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## ARTICLE

## Ion Speciation: A Key for the Understanding of the Solution Properties of Ionic Liquid Mixtures

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Recently, combination of two (or more) ionic liquids, known as ionic liquid mixtures, are becoming popular and have broad range of application. However, the fundamental knowledge on the molecular interaction that exist in the ionic liquid mixtures is far from being understood. In this work, the experimental measurement of water activity coefficient and computational modelling using Conductor-like Screening Model for Real Solvent (COSMO-RS) were carried out to get an insight into molecular interaction that present in the ionic liquids mixture in aqueous solution. The results shows that the combination of two ionic liquids of different basicity in aqueous solution allow to fine tune the water activities, covering a wide range of values that could replace several pure fluids. This is an important feature resulting from the unexpected ion speciation of the ionic liquid mixtures in aqueous solution.

### Introduction

Ionic liquids are an innovative class of compounds that have received enormous interest from both academy and industry. Their exceptional chemical and physical properties, such as wide liquidus range and negligible vapor pressure at room temperature, make of ionic liquids an alternative to the volatile organic solvents currently used in the industry.<sup>1</sup> Care should be taken as current finding shown that some ionic liquids have remarkable different chemical and thermal stability.<sup>2,3</sup> Nevertheless, the main interest of ionic liquids arise from the possibility to tune their chemical and physical properties by the suitable selection of a cation and an anion turning them designer solvents. In recent years, the design of ionic liquids has been taken to the next level by mixing two (or more) ionic liquids to achieve the desired properties, creating ionic liquids mixtures.<sup>4</sup> Not surprisingly these ionic liquids mixtures are becoming very popular and have known a plethora of applications.<sup>5-14</sup> While the application of ionic liquids mixtures

keeps growing, the fundamental knowledge of the interactions that occur in the system is only beginning to be understood.

Two types behaviour have been observed: (i) some properties of the ionic liquid mixtures could be simply predicted from an interpolation of the properties of the original constituents,<sup>15-25</sup> while (ii) other properties are influenced by numerous interactions occurring among the ions, giving rise to unique solvent properties to the mixture that cannot be easily estimated from the properties of the pure constituents.<sup>26-29</sup> From a thermodynamic point of view, the first type of behaviour is highly desirable as the properties of ionic liquids binary mixtures can be directly obtained from their corresponding values in the pure ionic liquids. In this regard, the desired properties of ionic liquids binary mixtures can be designed by mixing suitably two, or more, pure ionic liquids. Thus, it keeps ionic liquids with a true designer-solvent character. In the same way, insight into binary mixtures that give “unexpected” properties, which differs from the pure constituent, is an important key on developing ionic liquid mixtures with novel properties. The impact of mixing ionic liquids, either with molecular solvent or another ionic liquid, on their solution structure, and consequently on the chemical and physical properties of the obtained mixtures requires further studies.

As part of our studies towards understanding the interaction between ionic liquids and water,<sup>30-33</sup> the aim of this communication is manifold. First, we would like to show that aqueous solutions of ionic liquid binary mixtures (composed by two pure ionic liquids) can be used to target a specific water activity coefficient,  $\gamma_w$  and second, to understand the mixing behaviour of ionic liquid mixtures in aqueous solution at molecular level. This was attempted using a combination of experimental and computational modelling approaches that provide detailed information for the solvent-solute behaviour

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upon mixing. The Conductor-like Model for Real Solvent (COSMO-RS) allows a molecular insight for the interaction energies of ionic liquids in the pure and mixtures state.<sup>34</sup> In principle, the interaction energies between the cation and the anion of an ionic liquid, as well as between these ions with other solute, can be calculated using *ab initio* and density functional theory featured in COSMO-RS.<sup>34,35</sup> This has been done for a broad number of ionic liquids covering many different cations and anions. The estimated interaction energies are in perfect agreement with the measured cation-anion interaction strength using nuclear magnetic resonance spectroscopy.<sup>36</sup> Thus, we present here an approach for directly studying the strength of interaction energies between the cation and the anion in pure ionic liquid, as well as of these ions with water molecule in the mixture state. At the end, we expect to be able to evaluate how much of an ionic liquid is present as free cation and anion in aqueous solution, or exist as ion pair, or other speciation. The amount of these free cations and anions depends on the degree of dissociation,  $\alpha_D$ , similar to what has been observed for salts in aqueous solutions. This ion speciation is reflected on their affinity toward water molecules. We will then discuss the conditions under which ionic liquids will dissociate into free ions, or form ion pairs.

## Results and Discussions

The present study reconciles results, which have been published<sup>30-32</sup> by us recently, together with a set of new data, with particular emphasis on getting detail information about the structural features that may have impact on the physical and chemical properties of aqueous solutions of one or two ionic liquids. Firstly, we would like to discuss the  $\gamma_w$  in the aqueous solution of an ionic liquid.<sup>†</sup> In Figures 1 and 2, it is shown that the  $\gamma_w$  values in a series of ionic liquids with different head group and alkyl chain length, respectively, are lower than unity. This indicates the favourable interaction between ionic liquids with water in the aqueous solution. A good prediction of  $\gamma_w$  values using COSMO-RS was also observed, demonstrating the feasibility of this model to forecast the solution properties of ionic liquids. According to COSMO-RS, the dissolution of water into ionic liquids depends mainly on the hydrogen bonding of (i) cation-anion interaction energies in the pure state and (ii) anion-water interaction energies in aqueous solution.<sup>†</sup> For example, the stronger hydrogen bonding between cation – anion interaction of [C<sub>4</sub>C<sub>1</sub>im]Cl ( $\Delta H_{HB} = -29.48 \text{ kJ}\cdot\text{mol}^{-1}$ ) leads to its weaker interaction with water molecule compared to [C<sub>4</sub>C<sub>1</sub>pip]Cl ( $\Delta H_{HB} = -13.70 \text{ kJ}\cdot\text{mol}^{-1}$ ) because a higher energy is required to disrupt the hydrogen bonding in the former ionic liquid, so does to let Cl anion to interact with water molecule. Thus, the idea is, to maximize the interactions with water the anion should be “free” to interact with the water molecules.

Both experimental and COSMO-RS results confirm that the  $\gamma_w$  values in the presence of cations with different head group or alkyl chain length do not vary significantly. The situation changes enormously when  $\gamma_w$  is measured in a series of anions with the same cation, for instance 1-butyl-3-methylimidazolium cation. Figure S in reveals two different behaviours for the

activity coefficient of water in aqueous solution: (i) The  $\gamma_w$  value is higher than unity for ([C<sub>4</sub>C<sub>1</sub>im][CF<sub>3</sub>SO<sub>3</sub>] + H<sub>2</sub>O) binary mixture throughout all the composition range and for ([C<sub>4</sub>C<sub>1</sub>im][SCN] + H<sub>2</sub>O) binary mixture at at IL infinite dilution, and (ii) for the remaining aqueous solutions of ionic liquids the  $\gamma_w$  is lower than unity indicating favourable interactions between ionic liquid and water. The ([C<sub>4</sub>C<sub>1</sub>im][OAc] + H<sub>2</sub>O) binary mixture presents the strongest interaction, followed by ([C<sub>4</sub>C<sub>1</sub>im][DMP] + H<sub>2</sub>O), ([C<sub>4</sub>C<sub>1</sub>im][CH<sub>3</sub>SO<sub>3</sub>] + H<sub>2</sub>O), ([C<sub>4</sub>C<sub>1</sub>im]Cl + H<sub>2</sub>O). Note that the activity coefficient of water in these four binary mixtures are close to each other, differing slightly only. The other three binary mixtures also display values close with each other and can be ranked as ([C<sub>4</sub>C<sub>1</sub>im][TOS] + H<sub>2</sub>O), followed by ([C<sub>4</sub>C<sub>1</sub>im]Br + H<sub>2</sub>O) and the weakest interaction are in ([C<sub>4</sub>C<sub>1</sub>im][TFA] + H<sub>2</sub>O) mixture. It is, however, thought-provoking to highlight that while COSMO-RS is able to predict  $\gamma_w$  in ionic liquids that have activity coefficient of water lower than unity, the same cannot be said for the system with  $\gamma_w$  higher than 1.

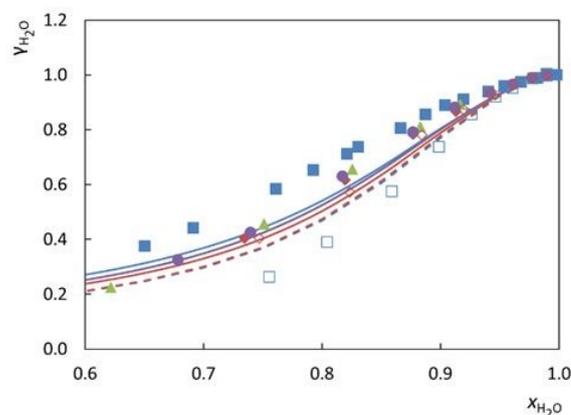


Figure 1. Water activity coefficient ( $\gamma_{H_2O}$ ) of (ionic liquids + H<sub>2</sub>O) as function of mole fraction of water,  $x_{H_2O}$ , in the mixture at 298.2 K. Symbols: (■), [C<sub>4</sub>C<sub>1</sub>im]Cl; (◆), o-[C<sub>4</sub>C<sub>1</sub>py]Cl; (▲), m-[C<sub>4</sub>C<sub>1</sub>py]Cl; (●), p-[C<sub>4</sub>C<sub>1</sub>py]Cl; (◻), [C<sub>4</sub>C<sub>1</sub>pip]Cl; and (◐), [C<sub>4</sub>C<sub>1</sub>pyrr]Cl. The symbols represent experimental<sup>32</sup> and lines the predicted values using COSMO-RS.

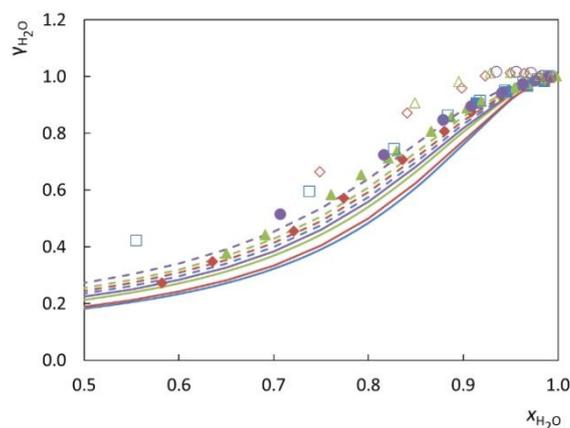


Figure 2. Water activity coefficient ( $\gamma_{H_2O}$ ) of (ionic liquids + H<sub>2</sub>O) as function of mole fraction of water,  $x_{H_2O}$ , in the mixture at 298.2 K. Symbols: (■), [C<sub>1</sub>C<sub>1</sub>im]Cl; (◆), [C<sub>2</sub>C<sub>1</sub>im]Cl; (▲), [C<sub>4</sub>C<sub>1</sub>im]Cl; (●), [C<sub>5</sub>C<sub>1</sub>im]Cl; (◻), [C<sub>6</sub>C<sub>1</sub>im]Cl; (◐), [C<sub>7</sub>C<sub>1</sub>im]Cl; (△), [C<sub>8</sub>C<sub>1</sub>im]Cl; and (◑), [C<sub>10</sub>C<sub>1</sub>im]Cl. The symbols represent experimental<sup>32</sup> and lines predicted values using COSMO-RS.

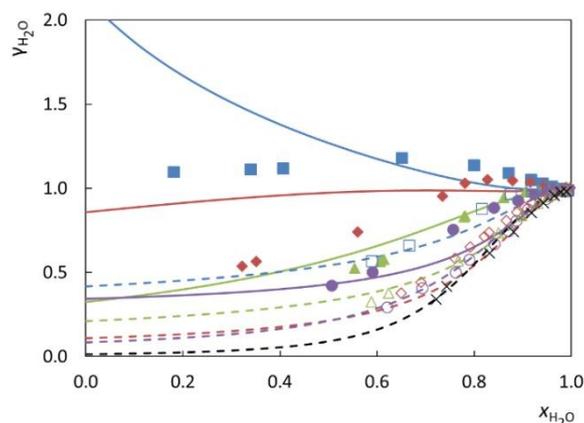


Figure 3. Water activity coefficient,  $\gamma_{H_2O}$ , of (ionic liquids +  $H_2O$ ) as function of mole fraction of water,  $x_{H_2O}$ , in the  $([C_4C_1im]A + H_2O)$  at 298.2 K. Symbols: (■),  $[C_4C_1im][CF_3SO_3]$ ; (◆),  $[C_4C_1im][SCN]$ ; (▲),  $[C_4C_1im][TFA]$ ; (●),  $[C_4C_1im]Br$ ; (□),  $[C_4C_1im][TOS]$ ; (◇),  $[C_4C_1im]Cl$ ; (△),  $[C_4C_1im][CH_3SO_3]$ ; (○),  $[C_4C_1im][DMP]$ ; and (×),  $[C_4C_1im][OAc]$ . The symbols represent experimental<sup>32</sup> and lines predicted values using COSMO-RS.

As previously mentioned, the interaction of ionic liquids and water depends on the availability of “free” ions to interact with the water molecules, and subsequently, throughout the computational modelling ionic liquids were always treated as completely dissociated into a cation and an anion. However, the inability of COSMO-RS to properly predict the  $\gamma_w$  in  $([C_4C_1im][CF_3SO_3] + H_2O)$  and  $([C_4C_1im][SCN] + H_2O)$  binary mixtures lead us to question whether these ionic liquids do exist as “free” cation and anion in the aqueous solution, or not. Herein we start to dissect the structure and equilibrium properties of ionic liquids in aqueous solution. Ionic liquids are, by definition, composed solely by cations and anions, similar to a salt. In aqueous solution, some salts dissociate to produce “free” cation and anions, which subsequently get hydrated by water molecules. The degree of dissociation and hydration depends on the nature of the counterion. Lima and co-workers<sup>37</sup> have showed that the degree of counterion dissociation,  $\alpha_D$ , of 0.1 M dodecyltrimethylammonium triflate,  $[N_{12,111}][CF_3SO_3]$ , in aqueous solution is just 0.1, considerably lower than that of dodecyltrimethylammonium chloride,  $[N_{12,111}Cl]$  ( $\alpha_D = 0.5$ ) and dodecyltrimethylammonium bromide,  $[N_{12,111}Br]$  ( $\alpha_D = 0.3$ ).<sup>38,39</sup> Using molecular dynamics, Lima and co-workers<sup>37</sup> showed that the interaction energies between dodecyltrimethylammonium cation and triflate anion were dominated by the electrostatic term, corresponding to nearly 70% of the total  $[N_{12,111}]^+ - [CF_3SO_3]^-$  interaction, strongly suggesting ion pair formation between these cation and anion at the micellar interface. In another communication, Benoit and Buisson<sup>40</sup> reported that the hydration of any large ions, such as tetraethylammonium cation ( $[N_{2222}]^+$ ), tetrabutylammonium cation ( $[N_{4444}]^+$ ),  $[CF_3SO_3]^-$ , is negligible compared to the hydration of the small ions, for instance  $Li^+$ ,  $Na^+$  and  $Cl^-$ . This finding on the ion pairing is supported by a recent report from Weingärtner and co-workers.<sup>41</sup> They showed that the formation of contact ion pairs, or at least neutral aggregates of ion pairs, lead to electrical conductance minima and liquid-liquid

miscibility gaps. Thus, their finding showed that salts composed by  $[CF_3SO_3]^-$  have a higher tendency for ion pairing with the respective cation, and consequently, a lower ability to completely dissociate into individual ions. This ion pairing obviously reduces the number of anions available to interact with water molecules. Therefore, the key to the description of the solution properties of ionic liquids is the concentration of “free” cations and, to a large extent, anions in the aqueous media.

Thus, for the purpose of investigating the possibility of the formation of free ions ( $[C]^+$  and  $[A]^-$ ) and ion-pair ( $[CA]$ ) in the aqueous solution of  $[C_4C_1im][CF_3SO_3]$  COSMO-RS was used to model the  $\gamma_w$  by varying speciation in the aqueous solution by varying the degree of dissociation. Note that in the previous COSMO-RS modelling, ionic liquids were always treated as individual cation + anion, or in other word as 100% free ions, ( $[C]^+$  and  $[A]^-$ ). As can be seen from Figure 4, when we assumed that all cation and anion available as free ion, the COSMO-RS model is unable to accurately depict the  $\gamma_w$  in aqueous solution of  $[C_4C_1im][CF_3SO_3]$ , especially in the ionic liquid-rich region. Better predictions can be achieved by reducing the amount of free ion as low as 10%. It seems that at 0% of free ions, this ionic liquid is slightly more repulsive toward water molecules. The presence of 10% of free ion, increases their interaction with water molecule, this is due to the presence of free  $[CF_3SO_3]^-$  to interact with the water molecules. Thus, the 10% of free ion, or  $\alpha_D = 0.1$ , is the optimum condition of  $[C_4C_1im][CF_3SO_3]$  in the aqueous solution. This value is similar to that reported by Lima and co-workers.<sup>37</sup> Therefore, the experiments and computational modelling reported here, shed light on the existence of ion speciation of ionic liquids in aqueous solution. In this regard, some ionic liquids, for example  $[C_4C_1im]Cl$  and  $[C_4C_1im][OAc]$  have a high dissociation degree in aqueous solution, while others, such as  $[C_4C_1im][CF_3SO_3]$  have just a minor degree of dissociation.

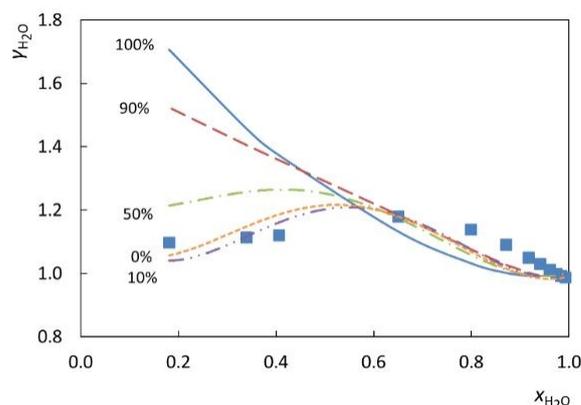


Figure 4. The experiment and predicted  $\gamma_w$  in aqueous solution of  $[C_4C_1im][CF_3SO_3]$  at 298.2 K. The symbols represent experimental and lines predicted values using COSMO-RS with different dissociation degrees of ionic liquid.

The ion pairing of ionic liquid  $[C_4C_1im][CF_3SO_3]$  in the aqueous solution might be explained in terms of the existence of more favourable interactions among salt ions agreement to the “law of matching water affinity” proposed by Collins.<sup>42</sup>

According to this law, opposite charged ions tend to form contact ion pairs in the solution if they have equal affinity for water molecule, but will separate if their water affinities are very different. It seems that since both  $[C_4C_1im]$  cation and  $[CF_3SO_3]$  anion have similar affinities toward water molecules, and as consequence, in aqueous solution they tend to bind together by electrostatic interactions. On the opposite,  $[C_4C_1im]$  cation and Cl anion arguably have very different affinities toward water molecules, the latter showing significantly higher interactions. As a result, the  $[C_4C_1im]$  cation and the Cl anion prefer to exist as free ions in the aqueous solution, with a small amount of other speciation that may be present.

One can argue that ion speciation is influenced by the concentration of salt, or in this case of the ionic liquid in the solution, as shown in a previous work using a polyvalent cations.<sup>43</sup> Nevertheless, at present time, the information about ion speciation of ionic liquid in aqueous solution as function of its concentration is still absent. The idea that we want to highlight here is that not all ionic liquids are present as free cation and anion in aqueous solution, some of them may exist as ion pairs like demonstrated using COSMO-RS modelling. This ion speciation seems to control the solution properties of ionic liquids.

Fostered by the results obtained for a single ionic liquid in aqueous solution we went further by studying solutions containing two ionic liquids. For this purpose, we combined the ionic liquids  $[C_4C_1im]Cl$  and  $[C_4C_1im][CF_3SO_3]$ , showing significant differences in their basicity and degree of dissociation in aqueous solution. Would these two ionic liquids keep their individual demeanor intact in the mixture? Or, would they interact with each other?

Figure 5 shows the plot of  $\gamma_w$  in the aqueous solution of  $([C_4C_1im][CF_3SO_3] + [C_4C_1im]Cl)$ . Interestingly, the  $\gamma_w$  values vary significantly in-between these parent ionic liquids, meaning that a suitable combination of these two ionic liquids in aqueous solution should be able to produce specific  $\gamma_w$  values as several pure ionic liquids could do, as depicted in Figure S3 in ESI<sup>†</sup>. This result further confirms the design-ability of ionic liquid mixtures. Nevertheless, our interest is not only to show the design-ability of ionic liquid mixtures, but also to understand the molecular mechanism behind this ternary mixture, in particular concerning ion speciation. Accordingly, COSMO-RS was also used to model the aqueous solution of  $([C_4C_1im][CF_3SO_3] + [C_4C_1im]Cl)$  that consist of  $H_2O$ ,  $[C_4C_1im]^+$ ,  $[CF_3SO_3]^-$ , and  $Cl^-$  as separate species. Unfortunately, but expectedly, this model is unable to predict the solution properties.<sup>†</sup> This suggests that  $[C_4C_1im]^+$ ,  $[CF_3SO_3]^-$ , and  $Cl^-$  for these mixtures in aqueous solution might not be present as fully dissociated ions. Thus, the first step is to venture the possibility of ion pairing in the system and redo the computational modelling using COSMO-RS. With the aid of mass spectroscopy,<sup>†</sup> we could identify several ion species that exist in aqueous solution composed of  $([C_4C_1im][CF_3SO_3] + [C_4C_1im]Cl)$ , which are depicted in Figure 6. Among these several species, only  $[C_4C_1im]^+$  and  $([C_4C_1im]_2Cl)^+$  have appreciable  $\gamma_w$  values, as predicted using COSMO-RS,<sup>†</sup> while other species does not have much interaction with water molecules.

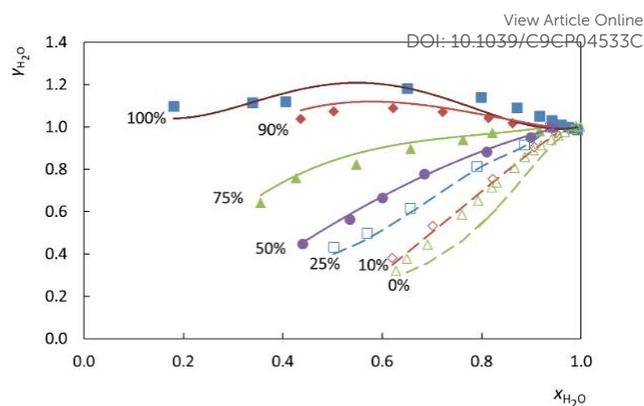
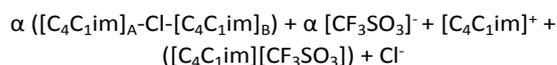


Figure 5. Experiment and predicted (COSMO-RS)  $\gamma_w$  at 298.2 K in aqueous solutions containing the ionic liquids mixtures of the type  $([C_4C_1im]Cl)_m([C_4C_1im][CF_3SO_3]_{1-m})$ , where  $m$  is weight fraction,

In the first binary mixture composition, with 0.1 weight fraction of  $[C_4C_1im]Cl$ , there are excess amount of  $[C_4C_1im][CF_3SO_3]$ . Taking cue from the dissociation degree, as mentioned above, we assumed that  $[C_4C_1im]Cl$  exists as “free”  $[C_4C_1im]$  cation and Cl anion in the aqueous solution, while  $[C_4C_1im][CF_3SO_3]$  follow the neutral ion pair  $[CA]$ .<sup>†</sup> In addition, based on the mass spectroscopy, it is also plausible that the cation prefers to interact with the stronger hydrogen bond acceptor anion, in this case the Cl anion, to form the cluster of  $([C_4C_1im]_A-Cl-[C_4C_1im]_B)$  cation. Note that the subscript A and B refers to the origin of  $[C_4C_1im]$  cation, either from  $[C_4C_1im]Cl$  or  $[C_4C_1im][CF_3SO_3]$ , respectively. If this interpretation is correct, we should observe a better prediction of  $\gamma_w$  in the aqueous solution of this binary mixture of ionic liquids. Indeed, applying the same procedure for aqueous solution of  $([C_4C_1im]Cl)_m([C_4C_1im][CF_3SO_3]_{1-m})$ , where  $m = 0.1$  and 0.25 weight fraction, Figure 5 shows the good results obtained for the prediction of  $\gamma_w$  using COSMO-RS. Thus, at  $m = 0.1$  and 0.25, according to COSMO-RS model, there are  $([C_4C_1im]_A-Cl-[C_4C_1im]_B)$  cations counter balanced by  $[CF_3SO_3]^-$ , and the ion pair  $([C_4C_1im][CF_3SO_3])$  in the aqueous solution. Accordingly, throughout the COSMO-RS modelling, it was assumed the following ion speciation exist in the aqueous solution of  $([C_4C_1im][CF_3SO_3] + [C_4C_1im]Cl)$ :



Throughout the modelling, it was always assumed that  $\alpha = 0.1$ , similar value to dissociation of  $[C_4C_1im][CF_3SO_3]$  in the aqueous solution as described above, and the remaining species sum to balance.<sup>†</sup> Note that, in order to predict the  $\gamma_w$  using COSMO-RS, the positive charge must be equal to the negative charge, so does in this work, the positive charge of  $([C_4C_1im]_A-Cl-[C_4C_1im]_B)$  cation is balanced by sum of  $[CF_3SO_3]^-$  and Cl anions. Remarkably, our strategy produces a very good description of the  $\gamma_w$  values in the aqueous solution of ionic liquids mixtures, suggesting that the proposed approach finely captures the ion speciation in these aqueous solutions.

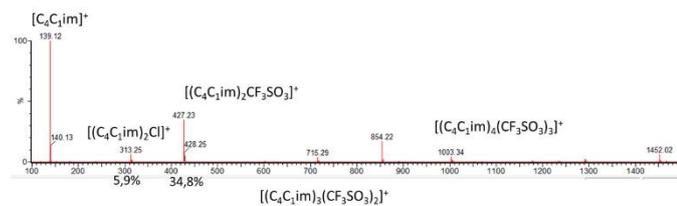


Figure 6. Mass spectroscopy spectrum of aqueous solution of  $[(C_4C_1im)[CF_3SO_3] + [C_4C_1im]Cl]$

To summarize, in this study, we have showed that the combination of two ionic liquids in aqueous solution could produce a broad range of  $\gamma_w$  values that could replace the use of several pure ionic liquids to achieve the same. Most importantly, using computational modelling, we have demonstrated that ion speciation, such as the presence of free ion,  $[C]^+$  and  $[A]^-$ ; ion pair  $[CA]$  and cluster  $[C-A-C]^+$  in aqueous solution can be estimated using COSMO-RS. The knowledge of ion speciation, although an estimate through computational modelling, allows us to determine the “free” ionic liquid cation and anion in the aqueous solution that is responsible for their interaction with water molecule. Overall, these results are a first step to a better understanding of the structural features of the ionic liquids in aqueous solution. A further step will be the ion speciation in the dynamics of these systems. This understanding, and obviously, a proper evaluation of exact amount of each species in the aqueous solution at given condition will allow better understanding how to design ionic liquids solutions presenting a given set of target properties.

## METHODOLOGY

### Chemicals

The ionic liquids  $[C_4C_1im]Cl$  and  $[C_4C_1im][CF_3SO_3]$  were acquired from Iolitec GmbH with a mass purity greater than 99%. Prior to the measurement of water activity, the ionic liquids were dried under vacuum ( $p = 1$  Pa), at moderate temperature (*circa* 303.15 K) and continues stirring for at least 48 hours. This procedure aimed at reducing the water content and other volatile compound that might presence in the sample. After drying, the water content was measured using a Metrohm 831 Karl Fischer coulometer, with the analyte Hydranal Coulomat AG from Riedel-de-Haën, and the values was found to be lower than 200 ppm. Ultra-pure water (double distilled, passed through a reverse osmosis unit, and further treated using a milli-Q plus 185 water purification apparatus) with a resistivity of 18.2  $M\Omega\cdot cm$ , a total organic carbon lower than 5  $\mu g\cdot L^{-1}$ , and particles smaller than 0.22  $\mu m$  was used to prepare the aqueous solution of binary mixture of ionic liquids.

### Measurement of water activity

The water activity,  $a_w$ , was measured using a Novasina hygrometer LabMaster- $a_w$ , Switzerland, similar to our previous work.<sup>30-32</sup> The instrument works based on the resistive-electrolyte method. Prior to the measurement of aqueous

solution of binary mixture of ionic liquids, the instruments were regularly calibrated using standard solution (with  $a_w$  values ranging from 0.0113 to 0.973) provided by the supplier. In addition, the instrument was also calibrated frequently using either aqueous solution of KCl or  $CaCl_2$  with different molalities, depending on the  $a_w$  values to be measured. The obtained  $a_w$  values were compared with data reported in the literature.

For each measurement, the samples were prepared by weighting predetermined composition of  $[C_4C_1im][OAc]$ ,  $[C_4C_1im][CF_3SO_3]$ , and water using analytical balance (model ALS 220-4N from Kern) with an accuracy of  $\pm 0.002$  g. Approximately 2-3  $cm^3$  of the mixtures were then transferred into the measuring dishes and put into the airtight equilibrium chamber inside the instrument. The instrument is equipped with built-in temperature sensor with the uncertainty of  $\pm 0.15$  K. The exchange of free water takes place until the partial pressure of water vapor reaches the equilibrium, which is confirmed by means of stable values of  $a_w$ . The water activity coefficient,  $\gamma_w$ , value is the calculated from the  $a_w$  according to the following equation:

$$\gamma_w = \frac{a_w}{x_w} \quad (1)$$

where  $x_w$  is the mole fraction of water in the mixture. The accuracy of the instruments is found to be  $0.001a_w$ .

### Measurement of mass spectroscopy

Electrospray ionization tandem mass spectra (ESI-MS-MS) were obtained using a Micromass Q-ToF 2 (Micromass, Manchester, U.K.), operating in the positive (or negative) ion mode, equipped with a Z-spray source. Source and desolvation temperatures were 353 and 373 K, respectively.<sup>44</sup> Aqueous solution of ionic liquid binary mixtures in methanol, at concentrations of  $\sim 10^{-4}$   $mol\cdot dm^{-3}$ , were introduced at a 10  $mm^3\ min^{-1}$  flow rate. The capillary and the cone voltage were 2600 V (or 3000 V) and 30 V, respectively. Nitrogen was used as the nebulization gas, whereas argon as the collision gas.

### Computational Modelling

The computational modelling used in this work is Conductor-like Screening Model for Real Solvents (COSMO-RS). It is well-established method based on unimolecular quantum calculations developed by Klamt and co-worker.<sup>34,45</sup> COSMO-RS is not only able to predict the thermophysical properties of compounds, but also can be used to understand the molecular interaction occur in the given system. The computational modelling to predict the water activity coefficient consists of two main steps. In the first step, the continuum solvation COSMO calculation of electronic density and molecular geometry of  $[C_4C_1im]$  cation, Cl and  $[CF_3SO_3]$  anions, and  $[C_4C_1im]-Cl-[C_4C_1im]$  complex cation were optimized using TURBOMOLE V7.3 2018 software program package on the density functional theory level, utilizing the BP functional B88-P86 with a triple- $\zeta$  valence polarized basis set (TZVP) and the resolution of identity standard (RI) approximation.<sup>46</sup> In the second step, the water activity coefficient in the aqueous

solution of ionic liquid mixture was determined by means of COSMOtherm software using parameter BP\_TZVP\_C30\_1701 (COSMOlogic, Levekusen, Germany).<sup>45</sup> Otherwise stated, the ionic liquids are always treated as a one to one cation/anion mixture, and the ions are treated at the quantum chemical level separately, and therefore, it is possible to analyze the contribution of cation and anion to the predicted properties. The detail of the COSMO-RS calculation on estimating the chemical potential is given in the COSMOtherm User's Manual.<sup>45</sup>

The activity coefficient of component  $i$  is related to its chemical potential  $\mu_i$  through the following equation,

$$\gamma_i = \exp\left(\frac{\mu_i - \mu_i^0}{RT}\right) \quad (2)$$

where  $\mu_i^0$  is the chemical potential of the pure compound  $i$ ,  $R$  is the ideal gas constant, and  $T$  is the absolute temperature.

The most important output from COSMO-RS model is the interaction energies between cation and anion of ionic liquid. Small changes in the electronic environment, for example, adding ionic liquid into water or vice versa, will cause a change in interaction energies between cation, anion, and water. Thus, the COSMO-RS model allows both chemical structure and cation – anion – water interactions to be probed on a molecular level providing vital information on the impact of structural changes upon mixing. In the molecular approach, COSMO-RS model focuses on three specific interaction, namely the electrostatic – misfit energy,  $H_{MF}$ , hydrogen bonding energy,  $H_{HB}$ , and van der Waals energy,  $H_{vdW}$ . These energies are described in Equations 3-5, respectively:

$$H_{MF} = a_{\text{eff}} \frac{\alpha}{2} (\sigma + \sigma')^2 \quad (3)$$

$$H_{HB} = a_{\text{eff}} c_{HB} (0; \min(0; \sigma_{\text{donor}} + \sigma_{HB}) \times \max(0; \sigma_{\text{acceptor}} - \sigma_{HB})) \quad (4)$$

$$H_{vdW} = a_{\text{eff}} (\tau_{vdW} + \tau'_{vdW}) \quad (5)$$

where  $a_{\text{eff}}$  is the effective contact area between two surface segments,  $\alpha$ 's is the interaction parameter,  $\sigma_{HB}$  is the hydrogen bond strength that the threshold for hydrogen bonding, and the last two  $\tau_{vdW}$  and  $\tau'_{vdW}$  are elements of specific van der Waals interaction parameters.

In addition, the cation – anion – water interaction energy was also estimated by COSMO-RS using the excess enthalpies as the difference in the enthalpy of the studied cation, anion, or water molecules in its mixture and pure state, according to the following equation:

$$H_{E,i}(\text{interaction}) = H_{i,\text{mixture}}(\text{interaction}) - H_{i,\text{pure}}(\text{interaction}) \quad (6)$$

The  $H_{E,i}$  (interaction) in the COSMO-RS model originates from summing the three specific interaction as described in Equations 3-5. Thus, it can be expressed as,

$$H_{E,m} = H_{E,MF} + H_{E,HB} + H_{E,vdW} \quad (7)$$

Therefore, the COSMO-RS model could provide the information required for the evaluation of molecular interaction occur of ionic liquids in the pure state, as well as in the aqueous solution, as contribution of cation, anion, and water molecules.

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## Conflicts of interest

There are no conflicts to declare.

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