



# Gibbs free energy of hydrogen bonding of aliphatic alcohols with liquid water at 298 K

Igor A. Sedov\*, Boris N. Solomonov

Department of Chemistry, Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

## ARTICLE INFO

### Article history:

Received 19 August 2011

Received in revised form

13 November 2011

Accepted 16 November 2011

Available online 25 November 2011

### Keywords:

Hydrogen bonding

Alcohols

Aqueous solutions

Cooperativity

## ABSTRACT

Thermodynamics of hydrogen bonding between water and molecules of aliphatic alcohols in dilute aqueous solutions is studied. The Gibbs free energies of hydrogen bonding of normal aliphatic alcohols from methanol to octanol with liquid water are determined from experimental data. The molar fractions of free unbonded molecules of alcohols and monomeric species of water are reported. Strong cooperative effects are observed when an alcohol molecule binds to an associate of water, leading to huge negative values of the Gibbs energies and an increased aqueous solubility. Formation of the second and third hydrogen bonds of an alcohol molecule with water is much less favorable, what can be described as an anti-cooperative effect.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

Hydrogen bonds between the molecules of aliphatic alcohols and water have attracted a close attention of researchers for a long time. They have been studied using experimental (Raman and infrared [1], NMR [2], X-ray [3], neutron diffraction [4], calorimetry [5], dielectric relaxation [6]) and theoretical (quantum chemistry calculations [7], molecular dynamics [8], thermodynamic models [9]) methods in different phases and media (water–alcohol mixtures [10], apolar solvent [11], gas phase [12], solid matrices [13], molecular beams [14], crystals [15], solid–gas [16] and solid–liquid interfaces [17]) in order to determine their energetic, dynamical and structural properties.

Such interest is explained by both practical importance of alcohol–water systems and simple chemical nature of aliphatic alcohols which allows using them as a model for more complicated hydrogen-bonding molecules. Alcoholic hydroxyls are one of the most common and important functional groups in organic and biological chemistry. They are present in many bioactive molecules and in the active sites of biomacromolecules. Hydroxylic groups are often involved in noncovalent hydrogen bonding between biomolecules or between a biomolecule and aqueous medium. They can also be introduced to a newly synthesized hydrophobic molecule in order to increase its hydrophilicity.

An increase in the solubility of a molecule due to the introduction of functional groups is determined by the strength of hydrogen bonds that these groups form with water. The process of binding of substrates with receptors and enzymes is accompanied with dehydration of the groups that take part in binding. Thus, the constants of binding are also strongly influenced by the hydrogen bonding of alcoholic hydroxyls with water.

The strength of hydrogen bonding of water with a dissolved compound (A) or its single functional group can be characterized with the standard Gibbs energy of bonding  $\Delta_{HB}G$ , which is related to the fraction of free non-bonded molecules (groups)  $\alpha$ , and to the effective constant of complexation with water  $K$ , through the following equation:

$$\Delta_{HB}G^{A/H_2O} = RT \ln \alpha^{A/H_2O} = -RT \ln(1 + K) \quad (1)$$

This quantity ( $\Delta_{HB}G^{A/H_2O}$ ) contributes to the Gibbs energy of hydration and to the Gibbs energy of dehydration or binding to another molecule in water with the opposite sign. Despite their importance, the Gibbs energies of H-bonding with liquid water at room temperature (298 K) for alcohols are still not reported. Their quantification is the goal of the present work.

## 2. Methodology

### 2.1. The problem of measuring thermodynamic functions of solute–solvent hydrogen bonding

The simplest systems to study the process of hydrogen bonding of alcohols with liquid water are their infinitely diluted aqueous

\* Corresponding author. Tel.: +7 9600503916; fax: +7 8432315346.

E-mail addresses: [igor\\_sedov@inbox.ru](mailto:igor_sedov@inbox.ru) (I.A. Sedov), [boris.solomonov@ksu.ru](mailto:boris.solomonov@ksu.ru) (B.N. Solomonov).

solutions, where the interactions between two alcohol molecules can be excluded from consideration. Constants of bonding with water are hard to measure using spectroscopic techniques because we cannot change the concentration of water in itself and thus we cannot change the degree of complexation of a solute with water. Fractions of alcohol molecules forming different numbers of hydrogen bonds (one, two, three) with water were reported in simulation studies [18], but the fraction of a non-hydrogen-bonded form of alcohols in water is very low, so that a simulation box can contain in average less than one such molecule. This makes difficult to calculate the free alcohol fraction from a simulation. Thermodynamic models of solutions are useful for such task. Starting with the experimental data on the Gibbs free energy of solvation in water (hydration)  $\Delta_{solv}G^{A/H_2O}$  at 298 K and 1 bar standard pressure, which are published in literature, we should somehow calculate the Gibbs energy of solute–solvent interactions that are not caused by hydrogen bonding. These interactions follow general laws and correlations, while the hydrogen bonding in water–alcohol system is a very complicated process. First, an alcohol molecule can act both as hydrogen bond donor and acceptor, and can simultaneously form one hydrogen bond as H-donor and one or two H-bonds as acceptor. Second, many possible structures of complexes with different clusters of water may form, and formation of some of them requires breaking or reorganization of H-bonds between molecules of water in the vicinity of a solute. Thus, the Gibbs energy of hydrogen bonding with bulk water is a weighted average of the Gibbs energies of all possible hydrogen-bonding processes. However, this average magnitude is of interest for us since it determines the influence of hydrogen-bonding processes on solute reactivity and other physico-chemical properties driven by the chemical potential.

Additionally, so-called cooperativity phenomenon [19] leads to a large difference in the energies of hydrogen bonds in complexes with one molecule of water and with a dimer or multimer of water. This effect limits our possibility to predict the Gibbs energy of bonding with clusters of water using the scales of hydrogen bond acidity and basicity that are based on the data for equimolar complexes with various proton acceptors and donors.

## 2.2. A model to describe the Gibbs energy of solvation in water

In our works we have shown [20–22] that the Gibbs energy of solvation in water can be represented as a sum of three contributions: due to nonspecific (van der Waals) solvation effects  $\Delta_{solv(nonsp)}G^{A/H_2O}$ , due to the hydrophobic effect  $\Delta_{h.e.}G^A$ , and the contribution of hydrogen bonding processes (specific interactions)  $\Delta_{int(sp)}G^{A/H_2O} = \Delta_{HB}G^{A/H_2O}$ :

$$\Delta_{solv}G^{A/H_2O} = \Delta_{solv(nonsp)}G^{A/H_2O} + \Delta_{h.e.}G^A + \Delta_{HB}G^{A/H_2O}. \quad (2)$$

The contributions of nonspecific solvation to the Gibbs energy of solvation for various solutes  $A$  in various solvents  $S$  are shown [23] to follow the empiric equation:

$$\begin{aligned} \Delta_{solv(nonsp)}G^{A/S} &= \Delta_{solv}G^{A/S_0} + (\delta g^S - \delta g^{S_0}) \cdot V_x^A + \left[ a + b \sqrt{\delta g^S} \right] \\ &\cdot \left[ (\Delta_{solv}G^{A/S_R} - \Delta_{solv}G^{A/S_0}) - (\delta g^{S_R} - \delta g^{S_0}) \cdot V_x^A \right]; \quad (3) \\ a &= -\frac{\sqrt{\delta g^{S_0}}}{\sqrt{\delta g^{S_R}} - \sqrt{\delta g^{S_0}}}; \\ b &= \frac{1}{\sqrt{\delta g^{S_R}} - \sqrt{\delta g^{S_0}}}. \end{aligned}$$

Here  $\Delta_{solv}G^{A/S_0}$ ,  $\Delta_{solv}G^{A/S_R}$  are the Gibbs energies of solvation of solute  $A$  in the standard solvents  $S_0$  and  $S_R$ ,  $V_x^A$  is McGowan characteristic volume [24] of solute  $A$  calculated by an atom-additivity

scheme,  $\delta g^S$ ,  $\delta g^{S_R}$ ,  $\delta g^{S_0}$  are the relative Gibbs energies of cavity formation for each solvent.  $\delta g^S$  is given by the following equation:

$$\delta g^S = \frac{\Delta_{solv}G^{C_8H_{18}/S} - \Delta_{solv}G^{C_8H_{18}/C_{16}H_{34}}}{V_x^{C_8H_{18}}}, \quad (4)$$

where  $C_8H_{18}$  = n-octane,  $C_{16}H_{34}$  = n-hexadecane. This parameter reflects the propensity of solvent molecules to the nonspecific interactions with both other solvent molecules and solute molecules. In the case of water, we also make a correction for the hydrophobicity of octane. The value of  $\delta_{cav}g^{H_2O}$  was found to be  $5.75 \times 10^{-2}$  kJ cm<sup>-3</sup>.

The contribution due to the hydrophobic effect reflects the difference in behavior of solutions in water from solutions in other solvents. We have shown that the Gibbs hydrophobic effect energy is linearly dependent on the characteristic molecular volume of solute [25]:

$$\Delta_{h.e.}G^A / (\text{kJ mol}^{-1}) = 22.02 V_x^A / (\text{cm}^3 \text{ mol}^{-1} 10^2) + 3.65. \quad (5)$$

The process of hydration of a hydrogen-bonding molecule can be dissected into two steps: transfer into water without formation of solute–water hydrogen bonds, and then bonding with water. The energy change in the first step is, as for all non-hydrogen-bonding molecules, the sum of the nonspecific hydration energy and the Gibbs hydrophobic effect energy. The energy difference between a non-hydrogen-bonded state of a solute in water (initial state of the second step) and an equilibrium mixture of solute–water associates in real solution (final state) is the Gibbs energy of specific interactions in water  $\Delta_{HB}G^{A/H_2O}$ , so the total Gibbs energy of hydration consists of three contributions (2) and

$$\Delta_{HB}G^{A/H_2O} = \Delta_{solv}G^{A/H_2O} - \Delta_{solv(nonsp)}G^{A/H_2O} - \Delta_{h.e.}G^A. \quad (6)$$

In a similar manner, we can calculate the Gibbs energy of self-association and the fraction of monomer of water in pure liquid water, using the Gibbs energy of vaporization of water with the opposite sign instead of  $\Delta_{solv}G^{A/H_2O}$  in Eq. (6).

## 2.3. Empiric parameters of aliphatic alcohols

In one of our previous works [20], we have discussed the difficulties of choice of the standard solvents in Eq. (3) for aliphatic alcohols. Good accuracy of Eq. (3) is achieved when two standard solvents have significantly different values of the  $\delta g^S$  parameter. However, the choice of standard solvents is reduced to alkanes and some of their halogenated derivatives, since alcohols form hydrogen bonds even with such weak proton acceptor as benzene. Thus, we would obtain more accurate results if we will write Eq. (3) in the equivalent form with empiric parameters of solute  $p^A$  and  $q^A$  that can be determined using a linear regression:

$$\Delta_{solv(nonsp)}G^{A/S} = V_x^A \cdot \delta g^S + p^A \sqrt{\delta g^S} + q^A. \quad (7)$$

A regression of  $\Delta_{solv}G^{A/S} - V_x^A \cdot \delta g^S$  versus  $\sqrt{\delta g^S}$  is conducted for each solute in all solvents  $S$  where solute–solvent hydrogen bonding interactions can be neglected. The parameters  $p^A$  and  $q^A$  for considered aliphatic alcohols were determined previously [20], and in the present work they were roughly estimated for water. The values of parameters used in Eqs. (3), (5) and (6) for considered species are given in Table 1.

## 3. Results and discussion

### 3.1. Gibbs energy of alcohol–water hydrogen bonding

Calculated values of the Gibbs energies of hydrogen bonding with water are given in Table 2. It is clear that they are not significantly dependent from the alkyl chain length, while two other

**Table 1**  
Parameters of monohydric aliphatic alcohols used to calculate their Gibbs energies of hydrogen bonding with water at  $T = 298$  K.

Alcohol (A)	$V_A^A / (\text{cm}^3 \text{mol}^{-1} 10^2)^a$	$p^A$	$q^A$	$\Delta_{\text{soliv}} G^{A/H_2O} / (\text{kJ mol}^{-1})^b$
Methanol	0.3082	-1.99	7.35	-3.4
Ethanol	0.4491	-2.01	4.01	-3.2
Propanol	0.5900	-2.17	1.12	-2.2
Butanol	0.7309	-2.36	-2.13	-1.7
Pentanol	0.8718	-2.76	-4.06	-0.8
Hexanol	1.0127	-2.49	-8.02	-0.1
Heptanol	1.1536	-2.80	-10.62	0.1
Octanol	1.2945	-2.93	-13.64	0.8
Water	0.1673	-1.0	9.8	-8.6

<sup>a</sup> See Ref. [21] for the procedure of calculation.

<sup>b</sup> Calculated from literature data [26].

contributions to the Gibbs energy of solvation in water depend on it.

### 3.2. Gibbs energy of formation of equimolar alcohol–water complexes

In order to see the influence of the cooperative effect on hydrogen-bonding strength for the complexes with water associates, it is necessary to know the Gibbs energies of bonding of alcohols with a monomer of water. They can form two types of equimolar complexes:  $\text{ROH} \cdots \text{OH}_2$  and  $\text{HOH} \cdots \text{ROH}$ . The Gibbs energies of their formation have also never been determined experimentally, but can be estimated from empiric correlation relationships for the binding constants in inert medium (tetrachloromethane). According to the scale of acidities and basicities of hydrogen bonds suggested by Abraham [27], the values of acidity parameters of methanol and water  $\alpha_2^H$  are respectively 0.37 and 0.35, and the basicity parameters  $\beta_2^H$  are 0.41 and 0.38. Other linear saturated alcohols have insignificantly different H-bond acidities and basicities. Parameters  $\alpha_2^H$  and  $\beta_2^H$ , based on experimental data for the 1:1 complexation constants  $K^{A \cdots B}$  in tetrachloromethane, are correlated with them through the equation:

$$\lg K^{A \cdots B} = 7.354 \alpha_2^H \beta_2^H - 1.094. \quad (8)$$

Here the constant  $K^{A \cdots B}$  is expressed in molarity scale. We can go to the molar fraction scale by dividing by the molar volume of solvent,  $\text{CCl}_4$ , and then convert the constant to the standard Gibbs energy of bonding:

$$\Delta_{\text{HB}} G^{A \cdots B} = -RT \ln 10 \cdot (\lg K^{A \cdots B} - \lg V_m(\text{CCl}_4)). \quad (9)$$

Then we receive the value  $-5.5 \text{ kJ mol}^{-1}$  for the standard Gibbs energy of formation of  $\text{ROH} \cdots \text{OH}_2$  complex and  $-5.6 \text{ kJ mol}^{-1}$  for  $\text{HOH} \cdots \text{ROH}$  complex. This result is interesting to compare with the Gibbs energies of bonding of alcohols with bulk water.

**Table 2**  
The Gibbs free energies at  $T = 298$  K of hydrogen bonding, hydrophobic effect, nonspecific solvation, and fractions of non-bonded form of aliphatic alcohols in their dilute aqueous solutions.

Alcohol (A)	$\Delta_{\text{soliv}(\text{nonsp})} G^{A/H_2O} / (\text{kJ mol}^{-1})$	$\Delta_{\text{h.e.}} G^A / (\text{kJ mol}^{-1})$	$\Delta_{\text{HB}} G^{A/H_2O} / (\text{kJ mol}^{-1})$	$\alpha \cdot 10^4$
Methanol	4.4	10.4	-18.2	6.5
Ethanol	1.8	13.5	-18.5	5.8
Propanol	-0.7	16.6	-18.1	6.6
Butanol	-3.6	19.7	-17.9	7.3
Pentanol	-5.7	22.8	-17.9	7.2
Hexanol	-8.2	25.9	-17.9	7.2
Heptanol	-10.7	29.1	-18.2	6.4
Octanol	-13.2	32.2	-18.2	6.6
Water	8.4	7.3	-24.3	0.56

### 3.3. Cooperativity and anticooperativity of alcohol–water H-bonds

Simulation studies and analysis of neutron diffraction data allow estimating fractions of different hydrogen-bonded forms of a solute, if they are not too small (like those of non-bonded alcohols in water) or too large. In a simulation of quite dilute (5 mol%) methanol solution [18] it was found that about 10% of methanol molecules have only one hydrogen bond with the associates of water through their lone pair electron (which may be represented as  $\text{W} \cdots \text{ROH}$ ), 5% of methanol molecules accept two hydrogen bonds with water using both lone pair electrons ( $\text{W}_2 \cdots \text{ROH}$ ), and the majority of methanol molecules accept one and donate one hydrogen bond ( $\text{W} \cdots \text{ROH} \cdots \text{W}$ , 45%) or accept two and donate one hydrogen bond ( $\text{W}_2 \cdots \text{ROH} \cdots \text{W}$ , 40%). These data can be analyzed in terms of the Gibbs energies.

For the process  $\text{ROH} + \text{W} = \text{W} \cdots \text{ROH}$

$$\Delta_{\text{HB}} G^\circ = \Delta_{\text{HB}} G^{A/H_2O} - RT \ln 0.1 = -18.2 + 5.7 = -12.5 \text{ kJ mol}^{-1};$$

This value includes the cost of breaking some water–water hydrogen bonds to free water hydroxyls, since we assumed the activity of “W” to be unity. In water the fraction of water molecules that are not involved in hydrogen bonds with other water molecules by at least one site is far from unity (below we show that about 10% of hydroxyls in liquid water are free). The standard Gibbs energy of complexation between methanol and water associate in a hypothetical inert solvent should be more negative by several  $\text{kJ mol}^{-1}$ . Anyway, this is already by far more negative than the Gibbs energy of formation of bimolecular  $\text{HOH} \cdots \text{ROH}$  complex.

It is now evident that the hydrogen bonds with water clusters in bulk water are much stronger than with a single molecule of water – the manifestation of cooperative hydrogen bonding phenomenon. At the same time, bonding of solute with more than one molecule of water is influenced by an opposite anti-cooperative effect [28]. We can calculate from the data above that for the process  $\text{W} \cdots \text{ROH} + \text{W} = \text{W}_2 \cdots \text{ROH}$

$$\Delta_{HB}G^\circ = -RT \ln(0.05/0.10) = 1.7 \text{ kJ mol}^{-1};$$

for  $W \cdots ROH + W = W \cdots ROH \cdots W$

$$\Delta_{HB}G^\circ = -RT \ln(0.45/0.10) = -3.7 \text{ kJ mol}^{-1};$$

and for  $W \cdots ROH \cdots W + W = W_2 \cdots ROH \cdots W$

$$\Delta_{HB}G^\circ = -RT \ln(0.40/0.45) = 0.3 \text{ kJ mol}^{-1}.$$

Hydrogen bonding with the second and third associates of water is much less favorable than with the first one. Accepting two hydrogen bonds is less favorable for an alcohol molecule than accepting one and donating one hydrogen bond.

#### 3.4. The fraction of monomer and free hydroxyls in liquid water. The entropy of alcohol–water bonding

Using Eq. (1), the Gibbs energy of hydrogen bonding can be transformed into another interesting quantity – the fraction of free monomeric molecules in solution. Their values are given in the last column of Table 2. Only about 0.07% of alcohol molecules are not bonded with water. We also calculated that in pure water 0.0056% of its molecules are not bonded with any other. In so-called 4C association scheme of water, the free monomer fraction is the fourth power of free OH-group fraction. Thus, our data indicate that the fraction of free hydroxyls in water is  $\sqrt[4]{5.6 \cdot 10^{-4}} = 0.086$  or 8.6%, while the estimates in literature are, 12% (analysis of IR-spectra [29]), 10% (Monte-Carlo simulation [30]), 8% (NRHB association model [31]), 6% (sPC-SAFT association model [31]). Our result is in general agreement with the other.

If we assume [32] that the enthalpy of alcohol–water bonding in aqueous solutions is about  $-15.1 \text{ kJ mol}^{-1}$ , then the entropy of this process will equal  $\Delta_{HB}S^{A/H_2O} = (-15100 + 18200)/(8.314 \cdot 298) = 10.4 \text{ J K mol}^{-1}$ . The typical values of the entropies of hydrogen-bonded complexes involving methanol are much less [33] (from  $-10$  to  $-30 \text{ J K mol}^{-1}$  in molar fractions scale). This fact may be attributed to the high positive entropy of reorganization of water. It should be noted that the hydrophobic effect which also accompanies hydration of alcohols leads to the opposite effect: a decrease of the entropy.

#### 3.5. The importance of cooperative effects for modeling aqueous solutions

There is a huge number of published experimental values of complexation constants for bimolecular hydrogen-bonded complexes involving various small organic molecules and simple empiric equations that describe these data well. However, the extension of such equations to more complicated systems with multiple hydrogen bonds between more than two molecules, which play an important role in real industrial and biological processes that take place in water and other associated solvents, is not so simple. Cooperative effect is responsible for the change in the energies of hydrogen bonds in such complexes, and the reorganization of solvent associates introduces its contribution to the thermodynamic functions. Binding with more than one molecule or associate of solvent has, again, different energy. These effects make acidity/basicity parameters obtained for equimolar complexes inappropriate for description of more complicated complexes without corrections dependent on both solute and solvent nature.

## 4. Conclusion

Obtained results indicate that cooperative effects of hydrogen bonding with water greatly accelerate solubilities of compounds containing hydroxylic groups and seriously affect reactivity of such groups. The constant of complexation of methanol as H-bond

acceptor with associates of water as donor in aqueous medium is at least 16 times larger than with water monomer in inert medium. Hydrogen bonds of the same alcohol molecule with the second and third associates of water are much weaker. Variation of the length of alkyl radical does not lead to a significant change of the Gibbs energy of bonding with water.

The values of the Gibbs energy of hydrogen bonding of various compounds and functional groups with water can be used in empiric models to reflect their HB-acidity and basicity, while parameters based on the data for equimolar complexes with proton acceptors and donors are not suitable for water and other associated solvents.

At the same time, the magnitude  $\Delta_{HB}G^{A/H_2O}$  reflects the energy of many complicated processes of creation, breaking, and rearrangement of hydrogen bonds. Its values can be a starting point to investigate these processes in more details.

## Acknowledgements

This work was supported by the Federal target program “Scientific and scientific-pedagogical personnel of innovative Russia in 2009–2013” (contract No. 16.740.11.0336) and RFBR (project No. 09-03-00751-a).

### List of symbols

$\Delta_{solv}G$	Gibbs energy of solvation
$\Delta_{solv(nonsp)}G$	Gibbs energy of nonspecific solvation
$\Delta_{int(sp)}G$	Gibbs energy of specific interactions
$\Delta_{HB}G$	Gibbs energy of hydrogen bonding
$\Delta_{h,e}G$	Gibbs energy of the hydrophobic effect
$\delta g^S$	relative cavity formation Gibbs energy in solvent S
$V_x^A$	McGowan characteristic molecular volume of A
$S_0, S_R$	standard solvents in Eq. (3)
$p^A, q^A$	parameters in Eq. (7)
$\alpha$	molar fraction of the non-hydrogen-bonded form of solute
$K$	complexation constant
$\alpha_2^H, \beta_2^H$	acidity and basicity parameters
$T$	temperature (K)
$R$	universal gas constant
$A/S$ (superscript)	solute A infinitely diluted in solvent S

## References

- [1] M. Nedic, T.N. Wassermann, Z. Xue, P. Zielke, M.A. Suhm, *Phys. Chem. Chem. Phys.* 10 (2008) 5953–5956.
- [2] K. Mizuno, Y. Miyashita, Y. Shindo, H. Ogawa, *J. Phys. Chem.* 99 (1995) 3225–3228.
- [3] T. Takamuku, K. Saisho, S. Nozawa, T. Yamaguchi, *J. Mol. Liq.* 119 (2005) 133–146.
- [4] S. Dixit, J. Crain, W.C.K. Poon, J.L. Finney, A.K. Soper, *Nature* 416 (2002) 829–832.
- [5] D.V. Batov, A.M. Zaichikov, V.P. Slyusar, V.P. Korolev, *Russ. J. Gen. Chem.* 71 (2001) 1208–1214.
- [6] S.S.N. Murthy, *J. Phys. Chem. A* 103 (1999) 7927–7937.
- [7] B.G. Oliveira, M.L.A.A. Vasconcellos, *J. Mol. Struct.: THEOCHEM* 774 (2006) 83–88.
- [8] T.S. van Erp, E.J. Meijer, *Chem. Phys. Lett.* 333 (2001) 290–296.
- [9] G.M. Kontogeorgis, M.L. Michelsen, G.K. Folas, S. Derawi, N. Von Solms, E.H. Stenby, *Ind. Eng. Chem. Res.* 45 (2006) 4869–4878.
- [10] M. Ferrario, M. Haughney, I.R. McDonald, M.L. Klein, *J. Chem. Phys.* 93 (1990) 5156–5166.
- [11] R. Iwamoto, H. Kusanagi, *J. Phys. Chem. A* 113 (2009) 5310–5316.
- [12] L.A. Curtiss, M. Blander, *Chem. Rev.* 88 (1988) 827–841.
- [13] N. Bakkas, Y. Bouteiller, A. Loutellier, J.P. Perchard, S. Racine, *J. Chem. Phys.* 99 (1993) 3335–3342.
- [14] U. Buck, F. Huisken, *Chem. Rev.* 100 (2000) 3863–3890.
- [15] T. Steiner, *Angew. Chem. Int. Ed.* 41 (2002) 48–76.
- [16] S. Bahr, C. Toubin, V. Kemper, *J. Chem. Phys.* 128 (2008).
- [17] T.R. Mattsson, S.J. Paddison, *Surf. Sci.* 544 (2003) L697–L702.
- [18] D.S. Venables, C.A. Schmuttenmaer, *J. Chem. Phys.* 113 (2000) 11222–11236.
- [19] M. Masella, J.P. Flament, *J. Chem. Phys.* 108 (1998) 7141–7151.
- [20] I.A. Sedov, B.N. Solomonov, *Fluid Phase Equilib.* 276 (2009) 108–115.

- [21] I.A. Sedov, B.N. Solomonov, *J. Chem. Eng. Data* 56 (2011) 1438–1442.
- [22] B.N. Solomonov, I.A. Sedov, A.A. Akhmediyarov, *J. Phys. Org. Chem.* 22 (2009) 1142–1147.
- [23] B.N. Solomonov, I.A. Sedov, *J. Mol. Liq.* 139 (2008) 89–97.
- [24] M.H. Abraham, J.C. McGowan, *Chromatographia* 23 (1987) 243–246.
- [25] I.A. Sedov, B.N. Solomonov, *J. Chem. Thermodyn.* 42 (2010) 1126–1130.
- [26] A.R. Katritzky, I. Tulp, D.C. Fara, A. Lauria, U. Maran, W.E. Acree, *J. Chem. Inf. Model.* 45 (2005) 913–923.
- [27] M.H. Abraham, *Chem. Soc. Rev.* 22 (1993) 73–83.
- [28] P.L. Huyskens, *J. Am. Chem. Soc.* 99 (1977) 2578–2582.
- [29] W.A.P. Luck, *Angew. Chem. Int. Ed. Engl.* 19 (1980) 28–41.
- [30] W.L. Jorgensen, J.D. Madura, *Mol. Phys.* 56 (1985) 1381–1392.
- [31] G.M. Kontogeorgis, I. Tsivintzelis, N. Von Solms, A. Grenner, D. Bagh, M. Frost, A. Knage-Rasmussen, I.G. Economou, *Fluid Phase Equilib.* 296 (2010) 219–229.
- [32] B.N. Solomonov, I.A. Sedov, *J. Phys. Chem. B* 110 (2006) 9298–9303.
- [33] M.D. Joesten, L.J. Schaad, *Hydrogen Bonding*, Marcel Dekker, New York, 1974.