

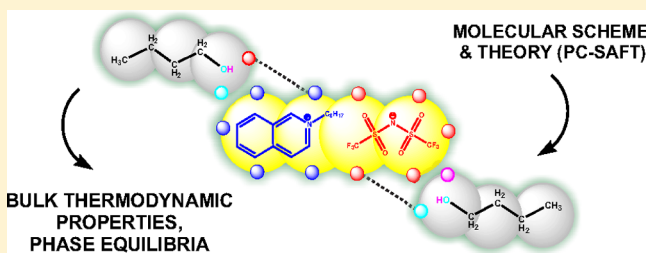
Perturbed-Chain SAFT as a Versatile Tool for Thermodynamic Modeling of Binary Mixtures Containing Isoquinolinium Ionic Liquids

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Supporting Information

ABSTRACT: This contribution reports a recapitulation of our experimental and modeling study on thermodynamic behavior of binary systems containing *N*-alkylisoquinolinium ionic liquids (ILs) based on bis(trifluoromethylsulfonyl)imide anion, $[C_n\text{iQuin}][\text{NTf}_2]$ ($n = 4, 6, 8$). In particular, we report isothermal vapor–liquid equilibrium (VLE) phase diagrams and molar excess enthalpies of mixing (H^E) for binary mixtures of $[C_8\text{iQuin}][\text{NTf}_2]$ IL with various organic solutes including benzene, toluene, thiophene, pyridine, and butan-1-ol. The measured VLE data represented simple homozeotropic behavior with either negative or positive deviations from ideality, depending on polarity of the solute, temperature, and mole fraction of IL. In turn, the obtained data on H^E were negative and positive for the mixtures containing aromatic hydrocarbons or thiophene and butan-1-ol, respectively, in the whole range of IL's concentration. All of the measured and some previously published data regarding phase behavior of $[C_8\text{iQuin}][\text{NTf}_2]$ IL were analyzed and successfully described in terms of perturbed-chain statistical associating fluid theory (PC-SAFT). The methodology used in this work was described by us previously. In general, the proposed modeling results in VLE diagrams, which are in excellent agreement with experimental data. In the case of H^E , the results obtained are good as well but not so satisfactory such as those for VLE. Nevertheless, they seem to be very promising if one take into account the simplicity of the utilized molecular model against significant complexity of IL-based systems. Thus, we concluded that PC-SAFT equation of state can be viewed as a powerful and robust tool for modeling of systems involving ILs.



INTRODUCTION

Ionic liquids (ILs) with their unique physicochemical properties have opened new frontiers in material sciences and new technologies, including synthesis and catalysis, analytical chemistry and separations.^{1–3} In particular, ILs have received increasing interest in recent years as selective solvents in separation processes such as aromatic/aliphatic hydrocarbons,^{4,5} sulfur compounds/alkanes,^{6,7} butan-1-ol/water,^{8,9} or in biosynthesis for 2-phenylethanol/water separation.¹⁰ In particular, the quinolinium-based ILs were showed earlier as good entrainers in the desulfurization of oils,¹¹ in the 1-hexene/*n*-hexane separation,¹² and in extraction of 2-phenylethanol from aqueous medium during the biosynthesis.¹³ It obviously makes those ILs interesting for new technologies employing liquid–liquid extraction.

In our recent contributions, we reported the phase equilibria diagrams, volumetric and transport properties, and activity coefficients at infinite dilution of diverse organic solutes for *N*-alkylisoquinolinium bis(trifluoromethylsulfonyl)imides homologous series (abbreviated in this work by $[C_n\text{iQuin}][\text{NTf}_2]$, where $C_n \equiv C_nH_{2n+1}$ and $n = 4, 6$, and 8).^{13–17} It was demonstrated that only $[C_8\text{iQuin}][\text{NTf}_2]$ IL forms liquid phase at room temperature and shows lower selectivity for different separation problems than other ILs with the same $[\text{NTf}_2]$ -anion

and different cations (with the exception of 2-phenylethanol/water separation problem).^{18,19} Furthermore, the larger capacity of $[C_8\text{iQuin}][\text{NTf}_2]$ IL in comparison with $[\text{NTf}_2]$ -based ILs was observed.¹⁴ Finally, we established that the solubility of isoquinolinium cation-based ILs in alcohols depends on the carbon chain length of an alcohol and the ILs $[C_4\text{iQuin}][\text{NTf}_2]$ and $[C_6\text{iQuin}][\text{NTf}_2]$ show complete miscibility in the liquid phase only with butan-1-ol.^{15,16}

A reliable knowledge of the phase equilibrium behavior, as vapor–liquid phase equilibrium (VLE), liquid–liquid equilibrium (LLE), or solid–liquid equilibrium (SLE), or excess enthalpy of mixing (H^E) is fundamental for the ILs to be effectively used as selective solvents in separation processes. Therefore, an accurate experimental data and tools for their modeling are crucial from the point of view of design and optimization of clean and sustainable technologies. Thus far, several approaches (including theoretical methodologies adopting equation of state²⁰ or quantum mechanics^{21,21} and empirical group contribution methods²²) have been used for the description of phase equilibria and volumetric/caloric

Received: April 25, 2012

Revised: June 19, 2012

Published: June 20, 2012

properties of ILs-based systems.^{23,24} In particular, predictions of diverse properties of ILs and their mixtures (density, gas solubility, VLE/LLE/SLE, H^E) with different versions of statistical associating fluid theory (SAFT) was successfully carried out and reported.^{20,25–28} Nevertheless, it should be stressed that the idea of modeling of such systems with SAFT may be perceived as controversial issue, mainly due to ambiguity of molecular scheme used to describe molecular characteristics and chemical nature of pure ILs. Moreover, in most cases, the parametrization of SAFT-based theories for ILs employs only volumetric data. Of course, the latter shortcoming follows from still scarce experimental data on vapor pressure of pure ILs.

We do not intend to provide here a detailed review of the state of the art of SAFT modeling of systems formed by ILs and/or molecular solvents. A brief overview can be found elsewhere, e.g., in our previous contributions^{25,26} or in the general review of Vega et al.²⁴ Nevertheless, we believe that there have been some new contributions worth to be mentioned in this summary.

Very recently, Paduszyński and Domańska reported a novel methodology of SAFT modeling of systems containing $[\text{NTf}_2]$ -based ILs, including those composed of imidazolium, pyridinium, pyrrolidinium, and piperidinium cations.²⁰ The method incorporates a combination of perturbed-chain SAFT (PC-SAFT) of Gross and Sadowski^{29,30} with the modified UNIFAC (Dortmund) of Gmehling et al.^{31–33} PC-SAFT was used to describe free energy of mixture, while the UNIFAC served as a tool for determination of limiting activity coefficients of molecular solutes in ILs (γ^∞), which were transformed into binary interaction parameters for the corresponding combining rules. The reliability and versatility of the method was demonstrated for a large number of systems (including mixtures with nonpolar, polar, and self-associating compounds) and thermodynamic properties (density, vapor pressure, surface tension, critical properties, VLE/LLE/SLE, H^E). In turn, solubility of CO_2 and CHF_3 in some imidazolium ILs was modeled by Alvarez and Saldaña.³⁴ The authors applied PC-SAFT coupled with artificial neural network (ANN) and COSMO-SAC approaches. The methodology was somewhat similar to that proposed by Paduszyński and Domańska, as it adopts γ^∞ data for determination of binary interaction parameters. A model to predict γ^∞ of molecular solutes in ILs or common liquid solvents was developed using an ANN with parameters of the COSMO-SAC model as inputs. The solubility of other gases (CO , H_2 , H_2S) in ILs has been also investigated by means of different SAFT approaches, including homonuclear SAFT models (PC-SAFT/SAFT-VR³⁵ and soft-SAFT²⁸) and those based on heteronuclear-group contribution models, e.g., SAFT- γ ,³⁶ heterosegmented SAFT (hs-SAFT).³⁷ Finally, the PC-SAFT have been recently applied to model density over wide pressure range and VLE phase behavior for binary system of 1-butyl-3-methylimidazolium tetrafluoroborate with 2,2,2-trifluoroethanol.³⁸ Pure fluid model parameters were obtained from atmospheric pressure density and then high pressure densities and VLE in binary systems was predicted. Satisfactory results were obtained only when binary interaction parameter for cross-dispersive interactions was provided.

There are the two main goals of this work. The first one is to assess the suitability of $[\text{C}_8\text{iQuin}][\text{NTf}_2]$ for use in solvent-enhanced separation processes by VLE and H^E measurements of this IL in binary systems with benzene, toluene, thiophene, pyridine and butan-1-ol. Afterward, the PC-SAFT equation of state capability of predicting thermodynamic phase behavior of

the studied binary systems is demonstrated and hence, the method proposed and developed by us previously²⁰ is extended to isoquinolinium $[\text{NTf}_2]$ -based ILs. Molecular model of IL adopted in the modeling is based on 10-site associating scheme proposed originally by Tsiptsias et al.³⁹ It has been already shown that this molecular picture mimics essential features of ILs and allows accurate correlations of temperature–pressure dependence of density and Hildebrand's solubility parameter simultaneously.^{25,26,39}

EXPERIMENTAL PROCEDURES

Materials. Synthesis of the IL *N*-octylisoquinolinium bis(trifluoromethylsulfonyl)imide, $[\text{C}_8\text{iQuin}][\text{NTf}_2]$, used the accepted technique of first preparing the halide salt of the appropriate cation followed by anion metathesis. Details for synthesis and purity were described in our previous work.¹⁴ The chemical structure of the investigated isoquinolinium series is presented in Figure 1. The IL was further purified by

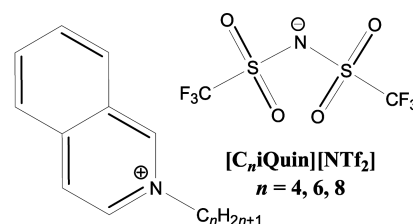


Figure 1. Chemical structure of *N*-alkylisoquinolinium bis(trifluoromethylsulfonyl)imide ionic liquids.

subjecting the liquid to a very low pressure of about 5×10^{-3} Pa at a temperature about 353 K for approximately 24 h. This procedure removed any volatile chemicals and water from the IL.

The other chemicals used were purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany. CAS registry numbers and mass fraction purities were as follows: benzene (71-43-2, >0.999), toluene (108-88-3, >0.997), thiophene (110-02-1, >0.99), pyridine (110-86-1, >0.999), and butan-1-ol (64-17-5, >0.999). All solvents were fractionally distilled over different drying reagents to mass fraction purity better than 0.998 and were stored over freshly activated molecular sieves of type 4A (Union Carbide). All compounds were checked by GLC analysis and Karl Fischer (KF) titration. No significant impurities were found. KF analysis showed that the water mass fraction in the IL were below 230×10^{-6} .

Vapor–Liquid Phase Equilibria (VLE) Apparatus and Measurements. The VLE was determined by an ebulliometric method, which reports, at constant temperature (T), the vapor pressure (P) as a function of the liquid-phase IL mole fraction (x_1) and the vapor-phase IL mole fraction (y_1). Of course, the vapor phase is composed only of molecular solvent in the studied systems. This is due to extremely low volatility of the IL. Indeed, it was checked that there were no measurable amounts of IL in the liquefied vapor phase samples and hence, $y_1 = 0$. The ebulliometer, designed by Rogalski and Malanowski, was used as described earlier.^{19,40,41} The modified Świątosławski ebulliometer was connected to the pressure stabilizing system consisting of the thermostatted container with volume of 50 L, enabling the pressure to be kept constant within ± 0.1 kPa and to dampen the pressure fluctuations caused by the bumping of the liquid boiling in ebulliometer or by the

variation of the temperature of the surroundings. Samples of the liquid were transferred from the ebulliometric still to evacuated ampules equipped with a needle and vacuum tight valve. The pressure was measured with tensiometric vacuum meter type CL 300 (ZEPWN, Poland) with the precision of ± 0.1 kPa. The equilibrium temperature was measured with a resistance thermometer, type P-550, produced by ROTH, Germany. The precision of the temperature measurements was ± 0.01 K and the reproducibility was ± 0.1 K. The composition of the liquid was determined by a densimeter (Anton Paar GmbH 4500 vibration-tube densimeter), with an accuracy of density of $\pm 10^{-5}$ g·cm $^{-3}$ at $T = 298.15 \pm 0.01$ K. A calibration curve of density vs mole fraction of IL was made for each system, and the uncertainty in the mole fraction composition was better than ± 0.0005 . The uncertainty of the method used for the VLE estimation is larger than the instruments error and was estimated as ± 0.5 kPa.

Excess Enthalpy Measurements. Excess molar enthalpies of mixing (H^E) were obtained by using an isothermal titration calorimeter (ITC) TAM III (TA Instruments, U.S.A.). A schematic diagram of the calorimeter is presented in Figure 1S in the Supporting Information. The titration cell and the reference cell were placed in the test wells of the highly stable thermostatic oil bath. Before the experiment, the temperature of the oil bath was maintained at 298.15 K for 24 h with a stability of ± 100 μ K. The whole apparatus was housed in a constant temperature booth maintained at very near 298 K as well.

Measurements were started from placing about 0.5 mL of pure IL in the stainless steel ampule (titration cell), which was placed into the thermostatic oil bath and equilibrated for a few hours. Depending on the change in mole fraction of IL, $2\text{--}15 \pm 0.001$ μ L of solute was injected into the titration cell using the precise syringe pump. The mixture was rigorously stirred during the titration with stirring speed of 100 rpm. The molar amount of the injected fluid was calculated from the volume with the known density, determined by the vibrating tube densimeter described in the previous section.

The actual property measured by TAM III is the difference in heat flow between sample and reference cells. Uncertainty of this measurement is about $\pm 0.2\%$. Exemplary heat flow-time titration curve is shown in Figure 2S in the Supporting Information. Integration of the heat flow peaks results in the total amount of heat effect during the j th injection, δq_j . This quantity is readily transformed into total molar excess enthalpy of mixing corresponding to i injections (H_i^E)

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

where n_1 is the number of moles of IL and $\Delta n_{2,j}$ stands for the number of moles of solvent injected during j th titration.

The uncertainty of the H^E data determined in the present study is estimated to be less than 0.5%. To verify the reliability of measurements, H^E for two reference systems, methanol with water and cyclohexane with *n*-hexane, were measured at $T = 298.15$ K. Those systems exhibit negative (exothermic) and positive (endothermic) heat effects of mixing, respectively. Figure 3S in the Supporting Information summarizes a comparison of experimental results obtained in this work with ITC TAM III calorimeter with literature values.

Activity Coefficients at Infinite Dilution Measurements. Limiting activity coefficients of various organic solutes

or water (2) in [C $_8$ iQuin][NTf $_2$] (1) (i.e., γ_2^∞) have been already measured by gas–liquid chromatography (GLC) and reported by us previously.¹⁴ In this work, we complement those data by the measurements of γ_2^∞ of pyridine in the studied IL. A comprehensive description of the experimental procedures can be found elsewhere.⁴² In particular, the equation developed by Everett and Cruickshank et al.^{43,44} was used once again to transform retention data (net retention volume) into γ_2^∞ . The overall error in γ_2^∞ was estimated to be less than 3%, taking into account the possible uncertainties in determining the chromatographic column loading, the retention times and solute properties (e.g., vapor pressure and liquid density). The reliability of GLC technique was confirmed for the system *n*-hexane in *n*-hexadecane at $T = 298.15$ K and the results were comparable very favorably with the respective literature values.⁴⁵

THEORETICAL BACKGROUND

Perturbed-Chain SAFT Equation of State. Statistical associating fluid theory (SAFT) was proposed and developed by Chapman et al.⁴⁶ in the beginning of the 1990s. Thus far, numerous modifications of that “SAFT-0” model have been elaborated and applied for description of thermodynamic properties of both simple and complex fluids, polymers, liquid crystals, electrolytes, and ILs.⁴⁷ In particular, perturbed-chain SAFT (PC-SAFT) of Gross and Sadowski^{29,30} has received attention because of its versatility and robustness in modeling phase behavior and/or volumetric/caloric properties demonstrated in the large number of scientific papers published up to date. Moreover, PC-SAFT equations and algorithms are nowadays implemented in many commercial process simulators and software packages such as Aspen or VLXE.

In terms of each SAFT-based model, the residual free energy of mixture (A^{res}) is defined as a series of contributions accounting for different types of structural/energetic effects. Each contribution is classified either as reference or perturbation term, as the SAFT is based on Wertheim’s thermodynamic perturbation theory.^{48–51} In PC-SAFT the major contributions to A^{res} are as follows:

$$\tilde{a}^{\text{res}} = \frac{A^{\text{res}}}{Nk_{\text{B}}T} = \tilde{a}^{\text{hc}} + \tilde{a}^{\text{disp}} + \tilde{a}^{\text{assoc}} + \dots \quad (2)$$

where N stands for the number of molecules, T is the system temperature, and k_{B} denotes the Boltzmann constant. In eq 2, hard-chain term (hc) serves as a reference for the perturbation expansion, whereas the remaining terms related to dispersive interactions (disp), association (assoc), and other types of molecular forces (dipole–dipole, quadrupole–quadrupole, ion–ion, polarizability, and so on) are formally the perturbations of the reference term. A general description of all of the contributions can be found elsewhere, for instance, in the recent compilation of Folas and Kontogeorgis⁵² and all of the references therein. Thus, only the model-specific parameters are briefly introduced in this paper.

Each pure component is characterized by three characteristic parameters: number of tangent spherical segments forming chain (m), the temperature-independent hard-sphere segment diameter (σ), and the depth of the dispersion energy potential (u/k_{B}). In the case of systems containing self- and/or cross-associating components (e.g., alcohols, ILs, etc.), the association contribution in eq 2 becomes essential. This kind of system is additionally characterized by the presence of different types of associating sites (A, B, ...) attached to molecules of different

components. To characterize a particular AB interaction, two additional parameters (per one pair of sites) describing strength of association are introduced: the energy potential well depth ($\epsilon^{\text{AB}}/k_{\text{B}}$) and/or the volume (κ^{AB}) of association AB. A common procedure for calculating all of those parameters rests on fitting the PC-SAFT predictions to experimental temperature dependent pure substance properties such as saturated and/or compressed liquid density, vapor pressure or solubility parameter. Moreover, the parameters for weakly characterized compounds can be readily obtained by means of various group contribution methods.^{53–55}

Finally, the relevant thermodynamic properties such as total pressure (P) and fugacity coefficients of all components (φ_k) can be derived by using common thermodynamic formulas, namely

$$Z = \frac{P}{\rho k_{\text{B}} T} = 1 + \rho \left(\frac{\partial \tilde{a}^{\text{res}}}{\partial \rho} \right)_{T,x} \quad (3)$$

$$\ln \varphi_k = \tilde{a}_k^{\text{res}} + (Z - 1) - \ln Z + \left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_k} \right)_{T,\rho,x_i \neq k} - \sum_j x_j \left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_j} \right)_{T,\rho,x_i \neq j} \quad (4)$$

where the symbols ρ and x_k denote the number density of mixture and mole fraction of component k , respectively.

Molecular Models. Application of PC-SAFT for ILs. ILs are fluids exhibiting extreme complexity at microscopic level. Particularly, effects of dispersive and polar–electrostatic interactions,⁵⁶ ion pairing,^{57–60} mesoscopic segregation^{61–65} and cavity formation effects^{66,67} have essential significance in those systems. Therefore, looking for versatile tools allowing chemists and chemical engineers prediction of physical properties of ILs is very attractive due to both scientific and practical purposes, e.g., for chemical engineering applications. The models for ILs are based mainly on empirical correlations like group-contribution methods as follows from recent review of Coutinho et al.²³ Therefore, exploring other approaches still remains essential. In particular, a lot of effort has been devoted to model ILs in terms of computer simulations^{68,69} and quantum chemical calculations (like COSMO-RS^{21,70}). It was shown by Huang et al. that molecular dynamics simulations elucidate some unusual phase behavior phenomena in CO₂/IL systems.⁶⁷ However, it is quite obvious that those methods are too sophisticated to be applied for practical purposes because they require specialist software, their cost is high and, finally, they are time-consuming. In turn, the “practical” modeling tools should be thermodynamic models which are (1) computationally simple and easy-to-use, (2) flexible in terms of a variety of molecular schemes that can be incorporated, and (3) derived from statistical mechanical, theoretically sounded, model allowing to disclose various molecular characteristics. Those three major requirements are fulfilled by approaches employing equations of state belonging to SAFT family. Indeed, SAFT-based approaches seem to be very promising as evidenced by numerous papers reported in many scientific journals (for detailed list of references the reader is directed to review of Vega et al.²⁴ and introductory sections of our recent contributions^{20,26}).

Different investigations have revealed that cations and anions forming ILs are associated together, forming neutral ionic pairs or hydrogen bonding ionic clusters in the bulk liquid state.^{56–59}

In particular, delocalization of the electric charge due to the oxygen groups in [NTf₂][−] anion enhances the possibility of interaction with the surrounding cations, as well as with the associating sites of other components in a mixture.⁷¹ Therefore, the investigated IL, namely [C₈iQuin][NTf₂], is modeled as a substance composed of strongly associating chain molecules. According to the proposed model, we used an A site representing a positive group corresponding to the positive charge of the cation and its proximity and a B site representing a negative site corresponding to the delocalized charge on the anion. Each type of associating site is identically defined, but only AB interactions between different IL molecules are allowed. The strength of association is reflected by the PC-SAFT parameters ($\epsilon^{\text{AB}}/k_{\text{B}}$ and κ^{AB}) and the number of associating sites per molecule. In this paper, the 10-site association scheme by Tsiopoulos et al.³⁹ was adopted following our previous investigations on PC-SAFT modeling of ILs-based system.^{25,26,20} This molecular scheme was selected because of its good performance compared with other models proposed in literature.^{27,28} In particular, simultaneous description of density and Hildebrand’s solubility parameters of ILs was readily feasible by using this model.^{25,26}

Molecular Solvents. The respective PC-SAFT parameters for the molecular solutes used in this study were extracted from the literature.^{29,30,72–74} Let us note that for ordinary chemicals such as hydrocarbons or alcohols, assigning an appropriate molecular picture is much more easier than for ILs. In particular, for hydrocarbons and weakly polar thiophene ($\mu \approx 0.53$ D), the only parameters required are m , σ , and u/k_{B} and the only two first terms in eq 2 necessary. For butan-1-ol, the association contribution with 2B association scheme (according to the nomenclature by Huang and Radosz⁷⁵) becomes relevant. Furthermore, in some cases it is recommended to model strongly polar compounds as built of self-associating molecules.⁷⁶ Therefore, the presence of two associating sites is assumed for pyridine ($\mu \approx 2.2$ D) and 2B scheme is assigned as for butan-1-ol. Finally, a 4-site 4C model was employed for water and the respective parameters were taken from Grenner et al.⁷⁴

Combining Rules and Application of γ_2^∞ Data. To model binary mixtures, the parameters corresponding to cross-dispersion and/or cross-association are required. The cross-dispersive energy between segments constituting [C₈iQuin]–[NTf₂][−] IL and molecular solvent (denoted by 1 and 2, respectively) can be approximated by using conventional quadratic combining rules of Lorentz–Berthelot:

$$u_{12} = \sqrt{u_1 u_2} (1 - k_{12}^{\text{LB}}) \quad \sigma_{12} = \frac{\sigma_1 + \sigma_2}{2} \quad (5)$$

For a cross-associating system such as [C₈iQuin][NTf₂][−] with butan-1-ol, the parameters for cross-association between sites A and B attached to molecules of distinct components 1 and 2 can be calculated with the relations proposed by Wolbach and Sandler,⁷⁷ as in the original PC-SAFT formulation by Gross and Sadowski³⁰

$$\epsilon^{\text{A}_1\text{B}_2} = \frac{\epsilon^{\text{A}_1\text{B}_1} + \epsilon^{\text{A}_2\text{B}_2}}{2} (1 - k_{12}^{\text{WS}}),$$

$$\kappa^{\text{A}_1\text{B}_2} = \sqrt{\kappa^{\text{A}_1\text{B}_1} \kappa^{\text{A}_2\text{B}_2}} \left(\frac{2\sqrt{\sigma_1 \sigma_2}}{\sigma_1 + \sigma_2} \right)^3 \quad (6)$$

The binary interaction parameters k_{12}^X ($X = \text{LB}$ or WS) appearing in eqs 5 and 6 are usually obtained from the binary phase equilibrium data by means of fitting.²⁵ In this work we follow the methodology employed by us previously.^{26,20} It rests on utilization of experimental activity coefficients of molecular solvent at infinite dilution in IL (γ_2^∞). The advantage of such way of modeling is that γ_2^∞ values are more easily accessible (mainly by GLC measurements) than other bulk phase equilibrium properties of ILs-based systems, e.g., VLE or H^E . The determination of k_{12}^X is based on iterative solving of the following equation (at defined temperature):

$$\Phi(k_{12}^X) = \varphi_2^{L,\infty}(k_{12}^X)/\varphi_2^{L,0} - \gamma_2^\infty = 0 \quad (7)$$

where $\varphi_2^{L,\infty}$ and $\varphi_2^{L,0}$ denote liquid phase fugacity coefficients of 2 at infinite dilution in 1 and in pure state, respectively. The fugacity coefficients are calculated from eq 4. In turn, X is set as LB or WS, depending on the type of molecular solute 2. For nonassociating and self-associating compounds $X = \text{LB}$ (and $k_{12}^{\text{WS}} = 0$) and $X = \text{WS}$ (and $k_{12}^{\text{LB}} = 0$), respectively. Finally, it is assumed that k_{12}^X is a function of temperature and follows experimental temperature dependence of γ_2^∞ , approximated by

$$\ln \gamma_2^\infty = -\frac{\Delta S_2^{E,\infty}}{R} + \frac{\Delta H_2^{E,\infty}}{RT} \quad (8)$$

Of course, eq 8 is implied by Gibbs–Helmholtz equation, $(\partial \ln \gamma_2^\infty / \partial T^{-1})_P = \Delta H_2^{E,\infty} / R$, and $\Delta H_2^{E,\infty}$ and $\Delta S_2^{E,\infty}$ stand for average

infinite dilution partial excess thermodynamic functions. Those quantities can be readily obtained from linear regression of $\ln \gamma_2^\infty$ as a function of $1/T$.

In present study, we used the experimental γ_2^∞ for benzene, toluene, thiophene and butan-1-ol measured by Domańska et al.¹⁴ Those data were complemented in this work by GLC measurements of γ_2^∞ for pyridine over the range of temperature at which VLE data were reported.

Summing up, the measured γ_2^∞ data were regressed with eq 8 and the resulting correlations were utilized in k_{12}^X determinations in terms of eq 7.

RESULTS AND DISCUSSION

In the following section we will discuss and analyze the new experimental data measured and PC-SAFT calculations carried out for a series of pure *N*-alkylisoquinolinium [NTf₂]-based ILs and all of the investigated binary systems formed by [C₈iQuin][NTf₂] and benzene, toluene, thiophene, pyridine, or butan-1-ol. Additionally, we present LLE calculations for some binary systems published previously.¹³ The mixtures containing [C₄iQuin][NTf₂] and [C₆iQuin][NTf₂] will not be discussed here although they were comprehensively reported in our recent contribution.^{15,16} This is due to the lack of experimental data on γ_2^∞ for those ILs. Characterization of the isoquinolinium series, including temperature-dependent ambient pressure densities^{15–17} and solubility parameters,⁷⁸ is summarized in Figure 2.

VLE, H^E , and γ_2^∞ Measurements. Although numerous measurements of VLE and H^E for ILs systems have been reported in literature so far (particularly significant are contributions by the research groups of Gmehling^{79–81} and Heintz^{82,83}), this is the very first time when VLE and H^E were measured for isoquinolinium ILs. Detailed tables listing all the experimental data points measured in this work (vapor pressures for the studied mixtures against temperature and their composition, excess enthalpies of mixing at $T = 298.15$ K and ambient pressure and γ_2^∞ for pyridine in [C₈iQuin][NTf₂]) are provided in Supporting Information, Tables 1S–7S. Representative results are shown in Figures 3 and 4 and discussed below.

Isothermal VLE phase diagrams for binary systems containing [C₈iQuin][NTf₂] IL and benzene, toluene, and thiophene at different temperatures are presented in Figure 3a. One could see that all of those binaries exhibit positive deviations from Raoult's law in the range of IL mole fraction covered by experimental data. However, one may expect that the negative deviations can be observed in more concentrated

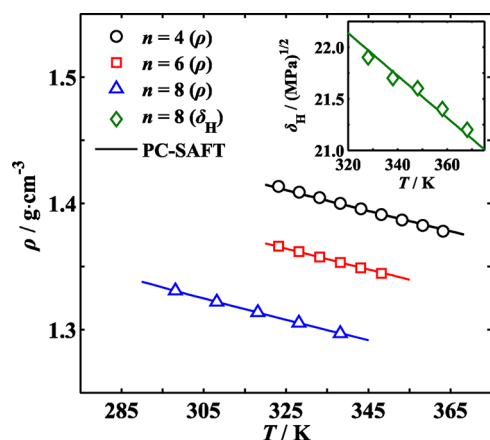


Figure 2. Experimental (points) and PC-SAFT calculated (lines) densities (ρ) and Hildebrand's solubility parameters (δ_H) vs temperature (T) for [C_{*n*}iQuin][NTf₂] series ($n = 4, 6$, and 8).

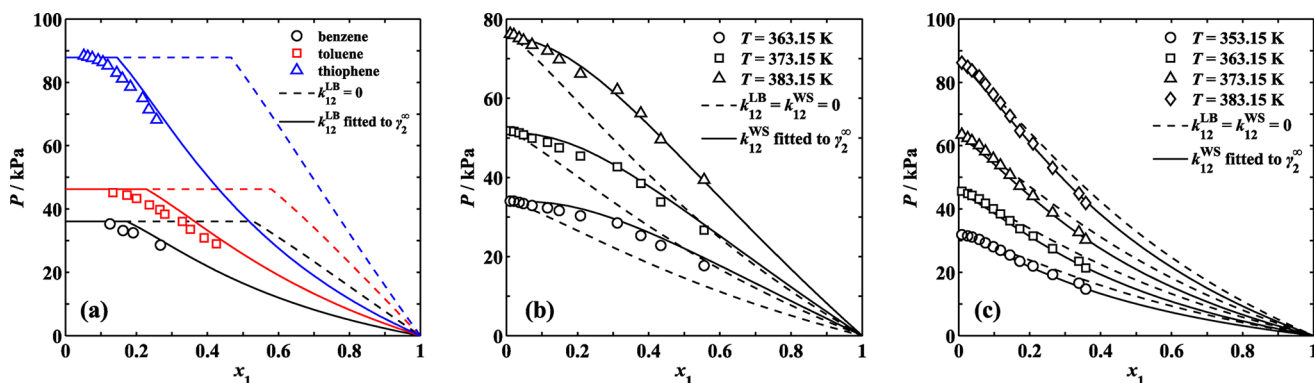


Figure 3. Experimental (points) and PC-SAFT calculated (lines) vapor pressure (P) vs IL mole fraction (x_1) for binary mixtures of [C₈iQuin][NTf₂] (1) with molecular solvent (2): (a) benzene (at $T = 323.15$ K), toluene (at $T = 358.15$ K), and thiophene (at $T = 353.15$ K); (b) butan-1-ol; and (c) pyridine.

IL solutions ($x_1 \rightarrow 1$), as it was proved and discussed by Verevkin et al.⁸² and Nebig and Gmehling³³ for imidazolium and pyrrolidinium [NTf₂]-based ILs, respectively. In the case of mixtures of [C₈iQuin][NTf₂] with benzene or toluene, liquid phase splitting occurs at mole fraction $x_1 \approx 0.20$. Indeed, liquid–liquid equilibrium (LLE) in those systems was captured in independent measurements and reported in our previous contribution.¹⁷ In Figure 3, panels b and c, experimental VLE

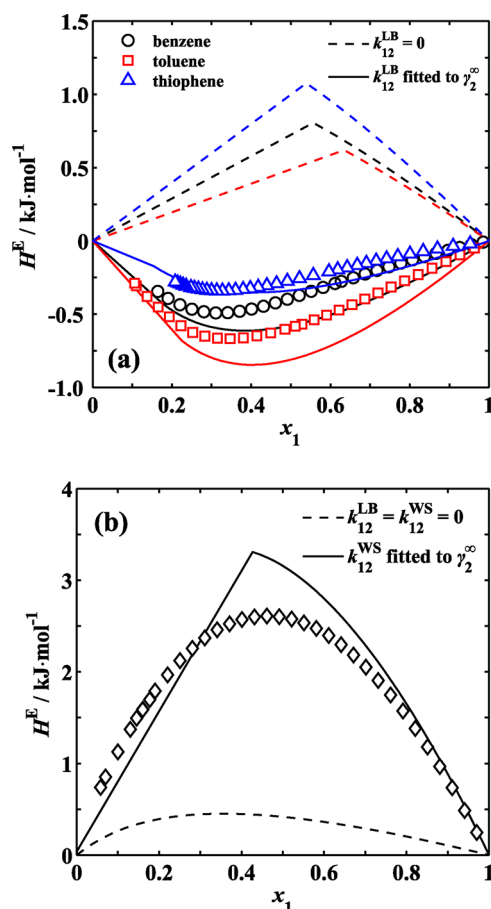


Figure 4. Experimental (points) and PC-SAFT calculated (lines) excess enthalpies of mixing (H^E) vs IL mole fraction (x_1) for binary mixtures of [C₈iQuin][NTf₂] with molecular solvent at $T = 298.15$ K: (a) benzene, toluene, and thiophene; (b) butan-1-ol.

data are summarized for binary systems [C₈iQuin][NTf₂] with butan-1-ol and pyridine, respectively, at four different temperatures. Positive (butan-1-ol) and negative (pyridine) deviations from ideal behavior were observed over the whole range of IL mole fraction. Eventually, it should be noted that the results obtained are similar to those published previously for analogous systems composed of imidazolium^{79,80,82} or pyrrolidinium⁸¹ ILs.

Excess enthalpies of mixing of [C₈iQuin][NTf₂] with benzene, toluene and thiophene at $T = 298.15$ K are shown in Figure 4(a). One can easily see that the values of H^E are negative for all three solvents in the whole range of concentration (exothermic effect). It means that interactions between unlike molecules are preferable over IL–IL and solvent–solvent interactions. This leads to an increase of γ_2^∞ with increasing temperature following the Gibbs–Helmholtz equation. Indeed, the sign of the measured H^E data agrees with the sign of partial enthalpy of mixing of the solvents in [C₈iQuin][NTf₂] at infinite dilution ($\Delta H_2^{E,\infty}$, see eq 8) measured by Domańska et al.¹⁴ with GLC.

In turn, the endothermic effect (H^E) was observed for mixing of [C₈iQuin][NTf₂] with butan-1-ol. Moreover, $\Delta H_2^{E,\infty} > 0$ was evidenced by the recent GLC measurements of γ_2^∞ .¹⁴ Hence, IL–IL interactions and hydrogen bonds between the alcohol molecules are stronger compared with IL–butan-1-ol interactions. In fact, [NTf₂]-based ILs mix with alcohols only in limited range of concentration and the width of the miscibility gap increases with an increase of the alkyl chain length of alcohol and decrease with the length of the alkyl side chain of cation.^{13,15,16,25} In this case (short-chain alcohol and long side chain of isoquinolinium cation) complete miscibility was observed.

PC-SAFT Modeling. Pure ILs. The resulting PC-SAFT parameters for [C_{*n*}iQuin][NTf₂] ILs ($n = 4, 6$, and 8) series are listed in Table 1. For [C₈iQuin][NTf₂] IL, all of the parameters were fitted simultaneously to experimental densities (ρ)¹⁷ and Hildebrand's solubility parameters (δ_H)⁷⁸ according to procedures describes in detail in our previous contribution.²⁵ Unfortunately, the number of experimental data points is limited and densities were reported only at ambient pressure. Therefore, in order to decrease the number of degrees of freedom of correlation it was assumed that the energetic parameters u/k_B , ϵ^{AB}/k_B , and κ^{AB} do not depend on the length of alkyl chain attached to the isoquinolinium cation core and only the remaining geometrical parameters m and σ were adjusted to experimental densities for [C₄iQuin][NTf₂]¹⁵ and [C₆iQuin][NTf₂].¹⁶ The results of the parametrization are

Table 1. Perturbed-Chain SAFT (PC-SAFT) Parameters of Pure Isoquinolinium Cation-Based Ionic Liquids and Investigated Molecular Compounds

compound	m	σ (Å)	u/k_B (K)	ϵ^{AB}/k_B (K)	κ^{AB}	ref ^a
Ionic Liquids ^b						
[C ₄ iQuin][NTf ₂]	9.2415	3.7611	228.181	2138.33	0.0713	Domańska et al. ¹⁵
[C ₆ iQuin][NTf ₂]	10.0233	3.7683	228.181	2138.33	0.0713	Domańska et al. ¹⁶
[C ₈ iQuin][NTf ₂]	10.7751	3.7947	228.181	2138.33	0.0713	Domańska et al.; ¹⁷ Marciniak ⁷⁸
Molecular Compounds						
benzene	2.4653	3.6478	287.35			Gross and Sadowski ²⁹
toluene	2.8149	3.7169	285.69			Gross and Sadowski ²⁹
thiophene	2.3644	3.5655	301.73			Zúñiga-Moreno et al. ⁷²
pyridine (2B) ^c	2.0352	3.8066	250.65	1890.3	0.189332	Van Niekerk et al. ⁷³
butan-1-ol (2B) ^c	3.2691	3.3761	243.22	2349.91	0.00970	Grenner et al. ⁸⁴
water (4C) ^c	1.5000	2.6273	180.30	1804.22	0.0942	Grenner et al. ⁷⁴

^aReferences for experimental data used in parameter determination and literature PC-SAFT parameters determined by other authors are given for ILs and molecular compounds, respectively. ^bThe 10-site associations scheme adopted (see details in text). ^cAssociation schemes (given in parentheses) according to Huang-Radosz nomenclature.⁷⁵

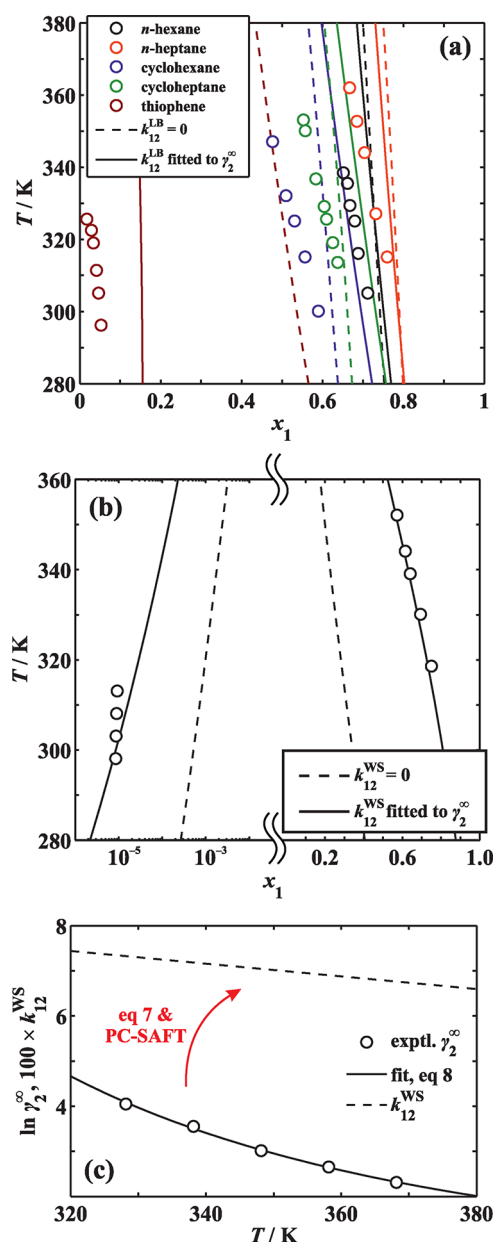


Figure 5. Experimental¹³ (points) and PC-SAFT calculated (lines) liquid–liquid equilibrium temperature (LLE) vs IL mole fraction (x_1) for binary mixtures of $[C_8iQuin][NTf_2]$ (1) with molecular solvent (2): (a) hydrocarbons and thiophene, (b) water, and (c) binary interaction parameter k_{12}^{WS} for mixture of the IL with water as a function of temperature and respective γ_2^∞ experimental data¹⁴ utilized in its determination in terms of eq 7.

illustrated in Figure 2. As can be easily seen, the PC-SAFT is capable of accurate description of all the pure ILs data, including ρ and δ_H . Average absolute relative deviation (%AARD)

$$\%AARD = \frac{1}{N} \sum_i \left| \frac{X_i^{\text{calcd}} - X_i^{\text{exptl}}}{X_i^{\text{exptl}}} \right| \times 100\% \quad (9)$$

of density ($X = \rho$) was 0.06%, 0.02% and 0.01% for $[C_niQuin][NTf_2]$ with $n = 4, 6$, and 8 , respectively, while % AARD of solubility parameter ($X = \delta_H$) of $[C_8iQuin][NTf_2]$ was 0.25%. Moreover, the obtained set of parameters is well-behaved since linear dependence of m and the “combined” PC-SAFT

parameters $\pi m \sigma^3/6$ (hard-core volume) and mu/k_B (dispersive energy per molecule) on molecular weight was observed.

Binary Mixtures. The γ_2^∞ -supported calculations compared with conventional PC-SAFT predictions ($k_{12}^X = 0$) and reported experimental data are demonstrated in Figures 3 and 4. The results of LLE modeling in binary mixtures of $[C_8iQuin][NTf_2]$ with *n*-hexane, *n*-heptane, cyclohexane, cycloheptane, and thiophene are shown in Figure 5 and compared with respective experimental data measured previously.¹³ A detailed list of the k_{12}^X values and %AARD of vapor pressure, H^E , and LLE composition (x_1) is summarized in Table 2.

Based on the results obtained, we can observe that adjusting k_{12}^X to γ_2^∞ gives excellent predictions of VLE over wide range of mixture's composition and temperature, including liquid–liquid phase splitting, see Figure 3a. Moreover, the γ_2^∞ -based predictions are substantially improved in comparison with those obtained with uncorrected combining rules given in eqs 5 and 6. Overall %AARD of vapor pressure obtained by those two approaches are respectively 3.9% and 11.1%. In particular, positive deviations from Raoult's law evidenced experimentally for system of $[C_8iQuin][NTf_2]$ with butan-1-ol are accurately captured by PC-SAFT, while assuming $k_{12}^{WS} = 0$ results in the negative deviations, see Figure 3b. On the other hand, the outcomes of both conventional and γ_2^∞ -based PC-SAFT modeling of VLE for mixtures of $[C_8iQuin][NTf_2]$ with pyridine are in good agreement with the measured vapor pressures, see Figure 3c. However, slight improvement in %AARD (about 2%; see Table 2) is evident when infinite dilution data are adopted in the calculations.

The H^E modeling results are presented in Figure 4. In particular, the results for binary systems of the studied IL with benzene, toluene, thiophene are shown in Figure 4a and for binary system with butan-1-ol in Figure 4b.

One could see that the conventional predictions with PC-SAFT are not in qualitative agreement with experimental data at all, whereas γ_2^∞ -based calculations reproduce experimental data at least semiquantitatively. However, the accuracy is still not satisfactory. Of course, the discrepancies are related to the difference in limiting partial enthalpy of mixing ($\Delta H_2^{E,\infty}$) derived either from the presented H^E data or γ_2^∞ measurements.¹⁴ The first quantity can be calculated as an intercept (i.e., the value for $x_1 = 0$) of tangent line to $x_1 - H^E$ graph at $x_1 = 1$, whereas the latter one is the slope of $\ln \gamma_2^\infty$ against $1/T$. Let us remind that the binary interaction parameters k_{12}^{LB} were adjusted to the γ_2^∞ data and thus, the PC-SAFT calculated value of $\Delta H_2^{E,\infty}$ is always equal to the latter.

In spite of a broad miscibility gap predicted by PC-SAFT for the system $[C_8iQuin][NTf_2]$ with butan-1-ol, the %AARD is low compared with pure predictions (15.7 and 82.6%, respectively). Besides, the symmetric shape and order of magnitude of H^E (including $\Delta H_2^{E,\infty}$) are correctly captured by the model. This makes the results obtained very promising in the context of future applications for other similar systems.

In Figure 5a, experimental¹³ and PC-SAFT calculated LLE phase diagrams for four binary mixtures with alkanes, cycloalkanes and thiophene are shown. As can be seen, both conventional and γ_2^∞ -based predictions provide qualitatively correct results. The effects of hydrocarbon structure (alkyl chain length of alkane and switching its structure from linear to cyclic) on phase equilibria are captured by the PC-SAFT. Unfortunately, accuracy of predictions is not satisfactory. On the other hand, the solubility of thiophene in $[C_8iQuin][NTf_2]$ predicted with k_{12}^{LB} adjusted to eq 8 is much closer to

Table 2. Summary of Vapor-Liquid Equilibrium, Excess Enthalpy of Mixing, and Liquid–Liquid Equilibrium Calculations with PC-SAFT Equation of State

solvent	X	T (K)	$k_{12}^X = 0$	k_{12}^X fitted to exptl. γ_2^∞	
			%AARD ^a	k_{12}^X	%AARD ^a
Vapor–Liquid Equilibrium (VLE)					
benzene	LB	323.15	12.0	−0.0553	6.2
		333.15	10.3	−0.0557	4.6
		343.15	9.8	−0.0561	4.1
		353.15	12.7	−0.0564	5.2
toluene	LB	348.15	26.1	−0.0503	9.6
		358.15	23.8	−0.0504	8.0
		368.15	21.8	−0.0505	6.7
		378.15	20.6	−0.0505	5.8
thiophene	LB	323.15	9.0	−0.0571	3.8
		333.15	8.6	−0.0575	3.4
		343.15	8.5	−0.0579	3.2
		353.15	8.5	−0.0583	3.0
butan-1-ol	WS	363.15	11.5	0.0748	4.2
		373.15	11.3	0.0682	2.3
		383.15	11.1	0.0609	1.3
pyridine	WS	353.15	5.0	−0.0189	3.0
		363.15	4.5	−0.0165	2.5
		373.15	3.9	−0.0141	2.0
		383.15	3.3	−0.0117	1.4
overall:			11.1		3.9
Excess Enthalpy of Mixing (H^E)					
benzene	LB	298.15	310.3	−0.0542	71.4
toluene	LB	298.15	188.4	−0.0493	37.2
thiophene	LB	298.15	439.4	−0.0561	36.1
butan-1-ol	WS	298.15	82.6	0.1050	15.7
overall:			257.0		38.7
Liquid–Liquid Equilibrium (LLE) ^b					
<i>n</i> -hexane	LB	305–338	0.05	-2×10^{-5}	0.05
<i>n</i> -heptane	LB	315–361	0.06	−0.0020	0.05
cyclohexane	LB	300–347	0.07	0.0074	0.13
cycloheptane	LB	314–353	0.04	0.0063	0.10
thiophene	LB	296–326	0.48	−0.0567	0.12
water	WS	298–352	0.23	0.0740	0.01
overall:			0.17		0.07

^a%AARD of VLE vapor pressure and H^E of mixing as defined in eq 9. For LLE compositions, average absolute deviation (AAD) of IL mole fraction (x_1) is used as a measure of prediction accuracy, $AAD = 1/N \times \sum_i |x_{1,i}^{calcd} - x_{1,i}^{exptl}|$. ^bAverage value of k_{12}^X in the temperature range given.

experimental solubility than in the case of calculations with k_{12}^{LB} set as zero.

To ultimately verify the performance of the proposed approach of equation-of-state modeling, we decided to apply it for LLE calculations in cross-associating systems. γ_2^∞ data are available only for water¹⁴ and thus, the only system possible to be modeled here was [C₈iQuin][NTf₂] with water. The results of calculations are shown in Figure 5b. Let us remind, that 4C association scheme was used for water to account for 3D structure of its molecules. In contrast to mixtures with hydrocarbons, surprisingly good results were obtained including both IL-rich and water-rich phases. The solubility of water in IL is predicted quantitatively, whereas the predicted solubility of IL in water is of the same order of magnitude as measured by Domańska et al. with UV/VIS spectrometry.¹³ The γ_2^∞ -based predictions are improved compared with conventional approach as well. As plotted in Figure 5c, the calculated binary correction to Wolbach-Sandler combining rules (k_{12}^{WS}) varies slightly with temperature. As can be seen, it is positive in the range of temperature covering LLE experimental

data. In fact, the sign of k_{12}^{WS} is consistent with LLE results: positive value of binary interaction parameter decreases cross-association energy and mutual solubility of water and IL.

Finally, we can state that the method of PC-SAFT calculations developed previously²⁰ was successfully extended for systems based on isoquinolinium [NTf₂]-based ILs.

CONCLUDING REMARKS

In summary, we presented experimental and theoretical study of some binary systems formed by [C₈iQuin][NTf₂] IL and molecular solvent. Typical results of VLE and H^E were obtained. In particular, in VLE positive deviations from Raoult's law were obtained for a mixture of [C₈iQuin][NTf₂] with butan-1-ol, hydrocarbons, and thiophene, whereas the IL–pyridine system exhibited the negative deviations. Exothermic effect of mixing (i.e., negative H^E) was observed for mixtures of [C₈iQuin][NTf₂] with hydrocarbons and thiophene, whereas it was positive for mixtures of IL with butan-1-ol.

The methodology for thermodynamic modeling based on the PC-SAFT model coupled with binary interaction parameters

(k_{12}^X) determined from γ_2^∞ data was demonstrated, and its performance was tested by applying it to reproduce the measured data.

We showed that satisfactory quality of predictions can be achieved in the case of both VLE saturation curves and H^E in the systems studied. We believe that this work will allow to get more insight into possible applications of ILs-based systems in technological processes involving phase equilibria (e.g., separations) as well as to better understand their phase behavior from the point of view of thermodynamic modeling.

■ ASSOCIATED CONTENT

■ Supporting Information

Tables listing all of the experimental data points measured in this work (vapor pressures for the studied mixtures against temperature and their composition as well as excess enthalpies of mixing at $T = 298.15$ K and ambient pressure). Schematic diagram of the isothermal titration calorimeter, exemplary power-time curve for the titration of solvent into IL, and the comparison of excess enthalpies for reference systems with literature data. 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.

■ ACKNOWLEDGMENTS

Funding for this research was provided by the National Science Centre in years 2011–2014 (Grant No. 2011/01/B/ST5/00800). M.Z., K.P., and M.K. wish to thank the support by the European Union in the framework of European Social Fund through the Warsaw University of Technology Development Programme, realized by Center for Advanced Studies.

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■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on July 6, 2012. The spelling of the first author's name was corrected, and the revised version was reposted on July 19, 2012.