

New data on phase diagram and clathrate formation in the system water–isopropyl alcohol

L. S. Aladko · A. Yu. Manakov · A. G. Ogienko ·
A. I. Ancharov

Received: 23 July 2008 / Accepted: 1 September 2008 / Published online: 17 September 2008
© Springer Science+Business Media B.V. 2008

Abstract The phase diagram of the binary system isopropyl alcohol–water was investigated by means of differential thermal analysis and powder X-ray diffraction. Two incongruently melting polyhydrates with the compositions close to the molar ratio of isopropanol to water 1:5 were found. The melting point of one of the polyhydrates is -49.6 °C, the melting point of the second one is within the range -38.8 to -30.6 °C. Assumptions concerning the structure of each compound were made on the basis of powder X-ray diffraction data.

Keywords Isopropyl alcohol · Hydrate · Phase diagram · Binary system · X-ray powder diffraction

Introduction

Clathrate hydrates of small organic molecules (amines, alcohols, salts of quaternary ammonium bases) acting as guests exhibit a surprising variety of structural types, which makes them interesting objects for supramolecular chemistry [1, 2]. The majority of these guests form several polyhydrates each, the hydrates being of different

compositions; they may be true clathrates (tert-butyl amine [3]), semi-clathrates (hydrates of many amines, considered in detail in [1, 2]; most likely, clathrate hydrates of ethanol belong to this group, too [4, 5]), layered compounds (hydrates of tert-butanol, piperazine, pinacol [6–8]). A peculiar group is formed by the so-called «ion hydrates» in which the salts of quaternary ammonium salts act as a guest [1, 2, 9]. A very informative procedure is the investigation of the phase diagrams of the corresponding binary systems with water (e.g. [9–11]), due to which it becomes possible to obtain comprehensive information, for example about the number of polyhydrates in the system and about the concentration ranges of their existence.

A factor bringing substantial complications into these investigations in the case of lower alcohols is the high viscosity of their aqueous solutions in the temperature range in which the formation of the majority of the corresponding polyhydrates occurs, that is, at low temperatures (e.g. [12]). In this case, the formation of hydrates occurs with large supercooling, vitrification of solutions is observed, the equilibrium gets established slowly. The same factors bring significant complications into obtaining the single crystals of alcohol polyhydrates for structural analysis. Due to these the polyhydrates of lower alcohols are rather poorly studied; in many cases the results obtained by different authors do not agree with each other. For example, the phase diagram of the system isopropyl alcohol–water was investigated in several groups [13–15]. The authors of [13] used the differential thermal analysis (DTA) and found two hydrates in this system: a stable one with the composition 1:3 (here and below alcohol:water ratio is given) melting incongruently at -37 °C and (presumably) a metastable one having the composition 1:5 and melting incongruently at -50 °C. Two groups of thermal effects observed by the authors of [13] at -100 °C

L. S. Aladko · A. Yu. Manakov · A. G. Ogienko (✉)
A.V. Nikolaev Institute of Inorganic Chemistry SB RAS,
Lavrentiev Ave., 3, Novosibirsk 630090, Russian Federation
e-mail: ogienko@che.nsk.su

A. Yu. Manakov · A. G. Ogienko · A. I. Ancharov
Novosibirsk State University, Pirogov Str., 2,
Novosibirsk 630090, Russian Federation

A. I. Ancharov
Institute of Solid State Chemistry SB RAS, Kutateladze 18,
Novosibirsk 630128, Russian Federation

and at $-108\text{ }^{\circ}\text{C}$ were related to eutectic equilibria; the latter one was considered as the metastable eutectics. In addition, monotectics with relatively small region of layering into two liquid phases with the upper critical dissolution temperature at $-12\text{ }^{\circ}\text{C}$ was discovered in the system at $-20\text{ }^{\circ}\text{C}$. Only one hydrate having the composition 1:5 (m.p. = $-53.2\text{ }^{\circ}\text{C}$) was found in a later work [14]; instead of monotectics with the layering region, a peculiarity on the liquidus curve was found. In the recent work [15], this system was investigated by means of the dielectric relaxation technique and differential scanning calorimetry. In general, the diagram presented by the authors is very similar to the result obtained in [13]; though the authors of [15] suggest the existence of only one polyhydrate having the composition within the range 1:5–1:6 (m.p. = $-41\text{ }^{\circ}\text{C}$), analysis of the dielectric relaxation data points to the clathrate nature of this hydrate. Double methane-alcohol clathrate hydrates with isopropanol and n-propanol were studied in [16–18].

In the present work we describe the new data on the polyhydrates of isopropyl alcohol and on the phase diagram of the corresponding system; these data were obtained by means of powder diffraction and differential thermal analysis.

Experimental

Isopropyl alcohol was used after triple distillation. The phase diagram was studied by differential thermal analysis (DTA); the experimental DTA curves were recorded in the course of heating. The reproducibility of temperature determination was $\pm 0.1\text{ }^{\circ}\text{C}$, the precision of the phase transition temperature determination was $\pm 0.2\text{ }^{\circ}\text{C}$, the heating rate of samples was $1\text{--}2\text{ }^{\circ}\text{C}/\text{min}$. The samples for DTA and powder X-ray diffraction measurements were prepared by mixing the weighted quantities of the components (isopropyl alcohol and water). The samples were frozen in liquid nitrogen and annealed for several hours at a temperature within the range -50 to $-70\text{ }^{\circ}\text{C}$.

X-ray diffraction studies were performed using synchrotron radiation at the fourth beamline of the VEPP-3 storage ring (Siberian synchrotron and terahertz radiation center, Budker Institute of Nuclear Physics SB RAS), at fixed wavelength of 0.3685 \AA [19]. The Debye-Scherrer scheme was applied. An imaging plate detector MAR345 (pixel dimension $100\text{ }\mu\text{m}$) was used to register the diffraction pattern. A fine-ground hydrate sample was placed in an aluminum cell with two foam-coated holes for the primary and diffracted beams. The cell was heated slowly from liquid nitrogen temperature; the diffraction patterns were recorded at several temperatures. Integration was carried out using FIT2D program [20], the distance from

the sample to the detector was determined using the diffraction patterns of a reference substance (NaCl, the distance was about 346 mm). Location of reflections, indexing trials, refinement of unit cell parameters and development of model diffraction patterns were carried out with the program FullProf [21].

Results and discussion

The phase diagram of the system isopropyl alcohol–water, composed on the basis of the data obtained in the present work by means of DTA and powder diffractometry, is presented in Fig. 1. The following designations will be used when discussing the results: i_{th} is ice, l_1 and l_2 are liquid phases (at a temperature above $-10\text{ }^{\circ}\text{C}$ $l_1 = l_2$), h_1 and h_2 are the corresponding hydrates, s is solid isopropanol. Our data on liquidus curves and the line of monotectic equilibrium observed at the temperature of $-20.3\text{ }^{\circ}\text{C}$ il_1l_2 are in good agreement with the data reported in [13] and will not be discussed further. Within the temperature range -30 to $-50\text{ }^{\circ}\text{C}$, three groups of thermal effects were clearly distinguished: at -30.6 , -38.8 and $-49.6\text{ }^{\circ}\text{C}$; initially they were explained as peritectic lines of decomposition of three hydrates existing in this system; further investigation compelled one to bring changes to this model. Two lines at -95.5 and $-97.8\text{ }^{\circ}\text{C}$ are exhibited at low temperatures, which satisfactorily agrees with the data on eutectic lines reported in [13–15]. The occurrence of

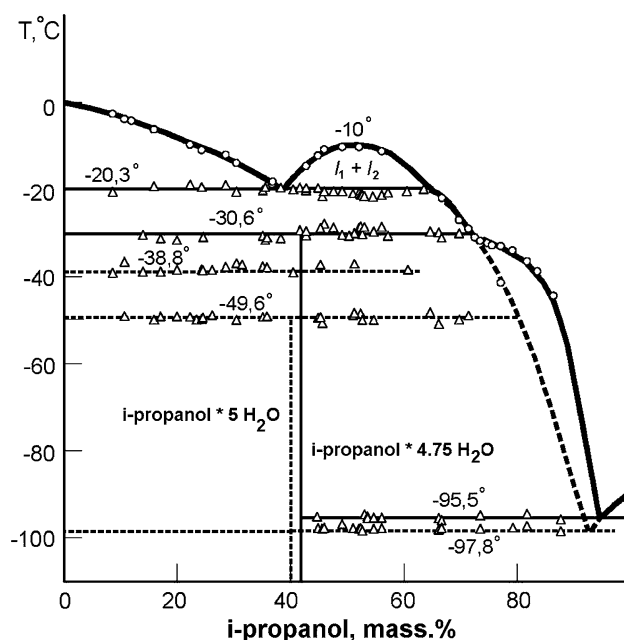


Fig. 1 Phase diagram of water–isopropyl alcohol system. The marks near the vertical lines correspond to supposed isopropanol:water molar ratio in corresponding hydrates

eutectic effects was successfully followed up to the point with isopropanol concentration of 45 mass%.

The above-mentioned high viscosity of isopropanol solutions (especially concentrated ones), their trend to become supercooled and vitrification, slow establishment of equilibrium caused the impossibility of reliable determination of hydrate formation in the system by composing Tammann's triangles. However, in all the cases the maximal values of the corresponding thermal effects were within the isopropanol concentration range 35–55 mass%. In the region of the high isopropanol content in solution, as a rule, thermal effects at -49.6 °C were substantially smaller than the effects at -30.6 or -38.8 °C; in the region of low isopropanol concentrations the effects were comparable. Under the cyclic (5–10 cycles) temperature variation within the range -100 to -45 °C within the whole range of isopropanol concentrations the thermal effects at -49.6 °C decreased systematically till disappearance, that is, the hydrate melting at this temperature is most probably metastable within the whole concentration range. This result corresponds to the data reported in [13].

Only two kinds of polyhydrates were detected in the diffraction experiment in the system isopropanol–water (see below). In our opinion, the composition of both polyhydrates is close to 40 mass% isopropanol, that is, to the molar ratio isopropanol:water equal to 1:5. This is confirmed by a break of the line of eutectics (Fig. 1) and change of the hydrate structure which crystallizing in the system (see below). The results obtained by building up Tammann's triangles do not contradict this assumption. In future, basing on the data presented in this work, we will make an attempt to grow the single crystals of isopropanol hydrates and carry out detailed investigations of the structure of these hydrates; however, some assumptions concerning the nature of these compounds can be made right now.

The X-ray diffraction patterns of the frozen samples of isopropanol–water mixtures were recorded within the range 10–80 mass% of isopropanol within the temperature range from -196 to -20 °C. Total number of phases recorded by means of X-ray diffraction in the system was 4, the existence of diffuse peaks on the low-temperature powder diffraction patterns pointed to the presence of a certain amount of an amorphous phase (most probably glassy phase of isopropanol) under these conditions. The powder diffraction patterns of i_{h} and s phases (ice Ih and solid isopropanol, respectively) were identified by comparing with the patterns calculated using the data reported in [22, 23]. For solid isopropanol, the determined values were $a = 6.62$ Å, $b = 13.55$ Å, $c = 14.56$ Å, $\beta = 100.06^\circ$ at -99 °C (literature data: $a = 6.56$ Å, $b = 13.39$ Å, $c = 14.45$ Å, $\beta = 99.75^\circ$, temperature was not indicated). The unit cells of h_1 and h_2 phases were obtained by indexing the powder diffraction patterns. For h_1 hydrate, the

parameters of the cubic unit cell were close to $a = 12.56$ Å in all the cases; for h_2 hydrate, a tetragonal cell with $a = 6.40$ Å, $b = 11.16$ Å was discovered (temperature was always within the range -40 to -60 °C). Some numerical data concerning powder diffraction patterns of h_1 and h_2 hydrates are presented in Table 1. Let us consider the typical experiments in more detail.

Typical diffraction patterns of the annealed sample with 10, 20 and 30 mass% isopropanol are shown in Fig. 2. At temperatures below -50 °C, the sample is a mixture of ice and h_2 hydrate (we estimate the error for the temperature boundaries of hydrate existence determined by X-ray diffraction to be ± 5 °C). Within the temperature range -50 to -35 °C we have a mixture of ice and h_1 hydrate, above this temperature there is pure ice. For the samples with isopropanol content 40 mass% and more, the transformations are essentially different (Fig. 3). At low temperatures, the powder diffraction patterns of the annealed samples exhibit a satisfactory correspondence to the picture expected for hydrate h_1 . The diffraction peaks are broadened. Some peaks are shifted with respect to the expected positions, which may point to a decrease of the symmetry in comparison with the cubic one expected for h_1 hydrate (Table 1, compare data for 51.7 mass% of isopropanol at different temperatures). As we approach the melting point of h_1 , the quality of the powder diffraction patterns improves substantially; we believe this is due to the annealing of defects in the crystal framework of hydrate h_1 . In our opinion, in general the low-temperature samples can be described as a mixture of hydrate h_1 having an imperfect crystal framework, and (probably) an amorphous isopropanol. Within the temperature range -110 to -90 °C, the powder diffraction patterns exhibit the reflections of a phase which we identify as the solid isopropanol. This crystal phase disappears at the eutectics melting temperature. Within the temperature range -90 to -35 °C the diffraction patterns correspond to the picture expected for h_1 hydrate, sometimes with the admixture of h_2 phase (Fig. 4). Only ice Ih is present in the system above -35 °C.

For non-annealed samples, the transformations occur in a more complicated manner. At the temperature of liquid nitrogen the only crystalline phase is ice Ih. Most probably, isopropanol is amorphous. At low concentrations of isopropanol hydrate h_2 start to form at temperature about -100 °C. At concentrations above 40 mass% of isopropanol its crystallization occurs near -100 °C; after melting of the crystal isopropanol (above the eutectic temperature) a slow formation of hydrate h_2 starts; it gets transformed into h_1 at a temperature above -50 °C. This observation allows us to interpret the appearance of additional eutectics in the system at -97.8 °C as the eutectic equilibrium of solid isopropanol, ice and liquid; the equilibrium is metastable with respect to the polyhydrate.

Table 1 Experimental and calculated values of **d** for some experiments

h₁	h₁, a = 12.57 Å <i>t</i> = −68 °C (51.7 mass%)		h₁, a = 12.55 Å <i>t</i> = −41 °C (51.7 mass%)		h₁, a = 12.57 Å h_h, a = 4.52 Å, c = 7.37 Å <i>t</i> = −43 °C (20.0 mass%)		h₂	h₂, a = 6.40 Å, c = 11.16 Å h_h, a = 4.51 Å, c = 7.37 Å <i>t</i> = −62 °C (20.0 mass%)	
	<i>hkl</i>	d_{obs.}	d_{calc.}	d_{obs.}	d_{calc.}	d_{obs.}		d_{calc.}	<i>hkl</i>
100	12.508	12.566	12.534	12.555	–	12.566	010	–	6.403
110	8.802	8.886	8.900	8.878	–	8.886	002	5.568	5.579
111	7.155	7.254	7.251	7.249	7.264	7.254	011	–	5.554
200	–	6.283	–	6.277	–	6.283	110	–	4.528
120	5.600	5.619	5.616	5.615	5.623	5.619	012	4.204	4.207
211	5.177	5.131	–	5.125	–	5.131	111	–	4.195
220	4.482	4.443	–	4.439	–	4.443	112	3.514	3.516
221, 300	4.176	4.188	4.187	4.185	4.192	4.188	013	3.216	3.216
130	3.950	3.974	3.969	3.970	–	3.974	020	–	3.201
311	–	3.789	–	3.785	–	3.789	021	–	3.077
222	3.636	3.628	3.622	3.624	–	3.628	113	2.870	2.874
230	3.493	3.485	3.481	3.482	–	3.485	120	–	2.863
231	3.362	3.358	3.354	3.355	3.359	3.358	004	–	2.790
400	3.130	3.142	3.138	3.139	3.142	3.142	002	2.778	2.777
140, 322	3.026	3.048	3.043	3.045	3.047	3.048	121	–	2.774
330, 411	2.920	2.962	2.958	2.959	2.962	2.962	014	2.551	2.558
331	–	2.883	2.876	2.880	2.882	2.883	122	–	2.547
240	2.820	2.810	2.805	2.807	2.809	2.810	023	–	2.426
241	2.755	2.742	2.738	2.740	2.743	2.742	114	2.374	2.375
332	2.688	2.679	2.675	2.677	–	2.679	123	–	2.269
422	2.624	2.565	–	2.563	–	2.565	220	2.260	2.264
340, 500	2.515	2.513	2.508	2.511	2.509	2.513	221	–	2.219
150, 341	2.468	2.464	2.460	2.462	2.466	2.464	030	–	2.134
333, 511	2.370	2.418	2.415	2.416	–	2.418			
250, 342	2.346	2.333	2.328	2.331	2.324	2.333			
251	2.302	2.294	2.291	2.292	–	2.294			
440	2.264	2.221	–	2.219	–	2.221			
441, 522	2.198	2.188	–	2.186	–	2.188			
433, 530	2.161	2.155	2.150	2.153	2.155	2.155			
351		2.124		2.122	–	2.124			
100 (Ih)					3.923	3.918	100 (Ih)	3.912	3.909
002 (Ih)					3.683	3.684	002 (Ih)	3.688	3.687
101 (Ih)					3.468	3.460	101 (Ih)	3.452	3.454
102 (Ih)					2.683	2.684	102 (Ih)	2.683	2.682
110 (Ih)					2.262	2.262	110 (Ih)		2.257

Types of hydrate, unit cell parameters, temperatures of X-ray experiment and concentration of the solution which was taken in the experiment are shown in the table. X-ray data for impurity of ice Ih are given in the bottom of the table

All the powder diffraction patterns of hydrate **h₁** obtained from solutions with different concentrations are indexes in the cubic unit cell with the parameter $a = 12.56 \pm 0.01$ Å (temperature −40 to −60 °C, in this case scattering characterizes the range of values obtained in refining the diffraction patterns of different samples). No systematic absence of reflections is observed, which allows

us to assume either a low-symmetry cubic cell or even lower symmetry. It is known from the data reported in [15] that this polyhydrate most probably has the clathrate nature. In this case, in the unit cell dimensions, the **h₁** hydrate is most close to the hydrates of cubic structure I (CS-I, $Pn\bar{3}m$, characteristic cell parameter $a = 12$ Å). It is usually accepted that the maximal size of guest molecules

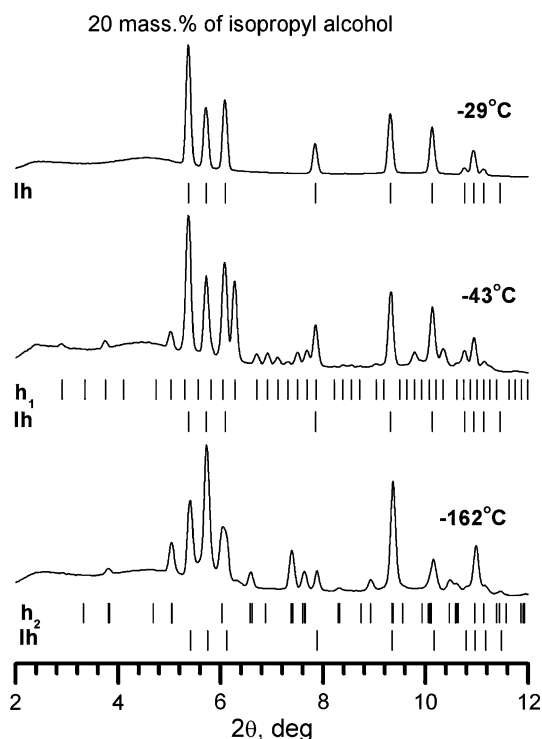


Fig. 2 Powder diffraction patterns of the annealed samples of water–isopropyl alcohol mixtures with 20 mass% of isopropyl alcohol taken at different temperatures

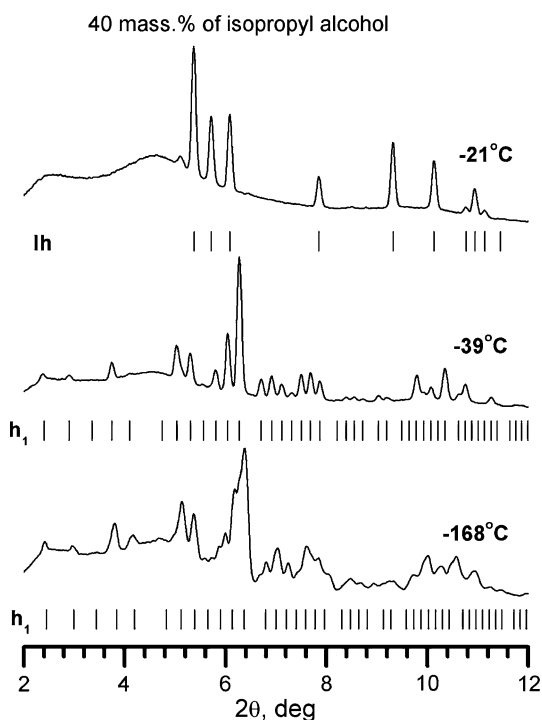


Fig. 3 Powder diffraction patterns of the annealed samples of water–isopropyl alcohol mixtures with 40 mass% of isopropyl alcohol taken at different temperatures

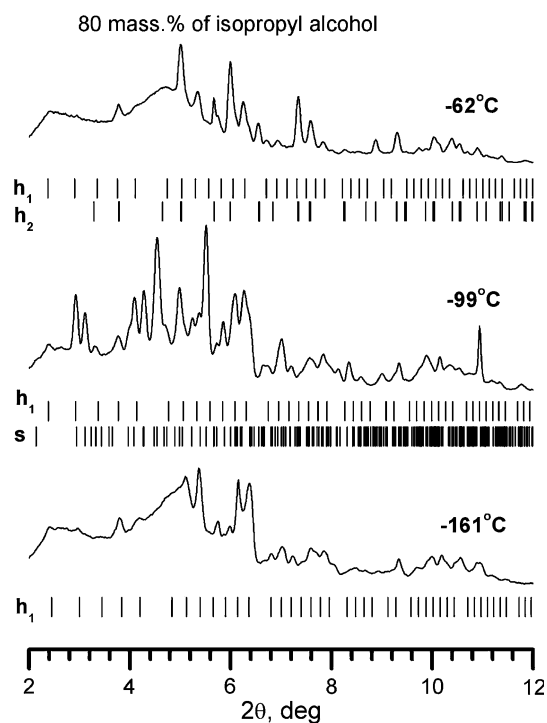


Fig. 4 Powder diffraction patterns of the annealed samples of water–isopropyl alcohol mixtures with 80 mass% of isopropyl alcohol taken at different temperatures

able to fit into the cavities of such a framework approximately corresponds to cyclopropane and ethylene oxide. Inclusion of hydrophilic part of the guest molecule into the hydrate framework makes possible inclusion of larger guests, e.g. occupation of large cavities of CS-I by butyl radicals of tetrabutylammonium cation is possible [24]. During the formation of the hydrate of isopropanol, its hydroxyl groups can be incorporated into the hydrate framework (similarly to the case of ethanol hydrate [4, 5]), which simplifies the arrangement of such a large molecule in the hydrate cavities of CS-I. A substantial extension of the framework and lowering the symmetry of hydrate h_1 can be explained similarly. The same situation, probably, takes place in the hydrate of dimethylamine [25]. It should also be stressed that there is partial similarity between the intensities of reflections of hydrate h_1 and a typical hydrate of CS-I (Fig. 5). It is well known that the ideal stoichiometry of the hydrate of cubic structure I with all the cavities filled up corresponds to $G \cdot 5.75H_2O$ (G is a guest molecule). In the case of a hydroxyl group displaces one water molecule from the framework, the stoichiometry will be $G \cdot 4.75H_2O$, which is close to the above estimation. It is interesting to note that the isopropanol–water system show several general features characteristic of the systems in which polyhydrates of organic molecules or polyhydrates of some ionic compounds form. First of all, several hydrates with different structures form in narrow range of

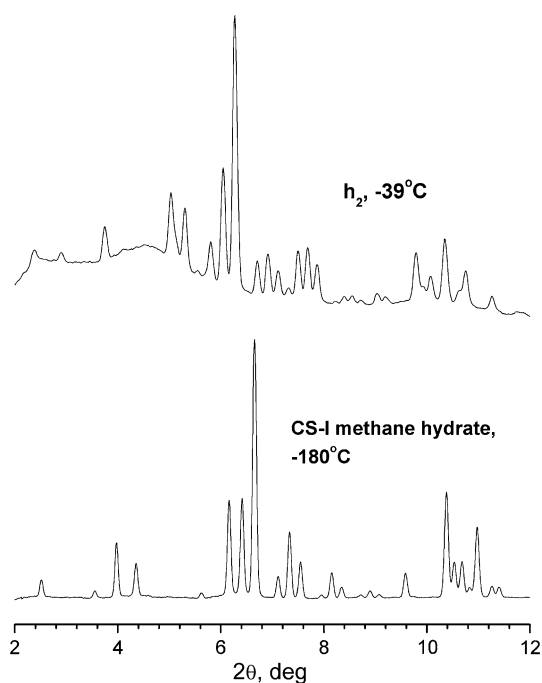


Fig. 5 Comparison of the powder diffraction patterns of the hydrate **h₂** and typical powder diffraction pattern of the cubic structure-I methane hydrate

guest concentrations; a lot of similar examples may be found in literature [1, 2, 9, 10, 26]. The second feature is coexistence of polyhydrates with different organization of water molecules in the same system (water framework with cavities, alternation of water and guest layers, water chains or clusters, e.g. [24, 27–29]).

It is difficult to explain the existence of two sets of thermal effects in the phase diagram that can be related to melting of **h₁** hydrate (Fig. 1). Either one or another effect was exhibited in thermograms, which does not allow us to explain the lower group of effects by the polymorphous transformation of hydrate **h₁**. We assume that the most probable reason of the appearance of a group of effects at $-38.8\text{ }^{\circ}\text{C}$ is the formation of the metastable crystal modification of hydrate **h₁** with close composition and unit cell parameters (for example, due to the variable occupancy of small cavities by isopropanol molecules).

Speaking of hydrate **h₂**, we may cautiously assume that its crystal framework has a layered character. It is known from [2, 7, 8, 30] that a tetragonal cell with the unit cell parameter a close to 6.4 \AA and widely varying parameter c is characteristic of layered hydrates composed of folded water layers of water pentagons in which often the hydrophilic groups of the guest are inserted; the manners of guest molecule inclusion are diverse, which determines the variations of parameter c within a broad range. The idealized stoichiometry of these hydrates corresponds to $\text{G}\cdot 6\text{H}_2\text{O}$, taking into account the displacement of one

water molecule by the hydroxyl group of the guest molecule— $\text{G}\cdot 5\text{H}_2\text{O}$.

Thus, the version of the phase diagram proposed by us for the system isopropanol–water (Fig. 1) is most close to the data of the oldest of available works [13]; we succeeded in achieving a good logical agreement between the data obtained using different methods. According to our data, two polyhydrates are formed in the system; the hydrate numbers of both of them are close to 5. Interpretation of powder diffraction patterns allowed us to make reasonable assumptions concerning the structure of these hydrates.

Acknowledgements This work was supported by the Integration Project No. 43 of the Siberian Branch of RAS, Project CRDF Y5-C-08-01, CRDF Y5-C-08-09, Projects DSP.2.2.2.3.16033, DSP.2.2.2.3.16035 program “Development of scientific potential of the higher school”.

References

- Jeffrey, G.A.: Hydrate inclusion compounds. In: Atwood, J.L., Davies, J.E.D., MacNicol, D.D. (eds.) *Inclusion Compounds*, vol. 1, pp. 135–190. Academic Press, London (1984)
- 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. 757–789. Elsevier Science Ltd., Oxford (1996)
- McMullan, R.K., Jeffrey, G.A., Jordan, T.H.: Polyhedral clathrate hydrates. XIV. The structure of $(\text{CH}_3)_3\text{CNH}_2 \cdot 9\frac{3}{4}\text{H}_2\text{O}$. *J. Chem. Phys.* **47**, 1229–1234 (1967). doi:10.1063/1.1712073
- Boutron, P., Kaufmann, A.: Metastable states in the system water–ethanol. Existence of a second hydrate; curious properties of both hydrates. *J. Chem. Phys.* **68**(11), 5032–5041 (1978). doi:10.1063/1.435619
- Jeffrey, G.A., McMullan, R.K.: Clathrate hydrates. *Prog. Inorg. Chem.* **8**(43), 43–108 (1967). doi:10.1002/9780470166093.ch2
- Schwarzenbah, D.: Structure of piperazine hexahydrate. *J. Chem. Phys.* **48**, 4134–4141 (1968). doi:10.1063/1.1669751
- Kim, H.S., Jeffrey, G.A.: Crystal structure of pinacol hexahydrate. *J. Chem. Phys.* **53**, 3610–3615 (1970). doi:10.1063/1.1674539
- Mootz, D., Staben, D.: Die hydrate von tert-butanol: Kristallstruktur von $\text{Me}_3\text{COH}\cdot 2\text{H}_2\text{O}$ und $\text{Me}_3\text{COH}\cdot 7\text{H}_2\text{O}$. *Z. Naturforsch.* **48b**, 1325–1330 (1993)
- Dyadin, Y.A., Udachin, K.A.: Clathrate polyhydrates of peralkylonium salts and their analogs. *J. Struct. Chem.* **28**, 394–432 (1987). (Translated from Russian *Zh. Strukt. Khim.* **28**, 75 (1987))
- Mootz, D., Seidel, R.: Polyhedral clathrate hydrates of a strong base: phase relations and crystal structures in the system tetramethylammonium hydroxide–water. *J. Incl. Phenom.* **8**, 139–157 (1990)
- Udachin, K.A., Lipkowski, J.: Channel polyhydrate $(\text{C}_2\text{H}_5)_4\text{NF}\cdot 11\text{H}_2\text{O}$. *Mendeleev Commun.* 92–93 (1996). doi:10.1070/MC1996v006n03ABEH000593
- Angell, C.A.: Liquid fragility and the glass transition in water and aqueous solutions. *Chem. Rev.* **102**, 2627–2650 (2002). doi:10.1021/cr000689q
- Rosso, M.J.-C., Carbonnel, L.: Le systeme eau–propanol₂. *C. R. Acad. Sci. Paris* **268**, 1012–1015 (1969)
- Ott, J.B., Goates, J.R., Waite, B.A.: (Solid + liquid) phase equilibria and solid-hydrate formation in water + methyl,

- +ethyl, +isopropyl, and tertiary butyl alcohols. *J. Chem. Thermodyn.* **11**, 739–746 (1979). doi:[10.1016/0021-9614\(79\)90109-5](https://doi.org/10.1016/0021-9614(79)90109-5)
15. Murthy, S.S.N.: Detailed study of ice clathrate relaxation: evidence for the existence of clathrate structures in some water-alcohol mixtures. *J. Phys. Chem. A* **103**, 7927–7937 (1999). doi:[10.1021/jp990518t](https://doi.org/10.1021/jp990518t)
16. Østergaard, K.K., Tohidi, B., Anderson, R., Todd, A.C., Danesh, A.: Can 2-propanol form clathrate hydrates? *Ind. Eng. Chem. Res.* **41**, 2064–2068 (2002). doi:[10.1021/ie010833d](https://doi.org/10.1021/ie010833d)
17. Chapoy, A., Anderson, R., Haghighi, H., Edwards, T., Tohidi, B.: Can n-propanol form hydrate? *Ind. Eng. Chem. Res.* **47**, 1689–1694 (2008). doi:[10.1021/ie071019e](https://doi.org/10.1021/ie071019e)
18. Maekawa, T.: Equilibrium conditions for clathrate hydrates formed from methane and aqueous propanol solutions. *Fluid Phase Equilib.* **267**, 1–5 (2008). doi:[10.1016/j.fluid.2008.02.006](https://doi.org/10.1016/j.fluid.2008.02.006)
19. Ancharov, A.I., Manakov, A.Y., Mezentsev, N.A., Tolochko, B.P., Sheromov, M.A., Tsukanov, V.M.: New station at the 4th beamline of the VEPP-3 storage ring. *Nucl. Instrum. Methods Phys. Res. A* **470**, 80–83 (2001). doi:[10.1016/S0168-9002\(01\)01029-4](https://doi.org/10.1016/S0168-9002(01)01029-4)
20. Hammersley, A.P.: Fit2D Program, 1987–2003. European Synchrotron Research Facility
21. Rodriguez-Carvajal, J.: FULLPROF: a program for Rietveld refinement and pattern matching analysis. In: Proceedings of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, p. 127, Toulouse, France (1990)
22. Rottger, K., Endriss, A., Ihringer, J., Doyle, S., Kuhs, W.F.: Lattice constants and thermal expansion of H₂O and D₂O ice Ih between 10 and 265 K. *Acta Crystallogr. B* **50**, 644–648 (1994). doi:[10.1107/S0108768194004933](https://doi.org/10.1107/S0108768194004933)
23. Cirkel, S.A., Boese, R.: The crystal structure of isopropanol. *Acta Crystallogr. A* **60**, s205 (2004)
24. Komarov, V.Y., Rodionova, T.V., Terekhova, I.S., Kuratieva, N.V.: The cubic superstructure-I of tetrabutylammonium fluoride (C₄H₉)₄NF·29.7 H₂O clathrate hydrate. *J. Incl. Phenom.* **59**, 11–15 (2007). doi:[10.1007/s10847-006-9151-9](https://doi.org/10.1007/s10847-006-9151-9)
25. McMullan, R.K., Jordan, T.H., Jeffrey, G.A.: Polyhedral clathrate hydrates. XII. The crystallographic data on hydrates of ethylamine, dimethylamine, trimethylamine, n-propylamine (two forms), iso-propylamine, diethylamine (two forms), and tert-butylamine. *J. Chem. Phys.* **47**(4), 1218–1222 (1967). doi:[10.1063/1.1712071](https://doi.org/10.1063/1.1712071)
26. Aladko, L.S., Dyadin, Y.A., Rodionova, T.V., Terekhova, I.S.: Effect of size and shape of cations and anions on clathrate formation in the system: halogenides of quaternary ammonium bases and water. *J. Mol. Liq.* **106**(2–3), 229–238 (2003). doi:[10.1016/S0167-7322\(03\)00111-9](https://doi.org/10.1016/S0167-7322(03)00111-9)
27. Udachin, K.A., Lipkowski, J.: Water-fluorine chains in (n-Bu)₄NF·5.5H₂O hydrate. *J. Supramol. Chem.* **2**, 449–451 (2002). doi:[10.1016/S1472-7862\(03\)00056-X](https://doi.org/10.1016/S1472-7862(03)00056-X)
28. Shimada, W., Shiro, M., Kondo, H., Takeya, S., Oyama, H., Ebinuma, T., et al.: Tetra-n-butylammonium bromide-water (1/38). *Acta Crystallogr. C* **61**(2), o65–o66 (2005). doi:[10.1107/S0108270104032743](https://doi.org/10.1107/S0108270104032743)
29. Lipkowski, J., Komarov, V.Y., Rodionova, T.V., Dyadin, Y.A., Aladko, L.S.: The structure of tetrabutylammonium bromide hydrate (C₄H₉)₄NBr·2.5H₂O. *J. Supramol. Chem.* **2**, 435–439 (2002)
30. Manakov, A.Y., Voronin, V.I., Kurnosov, A.V., Teplych, A.E., Komarov, V.Y., Dyadin, Y.A.: Structural investigations of argon hydrates at pressures up to 10 kbar. *J. Incl. Phenom.* **48**, 11–18 (2004)