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Overview of the Excess Enthalpies of the Binary Mixtures Composed of Molecular Solvents and Ionic Liquids and Their Modeling Using COSMO-RS

Kiki A. Kurnia and João A. P. Coutinho*

Departamento de Química, CICECO, Universidade de Aveiro 3810-193 Aveiro, Portugal

Supporting Information

ABSTRACT: In this work, an overview of the excess enthalpies of binary mixture containing ionic liquid and molecular solvent is reported, taking into account the various structural features of both the ionic liquid and molecular solvent. Subsequently, the capability of the conductor-like screening model for real system (COSMO-RS) to predict the excess enthalpies of the binary system of ionic liquid and molecular solvent was further evaluated. In general, a good agreement between experimental excess enthalpies and COSMO-RS prediction was obtained. In addition, the COSMO-RS was able to depict and screen the type of molecular interaction that governs the excess enthalpies of ionic liquid and molecular solvent. Thus, COSMO-RS proved very useful as an a priori method that could be used as a tool in the selection or design of a suitable ionic liquid candidate for a certain task and application before extensive experimental measurement.

1. INTRODUCTION

Ionic liquids (ILs) are salts composed by bulky organic cations, such as imidazolium, pyridinium, or pyrrolidinium, combined with organic or inorganic anions.[1] The main feature of ILs is the limitless variability of the physical and chemical properties that can be achieved by manipulating the core cation head, alkyl chain, as well as the anion, indicating that ILs may be regarded as designer solvents. As a consequence, in recent years, there has been a considerable amount of work devoted to the study of the structural relationship of ILs with their thermophysical properties.[2−6] ILs often tend to be more viscous than conventional organic solvents are, which may hamper the application of ILs in extraction or as a reaction medium. Fortunately, their mixtures with molecular solvent show reduced viscosity without jeopardizing their advantages as green solvents.[7] Thus, a study of the mixture of IL and molecular solvents may shed some light on the unique properties of IL solutions.

Several works have been devoted to study the thermophysical properties of binary mixtures composed of molecular solvent and IL for distinct application such as new absorbent of coolants for absorption refrigerators or absorption heat pumps.[8,9] Since many ILs are highly hygroscopic and fully miscible with water, the use of water and IL mixtures as working fluids in process is possible.[8] One of the most important properties for this specific application is excess enthalpies of binary mixture of IL and molecular solvent, yet there are few experimental data on these matters.[8−17] Constantinescu et al.[10] have reported the excess enthalpies for the mixture of cholinium lactate and cholinium glycolate with water over the entire composition range and temperatures of 303.15−323.15 K. The excess enthalpies of water and pyridinium-based ILs have been reported by Ortega et al.[11,12] Rebelo et al.[13] reported the excess enthalpies of 1-butyl-3-methylimidazolium tetrafluoroborate with water over the entire composition range and several temperatures from 278.15−333.15 K. Brennecke et al. have also reported the excess enthapies for a series of imidazolium-based ILs with different anions.[8,14,15] Excess enthalpies of water with quinolinium-based ILs were reported recently by Królikowska et al.[16,17] Given the wide field of potential applications involving ILs, this study was also extended to other solvents for which data on excess enthalpies of binary mixtures of (molecular solvent + ILs) are available.[11,18−20] The molecular solvents studied are alcohol, ketone, and nitromethane. They were chosen because these data allow us to study the effect of molecular liquid polarity on their interactions with ILs. These molecular solvents will cover a broad range of interactions between the molecular solvent and the ILs as discussed below.

Several models have been used for correlating experimental data of excess enthalpies involving IL such as modified UNIFAC,[21,22] the extended real associate solution theory,[18,23,24] and PC-SAFT modeling.[19] Nevertheless, these models are limited because their interaction parameters result from a large amount of experimental data, while the number of published data on the excess enthalpies of ILs and molecular solvents is still very limited. Taking into account the limitless combination of cation and anion to form ILs, it is necessary to employ an appropriate a priori method to adequately screen the best ILs for a given application. An alternative approach is the conductor-like screening model for real solvents (COSMO-RS) that can be used as predictive model for an initial screening of ILs for various applications.[25−28] This approach does not require large amounts of experimental data; in fact, it only uses the information on the molecular structure of the desired compounds. Therefore, COSMO-RS can be applied to a large number of ILs and molecular solvents. Our group has been

Received: June 4, 2013
Revised: August 27, 2013
Accepted: August 29, 2013
Published: August 29, 2013

dx.doi.org/10.1021/ie4017682 | Ind. Eng. Chem. Res. 2013, 52, 13862−13874

using COSMO-RS to the description of liquid−liquid equilibrium for the mixtures of ILs with water,[29] alcohol,[30] and hydrocarbons.[31,32] Palomar et al. have used COSMO-RS to predict the excess enthalpy in order to understand the physical absorption of CO_2[33] and various volatile organic compounds,[34] as well as solubility of cellulose and lignin,[35] in ILs. COSMO-RS has been previously applied by Navas et al. for the description of excess enthalpies of ILs with water, alcohol, and dibromoalkanes.[36−38] Although reasonable results were obtained,[36−38] the limited number of systems studied was insufficient for a detailed evaluation of the COSMO-RS performance and applicability. Therefore, this work aims at evaluating the effect of the structural characteristics of ILs and molecular solvents from the analysis of published experimental data, in order to get a better understanding of the main molecular interactions that control the excess enthalpies. In addition, the experimental data were then used to evaluate the ability of the COSMO-RS method in describing the excess enthalpies of these systems.

2. EXCESS ENTHALPIES PREDICTION OF SYSTEMS INVOLVING IONIC LIQUIDS

COSMO-RS is a quantum chemical based prediction method. The detail theory on COSMO-RS can be found at the original work of Klamt[39] and our recent works.[31,32] In brief, the standard procedure of COSMO-RS calculations consists essentially of two steps: First, the continuum solvation COSMO calculations of electronic density and molecular geometry were performed with the TURBOMOLE 6.1 program package on the density functional theory level, utilizing the BP functional B88-P86 with a triple-ζ valence polarized basis set (TZVP) and the resolution of identity standard (RI) approximation.[40] Then, the estimation of excess enthalpies was performed with the COSMOtherm program using the parameter file BP_TZVP_C30_1301 (COSMOlogic GmbH & Co KG, Leverkusen, Germany).[41] In all calculations, the ILs are always treated as a one to one cation/anion mixture, and the ions are treated at the quantum chemical level separately; thus, it possible to analyze the contribution of IL cation and anion to the total excess enthalpies of the system.

In the molecular approach, COSMO-RS focuses on three specific interactions. The electrostatic−misfit energy, E_{MF}, and hydrogen bonding energy, H_{HB}, are the most relevant and are described as a function of the polarization charge of the two interacting segments − (σ, σ') or $(\sigma_{acceptor}, \sigma_{donor})$. A third interaction, the van der Waals energy, H_{VdW}, only depends on the atoms involved. These energies are described in eqs 1−3, respectively:

$$E_{MF} = a_{eff}\frac{\alpha}{2}(\sigma + \sigma')^2 \tag{1}$$

$$E_{HB} = a_{eff}c_{HB}\min(0; \min(0; \sigma_{donor} + \sigma_{HB}) \times \max(0; \sigma_{acceptor} - \sigma_{HB})) \tag{2}$$

$$E_{VdW} = a_{eff}(\tau_{VdW} + \tau'_{VdW}) \tag{3}$$

There are five adjustable parameters fitted to the individual atoms properties, namely, the effective contact area between two surface segments, a_{eff}; interaction parameter, α'; hydrogen bond strength, σ_{HB}, which is the threshold for hydrogen bonding; and τ_{VdW} τ'_{VdW}, which are elements of specific van der Waals interaction parameters.

The COSMO-RS method defines the excess enthalpies as the difference in enthalpy of a cation, anion, or solute molecule i in its mixture and pure state,

$$H_i^E(\text{interaction}) = H_{i,\text{mixture}}(\text{interaction}) - H_{i,\text{pure}}(\text{interaction}) \tag{4}$$

The H_i^E (interaction) in the COSMO-RS method arises from summing the three specific interactions, namely, electrostatic−misfit, H_{MF}^E; hydrogen bonds, H_{HB}^E; and van der Waals forces, H_{VdW}^E that can be expressed as

$$H_m^E = H_{MF}^E + H_{HB}^E + H_{VdW}^E \tag{5}$$

Combining eqs 4 and 5,

$$H_m^E = H_{i,MF}^E + H_{i,HB}^E + H_{i,VdW}^E \tag{6}$$

Therefore, the COSMO-RS method uses inexpensive unimolecular quantum chemical calculations, which, combined with exact statistical thermodynamics, provide the information necessary for the evaluation of molecular interactions in liquids and their mixtures and can be used to evaluate the contribution of the specific interaction to the final values of the excess enthalpies of the mixture.

3. RESULTS AND DISCUSSION

The experimental and predicted excess enthalpies using COSMO-RS along with the average absolute deviation (AAD) calculate using Equation S1 are given in Tables S1−S4 in the Supporting Information. The effect of solute, cation, and anion of IL and positional isomerism of the alkyl chain of IL are analyzed and discussed below regarding the impact that they have on the excess enthalpies. The studied solutes were water, alcohol, ketone, and nitromethane. In this work, a critical evaluation of the experimental data was carried out by comparing similar systems, and whenever outsider results were observed, they were not considered in the following discussion. Unless otherwise stated, the symbols and the lines in the figures represent the experimental data and the COSMO-RS prediction calculations, respectively.

3.1. Binary Mixture of H_2O and Ionic Liquids. The excess enthalpies of binary mixtures of (H_2O + IL) are the most studied among the various solutes available in the literature. As an example, Figure 1 presents the predicted excess enthalpy of binary mixture {H_2O + [C_4mim][BF_4]} at 313 K along with the reported experimental data from the literature.[13] The excess enthalpies are positive as observed experimentally and predicted by COSMO-RS. The results obtained from COSMO-RS method show an acceptable agreement with the experimental data available. This shows the capability of COSMO-RS to predict the excess enthalpies of this system. Estimated by the COSMO-RS method, the dominant interactions present on this system are shown in Figure 1b. They are the hydrogen bonding, which regulates the endothermicity of the mixture, while the electrostatic interactions and van der Waals forces contribute only slightly to the excess enthalpy and their contributions are negative. It is interesting to note that H_2O highly contributes to the endothermicity of the system, while the cation and anion of ILs contribution were slightly negative; with the latter has more negative contribution, as depicted in Figure 1c. Therefore, from the COSMO-RS result, the scenario of the mixing between {H_2O + [C_4mim][BF_4]} can be described as follows: (i) The

dx.doi.org/10.1021/ie4017682 | Ind. Eng. Chem. Res. 2013, 52, 13862−13874

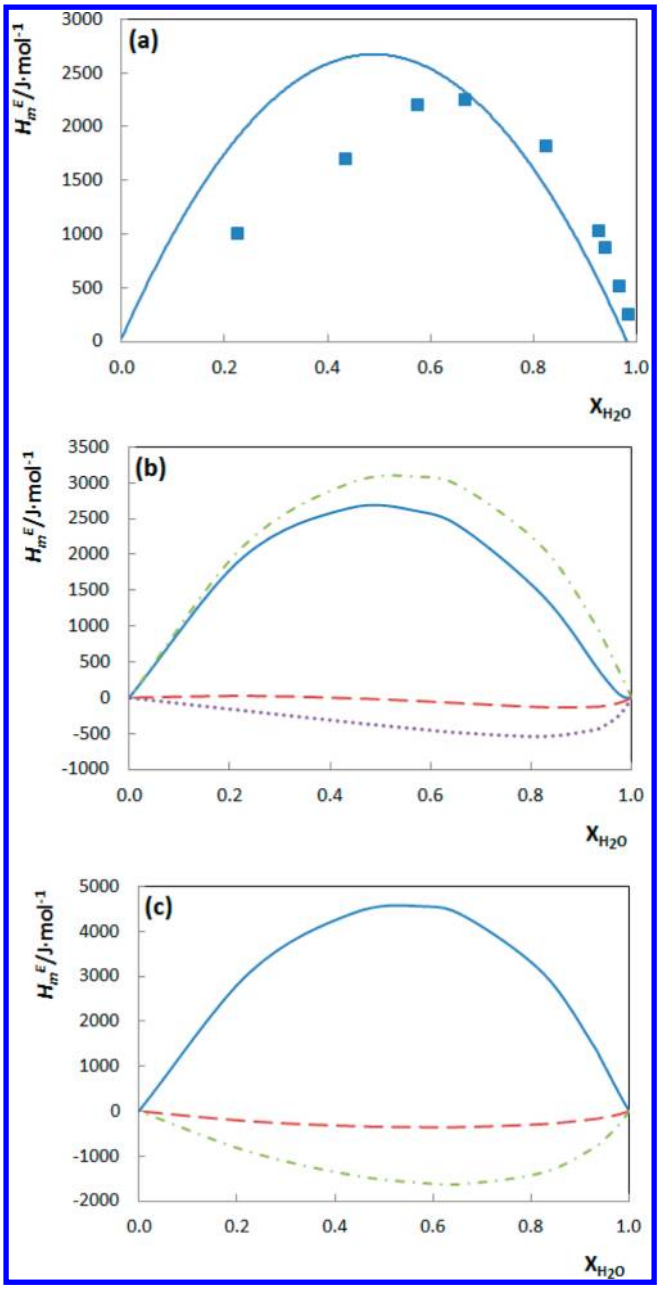

Figure 1. Excess enthalpies of binary mixtures {H_2O + [C_4mim][BF_4]}[13] at 313 K. (a) Comparison between experimental values and those predicted using COSMO-RS. (b) Total excess enthalpies (full line) as contribution of electrostatic interaction (dashed line), hydrogen bonding (dashed and dotted line), and van der Waals forces (dotted line). (c) Contribution of H_2O (full line), [C_4mim]$^+$ (dashed line), and [BF_4]$^-$ (dashed and dotted line) to the total excess enthalpies.

addition of H_2O reduces the electrostatic interaction between cation and anion of ILs, as observed from the negative contribution of H^E_{MF}; subsequently, it is followed by (ii) the rupture of the hydrogen bonding between H_2O−H_2O molecules and [C_4mim]$^+$−[BF_4]$^-$ ions in order to facilitate the mixing and (iii) the establishment of new hydrogen bonding between H_2O−[C_4mim]$^+$ and H_2O−[BF_4]$^-$. The hydrogen-bonding between H_2O−[C_4mim]$^+$ and H_2O−[BF_4]$^-$ are stronger than [C_4mim]$^+$−[BF_4]$^-$. However, the positive excess enthalpies of the system indicate that the hydrogen bonding of H_2O−[C_4mim]$^+$ and H_2O−[BF_4]$^-$ are energetically weak and do not overcome the loss of H_2O−H_2O hydrogen bonds upon mixing. In order to regain the lost hydrogen bonding network, the water molecules tend to use the energy of the system to reorient themselves.[42,43] Consequently, the process becomes endothermic in nature as observed experimentally and predicted by COSMO-RS. Therefore, the COSMO-RS method can be used to modulate and interpret the excess enthalpies taking into account the contribution of the specific interactions that occur between each species (molecules and ions).

3.1.1. Effect of Ionic Liquids Anion. The experimental data available allow a comparison of the effect of several ILs anions on the excess enthalpies of H_2O−IL mixtures. The systems here analyzed are mainly based on [C_2mim][anion] because they are the most studied, thus allowing a direct comparison of the effect of large number of anions on the excess enthalpies. Figure 2 presents the excess enthalpies of binary mixtures {H_2O + [C_2mim][anion]} at 313 K. The excess enthalpies at temperatures 303, 323, 333, and 348 K are given in Figures S1−S4 in the Supporting Information, respectively. The various binary mixtures of {H_2O + [C_2mim][anion]} studied presents a remarkably different excess enthalpy behavior. While [C_2mim]-[$EtSO_4$], [C_2mim][TFA], [C_2mim][$MeSO_3$], and [C_2mim]-[DEP] present negative excess enthalpies with water throughout the whole composition, [C_2mim][SCN] presents both negative and positive excess enthalpies depending on their concentration, and [C_2mim][CF_3SO_3] presents only positive excess enthalpies. For [C_2mim]-based ILs, the exothermicity of H_2O−IL increases in the following order: [CF_3SO_3] < [SCN] < [$EtSO_4$] < [TFA] < [$MeSO_3$] < [DEP]. The excess enthalpies decrease (become more negative) with the increasing hydrophilicity of the anions[44] or the hydrogen bonding acceptor ability, β.[45] Note that the same trend is also observed at different temperatures as shown in Figures S1−S4 in the Supporting Information.

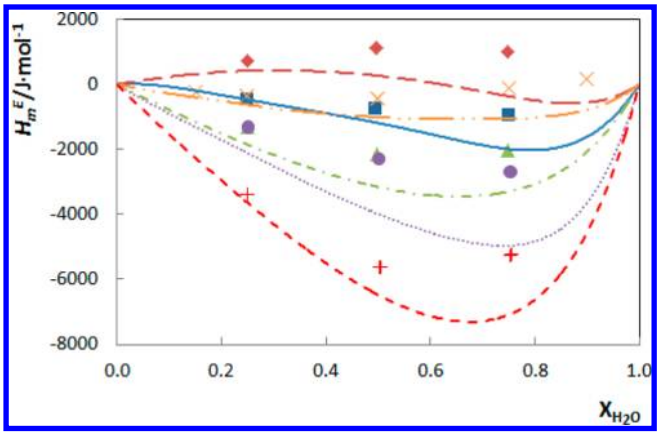

Figure 2. Excess enthalpies of binary mixtures of {H_2O + [C_2mim][$EtSO_4$]}[8] (blue square, full line), {H_2O + [C_2mim]-[CF_3SO_3]}[8] (red diamond, long dashed line), {H_2O + [C_2mim]-[TFA]}[8] (green triangle, dashed and dotted line), {H_2O + [C_2mim][$MeSO_3$]}[14] (purple circle, dotted line), {H_2O + [C_2mim]-[SCN]}[15] (orange X, dashed-dotted-dotted line), and {H_2O + [C_2mim][DEP]}[15] (red +, short dashed line) at 313 K.

Despite the limitation of COSMO-RS to describe the correct behavior of {H_2O + [C_2mim][SCN]} and {H_2O + [C_2mim]-[CF_3SO_3]} as depicted in Figure 2, the anion rank is correctly

dx.doi.org/10.1021/ie4017682 | Ind. Eng. Chem. Res. 2013, 52, 13862−13874

described. According to the COSMO-RS model, the major interaction present on these systems is the hydrogen bonding. As mentioned above, upon mixing water and ILs, there is establishment of new hydrogen bonding between H_2O−cation and H_2O−anion of the ILs. Figure 3 presents the contribution

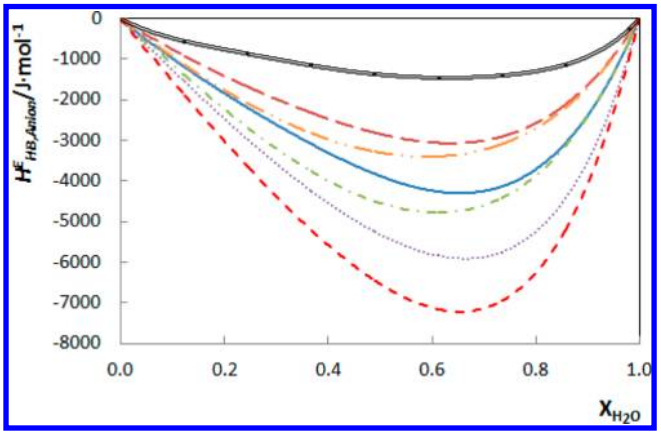

Figure 3. Contribution of hydrogen bonding of anion to the excess enthalpies of binary mixtures of {H_2O + [C_2mim][$EtSO_4$]}[8] (full line), {H_2O + [C_2mim][CF_3SO_3]}[8] (long dashed line), {H_2O + [C_2mim][TFA]}[8] (dashed and dotted line), {H_2O + [C_2mim]-[$MeSO_3$]}[14] (dotted line), {H_2O + [C_2mim][SCN]}[15] (dashed-dotted-dotted line), and {H_2O + [C_2mim][DEP]}[15] (short dashed line), and {H_2O + [C_4mim][BF_4]}[13] (double line) at 313 K predicted by COSMO-RS.

of hydrogen-bonding of the anion to the total excess enthalpies at 313 K. Because the contribution of H_2O−cation is small, as will be discussed in section 3.1.2, the binary mixtures of {H_2O + [C_4mim][BF_4]} are taken into consideration to get larger picture of anion effect on the excess enthalpies. Note that this contribution arises from the establishment of new hydrogen bonds between H_2O − anion of the ILs. H_2O presents the strongest hydrogen bonding with $[DEP]^-$ anion, followed by $[MeSO_3]^-$ > $[TFA]^-$ > $[EtSO_4]^-$ > $[SCN]^-$ > $[CF_3SO_3]^-$ and $[BF_4]^-$. These patterns closely follow the hydrogen bond basicity of [C_2mim]-based ILs regarding their anion. The hydrogen bond basicity, the β solvatochromic parameter, accordingly to the IL anion nature follows the sequence [DEP] > [$MeSO_3$] > [TFA] > [$EtSO_4$] > [SCN] > [CF_3SO_3] > [BF_4].[45] Therefore, it can be concluded that the interaction of water and ILs is highly governed by the hydrogen bond basicity of the respective anion shown in Figure 3 (the same being true at other temperatures presented in Figures S5−S8 in the Supporting Information). Therefore, for the systems here studied, the COSMO-RS model provides a qualitative description of the IL anion influence on the excess enthalpies and can be used as an a priori screening tool in system with particular characteristics.

In addition, it is striking the effect of fluorination of anion. Comparing the $[CF_3SO_3]^-$ to the $[MeSO_3]^-$ anion, according to their capacity to form hydrogen bonding with water, it seems that the fluorination reduces its ability to form hydrogen bonds. It should be highlighted that this phenomena was already discussed by Ficke and Brennecke using CHELPG Atomic Charge.[14] The CHELPG charges showed that the oxygen atoms in [CF_3SO_3] become less negative due to the electron-withdrawing nature of fluorine, preventing H_2O−[CF_3SO_3] interactions and accounting for the more endothermic excess enthalpy.[14]

3.1.2. Effect of Alkyl Chain of Ionic Liquid Anion. Figure 4 presents the excess enthalpies of binary mixtures of water and

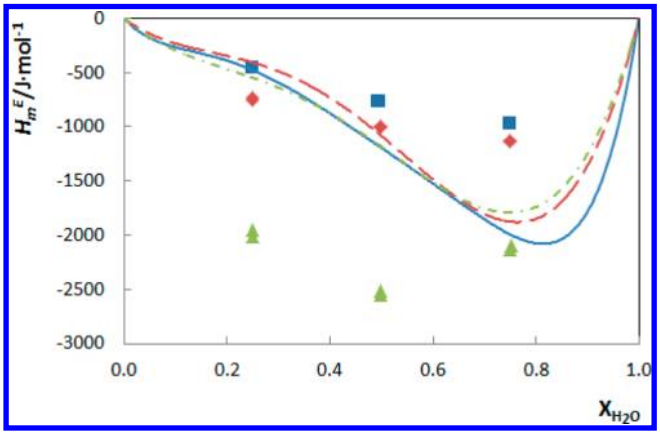

Figure 4. Excess enthalpies of binary mixtures of {H_2O + [C_2mim][$EtSO_4$]}[8] (blue square, full line), {H_2O + [C_2mim]-[$MeSO_4$]}[14] (red diamond, long dashed line), and {H_2O + [C_2mim][HSO_4]}[14] (green triangle, dashed and dotted line) at 313 K.

sulfate-based ILs at 313 K. The increase in alkyl chain length from [C_2mim][HSO_4] to [C_2mim][$EtSO_4$] decreases the exothermicity indicating a less favorable interaction with water. The binary mixtures {H_2O + [C_2mim][HSO_4]} showed the highest exothermicity, and a little decrement was observed from {H_2O + [C_2mim][$MeSO_4$]} to {H_2O + [C_2mim]-[$EtSO_4$]}. Although the COSMO-RS model, represented in Figure 4, is able to predict the exothermicity of these binary mixtures, it fails to correctly predict the effect of the alkyl chain of ILs anion. It is noteworthy to mention that the IL [C_2mim][$EtSO_4$] was found to decompose over time by reacting with water to form [C_2mim][HSO_4] and ethanol, as reported by the authors.[8] This finding was further validated by Jacquemin et al.[46] From their work, it is clear that methyl sulfate- and ethyl sulfate-based ILs are not stable in the presence of water, since hydrolysis of the methylsulfate or ethyl sulfate anions to methanol or ethanol and hydrogenate anion occurs.[46] By the other hand, the HSO_4^- anion is a protic anion and presents quite challenging pH equilibrium in ILs and in water[47] that is not easy to be described in COSMO-RS. Such observations could partly explain the differences observed between experimental and predicted excess enthalpy of binary mixtures of water and sulfate-based ILs.

Figure 5 presents the excess enthalpies for binary mixtures of water and cholinium-based ILs, namely, [Ch]Gly and [Ch]Lac, at 303 K.[10] The excess enthalpies for these two systems at 313 and 323 K are given in Figures S9 and S10, respectively, in the Supporting Information. Increasing alkyl chain length from [Ch]Gly to [Ch]Lac significantly increases the exothermicity of the mixture. This fact is contradictory with the effect of increasing alkyl chain of anion on imidazolium-based ILs as depicted in Figure 4. Again, the COSMO-RS model was not able to predict correctly the effect of the alkyl chain of ILs anion. Hitherto, the experimental data available are too scarce to draw any conclusions concerning this matter.

3.1.3. Effect of Alkyl Chain Length of Ionic Liquid Cation. To study the effect of the alkyl chain of ILs cation, Figure 6 presents the excess enthalpies of two binary mixtures of {H_2O + [C_2mim][CF_3SO_3]} and {H_2O + [C_6mim][CF_3SO_3]} at 313 K, whereas Figure S11 in Supporting Information presents the

dx.doi.org/10.1021/ie4017682 | Ind. Eng. Chem. Res. 2013, 52, 13862−13874

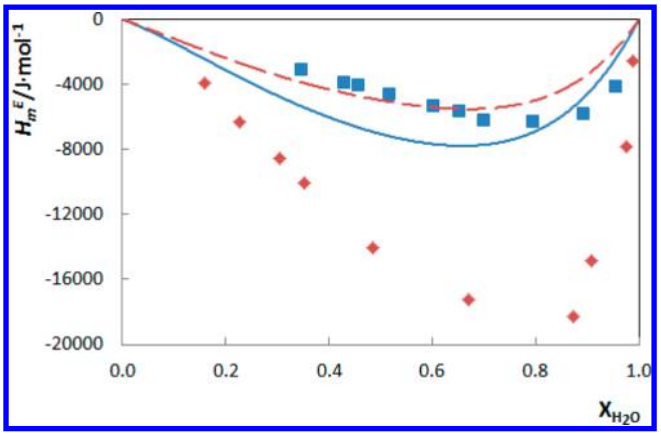

Figure 5. Excess enthalpies of binary mixtures of {H_2O + [Ch]Gly}[10] (blue square, full line) and {H_2O + [Ch]Lac}[10] (red diamond, long dashed line) at 303 K.

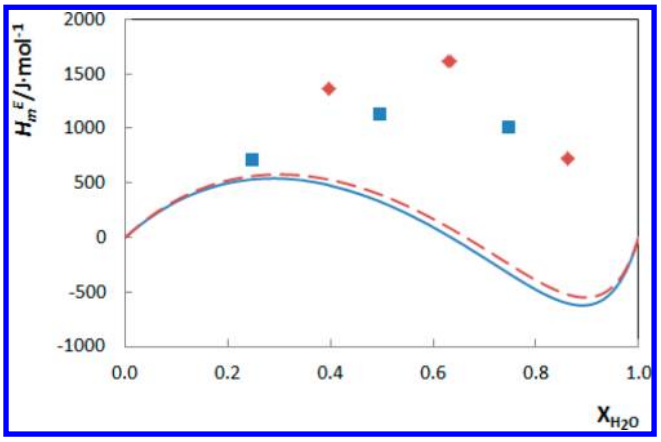

Figure 6. Excess enthalpies of binary mixtures of {H_2O + [C_2mim][CF_3SO_3]}[8] (blue square, full line) and {H_2O + [C_6mim][CF_3SO_3]}[14] (red diamond, long dashed line) at 313 K.

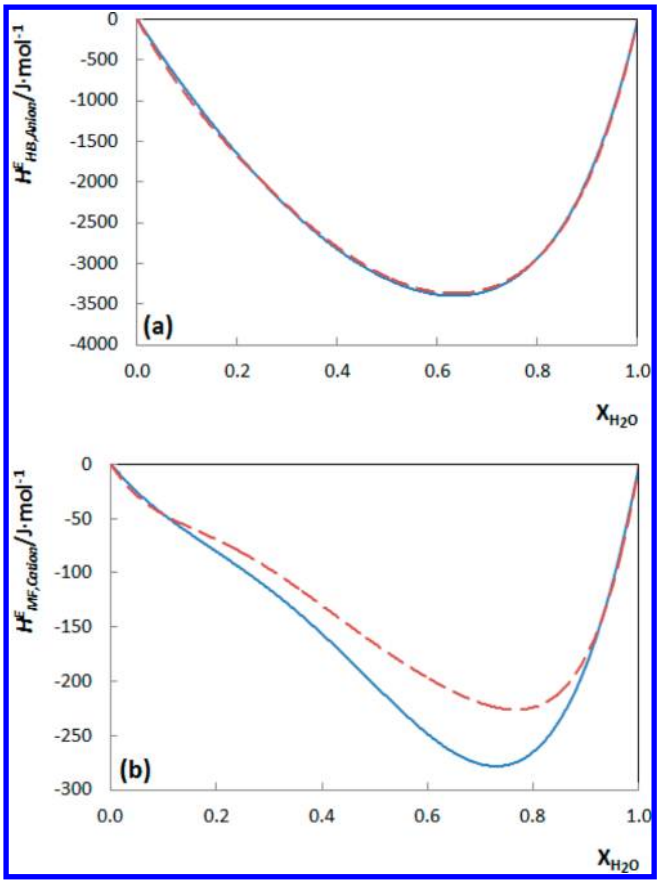

Figure 7. Contribution of specific interaction to the total excess enthalpies of the binary mixtures of {H_2O + [C_2mim][CF_3SO_3]}[8] (full line) and {H_2O + [C_6mim][CF_3SO_3]}[14] (long dashed line) at 313 K predicted by COSMO-RS. (a) Contribution of hydrogen bonding of the H_2O−anion. (b) Contribution of electrostatic−misfit interaction of H_2O−cation.

excess enthalpies of two binary mixtures of {H_2O + [C_2mim][CF_3SO_3]} and {H_2O + [C_4mim][CF_3SO_3]} at 303 K. The increase of the alkyl chain length from [C_2mim][CF_3SO_3] to [C_6mim][CF_3SO_3] slightly decreases the exothermicity indicating a less favorable interaction with water. The effect of the alkyl chain on cations is less significant than the anion effect as discussed above what suggests that the major interactions between the water and the ILs takes place, as discussed previously at the anions. Despite the inability of COSMO-RS to correctly describe the behavior of the $[CF_3SO_3]^-$ anion, as discussed previously, it can correctly predict the effect of the alkyl chain of the IL cation on the excess enthalpies trend observed experimentally in Figure 6 (as well as for the system presented in Figure S11 in Supporting Information).

According to the COSMO-RS model, the interaction of the H_2O−anion in [C_2mim][CF_3SO_3] is identical to [C_6mim][CF_3SO_3], as depicted in Figure 7a. However, increasing the alkyl chains increases the electrostatic−misfit interaction between H_2O−cation of the ILs, as shown in Figure 7b. The increased alkyl chain length of cation results in a more diffused charge density on the imidazolium ring, and the available charge is further hidden by these long alkyl chains in these cationic species. This leads to the dominance of strong hydrophobic effect of long alkyl chain.[42,43] Note that even though the H_2O−[C_2mim]$^+$, H_2O−[C_6mim]$^+$, and H_2O−$[CF_3SO_3]^-$ contributions are negative, they cannot compensate for the energy loss of H_2O−H_2O upon mixing that lead to observed positive excess enthalpies for this system.

Contrary to what has been observed for imidazolium-based ILs, increasing the alkyl chain length from [C_6iQuin][SCN][16] to [C_8iQuin][SCN][17] increased the exothermicity that enhance the favorable interaction with water, as shown in Figure 8 (and Figures S12 and S13 in the Supporting Information). Nevertheless, it is difficult at present to establish if this is a peculiar behavior related with the quinolinium-based ILs or is just a problem associated with the limited experimental data available. More data on these systems are required to establish the reason behind this particular trend.

3.1.4. Effect of Functionalized Alkyl Chain of Cation. Figure 9 shows the effect of adding hydroxyl groups to the cation by comparing the excess enthalpies of {H_2O + [C_2mim][TFA]} and {H_2O + [HO-C_2mim][TFA]}at 323 K. The excess enthalpies for these two systems at temperatures 333 and 348 K are given in Figures S14 and S15, respectively, in the Supporting Information. The excess enthalpies of {H_2O + [C_2mim][TFA]} are more exothermic than {H_2O + [HO-C_2mim][TFA]} indicating that addition of hydroxyl to the ethyl group of the cation, unexpectedly, decreases the interaction with water. The COSMO-RS model provides a correct qualitative description of the experimental data of the

dx.doi.org/10.1021/ie4017682 | *Ind. Eng. Chem. Res.* 2013, 52, 13862−13874

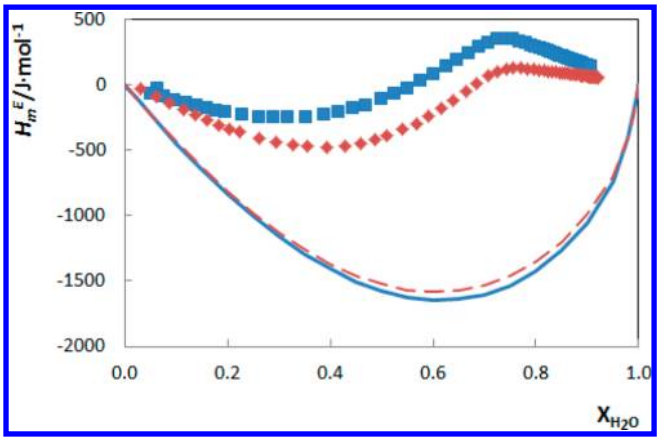

Figure 8. Excess enthalpies of binary mixtures of {H_2O + [C_6iQuin][SCN]}]}[16] (blue square, full line) and {[H_2O + [C_8iQuin][SCN]}[17] (red diamond, long dashed line) at 298 K.

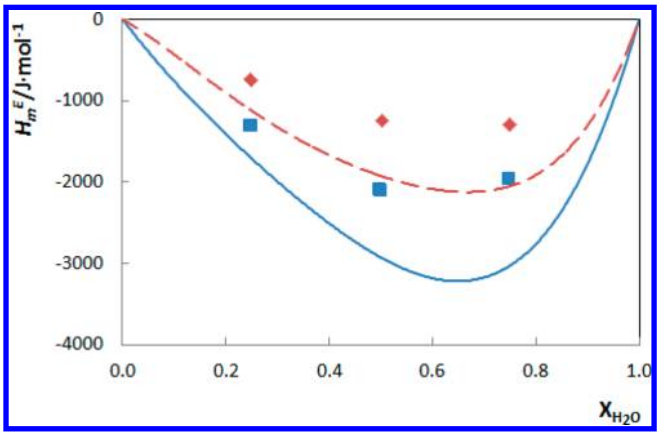

Figure 9. Excess enthalpies of binary mixtures of {H_2O + [C_2mim][TFA]}[14] (blue square, full line) and {H_2O + [HO-C_2mim][TFA]}[14] (red diamond, long dashed line) at 313 K.

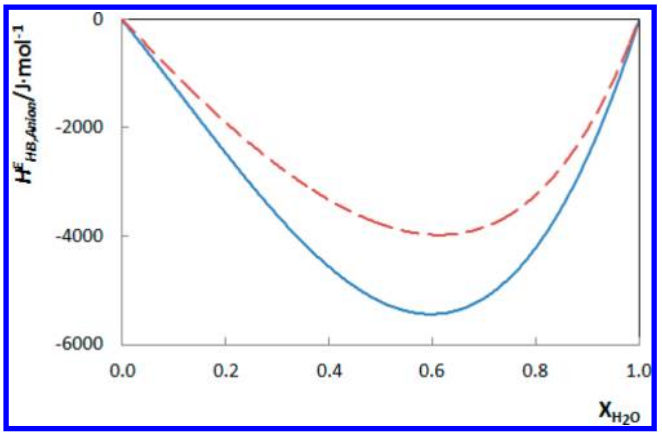

Figure 10. Contribution of hydrogen bonding of H_2O−anion for the binary mixtures {H_2O + [C_2mim][TFA]}[14] (full line) and {H_2O + [HO-C_2mim][TFA]}[14] (long dashed line) at 313 K predicted by COSMO-RS.

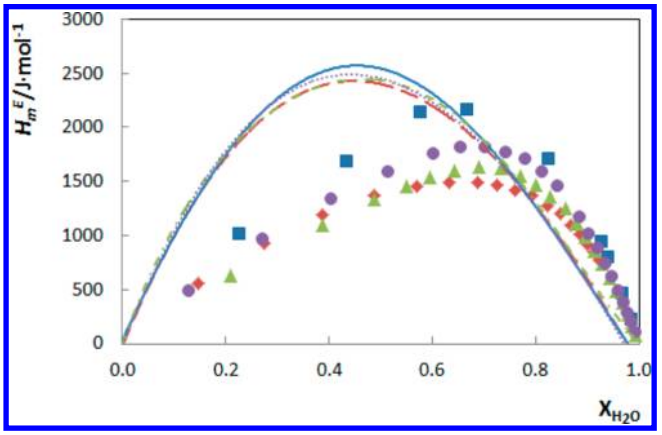

Figure 11. Excess enthalpies of binary mixtures of {H_2O + [C_4mim][BF_4]}[13] (blue square, full line), {H_2O + [(2)C_1bpy][BF_4]}[36] (red diamond, long dashed line), {H_2O + [(3)C_1bpy][BF_4]}[11] (green triangle, dashed and dotted line), and {H_2O + [(4)C_1bpy][BF_4]}[12] (purple circle, dotted line).

studied systems in Figure 9 (and Figures S14 and S15 in the Supporting Information).

On the basis of COSMO-RS model, introducing a hydroxyl group on the cation does not increase its hydrogen bonding with water, as anticipated. It is also observed that the hydrogen bonds of H_2O−[TFA]$^-$ anion in [C_2mim][TFA] are stronger than in [HO-C_2mim][TFA], as depicted in Figure 10 (and Figures S16 and S17 in Supporting Information). It should be emphasized that these peculiarities were already discussed by Ficke and Brennecke using CHELPG Atomic Charge.[14] As a result, the [TFA]$^-$ anion will preferentially associate with the hydroxyl group of the cation, thus increasing the IL−IL interactions for [HO-C_2mim][TFA].[14] Using the COSMO-RS model, the predicted hydrogen bonding at 323 K, in pure [HO-C_2mim][TFA] (−51.8 kJ·mol^{-1}) is much stronger than in pure [C_2mim][TFA] (−21.9 kJ·mol^{-1}), confirming the result from Ficke and Brennecke.[14] Consequently, more energy is required to disrupt the cation−anion interaction in the pure [HO-C_2mim][TFA] than in pure [C_2mim][TFA], and this leads to a less negative excess enthalpy for the {H_2O + [HO-C_2mim]-[TFA]} system.

3.1.5. Effect of Ionic Liquid Cation Core and Isomerism. The effect of the IL cation core can be examined by fixing the anion and the cation alkyl chain length. Figure 11 presents the excess enthalpies of [C_4C_1-cat][BF_4] where cat are imidazolium or pyridinium-based ILs. They exhibit similar excess enthalpies, with the former having a slightly more endothermic behavior. The position of the methyl group on the 1-butylpyridinium-based ILs, as in the case of [(2)C_1bpy][BF_4], [(3)C_1bpy][BF_4], and [(4)C_1bpy][BF_4], also has a slight effect on the excess enthalpies. At equimolar composition, the endothermicity increases in the following order: [(3)C_1bpy][BF_4] < [(2)-C_1bpy][BF_4] < [(4)C_1bpy][BF_4] < [C_4mim][BF_4] as can be observed both experimentally and predicted by the COSMO-RS method.

For the [BF_4]-based ILs, the endothermicity indicates that the H_2O−cation and H_2O−anion are energetically weak and could not compensate for the loss of H_2O−H_2O hydrogen bonds upon mixing. In order to regain the lost hydrogen bonding network, the water molecules tend to use the energy of the system to reorient themselves.[42,43] As can be observed from Figure 11, the excess enthalpies of binary mixtures {H_2O + [(4)C_1bpy][BF_4]} and {H_2O + [(2)C_1bpy][BF_4]} are slightly higher than those of {H_2O + [(3)C_1bpy][BF_4]}, indicating that the position of the −CH_3 group in the latter system favors the contraction effect more than in the other two systems, due to a better interstitial accommodation of the water molecule when they reorient themselves during mixing. It indicates that the

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solubility of [BF_4]-based ILs in water is an endothermic process and entropically driven. Such phenomena have also been observed for the solubility of [Tf_2N]− based IL reported by our group.[48]

3.1.6. Effect of Temperature. Figures 12 and 13 present the excess enthalpies for binary mixtures {H_2O + [C_2mim][TFA]}

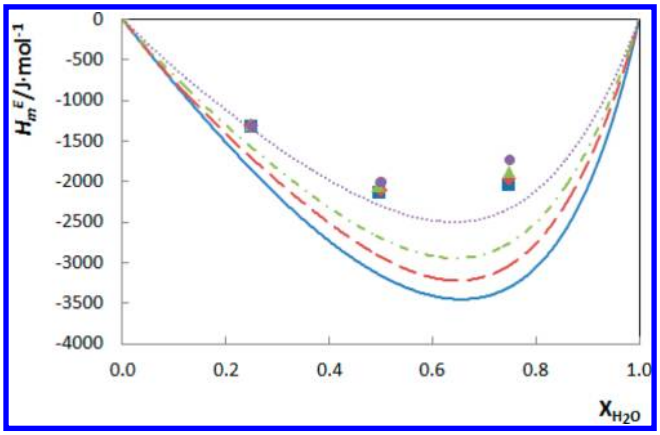

Figure 12. Excess enthalpy of binary mixture {H_2O + [C_2mim]-[TFA]}[8] at 313 K(blue square, full line), 323 K (red diamond, dashed line), 333 K (green triangle, dashed and dotted line), and 348 K (purple circle, dotted line).

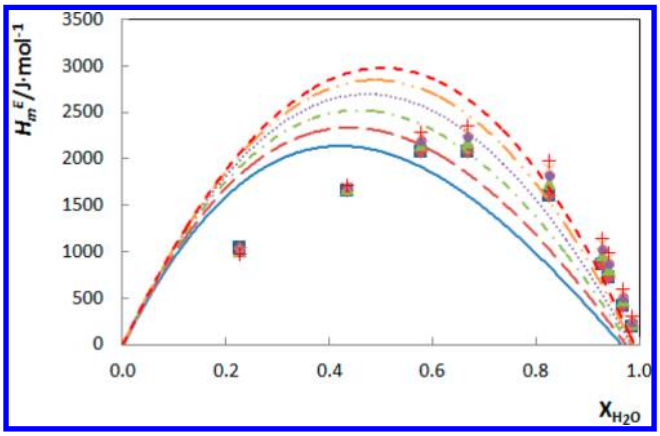

Figure 13. Excess enthalpy of binary mixture {H_2O + [C_2mim]-[BF_4]}[13] at 283 K (blue square, full line), 293 K (red diamond, long dashed line), 303 K (green triangle, dashed and dotted line), 313 K (purple circle, dotted line), 323 K (orange X, dashed, dotted, and dotted line), and 333 K (bright red +, short dashed line).

and {H_2O + [C_4mim][BF_4]}, respectively, at different temperatures. The excess enthalpies increase with temperature, indicating a less favorable interaction at higher temperature. This effect of temperature in H_m^E has also been observed in other binary mixtures of water and ILs.[8,10−12,14,15,21,22,36] The COSMO-RS model also provides a correct description of this behavior that can be interpreted as a loss of hydrogen bonding of H_2O−[anion] in the mixture with increasing temperature.

In summary, COSMO-RS seems to be able to produce at least a semiquantitative description of the experimental data. The exception was observed in a few cases such as the effect of the alkyl chain length of IL anion, which was not fully captured by the COSMO-RS. Also, COSMO-RS was not able to predict the correct behavior whenever chemical equilibrium occurs in the system, i.e., hydrolysis of sulfate-based ILs in the presence of water. The excess enthalpy of a binary mixture of water and ILs is dominated by the interaction of H_2O with the IL anion, while the IL cation plays a minor role. Therefore, future applications involving a binary mixture of water and IL can be enhanced by modifying the hydrogen bonding basicity of the IL anion.

3.2. Binary Mixtures of Alcohol and Ionic Liquids. *3.2.1. Effect of Alkyl Chain of Alcohol.* The effect of alkyl chain length of alcohol on their excess enthalpies with pyridinium-based and piperidinium-based ILs is given in Figures 14 and 15,

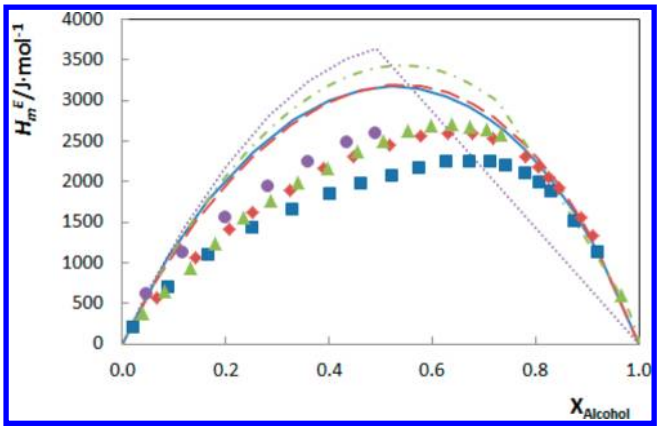

Figure 14. Excess enthalpy of binary mixture {methanol + [(2)C_1bpy][BF_4]}[36] (blue square, full line), {ethanol + [(2)C_1bpy]-[BF_4]}[36] (red diamond, long dashed line), {1-propanol + [(2)C_1bpy]-[BF_4]}[36] (green triangle, dashed and dotted line), and {1-butanol + [(2)C_1bpy][BF_4]}[36] (purple circle, dotted line) at 318 K.

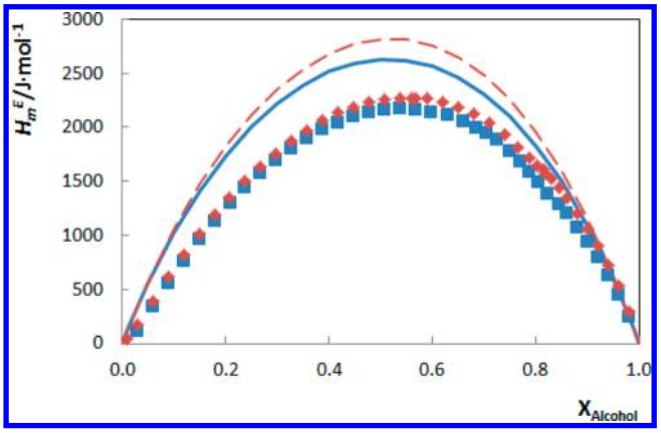

Figure 15. Excess enthalpy of binary mixture {ethanol + [C_4C_1pip]-[Tf_2N]}[19] (blue square, full line) and {1-propanol + [C_4C_1pip]-[Tf_2N]}[19] (red diamond, long dashed line) at 298 K.

respectively (and Figures S18−S23 in the Supporting Information). It can be seen that the endothermic effects are observed for all binary mixtures of alcohol and ILs. Increasing alkyl chain of linear alcohol from methanol to 1-butanol increases the endotherm excess enthalpies as observed experimentally and predicted by COSMO-RS. On the basis of COSMO-RS model, the excess enthalpies result from both their hydrogen bonds and the electrostatic−misfit interactions between the alcohol and IL. The highly positive contribution of hydrogen bond from alcohols indicates that more favorable interactions occur between alcohol−alcohol molecules rather than alcohol−cation and alcohol−anion of the IL, and it essentially governs the interaction of binary mixtures of alcohol and IL. The contributions of electrostatic of alcohols are also

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positive, meaning unfavorable interactions between the alcohol and IL. The electrostatic misfit becomes more unfavorable with increasing alkyl chain of the alcohol, as depicted in Figure 16

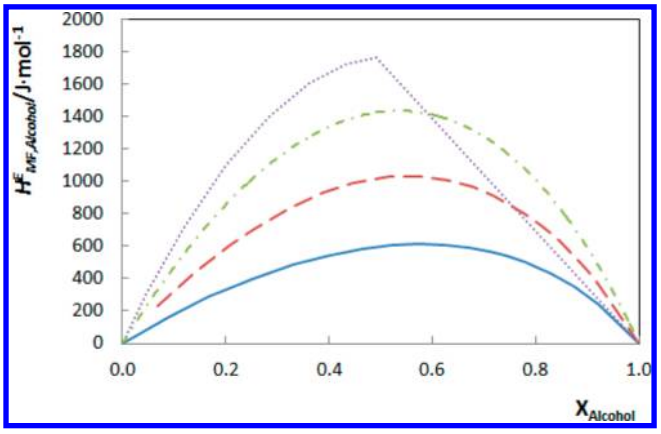

Figure 16. Contribution of electrostatic−misfit interaction of alcohol to the excess enthalpy of binary mixture {methanol + [(2)C_1bpy][BF_4]}[36] (full line), {ethanol + [(2)C_1bpy][BF_4]}[36] (long dashed line), {1-propanol + [(2)C_1bpy][BF_4]}[36] (dashed and dotted line), and {1-butanol + [(2)C_1bpy][BF_4]}[36] (dotted line) at 318 K predicted by COSMO-RS.

(and Figures S24−S28 in the Supporting Information). In other words, alcohol molecules do not like the presence of ILs. Contrarily, the slightly negative contribution of ILs specifies an attraction of cation and anion of ILs toward the alcohol molecule. Nevertheless, the endothermicity of the system indicates that the alcohol−cation and alcohol−anion interactions are weak and cannot compensate for the greater loss of alcohol−alcohol interaction.

Figure 17 (and Figures S29−S31 in the Supporting Information) presents the effect of hydroxyl group position

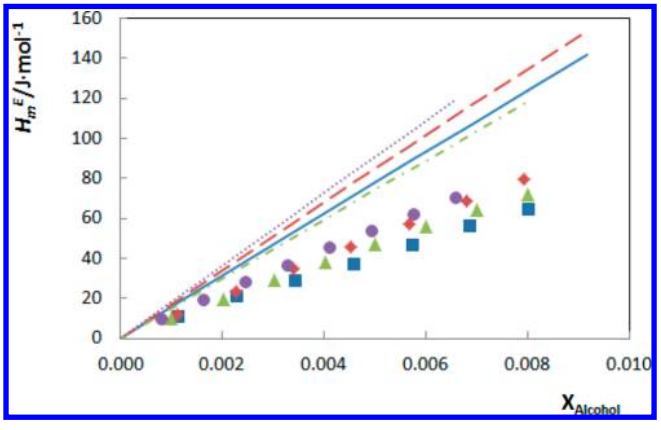

Figure 17. Excess enthalpy of binary mixture {ethanol + [C_4mim][PF_6]}[36] (blue square, full line), {1-propanol + [C_4mim][PF_6]}[36] (red diamond, long dashed line), {2-propanol + [C_4mim][PF_6]}[36] (green triangle, dashed and dotted line), and {1-butanol + [C_4mim][PF_6]}[36] (purple circle, dotted line) at 318 K.

of alcohol on the excess enthalpies. While COSMO-RS provides reliable prediction for binary mixtures of IL and linear alcohol, the same could not be observed for {2-propanol + [C_4mim][PF_6]. Yet again, due to limited experimental data available, we cannot draw definitive conclusions on the effect of the hydroxyl group position of alcohol on their excess enthalpies with ILs. More experimental data are required to establish this particular trend.

3.2.2. Effect of Ionic Liquid Anion. All the studied binary mixtures present an endothermic behavior (positive excess enthalpies) regardless the nature of the anion as depicted in Figures 18 and 19. Although the experimental data are scarce

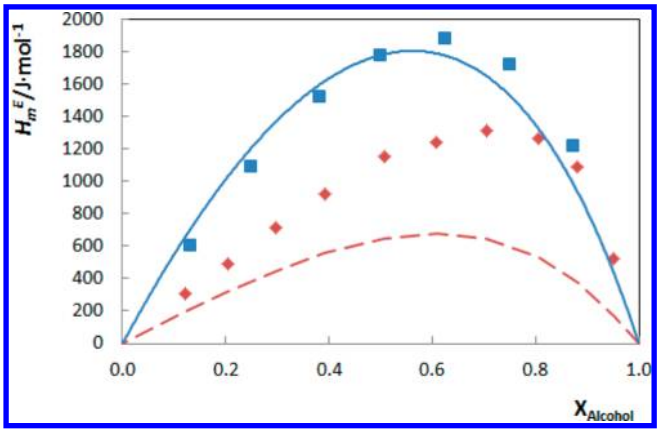

Figure 18. Excess enthalpy of binary mixture {ethanol + [C_2mim][CF_3SO_3]}[23] (blue square, full line) and {ethanol + [C_4mim][$EtSO_4$]}[23] (red diamond, long dashed line) at 308 K.

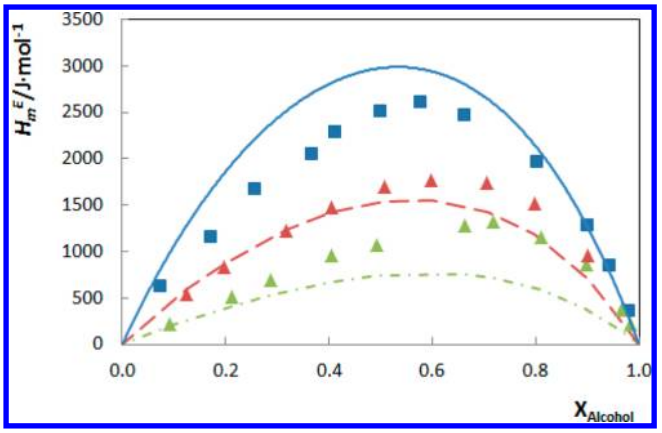

Figure 19. Excess enthalpy of binary mixture {ethanol + [C_4mim][BF_4]}[50] (blue square, full line), {ethanol + [C_4mim][CF_3SO_3]}[18] (red diamond, long dashed line), and {ethanol + [C_4mim][$MeSO_4$]}[50] (green triangle, dashed and dotted line) 308 K.

for a full evaluation of the anion rank, COSMO-RS can provide an excellent qualitative and quantitative description of the system behavior. In the aqueous binary mixtures, the basicity of the IL anion plays a dominant role in which highly basic anions hydrogen bond with water. Although hydrogen bonding between alcohols with IL anion is observed from COSMO-RS, their interaction is weak and cannot compensate for the cost of hydrogen bonding between alcohol−alcohol. This hydrogen bond loss, along with the alcohol electrostatic−misfit poor interaction with ILs, controls the behavior of alcohol + IL systems.

3.2.3. Effect of Alkyl Chain Length of Ionic Liquid Cation. Fixing the alcohol and IL anion, the alkyl chain length of IL influence in the excess enthalpies was studied in selected systems shown in Figure 20 and in the Supporting Information (Figures S32 and S33). The increase of the alkyl chain length of IL cation decreases the excess enthalpy of the binary mixture, as shown in Figure 18 for {ethanol + [C_4mim][BF_4]} and

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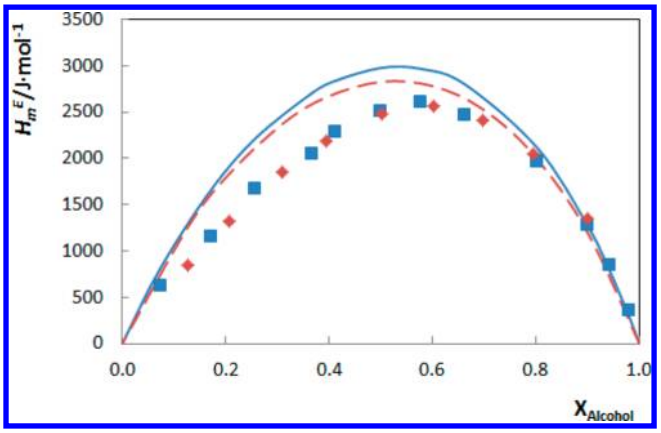

Figure 20. Excess enthalpy of binary mixture {ethanol + [C_4mim][BF_4]}[50] (blue square, full line) and {ethanol + [C_6mim][BF_4]}[23] (red diamond, long dashed line) at 303 K.

{ethanol + [C_6mim][BF_4]}. This trend is found to be independent of both the alcohol and IL nature. Although an alcohol and longer alkyl chain of IL cation leads to higher electrostatic−misfit repulsion forces, the decrease in excess enthalpies is due to a better interstitial accommodation of the alcohol molecule when they reorient themselves during mixing, accounting for higher efficiency of packing. COSMO-RS can satisfactorily predict the excess enthalpies dependency with the alkyl chain length of IL cation family as can be seen in Figure 20 (as well as in Figures S32 and S33 in the Supporting Information).

3.2.4. Effect of the Ionic Liquid Cation Core. As previously observed for binary mixtures of IL with water (Figure 11), the excess enthalpies of binary mixtures containing alcohol also do not vary appreciably with the aromatic nitrogen containing cation, such as imidazolium and pyridinium-based IL, as depicted in Figure 21. Again, slightly higher excess enthalpies

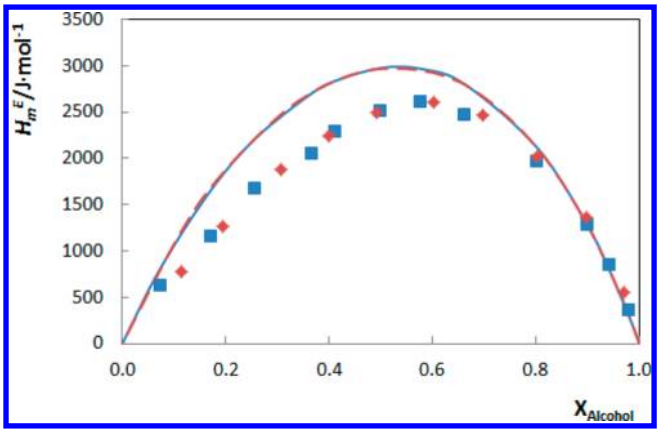

Figure 21. Excess enthalpy of binary mixture {ethanol + [C_4mim][BF_4]}[50] (blue square, full line) and {ethanol + [(3)C_1bpy][BF_4]}[23] (red diamond, long dashed line) at 303 K.

were observed with pyridinium-based ILs. COSMO-RS can correctly predict the excess enthalpies trend experimentally as observed in Figure 21. Other types of nitrogen-containing cations, such as pyrrolidinium and piperidinium, may present similar behaviors. Yet, the experimental data available are too scarce to draw any conclusions concerning this matter at the present.

3.2.5. Effect of Ionic Liquid Cation Isomerism. Figure 22 presents the experimental and the COSMO-RS predictions for

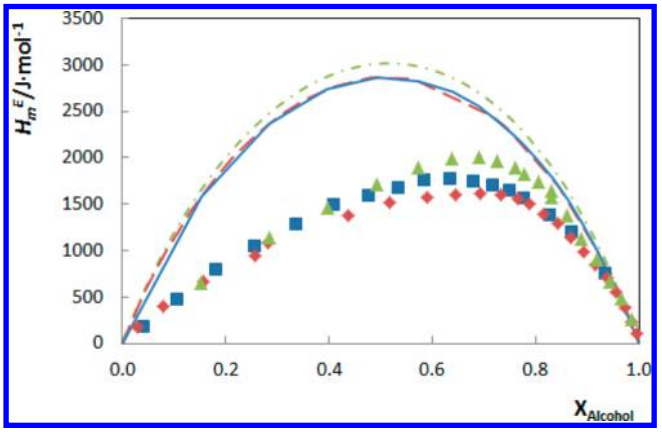

Figure 22. Excess enthalpy of binary mixture {methanol + [(2)C_1bpy][BF_4]}[36] (blue square, full line), {methanol + [(3)C_1bpy][BF_4]}[11] (red diamond, long dashed line), and {methanol + [(4)C_1bpy][BF_4]}[12] (green triangle, dashed and dotted line) at 298 K.

binary system of {methanol + [(x)C_1bpy][BF_4]} at 298 K, where x represents the position of the methyl group in the 1-butylpyridinium−cation. Experimentally, the excess enthalpies of these systems are almost identical, with {methanol + [(4)C_1bpy][BF_4]} presenting a slightly higher endothermic behavior compared to the other two. The prediction of the COSMO-RS method shows a fair quantitative agreement with the experimental data available. Nevertheless, the COSMO-RS adequately describes the higher excess enthalpies of [(4)-C_1bpy][BF_4] compared to the two other isomers, independently of the alcohol type and temperature (as indicated in Figures S34−S39, in the Supporting Information).

In general, it seems that the COSMO-RS proved to adequately predict the excess enthalpies for different alcohol and ILs. The effect of alkyl chain length of IL and alcohol, IL cation core, and anion nature is well described by the COSMO-RS method.

3.3. Binary Mixture of Ketone and Ionic Liquids. The experimental data available on the excess enthalpies of binary mixtures of (ketone + IL) are very scarce.[20,49] Figure 23 presents the experimental and COSMO-RS prediction of excess enthalpies for the binary mixture {acetone + [C_2mim][BF_4]} at

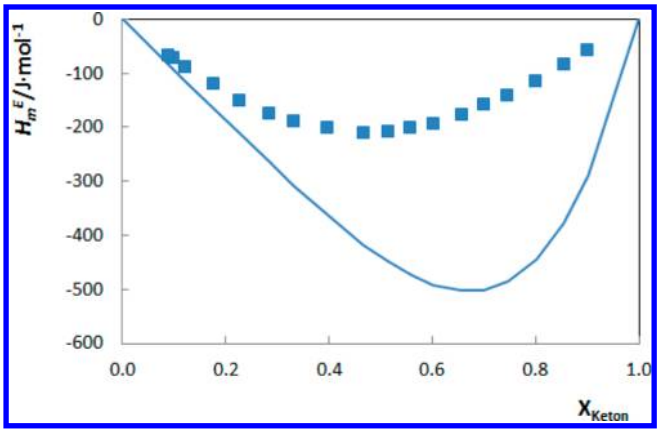

Figure 23. Excess enthalpy of binary mixture {acetone + [C_2mim][BF_4]}[20] (blue square, full line) at 298 K.

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298 K.[20] The excess enthalpies are negative as observed experimentally and predicted by COSMO-RS. On the basis of the COSMO-RS model, the exothermic behavior for this system arises from hydrogen bonding between acetone and the IL cation. On the other hand, the hydrogen bonding between acetone and the IL anion contribution is positive. Nevertheless, the hydrogen bonds of acetone−cation are stronger than acetone−anion and account for their exothermic behavior.

3.3.1. Effect of Alkyl Chain Length of Ketone. Figure 24 shows that exothermic effects are observed for all binary

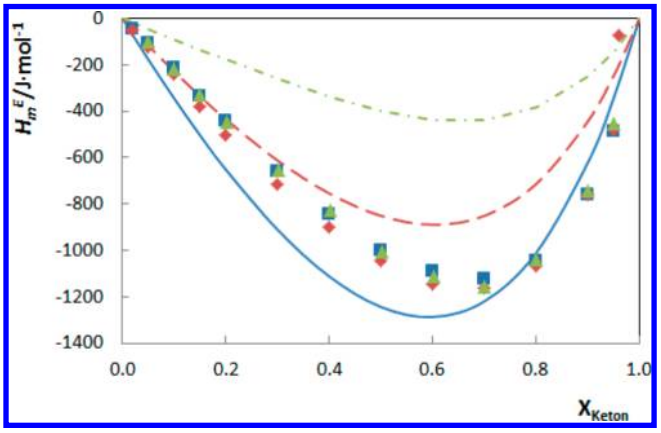

Figure 24. Excess enthalpy of binary mixture {acetone + $[C_6mim][Tf_2N]$}[49] (blue square, full line), {2-butanone + $[C_6mim][Tf_2N]$}[49] (red diamond, long dashed line), and {3-pentanone + $[C_6mim][Tf_2N]$}[49] (green triangle, dashed and dotted line) at 353 K.

mixtures of ketone and ILs, and experimentally, the excess enthalpies of these systems are almost identical. At equimolar concentration, the exothermicity slightly increases from acetone < 3-pentanone < 2-butanone. Despite the ability of COSMO-RS to predict the exothermic behavior for this system, the model fails in describing their correct trend. Yet, the experimental data available for these systems are too scarce to draw any definite conclusions on this matter.

3.3.2. Effect of Alkyl Chain of Ionic Liquid Cation. Figure 25 presents the excess enthalpies for binary systems of {2-butanone + $[C_4mim][Tf_2N]$} and {2-butanone + $[C_6mim][Tf_2N]$} at 353 K. Experimentally, the excess enthalpy for these two systems are almost identical, as is previously observed in

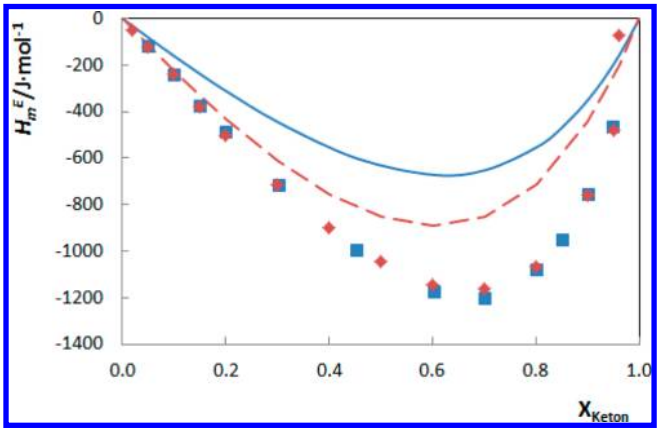

Figure 25. Excess enthalpy of binary mixture {2-butanone + $[C_4mim][Tf_2N]$}[49] (blue square, full line) and {2-butanone + $[C_6mim][Tf_2N]$}[49] (red diamond, long dashed line) at 353 K.

Figure 24. At equimolar composition, $[C_4mim][Tf_2N]$ shows a slightly higher exothermic behavior than $[C_6mim][Tf_2N]$. Again, despite the capability of COSMO-RS to predict the exothermic behavior for these systems, it also fails to produce the trend observed experimentally.

3.4. Binary Mixture of Nitromethane and Ionic Liquids. *3.4.1. Effect of Ionic Liquid Anion.* Figures 26 and

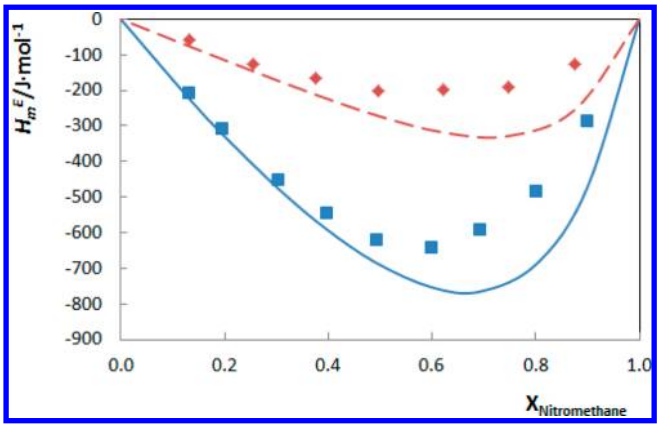

Figure 26. Excess enthalpy of binary mixture {nitromethane + $[C_2mim][EtSO_4]$}[18] (blue square, full line) and {nitromethane + $[C_2mim][CF_3SO_3]$}[18] (red diamond, long dashed line) at 303 K.

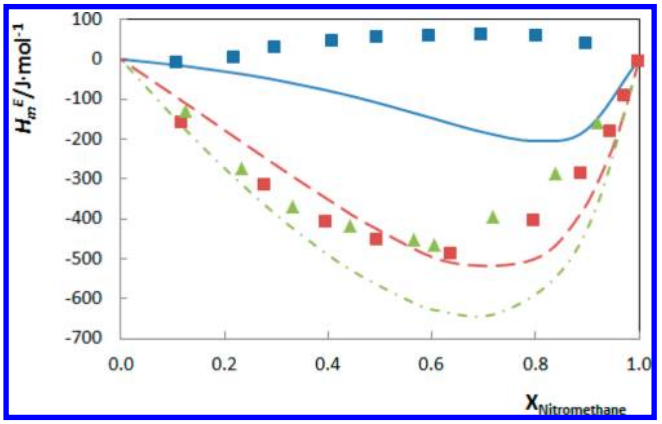

Figure 27. Excess enthalpy of binary mixture {nitromethane + $[C_4mim][CF_3SO_3]$}[18] (blue square, full line), {nitromethane + $[C_4mim][BF_4]$}[50] (red diamond, long dashed line), and {nitromethane + $[C_4mim][MeSO_4]$}[50] (green triangle, dotted and dashed line) at 303 K.

27 present the excess enthalpies of binary mixtures of nitromethane with $[C_2mim]$- and $[C_4mim]$-based ILs, respectively, at 303 K.[18,50] These systems present an exothermic behavior, except for binary mixtures of {nitromethane + $[C_4mim][CF_3SO_3]$} that is endothermic. For $[C_2mim]$-based, the excess enthalpies increase from $[C_2mim][CF_3SO_3]$ to $[C_2mim][EtSO_4]$, while for $[C_4mim]$-based, the exothermicity can be ranked as $[C_4mim][CF_3SO_3]$ < $[C_4mim][BF_4]$ ~ $[C_4mim][MeSO_4]$. Despite the inability of COSMO-RS to predict the behavior of {nitromethane + $[C_4mim][CF_3SO_3]$}, it can correctly predict the other excess enthalpies trend, and their anion dependency, experimentally observed in Figures 26 and 27. The exothermicity of these mixtures arises from strong van der Waals forces between nitromethane and

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ILs. The electrostatic−misfit interaction contributes slightly to the exothermicity, and the hydrogen bond contribution is, surprisingly, positive. Looking at the chemical structure of nitromethane, the oxygen of nitro group could provide a hydrogen bond acceptor. However, the COSMO-RS model shows that the hydrogen bonds interaction energies between nitromethane−cation and nitromethane−anion are positive. The only negative contribution comes from IL is the electrostatic−misfit interaction. It seems that the addition of nitromethane decreases the electrostatic−misfit interaction between cation and anion of IL. Even though the hydrogen bond between nitromethane−cation and nitromethane−anion is energetically unfavorable, the strong van der Waals forces cover the energy loss of hydrogen bond between cation−anion of IL. These strong van der Waals forces are observed for all studied binary mixtures of (nitromethane + IL).

3.4.2. Effect of Alkyl Chain Length of Ionic Liquid Cation. Figure 28 shows that the increase of cation alkyl chain length

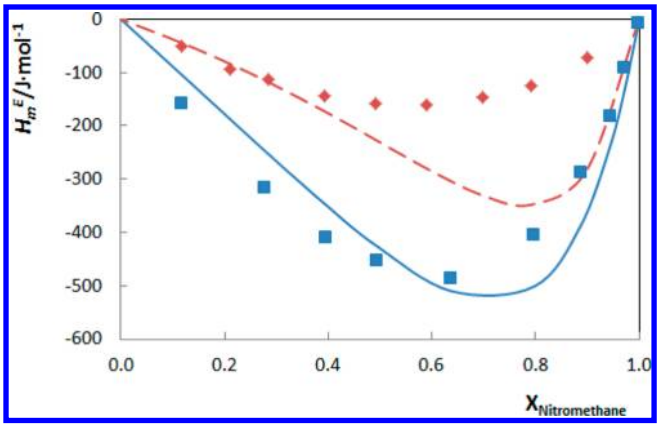

Figure 28. Excess enthalpy of binary mixture {nitromethane + $[C_4mim][BF_4]$}[50] (blue square, full line) and {nitromethane + $[C_6mim][BF_4]$}[18] (red diamond, long dashed line) at 303 K.

decreases the excess enthalpies, as observed experimentally and predicted by COSMO-RS. This is attributed to the stronger interaction of cation and anion in pure $[C_6mim][BF_4]$ than in pure $[C_4mim][BF_4]$. Consequently, more energy is required to disrupt the cation−anion, and this leads to a less negative excess enthalpy for the {nitromethane + $[C_6mim][BF_4]$.

4. CONCLUSION

ILs have been regarded as designer solvents due their tunable properties that can be modified to meet the requirements for task specific applications. However, more often than not, ILs are not expected to be used in the pure state but in mixtures with molecular solvents. To design an IL, it is thus important to understand the interaction between the IL and molecular solvent. COSMO-RS is shown here to be able to provide a priori predictions of the system thermodynamic involving IL and molecular solvents as well as to shed light on the mechanisms that govern their interaction, which is highly relevant for selecting a suitable IL for a practical application. For example, COSMO-RS showed that the interaction between water and IL anion dominates their excess enthalpies through hydrogen bonding; thus the basicity of anion can be modified to meet the requirements for a given application. COSMO-RS is shown to be a qualitative reliable predictive method to estimate the excess enthalpies of binary mixtures of IL and molecular solvents.

Despite the capability of COSMO-RS to correctly predict the behavior of IL and molecular solvent, a few exceptions were also observed, mainly for the system where (unknown) chemical composition changes may occur, as in the case of binary mixtures of water and sulfate-based ILs. Nevertheless, for a system with only physical interaction, COSMO-RS is a good a priori method in the selection or design of suitable IL candidates for a certain task and application before extensive experimental measurements.

■ ASSOCIATED CONTENT

Supporting Information

Supplementary figures as described in the text. This material is available free of charge via the Internet athttp://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +351 234 370200; fax: +351 234 370084; e-mail: jcoutinho@ua.pt.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financed by national funding from FCT-Fundação para a Ciência e a Tecnologia, through the projects PTDC/QUI-QUI/121520/2010 and Pest-C/CTM/LA0011/2013. K.A.K. also acknowledges *FCT* for the postdoctoral grant SFRH/BPD/88101/2012.

■ ABBREVIATIONS

$[C_2mim][EtSO_4]$ = 1-ethyl-3-methylimidazolium ethylsulfate

$[C_2mim][MeSO_4]$ = 1-ethyl-3-methylimidazolium methylsulfate

$[C_2mim][HSO_4]$ = 1-ethyl-3-methylimidazolium hydrogensulfate

$[C_2mim][MeSO_3]$ = 1-ethyl-3-methylimidazolium methanesulfonate

$[C_2mim][DEP]$ = 1-ethyl-3-methylimidazolium diethylphosphate

$[C_2mim][SCN]$ = 1-ethyl-3-methylimidazolium thiocyanate

$[C_2mim][CF_3SO_3]$ = 1-ethyl-3-methylimidazolium trifluoromethanesulfonate

$[C_2mim][TFA]$ = 1-ethyl-3-methylimidazolium trifluoroacetate

$[HO\text{-}C_2mim][TFA]$ = 1-(2-hydroxyethyl)-3-methylimidazolium trifluoroacetate

$[C_2mim][BF_4]$ = 1-ethyl-3-methylimidazolium tetrafluoroborate

$[C_4mim][BF_4]$ = 1-butyl-3-methylimidazolium tetrafluoroborate

$[C_4mim][PF_6]$ = 1-butyl-3-methylimidazolium hexafluorophosphate

$[C_4mim][CF_3SO_3]$ = 1-butyl-3-methylimidazolium trifluoromethanesulfonate

$[C_4mim][CF_3SO_3]$ = 1-butyl-3-methylimidazolium trifluoromethanesulfonate

$[C_4mim][Tf_2N]$ = 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

$[C_4mim][MeSO_3]$ = 1-butyl-3-methylimidazolium methanesulfonate
$[C_6mim][CF_3SO_3]$ = 1-hexyl-3-methylimidazolium trifluoromethanesulfonate
$[C_6mim][BF_4]$ = 1-hexyl-3-methylimidazolium tetrafluoroborate
$[C_6mim][Tf_2N]$ = 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
$[C_6iQuin][SCN]$ = 1-hexylisoquinolinium thiocyanate
$[C_8iQuin][SCN]$ = 1-octylisoquinolinium thiocyanate
$[(2)C_1bpy][BF_4]$ = 2-methyl-1-butylpyridinium tetrafluoroborate
$[(3)C_1bpy][BF_4]$ = 3-methyl-1-butylpyridinium tetrafluoroborate
$[(4)C_1bpy][BF_4]$ = 4-methyl-1-butylpyridinium tetrafluoroborate
[Ch]Lac = cholinium lactate
[Ch]Gly = cholinium glycolate

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