

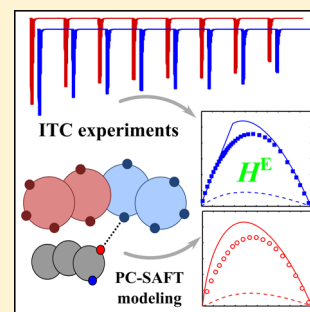
Excess Enthalpies of Mixing of Piperidinium Ionic Liquids with Short-Chain Alcohols: Measurements and PC-SAFT Modeling

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Supporting Information

ABSTRACT: This work is a continuation of our systematic study on thermodynamic properties of 1-*n*-alkyl-1-methylpiperidinium bis[(trifluoromethyl)sulfonyl]imides homologous series of ionic liquids ($[C_nC_1Pip][NTf_2]$). Excess enthalpies of mixing (H^E) of four binary systems containing two ionic liquids, namely $[C_4C_1Pip][NTf_2]$ and $[C_6C_1Pip][NTf_2]$, and two short-chain alcohols, namely ethanol and 1-propanol, were measured by isothermal titration calorimetry. Alcohol-to-ionic liquid and ionic liquid-to-alcohol titration experiments were carried out at temperature $T = 298.15$ K and atmospheric pressure. The experimental data were modeled in terms of perturbed-chain statistical associating fluid theory (PC-SAFT). Wolbach–Sandler combining rules were adopted in order to account for ionic liquid–alcohol cross-association. The model was applied in a conventional manner (i.e., without any binary corrections) as well as in a novel predictive mode developed previously by our group [Paduszyński, K.; Domańska, U. *J. Phys. Chem. B* **2012**, *116*, 5002–5018; Domańska et al. *J. Phys. Chem. B* **2012**, *116*, 8191–8200]. The latter approach employs temperature-dependent binary correction fitted to experimental limiting activity coefficient of alcohol in ionic liquid.



INTRODUCTION

For over two decades, ionic liquids (ILs), generally categorized as organic salts having a solid–liquid phase transition temperature below 100 °C, have gained a vast amount of attention and scientific activity.¹ This is due to their unique physical and thermodynamic characteristics which make ILs attractive from the point of view of sustainable and “green” applications in different fields of fundamental and applied chemical sciences.^{2–6}

The most interesting feature of ILs is their “tunability”. In fact, ILs are sometimes called “designer” (tunable) solvents. This is due to an overwhelming number of investigations which revealed that solvation properties of ILs can be easily modified by a proper selection and/or functionalization of cation or anion. Thus far, ILs have been shown to be promising media for dissolution of a great variety of materials ranging from inorganic salts⁷ and gases (e.g., carbon dioxide⁸), to biomass-based feedstocks, like carbohydrates.^{9,10} What is interesting is that ILs exhibit an enhanced selectivity in some separation processes and thus, they are regarded as good candidates for separating media of azeotropic mixtures.¹¹

There is no doubt that experimental knowledge of diverse thermophysical properties of ILs-based systems is essential, and not only from the utilitarian point of view. In fact, experimental data are required to better understand ILs at their molecular level. Furthermore, detailed information on the relationship between microscopic and macroscopic properties facilitate development of different theoretical tools (models, algorithms) for estimation or prediction of properties of other systems. Thus far, a great variety of approaches have been applied to

model pure ILs and their mixtures, including, for example, simple (but effective and robust) empirical correlations,¹² equations of state (empirical ones as well as those rooted in statistical mechanics),^{13,14} and force fields for large-scale computer simulations.^{15,16} As far as the thermodynamic equations of state are considered, statistical associating fluid theory (SAFT)¹⁷ seems to be one of the most promising theoretical tool for ILs systems. Recently, this approach has been successfully applied to model the thermodynamics of diverse cationic and anionic families of ILs.^{13,18–33} Unfortunately, SAFT-like models suffer from the incapability of accurately predicting properties of multicomponent properties, unless the binary corrections to combining rules are fitted. This problem was partially resolved very recently by Paduszyński and Domańska,^{21–23} who used limiting activity coefficients data to fit the binary corrections.

In our laboratory, we are concerned with experimental determination and equation-of-state modeling of thermodynamic properties and phase equilibria of ILs-based systems. Recently, we have focused our attention on 1-*n*-alkyl-1-methylpiperidinium cation-based ILs with bis[(trifluoromethyl)sulfonyl]imide anion.^{20,21,34–37} Throughout this work, we will abbreviate this class of ILs by $[C_nC_1Pip][NTf_2]$, where *n* stands for a number of carbon atoms in alkyl side chain of cation. Solid–liquid and liquid–liquid phase equilibrium diagrams of binary systems $[C_2C_1Pip][NTf_2]$ –alcohol (from ethanol to 1-

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nonanol),³⁵ [C₂C₁Pip][NTf₂]-water,³⁵ [C₃C₁Pip][NTf₂]-alcohol (from 1-pentanol to 1-undecanol),²⁰ [C₃C₁Pip][NTf₂]-hydrocarbon,²¹ [C₄C₁Pip][NTf₂]-alkane (*n*-alkane and cycloalkane),²¹ and limiting activity coefficients of diverse organic solutes (*n*-alkanes, alkenes, alkynes, aromatics, ketones, ethers), and water in [C_{3–6}C₁Pip][NTf₂]^{34,36,37} have been systematically measured and published. The results were discussed in terms of an impact of structure of both IL and solute on the observed phase behavior. Furthermore, the experimental data were analyzed in terms of modern molecular-based equations of state like perturbed-chain SAFT (PC-SAFT).^{20–22}

In this work, we present new sets of experimental data on excess enthalpies of mixing (H^E) in binary systems piperidinium IL–alcohol, measured by isothermal titration calorimetry. To the best of our knowledge, this is the very first work presenting H^E for mixtures containing piperidinium-based ILs. The study comprises four binary systems formed by [C₄C₁Pip][NTf₂] and [C₆C₁Pip][NTf₂] ILs with ethanol or 1-propanol. Those data are important from the standpoint of design and optimization of chemical engineering processes involving ILs and alcohols. Moreover, the results give an insight into mutual interactions between ionic liquid and alcohol moieties. Physical interpretation of the experimental data is supported by equation of state modeling adopting a PC-SAFT approach, applied in the predictive mode proposed previously by our group.²²

EXPERIMENTAL SECTION

Materials. The ionic liquids 1-butyl-1-methylpiperidinium bis[(trifluoromethyl)sulfonyl]imide ([C₄C₁Pip][NTf₂]; mass fraction purity ≥ 0.99) and 1-hexyl-1-methylpiperidinium bis[(trifluoromethyl)sulfonyl]imide ([C₆C₁Pip][NTf₂]; mass fraction purity ≥ 0.99) were purchased from IoLiTec (Ionic Liquids Technologies GmbH, Germany). The samples were further purified by subjecting the liquid to a low pressure of about 1 mPa at temperature 368 K for about 48 h. This procedure removed any volatile chemicals and water from samples. The sources and mass fraction purities of alcohols used in this study are as follows: ethanol (POCh, Poland; ≥ 0.999), 1-propanol (Sigma-Aldrich Chemie GmbH, Germany; ≥ 0.999). They were stored over freshly activated molecular sieves of type 4 A (Union Carbide), and the final purity was checked by gas–liquid chromatography before use.

The water content in ILs and alcohols was analyzed by the Karl Fischer titration technique (Schott Instruments Titro-Line KF). Samples of the ILs were dissolved in anhydrous methanol and titrated with steps of 2.5 μ L. The titrant CombiTitant 5 (no. 1.8805.1000, Merck; one-component reagent for volumetric Karl Fischer titration) was used. The results obtained have shown the water content to be less than 500 and 70 ppm in the cases of ILs and alcohols, respectively.

Excess Enthalpy Measurements. Excess enthalpies of mixing (H^E) of piperidinium ILs alcoholic solutions were determined according to procedures similar to those described previously.²³ A thermal activity monitor (TAM) III calorimeter (TA Instruments, U.S.), employing a technique called isothermal titration calorimetry (ITC), was used. The titration cell and the reference cell were placed in the test wells of the highly stable thermostatic oil bath of volume 22 L. Before the experiment, the temperature of the oil bath was maintained at a desired temperature (in this case, $T = 298.15$ K) for 24 h with a stability of ± 100 μ K.

The experiments were performed in two modes of titration. Alcohol-to-IL titration experiments were started from placing about 0.4 mL (approximately 0.5 g) of pure IL in the stainless steel ampule (titration cell) following by placing it in the thermostatic oil bath and equilibration for a few hours. Depending on the change in mole fraction of IL, $(2–15) \pm 0.001$ μ L of alcohol, was injected into the titration cell using the precise syringe pump provided by the manufacturer of the calorimeter. During the titration, the mixture was rigorously stirred with the maximum stirring speed of 100 rpm. The molar amount (required to calculate mole fraction of solution) of the titrant fluid was calculated on the basis of the volume with the known density of solute, determined in our laboratory directly prior the measurements by using vibrating tube densimeter (Anton Paar GmbH 4500), with an accuracy of density of $\pm 10^{-4}$ g·mL^{−1} at $T = 298.15 \pm 0.01$ K. The measured densities were (literature values³⁸ are given in parentheses): 0.78588 (0.7852) g·mL^{−1} for ethanol and 0.79987 (0.7995) g·mL^{−1} for 1-propanol. Titrations of ILs into alcohols were performed in an analogous manner. The initial volume of alcohol in the titration ampule was about 0.4 mL, while the injection volumes were in the range $(10–25) \pm 0.001$ μ L. Mole fractions of the resulting mixtures were calculated based on the densities of ILs at $T = 298.15$ K previously reported by our group: 1.3791 g·mL^{−1} for [C₄C₁Pip][NTf₂]²¹ and 1.3254 g·mL^{−1} for [C₆C₁Pip][NTf₂].³⁷

The actual property measured by TAM III calorimeter is the difference in heat flow between sample and the reference cell. Uncertainty of this measurement is estimated to be about $\pm 0.2\%$. Each injection is associated in heat flow peak on the power-time curve. Then, a heat effect corresponding to the *j*-th injection (δq_j) is obtained by integrating the heat flow peak over the injection time. The total molar excess enthalpy of mixing corresponding to a series of *i* consecutive injections (H_i^E) is readily calculated as follows:

$$H_i^E = \frac{\sum_{j=1}^i \delta q_j}{n_1 + \sum_{j=1}^i \Delta n_{2,j}} \quad (1)$$

where n_1 is the number of moles of solute 1 (IL in alcohol-to-IL titrations, or alcohol otherwise) and $\Delta n_{2,j}$ stands for the number of moles of solute 2 injected during *j*-th titration.

In order to verify and test the reliability of the apparatus, H^E for two reference systems, namely, methanol with water and cyclohexane with *n*-hexane, were measured at $T = 298.15$ K (see Supporting Information of our previous paper for details²³). The results obtained were compared to available literature data and an excellent agreement was observed. Finally, the uncertainty of the H^E data determined in the present study was estimated to be less than $\pm 0.5\%$.

THEORETICAL BACKGROUND

PC-SAFT Equation of State. Statistical associating fluid theory (SAFT) was derived in the beginning of the 1990s by Chapman et al.¹⁷ on the basis of the Wertheim's first-order thermodynamic perturbation theory.^{39–42} Among a vast number of SAFT modifications, the perturbed-chain SAFT (PC-SAFT) of Gross and Sadowski^{43,44} has received a lot of attention because of its excellent performance of predicting/correlating diverse thermodynamic properties of a great variety of simple and extremely complex molecular systems.⁴⁵

In terms of PC-SAFT model, the fluid mixture is assumed to be formed by molecules pictured as chains of tangent spherical segments. Thermodynamics of the mixture is given as the molar residual free energy, $\hat{a}^{\text{res}} \equiv A^{\text{res}}/RT$, assumed to be a sum of contributions accounting for various energetic/structural interactions:

$$\hat{a}^{\text{res}} = \hat{a}^{\text{hc}} + \hat{a}^{\text{disp}} + \hat{a}^{\text{assoc}} + \dots \quad (2)$$

The superscripts “hc”, “disp”, “assoc” in eq 2 denote contributions due to hard-chain formation, dispersive interactions between chains and association, respectively. Other types of intermolecular forces (like dipole–dipole, quadrupole–quadrupole) can also be taken into account, and the respective terms have been proposed and described in the literature. However, we will focus on the most “basic” version of PC-SAFT as only those terms given explicitly in eq 2 are important from the point of view of this study. Furthermore, we will not discuss in detail the expressions for the contributions, as they can be found elsewhere.^{43–45} In this work, we briefly introduce model-specific parameters only.

A pure component i (i.e., molecular chain consisted of segments of type i) is characterized by three constants: number of segments forming chain (m_i), the segment hard-sphere diameter (σ_i) and dispersion energy (u_i/k_B) accounting for the depth of the square-well potential of segment–segment interactions. In the case of substances composed of self- and/or cross-associating molecules, associating sites (A_i, B_i, \dots) located on chain segments and complementary parameters must be specified. To characterize a given A_i – B_i interaction, two additional parameters are introduced: the energy potential well depth ($\epsilon^{A_i B_i}/k_B$) and the relative volume ($\kappa^{A_i B_i}$). If A_i – B_i interaction is not allowed, then $\epsilon^{A_i B_i}/k_B = 0$ and $\kappa^{A_i B_i} = 0$.

A common procedure for calculating pure-fluid PC-SAFT parameters consists of fitting the model predictions to experimental pure-fluid properties such as saturated liquid density and vapor pressure. In the case of weakly characterized compounds (such as polymers, or multifunctional chemicals), the parameters can be estimated by means of empirical correlations, or group contribution methods,⁴⁶ or computer simulations.⁴⁷

Application of the PC-SAFT equation of state to mixtures requires some combining rules for cross-interaction parameters involved in the dispersion and association terms. The potential well depth for dispersive interactions of segments constituting different molecules i and j (i.e., u_{ij}/k_B) and the segment diameter corresponding to this interaction (i.e., σ_{ij}) are usually calculated by using the well-known quadratic combining rules of Lorentz–Berthelot:

$$u_{ij} = \sqrt{u_i u_j}, \quad \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (3)$$

In cross-associating systems, associating site A on molecule i (A_i) can interact with associating site B on molecule j (B_j). At the same time, associating site B on molecule i (B_i) is able to interact with associating site A on molecule j (A_j). To estimate the energy and volume of the cross-association (namely, $\epsilon^{A_i B_j}/k_B$ and $\kappa^{A_i B_j}$), other combining rules are needed. It was originally proposed⁴⁴ that the following relations proposed by Wolbach and Sandler⁴⁸ are suitable to account for cross-association when coupled with the PC-SAFT model:

$$\epsilon^{A_i B_j} = \frac{\epsilon^{A_i B_i} + \epsilon^{A_j B_j}}{2}, \quad \kappa^{A_i B_j} = \sqrt{\kappa^{A_i B_i} \kappa^{A_j B_j}} \left(\frac{\sqrt{\sigma_i \sigma_j}}{\sigma_{ij}} \right)^3 \quad (4)$$

Moreover, $\epsilon^{A_i B_i} = \epsilon^{A_i B_i}$ and $\kappa^{A_i B_i} = \kappa^{A_i B_i}$.

Provided that PC-SAFT pure fluid parameters are known, the model combined with eqs 3 and 4 can be used for mixtures in an entirely predictive manner. Satisfactorily accurate predictions can be obtained, however, only for relatively simple systems. To overcome this obstacle, binary interaction corrections to energetic cross-interaction parameters of Lorentz–Berthelot and Wolbach–Sandler combining rules (denoted by k_{ij}^{LB} and k_{ij}^{WS} , respectively) are introduced in accordance to the following definitions:²²

$$u_{ij} = \sqrt{u_i u_j} (1 - k_{ij}^{\text{LB}}) \quad (5)$$

$$\epsilon^{A_i B_j} = \frac{\epsilon^{A_i B_i} + \epsilon^{A_j B_j}}{2} (1 - k_{ij}^{\text{WS}}) \quad (6)$$

In equation-of-state modeling, the binary corrections (either k_{ij}^{LB} or k_{ij}^{WS} , depending of the system) are usually obtained by fitting them to experimental binary data of interest. Such a methodology is rather correlative and result in vanishing the predictive capacity of the model.

Molecular Scheme for Pure ILs. When SAFT modeling is going to be carried out, then the following question always arises: How to represent ILs in terms of PC-SAFT? Whereas the PC-SAFT representation is straightforward and intuitive for common molecular compounds, the problem is not easy to solve in the case of ILs. Of course, this is due to their complexity at the molecular level.⁴⁹

Thus far, there have been two main approaches proposed to model the ILs-based systems with different SAFT models. According to the first approach, the ILs are modeled as composed of neutral ion pairs capable of strong self- and cross-association.^{22,24–26,29} Although such a way of modeling may be viewed as controversial, it was shown that it provides very accurate results, including properties of pure ILs as well as their mixtures with a great variety of organic solvents and water.²² Very recently, Chen et al.³¹ presented a comprehensive study on application of PC-SAFT model to IL–CO₂ systems by using different association schemes depending on the anion. It was confirmed that utilization of the association term significantly improves description of vapor–liquid coexistence curve of pure ILs.³¹ Furthermore, Oliveira and co-workers³⁰ successfully applied soft-SAFT approach employing ion pairs picture of ILs to model surface tension of binary mixtures of imidazolium [NTf₂]-based ILs.

The second approach is a complete opposite of the first one. It assumes that ILs are completely dissociated into cations and anions and cation–anion Coulomb interactions are taken into account explicitly by electrostatic term included to eq 2.^{32,33} Ji et al. applied Debye–Hückel term in so-called ePC-SAFT (electrolyte PC-SAFT).³² Unfortunately, the model was tested only for solubility of CO₂ and CH₄ in a common series of imidazolium cation-based ILs, while other important properties like liquid–liquid equilibria phase diagrams or excess enthalpies of mixing were not taken into consideration. In turn, Shahriari and co-workers adopted a mean spherical approximation (MSA) approach to account for electrostatic effects in aqueous solutions of ILs.³³ There is no doubt that the methods involving electrostatic term are better-grounded physically compared to association-based methods. However, para-

metrization of such models may (in some cases) require binary experimental data, what significantly reduced their predictive power.

In calculations presented in this work, we follow the methodology for SAFT modeling of ILs-based systems developed and extensively tested previously by our group.^{20–23} According to this approach, $[C_4C_1Pip][NTf_2]$ and $[C_6C_1Pip][NTf_2]$ ILs are pictured as neutral ion pairs. Symmetric 10-site association scheme (five donor sites of type A_1 and five acceptor sites of type B_1) was adopted to mimic strong interactions between ion pairs and delocalization of negative charge on $[NTf_2]$ anion. The parameters m , σ , u/k_B , $\epsilon^{A_1B_1}/k_B$, and $\kappa^{A_1B_1}$ were taken from our previous works as well. In the case of ethanol and 1-propanol, 2B association scheme (according to Huang–Radosz nomenclature⁵⁰) was incorporated. In this scheme, one donor site of type A_2 corresponds to proton of the hydroxyl group, whereas one acceptor site of type B_2 mimics lone pairs on oxygen atom of the hydroxyl group. The PC-SAFT parameters for alcohols under consideration were taken from the original PC-SAFT paper of Gross and Sadowski et al.⁴⁴ Figure 1 demonstrates chemical structures of the investigated ILs and the corresponding molecular and association schemes in terms of PC-SAFT formalism.

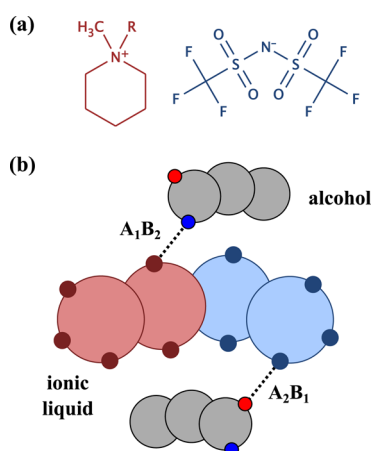


Figure 1. Representation to the investigated systems within the PC-SAFT approach: (a) Chemical structure of the ILs, where $R = n$ -butyl for $[C_4C_1Pip][NTf_2]$ and $R = n$ -hexyl for $[C_6C_1Pip][NTf_2]$; (b) Sketch illustrating molecular schemes adopted for ILs and alcohols (dashed lines indicate allowed cross-associations, see text for details).

IL–Alcohol Mixtures. In this work binary systems {IL (1) + ethanol, or 1-propanol (2)} are considered. The PC-SAFT model parameters representing IL–alcohol cross-interactions were determined following the methodology demonstrated and comprehensively tested in our previous work.²² The binary corrections k_{12}^{LB} , or k_{12}^{WS} given in eqs 3 and 4 are assumed to be dependent on temperature. Then they are adjusted to the experimental temperature dependence of limiting activity coefficient of molecular solute in IL, $\gamma_2^\infty(T)$.

Since formation of A_1 – B_2 and A_2 – B_1 complexes is (in terms of PC-SAFT) the most characteristic and the most relevant effect occurring in the IL–alcohol mixtures, k_{12}^{LB} correction is set equal to zero, while the remaining k_{12}^{WS} correction is fitted to experimental $\gamma_2^\infty(T)$ data reported recently by our group.^{36,37} The resulting predictions can be compared to purely predicted data, i.e., when $k_{12}^{LB} = k_{12}^{WS} = 0$.

Excess Enthalpy from PC-SAFT Model. Having specified residual free energy of a system, one can easily calculate residual molar enthalpy, $\hat{h}^{res} \equiv H^{res}/RT$, by using the following thermodynamic relation:

$$\hat{h}^{res} = -T \left(\frac{\partial \tilde{a}^{res}}{\partial T} \right)_{\rho, \mathbf{x}} + (Z - 1) \quad (7)$$

where Z stands for compressibility factor, while \mathbf{x} is the mole fractions vector. As the temperature-dependent binary interaction parameters k_{12}^{WS} are employed in this work, it is important to point out that the derivative with respect to temperature present in eq 7 must include term accounting temperature dependence of k_{12}^{WS} . When the chain rule for multivariable function is applied to \tilde{a}^{res} , the derivative can be rewritten as follows:

$$\left(\frac{\partial \tilde{a}^{res}}{\partial T} \right)_{\rho, \mathbf{x}} = \left(\frac{\partial \tilde{a}^{res}}{\partial T} \right)_{\rho, \mathbf{x}, k_{12}^{WS}} + \left(\frac{\partial \tilde{a}^{res}}{\partial k_{12}^{WS}} \right)_{\rho, T, \mathbf{x}} \frac{dk_{12}^{WS}}{dT} \quad (8)$$

Detailed expressions for the first term of the right-hand side of eq 8 can be found in the original work of Gross and Sadowski.⁴³ Since k_{12}^{WS} occurs in the association term in eq 2, the differentiation becomes complicated. Therefore, it is recommended to evaluate the derivative numerically, for example, by using central difference approximation:

$$\left(\frac{\partial \tilde{a}^{res}}{\partial T} \right)_{\rho, \mathbf{x}} \approx \frac{\tilde{a}^{res}[T + \tau, k_{12}^{WS}(T + \tau)] - \tilde{a}^{res}[T - \tau, k_{12}^{WS}(T - \tau)]}{2\tau} \quad (9)$$

In this work, we took $\tau = T\sqrt{\epsilon} = 4.4 \times 10^{-6}$ K, where ϵ is the “machine epsilon” (floating point-relative accuracy).

Finally, the excess enthalpy of mixing in binary mixture is calculated as follows:

$$\frac{H^E}{RT} = \hat{h}^{res} - \sum_i x_i \hat{h}_i^{res} \quad (10)$$

where \hat{h}^{res} and \hat{h}_i^{res} is the residual enthalpy of mixture and pure component i , respectively.

RESULTS AND DISCUSSION

Experimental Data. A complete list of experimental data measured (in total, 229 data points for four binary mixtures) can be found in the Supporting Information, Table S1. An exemplary power-time curve for $[C_4C_1Pip][NTf_2]$ –ethanol mixture and corresponding H^E as a function of IL mole fraction x_1 is given in Figure 2. It is clearly seen that both alcohol-to-IL and IL-to-alcohol titration experiments yield qualitatively and quantitatively consistent data. In fact, the produced H^E curves converge. This observation confirms the reliability of the apparatus as well as the method used.

The measured excess enthalpies were regressed by using the following Redlich–Kister equation:

$$\frac{H^E}{RT} = x_1 x_2 \sum_{i=0}^{k-1} A_i (x_2 - x_1)^i \quad (11)$$

where $x_2 = 1 - x_1$ and A_i ($i = 0, \dots, k - 1$) are fit coefficients, which are obtained by means of nonlinear least-squares optimization. In our calculations, *lsqnonlin* subroutine imple-

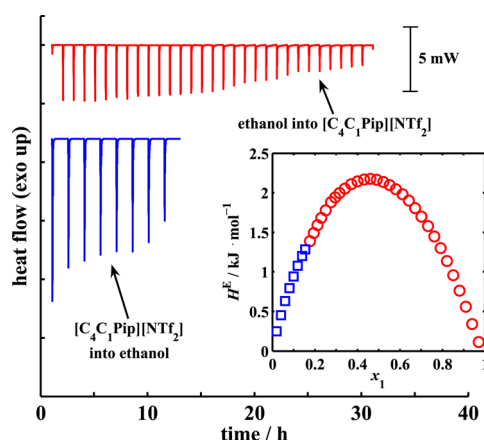


Figure 2. An exemplary raw signal from TAM III calorimeter and resulting excess enthalpies (H^E) as a function of IL mole fraction (x_1) calculated by using eq 1.

mented in Optimization Toolbox of MATLAB environment (MathWorks Inc.; version R2012a) was utilized. The number of coefficients k was adjusted on the basis of the residual variance analysis. Finally it was fixed as $k = 3$ for all the systems studied. The final values of Redlich–Kister coefficients are listed in Table 1 along with root-mean-square deviations, $\sigma(H^E)$, chosen as a measure of a quality of the fit:

$$\sigma(H^E) = \sqrt{\frac{1}{N-k} \sum_{i=1}^N (H_{i,\text{calcd}}^E - H_{i,\text{exptl}}^E)^2} \quad (12)$$

where N stands for a number of experimental data points.

The experimental data and the Redlich–Kister fits are presented in Figure 3. As can be seen, positive (endothermic) heat effect of mixing is observed for all systems in the full range of IL mole fractions. It means that the interactions between like molecules (IL–IL, alcohol–alcohol) are more preferable than interactions between alcohol and IL. Moreover, the maximum of each H^E curve is slightly shifted toward low IL mole fractions. The same was observed for similar system with imidazolium ILs based on $[\text{NTf}_2]^{51}$ and alkylsulfate⁵² anions.

Even though the differences in H^E are relatively small, one can deduce some trends governing an impact of structure of both IL and alcohol. First of all, an increase of the alkyl side chain of alcohol increases H^E . In particular, an increase in the maximum value of H^E of about $+100 \text{ J} \cdot \text{mol}^{-1}$ per CH_2 group is observed in systems with $[\text{C}_4\text{C}_1\text{Pip}][\text{NTf}_2]$, when changing from ethanol to 1-propanol, see Figure 3(a). In the case of mixtures containing $[\text{C}_6\text{C}_1\text{Pip}][\text{NTf}_2]$, the difference is slightly bigger, see Figure 3(b). Similar observation were made for mixtures containing 1-ethyl-3-methylimidazolium $[\text{NTf}_2]$ IL.⁵¹ One can suppose that this is related to more hydrophobic character of 1-propanol compared to ethanol. An impact of side

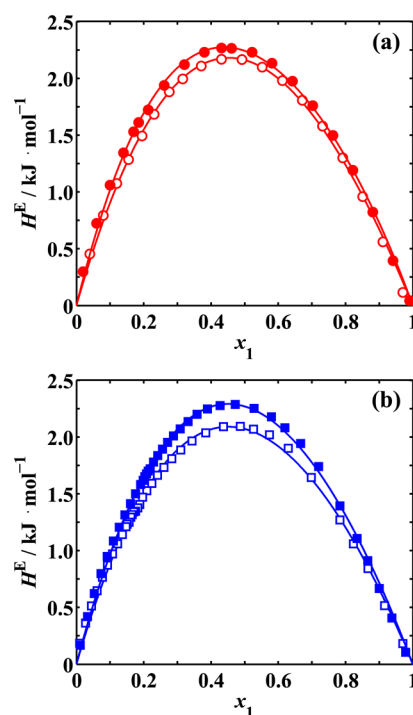


Figure 3. Experimental and correlated excess enthalpies (H^E) as a function of IL mole fraction (x_1): (a) $[\text{C}_4\text{C}_1\text{Pip}][\text{NTf}_2]$ with ethanol (empty markers), $[\text{C}_4\text{C}_1\text{Pip}][\text{NTf}_2]$ with 1-propanol (filled markers); (b) $[\text{C}_6\text{C}_1\text{Pip}][\text{NTf}_2]$ with ethanol (empty markers), $[\text{C}_6\text{C}_1\text{Pip}][\text{NTf}_2]$ with 1-propanol (filled markers). Solid lines have been designated by Redlich–Kister correlations, see eq 11 and Table 1.

chain of piperidinium cation is similar, although the differences in H^E are significantly smaller.

Finally, on the basis of Redlich–Kister correlations, infinite dilution partial enthalpies of ethanol and 1-propanol ($\bar{H}_2^{E,\infty}$) can be estimated. This quantity is calculated from an intercept of tangent line to H^E vs x_1 curve at $x_1 = 1$, namely:

$$\bar{H}_2^{E,\infty} = - \left(\frac{dH^E}{dx_1} \right)_{x_1 \rightarrow 1} = RT(A_0 - A_1 + A_2) \quad (13)$$

The obtained values of $\bar{H}_2^{E,\infty}$ are given in Table 2, where they were additionally compared with $\bar{H}_2^{E,\infty}$ obtained from gas–liquid chromatography measurements of γ_2^∞ reported previously by our group.^{36,37} It is seen that the values measured with completely different methods are in excellent agreement. This comparison proves thermodynamic consistency of both H^E and γ_2^∞ data measured in our laboratory.

Modeling. The PC-SAFT model parameters of pure ILs and alcohols are given in Table 3. The calculations for mixtures were performed by means of two methodologies. First, the model was used in a entirely predictive manner, namely, the ‘uncorrected’ combining rules, see eqs 3 and 4, were employed.

Table 1. Results of the Experimental Excess Enthalpy (H^E) Data Reduction by Using Redlich–Kister Correlation, See Eq 11

ionic liquid (1)	alcohol (2)	A_0	A_1	A_2	N^a	$\sigma(H^E/RT)^b$	$\sigma(H^E)^b$ ($\text{J} \cdot \text{mol}^{-1}$)
$[\text{C}_4\text{C}_1\text{Pip}][\text{NTf}_2]$	ethanol	3.4873	0.6526	0.0698	38	0.0131	32.4
$[\text{C}_4\text{C}_1\text{Pip}][\text{NTf}_2]$	1-propanol	3.6180	0.8104	0.4637	41	0.0132	32.8
$[\text{C}_6\text{C}_1\text{Pip}][\text{NTf}_2]$	ethanol	3.3422	0.6226	0.1883	75	0.0155	38.5
$[\text{C}_6\text{C}_1\text{Pip}][\text{NTf}_2]$	1-propanol	3.6615	0.6993	0.1805	75	0.0132	32.8

^aNumber of experimental data points. ^bDefined in eq 12.

Table 2. Comparison of Infinite Dilution Partial Excess Enthalpies of Alcohol ($\bar{H}_2^{\text{E},\infty}$) Determined from Excess Enthalpies Measured in This Work and Limiting Activity Coefficients of Alcohols in ILs (γ_2^∞) Measured with Gas-Liquid Chromatography (GLC)

solvent (1)	solute (2)	$\bar{H}_2^{\text{E},\infty}$ (kJ·mol ⁻¹)	
		H^{E} (this work)	γ_2^∞ (GLC) ^{36,37}
[C ₄ C ₁ Pip][NTf ₂]	ethanol	7.20	7.87
[C ₄ C ₁ Pip][NTf ₂]	1-propanol	8.11	8.04
[C ₆ C ₁ Pip][NTf ₂]	ethanol	7.21	7.81
[C ₆ C ₁ Pip][NTf ₂]	1-propanol	7.79	7.87

Table 3. PC-SAFT Parameters for the Ionic Liquids and Alcohols Considered in the Present Study

compound	m	σ (Å)	u/k_{B} (K)	$\varepsilon^{\text{AB}}/k_{\text{B}}$ (K)	κ^{AB}
[C ₄ C ₁ Pip][NTf ₂] ^a	9.1307	3.7414	233.190	1912.1	0.05734
[C ₆ C ₁ Pip][NTf ₂] ^a	9.6893	3.8003	245.271	1912.1	0.05734
ethanol ^b	2.3827	3.1771	198.24	2653.4	0.032384
1-propanol ^b	2.9997	3.2522	233.40	2276.8	0.015268

^aPaduszyński and Domańska;²² 10-site association scheme (see details in text). ^bGross and Sadowski;⁴⁴ 2B association scheme (see details in text).

In this case H^{E} of the IL–alcohol mixtures is expressed in terms of properties of pure components only. According to the second procedure, binary correction to Wolbach–Sandler combining rule given in eq 6 (k_{12}^{WS}) was adjusted to experimental γ_2^∞ vs T data.

Results of the calculations are shown in Figure 4 for each system separately. As seen, pure PC-SAFT predictions completely disagree with the experimental H^{E} data. Further-

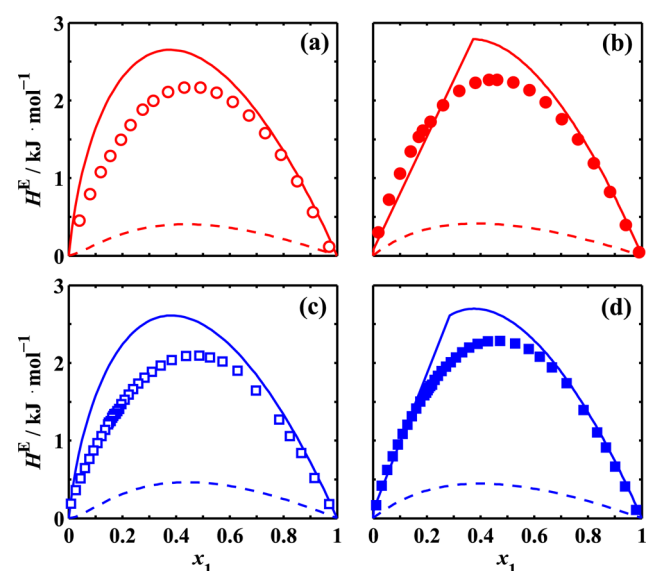


Figure 4. Experimental and predicted excess enthalpies (H^{E}) as a function of IL mole fraction (x_1): (a) [C₄C₁Pip][NTf₂] with ethanol; (b) [C₄C₁Pip][NTf₂] with 1-propanol; (c) [C₆C₁Pip][NTf₂] with ethanol; and (d) [C₆C₁Pip][NTf₂] with 1-propanol. Solid lines were designated by PC-SAFT equation of state employing binary correction k_{12}^{WS} , see eq 6, fitted to literature γ_2^∞ data. Dashed lines represent pure PC-SAFT predictions, i.e., $k_{12}^{\text{WS}} = 0$.

more, it is evidenced that incorporation of k_{12}^{WS} determined from γ_2^∞ essentially improves the representation of experimental data. The maximum on the H^{E} curve is overestimated roughly by 500 J·mol⁻¹. However, the influence of the length of alkyl chain of both piperidinium cation and alcohol is accurately captured by the model. These results confirm a good predictive capacity of the proposed methodology and extends its applications for H^{E} data for piperidinium [NTf₂]-based ILs with alcohols.

The values of k_{12}^{WS} are listed in Table 4 along with the root-mean-square deviations of predicted data. We emphasize that

Table 4. Binary Corrections to Wolbach–Sandler Combining Rules (k_{12}^{WS}) and Root Mean Square Deviations of PC-SAFT Predictions

ionic liquid (1)	alcohol (2)	k_{12}^{WS} ($T = 298.15$ K)	$\sigma(H^{\text{E}})$ (kJ·mol ⁻¹) ^a
[C ₄ C ₁ Pip][NTf ₂]	ethanol	0.09509	0.49 (1.3)
[C ₄ C ₁ Pip][NTf ₂]	1-propanol	0.11210	0.26 (1.4)
[C ₆ C ₁ Pip][NTf ₂]	ethanol	0.09652	0.59 (1.1)
[C ₆ C ₁ Pip][NTf ₂]	1-propanol	0.11450	0.28 (1.3)

^aThe values of $\sigma(H^{\text{E}})$ given in parentheses correspond to conventional PC-SAFT predictions ($k_{12}^{\text{WS}} = 0$).

the values shown correspond to constant temperature $T = 298.15$ K, while in calculations temperature-dependent k_{12}^{WS} s were adopted, see eq 9. As seen, $k_{12}^{\text{WS}} \approx +0.095$ for systems with ethanol and $k_{12}^{\text{WS}} \approx +0.11$ for systems with 1-propanol. Due to positive (and relatively high) values of k_{12}^{WS} the estimated IL–alcohol cross-interaction energy is significantly lower compared to energy obtained with Wolbach–Sandler combining rules. Unfortunately, decrease in $\varepsilon^{\text{AB}}/k_{\text{B}}$ results in prediction of liquid phase split for systems with 1-propanol. The predicted liquid–liquid equilibrium curves are shown in Figure 5. In fact,

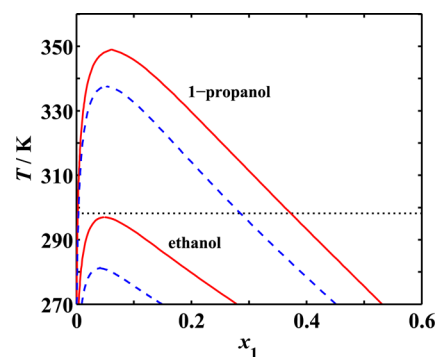


Figure 5. PC-SAFT predicted liquid–liquid equilibrium phase diagrams in the binary systems formed by [C₄C₁Pip][NTf₂] (solid lines) and [C₆C₁Pip][NTf₂] (dashed lines) with ethanol and 1-propanol. Temperature of excess enthalpy measurements ($T = 298.15$ K) is designated by dotted line.

for the systems with ethanol and 1-propanol the model predicts upper solution critical temperatures (UCST), which are lower and higher than $T = 298.15$ K, respectively. Therefore, the results as a whole may be thus viewed as disappointing. Nevertheless, in our opinion the predictions obtained should be perceived as (at least) satisfactory and promising, taking into account complexity of the systems and simplicity of the molecular schemes applied.

CONCLUSIONS

A new set of experimental data on molar excess enthalpies of mixing for binary mixtures of two piperidinium ILs ([C₄C₁Pip]⁺[NTf₂]⁻ and [C₆C₁Pip]⁺[NTf₂]⁻) with short-chain alcohols (ethanol and 1-propanol) have been presented and discussed. The excess enthalpies were measured with isothermal titration calorimetry at $T = 298.15$ K and ambient pressure. IL–alcohol cross-interactions are less preferable than the interactions between like molecules. It was evidenced by endothermic heat of mixing (a positive sign of H^E) in a full range of IL mole fractions. Moreover, H^E for systems with 1-propanol is higher than for systems with ethanol. Finally, a consistency of the measured data with previously published limiting activity coefficients was demonstrated.

The experimental data were reproduced by using PC-SAFT equation of state applied in accordance with a methodology of calculations developed and tested previously by our group.²² IL–alcohol cross-association was accounted for by Wolbach–Sandler combining rules employing binary correction fitted to limiting activity coefficients of alcohol in IL. A good predictive capacity of this approach (when compared to conventional PC-SAFT predictions) for the studied systems was demonstrated and hence, the range of its possible application is broadened. Unfortunately, for some systems, the calculations revealed liquid phase split, whereas such behavior was not evidenced by the H^E measurements. It may be related to the adopted temperature dependence of the binary corrections. The problem should be solved in further systematic investigations on application of the PC-SAFT approach to ionic liquid systems. Finally, we believe that the experimental and modeling contributions presented in this work will help the scientific community working in the field of solution thermodynamics of ILs-based system to get more physical insight into complex cross-associating IL–alcohol mixtures.

ASSOCIATED CONTENT

Supporting Information

Experimental excess enthalpies for all studied systems. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Freemantle, M. *An Introduction to Ionic Liquids*, 1st ed.; RSC Publishing: London, 2009.
- (2) Hallett, J. P.; Welton, T. Room-Temperature Ionic Liquids: Solvents for Synthesis and Catalysis. 2. *Chem. Rev.* **2011**, *111*, 3508–3576.
- (3) Opallo, M.; Leśniewski, A. A Review on Electrodes Modified with Ionic Liquids. *J. Electroanal. Chem.* **2011**, *656*, 2–16.
- (4) Koel, M., Ed. *Ionic Liquids in Chemical Analysis*; CRC Press, Taylor and Francis Group: Abingdon, UK, 2008.
- (5) Plechkova, N. V.; Seddon, K. R. Applications of Ionic Liquids in the Chemical Industry. *Chem. Soc. Rev.* **2008**, *37*, 123–150.
- (6) Roosen, C.; Müller, P.; Greiner, L. Ionic Liquids in Biotechnology: Applications and Perspectives for Biotransformations. *Appl. Microbiol. Biotechnol.* **2008**, *81*, 607–614.
- (7) Pereira, A. B.; Araújo, J. M. M.; Oliveira, F. S.; Bernandes, C. E. S.; Esperanca, J. M. S. S.; Canongia Lopes, J. N.; Marrucho, I. M.; Rebelo, L. P. N. Inorganic Salts in Purely Ionic Liquid Media: The Development of High Ionicity Ionic Liquids (HILs). *Chem. Commun.* **2012**, *48*, 3656–3658.
- (8) Zhang, X.; Zhang, X.; Dong, H.; Zhao, Z.; Zhang, S.; Huang, Y. Carbon Capture with Ionic Liquids: Overview and Progress. *Energy Environ. Sci.* **2012**, *5*, 6668–6681.
- (9) Zakrzewska, M. E.; Bogel-Lukasik, E.; Bogel-Lukasik, R. Solubility of Carbohydrates in Ionic Liquids. *Energy Fuels* **2010**, *24*, 737–745.
- (10) Conceicao, L. J. A.; Bogel-Lukasik, E.; Bogel-Lukasik, R. A New Outlook on Solubility of Carbohydrates and Sugar Alcohols in Ionic Liquids. *RSC Adv.* **2012**, 1846–1855.
- (11) Pereira, A. B.; Araújo, J. M. M.; Esperanca, J. M. S. S.; Marrucho, I. M.; Rebelo, L. P. N. Ionic Liquids in Separations of Azeotropic Systems—A Review. *J. Chem. Thermodyn.* **2012**, *46*, 2–28.
- (12) Coutinho, J. A. P.; Carvalho, P. J.; Oliveira, N. M. C. Predictive Methods for the Estimation of Thermophysical Properties of Ionic Liquids. *RSC Adv.* **2012**, *2*, 7322–7346.
- (13) Vega, L.; Vilaseca, O.; Llovel, F.; Andreu, J. Modeling Ionic Liquids and the Solubility of Gases in Them: Recent Advances and Perspectives. *Fluid Phase Equilib.* **2010**, *294*, 15–30.
- (14) Maia, F. M.; Tsivintzelis, I.; Rodriguez, O.; Macedo, E. A.; Kontogeorgis, G. M. Equation of State Modelling of Systems with Ionic Liquids: Literature Review and Application with the Cubic Plus Association (CPA) Model. *Fluid Phase Equilib.* **2012**, *332*, 128–143.
- (15) Maginn, E. Molecular Simulation of Ionic Liquids: Current Status and Future Opportunities. *J. Phys.: Condens. Matter* **2009**, *21*, 373101.
- (16) Dommert, F.; Wendler, K.; Berger, R.; Delle Site, L.; Holm, C. Force Fields for Studying the Structure and Dynamics of Ionic Liquids: A Critical Review of Recent Developments. *ChemPhysChem* **2012**, *13*, 1625–1637.
- (17) Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. New Reference Equation of State for Associating Liquids. *Ind. Eng. Chem. Res.* **1990**, *29*, 1709–1721.
- (18) Kroon, M. C.; Karakatsani, E. K.; Economou, I. G.; Witkamp, G.-J.; Peters, C. J. Modeling of the Carbon Dioxide Solubility in Imidazolium-Based Ionic Liquids with the tPC-PSAFT Equation of State. *J. Phys. Chem. B* **2006**, *110*, 9262–9269.
- (19) Karakatsani, E. K.; Economou, I. G.; Kroon, M. C.; Peters, C. J.; Witkamp, G.-J. tPC-PSAFT Modeling of Gas Solubility in Imidazolium-Based Ionic Liquids. *J. Phys. Chem. C* **2007**, *111*, 15487–15492.
- (20) Padaszyński, K.; Chiyen, J.; Ramjugernath, D.; Letcher, T.; Domańska, U. Liquid–Liquid Phase Equilibrium of (Piperidinium-Based Ionic Liquid + an Alcohol) Binary Systems and Modelling with NRHB and PCP-SAFT. *Fluid Phase Equilib.* **2011**, *305*, 43–52.
- (21) Padaszyński, K.; Domańska, U. Solubility of Aliphatic Hydrocarbons in Piperidinium Ionic Liquids: Measurements and Modeling in Terms of Perturbed-Chain Statistical Associating Fluid Theory and Nonrandom Hydrogen-Bonding Theory. *J. Phys. Chem. B* **2011**, *115*, 12537–12548.
- (22) Padaszyński, K.; Domańska, U. Thermodynamic Modeling of Ionic Liquid Systems: Development and Detailed Overview of Novel Methodology Based on the PC-SAFT. *J. Phys. Chem. B* **2012**, *116*, 5002–5018.
- (23) Domańska, U.; Zawadzki, M.; Padaszyński, K.; Królikowski, M. Perturbed-Chain SAFT as a Versatile Tool for Thermodynamic Modeling of Binary Mixtures Containing Isoquinolinium Ionic Liquids. *J. Phys. Chem. B* **2012**, *116*, 8191–8200.
- (24) Andreu, J.; Vega, L. Capturing the Solubility Behavior of CO₂ in Ionic Liquids by a Simple Model. *J. Phys. Chem. C* **2007**, *111*, 16028–16034.

- (25) Andreu, J.; Vega, L. Modeling the Solubility Behavior of CO₂, H₂, and Xe in [C_n-mim][Tf₂N] Ionic Liquids. *J. Phys. Chem. B* **2008**, *112*, 15398–15406.
- (26) Llovel, F.; Valente, E.; Vilaseca, O.; Vega, L. Modeling Complex Associating Mixtures with [C_n-mim][Tf₂N] Ionic Liquids: Predictions from the Soft-SAFT Equation. *J. Phys. Chem. B* **2011**, *115*, 4387–4398.
- (27) Llovel, F.; Marcos, R. M.; MacDowell, N.; Vega, L. F. Modeling the Absorption of Weak Electrolytes and Acid Gases with Ionic Liquids Using the Soft-SAFT Approach. *J. Phys. Chem. B* **2012**, *116*, 7709–7718.
- (28) Llovel, F.; Vilaseca, O.; Vega, L. F. Thermodynamic Modeling of Imidazolium-Based Ionic Liquids with the [PF₆][−] Anion for Separation Purposes. *Sep. Sci. Technol.* **2012**, *47*, 399–410.
- (29) Oliveira, M. B.; Llovel, F.; Coutinho, J. A. P.; Vega, L. F. Modeling the [NTf₂] Pyridinium Ionic Liquids Family and Their Mixtures with the Soft Statistical Associating Fluid Theory Equation of State. *J. Phys. Chem. B* **2012**, *116*, 9089–9100.
- (30) Oliveira, M. B.; Domínguez-Pérez, M.; Freire, M. G.; Llovel, F.; Cabeza, O.; Lopes-Da-Silva, J. A.; Vega, L. F.; Coutinho, J. A. P. Surface Tension of Binary Mixtures of 1-Alkyl-3-Methylimidazolium Bis(Trifluoromethylsulfonyl)Imide Ionic Liquids: Experimental Measurements and Soft-SAFT Modeling. *J. Phys. Chem. B* **2012**, *116*, 12133–12141.
- (31) Chen, Y.; Mutelet, F.; Jaubert, J.-N. Modeling the Solubility of Carbon Dioxide in Imidazolium-Based Ionic Liquids with the PC-SAFT Equation of State. *J. Phys. Chem. B* **2012**, *116*, 14375–14388.
- (32) Ji, X.; Held, C.; Sadowski, G. Modeling Imidazolium-Based Ionic Liquids with ePC-SAFT. *Fluid Phase Equilib.* **2012**, *335*, 64–73.
- (33) Shahriari, R.; Dehghani, M.; Behzadi, B. Thermodynamic Modeling of Aqueous Ionic Liquid Solutions Using PC-SAFT Equation of State. *Ind. Eng. Chem. Res.* **2012**, *51*, 10274–10282.
- (34) Domańska, U.; Paduszyński, K. Measurements of Activity Coefficients at Infinite Dilution of Organic Solutes and Water in 1-Propyl-1-Methylpiperidinium Bis{(Trifluoromethyl) Sulfonyl}Imide Ionic Liquid Using g.l.c. *J. Chem. Thermodyn.* **2010**, *42*, 1361–1366.
- (35) Domańska, U.; Królikowska, M.; Paduszyński, K. Physico-Chemical Properties and Phase Behaviour of Piperidinium-Based Ionic Liquids. *Fluid Phase Equilib.* **2011**, *303*, 1–9.
- (36) Paduszyński, K.; Domańska, U. Limiting Activity Coefficients and Gas-Liquid Partition Coefficients of Various Solutes in Piperidinium Ionic Liquids: Measurements and LSER Calculations. *J. Phys. Chem. B* **2011**, *115*, 8207–8215.
- (37) Paduszyński, K.; Domańska, U. Experimental and Theoretical Study on Infinite Dilution Activity Coefficients of Various Solutes in Piperidinium Ionic Liquids. *J. Chem. Thermodyn.* **2013**, *60*, 169–178.
- (38) Ortega, J. Densities and Refractive Indices of Pure Alcohols as a Function of Temperature. *J. Chem. Eng. Data* **1982**, *27*, 312–317.
- (39) Wertheim, M. S. Fluids with Highly Directional Attractive Forces. I. Statistical Thermodynamics. *J. Stat. Phys.* **1984**, *35*, 19–34.
- (40) Wertheim, M. S. Fluids with Highly Directional Attractive Forces. II. Thermodynamic Perturbation Theory and Integral Equations. *J. Stat. Phys.* **1984**, *35*, 35–47.
- (41) Wertheim, M. S. Fluids with Highly Directional Attractive Forces. III. Multiple Attraction Sites. *J. Stat. Phys.* **1986**, *42*, 459–476.
- (42) Wertheim, M. S. Fluids with Highly Directional Attractive Forces. IV. Equilibrium Polymerization. *J. Stat. Phys.* **1986**, *42*, 477–492.
- (43) Gross, J.; Sadowski, G. Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules. *Ind. Eng. Chem. Res.* **2001**, *40*, 1244–1260.
- (44) Gross, J.; Sadowski, G. Application of the Perturbed-Chain SAFT Equation of State to Associating Systems. *Ind. Eng. Chem. Res.* **2002**, *41*, 5510–5515.
- (45) Folas, G. K.; Kontogeorgis, G. M. *Thermodynamic Models for Industrial Applications: From Classical and Advanced Mixing Rules to Association Theories*; John Wiley & Sons: New York, 2010.
- (46) Rozmus, J.; de Hemptinne, J.-C.; Ferrando, N.; Mougin, P. Long Chain Multifunctional Molecules with GC-PPC-SAFT: Limits of Data and Model. *Fluid Phase Equilib.* **2012**, *329*, 78–85.
- (47) Ferrando, N.; de Hemptinne, J.; Mougin, P.; Passarello, J.-P. Prediction of the PC-SAFT Associating Parameters by Molecular Simulation. *J. Phys. Chem. B* **2012**, *116*, 367–377.
- (48) Wolbach, J.; Sandler, S. Using Molecular Orbital Calculations To Describe the Phase Behavior of Cross-Associating Mixtures. *Ind. Eng. Chem. Res.* **1998**, *37*, 2917–2928.
- (49) Weingärtner, H. Understanding Ionic Liquids at the Molecular Level: Facts, Problems, and Controversies. *Angew. Chem., Int. Ed.* **2008**, *47*, 654–670.
- (50) Huang, S. H.; Radosz, M. Equation of State for Small, Large, Polydisperse, and Associating Molecules. *Ind. Eng. Chem. Res.* **1990**, *29*, 2284–2294.
- (51) Nebig, S.; Bölts, R.; Gmehling, J. Measurement of Vapor–liquid Equilibria (VLE) and Excess Enthalpies (H^E) of Binary Systems with 1-Alkyl-3-Methylimidazolium Bis(Trifluoromethylsulfonyl)Imide and Prediction of These Properties and γ^∞ Using Modified UNIFAC (Dortmund). *Fluid Phase Equilib.* **2007**, *258*, 168–178.
- (52) Hector, T.; Uhlig, L.; Gmehling, J. Prediction of Different Thermodynamic Properties for Systems of Alcohols and Sulfate-Based Anion Ionic Liquids Using Modified UNIFAC. *Fluid Phase Equilib.* **2013**, *338*, 135–140.