

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

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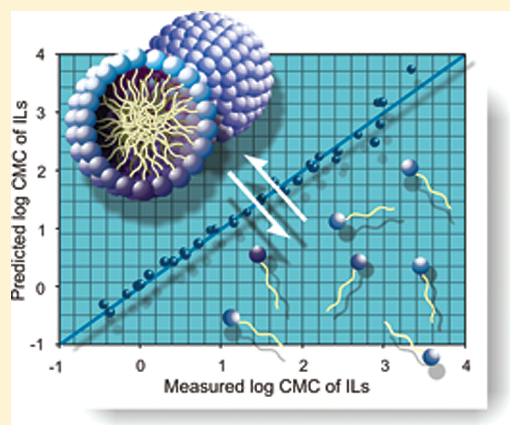
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## S Supporting Information

**ABSTRACT:** In this article, we present evolutionary models to predict the octanol–water partition coefficients ( $\log P$ ), water solubilities, and critical micelle concentrations (CMCs) of ionic liquids (ILs), as well as the anionic activity coefficients and hydrophobicities in pure water and octanol–water. They are based on a polyparameter linear free energy relationship (LFER) using measured and/or DFT-calculated LFER parameters: 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 errors of 0.182–0.217 for the octanol–water partition coefficient and 0.131–0.166 logarithmic units for the water solubility. Because experimentally determined solute parameters of anions are not currently available, the CMC, anionic activity coefficient, and hydrophobicity were predicted with quantum-chemical methods with  $R^2$  values of at least 0.99, as well as errors below 0.168 logarithmic units. These new approaches will facilitate the assessment of the technical applicability and environmental fate of ionic compounds even before their synthesis.



## INTRODUCTION

Over the past decade, interest in ionic liquids (ILs) has increased dramatically. ILs are alternative solvents, for example, for use as electrolytes,<sup>1</sup> in catalysis,<sup>2</sup> and in analytical chemistry.<sup>3</sup> This is because of 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. Because, according to serious estimates,  $10^6$ – $10^{18}$  ILs can be selectively designed by the combination of cations and anions, the contribution of ILs to science is expected to increase further.<sup>4</sup> However, the multitude of possible IL variations poses difficulties for the targeted synthesis of an IL with a specific property. Therefore, recent efforts have been directed toward understanding ILs on the molecular level<sup>5</sup> and predicting the basic physicochemical properties of ILs.<sup>6–13</sup> Our

groups have made some noteworthy additions in this respect, namely, approaches to understanding and predicting IL melting points,<sup>6,7</sup> viscosities and conductivities,<sup>8,9</sup> heat capacities, temperature-dependent densities,<sup>10</sup> and temperature-dependent liquid entropies.<sup>11</sup> Also, physicochemical properties related to biodegradation, such as the critical micelle concentration<sup>12</sup> or soil sorption coefficient,<sup>13</sup> can be predicted with the help of quantum-chemical calculations using the molecular volume  $V_m$ .<sup>10</sup> However, the insight into solute–solvent interaction of ILs is still in need of improvement. This effort holds the key to understanding various partitioning processes, such as liquid–gas,

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liquid–liquid, and liquid–surface partitioning. All of these processes have been described and studied in a variety of ways that are mutually largely incomparable. For example, Sprunger et al.<sup>14,15</sup> studied ILs in combination with gas or water. They reported cation- and anion-specific equation coefficients of ILs for predicting the partition coefficients of solutes in 32 different IL systems. Van Meter et al.<sup>16</sup> and Anderson et al.<sup>17</sup> characterized surface-confined ILs as a stationary phase in a high-performance liquid chromatography (HPLC) system. Their data are helpful for predicting the capacity factors of compounds in HPLC-confined ILs. The study of Sprunger et al.<sup>14,15</sup> allows predictions of the partition coefficients of compounds in IL mixtures. In general, predictions of solute–solvent interactions of relevant and experimentally hitherto-unavailable parameters can be obtained based on thermodynamically refined group contribution methods such as UNIFAC (universal functional activity coefficient),<sup>18</sup> polyparameter linear free energy relationships (pp-LFERs),<sup>19</sup> and methods based on quantum-chemical calculations such as continuum solvation models.<sup>20</sup> Among pp-LFERs, the most commonly used is the Abraham equation<sup>21–26</sup>

$$SP = c + eE + sS + aA + bB + \nu V \quad (1)$$

In eq 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  $(\text{cm}^3 \text{ mol}^{-1})/10$ , which models dispersive interactions arising from the greater polarizability of  $\pi$  and  $n$  electrons.  $S$  represents the solute dipolarity and polarizability due to solute–solvent interactions between bond dipoles and induced dipoles.  $A$  and  $B$  indicate the hydrogen-bond acidity and basicity, respectively, of the solute.  $V$  is the McGowan characteristic molar volume in units of  $(\text{cm}^3 \text{ mol}^{-1})/100$ . The coefficient  $e$  is a measure of the propensity of the phase to interact with solute  $\pi$ - 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  $\nu$  describes cavity formation in the case of bulk media. Finally, the parameter  $c$  is the property dependent offset of the LFER, which is obtained as regression constant. Recently, Abraham and Acree<sup>27–30</sup> reported an extended model by adding two additional terms to the model (eq 1), namely,  $j^+J^+$  (for the cation) and  $j^-J^-$  (for the anion), to describe solute transfer of ions and ionic species from water to organic solvents and successfully used it 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 HPLC<sup>31</sup> and then, as a complement, 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 solvents, which is a model combining quantum theory, surface interactions, and statistical thermodynamics),<sup>32</sup> and OBPROP (version 1.1.2)<sup>33</sup> were used. Here, we used a calculation model for  $S$ ,  $A$ , and  $B$  based on 470 nonionic compounds established by Zissimos et al.<sup>34</sup> that was extended for the first time to ionic compounds. The calculation methods for  $E$  and  $V$  values established in our previous study<sup>31</sup> and for  $S$ ,  $A$ , and  $B$  using COSMO-RS are explained in detail in the Supporting

Information. The Supporting Information also provides both measured and calculated LFER values (Tables S1 and S2).

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

## ■ RESULT AND DISCUSSION

Using the experimentally and computationally determined LFER parameters of the representative ion set (see Supporting Information), system parameters for the prediction of octanol–water partition coefficients, water solubilities, and critical micelle concentrations of ILs, anionic activity coefficients in water, and anionic hydrophobicities in octanol–water were established.

**Prediction of the Octanol–Water Partition Coefficient ( $\log P$ ).** The octanol–water partition coefficient ( $\log P$ ), as the ratio of the concentrations of a compound in two phases ( $n$ -octanol–water) at 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.<sup>35–39</sup> To choose an IL with a specific behavior in both the human body and the environment, it is necessary to establish a prediction model.

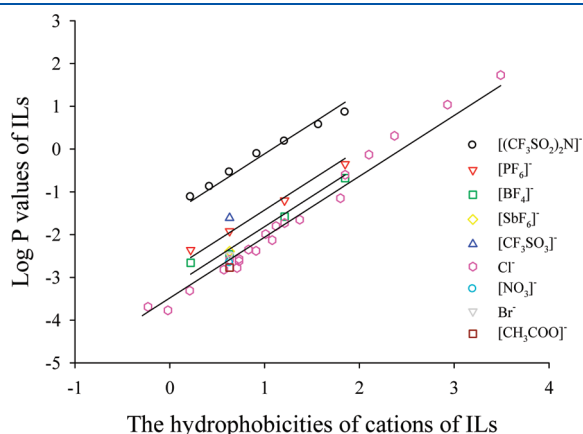
**Determination of Anionic Hydrophobicity.** For the partitioning behavior of salts including ILs, we assumed that both cationic ( $\log k_0$ ) and anionic ( $H_a$ ) hydrophobicity play an important role. The cationic hydrophobicity can be assessed by HPLC with a lipophilic stationary phase,<sup>40,41</sup> whereas it is difficult to directly measure anionic hydrophobicity, because most anions are rather small and, therefore, do not show significant retention in the stationary phase. Thus, to determine the anionic hydrophobicities of typical IL anions such as  $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ ,  $[\text{PF}_6]^-$ ,  $[\text{BF}_4]^-$ ,  $[\text{SbF}_6]^-$ ,  $[\text{CF}_3\text{SO}_3]^-$ ,  $\text{Cl}^-$ ,  $[\text{NO}_3]^-$ ,  $\text{Br}^-$ , and  $[\text{CH}_3\text{COO}]^-$ , we applied eq 2, as established by Ranke et al.,<sup>42</sup> to the model set

$$\log P = m \log k_0 + H_a + c \quad (2)$$

where  $k_0$  is the cationic capacity factor representing hydrophobicity, which was first used for ionic-liquid cations by Stepnowski and Storonik,<sup>43</sup>  $m$  is the slope, which ideally equals unity if all model assumptions are satisfied; and  $c$  is a constant. 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 is given by the capacity factor and the latter is extracted by a least-squares fit of the model to the data. For the determination of the anionic contribution, cationic capacity factors were collected from the literature<sup>40,41</sup> (Table S3, Supporting Information). 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 eq 2. By correlating the  $\log P$  values of 45 ILs with the  $\log k_0$  values of cations, we obtained  $m = 1.423$  and  $c = -3.039$ . Our results are given in Table 1.

To establish a prediction of the anionic hydrophobicity without any experimental input, we employed the LFER with the five computed<sup>34</sup> parameters  $E$ ,  $S$ ,  $A$ ,  $B$ , and  $V$ , for the prediction based on the Abraham model. One data point ( $[\text{SbF}_6]^-$ ) had to be excluded, because Sb is not parametrized in OBPROP's atomic contribution method.

The results show that the full Abraham model with our calculated parameters can be used to predict the anion hydrophobicity with a standard deviation (SD) of 0.079 (dimensionless), which has the expected statistical and physico-chemical meaning (Table 2). For a better understanding of



**Figure 1.** Measured octanol–water partition coefficient ( $\log P$ ) of ionic liquids as a function of the measured hydrophobicities of the cations<sup>40,41</sup> of various ionic liquids.

**Table 1. Dimensionless Hydrophobicities of Anions in the Octanol–Water Partitioning System**

anions	measured (from eq 2)	predicted [from eq 3 (Table 2)]
$[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$	$1.504 \pm 0.135$	1.423
$[\text{PF}_6]^-$	$0.191 \pm 0.136$	0.211
$[\text{BF}_4]^-$	$-0.197 \pm 0.177$	-0.186
$[\text{SbF}_6]^-$	-0.248	—
$[\text{CF}_3\text{SO}_3]^-$	0.533	0.509
$\text{Cl}^-$	$-0.443 \pm 0.220$	-0.537
$[\text{NO}_3]^-$	-0.518	-0.561
$\text{Br}^-$	-0.338	-0.261
$[\text{CH}_3\text{COO}]^-$	-0.628	-0.609

**Table 2. System Parameters (with Standard Deviations in Parentheses) for Predicting Anionic Hydrophobicities Using Calculated LFER Parameters of Anions**

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

**Table 3. System Parameters (with Standard Deviations in Parentheses) for Predicting Octanol–Water Partition Coefficients ( $\log P_{\text{O/W}}$ ) of Ionic Liquids Using 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

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, it is not surprising that the hydrophobicity correlates well with  $V_a$  according to eq 4 (Table 2), for which SD = 0.261. Here, we found that acetate, with its high hydrogen-bonding basicity ability, forms a large exception. To also include similarly basic anions, the hydrogen basicity value was added as a parameter. For the combination of  $V_a$  and  $B_a$ , we found the SD to decrease to 0.211, with all data points coming closer to the best-fit axis [eq 5 (Table 2)]. In the next step, the hydrogen-bonding acidity,  $A_a$ , was added [eq 6 (Table 2)]. 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 (Table 2)].  $E_a$  increased the accuracy only slightly (SD = 0.067), and  $S_a$  had very little importance, but in combination with  $V_a$ ,  $B_a$ , and  $A_a$  [eq 3 (Table 2)], they contributed to reaching the best prediction ( $R^2 = 0.997$ ).

**Prediction of  $\log P_{\text{O/W}}$ .** For predicting the octanol–water partition coefficient of ILs, we used both measured and calculated descriptors. Experimentally determined  $\log P_{\text{O/W}}$  values measured between very dilute conditions and around 15 mM were collected from the literature,<sup>44–49</sup> because  $\log P$  is dependent on concentration.<sup>45</sup> Values for 25 chloride-based ILs were also measured as part of this work (see Supporting Information). From theoretical considerations, we modified the Abraham equation by adding the anionic hydrophobicity parameter ( $H_a$ , dimensionless)

$$\log P_{\text{O/W}} = c + e_c E_c + s_c S_c + a_c A_c + b_c B_c + v_c V_c + d H_a \quad (8)$$

With the measured cationic LFER descriptors presented by our group in a previous study<sup>31</sup> and the experimentally determined anionic hydrophobicity constants,  $\log P_{\text{O/W}}$  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).

As shown by eq 10 (Table 3), the cationic volume term combined with the anionic hydrophobicity are the most important



**Table 4. System Parameters (with Standard Deviations in Parentheses) for Predicting Octanol–Water Partition Coefficients ( $\log P_{O/W}$ ) of Ionic Liquids Using 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

parameters for the  $\log P_{O/W}$  prediction of ILs, which already has a high accuracy with  $R^2 = 0.947$  and  $SD = 0.315$ . The next most important term is the hydrogen-bonding basicity [ $R^2 = 0.970$ ,  $SD = 0.234$  in eq 11 (Table 3)] and then the excess molar refraction, which together enhance the predicting accuracy to  $R^2 = 0.977$  and  $SD = 0.213$  [eq 12 (Table 3)]. 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 eqs 13 and 9, respectively (Table 3). The system parameters according to eqs 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<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N] were not investigated because their LFER parameters have not yet been measured.

Using only calculated cationic LFER descriptors (including the calculated anionic hydrophobicity), the  $\log P_{O/W}$  values of ILs were predicted following eq 8 giving an SD of 0.217 log units (Table 4). The order of importance of the contribution factors is similar to that with the measured parameters. The system parameters according to eqs 14–18 are shown in Table 4. Values measured experimentally and predicted using experimentally and computationally determined parameters are presented in Table 5 and Figure 2.

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

**Determination of the Anionic Activity Coefficient in Water.** The dimensionless activity coefficient of the anion in IL-saturated water<sup>42</sup> (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,  $f_a(-1/V_a)$  (where  $f_a$  is a system parameter). This modified equation can be used to predict anionic activity coefficients with an SD of 0.174 [eq 19 (Table 7)], which is better than can be achieved using the conventional Abraham model [eq 20 (Table 7),  $SD = 0.389$ ]. Table 7 gives the system parameters for all predictions of the activity coefficients using calculated parameters according to eqs 19–25.

The anionic activity coefficient  $B_a$  is the most important parameter and already leads to  $R^2 = 0.775$ ,  $SD = 0.721$  [eq 21 (Table 7)].  $C_a$  increases with  $B_a$ . As shown in eq 22 (Table 7), 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 (Table 7)]. The parameter  $E$  is also critical and leads to a significant increase in anionic activity, as shown in eq 24 (Table 7;  $SD = 0.234$ ). Adding the  $S$  and  $A$  terms

further slightly enhances the accuracy [eq 25 (Table 7)]. Again, one data point ([AsF<sub>6</sub>]<sup>−</sup>) had to be excluded because As is not parametrized in OBPROP's atomic contribution method.

Using the experimental and calculated LFER descriptors of the cations, the water solubilities of ILs were predicted. As for the  $\log P$  prediction model, we assumed that the cationic LFER parameters and the anionic contribution, expressed by  $dC_a$  (where  $C_a$  is the anionic activity coefficient in water and  $d$  is a system parameter), should be combined in one model as follows

$$\log(\text{water solubility}) \text{ (g L}^{-1}\text{)} = c + e_c E_c + s_c S_c + a_c A_c + b_c B_c \\ + v_c V_c + f_c(1/V_c) + dC_a \quad (26)$$

When using measured LFER parameters of the cation and activity coefficients of the anion, the water solubilities of ILs can be predicted within the small error range of 0.138 log units [eq 27 (Table 8), Figure 3].

Naturally, the molar fraction of ILs in water increases with decreasing cation volume and increasing anion activity coefficient. Therefore, with just these two terms, the water solubilities can be predicted with  $R^2 = 0.976$  and  $SD = 0.135$  [eq 28 (Table 8)]. 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 (Table 8)]. 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 yet available. The system parameters according to eqs 27–29 are provided in Table 8.

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

The system parameters in Tables 8 and 9 are different for the measured and calculated descriptors. This is likely due to the different statistical relations of the measured and calculated parameters, as already noted by Klamt and Abraham in their pioneering study<sup>34</sup> 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, that is, experimental or calculated LFER values. The water solubilities

**Table 5.**  $\log P_{O/W}$  Values of Ionic Liquids Measured Experimentally and Predicted Using Calculated (calcd) and Measured (exptl) LFER Parameters

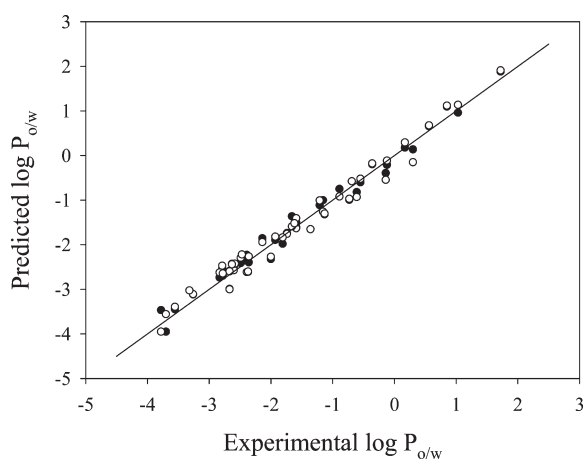
chemical	measured $\log P_{O/W}$	predicted $\log P_{O/W}$	
		calcd LFER parameters [eq 14 (Table 4)]	exptl LFER parameters [eq 9 (Table 3)]
[IM14]Cl	$-2.77 \pm 0.068^a$ , $-2.40^{46,47}$	-2.59	-2.53
[IM16]Cl	$-1.73 \pm 0.003^a$	-1.77	-1.75
[IM18]Cl	$-0.60 \pm 0.003^a$	-0.95	-0.83
[IM19]Cl	$-0.13 \pm 0.005^a$	-0.56	-0.41
[IM1-10]Cl	$0.31 \pm 0.030^a$	-0.16	0.12
[IM1-1Ph]Cl	$-2.35 \pm 0.008^a$	-2.28	-2.41
[IM1-(1Ph-4Me)]Cl	$-1.80 \pm 0.010^a$	-1.89	-1.99
[IM1-2Ph]Cl	$-1.99 \pm 0.017^a$	-2.29	-2.33
[IM12=1]Cl	$-3.25 \pm 0.007^a$	-3.12	-3.13
[N1,1,10, Bz]Cl	$1.04 \pm 0.014^a$	1.12	0.95
[N1,1,12, Bz]Cl	$1.73 \pm 0.017^a$	1.89	1.87
[IM12O1]Cl	$-3.77 \pm 0.060^a$	-3.96	-3.48
[IM13OH]Cl	$-3.69 \pm 0.010^a$	-3.57	-3.96
[IM11O2]Cl	$-3.31 \pm 0.005^a$	-2.04	—
[Py4-4NMe2]Cl	$-2.13 \pm 0.008^a$	-1.96	-1.87
[Py6-4NMe2]Cl	$-1.15 \pm 0.011^a$	-1.27	-1.02
[Py4-3Me-5Me]Cl	$-2.38 \pm 0.003^a$	-2.63	-2.24
[C2Py]Cl	$-3.55 \pm 0.011^a$	-3.41	-3.46
[C4Py]Cl	$-2.82 \pm 0.017^a$	-2.64	-2.75
[C8Py]Cl	$-0.72 \pm 0.001^a$	-0.99	-1.01
[Py4-2Me]Cl	$-2.78 \pm 0.002^a$	-2.49	-2.54
[Py4-4Me]Cl	$-2.57 \pm 0.020^a$	-2.44	-2.45
[Py4-3Me]Cl	$-2.62 \pm 0.007^a$	-2.45	-2.44
[Py6-3Me]Cl	$-1.58 \pm 0.005^a$	-1.65	-1.62
[Py6-4Me]Cl	$-1.65 \pm 0.008^a$	-1.61	-1.38
[IM14][NO <sub>3</sub> ]	$-2.42^{46,47}$ , $-2.9^{48}$	-2.61	-2.60
[IM14]Br	$-2.48^{47}$	-2.31	-2.43
[IM11][CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	$-1.35 \pm 0.040^{44}$	-1.67	—
[IM12][CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	$-1.18 \pm 0.03^{44}$ , $-1.01$ ( $-1.05$ to $-0.95$ ) <sup>47</sup>	-1.32	-1.33
[IM13][CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	$-0.88 \pm 0.02^{44}$	-0.93	-0.76
[IM14][CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	$-0.50 \pm 0.03^{44}$ , $-0.58$ ( $-0.96$ to $-0.208$ ) <sup>47</sup>	-0.54	-0.62
[IM15][CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	$-0.11 \pm 0.03^{44}$	-0.13	-0.22
[IM16][CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	$0.16 \pm 0.02^{44}$ , $0.19$ ( $0.15$ – $0.22$ ) <sup>47</sup>	0.28	0.16
[IM17][CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	$0.57 \pm 0.02^{44}$	0.66	0.64
[IM18][CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	$0.79 \pm 0.03^{44}$ , $0.93$ ( $0.80$ – $1.05$ ) <sup>47</sup>	1.11	1.08
[IM12][PF <sub>6</sub> ]	$-2.36 \pm 0.08^{44}$	-2.61	-2.62
[IM14][PF <sub>6</sub> ]	$-1.72 \pm 0.06^{44}$ , $-1.66^{46,49}$ , $-2.39^{48}$	-1.83	-1.91
[IM16][PF <sub>6</sub> ]	$-1.20 \pm 0.05^{44}$	-1.02	-1.13
[IM18][PF <sub>6</sub> ]	$-0.35 \pm 0.04^{44}$	-0.19	-0.21
[IM12][BF <sub>4</sub> ]	$-2.66 \pm 0.10^{44}$	-3.01	-3.01
[IM14][BF <sub>4</sub> ]	$-2.40 \pm 0.08^{44}$ , $-2.52^{46,49}$	-2.23	-2.29
[IM16][BF <sub>4</sub> ]	$-1.58 \pm 0.08^{44}$	-1.42	-1.51
[IM18][BF <sub>4</sub> ]	$-0.68 \pm 0.06^{44}$	-0.59	-0.59
[IM14][SbF <sub>6</sub> ]	$-2.39 \pm 0.08^{44}$	—	-2.34
[IM14][CF <sub>3</sub> SO <sub>3</sub> ]	$-1.61 \pm 0.05^{44}$	-1.53	-1.57
[IM14][CH <sub>3</sub> COO]	$-2.77 \pm 0.08^{44}$	-2.66	-2.71

<sup>a</sup> Measured for this study.

measured experimentally and predicted using measured and calculated LFER parameters according to eq 29 (Table 8) and eq 30 (Table 9), respectively, are provided in Table 10.

#### 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



**Figure 2.** Relationship between experimental and predicted  $\log P_{O/W}$  values determined using measured (●) and calculated (○) LFER parameters.

**Table 6.** Dimensionless Activity Coefficients of Ionic-Liquid Anions in Water Measured<sup>a</sup> and Predicted with the LFER Parameters Calculated According to Eq 19 (Table 7)

anion	measured	predicted [calcd, eq 19 (Table 7)]
[(6-2Et)2SS] <sup>−</sup>	0.521	0.501
[BF <sub>4</sub> ] <sup>−</sup>	−1.268	−1.219
[CF <sub>3</sub> SO <sub>3</sub> ] <sup>−</sup>	−1.343	−1.268
[PhBF <sub>3</sub> ] <sup>−</sup>	−1.853	−1.837
[B(CN) <sub>4</sub> ] <sup>−</sup>	−2.264	−2.209
[PF <sub>6</sub> ] <sup>−</sup>	−2.280, −2.178	−2.414
[(C <sub>4</sub> F <sub>9</sub> )SO <sub>3</sub> ] <sup>−</sup>	−2.610	−2.700
[(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N] <sup>−</sup>	−2.911, −2.868	−2.814
[AsF <sub>6</sub> ] <sup>−</sup>	−3.165	—
[(C <sub>2</sub> F <sub>5</sub> SO <sub>2</sub> ) <sub>2</sub> N] <sup>−</sup>	−3.363	−3.556
[(CF <sub>3</sub> SO <sub>2</sub> ) <sub>3</sub> C] <sup>−</sup>	−3.902, −3.841	−3.722
[(C <sub>2</sub> F <sub>5</sub> ) <sub>3</sub> PF <sub>3</sub> ] <sup>−</sup>	−4.883, −4.803	−4.788

<sup>a</sup>Experimental data from Ranke et al.<sup>42</sup>

**Table 7.** System Parameters (with Standard Deviations in Parentheses) According to Eqs 19–25 for the Prediction of the Anionic Activity Coefficient in IL-Saturated Water Using the Calculated LFER Parameters (calcd)

eq	<i>c</i>	<i>e<sub>a</sub></i>	<i>s<sub>a</sub></i>	<i>a<sub>a</sub></i>	<i>b<sub>a</sub></i>	<i>v<sub>a</sub></i>	<i>f<sub>a</sub></i>	<i>R</i> <sup>2</sup>	SD	<i>N</i>	<i>F</i>
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

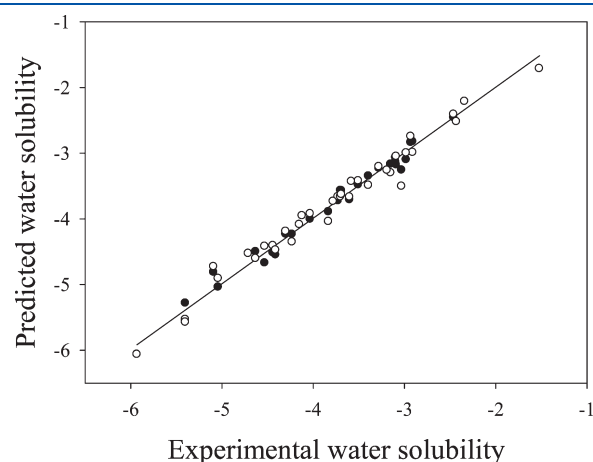
**Table 8.** System Parameters (with Standard Deviations in Parentheses) for Predicting the Water Solubilities of ILs Using Measured LFER Parameters and Anion Activities According to Eqs 27–29

eq	<i>c</i>	<i>e<sub>c</sub></i>	<i>s<sub>c</sub></i>	<i>a<sub>c</sub></i>	<i>b<sub>c</sub></i>	<i>v<sub>c</sub></i>	<i>f<sub>c</sub></i>	<i>d</i>	<i>R</i> <sup>2</sup>	SD	<i>N</i>	<i>F</i>
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

science. Specifically, it influences biological properties such as 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 interactions at rather high concentrations in water. Because 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 the literature<sup>12,61–84</sup> and are given in Table 8.

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

Here, the prediction was carried out exclusively with calculated descriptors, because experimental anionic descriptors are not yet available. The results show that the CMC can be predicted within an error range of about 0.179 log units according to eq 36. However, there are some marked



**Figure 3.** Relationship between experimental and predicted water solubility values determined with measured (●) and calculated (○) LFER parameters according to eq 29 (Table 8) and eq 30 (Table 9), respectively.

**Table 9. System Parameters (with Standard Deviations in Parentheses) for Predicting the Water Solubilities of ILs Using Calculated LFER Parameters and Anion Activities According to Eqs 30–35**

eq	$c$	$e_c$	$s_c$	$a_c$	$b_c$	$v_c$	$f_c$	$d$	$R^2$	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

**Table 10. Logarithms of the Water Solubilities ( $\text{g L}^{-1}$ ) of Ionic Liquids Measured Experimentally and Predicted with Measured (exptl) and Calculated (calcd) LFER Parameters According to Eqs 29 (Table <sup>8</sup>) and 30 (Table <sup>9</sup>), Respectively**

ionic liquid	measured	predicted	
		exptl LFER parameters	calcd LFER parameters
[IM12][B(CN) <sub>4</sub> ]	−2.46 <sup>49</sup>	−2.39	−2.41
[IM12][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−3.12, <sup>51</sup> −3.1, <sup>51</sup> −3.08, <sup>53</sup> −3.08, <sup>51</sup> −3.1 <sup>50</sup>	−3.04	−3.07
[IM13][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−3.29, <sup>51</sup> −3.28, <sup>51</sup> −3.27 <sup>51</sup>	−3.26	−3.21
[IM14][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> C]	−4.44 <sup>50</sup>	−4.55	−4.41
[IM14][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−3.51, <sup>51</sup> −3.51, <sup>51</sup> −3.54, <sup>51</sup> −3.53, <sup>51</sup> −3.49, <sup>51</sup> −3.46, <sup>51</sup> −3.5, <sup>51</sup> −3.5 <sup>59</sup>	−3.55	−3.42
[IM14][(C <sub>4</sub> F <sub>9</sub> )SO <sub>3</sub> ]	−3.15 <sup>52</sup>	−3.24	−3.30
[IM14][PF <sub>6</sub> ]	−3.0, <sup>54</sup> −2.92, <sup>54</sup> −2.96, <sup>54</sup> −2.93, <sup>57</sup> −2.89, <sup>55</sup> −2.87, <sup>55</sup> −2.8, <sup>53</sup> −2.9, <sup>59</sup> −2.9 <sup>50</sup>	−2.91	−2.99
[IM15][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−3.73, <sup>51</sup> −3.71, <sup>51</sup> −3.74 <sup>51</sup>	−3.74	−3.66
[IM16][(C <sub>2</sub> F <sub>5</sub> ) <sub>3</sub> PF <sub>3</sub> ]	−5.93 <sup>59</sup>	−5.99	−6.06
[IM16][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>3</sub> C]	−5.04 <sup>59</sup>	−5.00	−4.91
[IM16][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−4.02, <sup>51</sup> −4.18, <sup>59</sup> −3.86, <sup>53</sup> −4.03, <sup>50</sup> −4.05, <sup>51</sup> −4.05 <sup>51</sup>	−4.00	−3.92
[IM16][PF <sub>6</sub> ]	−3.41, <sup>54</sup> −3.45, <sup>54</sup> −3.35, <sup>59</sup> −3.36 <sup>54</sup>	−3.36	−3.49
[IM17][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−4.31, <sup>51</sup> −4.3, <sup>51</sup> −4.29 <sup>51</sup>	−4.19	−4.19
[IM18][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−4.7, <sup>61</sup> −4.6, <sup>61</sup> −4.59, <sup>59</sup> −4.14, <sup>50</sup> −4.1, <sup>52</sup> −4.1, <sup>61</sup> −4.5, <sup>51</sup> −4.49, <sup>51</sup> −4.47 <sup>51</sup>	−4.49	−4.48
[IM18][(C <sub>4</sub> F <sub>9</sub> )SO <sub>3</sub> ]	−4.23 <sup>52</sup>	−4.18	−4.35
[IM18][PF <sub>6</sub> ]	−3.93, <sup>59</sup> −3.92, <sup>54</sup> −3.9, <sup>54</sup> −3.46, <sup>56</sup> −3.95 <sup>54</sup>	−3.85	−4.04
[IM18][BF <sub>4</sub> ]	−2.93 <sup>54</sup>	−2.83	−2.75
[Py4-3Me][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−3.7 <sup>50</sup>	−3.67	−3.66
[Py4-4Me][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−3.69 <sup>52</sup>	−3.66	−3.63
[Py4-4Me][(C <sub>4</sub> F <sub>9</sub> )SO <sub>3</sub> ]	−3.03 <sup>52</sup>	−3.35	−3.51
[Py8-4Me][(C <sub>2</sub> F <sub>5</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−5.4 <sup>59</sup>	−5.18	−5.53
[Py8-4Me][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−5.09 <sup>59</sup>	−4.72	−4.73
[Py8-4Me][(C <sub>4</sub> F <sub>9</sub> )SO <sub>3</sub> ]	−4.63 <sup>59</sup>	−4.42	−4.60
[Py8-4Me][PhBF <sub>3</sub> ]	−3.6 <sup>59</sup>	−3.66	−3.67
[Py8-4Me][CF <sub>3</sub> SO <sub>3</sub> ]	−3.09 <sup>59</sup>	−3.14	−3.05
[Py8-4Me][BF <sub>4</sub> ]	−2.98 <sup>59</sup>	−3.07	−3.00
[Pyr14][(C <sub>2</sub> F <sub>5</sub> ) <sub>3</sub> PF <sub>3</sub> ]	−5.43 <sup>59</sup>	—	−5.57
[Pyr14][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−3.59, <sup>59</sup> −3.57 <sup>59</sup>	—	−3.43
[Pyr16][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−4.12 <sup>59</sup>	—	−3.95
[Pyr18][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−4.71 <sup>59</sup>	—	−4.53
[Py6-4NMe2][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−4.53, <sup>59</sup> −4.53 <sup>50</sup>	−4.66	−4.42
[IM16-2Me][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−4.15 <sup>50</sup>	—	−4.09
[Pip14][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−3.78 <sup>60</sup>	—	−3.73
[Mor11O2][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−3.19 <sup>59</sup>	—	−3.26
[Py3OH][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−2.43 <sup>59</sup>	—	−2.52
[IM12OH][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	−2.34 <sup>50</sup>	—	−2.21
[N4444][(6-2Et) <sub>2</sub> SS]	−1.52 <sup>58</sup>	—	−1.71

exceptions ([IM12]Br, [IM14]Br, [IM14][CF<sub>3</sub>SO<sub>4</sub>], and [IM14][C<sub>8</sub>SO<sub>4</sub>]). To include them, we introduced the charge

density term ( $1/V_c$  and  $-1/V_a$  for cation and anion, respectively). In this combination (eq 37), the correlation

**Table 11.** System Parameters (with Standard Deviations in Parentheses) for Predicting the Critical Micelle Concentrations of ILs Using Calculated LFER Parameters

eq	$c$	$e_c$	$s_c$	$a_c$	$b_c$	$v_c$	$e_a$	$s_a$	$a_a$	$b_a$	$v_a$	$g_c$	$f$
39 <sup>a</sup>	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)		
40 <sup>b</sup>	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)

<sup>a</sup>  $R^2 = 0.982$ , SD = 0.168,  $N = 36$ ,  $F = 139.3$ . <sup>b</sup>  $R^2 = 0.994$ , SD = 0.104,  $N = 36$ ,  $F = 307.3$ .

was improved to  $R^2 = 0.989$ .

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

$$R^2 = 0.989, \text{SD} = 0.128, N = 36, F = 345.7$$

In another approach, we rewrote eq 29 (Table 8) as eq 38 with the assumption that each parameter of the cation and anion is different

$$\begin{aligned} \log \text{CMC} = & c + e_c E_c + s_c S_c + a_c A_c + b_c B_c + v_c V_c + e_a E_a \\ & + s_a S_a + a_a A_a + b_a B_a + v_a V_a \end{aligned} \quad (38)$$

The results showed that the CMC can be predicted with an SD of 0.168 log units, which is similar to the case for eq 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 eqs 39 and 40 are given in Table 11, and the predicted and measured CMC values are given in Table 12 and Figure 4.

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.<sup>12</sup> The results give an  $R^2$  value of 0.994, equal to that in the present study. However, to use the previous method, it is necessary to calculate the enthalpies for each IL, because the values change with the combination of cation and anion, whereas the present approach is simpler, as the needed parameters can be easily derived by combining cation- and anion-specific LFER parameters without any quantum-chemical calculations.

## CONCLUSIONS

The extended models based on the Abraham equation can satisfactorily model log  $P$ , water solubility, and CMC values of rather concentrated aqueous solutions of ILs using measured and calculated LFER parameters. Activity coefficients and hydrophobicities 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 more easily accessible and provide an easy approach to investigate parameters for ILs that are not yet available experimentally.

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 the other terms ( $E$ ,  $S$ , and  $A$ ) make only slight—but not negligible—contributions. The combination of all parameters can enhance the predictability of IL 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 contribute significantly to IL partitioning 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 the hydrogen-bonding basicity of the cation. We assume that this is because 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-pairing and also for the ion-dissociated form. In both cases, good agreement was demonstrated, but the predictions using the ion-dissociated form were 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 follows: [IM1 $n$ ]<sup>+</sup>, 1-methyl-3-alkylimidazolium (with  $n = 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14$ , and 18 being the number of carbon atoms in the unbranched alkyl chain); [Pyn]<sup>+</sup>, alkylpyridinium (with  $n = 2, 4, 6, 8$ ); [N1,1,1, $n$ ]<sup>+</sup>, trimethylalkylammonium (with  $n = 8, 10, 12, 14, 16, 18$ ); [Pyr1 $n$ ]<sup>+</sup>, alkylmethylpyrrolidinium (with  $n = 4, 6, 8$ ); [N1,1, $n$ ,Bz]<sup>+</sup>, benzylalkyldimethylammonium (with  $n = 10, 12$ ); [Pyn-4NMe2]<sup>+</sup>, 1-alkyl-4-(dimethylamino)pyridinium (with  $n = 4, 6$ ); [Pyn-2Me]<sup>+</sup>, 1-alkyl-2-methylpyridinium (with  $n = 4, 6$ ); [Pyn-3Me]<sup>+</sup>, 1-alkyl-3-methylpyridinium (with  $n = 4, 6$ ); [Pyn-4Me]<sup>+</sup>, 1-alkyl-4-methylpyridinium (with  $n = 4, 6, 8$ ); [IM1-1Ph]<sup>+</sup>, 1-benzyl-3-methyl-imidazolium; [IM1-(1Ph-4Me)]<sup>+</sup>, 1-methyl-3-(4-methylbenzyl)-imidazolium; [IM1-2Ph]<sup>+</sup>, 1-methyl-3-(2-phenylethyl)-imidazolium; [IM1-2=1]<sup>+</sup>, (1-methyl-3-(2-propenyl)-imidazolium); [IM12O1]<sup>+</sup>, 1-(2-methoxyethyl)-3-methyl-imidazolium; [IM13OH]<sup>+</sup>, 1-(3-hydroxypropyl)-3-methyl-imidazolium; [IM11O2]<sup>+</sup>, 1-(ethoxymethyl)-3-methyl-imidazolium; [Py4-3Me-5Me]<sup>+</sup>, 1-butyl-3,5-dimethylpyridinium; [IM16-2Me]<sup>+</sup>, 1-hexyl-2,3-dimethyl-imidazolium; [Pip14]<sup>+</sup>, 1-butyl-1-methyl-piperidinium; [Mor11O2]<sup>+</sup>, 4-(ethoxymethyl)-4-methylmorpholinium; [Py3OH]<sup>+</sup>, 1-(3-hydroxypropyl)pyridinium; [IM12OH]<sup>+</sup>, 1-(3-hydroxyethyl)pyridinium; [N4,4,4,4]<sup>+</sup>, tetrabutylammonium

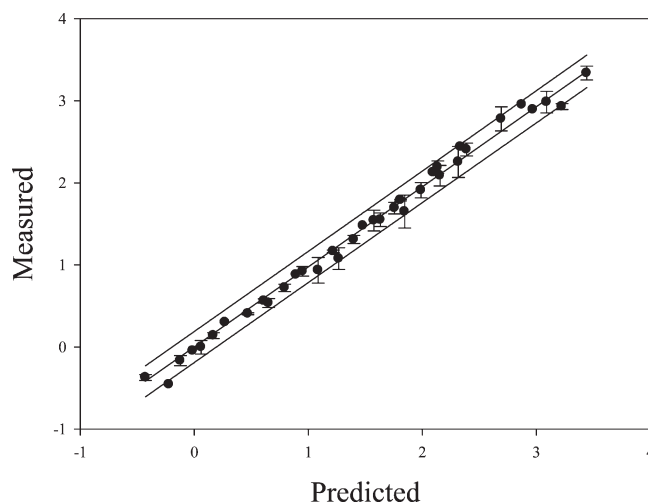


**Table 12.** Experimentally Measured and Predicted log CMC Values ( $\text{mmol L}^{-1}$ ) of Ionic Liquids Assessed with Calculated LFER Parameters According to Eq 40 (Table 11)

chemical	surface tension	conductivity	other	predicted
[N1,1,1,8]Br			2.352 <sup>61</sup> 2.462 <sup>62</sup>	2.388
[N1,1,1,10]Cl	1.845 <sup>63</sup>	1.976 <sup>64</sup>		1.988
[N1,1,1,10]Br		1.797 <sup>65</sup>	1.792 <sup>61</sup> 1.780 <sup>65</sup>	1.807
[N1,1,1,12]Cl	1.255 <sup>63</sup>	1.346 <sup>64</sup> 1.328 <sup>66</sup>		1.400
[N1,1,1,12]Br			1.155 <sup>60</sup> 1.176 <sup>67</sup>	1.218
[N1,1,1,14]Cl	0.740 <sup>68</sup> 0.653 <sup>63</sup>	0.751 <sup>64</sup> 0.740 <sup>69</sup>		0.793
[N1,1,1,14]Br		0.580 <sup>69</sup>	0.544 <sup>67</sup>	0.612
[N1,1,1,16]Cl	0.114 <sup>63</sup>	0.164 <sup>63</sup>		0.168
[N1,1,1,16]Br			−0.046 <sup>67</sup>	−0.013
[N1,1,1,18]Cl			−0.456 <sup>70</sup>	−0.221
[IM12]Br	3.398 <sup>71</sup>	3.279 <sup>71</sup>		3.442
[IM14]Br	2.903 <sup>71</sup>	2.954 <sup>71</sup>		3.225
[IM14][BF <sub>4</sub> ]	2.903 <sup>72</sup> 3.137 <sup>12</sup>	2.914 <sup>72</sup>		3.090
[IM14][CF <sub>3</sub> SO <sub>3</sub> ]	2.893 <sup>12</sup>			2.970
[IM14][C <sub>8</sub> SO <sub>4</sub> ]	1.608 <sup>12</sup>	1.491 <sup>73</sup>		1.632
[IM16]Cl	2.954 <sup>63</sup>			2.873
[IM16]Br	2.778 <sup>71</sup> 2.672 <sup>76</sup>	2.602 <sup>71</sup>	2.945 <sup>74</sup> 2.903 <sup>74</sup>	2.692
[IM18]Cl	2.342 <sup>76</sup> 2.000 <sup>72</sup> 2.342 <sup>63</sup>	2.369 <sup>76</sup> 1.954 <sup>72</sup>	2.301 <sup>63</sup>	2.316
[IM18]Br	2.176 <sup>71</sup> 2.083 <sup>76</sup>	2.176 <sup>71</sup>	2.255 <sup>74</sup> 2.279 <sup>74</sup>	2.135
[IM18]I	2.000 <sup>72</sup>	2.176 <sup>72</sup>		2.156
[IM19]Br	1.602 <sup>71</sup>	1.477 <sup>71</sup> 1.869 <sup>77</sup>		1.845
[IM1-10]Cl	1.777 <sup>76</sup> 1.740 <sup>63</sup> 1.601 <sup>78</sup>	1.731 <sup>76</sup> 1.607 <sup>78</sup>	1.653 <sup>63</sup> 1.740 <sup>63</sup>	1.756
[IM1-10]Br	1.301 <sup>75</sup> 1.467 <sup>80</sup>	1.602 <sup>79</sup> 1.613 <sup>77</sup> 1.517 <sup>80</sup>	1.623 <sup>74</sup> 1.663 <sup>74</sup>	1.575
[IM1-12]Cl	1.176 <sup>63</sup> 1.120 <sup>78</sup>	1.129 <sup>78</sup>	0.845 <sup>63</sup> 1.114 <sup>63</sup>	1.267
[IM1-12]Br	0.634 <sup>75</sup>	0.991 <sup>77</sup> 0.929 <sup>83</sup> 0.978 <sup>81</sup>	1.000 <sup>74</sup> 1.079 <sup>74</sup>	1.086
[IM1-12][BF <sub>4</sub> ]	0.964 <sup>80</sup>	0.881 <sup>80</sup>		0.952
[IM1-14]Cl	0.602 <sup>63</sup> 0.532 <sup>76</sup> 0.474 <sup>78</sup>	0.498 <sup>66</sup> 0.566 <sup>78</sup>	0.477 <sup>63</sup> 0.602 <sup>63</sup>	0.652
[IM1-14]Br		0.398 <sup>77</sup> 0.415 <sup>80</sup>		0.471
[IM1-16]Cl	0.114 <sup>76</sup> −0.056 <sup>82</sup> −0.061 <sup>78</sup>	0.057 <sup>76</sup> −0.066 <sup>78</sup>		0.060

**Table 12. Continued**

chemical	surface tension	conductivity	other	predicted
[IM1-16]Br		−0.097 <sup>75</sup> −0.215 <sup>77</sup> −0.187 <sup>81</sup>		−0.121
[IM1-18]Cl	−0.398 <sup>76</sup>	−0.347 <sup>76</sup>		−0.427
[Py <sub>8</sub> ]Cl		2.439 <sup>76</sup>		2.334
Na[C <sub>8</sub> SO <sub>4</sub> ]			2.127 <sup>83</sup>	2.094
Na[C <sub>10</sub> SO <sub>4</sub> ]			1.477 <sup>83</sup>	1.480
Na[C <sub>12</sub> SO <sub>4</sub> ]			0.881 <sup>84</sup>	0.892
Na[C <sub>14</sub> SO <sub>4</sub> ]			0.301 <sup>83</sup>	0.269

**Figure 4.** Relationship between experimental and predicted critical micelle concentrations ( $\text{mmol L}^{-1}$ ) determined with calculated parameters according to eq 40 (Table 11).

combined selectively with  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ;  $[\text{NO}_3]^-$ , nitrate;  $[\text{BF}_4]^-$ , tetrafluoroborate;  $[\text{PF}_6]^-$ , hexafluorophosphate;  $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ , bis(trifluoromethylsulfonyl)amide;  $[(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}]^-$ , bis(pentafluoroethanesulfonyl)imide;  $[\text{CF}_3\text{SO}_3]^-$ , trifluoromethanesulfonate;  $[\text{SbF}_6]^-$ , hexafluoroantimonate;  $[\text{CH}_3\text{COO}]^-$ , acetate;  $[(6\text{-}2\text{Et})_2\text{SS}]^-$ , bis(2-ethylhexyl)sulfosuccinate;  $[\text{PhBF}_3]^-$ , trifluorophenylborate;  $[\text{B}(\text{CN})_4]^-$ , tetracyanidoborate;  $[(\text{CF}_3\text{SO}_2)_3\text{C}]^-$ , tris(trifluoromethylsulfonyl)methide;  $[(\text{C}_2\text{F}_5)_3\text{PF}_3]^-$ , trifluorotris(pentafluoro-ethyl)phosphate;  $[\text{AsF}_6]^-$ , hexafluoroarsenate;  $[(\text{C}_4\text{F}_9)\text{SO}_3]^-$ , nonafluorobutyl sulfonate;  $[\text{C}_n\text{SO}_4]^-$ , alkyl sulfate ( $n = 8, 10, 12, 14$ ).

**Measurement of the Octanol–Water Partition Coefficient.** We measured the log  $P$  values of 25 chloride-based ILs (see the list of log  $P$  values in Table 5). Three 15 mL conical tubes with caps were filled with 3 mL of octanol and water, and 15.0 mM IL was added. The vials were vigorously shaken for 10 min and allowed to stabilize for at least 1 h, and then centrifugation was performed to eliminate the emulsion created by the shaking process prior to injection into the HPLC system. Then, samples of 5  $\mu\text{L}$  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 IL in each phase, we employed a Hilic stationary phase with acetonitrile (99.9%, Fluka) and buffer (15 mM  $\text{KH}_2\text{PO}_4$  and 30 mM  $\text{H}_3\text{PO}_4$ ) as the eluent in the HPLC instrument (Hewlett-Packard System Series 1100), because the

cation has good retention characteristics in HILIC systems and applying phosphate buffer to the mobile phase allows influence of the anion in the chromatographic system to be neglected.<sup>85</sup> The detection wavelengths were 211 nm for imidazolium-based ILs and 254 nm for pyridinium-based ILs and ammonium-based compounds with benzyl substituents. The partition coefficients of ILs were determined as the ratio of the solute peak area in the two phases

$$\log P = \log C_o^i / C_w^i \quad (41)$$

where  $C_o^i$  is the concentration of ILs in octanol phase and  $C_w^i$  is the concentration of ILs in water phase. The tests for partition coefficients of ILs were performed in triplicate. ILs were donated by Merck.

**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. First, (RI-)BP86/SV(P) optimizations<sup>86–89</sup> were carried out with the TURBOMOLE program package (version 5.10) using the Resolution of Identity (RI)<sup>89</sup> for reasonable starting structures. Using AOFORCE,<sup>90,91</sup> the vibrational frequencies of each ion were calculated. These structures were further refined with the TZVP<sup>92</sup> basis set, after which a full optimization with inclusion of COSMO<sup>32</sup> was performed ( $\epsilon_r = \infty$ ). Finally the sig 2, sig 3, HBD3, and HBA3 values of the optimized ion of ILs were calculated with COSMO-RS<sup>32</sup> using BP\_TZVP\_C21\_0108 parametrization. The calculated sig 2, sig 3, HBD3, and HBA3 values of all anions and cations ILs are given in Table S6 (Supporting Information).

## ■ ASSOCIATED CONTENT

**Supporting Information.** Measured and calculated LFER parameters of IL ions (Tables S1 and S2), detailed explanations of computational methods with subdata set (Table S3) and equations (eqs S1–S5) for LFER parameters, and lipophilicity of cation for determining anionic hydrophobicity (Table S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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