Available online at www.sciencedirect.com

ScienceDirect

Journal of Fluorine Chemistry 129 (2008) 397–401

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/fluor

On the miscibility of ethers and perfluorocarbons
An experimental and theoretical study

Peter Babiak, Adriana Němcová, Lubomír Rulíšek, Petr Beier *

Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic and Gilead Sciences Research Center, Flemingovo nám. 2, 166 10 Prague, Czech Republic

Received 19 December 2007; received in revised form 23 January 2008; accepted 24 January 2008
Available online 3 February 2008

Abstract

Despite their significant polar character, some organic ethers such as diethyl ether were found to be miscible with perfluorocarbon solvents. Solubilities of various ethers in perfluorocarbons and miscibility temperatures were determined. These properties were found to be greatly dependent on the polarity but also size and shape of the ether molecule. Theoretical calculations of the miscibility temperatures of organic solvents and perfluorocarbons using COSMO-RS method were correlated with experimental data. Considering the difficulties in the accurate description of the macroscopic properties, such as miscibility temperatures, from the first principles, the agreement between experimental and theoretical data is reasonable.

Keywords: Miscibility; Solubility; Ethers; Perfluorinated solvents; Fluorous biphase separation

1. Introduction

Perfluorinated hydrocarbons are recognized as liquids with unique characteristics. In these compounds, which contain only C–C and very strong C–F bonds, the presence of electron rich outer shell (molecular surface) comprised of fluorine atoms gives rise to unique properties such as high thermal and chemical stability, non-polar character, low polarizability and very weak intermolecular forces [1]. As a consequence, there is a large miscibility gap between perfluorocarbons and common organic solvents (including highly hydrophobic solvents). Perfluorocarbons thus form the third *fluorous* liquid phase in addition to the *organic* and *aqueous* phases and this fact has been utilized in the development of fluorous biphase chemistry and separation [2]. Standard biphasic system used in fluorous biphase chemistry is perfluoro(methylcyclohexane) (PFMCH) and toluene at 25 °C. There has been an extensive work done on the prediction and influence of the structure on the relative miscibility (partition coefficient) of various organic and polyfluorinated compounds [3]. However, data on absolute solubilities of compounds in perfluorocarbons are rather scarce [4]. Other common fluorous solvents are PFH (perfluorohexane) and PFD (perfluorodecalin, mixture of *cis* and *trans* isomers). In this report we attempt to broaden our understanding of solvation properties of organic ethers (miscibility and solubility) in fluorous solvents.

2. Results and discussion

The detailed investigation of the miscibility properties of ethers with perfluorocarbons was initiated by an interesting observation that various perfluorocarbons (such as PFH, PFD or PFMCH) are miscible in all proportions with diethyl ether at room temperature.[1] This behavior is quite unexpected because diethyl ether has relatively polar character. It is in contradiction with general experimental experience that only very hydrophobic solvents such as *n*-hexane or isooctane are miscible with perfluorocarbons. In Table 1 common organic solvents are ordered with respect to their polarity (dielectric constant) and experimentally determined values of miscibility temperatures (T_m) with fluorous solvents are shown. In all cases the miscibility is lower (i.e. T_m is higher) in PFH and PFD

---

* Corresponding author. Tel.: +420 220 183 273; fax: +420 220 183 578.
E-mail address: beier@uochb.cas.cz (P. Beier).

[1] Miscibility of diethyl ether with PFMCH and perfluoro(dimethylcyclohexane) has been briefly mentioned in literature [4a,4e].

0022-1139/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2008.01.014

Table 1
Measured and calculated miscibility temperatures (T_m) of common solvents with fluorous solvents

Entry	Solvent	ε_r[a]	δ [MPa$^{1/2}$][b]	$T_{m\ (PFH)}$ [°C][c,d] meas. (calc.)	$T_{m\ (PFD)}$ [°C][c,e] meas. (calc.)	$T_{m\ (PFMCH)}$ [°C][c,f] meas. (calc.)
1	*n*-Hexane	1.88	14.9	**21** (33)	**22** (51)	**7** (28)
2	Isooctane	1.94	14.1	**15** (88)	**12** (111)	**1** (82)
3	Cyclohexane	2.0	16.8	71 (101)	61 (122)	53 (95)
4	CCl_4	2.23	17.6	52 (−73)	32 (−62)	26.7 [4b] (−77)
5	Benzene	2.3	18.8	>95 (−29)	92 (−12)	84.9 [4b] (−28)
6	Toluene	2.4	18.2	>95 (−22)	>95 (−3)	88.6 [4b] (−20)
7	Et_2O	4.2	15.3	**14** (7)	**18** (21)	**3** (3)
8	$CHCl_3$	4.64	19.0	73 (−46)	61 (−33)	50.1 [4b] (−49)
9	EtOAc	6.0	18.6	76 (44)	73 (65)	59 (45)
10	THF	7.4	18.6	94 (61)	83 (82)	72 (61)
11	CH_2Cl_2	8.9	19.8	>92 (−5)	85 (8)	79 (−9)
12	Acetone	20.7	20.3	>95 (41)	>95 (63)	84 (42)
13	EtOH	24.3	26.0	>95 (124)	>95 (139)	>95 (123)
14	MeOH	32.6	29.7	>95 (157)	>95 (168)	>95 (154)
15	MeCN	36.2	24.3	>95 (82)	>95 (100)	>95 (82)
16	H_2O	78.5	48.0	>95 (345)	>95 (350)	>95 (341)

Experimental T_m values lower than 25 °C are highlighted in bold.

[a] Dielectric constant from literature (25 °C) [6].

[b] Hildebrand solubility parameter from literature [4a,5].

[c] Miscibility temperature (volume fraction of each solvent was 0.5).

[d] PFH—perfluorohexane.

[e] PFD—perfluorodecalin, T_m (calc.) refers to *cis* isomer.

[f] PFMCH—perfluoro(methylcyclohexane).

compared to PFMCH. In contrast to diethyl ether (entry 7), other common ether–tetrahydrofuran is not miscible with fluorous solvents at room temperature (entry 10). As suggested in the literature, Hildebrand solubility parameter (δ), which describes cohesive energy density of the solvent [5], is better parameter than dielectric constant for the prediction the mutual miscibility of fluorous and organic solvents [3a]. Indeed, diethyl ether unlike tetrahydrofuran has the δ value similar to that of saturated hydrocarbons.

We compared the experimental miscibility temperatures with the predicted ones calculated from the first principles. The theoretical calculations of miscibilities were carried out by COSMO*therm* program of COSMO*logic* [7]. The COSMO*therm* is based on COSMO-RS theory of interacting molecular surface charges [8] as computed by quantum chemical methods and it combines an electrostatic theory of locally interacting molecular surface descriptors (available from QM calculations) with a statistical thermodynamics theory.

The input data are the surface charge densities obtained by quantum chemical calculations in the context of conductor-like screening model (COSMO). COSMO model [9] effectively simulates the effect of the environment (solvent molecules) via solvent dielectric constant, thus perturbing the solute's electronic structure (wave function in *ab initio* or Kohn-Sham determinant in density functional theory (DFT) calculations).

It is apparent from the values shown in Table 1 and graphically more clearly presented in Fig. 1, that relatively good correlation is observed for hexane, diethyl ether and highly polar solvents; however the calculated T_ms are significantly underestimated for aromatics and chlorinated hydrocarbons. We can only speculate about the source of the observed discrepancies. We assume that in the case of chlorinated hydrocarbons it may be partially attributed to the incorrect description of halogen–halogen bonds between solvent molecules [10]. Their calculated properties were shown to be critically dependent on the accuracy of the quantum chemical method, including the correct treatment of dispersion energy (mostly neglected in popular DFT methods). Also, a part of the problem can be perhaps solved by including several explicit solvent molecules into the calculations. However, such an approach would also complicate the thermodynamics, since the variation of the chemical potential of the explicit solvent (which now is fixed) as a function of the concentration would have to be consistently taken into account for miscibility purposes. Besides, such an approach would need to be consistently repeated for the remaining solvents, where the agreement was satisfactory.

The unexpected miscibility of diethyl ether with fluorous solvents initiated our systematic search for other ethers that are miscible with fluorous solvents. We selected a range of aliphatic ethers, either commercially available or prepared by alkylation of alkyl bromides with anhydrous alkali metal alcoholate in a high boiling solvent (DMA). Table 2 summarizes measured temperatures (T_m) of miscibility of studied ethers with three fluorous solvents.

Several interesting observations can be made from data presented in Table 2. As expected, polar ethers containing two oxygen atoms such as 1,4-dioxane, dimethoxymethane and 1,2-dimethoxyethane (DME) are immiscible with fluorous solvents (i.e. T_m is high, entries 11, 12 and 14). Miscibility is largely dependent on the size of the molecule (e.g. Et_2O is miscible but *n*-Pr_2O and *n*-Bu_2O are not). Small increase of the chain length leads to a substantial change in miscibility (cf., entries 2–4). Branching increases miscibility (e.g. *i*-Pr_2O is miscible but *n*-

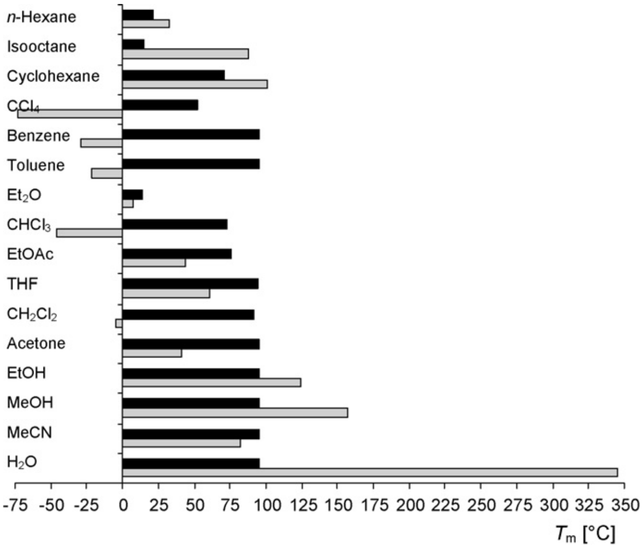

Fig. 1. Experimental (black bars) and calculated (grey bars) miscibility temperatures (T_m) of organic solvents and perfluorohexane.

Pr_2O is not). The best miscibility, as exemplified by the lowest miscibility temperature (T_m), has been observed for *t*-BuOMe and *i*-Pr_2O. However, the substitution of methyl group in *t*-BuOMe for ethyl or *n*-propyl groups results in the substantial increase of T_m (entries 8–10).

The results from calculations showed (see Table 2 and Fig. 2) a reasonably good agreement with experimental data for more polar ethers or the ones with linear structure. On the other hand the agreement is poor with ethers having branched structure. Nonetheless the trends in the homological series are preserved also in the calculated values.

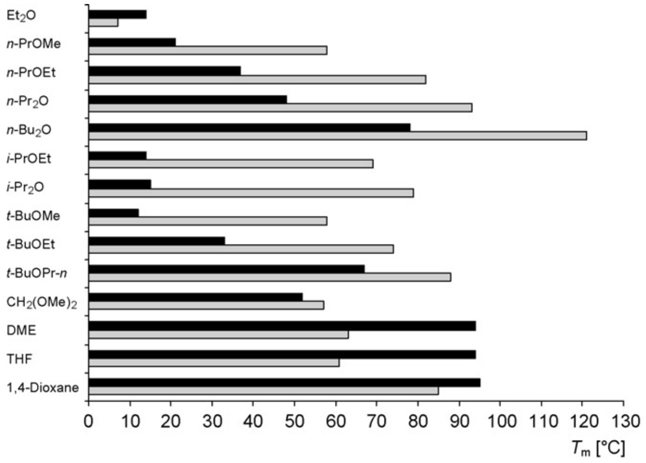

Fig. 2. Experimental (black bars) and calculated (grey bars) miscibility temperatures (T_m) of ethers and perfluorohexane.

We expected that ethers forming a two phase system at room temperature will have substantial solubilities with perfluorocarbons. To this aim, we measured mutual solubilities of studied ethers with PFH and PFD at 25 and −20 °C. The data are shown in Table 3.

As expected, at −20 °C the solubility of organic and fluorous phase is lower than at room temperature. In most cases solubilities of ethers in PFD were found to be slightly higher than in PFH. Except for more polar ethers (entries 12–14) we observed significant mutual solubilities at room temperature.

Table 2
Measured and calculated miscibility temperatures (T_m) of ethers with fluorous solvents

Entry	Ether	ε_r[b]	δ [$MPa^{1/2}$]	n_D[e]	m.p.[f] [°C]	$T_{m\ (PFH)}$ [°C][g,h] meas. (calc.)	$T_{m\ (PFD)}$ [°C][g,i] meas. (calc.)	$T_{m\ (PFMCH)}$ [°C][g,j] meas. (calc.)
1	Et_2O	4.2	15.3[c]	1.3526	−116.2	**14** (7)	**18** (21)	**3** (3)
2	*n*-PrOMe[a]	–	15.6[d]	1.3579	–	**21** (58)	**22** (79)	**10** (54)
3	*n*-PrOEt[a]	–	15.4[d]	1.3695	−127.5	37 (82)	37 (103)	**23** (77)
4	*n*-Pr_2O[a]	3.39	15.5[d]	1.3809	−114.8	48 (93)	48 (115)	33 (93)
5	*n*-Bu_2O	3.18	15.8[d]	1.3992	−95.2	78 (121)	72 (147)	58 (115)
6	*i*-PrOEt[a]	–	15.3[d]	1.3642	–	**14** (69)	**18** (90)	**3** (64)
7	*i*-Pr_2O	4.04	14.4[d]	1.3682	−85	**15** (79)	**14** (102)	**−2** (74)
8	*t*-BuOMe	–	15.1[d]	1.3736	−115.7	**12** (58)	**12** (79)	**0** (54)
9	*t*-BuOEt[a]	–	14.8[d]	1.4503	−94	33 (74)	35 (96)	**24** (69)
10	*t*-BuOPr-*n*[a]	–	15.2[d]	1.3856	−93.6	67 (88)	65 (112)	47 (88)
11	$CH_2(OMe)_2$	–	17.0[d]	1.3513	−105.1	52 (57)	54 (78)	41 (58)
12	DME	7.05	18.1[d]	1.377	−69.2	94 (63)	92 (85)	80 (59)
13	THF	7.4	18.6[c]	1.4050	−108.4	94 (61)	83 (82)	72 (61)
14	1,4-Dioxane	2.27	20.5[c]	1.4224	11.85	>95 (85)	>95 (107)	>95 (85)

Experimental T_m values lower than 25 °C are highlighted in bold.

[a] These ethers were synthesized.

[b] Dielectric constant from literature (25 °C) [6c,11].

[c] Hildebrand solubility parameter from literature [4a,5].

[d] Hildebrand solubility parameter calculated from literature ΔH_{vap} [12] and density [12a,12f,13,14] values.

[e] Refractive index from literature (25 °C) [12f,13,15].

[f] Melting point from literature [12a,13,16].

[g] Miscibility temperature (volume fraction of organic solvent was 0.5).

[h] PFH—perfluorohexane.

[i] PFD—perfluorodecalin, T_m (calc.) refers to *cis* isomer.

[j] PFMCH—perfluoro-(methylcyclohexane).

Table 3
Mutual binary solubilities of ethers (x_O) and fluorous solvents (x_F) at 25 and −20 °C

Entry	Ether	Solubility (vol%) PFH				Solubility (vol%) PFD			
		25 °C		−20 °C		25 °C		−20 °C	
		x_F[b]	x_O[c]	x_F[b]	x_O[c]	x_F[b]	x_O[c]	x_F[b]	x_O[c]
1	Et_2O	Miscible		7.5	10.6	Miscible		5.2	11.9
2	*n*-PrOMe[a]	Miscible		9	9	Miscible		2.5	23
3	*n*-PrOEt[a]	17.5	20	6.5	6	10	13	3	4
4	*n*-Pr_2O[a]	11	7	<1	3.5	12	6	<1	1.3
5	*n*-Bu_2O	3.1	4.4	1.6	2.6	7	5.8	5.5	2.7
6	*i*-PrOEt[a]	Miscible		7	7	Miscible		5.5	4
7	*i*-Pr_2O	Miscible		6	12.9	Miscible		13.5	12.5
8	*t*-BuOMe	Miscible		8	17	Miscible		13.5	7
9	*t*-BuOEt[a]	17	25	5	8	19	24	5	[d]
10	*t*-BuOPr-*n*[a]	1.5	19	<1	10	2	18	1	[d]
11	$CH_2(OMe)_2$	12	20	4	5	25	11	9	3
12	DME	2.6	3.1	2.4	2.8	1.3	4	<1	[d]
13	THF	4	6	3	2.5	2	6	<1	[d]
14	1,4-Dioxane	1.7	1.2	[d]	1.4	<1	2.5	[d]	[d]

PFH—perfluorohexane, PFD—perfluorodecalin.

[a] These ethers were synthesized.

[b] Solubility of fluorous solvent in ether phase.

[c] Solubility of ether in fluorous phase.

[d] Solvent solidified at this temperature.

When the solubility of ether in PFD (m.p. of pure liquid is −10 °C) was very low ($\ll 1\%$), the fluorous phase solidified at −20 °C.

Unfortunately, the difference of the miscibility of isomeric ethers cannot be used for their efficient separation by one step extraction with fluorous solvent. For example, after extraction of a mixture of *i*-Pr_2O (0.1 ml) and *n*-Pr_2O (0.1 ml) with PFD (0.2 ml) and separation at either 25 °C or −20 °C, we found that the upper organic phase had the volume ratio of ethers *i*-/*n*- of 49:51 at both temperatures, while the ratio in lower fluorous phase was 56:44 (at 25 °C) or 62:38 (at −20 °C) as determined by GC–MS. Clearly *i*-Pr_2O prefers to be solubilized by very similar *n*-Pr_2O rather than entering into the PFD phase.

In summary, the study of the solubility of ethers clearly shows that in the context of fluorous biphase separation it is important to realize that mutual solubilities can compromise the efficiency of extraction. In standard system of toluene and PFMCH we found solubilities (in vol%) of $x_F = 2.5$, $x_O = 6.7$ at 25 °C and $x_F = <1$, $x_O = 3$ at −20 °C as determined by GC–MS.[2] Although the presence of solutes can alter these values, fluorous biphase systems, especially those designed to form one phase under slight heating, cannot be considered as immiscible liquids.

3. Conclusions

Complete miscibility of diethyl ether with various fluorous solvents is recognized. A range of aliphatic ethers was employed for the determination of their miscibility temperatures and solubilities with various fluorous solvents. It is expected that perfluorinated solvents exert only very weak intermolecular forces and therefore, the solution contains larger cavities (free volumes) that can accommodate small molecules [4e]. We found that in a simple approximation most important factors necessary to achieve full miscibility of ethers in fluorous solvents are low polarity, small size and globular (bulky) rather than linear shape of the ether molecule.

4. Experimental and computational details

4.1. Materials and methods

Perfluoro(methylcyclohexane) (PFMCH, >97% purity) was purchased from Merck, perfluorohexane (PFH, 95% purity) and perfluorodecalin (PFD, mixture of *cis* and *trans*, >97% purity) were purchased from ABCR and Fluorochem, respectively. Ethers we either purchased (in >99% purity) or synthesized using general procedure. Reactions were performed under argon atmosphere and *N,N*-dimethylacetamide was dried using 4 Å molecular sieves prior to use. GC–MS analysis was conducted using an Agilent 7890A gas chromatograph equipped with a 5975C inert mass selective detektor (EI ionization) and 7683B autoinjector. NMR spectra were measured in $CDCl_3$ on a Bruker Avance 400 (^1H at 400 MHz). The temperature was controlled and measured using Memmert WB 14 water bath and JULABO FT 902 immersion cooler.

4.2. General procedure for ether synthesis

Alkyl bromide (50 mmol) was added dropwise to a stirred mixture of anhydrous alcoholate (60 mmol) (commercial MeONa, *t*-BuOK or prepared *n*-PrONa, *i*-PrONa) in *N,N*-dimethylacetamide (20 ml) cooled to −10 °C. The reaction

---

[2] Literature values (in vol%) at 25 °C are: $x_F = 2.9$, $x_O = 2.0$ measured by NMR [17].

mixture was warmed up to room temperature over 30 min and then the crude product was distilled under reduced pressure. The pure product was obtained as a colorless liquid in 62–79% yield (>98% GC purity) by washing several times with water to remove traces of alcohol and drying with anhydrous $MgSO_4$. MS and ^1H NMR spectra were in good agreement with published data.

4.3. Calculations of miscibility temperatures

All calculations were carried out within the framework of DFT using B-LYP [18] functional and TZVPP basis set [19]. The calculations were performed using Turbomole 5.8 program [20]. In COSMO*therm* program, default parameters were used in all cases. Calculated $T_{m\ (PFD)}$ values refer to *cis* isomer, $T_{m\ (PDF)}$ values for *trans* isomer were found to be very similar.

4.4. Determinations of miscibility temperatures

Mixture of organic and perfluorocarbon solvent (0.5 ml each) was placed in a glass vial and sealed. The vial was equilibrated for 5 min in a temperature controlled water bath and periodically shaken. The temperature of the bath was increased by 1 °C (the vial was equilibrated for another 5 min) until the formation of one phase system. In all cases sharp phase change over $\leq$1 °C was observed.

4.5. Solubility measurements

Mixture of organic and perfluorocarbon solvent (0.2 ml each) was manually shaken for 30 s and then equilibrated at 25 °C or −20 °C for at least 30 min. A portion (10 μl) was taken from each phase, diluted with diethyl ether (1 ml) and analyzed using GC–MS. In case of measuring solubilities of perfluorocarbons with diethyl ether, dibutyl ether was used for dilution. A four point calibration curve was made for each solvent. The solubility was calculated from the concentration ratio of each compound and is reported as an average of three separate measurements.

Acknowledgments

This work was supported by Research Plan AVZ40550506 from the Academy of Sciences of the Czech Republic and program LC512 from the Ministry of Education of the Czech Republic.

References

[1] (a) P. Kirsch, Modern Fluoroorganic Chemistry, Wiley-VCH, Weinheim, 2004, pp. 8–16;
(b) G. Sandford, Tetrahedron 59 (2003) 437–454.

[2] (a) I.T. Horváth, J. Rábai, Science 266 (1994) 72–75;
(b) I.T. Horváth, Acc. Chem. Res. 31 (1998) 641–650;
(c) J.A. Gladysz, D.P. Curran, I.T. Horváth, Handbook of Fluorous Chemistry, Wiley-VCH, Weinheim, 2004.

[3] (a) L.E. Kiss, I. Kövesdi, J. Rábai, J. Fluorine Chem. 108 (2001) 95–109;
(b) F.T.T. Huque, K. Jones, R.A. Saunders, J.A. Platts, J. Fluorine Chem. 115 (2002) 119–128;
(c) P.R. Duchowicz, F.M. Fernández, E.A. Castro, J. Fluorine Chem. 125 (2004) 43–48;
(d) E. de Wolf, P. Ruelle, J. van den Broeke, B.-J. Deelman, G. van Koten, J. Phys. Chem. B 108 (2004) 1458–1466.

[4] (a) R.L. Scott, J. Am. Chem. Soc. 70 (1948) 4090–4093;
(b) J.H. Hildebrand, D.R.F. Cochran, J. Am. Chem. Soc. 71 (1949) 22–25;
(c) J.H. Hildebrand, B.B. Fisher, H.A. Benesi, J. Am. Chem. Soc. 72 (1950) 4348–4351;
(d) G.S. Bernardo-Gil, L.J.S. Soares, J. Chem. Eng. Data 32 (1987) 327–329;
(e) L.P. Barthel-Rosa, J.A. Gladysz, Coord. Chem. Rev. 190–192 (1999) 587–605.

[5] (a) A.F.M. Barton, Chem. Rev. 75 (1975) 731–753;
(b) A.F.M. Barton, CRC Handbook of Solubility Parameters and Other Cohesion Parameters, CRC Press, Boca Raton, FL, 1983.

[6] (b) P. Mukerjee, C. Ramachandran, R.A. Pyter, J. Phys. Chem. 86 (1982) 3189–3197;
(b) J.L. Fulton, J.P. Blitz, J.M. Tingey, R.D. Smith, J. Phys. Chem. 93 (1989) 4198–4204;
(c) H. Hiemstra, H. Wynberg, J. Am. Chem. Soc. 103 (1981) 417–430.

[7] F. Eckert, A. Klamt, COSMO*therm*, Version C2.1, Release 01.05, COSMOlogic Gmbh & Co. KG, Leverkusen, Germany, 2005.

[8] (a) A. Klamt, J. Phys. Chem. 99 (1995) 2224–2235;
(b) A. Klamt, F. Eckert, Fluid Phase Equilib. 172 (2000) 43–72;
(c) F. Eckert, A. Klamt, AIChE J. 48 (2002) 369–385.

[9] (a) A. Klamt, G. Schuurmann, J. Chem. Soc. Perkin Trans. 2 (1993) 799–805;
(b) A. Schäfer, A. Klamt, D. Sattel, J.C.W. Lohrenz, F. Eckert, Phys. Chem. Chem. Phys. 2 (2000) 2187–2193.

[10] P. Politzer, P. Lane, M.C. Concha, Y. Ma, J.S. Murray, J. Mol. Model. 13 (2007) 305–311.

[11] (a) C. Laurence, P. Nicolet, M.T. Dalati, J.-L. Abboud, R. Notario, J. Phys. Chem. 98 (1994) 5807–5816;
(b) N. Gee, K. Shinsana, J.-P. Dodelet, G.R. Freeman, J. Chem. Thermodyn. 18 (1986) 221–234;
(c) H. Farber, S. Petrucci, J. Phys. Chem. 85 (1981) 1396–1401.

[12] (a) E.L. Krasnykh, S.V. Levanova, S.Y. Karaseva, I.N. Kirgizova, R.M. Varushchenko, A.I. Druzhinina, L.L. Pashchenko, Pet. Chem. 45 (2005) 92–95;
(b) V. Majer, Z. Wagner, V. Svoboda, V. Cadek, J. Chem. Thermodyn. 12 (1980) 387–391;
(c) S.P. Verevkin, E.L. Krasnykh, T.V. Vasiltsova, A. Heintz, J. Chem. Eng. Data 48 (2003) 591–599;
(d) W.V. Steele, R.D. Chirico, S.E. Knipmeyer, A. Nguyen, N.K. Smith, J. Chem. Eng. Data 41 (1996) 1285–1302;
(e) D.M. McEachern, J.E. Kilpatrick, J. Chem. Phys. 41 (1964) 3127–3130;
(f) M.G. Voronkov, L.A. Zhagata, Zh. Org. Khim. 4 (1968) 768–771.

[13] D.R. Lide, CRC Handbook of Chemistry and Physics, 88th edition, CRC Press, London, 2007.

[14] I.H. Peng, C.H. Tu, J. Chem. Eng. Data 49 (2004) 876–880.

[15] (a) M. Singliar, V. Macho, M. Kavala, Collect. Czech. Chem. Commun. 47 (1982) 1979–1987;
(b) J. Cidlinský, J. Polák, Collect. Czech. Chem. Commun. 34 (1969) 1317–1321.

[16] H.N. Huang, D.F. Persico, R.J. Lagow, L.C. Clark, J. Org. Chem. 53 (1988) 78–85.

[17] J.J.J. Juliette, D. Rutherford, I.T. Horváth, J.A. Gladysz, J. Am. Chem. Soc. 121 (1999) 2696–2704.

[18] (a) A.D. Becke, Phys. Rev. A 38 (1988) 3098–3100;
(b) C.T. Lee, W.T. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785–789.

[19] A. Schäfer, C. Huber, R. Ahlrichs, J. Chem. Phys. 100 (1994) 5829–5835.

[20] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, Chem. Phys. Lett. 162 (1989) 165–169.