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Designing ionic liquids for absorptive cooling†

Kiki Adi Kurnia,^a Simão P. Pinho^{b,c} and João A. P. Coutinho^{*a}

A computational methodology for designing ionic liquids (ILs) with an enhanced water absorption capacity to be used in absorption-refrigeration systems is presented here. It is based on increasing the hydrogen bond (HB)-acceptor ability of the anion and combining it with a cation that presents a weak cation–anion interaction. Employing this strategy, we identified and prepared three novel dianionic ILs with an enhanced water absorption capacity, larger than LiBr.

Ionic liquids (ILs) are novel compounds resulting from the combination of a large and asymmetric organic cation with weakly coordinating anions that have gained worldwide attention due to their unusual properties and wide application range.¹ In particular, the hydrophilic ILs have been considered to be promising alternatives as absorbents for absorption-refrigeration (AR) systems. The reason for the interest in using ILs as absorbents is the desire to improve the AR system cycle performance, due to the drawbacks of the conventional working-fluid pair combinations in the AR technology, such as low operating pressure, crystallization, and corrosion for the LiBr–H₂O system, and low system performance, the need for a rectification process of the refrigerant streams, and high driving heat source temperature for the H₂O–NH₃ system.^{2–4} Since the discovery of ILs, many families, especially those based on imidazolium cations, have been investigated as absorbent media in the AR systems. They have been studied

due to their high solvation toward water and organic compounds, thermal stability, and very low flammability that are well suited as absorbent media in AR systems. A number of brief overviews of the literature on using ILs as working fluids in the absorption-refrigeration system have appeared to keep readers abreast of the rapidly expanding subject.^{5–8}

One of the main features of ILs is that their physical properties can be finely tuned to meet the requirement of specific applications, and thus they are regarded as “designer” solvents. Yet, the rational designing of ILs, while targeting novel structures and desired properties, is still at the trial-and-error level, and therefore, remains a formidable task. Therefore, in this communication, the design-ability of these compounds is explored aiming at designing ILs with an enhanced water absorption capacity that can be used as absorbents in AR systems. To rationalize the design it is necessary to consider the behaviour of water molecules in the pure and mixture state. Using COSMO-RS, we observe that the σ -profile of water (*cf.* Fig. S1a in the ESI†) presents a series of peaks within three regions, with strong peaks in both positive and negative polar regions. The high polarized charge at 1.8 e nm⁻² corresponds to the oxygen atom fragment (red coloured polar surface of H₂O in Fig. S1a in the ESI†), indicating its ability to act as a strong hydrogen bond acceptor. As a consequence, H₂O has the potential to act as a hydrogen bond acceptor, as displayed in their σ -potential (*cf.* Fig. S1b in the ESI†). On the other hand, the hydrogen atoms present a peak within the positive region at -1.6 e nm⁻² (blue coloured polar surface of H₂O in Fig. S1a in the ESI†) allowing water to act as a strong hydrogen bond donor. This reflects the amphoteric character of the water molecule,⁹ with an excellent ability to act both as a donor and an acceptor for hydrogen bonding. This can be used as an input to design potential ILs with high affinity towards water molecules. In this way, it is necessary to design ILs that can act as either hydrogen bond donors or acceptors. However, it can be appreciated that conventional ILs behave mostly as hydrogen bond acceptors,¹⁰ hence as will be shown later the hydrogen bond (HB)-basicity of ILs plays a major role, and thus the design is focused on creating ILs with high

^aDepartamento de Química, CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal. E-mail: jcoutinho@ua.pt; Fax: +351-234-370084; Tel: +351-234-370200

^bAssociate Laboratory LSRE/LCM, Instituto Politécnico de Bragança, 5301-857 Bragança, Portugal

^cUNIFACS-Universidade de Salvador, 41770-235 Salvador, Brazil

† Electronic supplementary information (ESI) available: Sigma profile and potential of water and ions composing selected ILs; excess enthalpy of binary mixtures of water and selected ILs; name and abbreviation of ions composing the ILs; experimental activity coefficient of water at infinite dilution reported in the literature along with the predicted values using COSMO-RS; predicted activity coefficient of water at infinite dilution in 4760 screened ILs; experimental water activity and activity coefficient of binary mixtures of water and phosphonium-based ILs, along with COSMO-RS prediction. See DOI: 10.1039/c4gc00954a

HB-basicity. In addition, a series of small peaks within the non-polar region leads to a decrease in attraction of water molecules towards non-polar fragments of the other compounds in the mixture. Therefore, for example, increasing the alkyl chain of ILs increases their non-polar character and this leads to a decrease in their interaction with water molecules.

Knowing water behaviour, the next stage is to screen the potential ILs by tuning the cation and anion while targeting the desired properties, that is, the ILs with high water absorption capacity. In view of the thermodynamics criterion for selecting the AR working pair, the IL–water interaction can be characterized by the water activity coefficient at infinite dilution, γ_w^∞ .¹¹ In this way, the lower the γ_w^∞ is, the higher the solute–solvent interaction in the system, and *vice versa*. Based on this criterion, mixtures with γ_w^∞ lower than unity present absorption capacity and are usually classified as exhibiting negative deviations from Raoult's law (ideality) and this is often associated with exothermic mixing behaviour.¹¹ Prior to using COSMO-RS[‡] to screen the potential ILs, it is worth mentioning that in a previous work, we had evaluated the performance of this modelling tool to predict the γ_w^∞ in ILs.¹² The result is given in Tables S1 and S2 in the ESI.† The predictions obtained demonstrate the reliability of COSMO-RS to estimate the activity coefficient of water at infinite dilution in ILs.

Encouraged by the evaluation result, we then turned our attention to use COSMO-RS to screen and design ILs with enhanced water absorption capacity. In this way, we used COSMO-RS for screening 4760 ILs as potential absorbents. The

computational screening was performed over ILs covering an extensive variety of cation head groups that have been reported in the literature, such as imidazolium, pyridinium, pyrrolidinium, piperidinium, morpholinium, quinolinium, sulfonium, ammonium, and phosphonium. In regard to the anion, using experimental and COSMO-RS modelling, we recently reported an extended hydrogen bond basicity ranking for a wide range of anions.¹³ The carboxylate-based ILs are placed on the top position of ILs with higher HB basicity. Therefore, here we evaluated the dianionic oxalate, succinate, and maleic as anions with enhanced HB basicity. The name and abbreviation of all ions used in the screening are given in Table S3 in ESI,† while the predicted activity coefficient at infinite dilution in the screened ILs between 293.15 and 363.15 K is given in Table S4 in ESI.† For comparison, a contour plot of $\ln \gamma_w^\infty$ in 4760 screened ILs at 298.15 K is shown in Fig. 1. The series of ILs with the same anion share similar γ_w^∞ , as indicated by the colour. This further corroborates the idea that the basicity of the anion plays a major role on their interaction with water, whereas the cation head group has a secondary influence, and the alkyl chain has the smallest impact. These structural variations definitely can be used to fine-tune the physical properties of ILs to meet the requirement of task specific application. The ILs composed of carboxylate anions display higher affinity toward water molecules, regardless of the type of cation. Furthermore, the results also showed that the interaction of ILs with water can be enhanced by increasing the HB basicity of the anion while combining it with cations that have

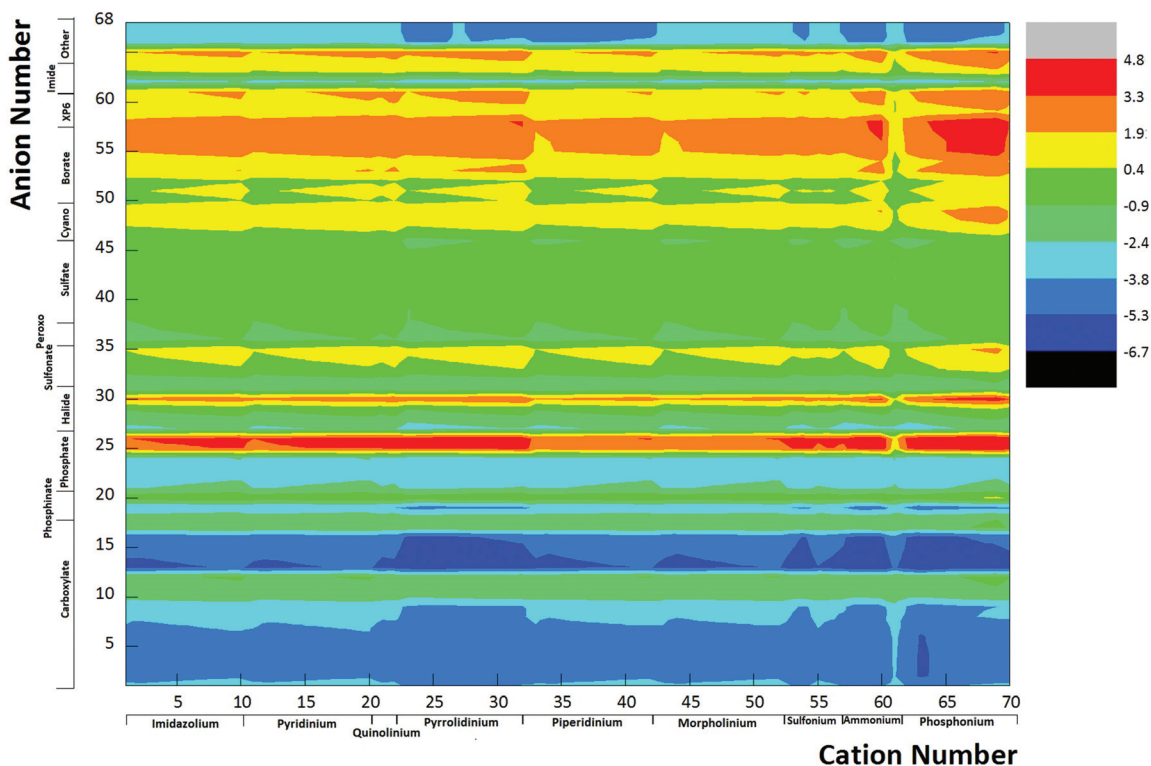


Fig. 1 Predicted natural logarithm of water activity coefficient at infinite dilution in 4760 ILs at 298.15 K using COSMO-RS.

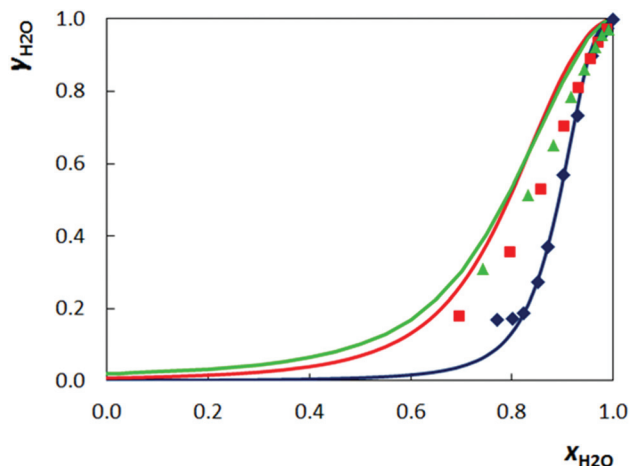


Fig. 2 Experimental and predicted activity coefficient of water in ILs using COSMO-RS at 298.15 K. Symbols: (◆, —), $[P_{4444}][Ac]$; (■, —), $[Ch][Ac]$;¹⁴ (▲, —), $[C_4C_1im][Ac]$.¹⁴ The symbols and lines represent experimental and COSMO-RS predictions, respectively.

weak cation–anion interactions. Fig. 2 presents a comparison of the activity coefficients for three ILs that share the same $[Ac]^-$ anion. The activity coefficient of water in $[P_{4444}][Ac]$ is the lowest among the ILs studied, and this is due to the weakest hydrogen bonding cation–anion interaction ($\Delta H_{HB}, [P_{4444}][Ac] = -20.69 \text{ kJ mol}^{-1}$) compared to the other ($\Delta H_{HB}, [Ch][Ac] = -81.25 \text{ kJ mol}^{-1}$ and $\Delta H_{HB}, [C_4C_1im][Ac] = -39.72 \text{ kJ mol}^{-1}$). The weakest hydrogen bonding between $[P_{4444}]^+$ and $[Ac]^-$ enhances the ability of the anion to hydrogen bond with water. On the other hand, strong hydrogen bonding between $[C_4C_1im]^+$ and $[Ch]^+$ with $[Ac]^-$ reduces the ability of the anion to hydrogen bond with water. A combination of dianionic carboxylates with non-cyclic cations leads to improved water absorption capacity, with phosphonium-based ILs displaying the strongest enhancement among them.

With the purpose of validating the strategy design used in this work to enhance ILs affinity toward water molecules, it can be summarized as by weakening the cation–anion interaction and enhancing the anion basicity, we prepared a series of novel dianionic phosphonium-based ILs, namely tetrabutylphosphonium oxalate, $[P_{4444}]_2[Ox]$; tetrabutylphosphonium succinate, $[P_{4444}]_2[Suc]$; and tetrabutylphosphonium maleate, $[P_{4444}]_2[Malc]$, and measured the water activity of their aqueous solution at 298.15 K by applying the method described by Khan *et al.*¹⁴ The results, along with the activity coefficients derived from them, are reported in Table S5 in ESI.†

In addition, we also prepared several other phosphonium-based ILs combined with different anions such as acetate, $[Ac]^-$, propanoate, $[Pro]^-$, butanoate, $[But]^-$, trifluoroacetate, $[TFA]^-$, and salicylate, $[Sal]^-$ aiming at further studying the impact of the anion on its interaction with water molecules. To the best of our knowledge, only $[P_{4444}][Ac]$ and $[P_{4444}][TFA]$ were previously reported in the literature.¹⁵ Fig. 3 shows the comparison between experimental and predicted activity coefficients of water using COSMO-RS. Experimental measurements

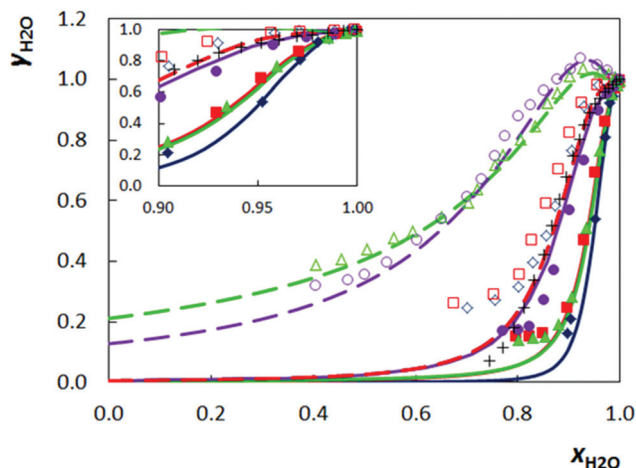


Fig. 3 Experimental and predicted activity coefficient of water in ILs using COSMO-RS at 298.15 K. Symbols: (◆, —), $[P_{4444}]_2[Ox]$; (■, —), $[P_{4444}]_2[Suc]$; (▲, —), $[P_{4444}]_2[Malc]$; (●, —), $[P_{4444}][Ac]$; (○, ---), $[P_{4444}][Pro]$; (□, ---), $[P_{4444}][But]$; (△, ---), $[P_{4444}][TFA]$; (◇, ---), $[P_{4444}][Sal]$; and (+), $LiBr$.¹⁶ The symbols and lines represent experimental and COSMO-RS predictions, respectively.

show that the selected dianionic ILs present a very high interaction with water as predicted by COSMO-RS. The best results are obtained for $[P_{4444}]_2[Ox]$ due to the highest anion basicity and weaker cation–anion interaction that lead to spontaneous interaction of the anion with water molecules. Increasing the number of anion alkyl chains, as in the case from $[P_{4444}]_2[Ox]$ to $[P_{4444}]_2[Suc]$, as anticipated, reduces their interaction with water due to an increase in the hydrophobic character of the anion. Substituting a single bond in $[P_{4444}]_2[Suc]$ with a more polar double bond, as in the case of $[P_{4444}]_2[Malc]$ just slightly increases the interaction of water with the latter ILs. Nevertheless, these three dianionic ILs possess improved affinity towards water molecules when compared to the monovalent anion phosphonium-based ILs. Accordingly, the anion can be ranked based on increasing interaction with water as the following: $[Sal]^- < [TFA]^- \ll [But]^- < [Pro]^- < [Ac]^- \ll [Suc]^{2-} \sim [Malc]^{2-} \ll [Ox]^{2-}$. In addition, it is striking to observe that the proposed novel dianionic ILs present superior interaction with the water molecule when compared to a conventional absorbent used in the current AR system, $LiBr$.¹⁶ This result shows that the proposed novel dianionic ILs may have potential to replace the $LiBr$ used in the AR technology.

The high water absorption capacity of dianionic ILs and the anion trend described above is well predicted by COSMO-RS. Based on COSMO both monovalent and divalent ions present peaks within the negative region with the latter possessing two times the intensity of the former, indicating their improved HB basicity character (*cf.* Fig. S2a in the ESI†). In regard to $[Ox]^{2-}$, it also displays a decrease of the peak within the non-polar region. Thus it translates into a high water affinity. The $[Suc]^{2-}$ and $[Malc]^{2-}$ present slightly higher peak intensities on the negative region, however it is also accompanied by an increment in their non-polar region that makes them less attracted towards water when compared to $[Ox]^{2-}$.

The systems studied also enable us to further evaluate the impact of the alkyl chain length as well as the fluorination and aromatization of the ILs anion. The decrease of water affinity with increasing the alkyl chain of the anion is due to the decrease of the anion polar character. As observed in Fig. S2b in the ESI,[†] the [Ac]⁻, [Pro]⁻, and [But]⁻ present a similar peak within the negative area, nevertheless the peak within the non-polar region increases from [Ac]⁻ to [Pro]⁻ to [But]⁻. On the other hand, the fluorination and aromatization of the anion, as in the case of [TFA]⁻ and [Sal]⁻, shift the peak in the negative area closer to the non-polar region. In addition, both [TFA]⁻ and [Sal]⁻ also present high peaks within the non-polar region. The fluorination and the aromatization both decrease the basicity of the anion and increase its hydrophobicity, thus decreasing their affinity towards water molecules. The decrement in basicity that translates directly into a reduction of its ability to form hydrogen bonding with water molecules is clearly displayed in Fig. S3a in the ESI,[†] in which [TFA]⁻ and [Sal]⁻ present relatively lower exothermicity compared to [Ac]⁻.

Aiming at further exploring the mechanism of water solvation, COSMO-RS was used to probe the type of interaction occurring in the system. It should be pointed out that in a previous work we established the reliability of COSMO-RS to estimate the excess enthalpies of binary mixtures composed of ionic liquids and water.¹⁰ Unfortunately, there are no experimental excess enthalpy data available in the literature for the systems studied, but the ability of the model to describe the activity coefficient data shown in Table S4 in ESI,[†] the highly consistent conclusions found in our previous work following a similar approach, and the demonstrated capability to describe the excess enthalpies^{10,17} gives us confidence on COSMO-RS to further characterize the interactions between water and ionic liquids. The dominant interactions present in the system, as expected, are hydrogen bonding between IL anion and water, as displayed in Fig. S3b in the ESI,[†] which highly contribute to the exothermicity of the system. The electrostatic-misfit interaction and van der Waals forces also contribute, albeit to a minor extent, to the exothermicity of the mixture. In addition, it is interesting to see the feature observed in Fig. S3a in the ESI,[†] while the monoanionic ILs present maxima of excess enthalpy at $x_{\text{H}_2\text{O}}$ ca. 0.6, dianionic ILs show maxima at regions of further water dilution, approximately at 0.9. This indicates that the dianionic ILs form hydration complexes with a higher number of water molecules when compared to the monoanionic ILs. In other words, the dianionic anion could absorb more water molecules than the monoanionic ILs.

In summary, in this work a design strategy to improve the water absorption capacity is proposed. It is based on decreasing the cation–anion interaction and enhancing the basicity of the anion, supported by the COSMO-RS results. Employing this strategy, the dianionic ILs selected and prepared are shown to present a remarkably high water absorption capacity. When the strong basic anions are combined with a cation that possesses weak cation–anion hydrogen bonding interaction, the affinity toward water molecules is greatly improved.

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Notes and references

[†]The prediction of γ_{∞}^{∞} in the ILs using COSMO-RS consists of two steps. In the first step, the distinct COSMO files were generated for cations and anions using the BP functional B88-p86 with a triple- ξ valence polarized (TZVP) basis set and the resolution of identity standard (RI) approximation using the TURBOMOLE 6.1 program package.¹⁸ The subsequent calculations consist mainly of statistical thermodynamics and were performed using COSMOtherm. The parameterization BP_TZVP_C30_1301 (COSMOlogic GmbH & Co KG, Leverkusen, Germany),¹⁹ which is required for the calculation of physicochemical data and contains intrinsic parameters of COSMOtherm and element specific parameters, was adopted.

[§]The phosphonium-based ILs were synthesized by the acid–base neutralization method. For example, synthesis of [P₄₄₄₄]₂[Ox] was achieved by stirring the mixture of [P₄₄₄₄][OH] (40%) aqueous solution and oxalic acid, with a molar ratio of 2 : 1, at the temperature 60 °C under reflux for 48 h. To remove the water by-product the mixtures were first subjected to rotary evaporator and then by drying the ILs under vacuum at 0.01 mbar with constant stirring for 96 hours at the temperature 60 °C. Note that a long time is required to dry [P₄₄₄₄]₂[Ox] due to its highly hygroscopic nature. After this procedure, the purity of the synthesized ILs was checked by ¹H and ¹³C NMR as well as their water content. The same method was also applied to prepare the other phosphonium-based ILs. The [P₄₄₄₄]₂[Ox], [P₄₄₄₄]₂[Suc], and [P₄₄₄₄]₂[Malc] are white solids with melting temperature 38, 41, and 40 °C, respectively, while the others are liquid. The water content of each ionic liquid was determined by Karl Fischer titration (Mettler Toledo DL32 Karl Fischer coulometer using the Hydranal – Coulomat E from Riedel-de Haen as an analyte) and found to be less than 100 ppm.

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