal analysis (DTA) in a cell specially developed for the studies of hydrate formation in the presence of a gaseous guest at high hydrostatic pressure [26]. A gas was taken in excess with respect to the expected hydrate composition. Hydrate decomposition temperatures were measured with a chromel–alumel thermocouple calibrated over standard compounds; the error of temperature measurement was  $\pm 0.3\text{ K}$ . Scale reading of a thermocouple of this type is almost independent of pressure. Pressure was measured with a manometric manometer calibrated at high pressures with respect to mercury melting. Error of pressure measurements was not more than 1%. The experimental procedure was described in detail in [26, 27].

The aqueous solution of tetrabutylammonium fluoride was obtained by neutralizing of tetrabutylammonium hydroxide solution (from “Chemapol”, “pure” grade) with the hydrofluoric acid. The crystals of tetrabutylammonium fluoride hydrate were deposited under cooling and then were recrystallized twice. The crystals of cubic and tetragonal polyhydrates of tetrabutylammonium fluoride were grown in accordance with the data of T, X-phase diagram of  $(n\text{-C}_4\text{H}_9)_4\text{NF-H}_2\text{O}$  binary system [20]. The composition of tetrabutylammonium fluoride polyhydrates was determined by means of the potentiometric titration of tetrabutylammonium cation with the solution of sodium tetraphenylborate using an ion-selective electrode. The crystals of the hydrate were collected in a cold chamber at a temperature about  $5\text{ }^{\circ}\text{C}$ , and were triturated in an agate mortar, then placed in an ampoule for differential thermal analysis at high gas pressures. In all cases first experiment after loading the ampoule was performed with the samples prepared in reaction of solid hydrate crystals saturated with gaseous guest under the high-pressure conditions. This method vouched for structural type of synthesized hydrate. Experiments of this type constituted 20% of total number of experiments. In other experiments double hydrate was synthesized from gas and aqueous solution of  $(n\text{-C}_4\text{H}_9)_4\text{NF}$  obtained by melting of the hydrate crystals. No significant differences were observed in both types of the experiments. The gases used contained the major substance not less than 99.99 mol.% and were used without additional purification.

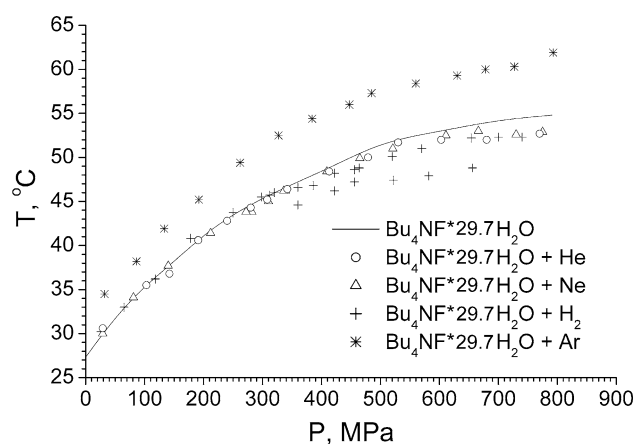
## Results and discussion

The experimental curves obtained are presented in Figs. 1, 2, 3, numerical data are listed in Table 1. In the system  $\text{Bu}_4\text{NF}-\text{H}_2\text{O}$ , there are two ionic clathrate hydrates having the composition  $\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O}$  (CSS-I) [20] and  $\text{Bu}_4\text{NF}\cdot 32.8\text{H}_2\text{O}$  (TS-I) [22], so the decomposition curves for double hydrates of  $\text{Bu}_4\text{NF}$  with gases were investigated for these two compositions. In Fig. 1, the curve of decomposition obtained by us for the double hydrate  $\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O}$  with hydrogen is compared with the results obtained at low pressure [16]; the agreement between the sets of data is satisfactory. The curves of decomposition for the hydrates obtained from the solutions of the compositions  $\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O}$  and  $\text{Bu}_4\text{NF}\cdot 32.8\text{H}_2\text{O}$  coincide within the investigated pressure range, temperatures of hydrate decomposition increase with pressure rise. A part of experiments was carried out with the solutions from which the dissolved gases were removed by bubbling with helium. We did not detect any differences between gas-free solutions and those containing gases. In both cases, the curves of decomposition of double hydrates with argon are situated by 4–6 °C higher than the curves of decomposition of the hydrates  $\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O}$  and  $\text{Bu}_4\text{NF}\cdot 32.8\text{H}_2\text{O}$ ; the difference increases with pressure rise (Figs. 2, 3). For the solutions having the composition  $\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O}$ , the curves of decomposition in the presence of hydrogen, helium and neon almost coincide up to the pressure of 300 MPa with the decomposition curve of the hydrate obtained from the solution with this composition, that is, hydrate stabilization is absent. It should be stressed that in the case of CS-II hydrate of tetrahydrofuran under 300 MPa of neon pressure the temperature of hydrate decomposition gets up to 21 °C [25]! At higher pressure, the curves obtained in the presence of gases are situated lower than the curve of decomposition of  $\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O}$  (Fig. 2). The solutions having the composition  $\text{Bu}_4\text{NF}\cdot 32.8\text{H}_2\text{O}$  demonstrate somewhat different behavior in the presence of hydrogen, helium and neon (Fig. 3). Within the whole pressure range, the curves of decomposition in the presence of gases lie higher by 1–3 °C than the curve of melting for the solution  $\text{Bu}_4\text{NF}\cdot 32.8\text{H}_2\text{O}$ , a small temperature decrease is observed only for neon and (in some experiments) for hydrogen (Fig. 3). It may be stated that any significant effect of helium, hydrogen and neon on the temperature of decomposition of the hydrates of  $\text{Bu}_4\text{NF}$  formed under the pressure of these gases is not observed.

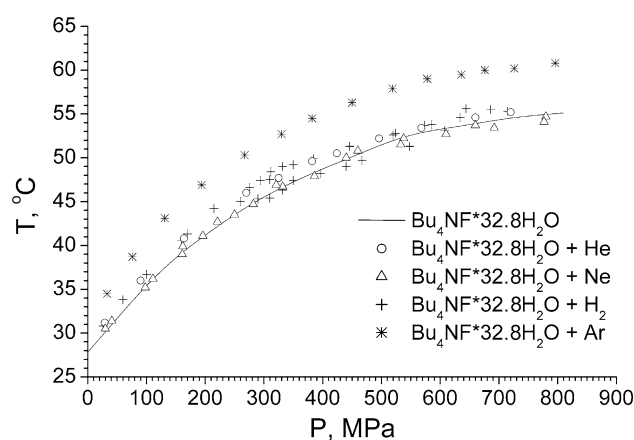
Analyzing the results, we first of all pay attention to the coincidence between the curves of decomposition of the hydrates obtained from the solutions having the composition  $\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O}$  (CSS-I) and  $\text{Bu}_4\text{NF}\cdot 32.8\text{H}_2\text{O}$  (TS-I). At atmospheric pressure, the corresponding hydrates have different structures but very close melting points and



**Fig. 1** The decomposition temperatures of the ionic clathrate hydrate  $\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O}$  and double hydrate  $\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O}$  with  $\text{H}_2$  at pressures up to 180 MPa in comparison with the data presented in [16]



**Fig. 2** The decomposition temperatures of the ionic clathrate hydrate  $\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O}$  and double hydrate  $\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O}$  with helium, neon, hydrogen and argon at pressures up to 800 MPa



**Fig. 3** Decomposition temperatures of the ionic clathrate hydrate  $\text{Bu}_4\text{NF}\cdot 32.8\text{H}_2\text{O}$  and double hydrate  $\text{Bu}_4\text{NF}\cdot 32.8\text{H}_2\text{O}$  with helium, neon, hydrogen and argon at pressures up to 800 MPa

**Table 1** Decomposition temperatures of ionic clathrate hydrates  $\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O}$ ,  $\text{Bu}_4\text{NF}\cdot 32.8\text{H}_2\text{O}$  and double clathrate hydrates formed by  $\text{Bu}_4\text{NF}$  with Ar, He, Ne and  $\text{H}_2$ 

$\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O}$		$\text{Bu}_4\text{NF}\cdot 32.8\text{H}_2\text{O}$	
P (MPa)	T (°C)	P (MPa)	T (°C)
0.1	27.4	0.1	27.9
32	30.2	31	30.2
85	34.3	86	34.4
143	37.8	140	38
212	41.7	205	41.4
277	44.5	274	44.5
330	46.3	340	46.9
412	48.8	375	48
496	51.3	450	50.1
602	53	541	52.4
695	54.1	633	53.6
791	54.8	729	54.6
		810	55.1
$\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O} + \text{He}$		$\text{Bu}_4\text{NF}\cdot 32.8\text{H}_2\text{O} + \text{He}$	
P (MPa)	T (°C)	P (MPa)	T (°C)
29	30.6	29	31.2
103	35.5	90	36
191	40.6	164	40.8
280	44.3	270	46
142	36.8	325	47.7
240	42.8	382	49.6
308	45.2	424	50.5
342	46.4	496	52.2
413	48.4	568	53.4
479	50	660	54.6
530	51.7	720	55.2
603	52		
680	52		
770	52.7		
	+		
$\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O} + \text{Ne}$		$\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O} + \text{Ne}$	
P (MPa)	T (°C)	P (MPa)	T (°C)
29	30	339	46.2
81	34.1	409	48.4
140	37.7	465	49.9
212	41.4	521	51
272	43.8	611	52.5
282	43.8	666	53
310	45	730	52.6
336	46.2	775	52.9

**Table 1** continued

$\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O} + \text{Ar}$		$\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O} + \text{Ar}$	
P (MPa)	T (°C)	P (MPa)	T (°C)
32	34.5	447	56.0
86	38.2	485	57.3
133	41.9	560	58.4
192	45.2	630	59.3
262	49.4	678	60.0
327	52.5	727	60.3
384	54.4	793	61.9
$\text{Bu}_4\text{NF}\cdot 29.7\text{H}_2\text{O} + \text{H}_2$		$\text{Bu}_4\text{NF}\cdot 32.8\text{H}_2\text{O} + \text{H}_2$	
P (MPa)	T (°C)	P (MPa)	T (°C)
26	30.2	26	30.8
65	33	60	33.8
118	36.2	100	36.7
178	40.8	160	40.6
250	43.7	170	41.3
298	45.5	215	44.2
312	45.7	260	45
320	46	276	46.6
360	46.6	290	45.3
360	44.6	294	47.4
386	46.8	310	45.4
422	46.2	310	47.5
422	48.2	312	48.4
456	48.6	332	46.3
456	47.2	332	49
464	48.8	350	49.2
520	50.1	350	47.4
522	47.4	385	49.9
570	51	396	48.2
582	47.9	440	49
654	52.2	446	51.3
656	48.8	467	49.7
700	52.3	520	52.6
740	52.3	524	52.8
		548	51.3
		573	53.7
		586	53.8
		608	53.1
		634	54.6
		644	55.6
		686	55.5
		715	55.3

**Table 1** continued

Bu <sub>4</sub> NF·32.9H <sub>2</sub> O + Ne		Bu <sub>4</sub> NF·32.9H <sub>2</sub> O + Ne	
P (MPa)	T (°C)	P (MPa)	T (°C)
30	30.5	332	46.7
32	29.4	386	47.9
41	31.4	440	50
98	35.2	460	50.8
111	36.2	533	51.5
161	39	538	52.2
162	39.9	610	52.7
196	41.1	660	53.7
221	42.7	692	53.4
250	43.5	777	54.1
282	44.7	780	54.7
321	46.9		
Bu <sub>4</sub> NF·32.9H <sub>2</sub> O + Ar		Bu <sub>4</sub> NF·32.9H <sub>2</sub> O + Ar	
P (MPa)	T (°C)	P (MPa)	T (°C)
33	34.5	450	56.3
76	38.7	519	57.9
131	43.1	578	59.0
194	46.9	676	60.0
267	50.3	636	59.5
330	52.7	796	60.8
382	54.5	726	60.2

liquidus lines [20]. It is known that the slope of the curve of decomposition of clathrate hydrates in the P–T space, that is, the rate of increase/decrease of decomposition temperature with pressure rise, is determined first of all by the tightness of packing of the hydrate framework (see Discussion in [28]). The ratio of the number of large cavities (filled with cation for both hydrates) and small cavities for CSS-I and TS-I are equal to 3 and 2, respectively. So, for the case of vacant small cavities, one may expect different packing densities for hydrates CSS-I and TS-I and, correspondingly, different slopes of the curves of decomposition of these hydrates on P, T diagram. This does not correspond to the available experimental data. We suppose that this is caused by the fact that small cavities are filled in the hydrates of both structures. As we have indicated above, the removal of dissolved atmospheric gases from the initial Bu<sub>4</sub>NF solutions does not affect the results of experiments, that is, the possibility of filling the small cavities with the molecules of atmospheric gases may be neglected. So, the most probable assumption is filling of the small cavities with water molecules [20–22]. As an alternative explanation, we may consider also the possibility of densifying of hydrate structures due to filling the small cavities in hydrates with the butyl groups of tetrabutylammonium

cations. Unfortunately, we are unable to discuss this possibility because of the absence of structural data concerning high-pressure ionic clathrate hydrates. Finally, the hypothetical possibility of crystallization of one and the same compound from both investigated solutions is to be considered. We think this is rather improbable because there are significant differences in the behavior of double hydrates formed from these solutions.

The assumption concerning the effect of filling of the small cavities in hydrates Bu<sub>4</sub>NF·29.7H<sub>2</sub>O and Bu<sub>4</sub>NF·32.8H<sub>2</sub>O with water molecules allows us to understand the features of the behavior of double hydrates. First of all, it should be stressed that the spectroscopic investigations reported in [16] showed that the inclusion of hydrogen molecules into the small cavities of these hydrates really occurs, that is, the double hydrate of hydrogen and tetrabutylammonium salt is formed. It is most probable that the corresponding double hydrates are formed with helium and neon. The formation of double hydrates occurs in this case not only due to the inclusion of the guest molecule into the vacant cavities but also due to the substitution of the guest molecules with hydrogen molecule, which is, most probably, a less profitable process. It is known [29] that the van der Waals radii of hydrogen, helium, neon and argon are equal to 1.2, 1.4, 1.5 and 1.9 Å, respectively; the van der Waals interactions for helium, neon and hydrogen are weak, that is, one may expect substantial stabilization of the hydrate phase due to the guest–host interactions only in the case of argon. Finally, at high pressures, one may expect substantial solubility of gases in the aqueous solutions of Bu<sub>4</sub>NF, which may cause a decrease of the decomposition temperature of the formed hydrates. In our opinion, experimentally observed behavior of the double hydrates of Bu<sub>4</sub>NF with helium, hydrogen and neon is the result of the joint action of three considered factors. The above-indicated guest molecules do not have any significant effect on decomposition temperature. Somewhat better pronounced effect in the case of solutions having the composition Bu<sub>4</sub>NF·32.8H<sub>2</sub>O may be attributed to the higher concentration of small cavities in the hydrate TS-I. Argon inclusion is more profitable from the point of view of energy; it causes a sharp increase in the temperature of decomposition of the double hydrate.

Thus, the results obtained in the present work show that the formation of double hydrates with helium, neon and hydrogen does not lead to any significant increase of the temperatures of decomposition of these hydrates; at high temperatures the hydrates may decompose even at lower temperatures than the hydrate of pure tetraalkylammonium salt does. We suppose that this behaviour is connected with the simultaneous effect of three factors on hydrate decomposition temperature: (1) partial filling of the small cavities in the host water framework of the hydrate with “guest” water molecules, (2) weakness of the van der

Waals interactions between the gas molecules and the host water molecules, and (3) dissolution of helium, hydrogen and neon in the solution of tetraalkylammonium salts, causing a decrease of melting temperatures of the hydrates formed from these solutions.

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