Journal of Molecular Liquids 167 (2012) 47–51

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Hydrogen bonding in neat aliphatic alcohols: The Gibbs free energy of self-association and molar fraction of monomer

Igor A. Sedov, Boris N. Solomonov *

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

ARTICLE INFO

Article history:
Received 11 May 2011
Received in revised form 12 December 2011
Accepted 21 December 2011
Available online 4 January 2012

Keywords:
Self-association
Hydrogen bonding
Gibbs energy
Monomer fraction
Cooperative effect

ABSTRACT

The magnitudes of the Gibbs free energies of self-association for several primary aliphatic alcohols at 298 K are calculated. The fraction of monomeric molecules in bulk alcohols is determined. We started from the experimental data on the Gibbs free energies of vaporization of alcohols, and quantified the contributions from three types of solvation effects: non-specific van der Waals interactions, solvophobic effects, and hydrogen-bonding processes (self-association) using an extrathermodynamic approach. Calculated values for monomer fractions are compared and found to be in general agreement with the results obtained from various association models: CPA, NRHB, sPC-SAFT, and other data reported in literature. The influence of hydrogen bond cooperativity on the process of self-association is shown.

1. Introduction

The process of self-association of aliphatic alcohols has attracted attention of scientists for a long time [1]. Simple molecules forming intermolecular hydrogen bonds are considered as convenient models that should help us to understand noncovalent binding processes in complicated biological and supramolecular systems. The energetic and structural properties of associates, dynamics of association processes have been extensively studied in neat monohydric aliphatic alcohols and their mixtures with other organic substances using thermodynamic [2–5], spectroscopic [6–8], and theoretical [9–11] methods. A large number of semi-empirical models for the association process were suggested [3–5,12–15].

There is a huge number of possible structures of alcohol associates, but in the simplest models of association process the number of considered associates is limited (e.g. only monomeric molecules and cyclic tetrameric associates are considered [16]). Less strict limitation used in many advanced models is that there may exist associates of any size, but the thermodynamic functions of H-bond formation are the same for all H-bonds either there is only a small number of H-bond types which differ by their energies. It is well-known that real hydrogen-bonding processes are cooperative [17–19]. The enthalpy and Gibbs energy of dimerization of alcohols are significantly less negative than that of addition of the third and subsequent monomeric molecules to the associate, and the corresponding constants of association are larger in magnitude [20–23]. Thus, at least two different values of each thermodynamic function – one for dimerization and one for subsequent self-association – are required to describe the process of association in realistic models.

In a number of spectroscopic studies, a simplified classification of the types of alcohol molecules and their OH groups that does not take cooperative effects into account is used [7]. Free monomer molecules and their hydroxyls are called type α, type β is for terminal free OH groups, γ for OH groups with non-H-bonded lone pair electrons of oxygen, and δ for molecules bonded with other alcohol molecules from both sides. All the molecules or bonds of each type are assumed to have similar OH frequencies in vibrational spectra and similar values of partial molar thermodynamic functions (enthalpy, Gibbs energy, entropy). In literature, the fractions of α–γ types in neat alcohols are obtained as a result of analysis of experimental data on the basis of various model assumptions.

2. Methodology

2.1. Gibbs energy and monomer fraction

Nevertheless, it is possible to characterize the thermodynamics of association processes in neat alcohols without any arbitrary assumptions about the energies of association and the structure of associates. One may use average thermodynamic function of association $\Delta_{ass}f^{ROH}(f=G,H,S)$ which reflects the change in the Gibbs energy, enthalpy, or entropy when one mole of alcohol ROH is changing from its monomeric state in the neat phase into the equilibrium mixture of associates that forms the same neat phase. In other words, the initial state of considered process is the monomer diluted in the bulk alcohol with the certain standard concentration

* Corresponding author. Tel./fax: +7 8432315346.
E-mail addresses: igor_sedov@inbox.ru (I.A. Sedov), Boris.Solomonov@ksu.ru (B.N. Solomonov).

0167-7322/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.molliq.2011.12.007

and the final state is just the bulk alcohol. If we assume that for monomer diluted in the neat phase the change of the chemical potential with concentration can be described by Flory–Huggins expression, then the Gibbs energy of self-association of alcohol $\Delta_{ass}G^{ROH}$ is related to the volume fraction of monomeric alcohol among all associates $\varphi_1 = V_m(ROH)[ROH]/\sum_{n=1} V_m((ROH)_n)[(ROH)_n]$ through $\Delta_{ass}G^{ROH} = RT\ln\varphi_1$. Here and below all possible isomers of associates (e.g. linear and cyclic) with the same n are supposed to be included in the sums as separate terms, i.e. $\sum_{n=1}$ means not only summation over n, but also over all possible isomers with the same n. The magnitude of φ_1 is almost equal to the fraction x_1 of free monomer among all molecules of alcohol engaging in different types of associates:

$$\begin{aligned} & V_m(ROH)[ROH]\Big/\sum_{n=1} V_m((ROH)_n)[(ROH)_n] \\ & \quad \approx V_m(ROH)[ROH]\Big/\sum_{n=1} nV_m(ROH)[(ROH)_n] = \\ & = [ROH]\Big/\sum_{n=1} n[(ROH)_n] = x_1, \text{and therefore } \Delta_{ass}G^{ROH} = RT\ln x_1. \end{aligned} \tag{1}$$

In contrast, the enthalpy of self-association $\Delta_{ass}H^{ROH}$ relating to the same process is described by a more complicated formula: it is the weighted average enthalpy of association over all possible associates:

$$\Delta_{ass}H^{ROH} = \sum_n x_n\Delta_{ass}H_n\Big/\sum_n nx_n \tag{2}$$

where $\Delta_{ass}H_n$ is the enthalpy of formation of the associate from n monomeric molecules, $x_n = [(ROH)_n]/\sum_{n=1} n[(ROH)_n]$. The entropy of self-association is given by

$$\Delta_{ass}S^{ROH} = \left(\Delta_{ass}H^{ROH} - \Delta_{ass}G^{ROH}\right)\Big/T. \tag{3}$$

It is important that the fraction of free monomer molecules x_1 keeps the same physical meaning in most of the association models, even if the energy of associates is dependent on their size and structure. The values of x_1 and $\Delta_{ass}G^{ROH}$ obtained from different models and experiments can be used to compare and justify them. One possible method is the analysis of intensities of OH vibrations in IR-spectrum of the neat alcohol and its solutions in inert solvents. Such study has been done by Luck [24]. Another way to estimate x_1 and $\Delta_{ass}G^{ROH}$ is comparing the vapor pressures of alcohol and its non-associated homomorph [2,25]. The data on free monomer fraction have also been obtained from various association models [26].

2.2. Intermolecular interactions in associated solvents and their contributions to the Gibbs energy

In our present work, we use an extrathermodynamic approach to determine the values of x_1 and $\Delta_{ass}G^{ROH}$ for a number of neat saturated alcohols from C_1 to C_8 on the basis of their experimental Gibbs free energies of vaporization $\Delta_{vap}G^{ROH}$.

All considered systems are at $T = 298$ K, $p = 1$ bar. We use the molar fractions-based standard state for the solutions.

In our recent work [27], we have shown that the Gibbs energy of solvation in self-associated solvents, e.g. aliphatic alcohols, can be represented as a sum of three contributions: due to nonspecific (van der Waals) solvation effects $\Delta_{solv(nonsp)}G^{A/ROH}$, due to the solvophobic effect $\Delta_{s.e.}G^{A/ROH}$, and the contribution of hydrogen bonding processes (specific interactions) $\Delta_{int(sp)}G^{A/ROH}$:

$$\Delta_{solv}G^{A/ROH} = \Delta_{solv(nonsp)}G^{A/ROH} + \Delta_{s.e.}G^{A/ROH} + \Delta_{int(sp)}G^{A/ROH}. \tag{4}$$

The Gibbs energy of vaporization can be considered as the Gibbs energy of solvation of compound in itself with the opposite sign: $\Delta_{vap}G^{ROH} = -\Delta_{solv}G^{ROH/ROH}$. Thus, for solvation of alcohol ROH in itself:

$$\begin{aligned} \Delta_{ass}G^{ROH} &= \Delta_{int(sp)}G^{ROH/ROH} \\ &= -\Delta_{vap}G^{ROH} - \Delta_{solv(nonsp)}G^{ROH/ROH} - \Delta_{s.e.}G^{ROH/ROH}. \end{aligned} \tag{5}$$

The contributions of nonspecific solvation to the Gibbs energy of solvation for various solutes A in various solvents S have been shown [28] to follow an empiric equation:

$$\begin{aligned} & \Delta_{solv(nonsp)}G^{A/S} = \Delta_{solv}G^{A/S_0} + \left(\delta g^S - \delta g^{S_0}\right)\cdot V_x{}^A + \\ & + \left[a + b\sqrt{\delta g^S}\right]\cdot\left[\left(\Delta_{solv}G^{A/S_R} - \Delta_{solv}G^{A/S_0}\right) - \left(\delta g^{S_R} - \delta g^{S_0}\right)\cdot V_x{}^A\right]; \\ & a = -\sqrt{\delta g^{S_0}}\Big/\left(\sqrt{\delta g^{S_R}} - \sqrt{\delta g^{S_0}}\right); \\ & b = 1\Big/\left(\sqrt{\delta g^{S_R}} - \sqrt{\delta g^{S_0}}\right). \end{aligned} \tag{6}$$

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 [29] of solute A calculated by an atom-additivity scheme, δg^S, δg^{S_R}, δg^{S_0} are the relative cavity formation Gibbs energies for each solvent. δg^S is given by the following equation:

$$\delta g^S = \left(\Delta_{solv}G^{C_8H_{18}/S} - \Delta_{solv}G^{C_8H_{18}/C_{16}H_{34}}\right)/V_x{}^{C_8H_{18}}, \tag{7}$$

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.

The standard solvents S_0 and S_R can be chosen arbitrarily, but they cannot form hydrogen bonds with solute A and should have different values of the δg^S parameter. If it is so, Eq. (6) allows to calculate the Gibbs energy of nonspecific solvation using one solute size parameter – V_x^A, and two experimental Gibbs solvation energies of A in the standard solvents that are required to know how the Gibbs energy of nonspecific interactions is changing with the growth of solvent propensity to intermolecular interactions described by δg^S parameter. We always used n-hexadecane as the standard solvent S_0 since it is inert, has $\delta g^S = 0$, and hundreds of values of the solvation Gibbs energies for various solutes in n-hexadecane are available. DMSO and benzene showed good performance as the standard solvents S_R.

δg^S is the only solvent parameter in Eq. (6). It is important to note that in the case of associated solvents such as aliphatic alcohols, it is necessary to take the solvophobic effects into account. For example, if we try to calculate the Gibbs energies of hydrogen bonding processes of various solutes with alcohols using Eq. (4) assuming $\Delta_{s.e.}G^{A/ROH} = 0$, we will obtain positive values for some solutes, which is an unphysical result that breaks the second law of thermodynamics. Moreover, in associated solvents the value of $\Delta_{solv}G^{C_8H_{18}/S}$ in Eq. (7) is influenced by the solvophobic effect. We have made a correction for the solvophobic effect of octane in order to calculate the values of δg^S for alcohols, what has been described in details in our previous paper [27].

2.3. Empiric parameters for description of solvation properties of aliphatic alcohols

In one of our previous works [30], we have discussed the difficulties of choice of the standard solvents in Eq. (6) for aliphatic alcohols. Good accuracy of Eq. (6) is achieved when two standard solvents have greatly different values of the δg^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 solvent as benzene. Thus, we would obtain more accurate results if we will write Eq. (6) in an equivalent form with empiric

Table 1
Parameters of monohydric aliphatic alcohols used in Eqs. (5), (8) and (9) (at 298 K).

Alcohol (ROH)	V_x^{ROH}/cm$^3\cdot$mol$^{-1}\cdot 10^2$ [a]	k^S [b]	b^S [b]	p^A [c]	q^A [c]	δg^S/kJ$\cdot$cm$^{-3}\cdot 10^2$ [b]	$\Delta_{vap}G^{ROH}$/kJ$\cdot$mol^{-1} [d]
Methanol	0.3082	5.17	0.23	−1.99	7.3	2.60	4.6
Ethanol	0.4491	3.98	0.83	−2.01	4.0	1.11	6.3
Propanol	0.5900	3.94	0.36	−2.17	1.1	0.94	8.9
Butanol	0.7309	3.06	0.50	−2.36	−2.1	0.65	11.6
Octanol	1.2945	1.78	0.60	−2.93	−13.6	0.20	21.9

[a] See ref [29] for the procedure of calculation.
[b] Taken from our previous work [27].
[c] Calculated in our previous work [30].
[d] Calculated from literature data [32,33].

parameters of solute p^A and q^A that can be determined using a linear regression:

$$\Delta_{solv(nonsp)}G^{A/S} = V_x{}^A\cdot\delta g^S + p^A\sqrt{\delta g^S} + q^A. \tag{8}$$

To determine the values of parameters p^A and q^A for a given solute A, a regression of the values of $\Delta_{solv}G^{A/S} - V_x^A\cdot\delta g^S$ versus the values of $\sqrt{\delta g^S}$ for various solvents S should be conducted. However, only the data for those solvents, where solute–solvent (A–S) hydrogen bonding interactions can be neglected, should be included in correlation. For considered aliphatic alcohols, the values of p^A and q^A have been determined previously [30].

The contribution due to the solvophobic effect reflects the difference in behavior of solutions in self-associated solvents from solutions in other solvents. We have shown that the solvophobic effect Gibbs energy in all considered alcohols [27] and in water [31] is found to be linearly dependent on the characteristic molecular volume of solute:

$$\Delta_{s.e.}G^{A/S} = k^S V_x{}^A + b^S. \tag{9}$$

The values of coefficients k^S and b^S in Eq. (9) for each of considered alcohols have been determined using a regression of $\Delta_{s.e.}G^{A/S}$ versus V_x^A for apolar solutes in our previous work [27]. They are given in Table 1, as well as other quantities and parameters that are required to calculate $\Delta_{int(sp)}G^{ROH/ROH}$.

3. Results and discussion

3.1. Gibbs free energies of self-association

Calculated values of the Gibbs free energies of self-association are given in Table 2. Taking into account the uncertainties of Eqs. (8) and (9), which are less than 1 kJ·mol^{-1}, the true values of $\Delta_{int(sp)}G^{ROH/ROH}$ are likely to lie in the interval ±1 kJ·mol^{-1} from calculated values. The borders of this interval and the middle value were then converted into the monomer molar fractions using Eq. (1) (columns 'min', 'max', and 'avg' in Table 3).

3.2. Monomer fractions calculated using different models

We wanted to compare our results with predictions of different association models. In the recent paper [26] of the authors of three of these models: CPA, sPC-SAFT and NRHB, the monomer fractions of alcohols were calculated over a broad temperature range. Unfortunately, only qualitative graphs showing the temperature dependence of the monomer fraction are given. Thus, we recalculated the monomer fractions for alcohols at 298 K using all three models: CPA, sPC-SAFT and NRHB. We used parameters from their previous papers [5,15]. A 2B association scheme of alcohols was assumed. The results are given in Table 3. In the last column of Table 3, the values obtained by Luck [34] are presented.

Table 2
The Gibbs free energies of self-association, solvophobic effect and nonspecific interactions in some monohydric aliphatic alcohols (at 298 K in kJ·mol^{-1}).

Alcohol (ROH)	$\Delta_{solv(nonsp)}G^{ROH/ROH}$	$\Delta_{s.e.}G^{ROH/ROH}$	$\Delta_{int(sp)}G^{ROH/ROH}$
Methanol	4.9	1.8	−11.4
Ethanol	2.4	2.6	−11.3
Propanol	−0.4	2.7	−11.1
Butanol	−3.5	2.7	−10.8
Octanol	−14.7	2.9	−10.1

The monomer molar fraction is increasing when we go from pure methanol to octanol. This result is reproduced by all models. In general, there is a very good agreement between the results of calculation by Eq. (3) and those of other considered models. The last ones fall into the range between minimum and maximum values of x_1 from the third and fourth columns of Table 3. One notable exclusion is that using our approach, we obtained larger percent of monomers in methanol, which are closer to those reported by Luck who analyzed the IR-spectra using his theory of self-associated liquids.

Some other results for monomer fractions in alcohols were obtained by Huyskens [35] who concluded that there is about 1.4% of monomer in liquid ethanol, and Benson [2] who estimated 0.3% of monomers in an "average" liquid aliphatic alcohol at 298 K.

3.3. Hydrogen bond cooperativity in self-association processes

An important feature of hydrogen bonding is its cooperativity: the strength of a hydrogen bond measured in terms of internal energy, enthalpy, or Gibbs free energy increases if it participates in a chain of hydrogen bonds [20–23]. This phenomenon has a large impact on the structure of self-associated fluids and stability of biological and artificial supramolecular structures. It should be taken into account in realistic models of association processes.

It is interesting to reveal the influence of cooperativity on the Gibbs energies of association between clusters of alcohol of various sizes. However, we would not be able to estimate exact values of subsequent constants of association of alcohols using only the data on monomer fractions unless we made some assumptions about the structures and energies of associates. Instead of making any arbitrary assumptions, we will calculate the magnitude of alcohol–alcohol dimerization constant from the above data on $\Delta_{ass}G^{ROH}$ using a 'model

Table 3
The monomer molar fractions (in percents) in some monohydric aliphatic alcohols (at 298 K) calculated using different models.

Alcohol (ROH)	x_1 [a] (avg)	x_1 [a] (min)	x_1 [a] (max)	x_1 (CPA)	x_1 (sPC-SAFT)	x_1 (NRHB)	x_1 (Luck)
Methanol	1.00	0.67	1.50	0.24	0.60	0.38	2.02
Ethanol	1.05	0.70	1.57	1.33	0.66	0.92	1.75
Propanol	1.13	0.75	1.69	1.56	1.01	1.16	
Butanol	1.27	0.85	1.91	1.50	1.36	1.40	
Octanol	1.71	1.14	2.56	6.39	2.07	2.32	

[a] Results of calculations by Eqs. (3), (6) and (7).

without cooperativity' where the difference in hydrogen bond strength due to the size of associate is neglected and compare it with the experimental Gibbs energy of dimerization of the alcohols in inert medium.

The following primitive model of association without cooperativity can be considered. Let us assume that only linear associates are present, and the constants of association are all equal when they are expressed through volume fractions: $K_2=K_3=\ldots=K_n$. In such case the constants K_n' in the scale of molar fractions defined as $x_n=\left[(ROH)_n\right]/\sum_{n=1} n\left[(ROH)_n\right]$ (x_n equals number of moles of associates containing n molecules of alcohol divided by total number of moles of alcohol molecules in all associates) are given by $K_n'=x_n/(x_1x_{n-1})=2K_2'(n-1)/n$, because $K_n=\varphi_n/(\varphi_1\varphi_{n-1})\approx x_n/(x_1x_{n-1})\cdot n/(n-1)\cdot const.$ Thus,

$$\sum_{n=1} nx_n=\sum_{n=1} x_1^n\left(2K_2'\right)^{n-1}=x_1/\left(1-2x_1K_2'\right)=1;\quad K_2'=(1-x_1)/(2x_1). \tag{10}$$

On the other hand, if we assume that association constants are all the same in molar fractions scale, then

$$\sum_{n=1} nx_n=\sum_{n=1} x_1^n K_2'^{\,n-1}=x_1/\left(1-x_1K_2'\right)=1;\quad K_2'=(1-x_1)/x_1. \tag{11}$$

The values of K_2' for methanol estimated using this model are 49.5 when using formula (10) and 99 when using formula (11). For ethanol, these values will be 47 and 94. The reference experimental values of dimerization constants in inert solvent (tetrachloromethane) obtained by different authors are reported [21,36] to be 11.2, 16.5, and 28.9 for ethanol and 32 for methanol (all values were converted to the molar fraction scale). A disagreement between these values and the result from a model of self-association without cooperativity is quite clear. This is an evidence of cooperative effects for associates larger than dimer, and it is likely that the constants of subsequent association exceed the dimerization constant in at least 2 times.

4. Conclusion

Studies of the properties of hydrogen bonds help to understand solvent effects on solute reactivity. The values of monomer fractions can also be used in parameterization of the association theories. We have applied a relatively simple extrathermodynamic method to determine the monomer fractions from thermodynamic data. A special attention should be paid on the fact that the solvophobic effects were explicitly treated as an additive contribution to the Gibbs energy. Neglection of these effects would lead to the results inconsistent with those obtained using different methods and models in literature. Another effect which cannot be neglected in self-associating systems is the cooperativity of hydrogen-bonding processes.

Out approach can be used not only for solvent itself, but also for any molecule dissolved in self-associated solvent in order to determine the contribution of hydrogen-bonding processes into the Gibbs free energy of solvation [37] and to judge about their influence on solute reactivity.

5. List of symbols

$\Delta_{ass}G^{ROH}$	Gibbs energy of self-association of alcohol ROH
$\Delta_{ass}f^{ROH}$	thermodynamic function of self-association of alcohol ROH ($f=H$, S)
φ_1	volume fraction of monomeric alcohol species among all associates
$V_m(A)$	molecular volume of compound A
$[(ROH)_n]$	concentration ($\mathrm{mol\cdot l^{-1}}$) of associate $(ROH)_n$
x_n	number of moles of associates containing n molecules of alcohol divided by total number of moles of alcohol molecules in all associates
x_1	fraction of free monomer among all molecules of alcohol engaging in different types of associates
$\Delta_{solv}G^{A/S}$	Gibbs energy of solvation of solute A in solvent S
$\Delta_{solv(nonsp)}G^{A/S}$	Gibbs energy of nonspecific solvation of solute A in solvent S
$\Delta_{int(sp)}G^{A/S}$	Gibbs energy of specific interactions of solute A in solvent S
$\Delta_{s.e.}G^{A/S}$	Gibbs energy of the solvophobic effect of solute A in solvent S
$\Delta_{vap}G^{A}$	Gibbs energy of vaporization of compound A
V_x^A	McGowan characteristic molecular volume of A
δg^S	relative cavity formation Gibbs energy in solvent S
S_0, S_R,	standard solvents in Eq. (6)
p^A, q^A	parameters of solute A in Eq. (8)
k^S, b^S	parameters of solvent S in Eq. (9)
K_n	constant of association between $(\mathrm{ROH})_{n-1}$ and ROH expressed through volume fractions
K_n'	constant of association between $(\mathrm{ROH})_{n-1}$ and ROH expressed through volume fractions
T	temperature (K)
R	universal gas constant

Acknowledgment

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.

References

[1] A. Apelblat, Journal of Molecular Liquids 128 (2006) 1.
[2] S.W. Benson, Journal of the American Chemical Society 118 (1996) 10645.
[3] M. Naoki, T. Seki, Fluid Phase Equilibria 281 (2009) 172.
[4] T. Hofman, Fluid Phase Equilibria 55 (1990) 39.
[5] A. Grenner, I. Tsivintzelis, I.G. Economou, C. Panayiotou, G.M. Kontogeorgis, Industrial and Engineering Chemistry Research 47 (2008) 5636.
[6] S. Woutersen, U. Emmerichs, H.J. Bakker, Journal of Chemical Physics 107 (1997) 1483.
[7] M. Paolantoni, P. Sassi, A. Morresi, R.S. Cataliotti, Chemical Physics 310 (2005) 169.
[8] N. Asprion, H. Hasse, G. Maurer, Fluid Phase Equilibria 186 (2001) 1.
[9] A. Staib, Journal of Chemical Physics 108 (1998) 4554.
[10] B. Chen, J.J. Potoff, J.I. Siepmann, The Journal of Physical Chemistry. B 105 (2001) 3093.
[11] J.W. Handgraaf, T.S. Van Erp, E.J. Meijer, Chemical Physics Letters 367 (2003) 617.
[12] P.L. Huyskens, M.C. Haulait-Pirson, G.G. Siegel, F. Kapuku, Journal of Physical Chemistry 92 (1988) 6841.
[13] V.A. Durov, Pure and Applied Chemistry 76 (2004) 1.
[14] A. Heintz, Berichte der Bunsengesellschaft/Physical Chemistry Chemical Physics 89 (1985) 172.
[15] G.M. Kontogeorgis, M.L. Michelsen, G.K. Folas, S. Derawi, N. Von Solms, E.H. Stenby, Industrial and Engineering Chemistry Research 45 (2006) 4855.
[16] G.M. Forland, F.O. Libnau, O.M. Kvalheim, H. Hoiland, Applied Spectroscopy 50 (1996) 1264.
[17] S.I. Sandier, Journal of Physical Chemistry A 104 (2000) 1121.
[18] H. Kleeberg, D. Klein, W.A.P. Luck, Journal of Physical Chemistry 91 (1987) 3200.
[19] R.B. Gupta, R.L. Brinkley, AIChE Journal 44 (1998) 207.
[20] F. Palombo, P. Sassi, M. Paolantoni, A. Morresi, R.S. Cataliotti, The Journal of Physical Chemistry. B 110 (2006) 18017.
[21] F. Schwager, E. Marand, R.M. Davis, Journal of Physical Chemistry 100 (1996) 19268.
[22] H. Shekaari, H. Modarress, N. Hadipour, Journal of Physical Chemistry A 107 (2003) 1891.
[23] B.N. Solomonov, V.B. Novikov, M.A. Varfolomeev, A.E. Klimovitskii, Journal of Physical Organic Chemistry 18 (2005) 1132.
[24] W.A.P. Luck, Angewandte Chemie (International Ed. in English) 19 (1980) 28.
[25] T. Hofman, I. Nagata, Fluid Phase Equilibria 25 (1986) 113.
[26] G.M. Kontogeorgis, I. Tsivintzelis, N. Von Solms, A. Grenner, D. B+¬gh, M. Frost, A. Knage-Rasmussen, I.G. Economou, Fluid Phase Equilibria 296 (2010) 219.

[27] I.A. Sedov, M.A. Stolov, B.N. Solomonov, Journal of Physical Organic Chemistry 24 (2011) 1088.
[28] I.A. Sedov, B.N. Solomonov, Russian Journal of Physical Chemistry A 82 (2008) 704.
[29] M.H. Abraham, J.C. McGowan, Chromatographia 23 (1987) 243.
[30] I.A. Sedov, B.N. Solomonov, Fluid Phase Equilibria 276 (2009) 108.
[31] B.N. Solomonov, I.A. Sedov, Journal of Molecular Liquids 139 (2008) 89.
[32] L.M. Sprunger, S.S. Achi, J. Acree, M.H. Abraham, Fluid Phase Equilibria 288 (2010) 139.
[33] EPI Suite, http://www.epa.gov/oppt/exposure/pubs/episuite.htm2007.
[34] W.A.P. Luck, H. Borgholte, T. Habermehl, Journal of Molecular Structure 177 (1988) 523.
[35] P.L. Huyskens, D.P. Huyskens, G.G. Siegel, Journal of Molecular Liquids 64 (1995) 283.
[36] B. Frange, J.L.M. Abboud, C. Benamou, L. Bellon, Journal of Organic Chemistry 47 (1982) 4553.
[37] I.A. Sedov, B.N. Solomonov, Journal of Chemical & Engineering Data 56 (2011) 1438.