Postprint of: Cho C., Preiss U., Jungnickel C., Stolte S., Arning J., Ranke J., Klamt A., Krossing I., Thöming J., Ionic liquids: predictions of physicochemical properties with experimental and/or DFT-calculated LFER parameters to understand molecular interactions in solution, JOURNAL OF PHYSICAL CHEMISTRY B, Vol. 115, Iss. 19 (2011), pp. 6040 - 6050.

Ionic Liquids: Predictions of Physicochemical Properties with Experimental and/or DFT-Calculated LFER Parameters to Understand Molecular Interactions in Solution

Journal:	*The Journal of Physical Chemistry*
Manuscript ID:	jp-2011-00042f.R1
Manuscript Type:	Article
Date Submitted by the Author:	n/a
Complete List of Authors:	Cho, Chul-Woong; Universität Freiburg Preiss, Ulrich; Insitut fuer Anorganische und Analytische Chemie, AK Krossing Jungnickel, Christian; Gdansk University of Technology, Department of Chemical Technology Stolte, Stefan; University of Bremen, Centre for Envirnmental Research and Sustainable Technology Arning, Juergen; University of Bremen, Centre for Envirnmental Research and Sustainable Technology Ranke, Johannes; Universität Bremen, UFT Department of Sustainable Chemistry Klamt, Andreas; COSMOlogic Krossing, Ingo; Albert-Ludwigs-Universität Freiburg, Institut für Anorganische und Analytische Chemie Thöming, Jorg; University of Bremen - Centre for Envirnmental Research and Sustainable Technology

Ionic Liquids: Predictions of physicochemical properties with experimental and/or DFT-calculated LFER parameters to understand molecular interactions in solution

Chul-Woong Cho[a,b], Ulrich Preiss[b], Christian Jungnickel[a,c], Stefan Stolte[a], Jürgen Arning[a], Johannes Ranke[a], Andreas Klamt[d,e], Ingo Krossing[b,f,*], Jorg Thöming[a,*]

[a] *Zentrum für Umweltforschung und nachhaltige Technologien (UFT) - Centre for Environmental Research and Technology, University of Bremen, Leobener Straße, 28359 Bremen, Germany*

[b] *Freiburger Materialforschungszentrum FMF, University of Freiburg, Stefan-Meier-Str. 21, 79104 Freiburg, Germany*

[c] *Chemical Faculty, Gdańsk University of Technology, ul. Narutowicza 11/12, 80-233 Gdańsk, Poland*

[d] *COSMOlogic GmbH & Co. KG, Burscheider Strasse 515, 51381 Leverkusen, Germany*

[e] *Institute of Physical and Theoretical Chemistry, University of Regensburg, Universitätsstrasse 31, 93040 Regensburg, Germany*

[f] *Institut für Anorganische und Analytische Chemie, Albertstraße 21, 79104 Freiburg, Germany and FRIAS Section Soft Matter Science*

*Corresponding author phone: +49(0)761 2036121(I.K); +49(0)421 21863300(J.T); fax: +49 (0)761 2036001 (I.K), +49 (0)421 2188297 (J.T); e-mail: krossing@uni-freiburg.de (I.K.), thoeming@uni-bremen.de (J.T.)

Abstract

In this paper we present evolutionary models to predict the octanol-water partitioning coefficient (Log P), the water solubility, and the critical micelle concentration (CMC) of ionic liquids (ILs) as well as the anionic activity coefficient and hydrophobicity in pure water and octanol-water respectively. They are based on a poly-parameter linear free energy relationship (LFER) using measured and/or DFT-calculated LFER parameters: the hydrogen-bonding acidity (A), hydrogen bonding basicity (B), polarizability/dipolarity (S), excess molar refraction (E), and McGowan volume (V) of IL ions. With both, calculated or experimental LFER descriptors of IL ions, the physicochemical parameters were predicted with an error bar of 0.182 to 0.217 for the octanol-water partitioning coefficient and 0.131 to 0.166 logarithmic units for the water solubility. Since experimentally determined solute parameters of anions are not available as of now, the CMC, anionic activity coefficient, and hydrophobicity was predicted with quantum-chemical methods with an R^2 of at least 0.99 as well as error bars below 0.168 logarithmic units. Prior to synthesis, these new approaches shall facilitate the assessment of the technical applicability of ionic compounds as well as their environmental fate.

Keywords: octanol-water partitioning coefficient, critical micelle concentration, water solubility, ionic liquids, cations, anions, DFT

Introduction

Over the past decade, the interest in ionic liquids (ILs) dramatically increased. They are alternative solvents, e.g. for use as electrolytes,[1] in catalysis,[2] and analytical chemistry.[3] This is due to their excellent solvating ability for organic and inorganic matter in combination with unusual properties such as low vapor pressure, low melting point, thermal stability, and high ionic conductivity. Since, according to serious estimates, 10^6 to 10^{18} ILs may be selectively designed by the combination of cations and anions, the ILs' contribution to science may further increase.[4] However, the multitude of possible IL variations poses difficulties for the targeted synthesis of an IL with a specific property. Therefore, recent efforts were devoted to the understanding of ILs on the molecular level[5] and to the prediction of the basic physicochemical properties of ILs.[6-13] Our groups have made some noteworthy additions here, *i.e.* an approach to understand and predict IL melting points,[6, 7] viscosities and conductivities,[8, 9] heat capacities, and temperature-dependent densities[10] as well as temperature-dependent liquid entropies.[11] Also, physicochemical properties related to biodegradation like the critical micelle concentration[12] or the soil sorption coefficient[13] can be predicted with the help of quantum chemical calculations using the molecular volume V_m.[10] However, the insight into solute-solvent interaction of ILs is still in need of improvement. It holds the key to understanding various partitioning processes, such as liquid-gas, liquid-liquid and liquid-surface partitioning. They all were described and studied in a variety of ways that are mutually largely incomparable. For example, Sprunger *et al.*[14, 15] studied ILs in combination with gas or water. They reported cation- and anion-specific equation coefficients of ILs for predicting the partitioning coefficient of solutes in 32 different IL systems. Van Meter *et al.*[16] and Anderson *et al.*[17] characterized surface-confined ILs as a stationary phase in the HPLC system. The data characterized by them is helpful to predict capacity factors of compounds in HPLC confined ILs. The study of Sprunger *et al.*[14, 15] allows predicting the partitioning coefficient of compounds in IL mixtures. In general, predictions of solute-solvent interactions of relevant and experimentally hitherto not available parameters may be obtained based on thermodynamically refined group contribution methods like UNIFAC[18], poly-parameter Linear Free Energy Relationships (pp-LFER)[19], and methods based on quantum chemical calculations like continuum solvation models.[20] Out of the pp-LFERs, the Abraham equation[21-26] (eq. 1) is the most commonly used one:

$$\mathrm{SP} = \mathrm{c} + e\,\mathrm{E} + s\,\mathrm{S} + a\,\mathrm{A} + b\,\mathrm{B} + v\,\mathrm{V} \qquad (1)$$

In equation (1), the dependent variable SP refers to some property of a series of solutes in a fixed phase. These solute descriptors are based on the physically meaningful cavity model of solute-system interactions. Here, E represents the excess molar refraction in units of $(\mathrm{cm}^3\ \mathrm{mol}^{-1})/10$, which models dispersive interactions arising from the greater polarizability of π and n- electrons. S represents the solute dipolarity and polarizability due to solute-solvent interaction between bond dipoles and induced dipoles. A and B indicate the hydrogen bond acidity and basicity of the solute, respectively. *V* is the McGowan characteristic molar volume in units of (cm^3 mol^{-1})/100. The coefficient *e* is a measure of the propensity of the phase to interact with solute π- and n-electron pairs; coefficient *s* is a measure of the system dipolarity/polarizability; coefficient *a* is a measure of the hydrogen bond basicity, which interacts with an acidic solute; and *b* is a measure of the hydrogen bond acidity, which interacts with a basic solute. The system parameter *v* describes cavity formation in the case of bulk media. Finally, the parameter c is the property dependent offset of the LFER and obtained as regression constant. Recently Abraham and Acree [27-30] has reported an extended model by adding two additional terms i.e. $j^+ J^+$ (for cation) and $j^- J^-$ (for anion) to the model (eqn. 1) to describe solute transfer of ions and ionic species from water to organic solvents, and successfully used to determine solute descriptors of ionic species.

For our predictive studies using the Abraham model, we experimentally determined the solute parameters of 30 different cations with high performance liquid chromatography[31] and then, complementary, employed computational methods. For the latter part, DFT-calculations at the (RI–)BP86/TZVP level in combination with COSMO (COnductor-Screening MOdel), COSMO-RS (COSMO for Real Solvent, which is a model combining quantum theory, surface interactions, and statistical thermodynamics),[32] and OBPROP (version 1.1.2)[33] were used. Here we used a calculation model for S, A, and B based on 470 non-ionic compounds established by Zissimos *et al.*[34] that was for the first time extended to ionic compounds. The calculation methods for E and V values established in our previous study,[31] and for S, A, and B using COSMO-RS, are in detail explained in the supporting information. It also provides both measured and calculated LFER values (Table S1 and S2).

The main goal of the present work is to predict physico-chemical quantities based on LFER, to find the most important contributing factors, and to thereby improve the understanding of the molecular interaction potentials of ILs as a solute.

Result and Discussion

Using the experimentally and computationally determined LFER parameters of the representative ion set (see S.I.), system parameters for the prediction of the octanol-water partitioning coefficient, water solubility, and critical micelle concentration of ILs and anionic activity coefficient in water and anionic hydrophobicity in octanol-water were established.

Prediction of the octanol-water partitioning coefficient (log P)

The octanol-water partitioning coefficient (log P) as the ratio of the concentrations of a compound in two phases (*n*-octanol/ water) at the equilibrium indicates hydrophobicity. This property can be strongly related to the adsorption of a drug in the human body as well as bioaccumulation and migration of dissolved hydrophobic compounds in soil, sediments and groundwater.[35-39] To choose an IL with a specific behavior in both the human body and the environment, it is necessary to establish a prediction model.

Determination of anionic hydrophobicity For the partitioning behavior of salts including ILs, we assumed that both cationic (log k_o) and anionic hydrophobicity (H_a) play an important role. The cationic hydrophobicity can be assessed by HPLC with a lipophilic stationary phase,[40, 41] while it is difficult to directly measure anionic hydrophobicity, because most anions are rather small and therefore do not show a significant retention in the stationary phase. Thus, in order to determine anionic hydrophobicity for the typical IL anions $[(CF_3SO_2)_2N]^-$, $[PF_6]^-$, $[BF_4]^-$, $[SbF_6]^-$, $[CF_3SO_3]^-$, Cl^-, $[NO_3]^-$, Br^-, and $[CH_3COO]^-$), we applied eq. 2, as established by Ranke *et al.*,[42] to the model set. This model is based on the idea that the excess molar free energy of dissolving the ILs in water can be expressed as the sum of cationic and anionic contributions, where the former one is given by the capacity factor, and the latter one is extracted by a least squares fit of the model to the data.

$$\text{Log P} = \text{m} \log k_o + H_a + \text{c} \qquad (2)$$

where k_o is the cationic capacity factor representing hydrophobicity defined by Stepnowski and Storoniak [43], m is the slope that ideally equals unity, if all model assumptions are satisfied, and c is a constant. For the determination of the anionic contribution, cationic capacity factors were collected from literature [40, 41] (Table S3). In Figure 1, log P data are plotted against the hydrophobicity of the cation. It turned out that the slopes are all equal, confirming the linear model specified in equation 2. By correlating the log P values of 45 ILs with log k_o of cations, we obtained m = 1.423, c = –3.039. Results are given in Table 1.

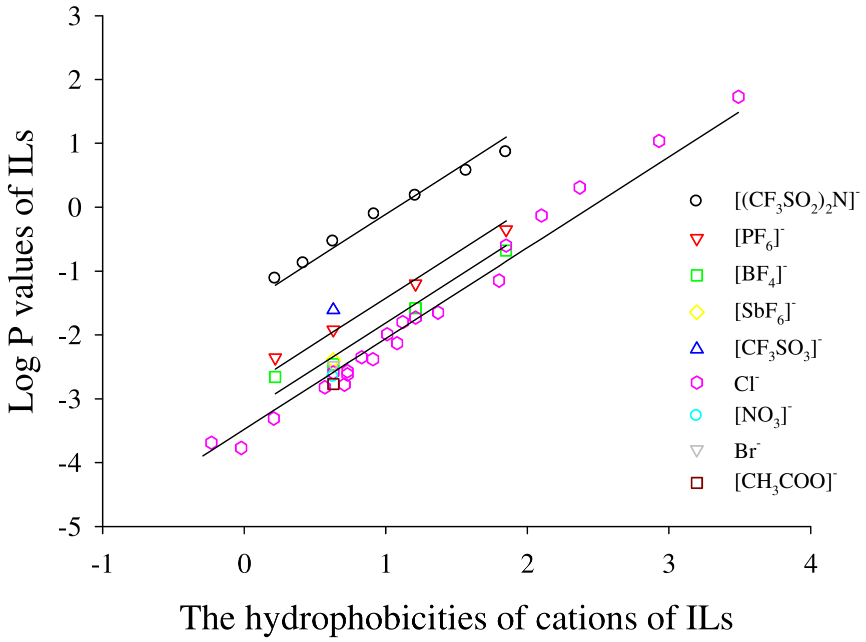

Figure 1. Measured octanol-water partitioning coefficient (log P) of ionic liquids as a function of the measured hydrophobicities of the cations[40, 41] of various ionic liquids.

Table 1. The dimensionless hydrophobicity of anions in the octanol-water partitioning system.

Anions	Measured hydrophobicity (from eq. 2)	Predicted Hydrophobicity (from eq. 3)
$[(CF_3SO_2)_2N]^–$	1.504 ± 0.135	1.423
$[PF_6]^–$	0.191 ± 0.136	0.211
$[BF_4]^–$	–0.197 ± 0.177	–0.186
$[SbF_6]^–$	–0.248	–
$[CF_3SO_3]^–$	0.533	0.509
$Cl^–$	–0.443 ± 0.220	–0.537
$[NO_3]^–$	–0.518	–0.561
$Br^–$	–0.338	–0.261
$[CH_3COO]^–$	–0.628	–0.609

In order to establish a prediction of the anionic hydrophobicity without any experimental input, we employed the LFER with the five computed[34] parameters E, S, A, B, and V, for the prediction based on the Abraham model. One data point ($[SbF_6]^–$) had to be excluded, because Sb is not parameterized in OBPROP's atomic contribution method.

Table 2. The system parameters (standard deviation) for predicting the anionic hydrophobicity with calculated LFER parameters of anion.

Eq.	c	e_a	s_a	a_a	b_a	v_a	R^2	SD	F	N
(3)	0.298(0.742)	–0.841(0.312)	0.263(0.660)	1.691(0.388)	–0.571(0.121)	1.319(0.149)	0.997	0.079	116.1	8
(4)	–0.956(0.169)					1.778(0.260)	0.886	0.261	46.7	8
(5)	–0.449(0.283)				–0.135(0.066)	1.503(0.249)	0.938	0.211	37.9	8
(6)	0.136(0.293)			0.844(0.246)	–0.370(0.100)	1.575(0.171)	0.977	0.143	57.5	8
(7)	0.581(0.178)	–0.756(0.193)		1.586(0.242)	–0.532(0.062)	1.288(0.108)	0.996	0.067	201.7	8

The results show that the full Abraham model with our calculated parameters can be used for prediction of the anion hydrophobicity with a standard deviation (SD) of 0.079 (dimensionless), which has the expected statistical and physicochemical meaning (Table 2). For a better understanding of the contribution of each parameter of the anion, we systematically simplified the Abraham equation in Table 2 to find the most important contributions for the molecular interactions. First of all, it is not surprising that the hydrophobicity correlates well with V_a according to equation (4) for which SD = 0.261. Here we found that acetate with its high hydrogen-bonding basicity ability forms a large exception. In order to also include similarly basic anions, the hydrogen basicity values were added as parameter. For the combination of V_a and B_a, we found SD to decrease to 0.211 with all data points coming closer to the best-fit axis (eq. 5). In the next step, the hydrogen bonding acidity A_a was added (eq. 6). Indeed, the SD decreased to 0.143. We then also added the refractive index (E_a) and dipolarity/polarizability (S_a), which further enhanced the accuracy (eq. 7). E_a only slightly increased the accuracy (SD = 0.067) and S_a has very little importance, but in combination with V_a, B_a, and A_a, (eq. 3), they contribute to reaching the best prediction (R^2 of 0.997).

Prediction of log $P_{O/W}$ – For predicting the octanol-water partitioning coefficient of ILs, we used measured as well as calculated descriptors. Experimentally determined log $P_{O/W}$ values measured between very dilute condition and around 15 mM were collected from literatures [44-49] because log P is dependent on concentration [45] and, for 25 chloride-based ILs, measured as part of this work (see S.I.). From theoretical considerations, we modified the Abraham equation by adding the anionic hydrophobicity parameter (H_a, dimensionless) (eq. 8).

$$\text{Log } P_{O/W} = c + e_c\,E_c + s_c\,S_c + a_c\,A_c + b_c\,B_c + v_c\,V_c + d\,H_a \tag{8}$$

With the measured cationic LFER descriptors presented by our group in a previous study[31] and the experimentally determined anionic hydrophobicity constants, log $P_{O/W}$ was predicted according to eq. (8) using a multiple linear regression with an SD of 0.182 log units and $R^2 = 0.984$ (eq. 9 in Table 3).

Table 3. The system parameters (standard deviation) for predicting the octanol-water partitioning coefficient (log $P_{O/W}$) of ionic liquids with measured cationic LFER parameters and including anionic hydrophobicity.

Eq.	c	e_c	s_c	a_c	b_c	v_c	d	R^2	SD	N	F
(9)	-4.678(0.190)	0.118(0.344)	-0.710(0.178)	-0.529(0.161)	-3.310(0.373)	2.985(0.139)	0.983(0.044)	0.984	0.182	44	373.3
(10)	-5.543(0.177)	-	-	-	-	2.653(0.113)	1.127(0.068)	0.947	0.315	44	363.2
(11)	-5.372(0.137)	-	-	-	-2.274(0.402)	2.576(0.086)	1.074(0.052)	0.970	0.234	44	435.9
(12)	-4.958(0.175)	-0.885(0.268)	-	-	-2.686(0.381)	2.932(0.133)	1.007(0.051)	0.977	0.213	44	410.4
(13)	-4.693(0.213)	-0.653(0.282)	-0.229(0.113)	-	-2.722(0.367)	2.803(0.143)	1.010(0.049)	0.979	0.204	44	355.6

As shown by equation (10), the cationic volume term combined with the anionic hydrophobicity are the most important parameters for the log $P_{O/W}$ prediction of ILs, which already has a high accuracy with $R^2 = 0.947$, SD = 0.315. The next important term is the hydrogen bonding basicity ($R^2 = 0.970$, SD = 0.234 in eq. 11), and then excess molar refraction, which both enhance the predicting accuracy to $R^2 = 0.977$ and SD = 0.213 (eq. 12). Inclusion of S_c and A_c contributes very slightly to the prediction quality as shown by the small reduction of the SD values in eq. (13) and eq. (9), respectively. The system parameters according to eq. (9) – (13) for predicting Log $P_{O/W}$ with measured LFER parameters and anionic hydrophobicity are shown in Table 3. Here [IM11O2][Cl] and [IM11][$(CF_3SO_2)_2N$] were not investigated because their LFER parameters were not measured so far.

Using only calculated cationic LFER descriptors (including the calculated anionic hydrophobicity), the log $P_{O/W}$ values of ILs were predicted following equation (8) giving a SD of 0.217 log units (Table 4). The order of importance of the contribution factors is similar to as with the measured parameters. The system parameters according to eq. (14) – (18) are shown in Table 4. Measured and predicted values using experimentally and computationally determined parameters are provided in Table 5.

Table 4. The system parameter (standard deviation) for predicting octanol-water partitioning coefficient (log $P_{O/W}$) of ionic liquids with calculated cationic LFER descriptors and including anionic hydrophobicity.

Eq.	c	e_c	s_c	a_c	b_c	v_c	d	R^2	SD	N	F
(14)	-6.239(0.481)	-0.603(0.347)	0.794(0.458)	-0.901(0.235)	-6.765(1.130)	2.976(0.143)	1.007(0.049)	0.977	0.217	45	272.1
(15)	-5.514(0.168)	-	-	-	-	2.671(0.109)	1.114(0.0624)	0.949	0.309	45	387.9
(16)	-6.104(0.182)	-	-	-	-4.911(1.013)	2.914(0.101)	1.032 (0.053)	0.967	0.250	45	404.9
(17)	-5.702(0.197)	-	-	-0.558(0.160)	-5.529(0.916)	2.874(0.090)	1.024(0.047)	0.975	0.221	45	389.2
(18)	-5.544(0.273)	-0.262(0.294)	-	-0.633(0.181)	-5.573(0.920)	2.977(0.146)	1.009(0.050)	0.975	0.222	45	309.9

Table 5. Measured and predicted log $P_{O/W}$ values of ionic liquids with calculated (calc.) and measured (exp.) LFER parameters.

Chemicals	Measured Log $P_{O/W}$	Predicted Log $P_{O/W}$ with	
		(calc. LFER parameters) according to eq. (14)	(exp. LFER parameters) according to eq. (9)
[IM14]Cl	-2.77 ± 0.068[a], -2.40[46, 47]	-2.59	-2.53
[IM16]Cl	-1.73 ± 0.003[a]	-1.77	-1.75
[IM18]Cl	-0.60 ± 0.003 [a]	-0.95	-0.83
[IM19]Cl	-0.13 ± 0.005[a]	-0.56	-0.41
[IM1-10]Cl	0.31 ± 0.030[a]	-0.16	0.12
[IM1-1Ph]Cl	-2.35 ± 0.008[a]	-2.28	-2.41
[IM1-(1Ph-4Me)]Cl	-1.80 ± 0.010[a]	-1.89	-1.99
[IM1-2Ph]Cl	-1.99 ± 0.017[a]	-2.29	-2.33
[IM12=1]Cl	-3.25 ± 0.007[a]	-3.12	-3.13
[N1,1,10, Bz]Cl	1.04 ± 0.014[a]	1.12	0.95
[N1,1,12, Bz]Cl	1.73 ± 0.017[a]	1.89	1.87
[IM12O1]Cl	-3.77 ± 0.060[a]	-3.96	-3.48
[IM13OH]Cl	-3.69 ± 0.010[a]	-3.57	-3.96
[IM11O2]Cl	-3.31 ± 0.005[a]	-2.04	--
[Py4-4NMe2]Cl	-2.13 ± 0.008[a]	-1.96	-1.87
[Py6-4NMe2]Cl	-1.15 ± 0.011[a]	-1.27	-1.02
[Py4-3Me-5Me]Cl	-2.38 ± 0.003[a]	-2.63	-2.24
[C2Py]Cl	-3.55 ± 0.011[a]	-3.41	-3.46
[C4Py]Cl	-2.82 ± 0.017[a]	-2.64	-2.75
[C8Py]Cl	-0.72 ± 0.001[a]	-0.99	-1.01
[Py4-2Me]Cl	-2.78 ± 0.002[a]	-2.49	-2.54
[Py4-4Me]Cl	-2.57 ± 0.020[a]	-2.44	-2.45
[Py4-3Me]Cl	-2.62 ± 0.007[a]	-2.45	-2.44
[Py6-3Me]Cl	-1.58 ± 0.005[a]	-1.65	-1.62
[Py6-4Me]Cl	-1.65 ± 0.008[a]	-1.61	-1.38
[IM14][NO$_3$]	-2.42[46, 47],-2.9[48]	-2.61	-2.60
[IM14]Br	-2.48[47]	-2.31	-2.43
[IM11][(CF$_3$SO$_2$)$_2$N]	-1.35 ± 0.040[44]	-1.67	--
[IM12][(CF$_3$SO$_2$)$_2$N]	-1.18 ± 0.03[44]; -1.01(-1.05 ~ -0.95)[47]	-1.32	-1.33

[IM13][$(CF_3SO_2)_2N$]	-0.88 ± 0.02[44]	-0.93	-0.76
[IM14][$(CF_3SO_2)_2N$]	-0.50 ± 0.03[44]; -0.58 (-0.96 ~ -0.208) [47]	-0.54	-0.62
[IM15][$(CF_3SO_2)_2N$]	-0.11 ± 0.03[44]	-0.13	-0.22
[IM16][$(CF_3SO_2)_2N$]	0.16 ± 0.02[44] ; 0.19 (0.15 ~ 0.22)[47]	0.28	0.16
[IM17][$(CF_3SO_2)_2N$]	0.57 ± 0.02[44]	0.66	0.64
[IM18][$(CF_3SO_2)_2N$]	0.79 ± 0.03[44] ; 0.93 (0.80 ~ 1.05)[47]	1.11	1.08
[IM12][PF_6]	-2.36 ± 0.08[44]	-2.61	-2.62
[IM14][PF_6]	-1.72 ± 0.06[44]; -1.66[46,49], -2.39[48]	-1.83	-1.91
[IM16][PF_6]	-1.20 ± 0.05[44]	-1.02	-1.13
[IM18][PF_6]	-0.35 ± 0.04[44]	-0.19	-0.21
[IM12][BF_4]	-2.66 ± 0.10[44]	-3.01	-3.01
[IM14][BF_4]	-2.40 ± 0.08[44]; -2.52[46, 49]	-2.23	-2.29
[IM16][BF_4]	-1.58 ± 0.08[44]	-1.42	-1.51
[IM18][BF_4]	-0.68 ± 0.06[44]	-0.59	-0.59
[IM14][SbF_6]	-2.39 ± 0.08[44]	--	-2.34
[IM14][CF_3SO_3]	-1.61 ± 0.05[44]	-1.53	-1.57
[IM14][CH_3COO]	-2.77 ± 0.08[44]	-2.66	-2.71

[a] Measured for this study

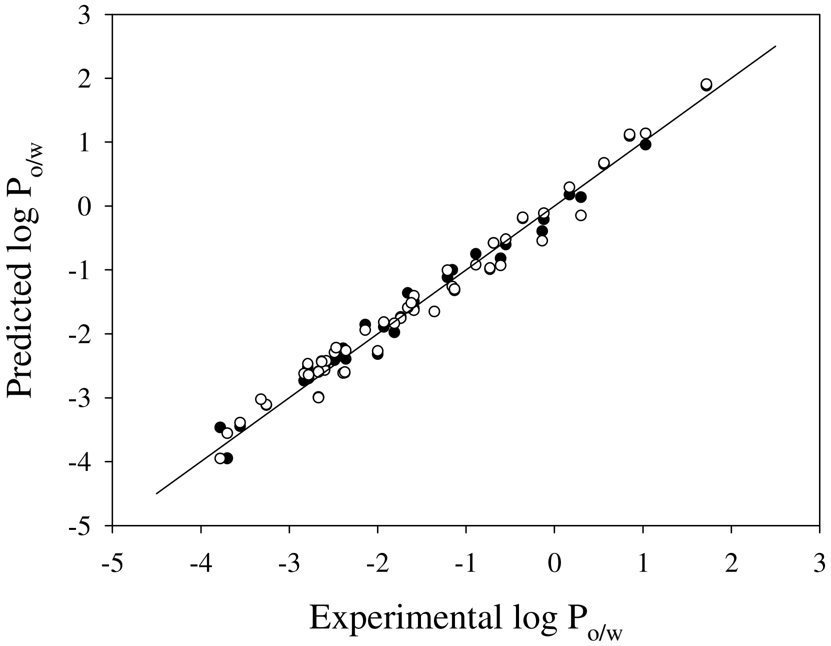

Figure 2. The relationship of experimental and predicted log $P_{O/W}$ values determined using measured (●) and calculated LFER parameters (○).

Prediction of the water solubility

Like log $P_{O/W}$, the water solubility is a useful quantity, since it influences release, transport, environmental fate, and risk of a compound. For its prediction, experimental values at 293 - 298 K were collected from literature [42, 50-60] and the anionic activity coefficients (C_a, determined by Ranke *et al.*[42] and given in Table 6) were combined with the Abraham model.

Table 6. Dimensionless activity coefficients of ionic liquid anions in water measured (exp. data from Ranke *et al*)[42] and predicted with the calculated LFER parameters (calc.) according to eq. (19).

Anions	Measured activity coefficient of anion in water	Predicted activity coefficient of anion in water (calc., eq. 19)
$[(6\text{-}2Et)2SS]^-$	0.521	0.501
$[BF_4]^-$	-1.268	-1.219
$[CF_3SO_3]^-$	-1.343	-1.268
$[PhBF_3]^-$	-1.853	-1.837
$[B(CN)_4]^-$	-2.264	-2.209
$[PF_6]^-$	-2.280; -2.178	-2.414

$[(C_4F_9)SO_3]^-$	-2.610	-2.700
$[(CF_3SO_2)_2N]^-$	-2.911; -2.868	-2.814
$[AsF_6]^-$	-3.165	--
$[(C_2F_5SO_2)_2N]^-$	-3.363	-3.556
$[(CF_3SO_2)_3C]^-$	-3.902; -3.841	-3.722
$[(C_2F_5)_3PF_3]^-$	-4.883, -4.803	-4.788

Determination of the anionic activity coefficient in water: The dimensionless activity coefficient of the anion in IL-saturated water[42] (Table 6) was correlated with the calculated anionic LFER descriptors to establish a prediction model. We modified the model by adding an anionic charge density term $f_a(-1/V_a)$ (f_a is a system parameter). This modified equation can be used to predict anionic activity coefficient with a SD of 0.174 (eq. 19), which is better than when using the conventional Abraham model (eq. 20, SD = 0.389). Table 7 gives the system parameters for all predictions of the activity coefficients using calculated parameters according to eq. (19) and (25).

Table 7. System parameters (standard deviation) according to eq. (19) – eq. (25) for the prediction of the anionic activity coefficient in IL-saturated water using the calculated LFER parameters (calc.).

Eq.	c	e_a	s_a	a_a	b_a	v_a	f_a	R^2	SD	N	F
(19)	-3.103(0.760)	4.110(1.287)	-7.084(2.524)	-7.543(2.712)	4.783(1.233)	0.670(0.303)	-0.715(0.157)	0.994	0.174	11	112.0
(20)	-2.651(1.679)	3.654(2.861)	-6.287(5.613)	-7.404(6.044)	4.710(2.748)	-0.136(0.623)		0.963	0.389	11	26.2
(21)	-4.811(0.490)				1.549(0.279)			0.775	0.719	11	30.9
(22)	-4.389(0.304)				1.923(0.186)	-0.690(0.162)		0.931	0.421	11	54.0
(23)	-5.880(0.278)				1.655(0.125)		-0.898(0.146)	0.961	0.319	11	97.6
(24)	-4.913(0.401)	0.556(0.198)			1.287(0.160)		-0.789(0.114)	0.981	0.234	11	123.5
(25)	-4.151(0.790)	1.518(0.709)	-2.016(1.412)	-2.183(1.621)	2.401(0.800)		-0.582(0.193)	0.987	0.233	11	75.1

The anionic activity coefficient B_a is the most important parameter and already leads to $R^2 = 0.775$, SD = 0.721 (eq. 21). C_a increases with B_a. As shown in eq. (22), inclusion of the two terms B_a and V_a leads to an improvement (SD = 0.421). However, exchanging the volume for $-1/V_a$, the anionic charge density, further reduces the SD value to 0.319 (eq. 23). The parameter E is also critical and leads to a significant increase in anionic activity, as shown in eq. 24 (SD = 0.234). Adding S and A terms further slightly enhances the accuracy (eq. 25). Again, one data point ($[AsF_6]^-$) had to be excluded because As is not parameterized in OBPROP's atomic contribution method.

Using the experimental and calculated LFER descriptors of the cation, the water solubility of ILs was predicted. Like for the log P prediction model, we assumed that the cationic LFER parameters and the anionic contribution, expressed by *d*Ca (C_a is the anionic activity coefficient in water and *d* is system parameter), should be combined in one model as shown in equation (26).

$$\text{Log water solubility [g L}^{-1}] = c + e_cE_c + s_cS_c + a_cA_c + b_cB_c + v_cV_c + f_c(1/V_c) + dC_a \qquad (26)$$

When using measured LFER parameters of the cation and activity coefficients of the anion, the water solubility of ILs can be predicted within the small error range of 0.138 log units (eq. 27, Figure 3).

Table 8. System parameters (standard deviation) for predicting the water solubility of ILs using measured LFER parameters and anion activity according to eq. (17) and (28).

Eq.	c	e_c	s_c	a_c	b_c	v_c	f_c	d	R^2	SD	N	F
(27)	1.395(0.265)	-0.429(0.453)	0.431(0.307)	0.280(0.206)	-	-1.769(0.170)	-	1.038(0.040)	0.979	0.138	27	198.9
(28)	1.662(0.183)	-	-	-	-	-1.734(0.081)	-	1.023(0.035)	0.976	0.135	27	513.8
(29)	6.061(2.078)	0.646(0.603)	-0.443(0.478)	-0.169(0.274)		-3.235(0.667)	-2.886(1.276)	1.043(0.036)	0.984	0.126	27	199.1

Naturally, the molar fraction of ILs in water increases with decreasing cation volume and increasing anion activity coefficient. Therefore, with just the two terms, we can predict the water solubility with $R^2 = 0.976$ and SD = 0.135

(eq. 28). Other parameters (E_c, S_c, and A_c) only slightly enhance the accuracy. B_c is not statistically important. The introduction of the $f_c 1/V_c$ charge density (f_c is the system parameter) term slightly reduces the SD values further (eq. 29). This means that the charge effect that accounts for IL-IL interactions plays a more important role in water than in the octanol-water system, where no IL phase is present and therefore, IL-IL interactions can be neglected. In the water solubility prediction with measured LFER parameters, 10 data points had to be excluded because their LFER parameters are not available so far. The system parameters according to eq. (27) and eq. (28) are provided in Table 8.

On the other hand, the water solubility of ILs was assessed using the predicted anion activity coefficient and the calculated cationic LFER descriptors according to equation 26 (eq. 30 to 35, Table 9).

Table 9. System parameters (standard deviation) for predicting the water solubility of ILs using calculated LFER parameters and anion activity according to eq. (30) – (35).

Eqn.	c	e_c	s_c	a_c	b_c	v_c	f_c	d	R^2	SD	N	F
(30)	4.586(1.548)	0.340(0.240)	-1.661(0.651)	1.166(0.359)	4.552(0.943)	-2.099(0.398)	-0.996(0.852)	1.085(0.041)	0.976	0.166	37	165.8
(31)	2.923(0.613)	0.289(0.237)	-1.405(0.617)	1.018(0.337)	4.205(0.900)	-1.660(0.132)		1.062(0.035)	0.974	0.167	37	190.9
(32)	2.536(0.518)		-0.907(0.457)	0.795(0.283)	3.433(0.632)	-1.598(0.122)		1.067(0.035)	0.973	0.168	37	214.1
(33)	1.677(0.298)			0.390(0.205)	2.474(0.427)	-1.734(0.105)		1.075(0.036)	0.970	0.176	37	256.5
(34)	2.074(0.216)				2.537(0.443)	-1.835(0.094)		1.082(0.038)	0.966	0.183	37	315.6
(35)	2.084(0.301)					-1.835(0.131)		1.102(0.052)	0.933	0.254	37	236.1

The system parameters in Tables 8 and 9 are different for the measured and calculated descriptors. This is likely due to the different statistical relation of measured and calculated parameters, as already noted by Klamt and Abraham in their pioneering study[34] on neutral molecules. By contrast, the interactions due to dispersion, volume, anion activity, and anionic charge density in water are almost the same as when using measured values. This implies that only one independently derived set of LFER descriptors should be used, i.e. experimental or calculated LFER values. The measured and predicted water solubility with measured and calculated LFER parameters according to eq. (29) and (30), respectively, are provided in Table 10.

Table 10. The measured water and predicted log water solubility [g L^{-1}] of ionic liquids with measured (exp.) and calculated (calc.) LFER parameters according to eq. (29) and (30), respectively.

Ionic liquids	Measured log water solubility	Predicted log water solubility with	
		(exp. LFER parameters)	(calc. LFER parameters)
[IM12][$B(CN)_4$]	-2.46[49]	-2.39	-2.41
[IM12][$(CF_3SO_2)_2N$]	-3.12[51]; -3.1[51]; -3.08[53], -3.08[51],-3.1[50]	-3.04	-3.07
[IM13][$(CF_3SO_2)_2N$]	-3.29[51]; -3.28[51];-3.27[51]	-3.26	-3.21
[IM14][$(CF_3SO_2)_2C$]	-4.44[50]	-4.55	-4.41
[IM14][$(CF_3SO_2)_2N$]	-3.51[51]; -3.51[51]; -3.54[51]; -3.53[51]; -3.49[51]; -3.46[51]; -3.5[51]; -3.5[59]	-3.55	-3.42
[IM14][$(C_4F_9)SO_3$]	-3.15[52]	-3.24	-3.30
[IM14][PF_6]	-3.0[54]; -2.92[54]; -2.96[54]; -2.93[57]; -2.89[55]; -2.87[55]; -2.8[53]; -2.9[59]; -2.9[50]	-2.91	-2.99
[IM15][$(CF_3SO_2)_2N$]	-3.73[51]; -3.71[51]; -3.74[51]	-3.74	-3.66
[IM16][$(C_2F_5)_3PF_3$]	-5.93[59]	-5.99	-6.06
[IM16][$(CF_3SO_2)_3C$]	-5.04[59]	-5.00	-4.91
[IM16][$(CF_3SO_2)_2N$]	-4.02[51]; -4.18[59]; -3.86[53]; -4.03[50]; -4.05[51]; -4.05[51]	-4.00	-3.92
[IM16][PF_6]	-3.41[54]; -3.45[54]; -3.35[59]; -3.36[54]	-3.36	-3.49
[IM17][$(CF_3SO_2)_2N$]	-4.31[51]; -4.3[51]; -4.29[51]	-4.19	-4.19
[IM18][$(CF_3SO_2)_2N$]	-4.7[61]; -4.6[61]; -4.59[59]; -4.14[50]; -4.1[52]; -4.1[61]; -4.5[51]; -4.49[51]; -4.47[51]	-4.49	-4.48
[IM18][$(C_4F_9)SO_3$]	-4.23[52]	-4.18	-4.35
[IM18][PF_6]	-3.93[59]; -3.92[54]; -3.9[54]; -3.46[56]; -3.95[54]	-3.85	-4.04
[IM18][BF_4]	-2.93[54]	-2.83	-2.75
[Py4-3Me][$(CF_3SO_2)_2N$]	-3.7[50]	-3.67	-3.66
[Py4-4Me][$(CF_3SO_2)_2N$]	-3.69[52]	-3.66	-3.63

[Py4-4Me][$(C_4F_9)SO_3$]	-3.03[52]	-3.35	-3.51
[Py8-4Me][$(C_2F_5SO_2)_2N$]	-5.4[59]	-5.18	-5.53
[Py8-4Me][$(CF_3SO_2)_2N$]	-5.09[59]	-4.72	-4.73
[Py8-4Me][$(C_4F_9)SO_3$]	-4.63[59]	-4.42	-4.60
[Py8-4Me][$PhBF_3$]	-3.6[59]	-3.66	-3.67
[Py8-4Me][CF_3SO_3]	-3.09[59]	-3.14	-3.05
[Py8-4Me][BF_4]	-2.98[59]	-3.07	-3.00
[Pyr14][$(C_2F_5)_3PF_3$]	-5.43[59]	--	-5.57
[Pyr14][$(CF_3SO_2)_2N$]	-3.59[59]; -3.57[59]	--	-3.43
[Pyr16][$(CF_3SO_2)_2N$]	-4.12[59]	--	-3.95
[Pyr18][$(CF_3SO_2)_2N$]	-4.71[59]	--	-4.53
[Py6-4NMe2][$(CF_3SO_2)_2N$]	-4.53[59]; -4.53[50]	-4.66	-4.42
[IM16-2Me][$(CF_3SO_2)_2N$]	-4.15[50]	--	-4.09
[Pip14][$(CF_3SO_2)_2N$]	-3.78[60]	--	-3.73
[Mor11O2][$(CF_3SO_2)_2N$]	-3.19[59]	--	-3.26
[Py3OH][$(CF_3SO_2)_2N$]	-2.43[59]	--	-2.52
[IM12OH][$(CF_3SO_2)_2N$]	-2.34[50]	--	-2.21
[N4444][$(6\text{-}2Et)_2SS$]	-1.52[58]	--	-1.71

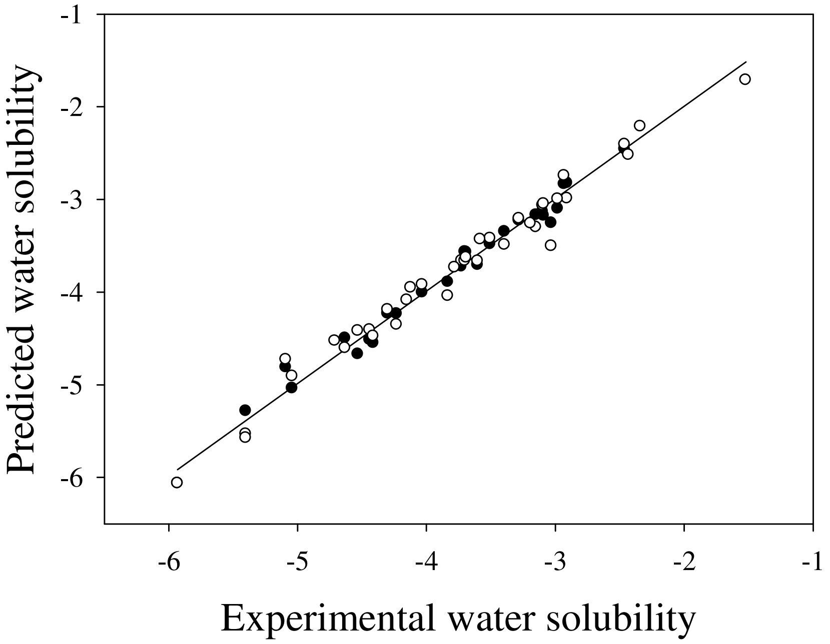

Figure 3. The relationship of experimental and predicted water solubility values determined with measured (●) and calculated LFER parameters (○) according to eq. (29) and eq. (30) respectively.

Prediction of the critical micelle concentration (CMC)

The critical micelle concentration (CMC) is a basic parameter of surface chemistry as well as colloid and environmental science. Specifically, it influences biological properties like toxicity and biodegradability. The process of micellization can be directly correlated to the interaction of amphiphiles with apolar surfaces such as micelles or cell membranes. Therefore, the CMC was predicted in order to investigate the molecular interaction at a rather high concentration in water. Since we assumed that cations and anions are forming aggregates, we used each parameter as the sum of cationic and anionic contributions (eq. 36). The CMC values of ILs at 293 - 298 K were collected from literature[12, 61-84] and are given in Table 8.

$$\text{Log CMC [mmol L}^{-1}] = e(E_c+E_a) + s(S_c+S_a) + a(A_c+A_a) + b(B_a+B_c) + v(V_c+V_a) + c \qquad (36)$$

Here, the prediction was carried out exclusively with calculated descriptors, because experimental anionic descriptors are not available so far. The results show that the CMC can be predicted within an error range of about 0.179 log units according to equation (36). However, there are some remarkable exceptions ([IM12]Br, [IM14]Br, [IM14][CF_3SO_4], and [IM14][C_8SO_4]). In order to include them, we introduced the charge density term ($1/V_c$ and $-1/V_a$ for cation and anion, respectively). In combination (eq. 37), the correlation was improved to $R^2 = 0.989$.

$$\text{Log CMC [mmol L}^{-1}] = 0.754(0.283)(E_c+E_a) - 1.174(0.704)(S_c+S_a) - 0.993(0.365)(A_c+A_a) + 0.531(0.169)(B_a+B_c) - 1.965(0.062)(V_c+V_a) - 0.123(0.033)1/V_c - 0.364(0.067)(-1/V_a) + 9.518(1.721) \qquad (37)$$

R^2=0.989, SD=0.128, N=36, F=345.7

In another approach, we rewrote equation (29) as equation (38) with the assumption that each parameter of cation and anion is different.

$$\text{Log CMC} = c + e_cE_c + s_cS_c + a_cA_c + b_cB_c + v_cV_c + e_cE_a + s_aS_a + a_aA_a + b_aB_a + v_aV_a \qquad (38)$$

The results showed that the CMC can be predicted with an SD of 0.168 log units, which is similar to equation (36), but with different system constants. To further reduce the SD, the charge density terms of cation and anion were added. Consequently, we found that this model can predict the CMC with the smallest error of 0.104 log units. The system parameters according to eq. (39) and (40) are given in Table 11 and predicted and measured CMC values are given in Table 12.

Table 11. System parameters (standard deviation) for predicting the critical micelle concentration of ILs using calculated LFER parameters.

Eqn.	c	e_c	s_c	a_c	b_c	v_c	e_a	s_a	a_a	b_a	v_a	g_c	f
(39)	4.838 (1.161)	-0.369 (0.257)	1.327 (0.263)	0.580 (0.765)	0.673 (1.864)	-2.010 (0.200)	0.212(0.368)	0.376 (1.014)	0.544 (0.673)	-0.299 (0.282)	-1.633 (0.247)		
		R^2=0.982	SD=0.168	N=36	F=139.3								
(40)	16.721 (0.265)	3.058 (0.814)	-7.647 (2.046)	-2.601 (0.868)	1.696 (1.189)	-1.648 (0.141)	0.796 (0.263)	-2.024 (0.802)	-2.731 (0.803)	1.452 (0.400)	-2.099 (0.184)	-0.411 (0.095)	0.623 (0.130)
		R^2=0.994	SD=0.104	N=36	F=307.3								

Table 12. The experimentally measured and predicted log CMC values [mmol L^{-1}] of ionic liquids assessed with calculated LFER parameters according to eq. (40).

Chemicals	Surface tension	Conductivity	Other	Predicted
[N1,1,1,8]Br			2.352[61]	2.388
			2.462[62]	
[N1,1,1,10]Cl	1.845[63]	1.976[64]		1.988
[N1,1,1,10]Br		1.797[65]	1.792[61]	1.807
			1.780[65]	
[N1,1,1,12]Cl	1.255[63]	1.346[64]		1.400
		1.328[66]		
[N1,1,1,12]Br			1.155[60]	1.218
			1.176[67]	
[N1,1,1,14]Cl	0.740[68]	0.751[64]		0.793
	0.653[63]	0.740[69]		
[N1,1,1,14]Br		0.580[69]	0.544[67]	0.612
[N1,1,1,16]Cl	0.114[63]	0.164[63]		0.168
[N1,1,1,16]Br			-0.046[67]	-0.013
[N1,1,1,18]Cl			-0.456[70]	-0.221
[IM12]Br	3.398[71]	3.279[71]		3.442
[IM14]Br	2.903[71]	2.954[71]		3.225
[IM14][BF_4]	2.903[72]	2.914[72]		3.090
	3.137[12]			
[IM14][CF_3SO_3]	2.893[12]			2.970
[IM14][C_8SO_4]	1.608[12]	1.491[73]		1.632
[IM16]Cl	2.954[63]			2.873
[IM16]Br	2.778[71]	2.602[71]	2.945[74]	2.692
	2.672[76]		2.903[74]	
[IM18]Cl	2.342[76]	2.369[76]	2.301[63]	2.316
	2.000[72]	1.954[72]		
	2.342[63]			
[IM18]Br	2.176[71]	2.176[71]	2.255[74]	2.135

	2.083[76]		2.279[74]	
[IM18]I	2.000[72]	2.176[72]		2.156
[IM19]Br	1.602[71]	1.477[71]		1.845
		1.869[77]		
[IM1-10]Cl	1.777[76]	1.731[76]	1.653[63]	1.756
	1.740[63]	1.607[78]	1.740[63]	
	1.601[78]			
[IM1-10]Br	1.301[75]	1.602[79]	1.623[74]	1.575
	1.467[80]	1.613[77]	1.663[74]	
		1.517[80]		
[IM1-12]Cl	1.176[63]	1.129[78]	0.845[63]	1.267
	1.120[78]		1.114[63]	
[IM1-12]Br	0.634[75]	0.991[77]	1.000[74]	1.086
		0.929[83]	1.079[74]	
		0.978[81]		
$[IM1\text{-}12][BF_4]$	0.964[80]	0.881[80]		0.952
[IM1-14]Cl	0.602[63]	0.498[66]	0.477[63]	0.652
	0.532[76]	0.566[78]	0.602[63]	
	0.474[78]			
[IM1-14]Br		0.398[77]		0.471
		0.415[80]		
[IM1-16]Cl	0.114[76]	0.057[76]		0.060
	-0.056[82]	-0.066[78]		
	-0.061[78]			
[IM1-16]Br		-0.097[75]		-0.121
		-0.215[77]		
		-0.187[81]		
[IM1-18]Cl	-0.398[76]	-0.347[76]		-0.427
$[Py_8]Cl$		2.439[76]		2.334
$Na[C_8SO_4]$			2.127[83]	2.094
$Na[C_{10}SO_4]$			1.477[83]	1.480
$Na[C_{12}SO_4]$			0.881[84]	0.892
$Na[C_{14}SO_4]$			0.301[83]	0.269

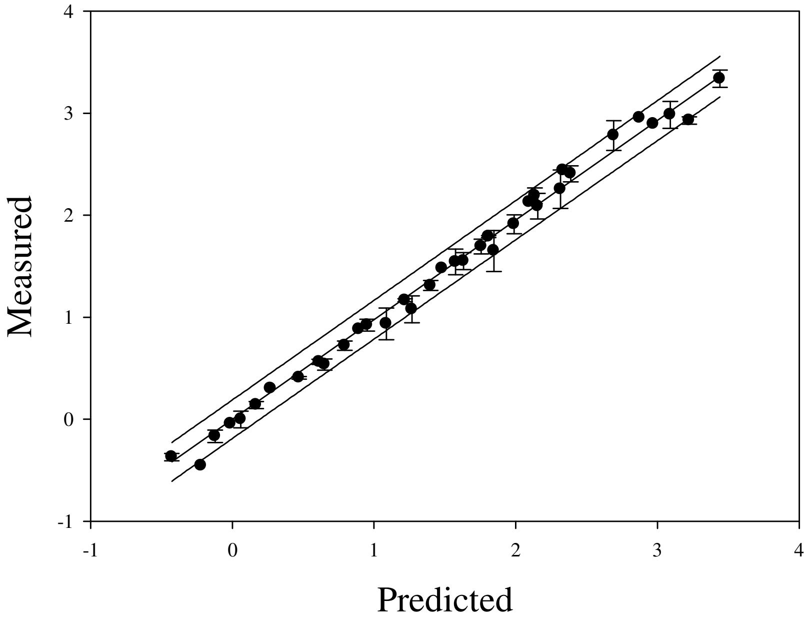

Figure 4. The relationship of experimental and predicted critical micelle concentration [mmolL^{-1}] determined with calculated parameters according to eq. (40).

Recently, we introduced a CMC prediction method for ILs using the cubed molecular radius, the solvent-accessible surface, and COSMO-RS interactions such as hydrogen bonding, van der Waals, and misfit enthalpies.[12] The results give an R^2 of 0.994, equal to that in the present study. However, in order to use this method, it is necessary to calculate the enthalpies for each IL, because the values change with the combination of cation and anion, while the present approach may be more comfortable, as the needed parameters can be easily derived by combining cation- and anion-specific LFER parameters without any quantum chemical calculation.

Conclusions

The extended models based on the Abraham equation can satisfactorily model log P, water solubility, and CMC of rather concentrated aqueous solutions of ILs using measured as well as calculated LFER parameters. Activity coefficient and hydrophobicity of the anion in water and octanol-water can equally be modeled using the calculated LFER descriptors. For the prediction of log P and water solubility, it is slightly advantageous to use the measured LFER descriptors over the calculated ones. However, the calculated parameters are much easier accessible and provide an easy approach to investigate parameters for ILs, which are experimentally not yet available.

In our prediction studies, the volume term (V) is the most important factor to determine physicochemical properties of ILs in solution. B is the second-most important contribution parameter, and other terms (E, S, and A) have only slight - but not ignorable - contributions. The combination of all parameters can enhance the predictability of the ILs' behavior in solution. For the anionic hydrophobicity hydrogen bonding basicity as a second key parameter in combination with V significantly contributes to the anionic molecular interaction in the octanol-water system. Similarly, both cationic volume and hydrogen bonding basicity with anionic hydrophobicity cause importantly ILs to partition in octanol-water. On the other hand, for the anionic activity coefficient in water, the single anionic hydrogen-bonding basicity term gives a better correlation than the volume, and changing the charge density term from V_c to $1/V_a$ with inclusion of the hydrogen-bonding basicity of the anion improves the prediction. In the case of the cationic contribution to the solubility in water, unlike the anionic activity coefficient, the $1/V_c$ term includes more molecular interaction than hydrogen-bonding basicity of cation: we assume that this has to be attributed to the fact that cations (e.g. imidazolium and pyridinium) have larger volumes and are less functionalized than anions. Moreover, the CMC at high concentrations was predicted with the assumption of ion-paring and as well for the ion-dissociated form. In both cases, a good agreement was demonstrated, but the prediction using the ion-dissociated form is more accurate. The CMC also correlates readily with the volume term, but to include amphiphiles, the consideration of hydrogen bonding is required.

Experimental Section

Nomenclature

IL ions are abbreviated as $[IM1n]^+$ 1-methyl-3-alkylimidazolium (with *n* = 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 18 being the number of carbon atoms in the unbranched alkyl chain), $[Py\ n]^+$ alkylpyridinium (with *n* = 2, 4, 6, 8), $[N1, 1, 1, n]^+$ trimethylalkylammonium (with *n* = 8, 10, 12, 14, 16, 18), $[Pyr1n]^+$ alkylmethylpyrrolidinium (with *n* = 4, 6, 8), $[N1,1,n,Bz]^+$ benzylalkyldimethylammonium (with *n* = 10, 12), $[Pyn\text{-}4NMe2]^+$ 1-alkyl-4-(dimethylamino)pyridinium (with *n* = 4, 6), $[Pyn\text{-}2Me]^+$ 1-alkyl-2-methylpyridinium (with *n* = 4, 6), $[Pyn\text{-}3Me]^+$ 1-

alkyl-3-methylpyridinium (with *n* = 4, 6), [Py*n*-4Me]$^+$ 1-alkyl-4-methylpyridinium (with *n* = 4, 6, 8), [IM1-1Ph]$^+$ 1-benzyl-3-methyl-imidazolium, [IM1-(1Ph-4Me)]$^+$ 1-methyl-3-(4-methylbenzyl)-imidazolium, [IM1-2Ph]$^+$ 1-methyl-3-(2-phenylethyl)-imidazolium, [IM1-2=1]$^+$ (1-methyl-3-(2-propenyl)-imidazolium), [IM12O1]$^+$ 1-(2-methoxyethyl)-3-methyl-imidazolium, [IM13OH]$^+$ 1-(3-hydroxypropyl)-3-methyl-imidazolium, [IM11O2]$^+$ 1-(ethoxymethyl)-3-methyl-imidazolium, [Py4-3Me-5Me]$^+$ 1-butyl-3,5-dimethylpyridinium, [IM16-2Me]$^+$ 1-hexyl-2,3-dimethyl-imidazolium, [Pip14]$^+$ 1-butyl-1-methylpiperidinium, [Mor11O2]$^+$ 4-(ethoxymethyl)-4-methylmorpholinium, [Py3OH]$^+$ 1-(3-hydroxypropyl)pyridinium, [IM12OH]$^+$ 1-(3-hydroxyethyl)pyridinium, [N4,4,4,4]$^+$ tetrabutylammonium combined selectively with Cl^-, Br^-, I^-, $[NO_3]^-$ Nitrate, $[BF_4]^-$ tetrafluoroborate, $[PF_6]^-$ hexafluorophosphate, $[(CF_3SO_2)_2N]^-$ bis(trifluoromethylsulfonyl)amide, $[(C_2F_5SO_2)_2N]^-$ bis(pentafluoroethanesulfonyl)imide, $[CF_3SO_3]^-$ trifluoromethanesulfonate, $[SbF_6]^-$ hexafluoridoantimonate, $[CH_3COO]^-$ acetate, [(6-2Et)2SS]$^-$ bis(2-ethylhexyl)sulfosuccinate, $[PhBF_3]^-$ trifluorophenylborate, $[B(CN)_4]^-$ tetracyanidoboranate, $[(CF_3SO_2)_3C]^-$ tris(trifluoromethylsulfonyl)methide, $[(C_2F_5)_3PF_3]^-$ trifluorotris(pentafluoroethyl)phosphate, $[AsF_6]^-$ hexafluoroarsenate, $[(C_4F_9)SO_3]^-$ nonafluorobutyl sulfonate, $[C_nSO_4]^-$ alkyl sulfate (*n* = 8, 10, 12, 14).

Measurement of the octanol-water partitioning coefficient

We measured the log P values of 25 chloride-based ILs (see the list of log P). Three 15 ml conical tube with cap were filled with 3 ml of octanol and water respectively, and 15.0 mM of IL were added. The vials were vigorously shaken for 10 min and allowed to stabilize for at least an hour and then centrifugation was performed to eliminate the emulsion created by shaking process prior to injection into the HPLC system. Then, samples of 5 μL from each phase were carefully withdrawn with a syringe. The withdrawn samples were diluted by a factor of 10 or 100 prior to HPLC analysis.

For analyzing the quantity of ILs in each phase, we employed a Hilic stationary phase with acetonitrile (99.9 %, Fluka) and buffer (15 mM KH_2PO_4 and 30 mM H_3PO_4) as eluent in the HPLC (Hewlett Packard System Series 1100), because cation has a good retention characteristic in Hilic system and applying phosphate buffer into the mobile phase allows us to neglect influence of anion in the chromatographic system [85]. The detection wavelengths were 211 nm for imidazolium based ILs and 254 for pyridinium based ILs and ammonium based compounds with benzyl substituents. The partitioning coefficients of ILs were determined as the ratio of the solute peak area in both phases (eq. 41). The tests for partition coefficient of ILs were triplicate. C^i_o is the concentration of ILs in octanol phase, and C^i_w is the concentration of ILs in water phase. ILs were donated by Merck.

$$\text{Log P} = \text{Log } C^i_o/C^i_w \qquad (41)$$

Computational details

For the COSMO calculations of all parameters of ILs (sig2, sig3, HBD3, and HBA3), the structures of the single IL ions were optimized. Firstly, (RI-)BP86/SV(P) optimizations[86-89] were carried out with the TURBOMOLE program package (version 5.10) using the Resolution of Identity (RI) [89] for reasonable starting structures. Using AOFORCE[90, 91], the vibrational frequencies of each ion were calculated. These structures were further refined with the TZVP[92] basis set, after which a full optimization with inclusion of COSMO[32] was performed ($\varepsilon_r = \infty$). Finally sig 2, sig 3, HBD3, and HBA3 of the optimized ion of ILs were calculated with COSMO-RS[32] using BP_TZVP_C21_0108 parameterization. The calculated sig 2, sig 3, HBD3, and HBA3 of all anions and cations ILs are given in Table S6.

Acknowledgment

This work was supported by the Universität Bremen, the Universität Freiburg, the Deutsche Bundesstiftung Umwelt DBU, and the DFG priority program SPP 1191. The authors acknowledge the use of the computing resources provided by the Black Forest Grid Initiative (BFG) (http://www.bfg.uni-freiburg.de) and the donation of IL samples by Merck Germany and by Prof. Bernd Ondruska in the Universität Jena.

Supporting information

We address measured and calculated LFER parameters of IL ions (Table S1 and S2), explanations in detail computational methods with sub-dataset (Table S3) and equations (Eq. S1–S5) for LFER parameters, and lipophilicity of cation for determining anionic hydrophobicity (Table S4). Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.2010xxxxx.

References

[1] M. Galinski, A. Lewandowski, I. Stepnowski, *Electrochim. Acta* **2006**, *51*, 5567–5580.

[2] T. Welton, *Coordin. Chem. Rev.* **2004**, *248*, 2459–2477.

[3] J. F. Liu, J. A. Jonsson, G. B. Jiang, *Trac-Trends Anal. Chem.* **2005**, *24*, 20–27.

[4] K. R. Seddon, The International George Papatheodorou Symposium: Proceedings, S. Boghosian, V. Dracopoulos, C. G. Kontoyannis, G. A. Voyiatzis (Eds.), Institute of Chemical Engineering and High Temperature Chemical Processes, Patras, Greece, **1999**, pp. 131.

[5] H. Weingärtner, *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 654–670.

[6] I. Krossing, J. M. Slattery, C. Daguenet, P. J. Dyson, A. Oleinikova, H. Weingärtner, *J. Am. Chem. Soc.* **2006**, *128*, 13427–13434.

[7] U. Preiss, S. Bulut, I. Krossing, *J. Phys. Chem. B* **2010**, *114*, 11133–11140.

[8] J. M. Slattery, C. Daguenet, P. J. Dyson, T. J. S. Schubert, I. Krossing, *Angew. Chem. Int. Ed.* **2007**, *46*, 5384–5388.

[9] P. Eiden, C. Friedrich, S. Bulut, I. Krossing, **2010**, *J. Phys. Chem.*, accepted for publication..

[10] U. P. R. M. Preiss, J. M. Slattery, I. Krossing, *Ind. Eng. Chem. Res.* **2009**, *48*, 2290–2296.

[11] U. Preiss, V. N. Emel'yanenko, S. P. Verevkin, D. Himmel, Y. U. Paulechka, I. Krossing, *ChemPhysChem* **2010**, DOI: 10.1002/cphc.201000614.

[12] U. Preiss, C. Jungnickel, J. Thöming, I. Krossing, J. Luczak, M. Diedenhofen, A. Klamt, *Chem. Eur. J.* **2009**, *15,* 8880–8885.

[13] C. Jungnickel, M. Markiewicz, U. Preiss, W. Mrozik, P. Stepnowski, J. Optoelectron, *Adv. Mater. Symposia* **2009**, *1*, 82–87.

[14] L. M. Sprunger, J. Gibbs, A. Proctor, W. E. Acree, Jr., M. H. Abraham, Y. Meng, C. Yao, J. L. Anderson, *Ind. Eng. Chem. Res.* **2009**, *48*, 4145–4154.

[15] L. Sprunger, M. Clark, W. E. Acree, Jr., M, Abraham, *J. Chem. Inf. Model.* **2007**, *47*, 1123–1129.

[16] D. S. Van Meter, O. D. Suart, A. B. Carle, A. M. Stalcup, *J. Chromatogr. A* **2008**, *1191*, 67–71.

[17] J. L. Anderson, J. Ding, T. Welton, D. W. Armstrong, *J. Am. Chem. Soc.* **2002**, *124 (47)*, 14247–14254.

[18] A. Fredenslund, R. L. Jones, T. H. Prausnitz, *AIChe J.* **1975**, *21(6)*, 1086–1099.

[19] K.-U. Goss, R. P. Schwarzenhach, *Envion. Sci. Technol.* **2001**, *35(1)*, 1–9.

[20] B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *106*, 5151–5158.

[21] M. H. Abraham, A. Ibrahim, A. M. Zissimos, *J. Chromatogr. A* **2004**, 29–47.

[22] M. H. Abraham, J. M. Al-Hussaini, *J. Environ. Monit.* **2005**, *7*, 295–301.

[23] M. H. Abraham, P. L. Grellier, R. A. McGill, *J. Chem. Soc. Perkin. Trans. 2* **1987**, 797–803.

[24] M. H. Abraham, G. S. Whiting, *J. Chromatogr.* **1991**, *587*, 229–236.

[25] M. H. Abraham, *J. Phys. Org. Chem.* **1993**, *6*, 660–684.

[26] M. H. Abraham, H. S. Chadha, G. S. Whiting, R. C. Mitchell, *J. Pharm. Sci.* **1994**, *83*, 1085–1100.

[27] M. H. Abraham, W. E. Acree, Jr., *J. Org. Chem.* **2010**, *75(4)*, 1006–1015.

[28] M. H. Abraham, W. E. Acree, Jr., *J. Org. Chem.* **2010**, *75(9)*, 3021–3026.

[29] M. H. Abraham, W. E. Acree, Jr., *New J. Chem.* **2010**, *34(10)*, 2298–2305.

[30] M. H. Abraham, W. E. Acree, Jr., *Phys. Chem. Chem. Phys.* **2010**, *12(40)*, 13182–13188.

[31] C.-W. Cho, C. Jungnickel, S. Stolte, U. Preiss, J. Arning, J. Ranke, A. Klamt, I. Krossing, J. Thöming, **2010**, *Submitted to Journal of Chromatography A*

[32] A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans. 2* **1993**, 799–805.

[33] OBPROP (http://openbabel.sourceforge.net)

[34] A. M. Zissimos, M. H. Abraham, A. Klamt, F. Eckert, J. Wood, *J. Chem. Inf. Comput. Sci.* **2002**, *42*, 1320–1331.

[35] S. H.Yalkowsky, S. C. Valvani, *J. Pharm. Sci.* **1981**, *70*, 1177–1178.

[36] W. M. Meylan, P. H. Howard, R. S. Boethling, D. Aronson, H. Printup, S. Gouchie, *Environ. Toxicol. Chem*. **1999**, *18*, 664–672.

[37] R. L. Swann, D. A. Laskowski, P. J. Mccall, K.Vanderkuy, H. J. Dishburger, *Residue Rev*. **1983**, *85*, 17–28.

[38] Y. H. Zhao, M. T. D. Cronin, J. C. Dearden, *Quant. Struct.-Act. Relat.* **1998**, *17*, 131–138.

[39] Y. H. Zhao, M. H. Abraham, J. Le, A. Hersey, C. N. Luscombe, G. Beck, B. Sherborne, I. Cooper, *Pharm. Res*. **2002**, *19*, 1446–1457.

[40] J. Ranke, A. Müller, U. Bottin-Weber, F. Stock, S. Stolte, J. Arning, R. Störmann, B. Jastorff, *Ecotoxicol. Environ. Safety* **2007**, *67*, 430–438.

[41] http://chem.uft.uni-bremen.de/il-eco/ supported by Zentrum für Umweltforschung und nachhaltige Technologien (UFT) and Merck, University of Bremen, Germany

[42] J. Ranke, A. Othman, P. Fan, A. Müller, *Int. J. Mol. Sci.* **2009**, *1037*, 1271–1289.

[43] P. Stepnowski, P. Storoniak, *Environ. Sci. Poll. Res.* **2005**, *12*, 199.

[44] S. H. Lee, Biocatalysis in ionic liquids: Influence of physicochemical properties of ionic liquids on enzyme activity and enantioselectivity, **2005**, Pohang University of Science and Technology, Korea

[45] S. H. Lee, S. B. Lee, *J. Chem. Technol. Biotechnol.* **2009**, *84(2)*, 202–207.

[46] L. J. Ropel, Diffusion coefficients and 1-octanol-water partitioning coefficient of ionic liquids, **2004,** Notre Dame, Indiana, IN, USA

[47] L. Ropel, L. S. Belvéze, S. N. V. Aki, A. Stadtherr, J. F. Brennecke, *Green Chem.* **2005**, *7*, 83–90.

[48] J. L. Kaar, A. M. Jesionowski, J. A. Berberich, R. Moulton, A. J. Russell, *J. Am. Chem. Soc.* **2003**, *125*, 4125–4131.

[49] L. S. Belvéze, Modeling and Measurement of Thermodynamic Properties of Ionic Liquids, **2004,** University of Notre Dame, Notre Dame, IN, USA

[50] A. Chapeaux, L. D. Simoni, M. A. Stadtherr, J. F. Brennecke, *J. Chem. Eng. Data* **2007**, *52*, 2462–2467.

[51] M. G. Freire, P. J. Carvalho, R. L. Gardas, I. M. Marrucho, L. M. N. B. F. Santos, J. A. P. Coutinho, *J. Phys. Chem. B* **2008**, *112*, 1604–1610.

[52] N. Papaiconomou, N. Yakelis, J. Salminen, R. Bergman, J. M. Prausnitz, *J. Chem. Eng. Data* **2006**, *51*, 1389–1393.

[53] H. Luo, S. Dai, P. V. Bonnesen, *Anal. Chem.* **2004**, *76*, 2773–2779.

[54] M. G. Freire, C. M. S. S. Neves, P. J. Carvalho, R. L. Gardas, A. M. Fernandes, I.M. Marrucho, L.M. N. B. F. Santos, J. A. P. Coutinho, *J. Phys. Chem. B* **2007**, *111*, 13082–13089.

[55] N.V. Shvedene, S.V. Borovskaya, V.V. Sviridov, E. R. Ismailova, I. V. Pletnev, *Anal. Bioanal. Chem.* **2005**, *381*, 427–430.

[56] J. L. Anthony, E. J. Maginn, J. F. Brennecke, *J. Phys. Chem. B* **2001**, *105*, 10942–10949.

[57] S. Carda-Broch, A. Berthod, D. W. Armstrong, *Anal. Bioanal. Chem.* **2003**, *375*, 191–199.

[58] N. Nishi, T. Kawakami, F. Shigematsu, M. Yamamoto, T. Kakiuchi, *Green Chem.* **2006**, *8*, 349–355.

[59] N. Papaiconomou, J. Salminen, J.-M. Lee, J. M. Prausnitz, *J. Chem. Eng. Data* **2007**, *52*, 833–840.

[60] J. Salminen, N. Papaiconomou, R. A. Kumara, J. Lee, J. Kerr, J. Newmana, J. M. Prausnitz, *Fluid Phase Equilib.* **2007**, *261*, 421–426.

[61] G. D'Errico, O. Ortona, L. Paduano, V. Vitagliano, *J. Colloid Interface Sci.* **2001**, *239*, 264–271.

[62] W. Mosquera, *J. Colloid Interface Sci.* **1998**, *206*, 66–76.

[63] M. Blesic, M. H. Marques, N. V. Plechkova, K. R. Seddon, L. P. N. Rebelo, A. Lopes, *Green Chem.* **2007**, *9*, 481–490.

[64] T. M. Perger, M. Bester-Rogac, *J. Colloid Interface Sci.* **2007**, *313*, 288–295.

[65] I. Chakraborty, S. P. Moulik, *J. Phys. Chem. B* **2007**, *111*, 3658–3664.

[66] S. K. Mehta, K. K. Bhasin, R. Chauhan, S. Dham, *Colloids Surf. A* **2005**, *255*, 153–157.

[67] P. Hansson, B. Joensson, C. Stroem, O. Soederman, *J. Phys. Chem. B* **2000**, *104*, 3496–3506.

[68] Y. Hayami, H. Ichikawa, A. Someya, M. Aratono, K. Motomura, *Colloid Polym. Sci*. **1998**, *276*, 595–600.

[69] S. Durand-Vidal, M. Jardat, V. Dahirel, O. Bernard, K. Perrigaud, P. Turq, *J. Phys. Chem. B* **2006**, *110*, 15542–15547.

[70] R. Ueoka, Y. Murakami, *J. Chem. Soc. Perkin Trans. 2* **1983**, 219–224.

[71] I. Goodchild, L. Collier, S. L. Millar, I. Prokeš, J. C. D. Lord, C. P. B. Butts, J. Bowers, J. R. P. Webster, R. K. Heenan, *J. Colloid Interface Sci.* **2007**, *307*, 455–468.

[72] J. Bowers, C. P. Bitts, P. J. Matin, M. C. Vergara-Gurierrez, *Langmuir* **2004**, *20*, 2191–2198.

[73] Z. Miskolczy, K. Sebok-Nagy, L. Biczok, S. Gokturk, *Chem. Phys. Lett.* **2004**, *400*, 296–300.

[74] J. Wang, H. Wang, S. Zhang, H. Zhang, Y. Zhao, *J. Phys. Chem. B* **2007**, *111,* 6181–6188.

[75] Q. Q. Baltazar, J. Chandawalla, K. Sawyer, J. L. Anderson, *Colloids Surf. A* **2007**, *302*, 150–156.

[76] C. Jungnickel, J. Łuczak, J. Ranke, J. F. Fernandez, A. Müller, J. Thöming, *Colloids Surf. A* **2008**, *316*, 278–284.

[77] R. Vanyúr, L. Biczok, Z. Miskolczy, *Colloids Surf. A* **2007**, *299*, 256–261.

[78] O. A. El Seoud, P. A. R. Pires, T. Abdel-Moghny, E. L. Bastos, *J. Colloid Interface Sci.* **2007**, *313*, 296–304.

[79] J. Sirix-Plenet, L. Gaillon, P. Letellier, *Talanta* **2004**, *63*, 979–986.

[80] B. Dong, N. Li, L. Zheng, L. Yu, T. Inoue, *Langmuir* **2007**, *23*,4178–4182.

[81] T. Inoue, H. Ebina, B. Dong, L. Zheng, *J. Colloid Interface Sci.* **2007**, *314*, 236–241.

[82] S. Thomaier, K. Werner, *J. Mol. Liq.* **2007**, *130*, 104–107.

[83] F. Quina, *J. Phys. Chem.* **1995**, *99*, 17028–17031.

[84] T. Sasaki, M. Hattori, J. Sasaki, K. Nukina, *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1397–1403.

[85] P. Stepnowski, A. Muller, P. Behred, J. Ranke, J. Hoffmann, *J. Chromatogr. A* **2003**, *993 (1–2)*, 173–178.

[86] A. Schäfer, C. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577.

[87] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100.

[88] S. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200–1211.

[89] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822–8824.

[90] P. Deglmann, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2002**, *362*, 511–518.

[91] P. Deglmann, F. Furche, *J. Chem. Phys.* **2002**, *117*, 9535 – 9538.

[92] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829–5835.

[93] T. Sasaki, M. Hattori, J. Sasaki, K. Nukina, *Bull. Chem. Soc. Jpn.* **1975**, *38*, 1397–1403.