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A. Maiti, A. Kumar, R. D. Rogers

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Water-clustering in hygroscopic Ionic Liquids – an implicit solvent analysis

Amitesh Maiti,[§,*] Arvind Kumar,[¶] and Robin D. Rogers[¶]

Lawrence Livermore National Laboratory, Livermore CA 94550

Center for Green Manufacturing and Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487

Abstract:

Most ionic liquids are known to be hygroscopic to varying degrees, and that can be detrimental or useful depending upon the application in question. Water can accumulate slowly over hours or days to saturation levels corresponding to the humidity level. When designing or deploying a new ionic liquid it is important to be able to estimate its maximum moisture absorbing ability at the temperature and pressure of its operation. With this goal in mind we have carried out computational studies on three ionic liquid systems based on $[BF_4]^-$, $[PF_6]^-$, and $[Tf_2N]^-$ anions and 1–alkyl-3-methyl-imidazolium ($[C_n mim]^+$) cations within an implicit solvent formalism. For highly hygroscopic systems like $[C_n mim][BF_4]$ we find that non-iterative calculations with single water molecules can lead to significant underestimation of the maximum moisture content, while iterative calculations can result in miscibility behavior qualitatively different from experimental observations. On the other hand, the inclusion of small hydrogen-bonded water-clusters up to an appropriately chosen size not only yields quantitative consistency, but also leads to the reproduction of a number of thermodynamically interesting phase behaviors, including limited-solubility to full-miscibility transitions as a function of temperature and as a function of the alkyl chain length of the imidazolium cation. For hydrophobic systems like $[C_n mim][PF_6]$ and $[C_n mim][Tf_2N]$ the computed solubility (for each n) is found to have a smooth convergence behavior as a function of the largest cluster-size considered, with the results for the larger clusters being close to that obtained by iterative calculations with single water molecules.

[§] Lawrence Livermore National Laboratory

[*] Corresponding author, E-mail: amaiti@llnl.gov

[¶] The University of Alabama

I. Introduction:

Ionic Liquids (ILs) (salts with melting points <100 ^{o}C) [1] normally comprise of large asymmetric organic cations and inorganic or organic anions of varying sizes. Because of their modular nature and unique accessible physicochemical properties, which may include very low vapor pressure, high thermal stability, large liquidus range, high ionic conductivity, and high solvating ability towards organic or inorganic solutes, ILs have found widespread applications in many areas of chemistry [2]. The ionic nature of the ILs essentially makes them hygroscopic, and complete drying of ILs is extremely difficult [3]. The presence of water in the ILs largely affects the interionic interactions and alters their physical properties such as viscosity, electrical conductivity, reactivity or solvating ability to a significant extent [4]. Therefore, it is important to understand the details of ion-water interactions at a molecular-level both experimentally and theoretically. Knowledge of the mutual solubility of water and ILs is essential for a variety of reasons, including; (i) for the utilization of very low water solubility (hydrophobic) ILs as an extraction media for organic compounds from aqueous solutions and consequently developing novel separation processes [5], (ii) for assessing the bioaccumulation impact of ILs, mainly the toxicity in aquatic environments [6], (iii) for enhancing or reducing the mutual solubility of organic solvents with the ILs where water acts as a cosolvent or antisolvent [7, 8], or (iv) for investigations on the effects of moisture content on the rates and selectivity of organic reactions in the IL media [9].

The mutual solubility of IL-water systems has been extensively studied experimentally [9-13]. The role of water in ILs is complex, and depends on the constituent ions and supramolecular structure of the IL. Interactions between water and ILs have been studied at the molecular level using light scattering and various spectroscopic techniques, particularly vibrational spectroscopy [9a, 16]. Molecular level studies reveal the existence of different molecular states of water in the IL rich region wherein the water interacts with the anion. It is also inferred that the water molecules can change the conformation of the alkyl side chain of the cation by making a hydrogen bonding network with the anions and consequently displacing the anion positions.

It has been observed that for a given dialkyl-imidazolium cation the amount of water that can be taken up by the IL increases with the increasing hydrogen bond basicity of the anion [16e], whereas for a given anion it decreases with the increase in alkyl chain length of the cation. Imidazolium ILs having $[Tf_2N]^-$ anions are highly hydrophobic with relatively low viscosity [9a] and are interesting for organics extraction from aqueous phases. ILs with $[PF_6]^-$ are also highly hydrophobic and usually show a phase split with water [9r,s]. Extremely low solubility of these ILs with water can be decisive in extraction applications and needs to be modeled accurately.

On the other hand, $[C_n mim][BF_4]$ ILs show interesting phase behavior depending upon the length of the alkyl chain of the imidazolium cation. $[C_2mim][BF_4]$ and $[C_4mim][BF_4]$ are completely miscible with water at room temperature [7, 9b,i, 11]. The phase behavior of $[C_4mim][BF_4]$ suggests an upper critical temperature of ~ 5 ^{o}C above which it is completely miscible and below which it displays finite solubility [12], which decreases with decrease in temperature [9b]. ILs for $n > 4$ are hygroscopic at room temperature with a finite moisture adsorption ability that decreases with increasing n [8, 13]. With increasing temperature the degree of hygroscopicity in all

these ILs increases. Thus, $[C_6mim][BF_4]$ and $[C_8mim][BF_4]$ become fully miscible at temperatures above ~ 60 ^oC and 70 ^oC, respectively [10c, 14-16]. Such temperature-controlled biphasic or homogeneous IL-water systems can be highly important in useful chemical reactions and product separation [17].

It is clear from the experimental results published to date, that the interactions of ILs with water can be as varied as the nature of the ions that can form ILs themselves, but also that when developing an IL application it is critical to be able to estimate its maximum moisture absorbing ability at the temperature and pressure of its operation. In this report we present our initial results aimed at understanding and predicting the interactions of water with ILs by computationally exploring interactions of water with ILs based on 1–alkyl-3-methyl-imidazolium $[C_nmim]^+$ cations and three anions of various degrees of hygroscopicity, i.e., $[BF_4]^-$, $[PF_6]^-$, and $[Tf_2N]^-$.

II. Common Theoretical Methods:

To cut down on the number of experiments that can be both time-consuming and expensive, it is often desirable to estimate the maximum solubility of water (i.e., maximum moisture content) in various solvent media through computational means. In addition, computational methods can often provide molecular-level insights into various interactions that may not be easily discernable from experiments. A computation of water-solubility in an IL involves determining the difference in chemical potential between the solute (water) in the solvent phase (IL) and the solute in its source phase (liquid water or water vapor). There are theoretical procedures to compute such chemical potential differences from first-principles, e.g., through simulations using advanced sampling techniques, e.g., umbrella sampling [18], free energy perturbation [19], thermodynamic integration [20], or constrained molecular dynamics [21]. However, several roadblocks to the accurate usage of any of the above techniques remain. For instance, although first-principles calculations can yield accurate forces for any given solute-solvent configuration, they are limited to very small system sizes, while developing accurate interaction potentials (or force fields) can become an intensive effort in itself. In addition, the internal degrees of freedom of complex IL molecules make it difficult to sample all relevant phase space within limited simulation times.

Given the above challenges to first-principles simulations, researchers have developed alternative statistical mechanical, equation-of-state (EoS), or correlation-based methods to model the vapor-liquid equilibrium (VLE) or liquid-liquid equilibrium (LLE) of water-IL systems [22]. Wang *et al.* [22a] presented a heteronuclear-square-well chain fluid (SWCF) EoS to estimate the VLE of several members of the $[Tf_2N]^-$ IL family in alcohols and water, whereas, similar systems were modeled by Llovell *et al.* [22b] using statistical associating fluid theory (SAFT) EoS. A new pathway to the quantification of aqueous ion solvation was shown by Ranke *et al.* [22c], making use of the relative weakness of interactions between IL ions as compared to their hydrophobicities. Tsioptsias *et al.* [22d] described the phase behavior of binary systems containing $[Tf_2N]^-$ imidazolium ILs with several organic solvents and water using the non-random hydrogen-bonding (NRHB) model. Other models such as NRTL, Wilson, UNIQUACK, UNIFAC, or modified UNIFAC have also been used to correlate the LLE or VLE of organic solvents or water with ILs [22e-h].

COSMO-RS [23, 24], a model based on unimolecular quantum chemistry calculations has been used for the prediction of LLE of systems containing ILs and organic solvents or water [9m-o, 25]. This model has some advantages over traditional approaches such as the structure-interpolating group-contribution methods (GCMs), EoS, and correlation-based methods, all of which require a large experimental database prior to their effective use. COSMO-RS is readily able to provide a qualitative description of the solubility dependence on temperature and IL structural variations.

III. Basic hygroscopicity calculation with COSMO-RS

The simplest calculation of maximum water solubility involves computing the pseudo-chemical potential (μ^*) [26] of a water molecule in the IL environment and determining the difference ($\Delta\mu = \mu_{IL}^* - \mu_{self}^*$) from the chemical potential in its own liquid environment. Then the maximum equilibrium mole fraction of water in the IL is given by:

$$x_{water} = \exp(-\beta\Delta\mu), \text{ where } \beta = (k_B T)^{-1} \quad (1)$$

where k_B and T are the Boltzmann constant and the absolute temperature respectively. The above equation is accurate under the condition of high dilution, i.e., low mole fraction of water in the IL when any possible water-water interaction within the IL environment can be neglected. On the other hand for ILs that are even moderately hygroscopic, the above assumption breaks down. In such a situation one would like to solve the above equation iteratively, i.e., the mole fraction $x^{(i)}$ at iteration i is given by:

$$x^{(i)} = \exp(-\beta\Delta\mu^{(i-1)}) \quad (2)$$

where $\Delta\mu^{(i-1)}$ is the change in pseudo-chemical potential when one removes a water molecule from its own liquid environment to a water/IL solution consisting of $x^{(i-1)}$ mole fraction of water (the initial condition being set as $x^{(0)} = 0$). Ideally, for a system with limited hygroscopicity one expects that the difference between the computed x between successive iterations decreases, thereby leading to a converged value of x within a few iterations, while for a miscible system one expects to see a progressive increase of $x^{(i)}$ with increasing iterations, thereby leading to divergence in solution.

In the COSMO-RS method [23, 24] one represents both the solute and solvent molecules by the histogram of their surface screening charges called the σ-profile. All interactions, including coulombic, van der Waals, and hydrogen bond interactions are then defined in terms of these σ-profiles. One can use this formalism to compute the partition function, the Gibbs free energy, and many other thermodynamic quantities, including pseudo-chemical potentials that can be used to estimate the quantity $\Delta\mu$ discussed above. COSMO-RS has been parameterized and widely tested for small charge-neutral solute species in a variety of solvent systems, both charge-neutral and ionic, including a wide variety of ILs.

As in our previous work [27, 28] we used the Density Functional Theory (DFT) code Turbomole [29, 30] to compute the σ-profile for each molecule or ion using the Becke-Perdew (BP) exchange-correlation functional [31, 32] and an all-electron representation using the triple-zeta valence basis set with correlation (TZVP) [33, 34]. From extensive tests on the aqueous solubility a large dataset of drug molecules or organic solutes it appears that COSMO-RS incurs an average error of the order of ≥ 0.3 log units [24, 35]. Based on the above, an accuracy of the computed solubility to within a factor of ~3 can be considered reasonable. At the same time, the COSMO-RS errors appear to be systematic within a given class of IL solvents, and accurate *trends* can still be obtained [28, 36], e.g., as a function of the length of the alkyl functional groups on the cation, or as a function of the basicity of the anion.

The aim of the present paper is to see if the COSMO-RS computed $\Delta\mu$ is able to quantitatively reproduce the experimentally observed water-solubility in various ILs, more specifically in the IL series [$C_n$mim][BF_4], [$C_n$mim][PF_6], and [$C_n$mim][Tf_2N] [n = 2, 4, 6, 8, 10]. In particular, we wanted to determine the accuracy of such a method in computing the maximum water-solubility, and also to see if such an approach can reproduce the limited-solubility to miscibility transitions displayed by the [$C_n$mim][BF_4] system as a function of n and temperature T.

IV. Solubility calculations with single water molecules

The first set of COSMO-RS calculations was carried out on the solubility of single water molecules in the [$C_n$mim][BF_4] system [n = 2, 4, 6, 8, 10] at two different temperatures, i.e., 0 ^{o}C and 25 ^{o}C. The $\Delta\mu$ values were computed using the parameter settings discussed in the previous section. The results are listed in Table 1. Some of the interesting points of note are:

(1) When using eq. (1) (i.e., non-iterative solution) the computed solubility for all n at both temperatures are at least a factor of 5 (or more) smaller than the corresponding experimental value. It also yields $\Delta\mu > 0$ in all cases, and therefore does not yield the known miscibility for smaller-alkyl-chain cations at room temperature.

(2) The iterative solution yields acceptable agreement (within a factor of 2-3) for [C_8mim][BF_4] and [C_{10}mim][BF_4], and correctly predicts full miscibility for [C_2mim][BF_4] and [C_4mim][BF_4]. However, the iterative solution incorrectly predicts full miscibility for [C_6mim][BF_4] at all three temperatures.

(3) Both the non-iterative and iterative solutions correctly predict the *trend* of decreasing solubility with increasing n. However, the iterative solution predicts a much stronger variation of solubility as a function of n than experimentally observed, while the variation predicted by the non-iterative solution as a function of n is in better agreement with the experimental solubility values.

V. Inclusion of water clusters

Given the discussion in the previous section we deemed it an interesting exercise to perform non-iterative calculations in which small hydrogen-bonded water clusters are explicitly considered. We wondered if such a strategy could lead to an overall improvement of the solubility results, including the limited-solubility to miscibility transition at around 5 ^{o}C as exhibited by the [C_4mim][BF_4] system. To employ this strategy we interpret the IL as providing a solvent environment in which a finite number of single water molecules and small hydrogen-bonded water clusters form in the IL medium. The solute molecules and clusters are assumed to interact with the IL only and not with each other, thereby justifying a non-iterative procedure.

In order to derive an expression for the maximum water solubility in this case, consider a system of N IL molecules (i.e., ion-pairs) in contact with pure liquid water. Suppose that at thermodynamic equilibrium a set of $\{n_i\}$ water clusters of size i are adsorbed in it, where i = 1,2, 3, …., i_{max}, and a cluster of size i means a hydrogen-bonded complex of i water molecules. For a fixed number of IL pairs one can obtain the equilibrium number of absorbed water clusters $\{n_i\}$ by maximizing the following partition function:

$$Z = \frac{(N + \sum_{i=1}^{i_{max}} n_i)!}{N! n_1! n_2! .. n_{i_{max}}!} \exp\left\{ -\beta \sum_{i=1}^{i_{max}} n_i \Delta\mu_i \right\} \tag{3}$$

where $\Delta\mu_i$ is the pseudo-chemical potential difference of a water-cluster of size i between the IL environment and a pure liquid water environment. Maximizing ln(Z) above with respect to $\{n_i\}$ yields the following set of coupled equations:

$$\frac{y_i}{1 + \sum_{j=1}^{i_{max}} y_j} = \exp(-\beta\Delta\mu_i) \, , \; i = 1, 2, \ldots, i_{max} \tag{4}$$

where $y_i = n_i/N$, i.e., the mole ratio of water-clusters of size i relative to the number of IL pairs.

Finally, the net mole ratio of water: IL is computed as:

$$y = \sum_{i=1}^{i_{max}} i y_i = \frac{n_{water}}{n_{IL}} \qquad . \tag{5}$$

If we neglect any cluster-cluster interaction (our basic assumption) all chemical potentials $\Delta\mu_i$ are concentration-independent, and dependent only on the chemical structure of the IL and temperature. This makes eq. (4) a linear system that can be solved by simple Matrix inversion. As a consistency check, we note that eq. (4) becomes identical to eq. (1) when for $i > 1$ the condition $\beta\Delta\mu_i >> 1$ is satisfied (i.e., $\Delta\mu_i >> k_B T$ for $i > 1$), i.e., only single water molecules are allowed and any cluster formation is thermodynamically prohibitive.

In order to use eqs. (4) and (5) one first needs to decide on the maximum cluster size i_{max}. To this end, we note that any reasonable calculation should be limited to small values of i_{max}. This is because: (1) COSMO-RS parameters were optimized for relatively small (and charge-neutral), compact solute molecules. Clusters larger than a few molecules are likely to undergo significant structural deformation or changes within the confined geometries of IL adsorption sites. Such deformations are not taken into account into the COSMO-RS formalism. (2) The lowest-energy hydrogen-bonded water clusters of sizes 2, 3, 4, and 5 have well-defined cyclical structures (for n = 3, 4, 5) (see Fig. 1); larger clusters (beginning with n = 6) have non-cyclical structural isomers [37] which makes the analysis complicated. We show below that clusters of size up to 4 yields interesting results for the [$C_n$mim][BF_4] system. All results shown below involve calculating the pseudo-chemical potentials $\Delta\mu_i$ by COSMO-RS using the standard BP-TZVP settings as mentioned in section II.

Fig. 2 displays the cluster-calculation results for maximum water solubility at 25 ^oC in the [$C_n$mim][BF_4] system [n = 2, 4, 6, 8, 10]. Four different cluster results are shown for each IL, i.e., in which water-clusters up to (and including) size 1, 2, 3, and 4 were considered. To clarify, the calculation with i_{max} = 3 includes clusters of sizes 1, 2, and 3, while the calculation with i_{max} = 4 includes clusters of sizes 1, 2, 3, and 4, etc. Fig. 2 also includes the corresponding iterative solution using single water molecules (from Table 1) and experimental numbers from two different research groups. From the results of Fig. 2 some of the interesting points of note are:

(1) The experimental numbers fall somewhere between i_{max} = 3 and i_{max} = 4 results except for [C_{10}mim][BF_4] where the experimental number is slightly higher than the i_{max} = 4 value. This would suggest that the maximum size of the clusters formed in such IL's is 4 or less.

(2) All cluster calculations consistently predict decreasing solubility with increasing alkyl-chain-length n. However, the variation as a function of n increases with increasing cluster size, although it is not as high as that predicted from the iterative solution.

(3) At T = 25 ^oC the i_{max} = 4 calculation correctly predicts full miscibility of water with [C_2mim][BF_4] and [C_4mim][BF_4], and finite solubility in [C_6mim][BF_4], [C_8mim][BF_4], and [C_{10}mim][BF_4], while the iterative solution predicts miscibility with the [C_6mim][BF_4] system at all temperatures.

Since the LLE phase diagram for the water-[$C_n$mim][BF_4] system has been experimentally studied for various values of n, particularly for the common case of n = 4 [12], and higher [10c, 14-16], it was of interest to compute the maximum water-solubility in this IL as a function of temperature. Fig. 3 compares the experimental water-solubility in the IL [C_4mim][BF_4] (obtained from the molar composition at the water-saturation point at temperatures below $T_c \sim 5$ ^oC) and the value computed by eq. (5) using water clusters of size up to i_{max} = 4. We find that the computed solubility is in good agreement with the experimental numbers at all temperatures, and within the acceptable error range of COSMO-RS. More specifically, the experimentally observed critical temperature of 5 ^oC is accurately mimicked by the cluster-computed results. This is a great improvement over the iterative solution (by eq. (2)), which predicts full miscibility of water with the [C_4mim][BF_4] system at all temperatures (see Table 1 and the discussion in

section IV). Carrying out similar calculations for the $[C_6mim][BF_4]$ and $[C_8mim][BF_4]$ systems yield upper critical temperatures of ~ 30 ^oC and50 ^oC respectively. Although these numbers are somewhat below what is observed experimentally [10c, 14-16], the overall trend and semi-quantitative agreement is quite encouraging.

VI. Water-solubility in the $[C_nmim][PF_6]$ and $[C_nmim][Tf_2N]$ system

As a qualitatively different example, we now turn to the hydrophobic IL systems $[C_nmim][PF_6]$ and $[C_nmim][Tf_2N]$, which although less hygroscopic than $[C_nmim][BF_4]$ still display finite affinity for taking in water. The motivation is to check the accuracy and consistency of the two approaches discussed above to compute the maximum solubility of water in these systems. Figs. 4 and 5 summarize the results at 25 ^oC. The important points of note are:

(1) The results for the $[PF_6]^-$ and the $[Tf_2N]^-$ systems are remarkably similar, with the maximum water-solubility in the $[PF_6]^-$ system being somewhat higher than that in the $[Tf_2N]^-$ system. The difference between the two systems is the highest for the smallest alkane-chain length of the cation, and decreases with increasing chain-length.

(2) As opposed to the water solubility in the $[C_nmim][BF_4]$ system, the solubility numbers in both the $[C_nmim][PF_6]$ and $[C_nmim][Tf_2N]$ systems display a smooth convergence behavior as a function of increasing i_{max}. This results from the overall increasing values of the pseudo-chemical potentials $\Delta\mu_i$ in both systems as a function of cluster size i, thus making the formation of larger clusters energetically unfavorable. For instance, the difference in results between including clusters of up to size 4 and clusters of up to size 5 is only 3% for $[C_{10}mim][Tf_2N]$ and 9% for $[C_2mim][Tf_2N]$.

(3) The cluster results for each chain-length n appear to converge toward the iterative solution, providing a consistency check on our approach, and some confidence in the $\Delta\mu_i$ values computed by COSMO-RS.

(4) All calculations are consistent with the trend that the degree of hygroscopicity decreases with increasing alkyl-chain-length n. However, the rate of change as a function of n is underestimated as compared to the experimental trends. This rate appears to get better with the inclusion of larger clusters.

(5) The results from the iterative calculation and calculations with clusters of size 4 or 5 molecules are all within an acceptable factor of 2-3 compared to the experimental results for all n.

VII. Conclusions

In this work we carry out a brief analysis of plausible computational procedures for the maximum water solubility in ionic liquids. Two different types of ILs are used as example systems, i.e., the very hygroscopic (or even miscible) $[C_nmim][BF_4]$ system, and the hydrophobic $[C_nmim][PF_6]$ and $[C_nmim][Tf_2N]$ systems. Ideally one would like to perform such calculations from first-principles with detailed free-energy simulations, either with classical or quantum-mechanical force evaluations. However, such an approach requires extensive parameter development and very long simulation runs to ensure adequate sampling of a complex phase space. We demonstrate

here a computationally fast yet viable alternative in which an implicit solvent model (COSMO-RS) is used to compute the pseudo-chemical potential difference $\Delta\mu_i$ of the water solute between the IL environment and its own liquid environment. Within this framework three different solubility computation schemes are compared, i.e., a standard non-iterative calculation with single water molecules, iterative calculations with single-water molecules, and calculations using small hydrogen-bonded water clusters. For the $[C_n\text{mim}][BF_4]$ system the cluster calculations of size up to 4 waters are shown to be the ones that are not only quantitatively predictive, but also reproduce interesting limited-solubility to miscibility transitions as a function of n and temperature. Although larger clusters are still allowed in terms of COSMO-RS chemical potentials, such clusters need to be excluded based on physical (e.g., steric) arguments and the fact that the COSMO-RS methodology is appropriate only for small, compact molecules. On the other hand, for the $[C_n\text{mim}][PF_6]$ and the $[C_n\text{mim}][Tf_2N]$, systems the solutions converge smoothly as a function of the maximum cluster-size $i_{\max}$ (up to size 5 were considered here) and are close to the iterative results for all values of n. Several known experimental trends are consistently reproduced in this work, including decreasing solubility in the order $[C_n\text{mim}][BF_4] > [C_n\text{mim}][PF_6] > [C_n\text{mim}][Tf_2N]$, and decreasing solubility and increasing upper critical temperature with increasing n.

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References:

1. Green Industrial Applications of Ionic Liquids (Eds.: R. D. Rogers, K. R. Seddon, S. Volkov), NATO Science Series, Kluwer, Dordrecht, 2002.

2. (a) N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* 2008, **37**, 123; (b) O. A. El Seoud, A. Koschella, L. C. Fidale, S. Dorn, T. Heinze, *Biomacromolecules* 2007, **8**, 2629; (c) S. Werner, M. Haumann, P. Wasserscheid, *Chem. Biomol. Eng.* 2010, **1**, 203.

3. M. Ó Mahony, D. S. Silvestor, L. Aldous, C. Hardacare, R. G. Compton, *J. Chem. Eng. Data* 2008, **53**, 2884.

4. (a) J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, *Green Chem.* 2001, **3**, 156; (b) J. Wang, Y. Tian, Y. Zhao, K. Zhuo, *Green Chem.* 2003, **5**, 618; (c) J. A. Widegren, E. M. Saurer, K. N. Marsh, J. W. Magee, *J. Chem. Thermodyn.* 2005, **37**, 569; (d) R. A. Brown, P. Mollet, E. McKoon, C. A. Eckert, C. L. Liotta, P. G. Jessop, *J. Am. Chem. Soc.* 2001, **123**, 1254; (e) V. Najdanovic-Visak, J. M. S. S. Esperancüa, L. P. N. Rebelo, M. Nunes da Ponte, H. J. R. Guedas, K. R. Seddon, H. C. de Souza, J. Szydlowski, *J. Phys. Chem. B* 2003, **107**, 12797; (f) J. A. Widegren, A. Laesecke, J. W. Magee, *Chem. Commun.* 2005, 1610; (g) E. Gomez, B. Gonzalez, A. Dominguez, E. Tojo, J. Tojo, *J. Chem. Eng. Data* 2006, **51**, 696; (h) J.-Z. Yang, J. Tong, J.-B. Li, J.-G. Li, J. Tong, *J. Colloid Interface Sci.* 2007, **313**, 374; (i) M. Kanakubo, T. Umecky, T. Aizawa, Y. Kurata, *Chem. Lett.* 2005, **34**, 324.

5. (a) J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser, R. D. Rogers, *Chem. Commun.* 1998, **16**, 1765; (b) A. G. Fadeev, M. M. Meagher, *Chem. Commun.* 2001, 295; (c) J. McFarlane, W. B. Ridenour, H. Luo, R. D. Hunt, D. W. DePaoli, R. X. Ren, *Sep. Sci. Technol.* 2005, **40**, 1245.

6. (a) K. M. Docherty, C. F. Jr Kulpa, *Green Chem.* 2005, **7**, 185; (b) P. Stepnowski, P. Storoniak, *Environ. Sci. Pollut. Res.* 2005, **12**, 199; (c) D. J. Couling, R. J. Bernot, K. M. Docherty, J. K. Dixon, E. J. Maginn, *Green Chem.* 2006, **8**, 82; (d) D. Zhao, Y. Liao, Z. Zhang, *Clean* 2007, **35**, 42; (e) J. Ranke, A. Müller, U. Bottin-Weber, F. Stock, S. Stolte, J. Arning, R. Störmann, B. Jastorff, *Ecotoxicol. Environ. Saf.* 2007, **67**, 430.

7. (a) D. B. Fu, X. W. Sun, J. J. Pu, S. Q. Zhao, *J. Chem. Eng. Data* 2006, **51**, 371; (b) M. G. Freire, P. J. Carvalho, A. M. Fernandes, I. M. Marrucho, A. J. Queimada, J. A. P. Coutinho, *J. Colloid Interface Sci.* 2007, **314**, 621; (c) R. L. Gardas, M. G. Freire, P. J. Carvalho, I. M. Marrucho, I. M. A. Fonseca, A. G. M. Ferreira, J. A. P. Coutinho, *J. Chem. Eng.Data* 2007, **52**, 80.

8. K. R. Seddon, A. Stark, M.-J. Torres, *Pure Appl. Chem.* 2000, **72**, 2275.

9. (a) C. G. Hanke, R. M. Lynden-Bell, *J. Phys. Chem. B* 2003, **107**, 10873; (b) N. D Khupse, A. Kumar, *J. Phys. Chem. A*, 2011, **115,** 10211; (c) C. Chiappe, D. Pieraccini, *J. Phys. Org. Chem.* 2005, **18**, 275–297.

10. (a) P. Bonhôte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, *Inorg. Chem.* 1996, **35**, 1168; (b) J. E. L. Dullius, P. A. Z. Suarez, S. Einloft, R. F. de Souza, J. Dupont, J. Fischer, A. De Cian, *Organometallics,*1998, **17***,* 815; (c) J. L. Anthony, E. J. Maginn, J. F. Brennecke, *J. Phys. Chem. B* 2001, **105**, 10942; (d) D. S. H. Wong, J. P. Chen, J. M. Chang, C. H. Chou, *Fluid Phase Equilib.* 2002, **194-197**, 1089; (e) V. Najdanovic-Visak, J. M. S. S. Esperancüa, L. P. N. Rebelo, M. N. Ponte, H. J. R. Guedes, K. R. Seddon, J. Szydlowski, *Phys. Chem.Chem. Phys.* 2002, **4**, 1701; (f) Z. B. Alfassi, R. E. Huie, B. L. Milman, P. Neta, *Anal. Bioanal. Chem.* 2003, **377**, 159; (g) J. M. Crosthwaite, S. N. V. K. Aki, E. J. Maginn, J. F. Brennecke, *J. Phys. Chem. B* 2004, **108**, 5113; (h) N. V. Shvedene, S. V. Borovskaya, V. V. Sviridov, E. R. Ismailova, I. V. Pletnev, *Anal. Bioanal. Chem.* 2005, **381**, 427; (i) A. Arce, M. J. Earle, S. P. Katdare, H. Rodr□guez, K. R. Seddon, *Chem. Commun.* 2006, 2548; (j) S. L. I. Toh, J. McFarlane, C. Tsouris, D. W. DePaoli, H. Luo, S. Dai, *Solvent Extr. Ion Exch.* 2006, **24**, 33; (k) N. Papaiconomou, N. Yakelis, J. Salminen, R. Bergman, J. M. Prausnitz, *J. Chem. Eng. Data* 2006, **51**, 1389; (l) U. Domańska, A. Marciniak, *Green Chem.* 2007, **9**, 262; (m) U. Domańska, I. Bakala, J. Pernak, *J. Chem. Eng. Data* 2007, **52**, 309; (n) M. G. Freire, L. M. N. B. F. Santos, A. M. Fernandes, J. A. P. Coutinho, I. M. Marrucho, *Fluid Phase Equilib.* 2007, **261**, 449; (o) M. G. Freire, P. J. Carvalho, R. L. Gardas, I. M. Marrucho, L. M. N. B. F. Santos, J. A. P. Coutinho, *J. Phys. Chem. B* 2008, **112**, 1604; (p) M. G. Freire, S. P. M. Ventura, L. M. N. B. F. Santos, I. M. Marrucho, J. A. P. Coutinho, *Fluid Phase Equilib.* 2008, **268**, 74; (q) T. Kakiuvhi, *Anal. Sci.* 2008, **24**, 1221;(r) Y. Zhao, Z. Chen, J. Wang, K. Zhuo, *Z. Phys. Chem.* 2009, **223**, 857; (s) Y. Li, L. Wang, S. Cai, *J. Chem. Eng. Data* 2010, 55*,* 5289.

11. M. G. Freire, C. M. S. S. Neves, P. J. Carvalho, R. L. Gardas, A. N. Fernandes, I. M. Marrucho, L. M. N. B. F.; Santos, J. A. P. Coutinho, *J. Phys. Chem. B* 2007, **111**, 13082.

12. L. P. N. Rebelo, V. Najdanovic-Visak, Z. P. Visak, M. N. Ponte, J. Szydlowski, C. A. Cerdeirina, J. Troncoso, L. Romani, J. M. S. S. Esperancüa, H. J. R. Guedes, H. C. Sousa, *Green Chem.* 2004, **6**, 369.

13. T. Masaki, K. Nishikawa, and H. Shirota, *J. Phys. Chem. B* 2010, **114**, 6323.

14. M. Wagner, O. Stanga, and W. Shroer, *Phys. Chem. Chem. Phys*. 2003, **5**, 3943.

15. F. M. Maia, O. Rodriguez, and E. A. Macedo, *Fluid. Phase. Equilib.* 2010, **296**, 184.

16. (a) T. Singh, A. Kumar, *J. Phys. Chem. B* 2007, **111**, 7843; (b) L. Almásy, M. Turmine, A. Perera, *J. Phys. Chem. B* 2008, **112**, 2382; (c) W. Jiang, Y. Wang, G. A. Voth, *J. Phys. Chem. B* 2007, **111**, 4812; (d) L. Zhang, Z. Xu, Y. Wang, H. Li, *J. Phys. Chem. B* 2008, **112**, 6411; (e) L. Cammarata, S. G. Kazarian, P. A. Salter, T. Welton, *Phys. Chem. Chem. Phys.* 2001, **3**, 5192; (f) C. D. Tran, S. H. D. Lacerda, D. Oliveira, *Appl. Spectrosc.,* 2003, **57**, 152; (g) T. Köddermann, C. Wertz, A. Heintz, R. Ludwig, *Angew. Chem. Int. Ed*. 2006, **45**, 3697; (h) A. Dominguez-Vidal, N. Kaun, M. J. Ayora-Cãnada, B. Lendl, *J. Phys. Chem. B* 2007, **111**, 4446; (i) Y. Jeon, J. Sung, D. Kim, C. Seo, H. Cheong, Y. Ouchi, R. Ozawa, H. Hamaguchi, *J. Phys. Chem. B* 2008, **112**, 923; (j) T. Singh, A. Kumar, *Vib. Spec.* 2011, **55**, 119.

17. P. J. Dyson, D. J. Ellis, T. Welton, *Can. J. Chem.,* 2001, **79**, 705.

18. G.M. Torrie and J.P. Valleau, *J. Comput. Phys.*, 1977, **23**, 187.

19. W.L. Jorgensen, J.K. Buckner, S. Boudon and J. Tirado-Reeves, *J. Chem. Phys*., 1988, **89**, 3742.

20. M. Mezei and D.L. Beveridge, *Ann. NY Acad. Sci.*, 1986, **482**, 1.

21. G. Ciccotti, M. Ferrario, J.T. Hynes and R. Kapral, *Chem. Phys.*, 1989, **129**, 241.

22. (a) T. Wang, C. Peng, H. Liu, Y. Hu, J. Jiang, *Ind. Eng. Chem. Res.* 2007, **46**, 4323; (b) F. Llovell, E. Valente, O. Vilaseca, L. F. Vega, *J. Phys. Chem. B* 2011, **115**, 4387; (c) J. Ranke, A. Othman, P. Fan, A. Müller, *Int. J. Mol. Sci.* 2009, **10**, 1271; (d) C. Tsioptsias, I. Tsivintzelis, C. Panayiotou, *Phys. Chem. Chem. Phys.* 2010, **12**, 4843; (e) U. Domańska, A. Marciniak, *Fluid Phase Equilib.* 2007, **260**, 9; (f) S. Nebig, R. Bölts, J. Gmehling, *Fluid Phase Equilib.* 2007, **258**, 168; (g) R. S. Santiago, *Braz. J. Chem. Eng.* 2007, **24**, 143; (h) J. A. Lazzús, J. Mar□n, *J. Eng. Thermophys.*, 2010, **19**, 170.

23. A. Klamt, *J. Phys. Chem.*, 1995, **99**, 2224.

24. A. Klamt, *COSMO-RS: From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design*, Elsevier, 2005.

25. (a) K. N. Marsh, A. V. Deev, A. C. -T. Wu, E. Tran, A. Klamt, *Korean J. Chem. Eng.* 2002, **19**, 357; (b) C.-T. Wu, K. N. Marsh, A. V. Deev, J. A. Boxall, *J. Chem. Eng. Data* 2003, **48**, 486; (c) T. Banerjee, M. K. Singh, A. Khanna, *Ind. Eng. Chem. Res.* 2006, **45**, 3207–; (c) U. Domańska, A. Pobudkowska, F. Eckert, *Green Chem.* 2006, **8**, 268; (d) U. Domańska, A. Pobudkowska, F. Eckert, *J. Chem. Thermodyn.* 2006, **38**, 685; (e) K. Sahandzhieva, D. Tuma, S. Breyer, A. P.-S. Kamps, G. Maurer, *J. Chem. Eng. Data* 2006, **51**, 1516.

26. A. Ben-Naim, *Solvation Thermodynamics*, 1st Ed., Plenum Press, New York, USA, 1987.

27. A. Maiti, P. Pagoria, A. Gash, T. Y. Han, C. Orme, R. Gee, and L. Fried, *Phys. Chem. Chem. Phys*. 2008, **10**, 5050.

28. A. Maiti, *ChemSusChem* 2009, **2**, 628.

29. R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*1989, **162**, 165.

30. A. Schäfer, A. Klamt, D. Sattel, J. C. W. Lohrenz and F. Eckert, *Phys. Chem. Chem. Phys.* 2000, **2**, 2187.

31. A. D. Becke, *Phys. Rev. A* 1988, **38**, 3098.

32. J. P. Perdew, *Phys. Rev. B* 1986, **33**, 8822; J. P. Perdew, *Phys. Rev. B* 1986, **34**, 7406.

33. K. Eichkorn, F. Weigend, O. Treutler and R. Ahlrichs, R. *Theor. Chim. Acta* 1997, **97**, 119.

34. A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.* 1994, **100**, 5829.

35. (a) M. Fujisawa, H. Tsutsumi, T. Kimura, *J. Chem. Pharm. Res.,* 2011*,* **3,** *750;* (b) M. Diedenhofen, A. Klamt, *Fluid Phase Equilib.* 2010, **294**, 31; (c) M. Buggert, L. Mokrushina, I. Smirnova, R. Schomäcker, W. Arlt, *Chem.Eng. Technol.* 2006, **29**, 567; (d) L. Mokrushina, M. Buggert, I. Smirnova, W, Arlt, R. Schomäcker, *Ind. Eng. Chem. Res.* 2007**, 46***,* 6501.

36. A. Maiti and R. Rogers, *Phys. Chem. Chem. Phys.* 2011, **13**, 12138.

37. (a) K. S. Kim, K. D. Jordan, T. S. Zwier, *J. Am. Chem. Soc.* 1994, **116**, 11568; (b) K. S. Kim, M. Dupuis, G. C. Lie, E. Clementi, *Chem. Phys. Lett.*1986, **131**, 451; (c) R. N. Pribble, T. S. Zwier, *Science* 1994, **265**, 75; (d) U. Buck, I. Ettischer, M. Melzer, V. Buch, V. Sadlej, *Phys. Rev. Lett.* 1998, **80**, 2578; (e) S. Maheshwary, N. Patel, N. Sathyamurthy, A. D. Kulkarni, S. R. Gadre, *J. Phys. Chem. A* 2001**, 105***,* 10525 and references therein.

Table 1: Maximum solubility of water in the IL series $[C_n mim][BF_4]$ [n = 2, 4, 6, 8, 10] computed by non-iterative (eq. (1)) and iterative procedure (eq. (2)) by considering single water molecules only. Results are shown for T = 0 °C and 25 °C. Also shown are available experimental data from the literature (references indicated by the side).

T	Alkyl chain-length in cation (n)	n_{water}/n_{IL} (non-iterative)	n_{water}/n_{IL} (iterative)	n_{water}/n_{IL} (Experiment)
0 °C	2	0.40	Miscible	---
	4	0.32	Miscible	4.65 [12]
	6	0.28	Miscible	---
	8	0.24	1.40*	---
	10	0.21	0.69	---
25 °C	2	0.61	Miscible	Miscible
	4	0.48	Miscible	Miscible
	6	0.41	Miscible	2.20 [8], 3.57 [13]
	8	0.35	1.60	1.96 [8], 2.89 [13]
	10	0.30	0.81	1.83 [8], 2.82 [13]

*Unstable in favor of miscibility

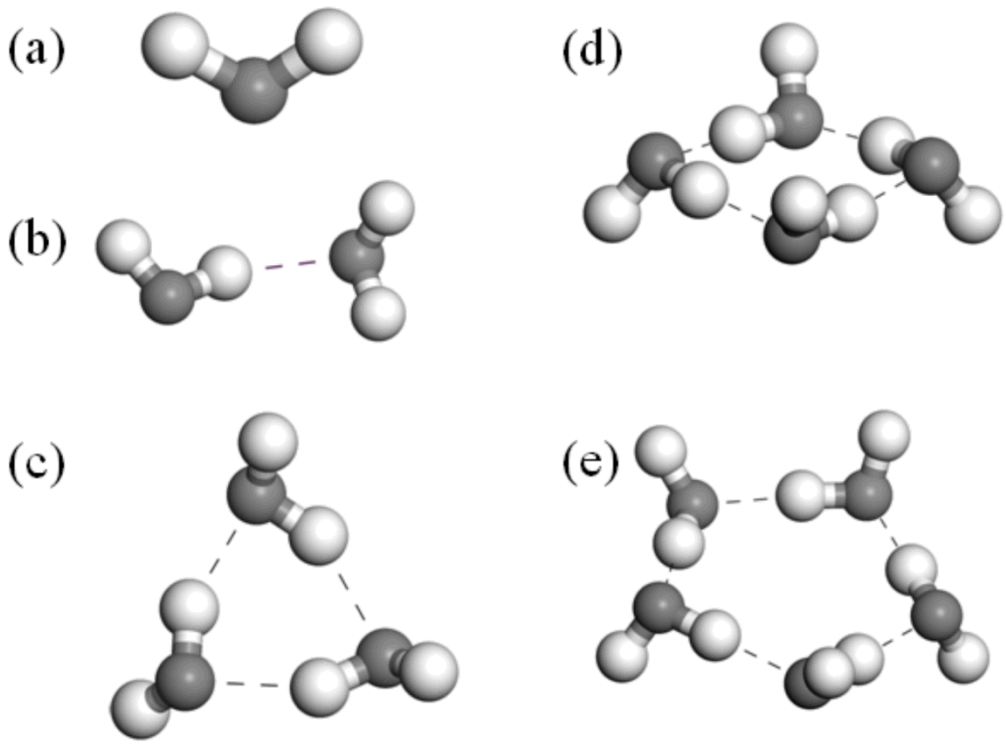

Fig. 1. Ground-state structures of hydrogen-bonded clusters of water of size (a) single molecule; (b) 2 molecules; (c) 3 molecules; (d) 4 molecules; and (e) 5 molecules. The hydrogen bonds are indicated by dashed lines.

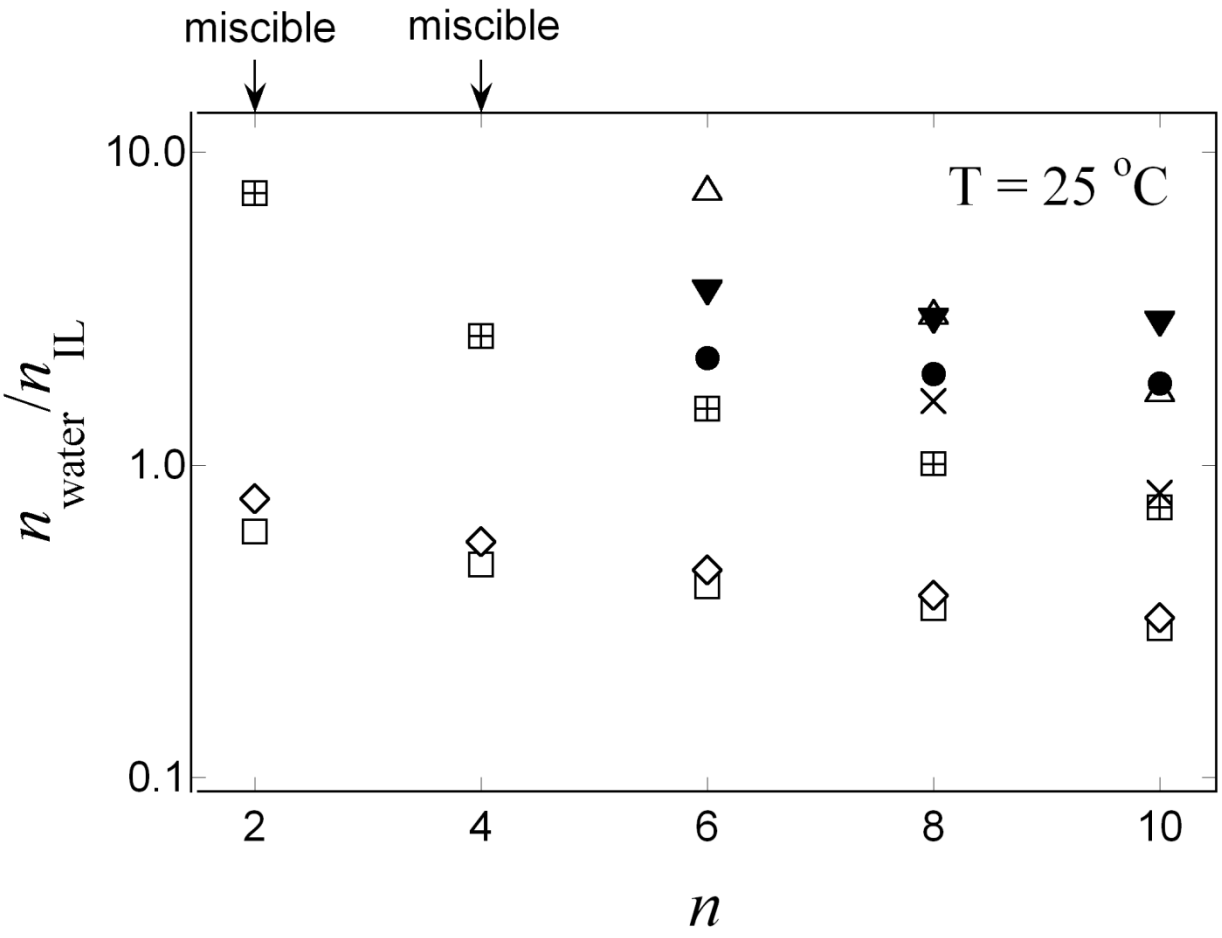

Fig. 2. Maximum solubility of water at 25 °C in the IL series [$C_n$mim][BF_4] [n = 2, 4, 6, 8, 10] by explicitly considering water clusters (eqs. (4) and (5)). The solubility is expressed as the mole ratio of water to IL (n_{water}/n_{IL}). Four different computed results are shown for each IL, corresponding to water cluster-sizes up to i_{max} = 1 water (□), 2 waters (□), 3 waters (∧), and 4 waters (Δ). Also shown are the results for the iterative solution (X) (see Table 1). The experimental data correspond to Seddon et al. (●), ref. [8] and Masaki et al. (▼), ref. [13].

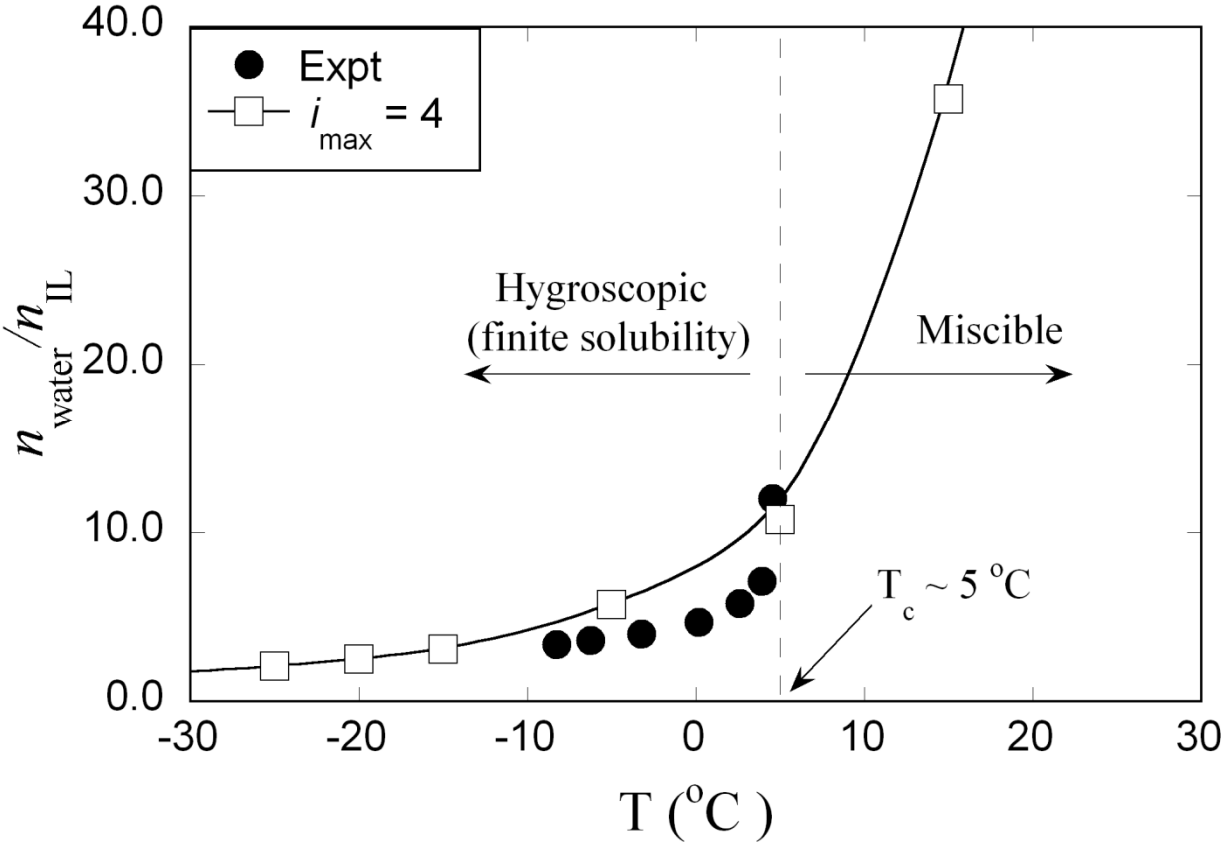

Fig. 3. Predicted maximum solubility of water (□) in $[C_4mim][BF_4]$ as a function of temperature by considering water-clusters of size up to four molecules compared with experimental numbers (●) [12]. The solubility is expressed as the mole ratio of water to IL (n_{water}/n_{IL}).

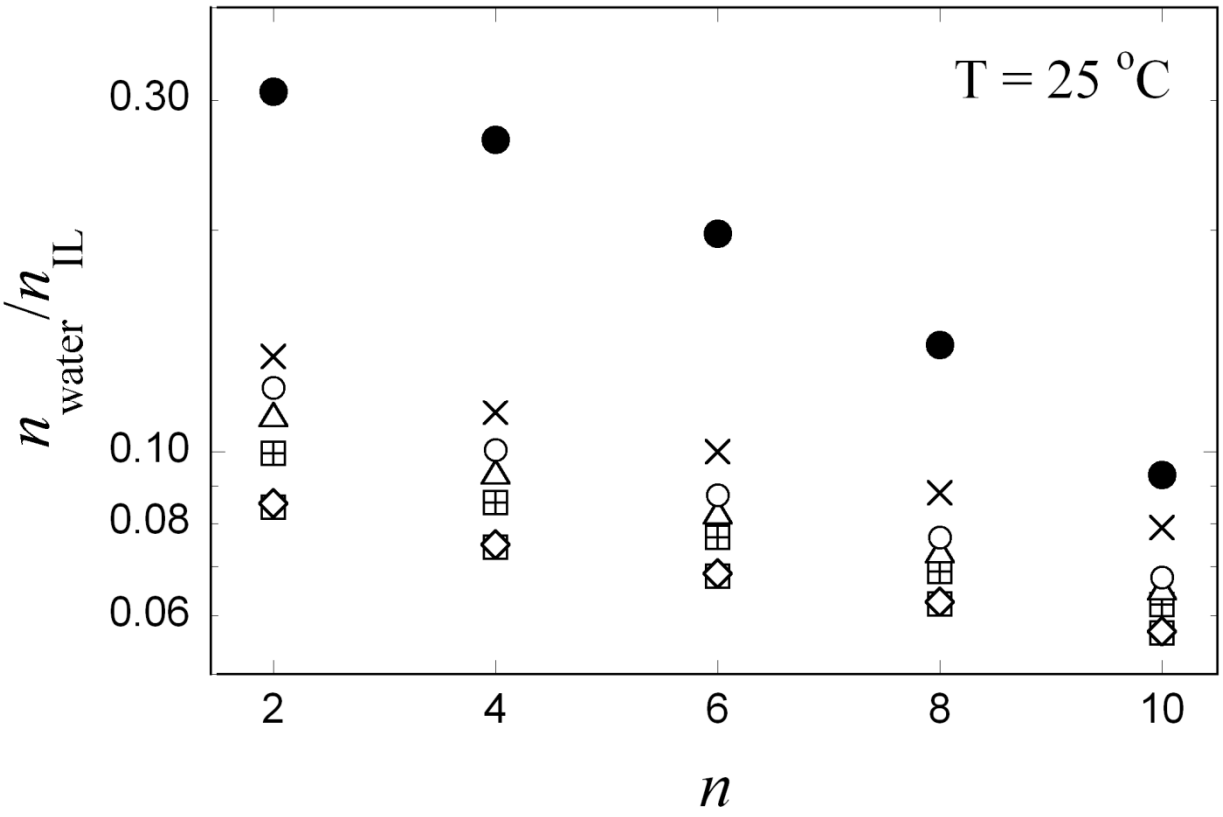

Fig. 4. Predicted maximum solubility of water at 25 °C in the IL series [C$_n$mim][Tf$_2$N] [n = 2, 4, 6, 8, 10] from our calculations (expressed as the mole ratio of water to IL). Six different computed results are shown for each IL, including clusters of size up to i_{max} = 1 water (□), 2 waters (▯), 3 waters (∧), 4 waters (Δ), 5 waters (○), as well as the iterative solution (X). The experimental numbers (●) are from ref. [13].

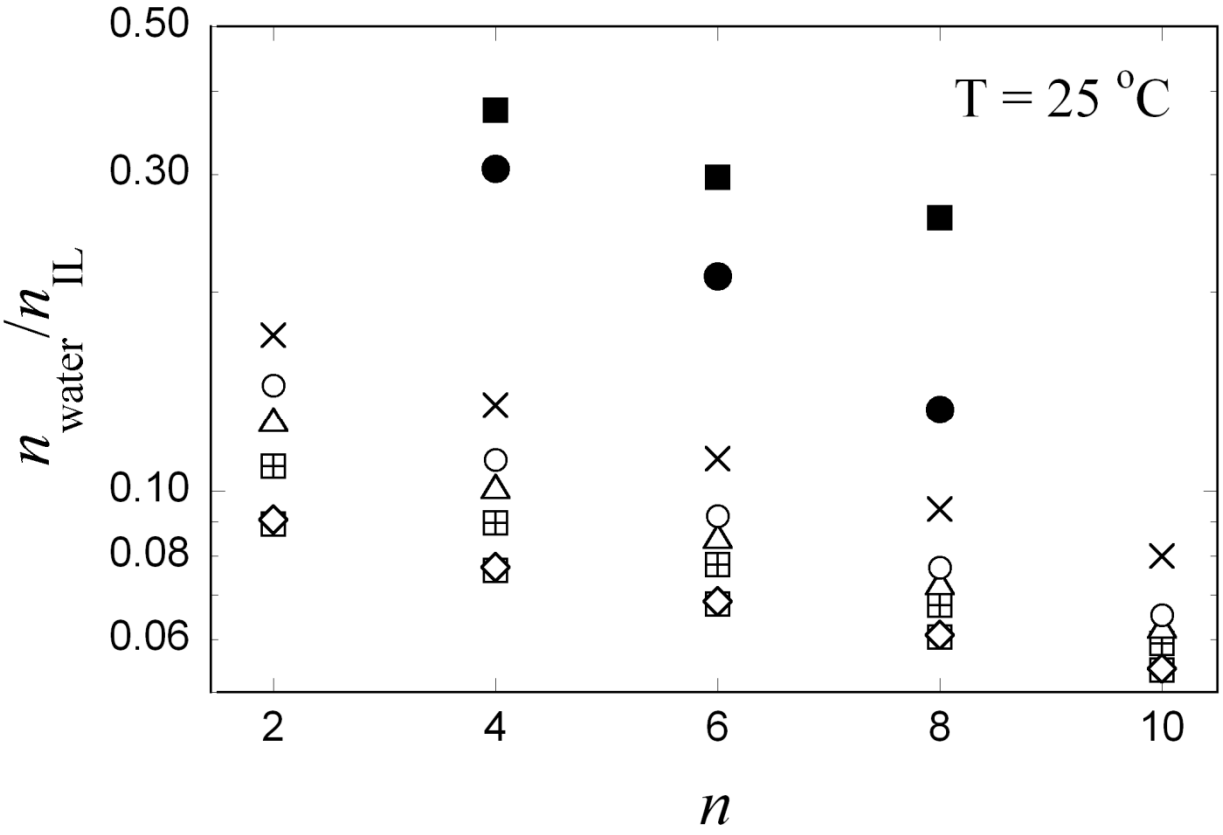

Fig. 5. Predicted maximum solubility of water at 25 °C in the IL series [$C_n$mim][PF_6] [n = 2, 4, 6, 8, 10] from our calculations (expressed as the mole ratio of water to IL). Six different computed results are shown for each IL, including clusters of size up to i_{max} = 1 water (□), 2 waters (⬚), 3 waters (∧), 4 waters (Δ), 5 waters (○), as well as the iterative solution (X). The experimental numbers (●) are from ref. [8] and (■) from ref [11].