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Description of the Behavior of Dichloroalkanes-Containing Solutions with Three [bXmpy][BF_4] Isomers, Using the Experimental Information of Thermodynamic Properties, ^{1}H NMR Spectral and the COSMO-RS-Methodology

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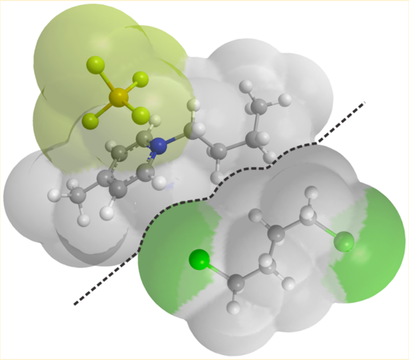
Supporting Information



ABSTRACT: This work studies the binaries of 1-butyl-*X*-methylpyridinium tetrafluoroborate [b*X*mpy][BF_4] (*X* = 2, 3, and 4) with four 1,ω-dichloroalkanes, ω = 1−4, using the results obtained for the mixing properties h^E and v^E at two temperatures. The three isomers of the ionic liquid (IL) are weakly miscible with the 1,ω-dichloroalkanes when $\omega \geq 5$ and moderately soluble for $\omega = 4$. The v^Es of all the binaries present contractive effects, $v^E < 0$, which are more pronounced with increasing temperature; the variation in v^E with ω is positive, although this changes after $\omega = 4$ due to problems of immiscibility. The energetic effects of the mixing process are exothermic in the solutions with the shorter dichloroalkanes, $\omega = 1$ and 2, and this effect increases slightly with temperature. However, mildly exothermic effects are found in the binaries with larger halides, where $(dh^E/dT) > 0$. The experimental data are correlated with a suitable equation. The study is completed with ^{1}H NMR measurements of both the pure compounds and some of the solutions, which showed minor diamagnetic shifts with increasing IL compositions, related to the anisotropy of the pyridine ring. The variation in h^E with ω for a same IL, due to an increase in the contact surfaces, is related to the reduction in polarity which, in turn, depends on the smaller chemical shifts of the pure dihalide compounds. The COSMO-RS method determines the energetic effects of the mixing process and predicts an exothermic contribution for the electrostatic Misfit-interaction which is quantitatively very similar for the three IL isomers. The differences proposed by the model are mainly reflected in the van der Waals interactions, which are exothermic and clearly influenced by the position of the methylene group in the IL. The contribution made by hydrogen bonds is negligible.

INTRODUCTION

Much emphasis has been placed by researchers on studies into ionic liquids (ILs) and their mixtures with a wide range of substances, and an increasing number of publications relate to applications for these materials. One of the most interesting of these corresponds to the use of ILs in separation processes to replace the current organic solvents, which are polluting and unselective agents, in some industrial processes.[1,2] One of the advantages of ILs is that they can help to develop clean processes, as they can be reused with minimum losses. An example of this corresponds to the use of ILs in the treatment of effluents containing substances with a high environmental impact, such as halide compounds.[3,4] Before deploying this application, previous knowledge is required of the behavior of solutions of ILs + haloalkanes.

As background to the projected research work, in previous articles[5−7] the behavior of solutions of three isomers of 1-butyl-*X*-methylpyridinium tetrafluoroborate, [b*X*mpy][BF_4] (*X* = 2, 3, and 4) with alkanols, water, and dibromide hydrocarbons[8] was analyzed. Moreover, in a recent study,[9] the liquid−liquid equilibria (LLE) of the same ILs with mono and dihalide hydrocarbons (Cl and Br) were determined. The latter was a preliminary step to the present work since it involved determination of the miscibility ranges (i.e., the area where the principles of thermodynamic of solutions are applied). Except the short-chained 1,ω-dichloroalkanes (ω = 1−3), the other dihalides showed a limited solubility with the ILs selected. Hence, the binary [b2mpy][BF_4]+1,4-dichlorobutane, with critical coordinates of $x_{IL} = 0.120$ and $T = 323.98$ K was partially miscible. The immiscibility increased with the alkyl dihalide chain length.[9]

It is difficult to interpret the behavior of solutions with ILs from the results of these studies, owing to the influence of certain structural factors. Therefore, in addition to experimentation on the macroscopic properties generated in the mixing processes, other more sensitive techniques have been employed to assess the microscopic nature, such as the analysis of the ^{1}H NMR spectra. This technique can establish the presence of hydrogen

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bonds,[10−12] hence the formation of molecular aggregates,[12,13] although the nature of the interactions of ILs pyridinium-derived have been less studied.[12−14] Here, we propose to continue the research started in previous works,[8,9] by analyzing the results of thermodynamic quantities measured for the binary systems of three IL, isomers of [b*X*mpy][BF$_4$] (X = 2, 3, and 4), with 1,ω-dichloroalkanes, Cl(CH)$_n$Cl ($\omega = n = 1{-}4$), to study the influence of the dihalide chain, on the one hand, and the position of the methyl group in the cation, [b*X*mpy]$^+$, on the other. Several articles in the literature have recorded properties of the pure compounds [b*X*mpy][BF$_4$] (X = 2, 3, and 4)[5−9,15−18] at different temperatures, but property values have not been found for the binaries [b*X*mpy][BF$_4$]+1,ω-dichloroalkanes.

Theoretical modeling is an important tool to provide additional information to help interpret the behavior of solutions. Here, the COSMO-RS methodology has been used[19] to estimate the mixing enthalpies from the structural data (obtained previously by quantum-mechanics calculations) of individual molecules. Hence, this model is recommended when further data of the systems investigated are required to complement the experimental study.[5,8,20] COSMO-RS has been used by several authors to estimate the properties of pure ILs[21,22] and the thermodynamic behavior of their solutions with a wide range of chemical compounds, including liquid−liquid equilibria (LLE),[5,8,23−27] the solubility of gases,[28,29] and activity coefficients at infinite dilution.[30−32] For this line of work, the model is especially used to estimate the mixing energies, h^E, a measurable property resulting from interactions occurring in the mixing process.[5−8] The results obtained with COSMO-RS are presented to provide information about the interactions that influence the properties of solutions of three isomers of IL [b*X*mpy][BF$_4$] (X = 2−4) with 1,ω-dichloroalkanes (ω = 1−4).

■ EXPERIMENTAL SECTION

Apparatus and Procedures. The refractive indices n_D, of the pure compounds were measured with a 320 Abbe refractometer by Zuzi, with a reading error of ±0.0002. The apparatus was thermostatized with an external circulating water bath by Haake Phenix II, with a temperature control of ±0.02 K.

Excess volumes were estimated from the density values of the pure products, and the mixtures that were determined with a DMA-58 Anton-Paar digital densimeter, with a reading error of ±0.02 kg m^{-3}. The densimeter was thermostated by a Peltier effect, and the temperature control improved further by circulating water from the aforementioned water bath at a constant temperature of $(T - 0.5)$ K, where T is the working temperature, 298.15 or 318.15 K. The apparatus was fine-tuned electronically. Binary mixtures were prepared synthetically by weighing them in airtight closed phials and placing them in an ultrasound bath for 5 min to homogenize the mixture. The error of the molar fractions in [b*X*mpy][BF$_4$], x_{IL}, was estimated to be ±0.0002.

Direct measurements of the mixing enthalpies h^E were made using a Calvet MS80D conduction calorimeter by Setaram, calibrated by applying a Joule-effect with a power source model EJ3 by Setaram, which reproduced analogous thermograms to the mixing process when different powers are applied to the calibration cell. Electrical calibration of the apparatus was checked at two working temperatures with the mixture propan-1-ol+benzene,[33] with an uncertainty of 1% for h^E. In this work, for mixtures with isomers of [b*X*mpy][BF$_4$], a special cell was used equipped with a gentle stirring mechanism, described previously,[8] that maintained a constant stirring action during the entire process. The net interaction energy is obtained from the difference between the thermogram of the process and that corresponding to the stirring, previously estimated in a pilot experience using IL.

^{1}H NMR spectra were obtained at 293.15 K in a 300 MHz spectrometer, AMX model by Bruker. The solvent, deuterated chloroform, Cl$_3$CD, was introduced into the sample tube through closed concentric capillaries, avoiding interactions between the components of the mixture and the solvent of the lock. The tetramethylsilane signal ($\delta = 0$) was used to calibrate the spectra.

Materials. The isomers of [b*X*mpy][BF$_4$] (X = 2−4) used in this work were supplied by IoLiTec (Ionic Liquid Technologies), GmbH & Co. KG, with a commercial purity of 99% and a water content <300 ppm for the isomer with X = 2 and <100 ppm for the isomers with X = 3, 4, and of the halides <100 ppm according to the manufacturer. Values provided by the manufacturer were verified by a coulometric Karl Fischer titrator C-20, from Mettler. To avoid contact with the ambient air, the IL was stored in a hermetic chamber filled with dry nitrogen gas. The 1,ω-dichloroalkanes (ω = 1−4) also were of high purity and supplied by Fluka and Aldrich. These substances were checked with a GC manufactured by Agilent, model 6890N, equipped with FID and an electron capture detector (ECD), to verify the manufacturer's values. Before preparing the samples, all products used in this work were degassed in an ultrasound bath for several hours and the dichloroalkanes stored over 0.3 nm sieve from Fluka.

Table S1 of the Supporting Information gives the experimental values for the densities and refractive indices measured at working temperatures, and comparisons were acceptable with data published in the literature.[34−39]

■ RESULTS AND DISCUSSION

Mathematical Treatment of Properties. Experimental data of the thermodynamic quantities obtained in the mixing processes for x_{IL}[b*X*mpy][BF$_4$] (X = 2−4)+(1-x_{IL})1,ω-dichloroalkanes (ω = 1−4) at temperatures of 298.15 and 318 K were correlated with a polynomial equation, frequently used by our group.[5−8] For a generic property, $y^E[h^E(\text{in J mol}^{-1}), v^E\ (\text{in m}^3\ \text{mol}^{-1})]$, it takes the form:

$$y^E = z_{IL}(1 - z_{IL}) \sum_{i=0}^{2} y_i z_{IL}^i \text{ where } z_{IL} = \frac{x_{IL}}{x_{IL} + k(T, p)(1 - x_{IL})} \quad (1)$$

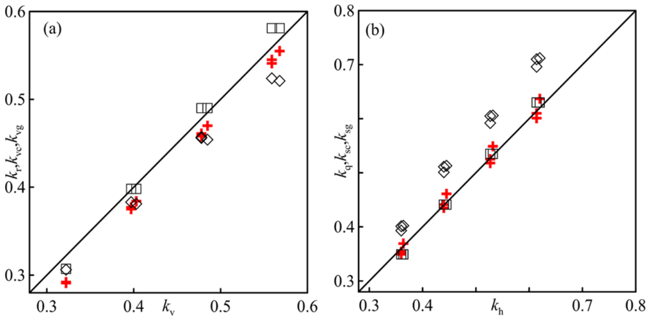

Figure 1. Comparison between different k-values (volume and surface) calculated using several procedures (a) for k_v and (b) for k_h. (□) Bondi, k_r,k_q; (red +) Connolly, k_{vc},k_{sc}; and (◇) Gaussian03, k_{vg},k_{sg}.

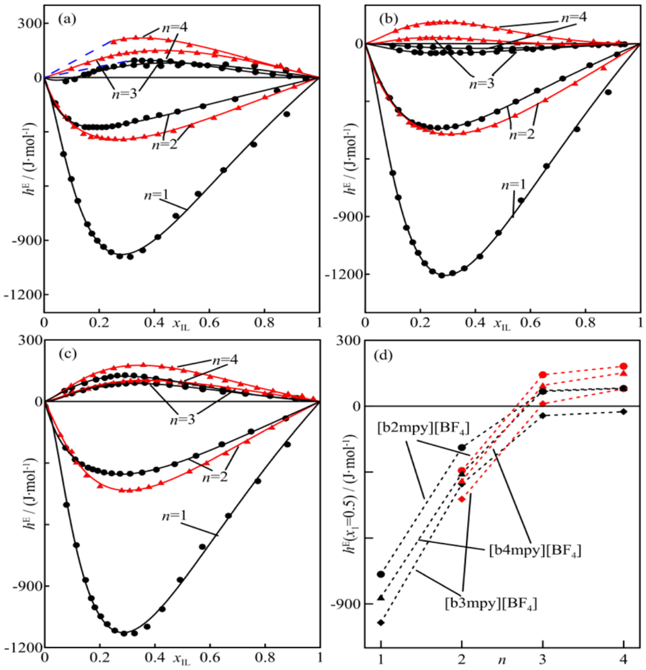

Figure 2. Plots of h^E experimental values and correlation curves at T = 298.15 K (●) and T = 318.15 K (red ▲) for the binaries [bXmpy][BF$_4$](IL)+Cl(CH$_2$)$_n$Cl, n = 1−4. Labels indicate n. (a) For X = 2; dashed-line (---) shows the immiscible-region. (b) For X = 3; (c) for X = 4. (d) Equimolar excess enthalpies as a function of dichloroalkanes chain, n; for X = 2, (●) T = 298.15 K and (red ●) T = 318.15 K; for X = 3, (◆) T = 298.15 K, (red ◆) T = 318.15 K; for X = 4, (▲) T = 298.15 K and (red ▲) T = 318.15 K.

resulting in $y_i = Y_{i0} + Y_{i1}/T$ (2)

where the coefficients Y_{ij} correspond to the correlation of h^E, h_{ij} or of v^E, v_{ij}; these parameters are obtained by a regression of the model to the experimental values (x_{IL},T,h^E) and (x_{IL},T,v^E), respectively. With the use of a combination of eqs 1 and 2, a single correlation can be made of the properties as a function of T and x_{IL}, for the purposes of inter- and extrapolation. Since the substances studied are liquids and p = Cst, here the parameter $k(T,p)$ only depends on the temperature. To carry out the data correlation, this parameter is obtained by (a) the same regression procedure as for the y_i coefficients or (b) through other specified procedures.

Other studies by our research group[40] found that when the volumes v^E are correlated, the active fractions z_i are directly related to the molar volumes of the substances in the solution; a specific parameter was proposed for this case, relating to the binaries IL (1)+compound (2), as

$$k_v^{2\text{-IL}}(T) = \frac{v_2^o(T)}{v_{IL}^o(T)} = \frac{v_2^o(T_0)}{v_{IL}^o(T_0)}\exp[(\alpha_2-\alpha_{IL})(T-T_0)] = k_{v,0}^{2\text{-IL}}(T_0)\exp[\delta(T-T_0)] \quad (3)$$

being α the isobaric expansion coefficients of the compounds involved and $\delta = \alpha_2$-α_{IL}; T_0 is a reference temperature chosen by the researcher. On the other hand, when the sets of (x_{IL},T,h^E) values are correlated, the surface active fractions are related to the contact surfaces of the molecules which, in turn, depend on the molecular surfaces. Now, the parameter k is represented by $k_h^{2\text{-IL}}$, which is expressed as a function of temperature[40] as

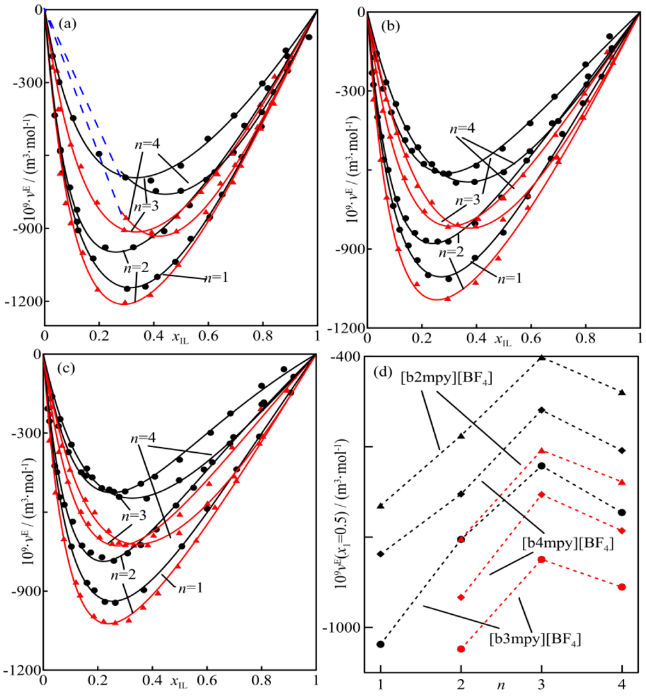

Figure 3. Plots of v^E experimental values and correlation curves at T = 298.15 K (●) and T = 318.15 K (red ▲), for [bXmpy][BF$_4$](IL)+Cl-(CH$_2$)$_n$Cl (n = 1−4). Labels indicate n. (a) For X = 2; Dashed-lines (red ▲) show the immiscibility-region. (b) For X = 3; (c) for X = 4. (d) Equimolar excess enthalpies as a function of dichloroalkanes chain, n; for X = 2, (●) T = 298.15 K and (red ●) T = 318.15 K; for X = 3, (◆) T = 298.15 K and (red ◆) T = 318.15 K; for X = 4, (▲) T = 298.15 K and (red ▲) T = 318.15 K.

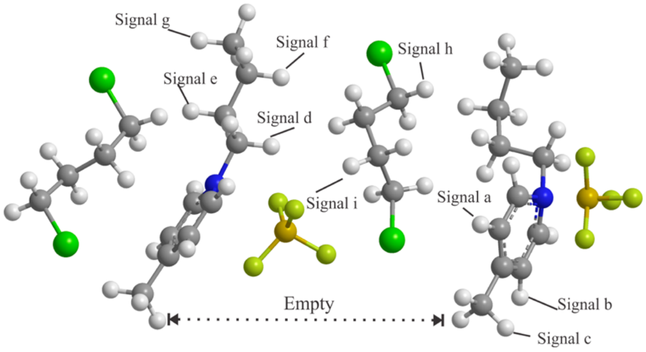

Figure 4. Schema of molecular structure of the [b4mpy][BF$_4$]+Cl-(CH$_2$)$_4$Cl binary solution, obtained by ChemOffice. The signals analyzed by ^{1}H NMR are indicated for each proton group.

$$k_h^{2\text{-IL}}(T) = \frac{S_2^o}{S_{IL}^o} = \left(\frac{q_2}{q_{IL}}\right)\left(\frac{r_{IL}}{r_2}\right)^{2/3}\left[\frac{v_2^o(T)}{v_{IL}^o(T)}\right]^{2/3} = k_q\left[\frac{k_v(T_0)}{k_r}\right]^{2/3}\exp\left[\left(\frac{2}{3}\right)(\alpha_2-\alpha_{IL})(T-T_0)\right] = k_{h,0}^{2\text{-IL}}\exp\left[\left(\frac{2}{3}\right)\delta(T-T_0)\right] \quad (4)$$

Equation 4 needs the parameters of area q_k and volume r_k for each compound, which can be determined by Bondi's group contribution method.[41] This calculation is simple for the 1,ω-dichloroalkanes, since the parameters have been well-identified

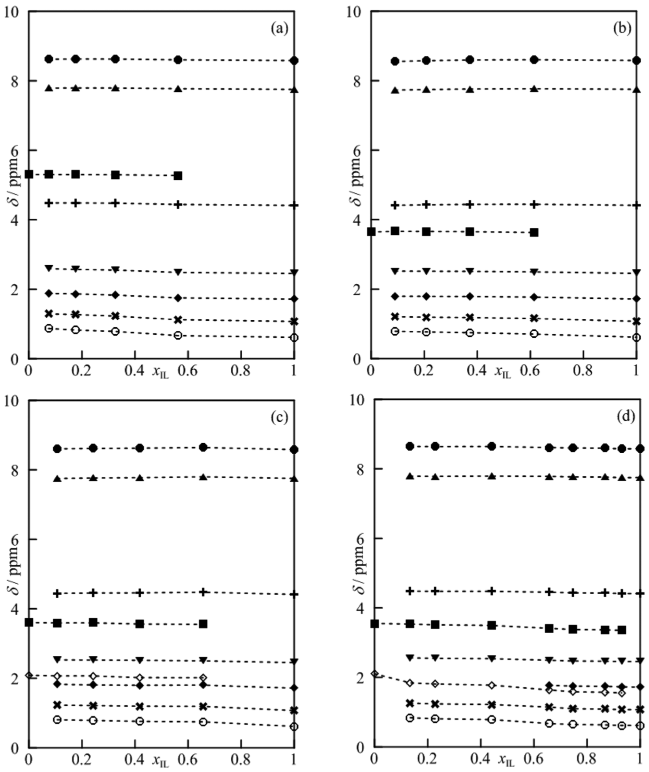

Figure 5. Shifts for mixtures [b4mpy][BF_4] + dichloroalkanes $Cl(CH_2)_nCl$. (a) $n = 1$, (b) $n = 2$, (c), $n = 3$, and (d) $n = 4$. (●) Ha, (▲) Hb, (+) Hc, (▼) Hd, (◆) He, (×) Hf, (○) Hg, (■) Hh, and (◇) Hi. These shifts correspond to signals indicated in Figure 4.

in the literature.[42] However, this is not the case for the ILs, for which an additional procedure is required. In previous works,[5−7] the following approximations are considered $k_v = r_{dichlorides}/r_{IL}$ and $k_S = q_{dichlorides}/q_{IL}$, which permit approximate values to be estimated for the parameters r_{IL} and q_{IL}. When recalculated now these give similar values to the previous ones.

It is important to bear in mind that the objective is to obtain values of $k_v^{2\text{-IL}}$ and $k_h^{2\text{-IL}}$, and the method proposed previously must be tested. To do this, two procedures are used to calculate the values of r_k and q_k: the empirical method by Connolly[43] implemented in the commercial software PCMODEL, and the quantum-chemistry approach GAUSSIAN03[44] that can optimize the molecules and calculate the areas and volumes following the procedure used in COSMO-RS.[19] In both cases, the ILs were considered as a single cation−anion [CA] aggregate and not as the sum of the areas and volumes of the ions, in other words [C^+] + [A^-]. The values obtained are recorded in Table S2 of the Supporting Information. The normalization of areas and volumes gives rise to the corresponding parameters q_k and r_k, compiled in Table S3 of the Supporting Information. Figure 1 shows a comparison of the values of $k_v^{2\text{-IL}}$ and $k_h^{2\text{-IL}}$ obtained by eqs 3 and 4 and those calculated by the indicated methods. It is found that, in spite of the differences in the calculations of areas and volumes, those corresponding to the parameters $k^{2\text{-IL}}$ are actually quite similar, although there is a greater difference with those obtained by Gaussian03. Moreover, our results are quite similar to those obtained by Connolly.[43] Hence, the values used for the correlation of experimental data are those obtained by eqs 3 and 4, see Table S3 of the Supporting Information. This procedure confirms the proposed methodology above-mentioned.

Behavior of the Binaries [b*X*mpy][BF_4]+1,*ω*-dichloroalkanes in Relation to Mixing Properties. Data for the properties (x_{IL},h^E,T) and (x_{IL},v^E,T) for the systems ([b*X*mpy][BF_4]+1,*ω*-$Cl(CH)_nCl$) (with $X = 2$, 3, and 4 and $n=\omega = 1−4$) at $T = 298.15$ K and $T = 318.15$ K are shown, respectively, in Tables S4 and S5 of the Supporting Information. Equation 1 is used to correlate the mixing properties (x_{IL},T,h^E) and (x_{IL},T,v^E), using a least-squares regression procedure with Matlab commercial software. The values obtained for the coefficients are shown in Table S6 of the Supporting Information together with the standard deviations, $s(y^E)$, for each case and the values of the parameter $k^{2\text{-IL}}$, taken from Table S3 of the Supporting Information, as mentioned before. The quality of fit is acceptable for all the binaries. Figure 2 (panels a−c) represents the experimental values of $h^E(x_{IL})$ at 298.15 and 318.15 K for mixtures of [b*X*mpy][BF_4]+1,*ω*-dichloroalkanes and the curves obtained using eq 1. Figure 2d represents the values of h^E (at $x = 0.5$) with n, showing that the binaries comprised of the first 1,*ω*-dichloroalkanes ($\omega = 1$ and 2) with any of the ionic liquids are exothermic. On the one hand, the progressive increase in the molecular surface of the dihaloalkanes (with n) gives rise to a quasiproportional response to n, where the h^E (as absolute values) are smaller and become endothermic when $n \geq 3$. With regard to the [b*X*mpy][BF_4], the order of the enthalpic effects is [b2mpy][BF_4] > [b4mpy][BF_4] > [b3mpy][BF_4], for a same dichloroalkane composition and temperature. In other words, the meta-methylated isomer produces less endothermic effects. This ordinance does not coincide with the solubility,[9] since in such cases the mixing energetic effects are not predominant in the phase instability. In summary, the results suggest that the insolubility in binaries with the larger molecular weight haloalkanes are mainly due to an entropic contribution that is greater than the corresponding enthalpic one. It is interesting to note the effect of temperature on the systems, since there appears to be an increased exothermicity, $(dh^E/dT) < 0$, in the binaries [b*X*mpy][BF_4]+1,2-dichloroethane, while the opposite occurs, $(dh^E/dT) > 0$, in the binaries with the other 1,*ω*-dichloroalkanes.

With regard to the v^E results, the binaries studied present contractions, $v^E < 0$, see Figure 3 (panels a−d). On the one hand, the increase in n reflects less negative values of v^E, and a change in tendency can be observed in the system with 1,4-dichlorobutane (see Figure 3d). This dichloroalkane already presented partial miscibility with [b2mpy][BF_4] in zones of $x_{IL} \leq 0.2$, whereas the variation in this property with isomers of the IL and the other dichloroalkanes where $n < 4$ is positive. In other words, the absolute values of v^E decrease with n. The increase in temperature produces greater contractive effects, with a weaker packing. Figure 4 shows the structural model of an example solution, showing alternative locations for the compounds involved, after optimization with the ChemOffice software and testing with the PCMODEL.

It is noteworthy that both properties, h^E and v^E, have lower values (are more contractive and more exothermic) than the corresponding binaries of the same ILs with dibromide compounds 1,*ω*-$C_nH_{2n}Br_2$,[8] since these have less electronegative heteroatoms, therefore present a reduced capacity to interact with the ILs, and are less soluble than the corresponding dichlorides.

Analysis of the Behavior of the Binaries IL+dichloroalkanes by ^{1}H NMR. Figure 4 identifies the proton signals for the two types of compounds studied in this work. Figure 5(panels a−d) represents the results obtained using ^{1}H NMR, of the

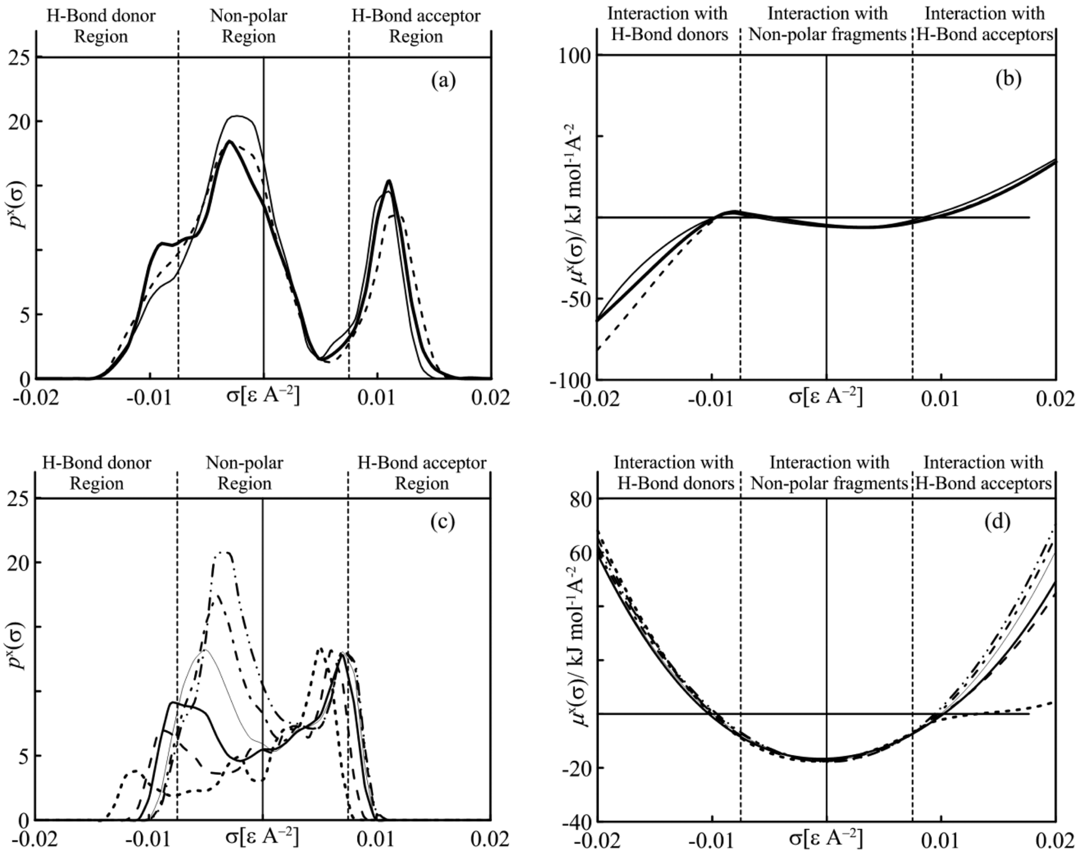

Figure 6. (a) σ-profile using the $p^x(\sigma)$ charge for the ILs [b*X*mpy][BF_4], (b) σ-potential for pure ILs, bold —— X = 2; —— X = 3; - - - X = 4, (c) σ-profile using the $p^x(\sigma)$ charge for $Cl(CH_2)_nCl$, (d) σ-potential for $Cl(CH_2)_nCl$. ······ *n* = 1; - - - *n* = 2; bold —— *n* = 3; —— *n* = 4; — · — *n* = 5; — · · · *n* = 6.

chemical shifts of the [b4mpy][BF_4]+ 1,ω-dichloroalkanes solutions, for samples of different composition.

The different signals present only minor diamagnetic shifts as the quantity of the IL increases, associated with the increase in anisotropies of the pyridine ring, which is aromatic. For a same IL, the h^E vary with the dichloroalkane chain, since the Van der Waals attractions increase with the molecular surface of the pure compound (see Table S2 of the Supporting Information), thus increasing the contact surfaces of the molecules. The increase is opposed by the diminished dipolar density. This is related with a decrease in the chemical shifts of the germinal hydrogens toward the chlorine of the pure dichloroalkanes, for equimolar mixtures of [b4mpy][BF_4]+$C_nH_{2n}Cl_2$ as shown in Figure 5 (panels a–d): H_h ($\delta = 5.29 \rightarrow \delta = 3.66 \rightarrow \delta = 3.57 \rightarrow \delta = 3.45$), and Hi ($\delta = 2.04 \rightarrow \delta = 1.70$). Similar experimentation was carried out with the binaries of the other ILs, resulting in analogous variations to those described here.

■ METHODOLOGY OF THE COSMO-RS MODEL

Calculation Procedure. The molecular geometry of all compounds (common solvents and ionic liquids) was optimized at the B3LYP/6-31++G** computational level in the ideal gas-phase using the quantum chemical Gaussian03 package.[44] As a molecular model to simulate the pure ionic liquid, ion-paired structures including both counterions were optimized as a whole. Vibrational frequency calculations were performed for each case to confirm the presence of an energy minimum. Then, the standard procedure was applied for COSMO-RS calculations, which consists of two steps: first, Gaussiano03 was used to compute the COSMO files. The ideal screening charges on the molecular surface for each species were calculated by the continuum solvation COSMO model using the BVP86/TZVP/DGA1 level of theory. Subsequently, COSMO files were used as input in the COSMOtherm[45] statistical thermodynamic code to calculate the excess enthalpy of the mixtures studied at 298.15 K. According to the chosen quantum method, the functional and the basis set, we used the corresponding parametrization (BP_TZVP_C21_0105) that is required for the calculation of physicochemical data and contains intrinsic parameters of COSMOtherm as well as element-specific parameters.

COSMO-RS Description of Pure Compounds. One advantage of the COSMO-RS methodology is that it provides the charge distribution (σ, sigma) of a given polarity on the molecular surface, which is easily visualized by the "σ-profile" histogram, which the method uses to calculate the interaction energy between pairs of surface segments. Consequently, the "σ-profile" determines the electrostatic and of hydrogen bond interactions of the COSMO-RS model. In fact, the qualitative analysis of the "σ-profile" of the components of a mixture can be used to predict its behavior. Figure 6a presents the σ-profile of the three isomers of the ionic liquid studied [b*X*mpy][BF_4] with *X* = 2, 3, and 4, which can be seen to be similar. The peak at 0.011 corresponds to the anion $[BF_4]^-$ and can be found in the region of high polarity ($\sigma_{HB} > 0.0085$ e/Å^2), showing that this group is a hydrogen bond acceptor. On the negative side, unresolved peaks of low intensity can be observed, located at values lower than the cut off −0.0085 e/Å^2. These signals are associated with hydrogen atoms of the pyridine ring and can contribute to hydrogen bonds as donors. The distribution of charge densities around "zero" corresponds to nonpolar alkyl groups of the cation and to the

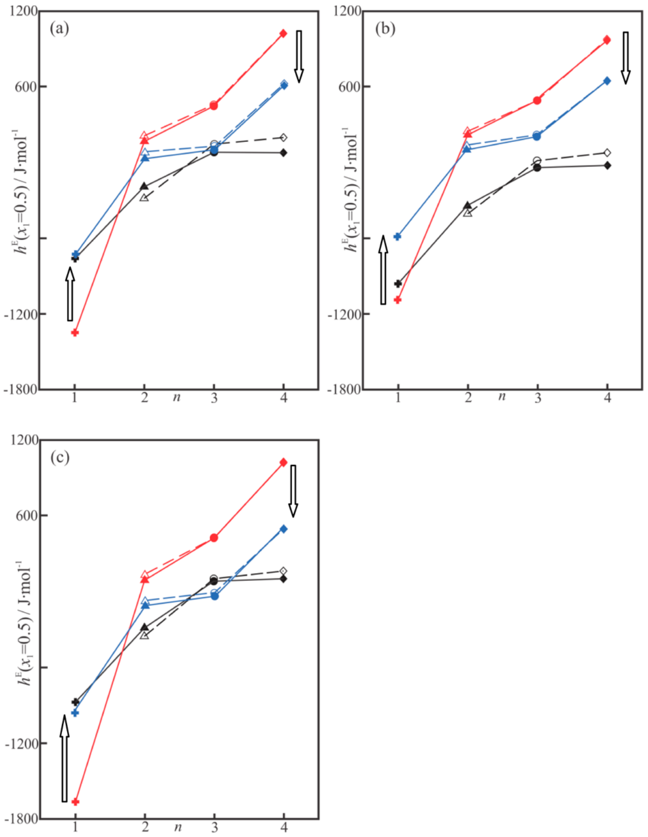

Figure 7. Plot of experimental h^E values (black) and those estimated by standard-COSMO-RS (red) and by optimized-COSMO-RS (blue) as a function of dichloroalkane chain, *n*; for the binaries [bXmpy][BF_4]-(IL)+Cl(CH_2)$_n$Cl, $n = 1-4$ at $T = 298.15$ K (close symbol, solid line) and $T = 318.15$ K (open symbols, dashed line). (a) X = 2; (b) X = 3; (c) X = 4. (+) *n* = 1; (▲) *n* = 2; (●) *n* = 3; and (◆) *n* = 4.

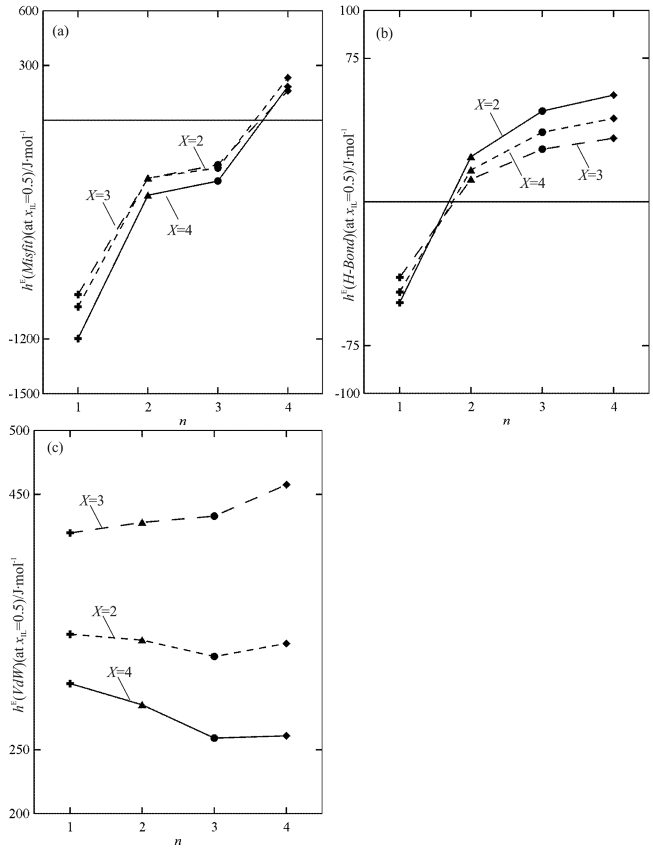

Figure 8. Values of the different contributions: (a) Misfit, (b) *H*−*B*, (c) VdW obtained by COSMO-RS for estimating the equimolar h^E values at 298.15 K of the binaries [bXmpy][BF_4](IL)+Cl(CH_2)$_n$Cl ($n = 1-4$) as a function of the dichloroalkane chain length, *n*. X = 2 (---) ; X = 3 (− − −); X = 4 (——). (+) *n* = 1; (▲) *n* = 2; (●) *n* = 3; (◆) *n* = 4.

carbon atoms of the aromatic ring. The different position of the −CH_3 in the pyridine ring gives rise to slight differences in the intensity and position of the peaks of the σ-profile of the ionic liquids studied. The significance of these differences is more clearly revealed by the representation of the σ-potential (see Figure 6b). The ILs studied in this research present attractive interactions with acid groups and repulsive ones with basic groups. The capacity of these ILs as hydrogen bond acceptors is represented by the order [b3mpy][BF_4] > [b4mpy][BF_4] > [b2mpy][BF_4], while repulsions of the three compounds with electro-donor species are similar. On the other hand, alkyl groups of the cation promote mildly attractive interactions with apolar compounds.

Differences are observed among the alkyl halides, for which the σ-profiles are represented in Figure 6c. The σ-profile is characterized by a peak caused by the chlorine atom at 0.007 e/Å^2 that diminishes its basicity in the dichloromethane with a slight increase in its acidic character. In the nonpolar region of the σ-profile, peaks associated with the alkyl groups can be observed that increase in intensity with the dichloroalkane chain length. A peak can also be observed in the interval between −0.007 and −0.013 for which the σ value depends on 1,ω-dichloroalkane, such that its acidity increases as the aliphatic chain of the halide diminishes. Figure 6d shows how the σ-potential of the 1,ω-dichloroalkanes corresponds to a parabola centered around $\sigma = 0$, indicating strong repulsive interactions of both acidic and basic groups. The latter decrease with the chain length of the 1,ω-dichloroalkane, with a sharp drop observed for the dichloromethane. There are also mildly attractive interactions with nonpolar fragments.

COSMO-RS Description of h^E for [b*X*mpy][BF_4]+Cl-(CH)$_n$Cl. Figure 7 (panels a−c) represents the h^E values calculated at equimolar composition, together with experimental data at the temperatures of 298.15 and 318.15 K estimated by the COSMO-RS methodology of the binaries indicated. The prediction gives an acceptable picture of the qualitative behavior of the solutions, although quantitative errors can be detected which increase with the haloalkane chain length. The parameters used in the COSMO-RS method are not associated with functional groups or types of molecules but are of general application for the prediction of thermodynamic properties of any kind of compound or solution. However, some authors[46] have found it useful to adjust these for application with halogen elements. Owing to the special polarizability of these compounds, these interactions have not been well-described.

To obtain a better estimation of the excess enthalpies of [bXmpy][BF_4]+1,ω-dichloroalkanes, the hydrogen bonding (HB) parameter was recalculated to get the best fit. Figure 7 (panels a−c) presents the results obtained with the COSMO-RS estimates for these binaries with the optimized hydrogen bonding parameter at a value of c_{HB} = 8369 kJ/mol/Å^2, corresponding to a 90% decrease. The predictions made now with the COSMO-RS still do not accurately reflect the behavior shown by the experimental values, although acceptable quantitative estimates are obtained and a more realistic representation in systems containing long-chained compounds.

In the COSMO-RS model, h^E are estimated from the sum of three contributions associated with interactions: electrostatic or "polar misfit", h^E(Misfit), those due to "hydrogen bonds" h^E(H-Bond), and the "van der Waals forces" h^E(VdW). In other words,

$$h^E = h^E(\mathrm{H-Bond}) + h^E(\mathrm{Misfit}) + h^E(\mathrm{VdW}) \quad (5)$$

To study the contribution of each type of interaction in the h^E of [b*X*mpy][BF_4]+1,*ω*-dichloroalkane solutions, the equimolar values of h^E (Misfit) are shown in Figure 8a, of h^E (H-Bond) in Figure 8b and, finally, h^E (VdW) in Figure 8c. In Figure 8a, the contribution of the electrostatic interactions-Misfit is predominantly exothermic. These diminish with the chain length of the *α*,*ω*-dichloroalkane, $n = \omega$, until it becomes endothermic for 1,4-dichlorobutane. This contribution is similar for the three IL isomers.

The contribution of the hydrogen bond interactions is only negligible compared with that of the Misfit and van der Waals interactions. It is exothermic for dichloromethane but endothermic (Figure 8b) for the other dihalides. Finally, the contributions of the van der Waals forces, Figure 8c, are endothermic and quite significant and decrease with increasing length of the *α*,*ω*-dichloroalkane chain, for the isomer X = 4, presenting the opposite behavior when $X = 3$ and an intermediate behavior for $X = 2$. This interaction is more influenced than others by the position of the methyl group in the IL, which is to be expected if these interactions are considered as contact surfaces. Hence, the structure of the IL isomer becomes important, presenting an order of [b4mpy][BF_4] < [b2mpy]-[BF_4] < [b3mpy][BF_4] for this interaction.

CONCLUSIONS

An overall theoretical and experimental evaluation can be established, taking as base the two findings of this study: one, relating to the molecular structure of the compounds, and another, to the working conditions. In other words, the effect of the 1,*ω*-dichloroalkane chain in its interaction with a given IL and that corresponding to the type of [b*X*mpy][BF_4] isomer with a specific alkyl dihalide on the one hand and the effect of temperature on the other. The mixing processes are exothermic in the binaries of ILs with short-chained dichloroalkanes, and endothermicity increases (less exothermic) with increasing *ω*. These effects increase with temperature that also favors packing, especially in the smaller dichloroalkanes, as reflected by the increased contraction of the final solution. Enthalpic estimates made with COSMO-RS at the temperature of 298.15 K, confirm the effects of the dichloroalkane chain, as shown in COSMO-RS Description of hE for [bXmpy][BF4]+Cl(CH)nCl, giving acceptable values for the h^E. When the analysis of the results was based on the different position of the methyl group $-CH_3$ in the IL ($X = 2$, 3, and 4), the theoretical model did not detect any differences in two of the three contributions for the three of the ILs isomers, except for those due to the van der Waals forces.

This behavior of the properties is to be expected, owing to the nature of the halogen, for a same dihalide chain length, thus confirming the results of a previous work with 1,*ω*-dibromoalkanes,[8] which have quantitatively higher properties. Bromine derivatives are less polar than the corresponding chlorinated compounds, due to a lower electronegativity of the bromine atoms and are also less soluble in the [b*X*mpy][BF_4] compounds.

ASSOCIATED CONTENT

Supporting Information

Table S1: Experimental values of pure compounds and comparison with literature. Table S2: Information on molecular volumes and surfaces calculated by different methods. Table S3: Information on the *k*-parameter obtained by different procedures. Table S4: Experimental h^E values for binaries [b*X*mpy][BF_4] + a dichloroalkane at T = 298.15 K and T = 318.15 K. Table S5: Experimental v^E values for binaries [b*X*mpy][BF_4] + a dichloroalkane at T = 298.15 K and T = 318.15 K. Table S6: Coefficients obtained in the data correlation using eq 1. 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) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. Room Temperature of Ionic Liquids as Novel Media for 'Clean' liquid-liquid extraction. *Chem. Commun.* **1988**, 1765−1766.

(2) Cull, S. G.; Holbrey, J. D.; Vargas-Mora, V.; Seddon, K. R.; Lye, G. J. Room-Temperature Ionic Liquids as Replacements for Organic Solvents in Multiphase Bioprocess Operations. *Biotechnol. Bioeng.* **2000**, *69*, 227−233.

(3) Fuerharcker, M.; Haile, T. M.; Kogelnig, D.; Stojanovic, A.; Keppler, B. Application of Ionic Liquids for the removal of Heavy Metals from Wastewater and Activated Sludge. *Water Sci. Technol.* **2012**, *65*, 1765−1773.

(4) Vijayaraghavana, R.; Vedaramanb, N.; Surianarayananb, M.; MacFarlanea, D. R. Extraction and Recovery of Azo Dyes Into an Ionic Liquid. *Talanta* **2006**, *69*, 1059−1062.

(5) Navas, A.; Ortega, J.; Vreekamp, R.; Marrero, E.; Palomar, J. Experimental Thermodynamic Properties of 1-Butyl-2-methylpyridinium Tetrafluoroborate [b2mpy][BF4] with Water and with Alkan-1-ol and Their Interpretation with the COSMO-RS Methodology. *Ind. Eng. Chem. Res.* **2009**, *48*, 2678−2690.

(6) Ortega, J.; Vreekamp, R.; Penco, E.; Marrero, E. Mixing Thermodynamic Properties of 1-butyl-4-methylpyridinium Tetrafluoroborate [b4mpy][Bf4] with Water and With an Alkan-1ol (Methanol to Pentanol). *J. Chem. Thermodyn.* **2008**, *40*, 1087−1094.

(7) Ortega, J.; Vreekamp, R.; Marrero, E.; Penco, E. Thermodynamic Properties of 1-butyl-3-methylpyridinium Tetrafluoroborate and Its Mixtures with Water and Alkanols. *J. Chem. Eng. Data* **2007**, *52*, 2269−2276.

(8) Navas, A.; Ortega, J.; Palomar, J.; Díaz, C.; Vreekamp, R. COSMO-RS Analysis on Mixing Properties Obtained for the Systems 1-butyl-*X*-methylpyridinium Tetrafluoroborate [X = 2,3,4] and 1,*ω*-dibromoalkanes [ω=1−6]. *Phys. Chem. Chem. Phys.* **2011**, *13*, 7751−7759.

(9) Fernández, L.; Montaño, D.; Ortega, J.; Toledo, F. Binary Liquid-Liquid Equilibria for Systems of Mono or Disubstituted Haloalkanes (Cl, Br) and Pyridinium Based Ionic Liquids. Advances in the Experimentation and Interpretation of Results. *Ind. Eng. Chem. Res.* **2013**, *52*, 11758−11766.

(10) Kamlet, J. M.; Taft, R. W. The Solvatochromic Comparison Method. I. The.Beta.-Scale of Solvent Hydrogen-Bond Acceptor (HBA) Basicities. *J. Am. Chem. Soc.* **1976**, *98*, 377−383.

(11) Gellman, S. H.; Dado, G. P.; Liang, G. B.; Adams, B. R. Conformation-Directing Effects of a Single Intramolecular Amide-Amide Hydrogen Bond: Variable-Temperature NMR and IR Studies on a Homologous Diamide Series. *J. Am. Chem. Soc.* **1991**, *113*, 1164−1173.

(12) Singh, T.; Kumar, A. Aggregation Behaviour of Ionic Liquids in Aqueous Solutions: Effect of Alkyl Chain Length, Cations, and Anions. *J. Phys. Chem. B* **2007**, *111*, 7843−7851.

(13) Bankmann, D.; Giernoth, R. Magnetic Resonance Spectroscopy in Ionic Liquids. *Prog. Nucl. Magn. Reson. Spectrosc.* **2007**, *51*, 63−90.

(14) Palomar, J.; Ferro, V. R.; Gilarranz, M. A.; Rodriguez, J. J. Computational Approach to Nuclear Magnetic Resonance in 1-Alkyl-3-methylimidazolium Ionic Liquid. *J. Chem. Phys. B* **2007**, *111*, 168−180.

(15) Bandres, I.; Martin, G.; Martin, S.; Castro, M.; Lafuente, C. Thermophysical Study of 1-Butyl-2-Methylpyridinium Tetrafluoroborate Ionic Liquid. *J. Phys. Chem. B* **2009**, *113*, 11936−11942.

(16) Bandrés, I.; Giner, B.; Artigas, H.; Royo, F. M.; Lafuente, C. Thermophysic Comparative Study of Two Isomeric Pyridinium-Based Ionic Liquids. *J. Phys. Chem. B* **2008**, *112*, 3077−3084.

(17) Heintz, A.; Klasen, D.; Lehmann, J. K. Excess Molar Volumes and Viscosities of Binary Mixtures of Methanol and the Ionic Liquid 4-Methyl-*N*-butylpyridinium Tetrafluoroborate at 25, 40, and 50 °C. *J. Solution Chem.* **2002**, *31*, 467−475.

(18) Heintz, A.; Kulikov, D. V.; Verevkin, S. Thermodynamic Properties of Mixtures Containing Ionic Liquids. 1. Activity Coefficients at Infinite Dilution of Alkanes, Alkenes, and Alkylbenzenes in 4-Methyl-*n*-butylpyridinium Tetrafluoroborate Using Gas-Liquid Chromatography. *J. Chem. Eng. Data* **2001**, *46*, 1526−1529.

(19) Klamt, A. *COSMO-RS: From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design*, 1st ed.; Elsevier: Amsterdam, 2005.

(20) Ortega, J.; Marrero, E.; Palomar, J. Description of Thermodynamic Behavior of the Systems Formed by Alkyl Ethanoates with 1-Chloroalkanes Using COSMO-RS Methodology Contributing with New Experimental Information. *Ind. Eng. Chem. Res.* **2008**, *47*, 3253−3264.

(21) Palomar, J.; Ferro, V. R.; Torrecilla, J. S.; Rodríguez, F. Density and Molar Volumen Predictions Using COSMO-RS for Ionic Liquids. An Approach to Solvent Desing. *Ind. Eng. Chem. Res.* **2007**, *46*, 6041−6048.

(22) Palomar, J.; Torrecilla, J. S.; Ferro, V. R.; Rodríguez, F. Development of an a Priori Ionic Liquid Desing Tool. 1. Integration of a Novel COSMO-RS Molecular Descriptor on Neural Networks. *Ind. Eng. Chem. Res.* **2008**, *47*, 4523−4532.

(23) Domanska, U.; Pobudkowska, A.; Eckert, F. Liquid-Liquid) Phase Equilibria of 1-Alkyl-3-methylimidazolium Methylsulfate with Alcohols, or Ethers, or Ketones. *J. Chem. Thermodyn.* **2006**, *38*, 685−695.

(24) Domanska, U.; Pobudkowska, A.; Eckert, F. Liquid-Liquid Equilibria in the Binary Systems (1,3-Dimethylimidazolium, or 1-Butyl-3-methylimidazolium Methyl Sulfate + Hydrocarbons). *Green Chem.* **2006**, *8*, 268−276.

(25) Sahandzhieva, K.; Tuma, D.; Breyer, S.; Pérez-Salado, A.; Maurer, J. Liquid-Liquid Equilibrium in Mixtures of the Ionic Liquid 1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate and an Alkanol. *J. Chem. Eng. Data* **2006**, *51*, 1516−1525.

(26) Freire, M. G.; Santos, L. M. N. B. F.; Marrucho, I. M.; Coutinho, J. A. P. Evaluation of COSMO-RS for the Prediction of LLE and VLE of Alcohols + Ionic Liquids. *Fluid Phase Equilib.* **2007**, *255*, 167−178.

(27) Lei, Z.; Arlt, W.; Wasserscheid, P. Selection of Entrainers in the 1-Hexene/n-Hexane System with a Limited Solubility. *Fluid Phase Equilib.* **2007**, *260*, 29−35.

(28) Marsh, K. N.; Boxall, J. A.; Lichtenthaler, R. Room Temperature Ionic Liquids and Their Mixtures-a Review. *Fluid Phase Equilib.* **2004**, *219*, 93−98.

(29) Manan, A. N.; Hardacre, C.; Jacquemin, J.; Rooney, D. W.; Youngs, T. G. A. Evaluation of Gas Solubility Prediction in Ionic Liquids using COSMOthermX. *J. Chem. Eng. Data* **2009**, *54*, 2005−2022.

(30) Diedenhofen, M.; Eckert, F.; Klamt, A. Prediction of Infinite Dilution Activity Coefficients of Organic Compounds in Ionic Liquids Using COSMO-RS. *J. Chem. Eng. Data* **2003**, *48*, 475−479.

(31) Lei, Z.; Arlt, W.; Wasserscheid, P. Separation of 1-Hexene and n-Hexane with Ionic Liquids. *Fluid Phase Equilib.* **2006**, *241*, 290−299.

(32) Banerjee, T.; Khanna, A. Infinite Dilution Activity Coefficients for Trihexyltetradecyl Phosphonium Ionic Liquids: Measurements and COSMO-RS Prediction. *J. Chem. Eng. Data* **2006**, *51*, 2170−2177.

(33) Van Ness, H. C.; Abbott, M. M. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1976**, *1*, 22.

(34) Garcia-Miaja, G.; Troncoso, J.; Romani, L. Density and Heat Capacity As a Function of Temperature for Binary Mixtures of 1-Butyl-3-Methylpyridinium Tetrafluoroborate Plus Water, Plus Ethanol, and Plus Nitromethane. *J. Chem. Eng. Data* **2007**, *52*, 2261−2265.

(35) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents of Chemistry*, 4th ed., Vol. 2, Wiley-Interscience: New York, 1986.

(36) Ortega, J.; Marrero, E.; Toledo, F. J.; Espiau, F. Thermodynamic study of (alkyl esters + α,ω-alkyl dihalides) I: H^E and V^E for 25 binary mixtures $\{xC_{u-1}H_{2u-1}CO_2C2H_5 + (1 - x)\alpha,\omega\text{-}ClCH_2(CH2)_{v-2}CH_2Cl\}$, where u = 1 to 5, $\alpha = 1$ and v= ω=2 to 6. *J. Chem. Thermodyn.* **2005**, *37*, 1332−1346.

(37) TRC Tables Non-Hydrocarbons, Thermodynamics Research Center, Texas A&M University: Collage Station, TX, 1991.

(38) Ortega, J.; Plácido, J. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1993**, *21*, 1−37.

(39) Garcia-Gimenez, P.; Martinez-Lopez, J. F.; Blanco, S. T.; Velasco, I.; Otin, S. Densities and Isothermal Compressibilities at Pressures up to 20 MPa of the Systems *N,N*-Dimethylformamide or *N,N*-Dimethylacetamide+α,ω-Dichloroalkane. *J. Chem. Eng. Data* **2007**, *52*, 2368−2374.

(40) Fernandez, L.; Ortega, J.; Sabater, G.; Espiau, F. Experimentation and Thermodynamic Representations of Binaries Containing Compounds of Low Boiling Points: Pentane and Alkyl Methanoates. *Fluid Phase Equilib.* **2014**, *363*, 167−179.

(41) Bondi, A. *Physical Properties of Molecular Crystals, Liquids and Glasses*; Wiley: New York, 1968.

(42) Hansen, H. K.; Rasmussen, P.; Fredenslund, A.; Schiller, M.; Gmehling, J. Vapor-Liquid Equilibria by UNIFAC Group Contribution. 5. Revision and Extension. *Ind. Eng. Chem. Res.* **1991**, *30*, 2352−2355.

(43) Connolly, M. L. Analytical Molecular Surface Calculation. *J. Appl. Crystallogr.* **1983**, *16*, 548−558.

(44) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N., et al. *Gaussian03*, revision B.05; Gaussian, Inc.: Wallingford, CT, 2004.

(45) *COSMOtherm C2.1*, release 01.06; GmbH&CoKG: Leverkusen, Germany, 2003; http://www.cosmologic.de.

(46) Klamt, A.; Eckert, F. Prediction, Fine Tuning, And Temperature Extrapolation of a Vapor Liquid Equilibrium Using COSMOtherm. *Fluid Phase Equilib.* **2007**, *260*, 183−189.