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Structure and properties of congruent melting 18-crown-6 crystalline hydrates

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ABSTRACT

Crystallographic characteristics of congruent melting 18-crown-6 crystalline hydrates were specified using X-ray structure analysis. Melting enthalpies of 18-crown-6 tetra- and hexahydrates have been determined; melting points of these compounds have been specified. Liquidus of 18-crown-6–water system has been calculated in the concentration range $x_{H_2O} = 0.750–0.935$ by using the received data and known thermodynamic properties of the solution.

1. Introduction

Crown ethers are widely applied in supramolecular and coordination chemistry due to the unusual structure of resulting complexes and various types of generating bonds. Hydration plays a major role in the stabilization of 18-crown-6 (18C6) complexes, that is why many studies of 18-crown-6 crystalline hydrates structures and phase equilibria in the H_2O–18C6 system have been reported over the years [1–6]. The phase diagram of the system 18-crown-6–water has been studied since 1989 when the work [2] was published. Mixtures of 18-crown-6 with water have been investigated by Raman spectroscopy in a temperature range −195 to 40 °C (78–313 K) in a solid and liquid state. The analysis of the Raman spectra shows the formation of congruent melting phase with the D_{3d} structure, which confirmed the earlier results of work [1]. The ratio of 18-crown-6 to water for this hydrate is assumed to be approximately 1:4–6 (melting point ∼24 °C). Phase diagram of the system 18-crown-6–water was specified later [4]. The analysis of the Raman spectra in combination with the examination of the liquidus curve of the 18-crown-6–water system shows the formation of at least four distinct hydrates. Almost at the same time the authors [5] established the formation of only three crystalline hydrates of the following composition: 1:6, 1:8.25 and 1:12; and the melting points of incongruent melting compounds were 1–1.5 °C higher than it was in paper [4]. In the work [6] according to DSC and X-ray structure analysis the existence of four binary hydrates of the 1:*N* (*N* = 4, 6, 8, and 12) were confirmed. Crystal structures for three of them were determined in work [6], and hexahydrate was described in detail in paper [3]. The results of processing the curves of differential thermal analysis (DTA) were summarized in the melting diagram of the system 18-crown-6–water with indicating of liquidus and solidus effects. Authors noted that anomalies were observed in DSC curves, which could not be explained. It may be one of the reason why there were not any data concerning to measuring accuracy of liquidus and solidus coordination. It was mentioned [6] that in general the liquidus was similar to that one in work [4]. Evidently, these data are more accurate nowadays and that is why first of all we took them into account by comparison the results of this work with the literature date.

This work was aimed to synthesize and identify congruent melting crystalline hydrates, to determine melting points and melting enthalpies of these compounds. In the literature date we could not find any information about thermodynamic properties of the complexes.

2. Experimental

2.1. Material

18-Crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) was supplied by «Reanal». To control the quality of this compound its melting point was measured by differential scanning calorimetry (DSC). It was found that the melting point is falling gradually

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Table 1
Crystal structure data and refinement results for **I** and **II**.

Compound	**I**		**II**	
	This work	[6]	This work	[3]
Bulk formula	$C_{12}H_{32}O_{10}$		$C_{12}H_{36}O_{12}$	
Molecular weight	336.38	372.41		
T, K	150	123	200	123
Crystal system	Monoclinic		Monoclinic	
Space group	$P2_1/c$		$P2_1/n$	
a, Å	7.5070(13)	7.484(8)	7.4713(6)	7.431(5)
b, Å	14.287(2)	14.26(1)	8.1116(6)	8.083(6)
c, Å	8.3904(15)	8.37(1)	17.0722(13)	17.02(1)
β,°	95.270(5)	95.1(1)	95.1350(10)	94.97(5)
V, Å^3	896.1(3)	890(2)	1030.49(14)	1018(1)
Z	2	2		
ρ_{calc}, g cm^{-3}	1.247	1.256	1.200	1.40
μ, cm^{-1}	1.08	–	1.07	1.10
θ limits,°	2.72–26.37	1.5–32.5	2.40–28.32	1.5–32.5
$T_{min/max}$	0.9531/0.9582	–	0.9585/0.9738	–
Total number of reflections/unique	5119/1832	3085/2350	6913/2562	–/2366
R_{int}	0.0275		0.0152	–
R_1 ($I > 2\sigma(I)$)	0.0485	0.040	0.0357	–
wR_2 ($I > 2\sigma(I)$)	0.1891	0.120	0.1317	–
R_1	0.0582		0.0439	–
wR_2	0.2075		0.1448	–

while it is keeping in a closed container. This effect can be related to high hygroscopicity of this compound. To remove the traces of water the reagent was placed in a desiccator, phosphorus pentoxide was used as a drying agent. 18-Crown-6 was keeping in desiccator at room temperature for 24 h and residual pressure of gases in the system was 10 Pa. Then the melting point of crown ether agreed well with the literature data (mp = 39.1 °C [7,8]). The standard recrystallization procedure from acetonitrile was used for additional purification of 18-crown-6 [9].

Distilled water was used to prepare all water solutions.

2.2. *Synthesis of crystalline hydrates*

2.2.1. *Tetrahydrate of 18-crown-6 (**I**)*

Mixture of 18-crown-6 and hyperstoichiometric quantity of distilled water was heated to 40 °C (313 K) with continuous stirring. We needed to use small excess of water because there is doubt about true hydrate composition [4,6]. Our structural analysis results confirmed data from the [6]. In addition, there were attempts to prepare compound from stoichiometric quantities of reagents but they were unsuccessful. After homogenization, solution was cooled rapidly prior to the beginning of crown tetrahydrate crystallization, and then the temperature was kept at 294–295 K. The formed crystals were separated by filtration.

2.2.2. *Hexahydrate of 18-crown-6 (**II**)*

Mixture containing stoichiometric amounts of 18-crown-6 and water was heated to 40 °C (313 K) with continuous stirring. After homogenization, solution was cooled rapidly prior to the beginning of crown hexahydrate crystallization. Reactive mixture was kept above incogruent melting point of dodeca- and octohydrates to avoid formation of higher order hydrates (294–295 K). The formed crystals were separated by filtration.

2.3. *Sample analysis*

The target crystalline hydrates of 18-crown-6 were investigated using X-ray structure analysis and differential scanning calorimetry (DSC).

2.3.1. *The X-ray diffraction study*

The X-ray diffraction study of crystalline hydrates **I** and **II** were carried out on a Bruker SMART APEX II diffractometer equipped with a CCD detector (graphite-monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å) according to a standard procedure [10]. A semiempirical correction was applied to absorption [11]. The structure of the compounds **I** and **II** were solved by direct methods [12] and refined in the full-matrix least-squares on F^2 [13] with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms on 18-crown-6 were positioned geometrically and refined using a riding model; those associated with the H_2O molecules were located on a difference map and not refined. Crystallographic parameters and details of structure refinement are listed in Table 1. The corresponding parameters received in works [3,6] are given for comparison.

2.3.2. *Differential scanning calorimetry*

Thermograms of the samples were obtained by DSC on a NETZSCH 204 F1 in a dry argon flow (10 ml/min) in the −10 to 40 °C (263–313 K) temperature range at a heating rate of 2 K/min in covered aluminum specimen containers ($V = 56$ mm^3, $d = 6$ mm). Each experiment was carried out at least in triplicate. The controlled cooling of the measuring cells was performed manually using a liquid-nitrogen cooling system. The temperature calibration of calorimeter was carried out against phase-transition points in references (C_6H_{12}, Hg, KNO_3, In, Sn, Bi, and CsCl; all 99.99% pure) according to the ISO/CD 11357-1 standard. The accuracy in temperatures and heats of processes in DSC curves was ±0.2 K and ±5.0%, respectively. Sample sizes in experiments were 5–10 mg. Samples were weighed on a SARTORIUS RESEARCH R 160P analytical balance with an accuracy of 1×10^{-2} mg. Software package NETZSCH Proteus Thermal Analysis was employed for experimental data processing. The temperature of phase transition was determined by T_{onset} (the temperature of the point of intersection of the inflectional tangent through the ascending peak slope with the interpolated baseline).[1] The enthalpy was defined as area between peak and interpolated baseline.Selected crystals were "tempered" before the experiment, cooling them in liquid-nitrogen.

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[1] Standart ISO 11357-1.

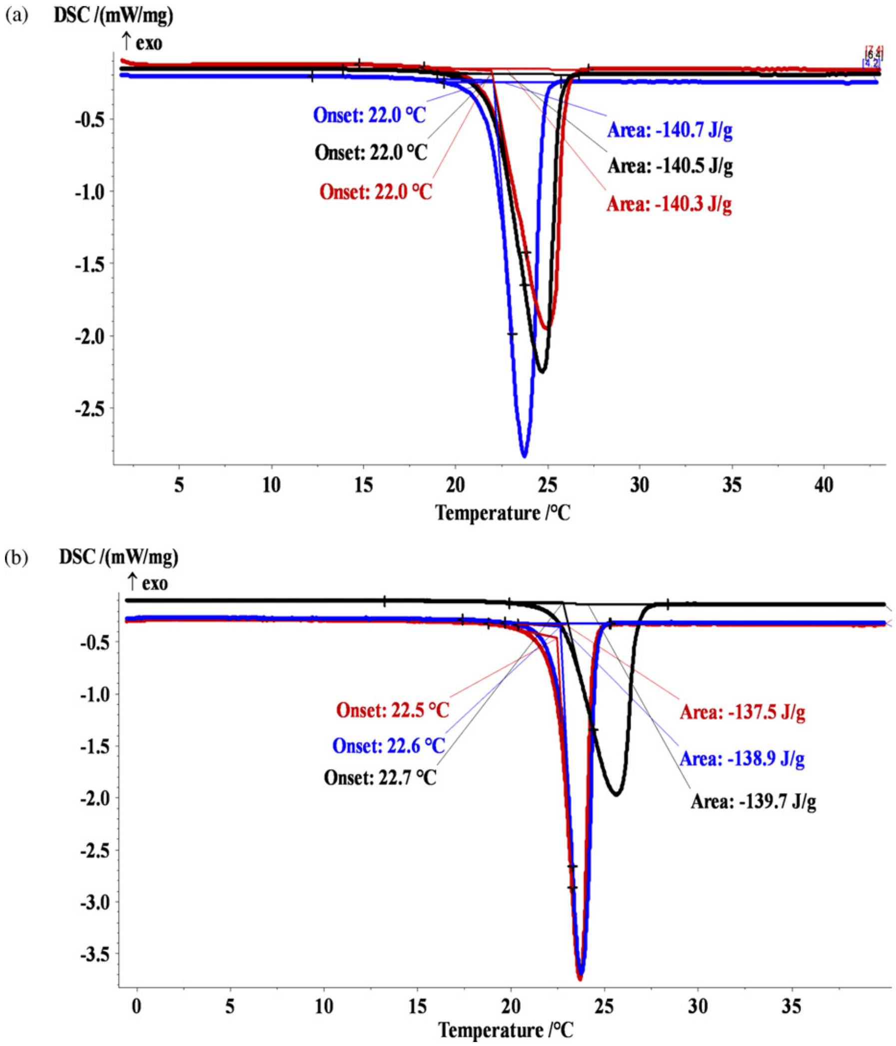

Fig. 1. DSC curves: (a) 18-crown-6 hexahydrate, (b) 18-crown-6 tetrahydrate. Measurement conditions: closed standard aluminum crucibles, heating rate 2 °C/min, flow of dry argon 10 ml/min.

Table 2
Characteristics of $C_{12}H_{24}O_6 \cdot nH_2O$ crystalline hydrates phase transition.

Hydrate	n	T_m °C	K	$\Delta_m H^\circ$ J g^{-1}	kJ mol^{-1}	$\Delta_m S$ J mol^{-1} K^{-1}
Tetrahydrate	4	22.6 ± 0.2	295.8 ± 0.2	138.7 ± 3.9	46.7 ± 1.3	157.9
Hexahydrate	6	22.0 ± 0.2	295.2 ± 0.2	140.5 ± 0.7	52.32 ± 0.26	177.3

Each crystal was placed into a crucible and cooled rapidly to −10 °C (263 K), thus preventing premature melting of crystalline hydrates. Then samples were heated to 40 °C (313 K) at a heating rate of 2 °C/min. To obtain more accurate results and provide better contact of the sample with cell bottom, cooling–heating cycle was repeated (cooling rate 1 K/min, heating rate 2 K/min). Fig. 1a and b shows some DSC curve of the samples **I**, **II** as an example. The melting point and the enthalpy of hydrates[2] fusion are listed in Table 2.

3. Calculation

Liquidus calculation of congruent melting compound was carried out using the method described at [14]. Equilibrium conditions of solution and congruent melting stoichiometric phase give a binding equation for enthalpy of compound fusion $\Delta_m H$ and liquidus coordinate x:

$$\Delta_m H = \frac{(x_0 - 4x)(x_0 - x)^2 T_m}{6x^2 (T_m - T)} \beta(x, T), \qquad (1)$$

where x_0—phase composition (mole fraction of the 2nd compound–water), x,T—liquidus coordinates, T_m—melting point of the compound. Function $\beta(x,T)$ is connected with relative chemical

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[2] The product of root-mean-square deviation and St. coefficient by confidence probability 0.95 is listed in Table 2 as a confidence interval of melting enthalpy's value.

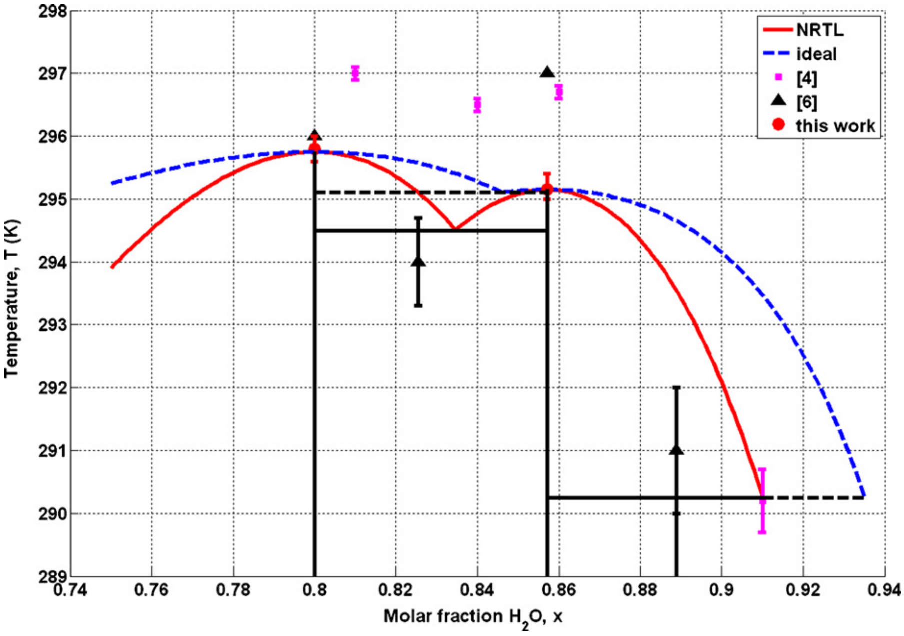

Fig. 2. Fragment of phase diagram of 18-crown-6–water system. Calculation results of liquidus line: ideal solution (dotted line), model NRTL (solid line); experimental data: squares – [4]; triangles – [6] (errors for the solidus line were estimated by averaging deviations of experimental points, which were obtained by digitizing the figure); circles – this work.

potentials of the components:

$$\beta(x,T)=\left(\frac{\partial(\Delta\mu_1)}{\partial x}\right)_T=-\frac{x}{1-x}\left(\frac{\partial(\Delta\mu_2)}{\partial x}\right)_T. \qquad (2)$$

Chemical potentials are defined by the Gibbs energy of mixing using well-known formulas:

$$\begin{aligned}\Delta\mu_1 &= G-x(\partial G/\partial x)_{p,T}-RT\ln(1-x)+\mu_1^{\mathrm{ex}}\\ &= RT\ln(1-x)+RT\ln\gamma_1, \qquad (3)\end{aligned}$$

$$\Delta\mu_2 = G+(1-x)(\partial G/\partial x)_{p,T}=RT\ln x+RT\ln\gamma_2. \qquad (4)$$

In case of ideal solution μ_1^{ex} and μ_2^{ex} are zero. In the NRTL model the activity coefficients are derived as [15]:

$$\ln\gamma_1=x^2\left(\frac{\tau_{21}G_{21}^2}{((1-x)+xG_{21})^2}+\frac{\tau_{12}G_{12}}{(x+(1-x)G_{12})^2}\right), \qquad (5)$$

$$\ln\gamma_2=(1-x)^2\left(\frac{\tau_{12}G_{12}^2}{(x+(1-x)G_{12})^2}+\frac{\tau_{21}G_{21}}{((1-x)+xG_{21})^2}\right), \qquad (6)$$

$$G_{ij}=\exp\left(-\alpha_{ij}\tau_{ij}\right),\quad \alpha_{ij}=\alpha_{ji} \qquad (7)$$

Taking into account the relationship between excess chemical potential of components and $\beta(x,T)$, it is possible to get the following equation:

$$\begin{aligned}\beta(x,T)=-\frac{RT}{1-x}+2RT\Bigg[&\frac{\tau_{21}G_{21}^2x}{(1+(G_{21}-1)x)^2}\left(1-\frac{(G_{21}-1)x}{1+(G_{21}-1)x}\right)\\ &+\frac{\tau_{12}G_{12}x}{(G_{12}+(1-G_{12})x)^2}\left(1-\frac{(1-G_{12})x}{G_{12}+(1-G_{12})x}\right)\Bigg] \qquad (8)\end{aligned}$$

Using the expression (1), we may obtain an equation that can be solved relative to the composition x or T when the second variable is desired and model parameters,melting point and enthalpy of compound fusion are known:

$$\begin{aligned}\Delta_m H =& \frac{RT(x_0-4x)(x_0-x)^2T_m}{6x^2(T_m-T)}\\ &\times\Bigg[-\frac{1}{1-x}+2\Bigg[\frac{\tau_{21}G_{21}^2x}{(1+(G_{21}-1)x)^2}\left(1-\frac{(G_{21}-1)x}{1+(G_{21}-1)x}\right)\\ &+\frac{\tau_{12}G_{12}x}{(G_{12}+(1-G_{12})x)^2}\left(1-\frac{(1-G_{12})x}{G_{12}+(1-G_{12})x}\right)\Bigg] \qquad (9)\end{aligned}$$

Thermadynamics of hexa- and tetrahydrate melting are estimated in the issue of this work, the numerical value of interaction parameters for water and 18-crown-6 were presented in a paper [16]:

$$\tau_{12}=\frac{-1033.48}{T},\quad \tau_{21}=\frac{-1530.34}{T}$$

$$\alpha=(0.35+0.0016(T-298.15))$$

Calculated liquidus fragment of 18-crown-6–H$_2$O system in the composition range 0.750–0.935 mole fraction of water is presented in Fig. 2. The solid line shows the results of calculation with non-ideal liquid phase (model NRTL), dotted line – in the assumption of ideal solution of components.

4. Results and discussion

According to the available literature data, it is possible to conclude that there are four hydrates of the composition 1:4, 1:6, 1:8 and 1:12 in the system water–18-crown-6. During the work two congruent melting crystalline hydrates **I** and **II** were synthesized and characterized with X-ray structure analysis.

In conformity with X-ray structure analysis the compound **I** is a solvate of 18-crown-6 with four molecules of water. Center of inversion is situated in the geometrical center of 18-crown-6 molecule. In a crystal water molecule (O(1w)) donate a hydrogen bonds each to crown ether atoms O(1) and O(3) (Fig. 3a and Table 3). At the same time each of two bridging water molecules

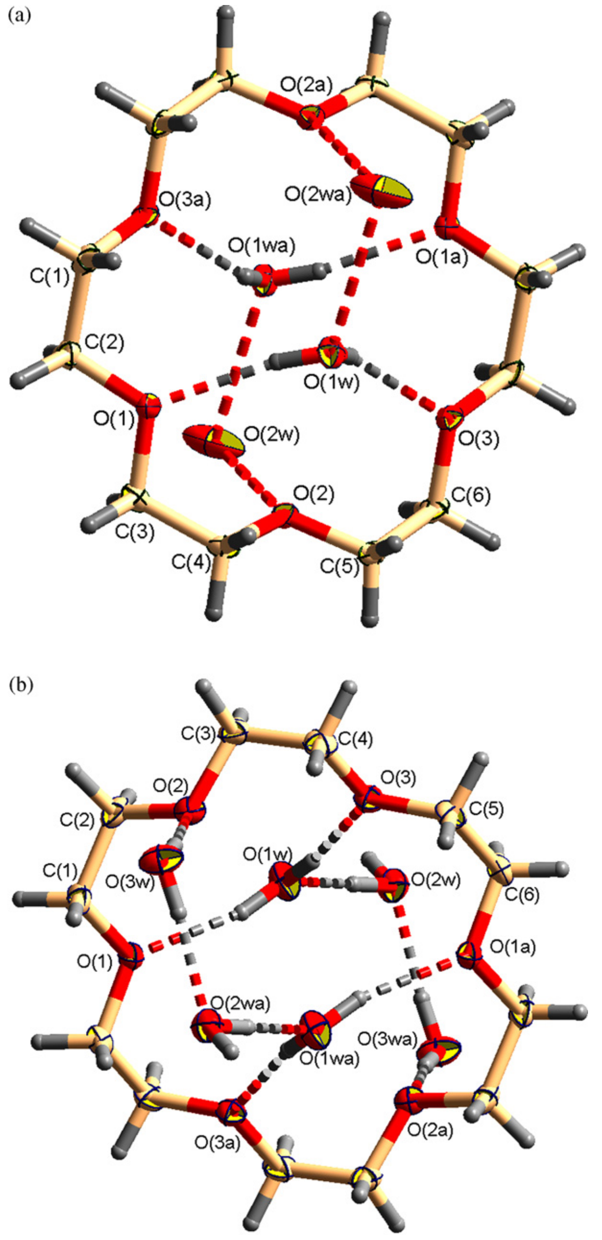

Fig. 3. Structure of 18-crown-6 crystalline hydrates (30% thermal probability ellipsoids): (a) compound **I** and (b) compound **II**.

(O(1w) and O(1wa)) binds directly to one solvated water molecule O(2w) (or O(2wa)), which in one's turn formed hydrogen bonds with remaining ring O atom O(2) (or O(2a)).

The compound **II** is a solvate of 18-crown-6 with six molecules of water. As well as in the compound **I** the center of inversion is situated in the geometrical center of 18-crown-6 molecule. Hydrogen bonds are formed between atoms O(1) and O(3) of 18-crown-6 molecule and H atoms of water molecules (O(1w)) (Fig. 3b and Table 2), while water molecule (O(3w)) makes one of the bond to the remaining independent ring O (O(2)) and the second with the available molecule (O(2w)), that form second hydrogen bond with the water molecules (O(1w) and O(3w)).

As it can be observed from Table 1 the results of this work are in a good agreement with the literature data [3,6], but the X-ray structure analysis of obtained compounds **I**, **II** is characterized with the better value of *R*-factor in this work. One of the reasons for the differences in the lattice parameters is the various temperature conditions during investigations (Table 1).

Table 3
Bond length (Å) and bond angle (°) parameters and geometry of hydrogen bonds for compounds **I** and **II**.

Parameter	**I**	**II**
C–C	1.499(3), 1.500(3), 1.501(3)	1.4929(17), 1.4938(17), 1.4957(18)
C–O	1.417(2)–1.425(2)	1.4188(14)–1.4243(13)
Angle C–O–C	112.55(13), 112.54(13), 111.36(14)	111.30(9), 112.99(8), 112.18(8)
Angle C–C–O	108.74(14)–110.34(14)	108.41(9)–110.18(9)
O(1)···O(1w), O(1w)–H	2.88, 0.85	2.90, 0.88
Angle O(1)–H–O(1w)	170.0	165.5
O(3)···O(1w), O(1w)–H	2.95, 0.85	2.88, 0.88
Angle O(3)–H–O(1w)	162.3	170.8
O(2)···O(3w), O(3w)–H		2.87, 0.82
Angle O(2)–H–O(3w)		171.5
O(1w)···O(2w), O(2w)–H	2.76, 0.85	2.75, 0.87
Angle O(1w)–H–O(2w)	176.8	170.2
O(2w)···O(3w), O(3w)–H		2.75, 0.87
Angle O(2w)–H–O(3w)		176.4
O(2w)···O(3w), O(2w)–H		2.72, 0.88
Angle O(2w)–H–O(3w)		172.7
O(2w)···O(2wa), O(2w)–H	2.47, 0.83	
Angle O(2w)–H–O(2wa)	139.8	

According to experimental results and literature data [3,6] molar volume at $T = 0$ K and isobaric coefficient of thermal expansion for both hydrates were estimated (Table 4).

All information concerning to stability conditions of 18-crown-6 crystalline hydrates are listed in Table 5. Tetra- and hexahydrate are melted congruently. The melting point of 1:4 compound determined in this work agrees well to the literature data [6], but it is the first time that $\Delta_m H$ (1:4) has been determined. According to different data upper limit of hexahydrate stability varied in two degrees. Unfortunately, there is no information about the way of melting point determination in the literature data (according to peak $T_{\max}$ or T_{onset}) and there are not any DSC curves in the papers [5,6]. So it makes difficult to find out the reason of the difference between the results of this work and literature data. Considering that data scattering of solidus temperature is about 1.5 °C in work [6], it can be assumed that the same accuracy is for the liquidus coordination. In this work as opposed to published papers the main problems were that we needed to focus on the synthesis and separation of hydrates, their identification by X-ray structure analysis and melting point and enthalpy of fusion determination with reproducibility of results monitoring. That is why it is possible to suggest that these results are more accurate.

According to the literature data the liquidus and solidus coordinates were estimated by thermal analysis. As liquation can be observed in the 18-crown-6–water system, measurement conditions have an influence on the final results. Studying solidus it is possible to average out the temperature of phase transition, which are measured for different compositions of the same heterogeneous area. It helps to evaluate the error of solidus coordinates. As for liquidus the same information can be obtained as the result of set of measurements of the same compositions. Unfortunately, in the papers [4,5] there is no information concerning results reproducibility.

So it is interesting to calculate the lines of phase equilibrium, because it can be done on the basis of equilibrium behavior of coexisting phases. Calculation results of liquidus in the concentra-

Table 4
Molar volume, V_0, and isobaric coefficient of thermal expansion, α, of 18-crown-6 ($C_{12}H_{24}O_6$) hydrates.

Hydrate	V_0, cm^3 mol^{-1}	α, K^{-1}
Tetrahydrate	260	2.62×10^{-4}
Hexahydrate	300	1.62×10^{-4}

Table 5
Temperatures of 18-crown-6 ($C_{12}H_{24}O_6$) crystalline hydrates fusion.

Composition	Weight % 18C6 (*w*)	*x*(18C6)	*t*, °C	Type of melting	Reference
1:4	78.6	0.2	23	Congruent	[6]
			22.6 ± 0.2		[this work]
1:4.5	76.5 ± 1	0.182	24.0 ± 0.1	Congruent	[4]
1:6	71.0 ± 1	0.143	24	Congruent	[6]
			23.7 ± 0.1		[4]
			23.6		[5]
			24.0		[2]
			22.0 ± 0.1		[this work]

tion range $x_{H_2O} = 0.750–0.935$ are presented in Fig. 2. It can be observed that the curve and coordinates of singular points depend on the model of solution (ideal or real solution), that is why the simulation accuracy of phase curves mostly depends on the data adequacy for partial and integral solution properties. Calculating NRTL parameters authors [16] used the measured osmotic coefficient [17] and enthalpy of mixing for 18-crown-6 aqueous solutions [18]. The measurements were carried out in the range of diluted solutions ($x_{H_2O} > 0.95$), so the error of extrapolation can be essential, especially for the compound with high fraction of 18-crown-6. It is impossible to calculate the coordinates of liquidus near the pure water because nowadays there is no information about standard thermodynamic functions of incongruent melting crystalline hydrates.

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Appendix A. Supplementary data

CCDC 772294 and 772295 contain the supplementary crystallographic data for compounds I and II. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033 or e mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2010.07.009.

References

[1] G. Ranghino, S. Romano, J.M. Lehn, G. Wipff, J. Am. Chem. Soc. 107 (1985) 7873–7877.
[2] H. Matsuura, K. Fukuhara, K. Ikeda, M. Tachikake, J. Chem. Soc., Chem. Commun. 23 (1989) 1814–1816.
[3] D. Mootz, A. Albert, S. Schaefgen, D. Staben, J. Am. Chem. Soc. 116 (1994) 12045–12046.
[4] K. Fukuhara, M. Tachikake, S. Matsumoto, H. Matsuura, J. Phys. Chem. 99 (1995) 8617–8623.
[5] K. Udachin, J. Lipkowski, Mendeleev Commun. 6 (1996) 133–134.
[6] A. Albert, D. Mootz, Z. Naturforsch. 52b (1997) 615–619.
[7] U. Domanska, P. Venkatesu, J. Chem. Eng. Data 43 (1998) 919–924.
[8] G. Nichols, J. Orf, S.M. Reiter, J. Chickos, G.W. Gokel, Thermochim. Acta 346 (2000) 15–28.
[9] G.W. Gokel, D.J. Cram, C.L. Liotta, H.P. Harris, F.L. Cook, J. Org. Chem. 39 (1974) 2445–2446.
[10] SMART (Control) and SAINT (Integration) Sofware, Version 5.0, Bruker AXS Inc., Madison, WI, 1997.
[11] G.M. Sheldrick, SADABS, University of Göttingen, 1997.
[12] G.M. Sheldrick, Acta Crystallogr. A 46 (1990) 467–473.
[13] G.M. Sheldrick, SHELXL93, University of Göttingen, 1993.
[14] G.F. Voronin, Russ. J. Phys. Chem. 45 (1971) 2100–2101.
[15] H. Renon, J.M. Prausnitz, AIChE. J. 14 (1968) 135–144.
[16] N.A. Kovalenko, S.N. Igumnov, N.B. Golovina, A.G. Bogachev, Vestn. KGTU N1 (2010) 153–156.
[17] K. Patil, R. Pawar, D. Dagade, J. Phys. Chem. A 106 (2002) 9606–9611.
[18] W. Zielenkiewicz, O.V. Kulikov, I. Kulis-Cwikla, J. Sol. Chem. 22 (1993) 963–973.