J Incl Phenom Macrocycl Chem (2010) 67:13–18
DOI 10.1007/s10847-009-9662-2

ORIGINAL ARTICLE

Double clathrate hydrates of cross-linked tetrabutylammonium polyacrylate and noble gases at high pressures

E. Ya. Aladko · E. G. Larionov · A. Yu. Manakov · I. S. Terekhova

Received: 27 May 2009 / Accepted: 6 August 2009 / Published online: 22 September 2009

Abstract Temperatures of hydrate decomposition were measured by means of the differential thermal analysis at a pressures up to 800–900 Mpa in the systems: cross-linked tetrabutylammonium polyacrylate–water and cross-linked tetrabutylammonium polyacrylate–water–noble gas (He, Ne, Ar, Kr, Xe). The effect of the deformation of *D*-cavities of the hydrates on the temperature of their decomposition is discussed on the basis of the experimental data.

Keywords Clathrate hydrate · Tetrabutylammonium polyacrylates · Noble gas · High pressure · Phase diagram

Introduction

Clathrate hydrates are crystalline inclusion compounds in which the host framework is formed by water molecules bound to each other with hydrogen bonds. The guest molecules of suitable size and molecular shape occupy the cavities of the framework. Hydrates formed by gases or volatile liquids are usually called gas hydrates. As a rule, the interaction between guests and hosts in gas hydrates is purely Van der Waals.

E. Ya. Aladko · E. G. Larionov (✉) · A. Yu. Manakov · I. S. Terekhova
A.V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Akad. Lavrent'ev Av. 3, 630090 Novosibirsk, Russian Federation
e-mail: larionov@che.nsk.su

A. Yu. Manakov
Novosibirsk State University, Pirogova Str. 2, Novosibirsk 630090, Russian Federation

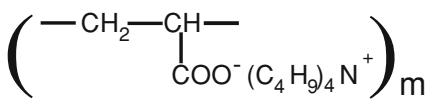
Jeffrey [1] introduced the term "ionic hydrates" for polyhydrates of tetraalkyl ammonium salts. Among them, the compounds studied most thoroughly are the hydrates of tetrabutyl- and tetraisoamylammonium salts [2]. The size of the cations under consideration does not allow them to occupy any simple cavities characteristic of gas hydrate structures [5^{12}(*D*), $5^{12}6^2$(*T*), $5^{12}6^3$(*P*), $5^{12}6^4$(*H*)], so combined cavities are formed in the structures of ionic hydrates. They consist of four simple cavities having a common vertex. The nitrogen atom of the cation occupies the position of water molecule located in the common vertex, while alkyl groups occupy adjacent simple cavities. Such a type of guest inclusion is called hydrophobic-hydrophilic. Anions (in the simplest cases—halide, hydroxide etc.) get included in the hydrophilic manner, that is, they replace one or several water molecules from the framework forming hydrogen bonds with the neighbouring water molecules. In the case of tetraalkylammonium carboxylates, the carboxylic group of an anion gets included in the hydrophilic manner replacing two water molecules, while the hydrocarbon chain occupies the positions in the cavities of the framework [2]. At atmospheric pressure, temperature of decomposition of the majority of the hydrates of quaternary ammonium salts under consideration is within the range 0–30 °C [2].

Quite unusual group of the hydrates of quaternary ammonium salts is comprised by the hydrates based on carboxylic cationic salt, that is, cross-linked polyacrylates of tetrabutylammonium (TBA) and tetraisoamylammonium (TiAA) [3–5]. At atmospheric pressure, decomposition temperatures of these compounds are above 0 °C. The general formula of these compounds may be represented as $(C_nH_{2n+1})_4NCOOR_m$, where R_m is the polymer cross-linked polyacrylate ion, *m* is the degree of cross-linking with divinyl benzene or divinyl sulphide. These systems

are interesting from several points of view. It is known that water molecules in polypeptides and proteins are in many cases arranged into semi-clathrate-like structures [6, 7]. Synthetic polyelectrolytes containing carboxylic groups possess a simpler and more regular structure; however, one may expect that the structure of hydrate shells in the systems of both types will have a similarity. So, investigation of the features of hydration of the polyelectrolytes under consideration may be useful for better understanding of the structure of more complicated systems. These polyelectrolytes themselves have excellent prospects for application in biology and medicine [8]. In addition, recent publications [9, 10] point to the possibility to use the hydrates of quaternary ammonium salts for gas storing and for separating gas mixtures (Scheme 1).

Investigation of the hydrates of cross-linked polyacrylates by means of powder diffractometry [11] confirmed the existence of the crystal hydrate phase in swollen granules of ion-exchange resins. Single crystal diffraction studies of the polyhydrates of cross-linked carboxylic cationic salt is impossible, so polyhydrates of non-crosslinked polyacrylates TBA [12] and TiAA [13] were investigated as the model compounds. It turned out that the TBA and TiAA cations occupy the four-sectioned T_3P and P_2T_2 cavities, respectively, while polyacrylate ions of these salts are inserted into the channels formed by the deformed and partially destroyed *T*- cavities for TBA- and *D*- cavities for TiAA-polyacrylates. In this situation, the *D*-cavities remain entirely vacant for TBA- polyacrylates and partially vacant for TiAA-polyacrylates. It follows from the results of powder X-ray diffraction experiment that the unit cell parameters for the hydrates of non-linked and cross-linked polyacrylates are in good agreement with reach other [13]. It was concluded that the polyhydrates of cross-linked and non-linked polyacrylates are isostructural.

It is known that decomposition temperatures of gas hydrates formed by a mixture of the molecules which substantially differ from each other in size are often higher than decomposition temperatures of the hydrates of pure components [14]. For instance, the decomposition temperature of a double hydrate of xenon and tetrahydrofuran, having cubic structure II, is 13.5 °C at atmospheric pressure, while the hydrates of pure tetrahydrofuran and xenon decompose at +4.3 and –10.4 °C, respectively [15]. As considered above, polyhydrates of cross-linked polyacrylates TBA and TiAA have a system of vacant small



Scheme 1 An elementary unit of the polymeric chain of tetrabutylammonium polyacrylate

D-cavities; in principle, they may be filled with the molecules of help gases. Some data confirming this assumption are available from literature [3, 10]. At present, clathrate hydrates based on cross-linked polyacrylates of TBA and TiAA are the only known compounds of this type that do not change their aggregative state during decomposition. The systems of this kind are certainly interesting for gas storage and separation of gas mixtures, which has defined out attention to this subject. The goal of the present investigation was to study the behaviour of double clathrate hydrates of polyacrylate ion-exchange resins in the form of tetrabutylammonium with noble gases from xenon to helium as help atoms at pressures up to 800 MPa.

Experimental

Hydrate decomposition temperatures in the system cross-linked tetrabutylammonium polyacrylate–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 [16]. 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 ±0.3 K. Scale reading of a thermocouple of this type is almost independent of pressure. Pressure was measured with a manganine manometer calibrated at high pressure withr espect to mercury melting. Error of pressure measurements was not more than 1%. The experimental procedure was described in detail in [16, 17]. Hydrate decomposition temperature in the system cross-linked tetrabutylammonium polyacrylate–water without any help gas was determined using a cell described in [18].

The samples of ion-exchange resin was prepared as follows. The carboxylic cationite with the cross-linking degree 0.5% was conditioned preliminarily with cyclic acid-base treatment using 0.1 N NaOH and HCI solutions, washed with ethanol; then ethanol was removed by washing with a large volume of distilled water. The TBA form of carboxylic cationic salt was obtained under the static conditions by neutralizing the polyacid with a three-fold excess (over the stoichiometric amount) of 0.1 N solution of tetrabutylammonium hydroxide. After neutralization, the samples were centrifuged, washed with distilled water and dried to the air-dry state. The residual water content of the samples was determined by titration according to Fisher's procedure; it was 7–10 mass%. In order to prepare the samples with water content corresponding to that in the hydrate phase [4, 11], a calculated amount of water was added to a weighed portion of the air-dry cationic salt; then

the samples were kept for 24 h in a closed ampoule for swelling. The gases used in the work contained not less than 99.95% of the major substance; no additional purification was carried out.

Results and discussion

Hydrate decomposition curves obtained by means of DTA in the systems cross-linked tetrabutylammonium polyacrylate + H_2O and cross-linked tetrabutylammonium polyacrylate + H_2O + gas under the excess of the help gas at pressures up to 800–900 MPa are shown in Figs. 1 and 2. The numerical experimental data are listed in Table 1. The positions of phase transition points were determined from the presence of a break on the curve of hydrate decomposition or from the site of crossing of the equilibrium and metastable decomposition curves. It follows from Fig. 1 that at least three hydrates are formed in the system cross-linked tetrabutylammonium polyacrylate + H_2O within the investigated pressure range. The TS-I hydrate [1, 2, 12] exists up to the pressure of 83 MPa. Further on, following pressure increase, hydrate phases with unknown structures h_x and h_y are formed within the ranges 83–367 MPa and 367–808 MPa. When moving along the pressure from above downward, the branch of decomposition of h_y hydrate was successfully followed to 164 MPa (8.6 °C), that is, into the P, T-region where it is metastable. In this region, when heating the system, two peaks were observed in the DTA diagram at the first rans; they corresponded to the decomposition of the stable and metastable hydrates. However, on repeated cycles of formation and decomposition, the peak of the metastable hydrate disappeared.

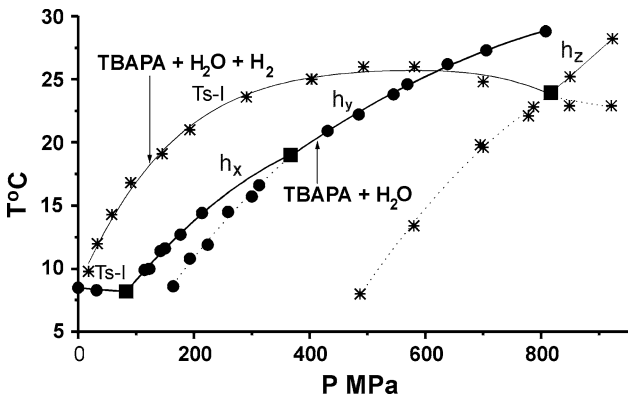


Fig. 1 Decomposition curves of clathrate hydrates formed by cross-linked tetrabutylammonium polyacrylate (TBAPA) + H_2O (*solid rings*) and cross-linked tetrabutylammonium polyacrylate + H_2O + H_2 (*asterisks*). Points of phase transformations are marked by solid squares. Metastable parts of the decomposition curves are marked by dotted lines. Ts–I—hydrate of tetragonal structure I, h_x, h_y and h_z—hydrates with unknown structures

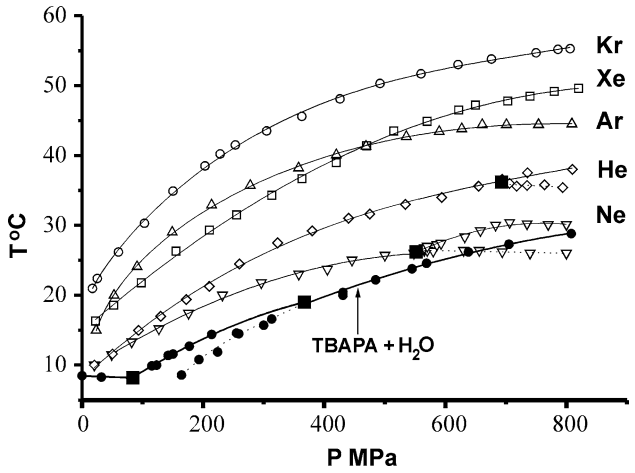


Fig. 2 Decomposition curves of clathrate hydrates formed by cross-linked tetrabutylammonium polyacrylate (TBAPA) + H_2O (*solid rings*) and cross-linked tetrabutylammonium polyacrylate + H_2O + help gas. Points of phase transformations are marked by solid squares. Metastable parts of the decomposition curves are marked by dotted lines

According to the data reported in [12], all the *D*-cavities in TS–I ($4P^{\cdot}16T^{\cdot}10D^{\cdot}172H_2O$) hydrate of tetrabutylammonium polyacrylate are vacant in the absence of the help gas. The structure of this compound is rather friable. For the compounds of this kind, application of pressure causes a decrease in the temperature of their decomposition because the total volume of the products of decomposition turns out to be smaller than the volume of the initial compound [19]. With an increase in pressure, these compounds are replaced by the hydrates with tighter packing. This phase transition TS–I → h_x is observed for the system TBAPA + H_2O at 83 MPa. With further increase in pressure, we observe one more phase transition from a less dense hydrate h_x to a denser hydrate h_y at a pressure of 367 MPa (19.0 °C).

When hydrogen in added to the system TBAPA + H_2O, H_2 molecules occupy vacant *D*-cavities in the tetragonal structure of tetrabutylammonium polyacrylate, which causes an increase in the decomposition temperature of the formed hydrate. One can see in Fig. 1 that the hydrate of the TS–I structure exists in the system TBAPA + H_2O + H_2 up to the pressure of 817 MPa (23.9 °C), denser hydrate h_z is formed in the system at higher pressures. We succeeded in following the metastable branch of the curve of TS–I hydrate decomposition to the pressure of 921 MPa (22.9 °C). Here Fig. 1 shows also the metastable continuation of the curve of h_z hydrate decomposition recorded in the DTA experiment when moving from above downward along pressure.

It was shown in [20] that at high pressures the decomposition temperatures of double hydrates of tetrahydrofuran (THF) with noble gases increases regularly with an

Table 1 Numerical experimental data on the decomposition temperatures of clathrate hydrates formed in the binary system cross-linked tetrabutylammonium polyacrylate (TBAPA) + H_2O and ternary system cross-linked tetrabutylammonium polyacrylate + H_2O + gas (G)

TBAPA + H_2O		TBAPA + H_2O + G											
		G = Xe		G = Kr		G = Ar		G = Ne		G = He		G = H_2	
P, MPa	T, °C	P, MPa	T, °C	P, MPa	T, °C	P, MPa	T, °C	P, MPa	T, °C	P, MPa	T, °C	P, MPa	T, °C
0.1	8.5	22	16.3	17	21.0	23	15.0	20	10.0	20	10.0	18	9.8
32	8.3	52	18.6	25	22.4	53	20.0	49	11.5	50	11.6	33	12.0
83	8.2	97	21.8	60	26.2	91	24.1	82	13.3	93	15.0	58	14.3
115	9.9	155	26.3	103	30.3	149	29.0	127	15.2	130	17.0	91	16.8
123	10.0	210	29.3	150	34.9	214	32.9	232	17.4	172	19.4	145	19.1
142	11.4	255	31.5	203	38.5	278	35.7	176	20.0	210	21.3	193	2.01
150	11.6	313	34.3	228	40.2	357	38.2	296	21.8	260	24.5	291	23.6
177	12.7	363	36.7	253	41.5	420	40.1	358	23.0	323	27.5	403	25.0
214	14.4	420	39.0	305	43.5	469	41.3	405	23.7	380	29.2	404	25.0
367	19.0	470	41.4	363	45.6	535	42.7	446	25.0	440	31.0	493	26.0
431	20.9	515	43.5	426	48.1	590	43.4	500	25.7	475	31.6	581	26.0
485	22.2	570	44.9	492	50.3	627	43.8	548	26.0	534	33.0	700	24.8
545	23.8	622	46.5	560	51.7	661	44.4	558	26.6	594	34.0	816	23.9
569	24.6	650	47.2	621	53.0	701	44.4	565	26.8	655	35.6	850	25.2
638	26.2	703	47.8	676	53.8	754	44.4	570	27.0	694	36.6	923	28.2
705	27.3	740	48.5	750	54.7	809	44.5	586	27.2	736	37.5		
808	28.8	780	49.2	786	55.2			593	27.4	810	38.0		
		820	49.6	806	55.3			632	28.3			m-stab 1	
								658	29.2			487	8.0
m-stab								683	30.0	m-stab		580	13.4
164	8.6							706	30.4	706	36.0	695	19.8
193	10.8							735	30.2	718	35.6	700	19.6
224	11.9							770	30.1	735	35.7	778	22.1
259	14.5							800	30.1	764	35.8	787	22.8
300	15.7									794	35.4		
												m-stab	
												849	22.9
												921	22.9

m-stab metastable parts of the decomposition curves

increase in the atomic size of help gases from He to Xe. Most probably, this regularity is caused by the improvement of the spatial conformity between the atom of a help gas and the D-cavity occupied by it. The second reason is an increase in the energy of Van der Waals guest–host interactions in this sequence. The situation observed in the systems with cross-linked tetrabutylammonium polyacrylate (Fig. 2) has some essential differences from the former one. Similarly to the systems with THF, the addition of a help gas causes an increase in the temperature of decomposition of double hydrates in comparison with the hydrates of pure TBAPA within the whole pressure range investigated. However, the order or the mutual arrangement of decomposition curves is different. The formation of the double hydrate of krypton with cross-linked tetrabutylammonium polyacrylate gives a higher decomposition temperature of the formed double hydrates than that for the case when the double hydrate with xenon is formed. In our opinion, this is explained by the fact that the vacant *D*-cavities are distorted in cross-linked tetrabutylammonium polyacrylate because of (1) the presence of cross-linking groups in the structure of the hydrate, and (2) framework distortions which are necessary to include a polymeric molecule in the framework. The Van der Waals diameter of xenon atom is larger than that of krypton atom. As a result, in order to insert a xenon atom into such a cavity, the deformed *D*-cavity should be somewhat stretched, which is disadvantageous from the point of view of energy. This decreases the temperature of decomposition of the double hydrate in comparison with the hypothetic

situation of non-deformed *D*-cavities. At the same time, insertion of a smaller krypton atom into the deformed *D*-cavity stabilizes it but does not require any deformation of the framework. As a result, gain in the free energy of formation of the double hydrate for the system with krypton exceeds that for the system with xenon.

One can see in Fig. 2 that at low pressures (about 22 MPa) the angle of inclination to the abscissa axis is larger for the curve of decomposition of the system with argon than that for the system with xenon, that is, under these conditions $(\partial T/\partial P)_{Ar} > (\partial T/\partial P)_{Xe}$. According to Clausius–Clapeyron equation,

$$\frac{dT}{dP} = \frac{T\Delta V}{\Delta H}$$

where ΔH is change of enthalpy during phase transition; ΔV is change of volume during phase transition. Temperatures of hydrate decomposition for both systems at a pressure of 22 MPa are close to each other: 16.3 and 15.0 °C (see Table 1). Enthalpies of formation/decomposition of double hydrates should be close, too, since the xenon atom gets inserted into the deformed *D*-cavity with its stretching; as the first approximation, the enthalpies can be accepted to be identical. If this is the case, $\Delta V_{Ar} > \Delta V_{Xe}$. This inequality is fulfilled only in the case if the degree of filling the *D*-cavities with argon atoms is higher than that with xenon atoms in the systems under consideration, other conditions being kept the same. This conclusion is in agreement with the general considerations suggesting that the deformation of *D*-cavities causes a decrease in the degree of their filling with large xenon atoms due to the necessity to stretch the cavities during filling. However, while pressure increases, the degree of filling *D*-cavities in both systems should tend to a definite common limit, which finally is likely to result in the higher decomposition temperature for the system with xenon than the decomposition temperature of the system with argon. A similar situation is observed also in the case of double hydrates with helium and neon (Fig. 2). The atoms of these gases certainly can get included into the D-cavities of the hydrate. Assuming that single filling of the cavities occurs in both cases, we cannot explain the observations. It is most probable that somewhat smaller size of the helium atom in comparison with neon (Van der Waals diameters of helium and neon are $d_{He} = 2.8$ Å and $d_{Ne} = 3.0$ Å [21]) allows multiple filling of D-cavities with helium atoms. This provides the higher stability of the double hydrate with helium.

Authors admit the debatable character of the above considerations. It is necessary to carry out further investigations involving structural and physicochemical methods.

Acknowledgements This work was financially supported by the Integration project of the Presidium of SB RAS No 62.

References

1. Jeffrey, G.A.: Hydrate inclusion compounds. In: Atwood, J.L., Davies, J.E.D., MacNicol, D.D., Vogtle, F. (eds.) Comprehensive Supramolecular Chemistry, vol. 6, pp. 757–788. Pergamon Press, Oxford (1996)
2. Dyadin, Y.A., Udachin, K.A.: Clathrate polyhydrates of peralkylonium salts and their analogs. J. Struct. Chem. **28**(3), 394–432 (1987)
3. Bogatyryov, V.L.: Clathrate-forming ion exchangers. In: Muraviev, D., Gorshkov, V., Warshawsky, W. (eds.) Ion Exchange, vol. 1, p. 223. Marcel Dekker, New York (1998)
4. Terekhova, I.S., Bogatyryov, V.L., Dyadin, Yu.A.: Clathrate hydrates of cross-linked tetraisoamylammonium polyacrylates. J. Supramol. Chem. **2**, 393–399 (2002)
5. Nakayama, H.: Hydrates of organic compounds. XIII. The confirmation of the formation of clathrate-like hydrates of tetrabutylammonium and of tetraisopentylammonium polyacrylates. Bull. Chem. Soc. Jpn. **60**, 2319–2326 (1987)
6. Bella, J., Brodsky, B., Berman, H.: Hydration structure of a collagen peptide. Structure **3**(9), 893–906 (1995)
7. Nakasako, M.: Structural characteristics in protein hydration investigated by cryogenic X-ray crystal structure analyses. J. Biolog. Phys. **28**, 129–137 (2002)
8. Shataeva, L.K., Kuznetsova, N.N., El'kin, G.E.: Karboxyl'nye kationity v biologii (The use of Carboxylic Cation-Exchange Resins in Biology). Nauka, Leningrad (1979). (in Russian)
9. Chapoy, A., Anderson, R., Tohidi, B.: Low pressure molecular hydrogen storage in semi-clathrate hydrates of quaternary ammonium compounds. J. Am. Chem. Soc. **129**, 746–747 (2007)
10. Skiba, S.S., Terekhova, I.S., Larionov, E.G., Manakov, A.Y.: Incorparation of gas molecules into the frameworks of clathrate hydrates of ion-exhange resins in tetraalkylammonium form. Mendeleev Commun. **18**, 126–127 (2008)
11. Terekhova, I.S., Manakov, A.Yu., Feklistov, V.V., Dyadin, Yu.A., Komarov, V.Yu., Naumov, D.Yu.: X-ray powder diffraction studies of polyhydrates of cross-linked tetraisoamylammonium polyacrylates. J. Incl. Phenom. Macro. Chem. **52**, 207–211 (2005)
12. Udachin, K.A., Ripmeester, J.A.: A polymer guest transforms clathrate cages into channels: the single-crystal X-ray structure of tetra-*n*-butylammonium polyacrylate hydrate, nBu$_4$NPA·40 H$_2$O. Angew. Chem. Int. Ed. **38**(13/14), 1983–1984 (1999)
13. Soldatov, D.V., Suwinska, K., Terekhova, I.S., Manakov, A.Y.: Structural study of hydrate compounds of polyacrylate resins in tetraisoamylammonium form. crystal structure of a clathrate hydrate of linear polyacrylate in tetraisoamylammonium form. J. Struct. Chem. **49**(4), 712–718 (2008)
14. Glew, D.N., Mak, H.D., Rath, N.S.: Aqueous non-electrolyte solutions: Part VII. Water shell stabilization by interstitial non-electrolytes. In: Covington, A.K., Jones, P. (eds.) Hydrogen-Bonded Solvent Systems, pp. 185–193. Taylor & Francis Ltd, London (1968)
15. Dyadin, Y.A., Larionov, E.G., Manakov, A.Y., Zhurko, F.V.: Double clathrate hydrate of tetrahydrofuran and xenon at pressures up to 15 kbar. Mendeleev Commun. **2**, 80–81 (1999)
16. Dyadin, A.Yu., Larionov, E.G., Mirinskij, D.S., Mikina, T.V., Aladko, E.Ya., Starostina, L.I.: Phase diagram of the Xe-H$_2$O system up to 15 kbar. J. Incl. Phenom. **28**, 271–285 (1997)
17. Dyadin, Yu.A., Larionov, E.G., Mikina, T.V., Starostina, L.I.: Clathrate hydrate of xenon at high pressure. Mendeleev Commun. **6**, 44–45 (1996)
18. Dyadin, A.Yu., Zelenin, Yu.M., Bezuglov, S.G., Bondaryuk, I.V.: Clathrate hydrates and phase diagram of the system water-

acetone under pressure to 10 kbar. Izv Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk **7**, 70 (1978)
19. Larionov, E.G., Manakov, A.Y., Zhurko, F.V., Dyadin, Y.A.: Double clathrate hydrate CS-II at pressures up to 15 kbar. J. Struct. Chem. **41**(3), 476–482 (2000)
20. Larionov, E.G., Zhurko, F.V., Dyadin, Y.A.: Gas-hydrate packing and stability at high pressures. J. Struct. Chem. **43**(6), 985–989 (2002)
21. Batsanov, S.S.: Atomic radii of elements. Zhurnal Neorganicheskoi Khimii **36**(12), 3015–3047 (1991)