

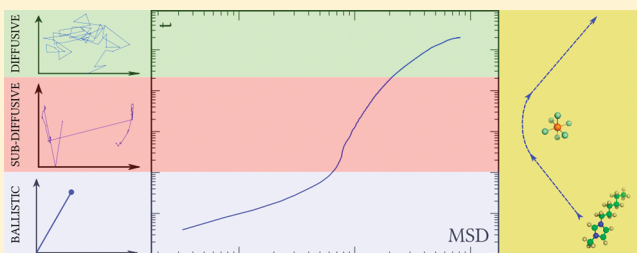
Dynamical Properties of Alcohol + 1-Hexyl-3-methylimidazolium Ionic Liquid Mixtures: A Computer Simulation Study

Trinidad Méndez-Morales,[†] Jesús Carrete,[†] Manuel García,[†] Oscar Cabeza,[‡] Luis J. Gallego,[†] and Luis M. Varela^{*,†}

[†]Grupo de Nanomateriales y Materia Blanda. Departamento de Física de la Materia Condensada, Universidad de Santiago de Compostela, E-15782 Santiago de Compostela, Spain

[‡]Facultad de Ciencias, Universidade da Coruña, Campus A Zapateira s/n, E-15008, A Coruña, Spain

ABSTRACT: In this work, extensive molecular dynamics simulations of the dynamics of mixtures of ionic liquids (ILs) composed of the cation 1-hexyl-3-methylimidazolium and several anions of different hydrophobicity degrees (Cl^- , BF_4^- , PF_6^-) with alcohols of different chain lengths (methanol and ethanol) are reported. We evaluated the influence of the nature of the anion, the length of the molecular chain of the alcohol, and the alcohol concentration on some dynamical properties of the mixtures, such as self-diffusion coefficients of all the species, mean square displacements (with an analysis of both ballistic and diffusive regimes), and velocity autocorrelation functions of alcohol molecules. The diffusivity of the mixtures was found to be highly dependent on the nature of the anion since the interaction between chloride and alcohols is greater than that with fluorinated anions and leads to slower dynamics. Additionally, our results show that self-diffusion coefficients increase with alcohol concentration. On the other hand, a subdiffusive regime over thousands of picoseconds was detected at intermediate times through analysis of the center-of-mass mean square displacements of alcohol molecules, a region that becomes narrower as alcohol concentration increases. Finally, the study of the role of the anion and of solvent concentration on velocity autocorrelation functions reflects an increase in mean collision times as the amount of alcohol increases until the value of pure alcohols is reached. These collision times are smaller in mixtures with halogenated ILs.



INTRODUCTION

Room temperature ionic liquids (ILs) have attracted increasing attention in recent years^{1–5} from both academia and industry due to their interesting properties and potential applications. ILs exhibit some unique characteristics, such as negligible vapor pressure, high thermal and electrochemical stability, nonvolatility, nonflammability, low viscosity, high ionic conductivity, and miscibility, with a wide range of organic and inorganic compounds,^{1,3,6–12} which confer them their reputation as “green solvents” and make them a good alternative to traditional organic solvents.^{7,10,13–18} Because of these properties, ILs have been investigated for many applications in different fields of chemistry: catalysis, synthesis, lubrication, thermal separation processes, and electrochemistry.^{4,13,19–25}

As with any salt, these systems are formed entirely by ions: an organic cation such as those based on imidazolium, pyridium, pyrrolidinium, ammonium, phosphonium, or guanidinium and an anion like PF_6^- , BF_4^- , Cl^- , Br^- , NTf_2^- , NO_3^- , etc.^{12,17,26,27} The physicochemical properties of ILs can be easily modified simply by a proper choice of ions.^{13,17} Because of this potential tunability for any particular application,^{4,16,28,29} ILs are usually called “designer solvents”.^{3,18} In practice, however, the design and development of ILs for a specific role requires a detailed understanding of their molecular and thermodynamic behavior. In particular, a systematic understanding of the correlation between the composition of mixtures of ILs with (organic or

inorganic) solvents, their dynamical features, and their bulk physicochemical properties is of extreme importance for both theoretical and practical reasons. Accordingly, extensive computational and experimental research of the properties of ILs has been carried out during the last years (see, for example, refs 30 and 31 and references therein). However, the understanding of the dynamical properties of ILs and their mixtures, even with water, is still very limited, and studies devoted to quantifying the relationship between the structure of the mixture and the dynamics of the molecules (which has a direct influence on the physicochemical properties) have as of yet been scarce, especially if we compare the number of ILs whose dynamical properties have been broadly studied and the immense number of ILs synthesized so far.

As regards experimental studies of dynamical magnitudes, a number of reports of mutual and self-diffusion coefficients of pure ILs can be found in the literature,^{4,32–43} as well as some measurements dealing with the diffusion of solid, liquid, and gaseous solvents in ILs.^{44–56} Among the latter, however, papers concerned with IL + alcohol mixtures have not been abundant. As far as we know, the first measurements of mutual diffusion coefficients of mixtures between 1-butyl-3-methylimidazolium

Received: October 4, 2011

Revised: November 14, 2011

Published: December 06, 2011

hexafluorophosphate ([BMIM][PF₆]) and methanol, using digital image holography, were published by Ritcher et al. in 2003.⁵⁵ Another example is the study, by Sarraute et al.,⁵⁰ of the diffusion coefficients of several ILs based on the 1-alkyl-3-methylimidazolium cation (AMIM⁺) in methanol, for temperatures ranging from 283 to 333 K, using the Taylor dispersion method.

Unfortunately, it is usually very complicated to experimentally or theoretically achieve a detailed knowledge of the correlation between structure and molecular mobility of ILs. To overcome this lack of information, computer simulations are often used to improve the understanding about the behavior of ILs at the molecular level. Due to the high computational cost of ab initio techniques, the best simulation method to probe the dynamical behavior of these systems is classical molecular dynamics (MD).^{4,30,57–80} So far, MD studies have concerned themselves mainly with pure components,^{30,62–73} while IL + solvent mixtures have received much less attention. A notable example of the former is the study, by del Pópolo and Voth,⁶³ of the structure and dynamics of 1-ethyl-3-methylimidazolium nitrate ([EMIM][NO₃]), including dynamical magnitudes such as the center-of-mass velocity autocorrelation functions (VACFs) and the mean square displacements (MSDs) of the ions. Although the most studied among IL mixtures have been those with water,^{60,61,75–80} a few instances of computational research about mixtures with other compounds such as acetonitrile⁷⁴ or supercritical carbon dioxide⁵⁸ can also be found. Like for experimental studies, the number of reported MD results regarding the dynamical properties of IL + alcohol mixtures is much lower. In 2008, Raabe and Köhler⁸¹ performed MD simulations of mixtures of 1-alkyl-3-methylimidazolium chloride ([AMIM][Cl]) with ethanol and 1-propanol to calculate the diffusion coefficients and some structural properties of those systems. That same year, Jahangiri et al.⁵⁷ reported results of excess, dynamical, and structural properties of mixtures of 1-ethyl-3-methylimidazolium chloride ([EMIM][Cl]) and 1-ethyl-3-methylimidazolium hexafluorophosphate ([EMIM][PF₆]) with both methanol and ethanol obtained by MD simulations. A larger computational study of dynamical properties was carried out by Heintz et al.,⁵⁴ who performed MD simulations with the aim to investigate tracer diffusion coefficients of the IL ions in mixtures of [EMIM][NTf₂] and [BMIM][NTf₂] with water or methanol at different temperatures between 288 and 313 K.

Even though a molecular understanding of the dynamical properties of alcohol + IL mixtures is of fundamental importance from both a fundamental and a practical standpoint, a systematic study of the role of different parameters such as alkyl chain length, anion nature, concentration of solvent, and alcohol chain size on the dynamical properties of this kind of mixtures is, as far as we know, still missing. As we reported in our previous work,⁸² the length of the chain of the alcohol and, above all, the nature of the anion have a direct influence on the solvation process of ILs and on the mixture structure, and consequently they are expected to have a deep impact on the transport properties.

Using previously reported simulation models,⁸² in this work we performed extensive MD simulations of mixtures of alcohols and 1-hexyl-3-methylimidazolium (HMIM⁺) with three different anions of various solvophobicity degrees to investigate several dynamical properties of the systems: PF₆[−], the one with the higher level of hydrophobicity; Cl[−], with a great effect on water structure according to the Hoffmeister series; and BF₄[−], with intermediate characteristics. Moreover, the impact of the length of the chain in the chosen alcohols (methanol and ethanol) on

the dynamic behavior was studied and compared. Additionally, we analyzed the influence of the anionic species and alcohol concentration on the single-particle dynamics of the mixtures by analyzing the self-diffusion coefficients of the involved species, MSDs (with an analysis of the ballistic and diffusive regimes), and VACFs of alcohol molecules.

This paper is organized as follows. We begin by giving a detailed description of the computational procedure used in our study. In the next section we present and discuss the obtained results, and in the final part we summarize our main conclusions.

SIMULATION DETAILS

The MD simulations for pure ILs and their mixtures with alcohols were performed using the GROMACS package.⁸³ All the simulations were run at 298.15 K, and the analyzed mole fractions of alcohol in the IL + alcohol mixtures were $x_{\text{alcohol}} = \{0.00, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, 0.95, 0.98, \text{ and } 1.00\}$ since both ethanol and methanol are miscible with all the selected ILs ([HMIM][PF₆], [HMIM][BF₄], and [HMIM][Cl]) over the whole concentration range.^{84–86} The number of IL molecules in the cubic box was set to 300, except for $x_{\text{alcohol}} = 1.00$, a case in which only alcohol molecules are present, $x_{\text{alcohol}} = 0.95–0.98$, where just 50 ionic pairs were introduced to keep the system size small enough, and $x_{\text{alcohol}} = 0.10$, where we considered 450 IL molecules to have enough alcohol to yield statistically significant trajectories. The number of alcohol molecules was adjusted in each situation counting each ionic pair as a single molecule in the calculation of mole fractions.

The parametrization of the ions was carried out in the framework of the all-atom version of the fully flexible OPLS force field developed by Jorgensen and co-workers⁸⁷ for different organic fluids. The details of the parametrization used have been reported elsewhere,⁸² but it is important to remark, with regard to our description of the ions, that we used a nonpolarizable model with static partial charges adding up to +1 and −1 for the cation and anion, respectively; i.e., full (nonreduced) charges were used. Our all-atom representation of 1-hexyl-3-methylimidazolium is shown in Figure 1. Other relevant details of the simulation include the fact that a neighbor search was made up to 1.1 nm from the central ion and updated every five simulation steps and that the cutoff distance for Lennard-Jones interactions was set to this same distance. Long-range electrostatic interactions were computed using the Particle-Mesh Ewald (PME)⁸⁸ method with a grid spacing of 0.12 nm and cubic interpolation. When needed, the Linear Constraint Solver (LINCS) algorithm^{89,90} with a fourth-order expansion of the constraint coupling matrix was used to constrain the bonds, and long-range dispersion corrections were used for energy and pressure.

To remove bad contacts resulting from the initial random configuration of ions, initial configurations were energy-minimized for 10⁶ steps using a conjugated gradients algorithm. The maximum step size and the tolerance were set to 0.01 nm and 0.1 kJ · nm^{−1} · mol^{−1}, respectively. The equilibration phase was performed in the isothermal–isobaric (*NpT*) ensemble during 100 ps to ensure the full equilibration of all the properties of the system. The analysis was carried out using the results of an additional 2 ns simulation in the isothermal–isobaric ensemble. This very long simulation time is in keeping with the findings of recent MD studies, which remark that the simulation time used for analysis must be in the order of nanoseconds to ensure that

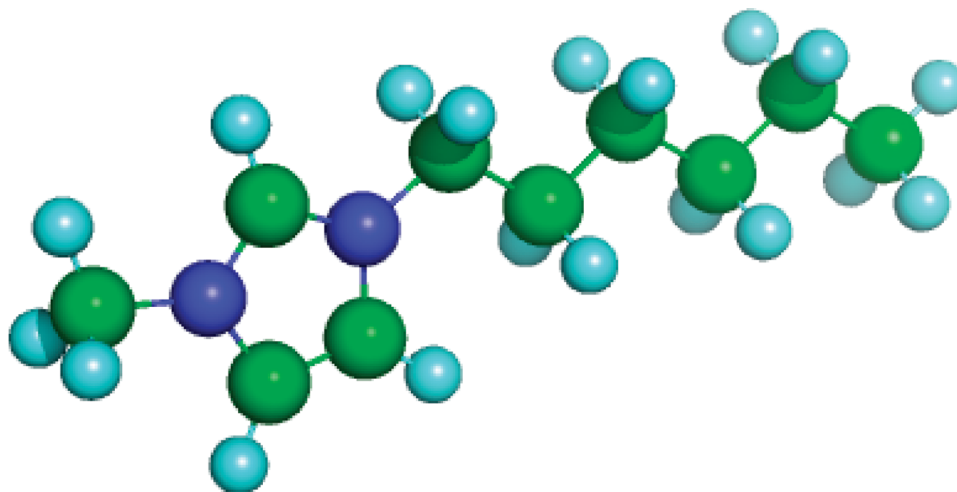


Figure 1. Molecular structure of 1-hexyl-3-methylimidazolium, modeled using an all-atom representation.

the particles of the ILs have reached a diffusive behavior during the simulation since trajectories that seem to be in the linear diffusive regime are often still subdiffusive.^{4,30,57–62} The temperature control was implemented using a velocity rescaling thermostat.⁹¹ Cations and anions (and alcohols in those cases where we include a solvent) were separated in two (three) baths with temperature coupling constants of 0.1 ps. The pressure control was set using the Parrinello-Rahman barostat⁹² with a reference pressure of 1 atm, an isothermal compressibility of $4.5 \times 10^{-5} \text{ bar}^{-1}$, and a relaxation time of 1.0 ps. Tests performed prior to the simulation revealed that our results are largely insensitive to the choice of time scales of the thermostat and barostat.

Each of these simulations provided us with a sequence of configurations, i.e., positions and instantaneous velocities of all atoms of the system, which was analyzed to obtain dynamical information about the mixtures previously mentioned.

RESULTS AND DISCUSSION

In addition to thermodynamical or structural properties, MD simulations are an efficient method to get a molecular understanding of the dynamical behavior of pure ILs and their mixtures. As it is well-known, the reliability of the properties obtained by computational studies depends on the accuracy of the employed force field, and density is usually the magnitude used to estimate the precision of this force-field-based simulation.^{77,81} This precision was tested for IL + alcohol mixtures in our previous work,⁸² where the comparison between our simulated densities of both pure ILs and alcohols with the experimental data showed deviations smaller than 2.0%.

Single-particle dynamics of these systems can be described by means of the self-diffusion coefficient of species i , which is particularly amenable for calculation with MD simulations as it can be obtained from the well-known Einstein equation^{93,94}

$$D_i = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle [\vec{r}_i(t) - \vec{r}_i(0)]^2 \rangle \quad (1)$$

where $\langle [\vec{r}_i(t) - \vec{r}_i(0)]^2 \rangle$ is the ensemble-averaged MSD of component i and positions of molecules have been calculated from their center of mass at time t . The above equation is valid only at long simulation times, when the MSD exhibits a linear

Table 1. Simulated Self-Diffusion Coefficients and Uncertainties for Pure IL and Alcohols at 298.15 K and 1 atm

compound	$D \text{ (} 10^{-5} \text{ cm}^2/\text{s} \text{)}$	
	D_{cation}	D_{anion}
[HMIM][PF ₆]	0.00463 ± 0.00035	0.00319 ± 0.00026
[HMIM][BF ₄]	0.00600 ± 0.00067	0.00521 ± 0.00011
[HMIM][Cl]	0.00258 ± 0.00064	0.00202 ± 0.00014
methanol	2.57 ± 0.20	
ethanol	1.207 ± 0.033	

behavior with time and a truly diffusive regime is reached, since too short MD trajectories usually lead to overestimations of self-diffusion coefficients.^{30,62} In particular, for this work the data between 200 and 1800 ps were fitted to a straight line to apply eq 1.

An additional validation of the accuracy of our force field, and therefore of the dynamical and transport properties of our model, can be made by calculating the self-diffusion coefficients of pure ILs and alcohols and contrasting them with some available experimental and computational values. Table 1 shows the simulated self-diffusion coefficients for cation (D_{cation}) and anion (D_{anion}) species in each pure IL and for pure methanol and ethanol, together with their respective uncertainties, provided by the GROMACS package. The computed self-diffusion coefficients for both pure methanol and ethanol are very similar to the ones reported by Karger et al.⁹⁵ using NMR techniques, whose measured self-diffusivities were $2.3 \times 10^{-5} \text{ cm}^2/\text{s}$ for pure methanol at 292 K and $0.946 \times 10^{-5} \text{ cm}^2/\text{s}$ for pure ethanol at 290 K, both with a pressure of 0.1 MPa. These are largely due to the fact that the experimental studies of Karger et al. were done at lower temperatures than the present simulations. Our computational results for pure alcohols are also in good agreement with some previous values obtained by Martí et al.,⁹⁶ Haughney et al.,⁹⁷ and Guevara-Carrión et al.⁹⁸ using MD simulations. Concerning the obtained values of pure ILs, self-diffusion coefficients for HMIM⁺ and PF₆[−] are comparable to those reported by Jacob et al.⁴⁸ from their NMR measurements and the ones calculated by Liu et al.⁷⁴ from MD simulations. The values corresponding to HMIM⁺ and BF₄[−] are slightly smaller than the experimental results measured by Jin et al.³⁹ for

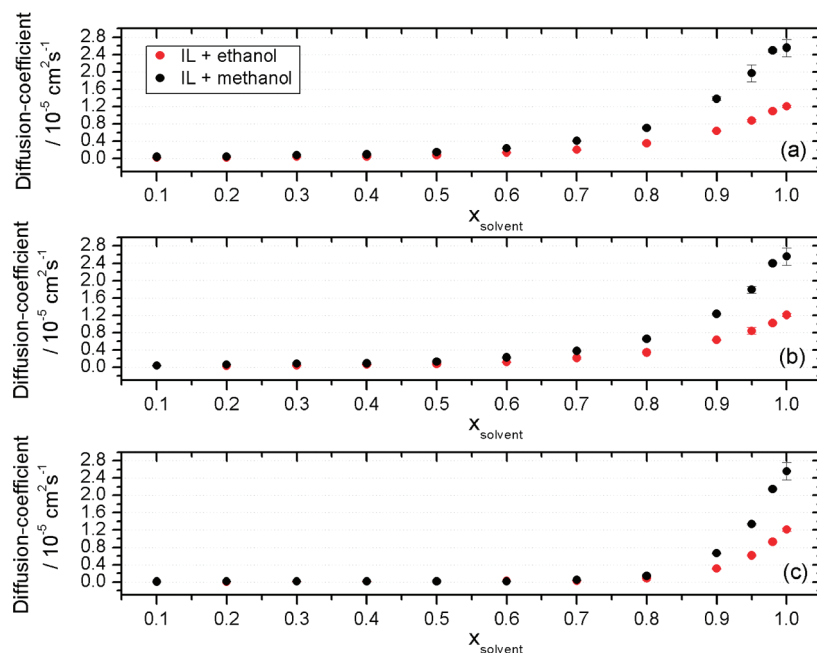


Figure 2. Concentration dependence of the self-diffusion coefficients of alcohol molecules in (a) [HMIM][PF₆] + alcohol, (b) [HMIM][BF₄] + alcohol, and (c) [HMIM][Cl] + alcohol mixtures, calculated by the Einstein relation.

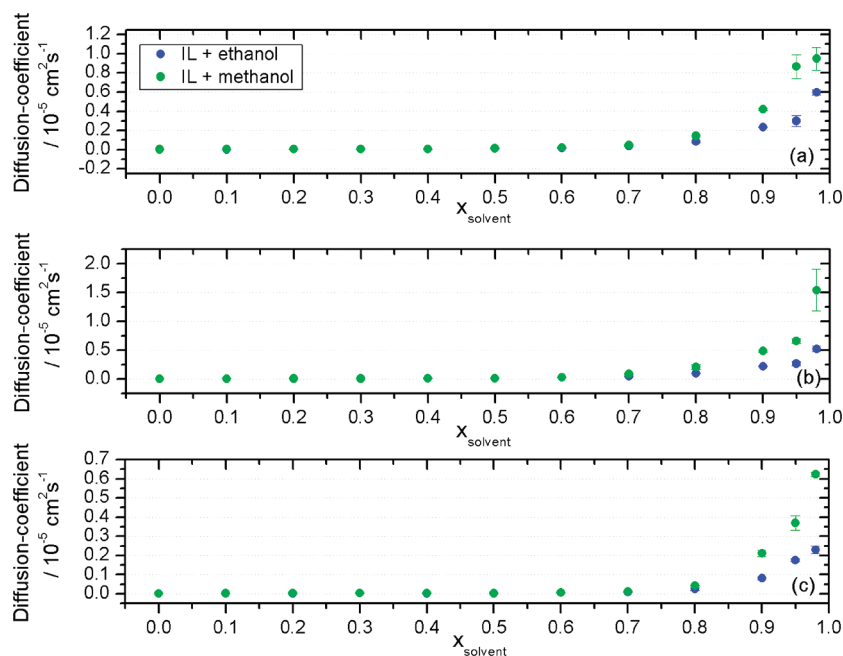


Figure 3. Concentration dependence of the self-diffusion coefficients of anions in (a) [HMIM][PF₆] + alcohol, (b) [HMIM][BF₄] + alcohol, and (c) [HMIM][Cl] + alcohol mixtures, calculated by the Einstein relation.

[BMIM][BF₄] and those simulated by Liu et al.,⁷⁴ Andrade et al.,⁷² and Prado et al.⁷³ for the same IL, all of them at room temperature. This is not surprising if we take into account that the self-diffusion coefficient decreases with increasing alkyl chain length as reflected in the increase of the viscosity.⁴² Finally, our self-diffusion coefficients for HMIM⁺ and Cl[−] agree reasonably well with the ones computed by Jahangiri et al.⁵⁷ for [BMIM]-[Cl]. Interestingly, cation and anion were found to exhibit similar

diffusion behavior for each IL, but self-diffusion coefficients of the cations are slightly greater than those of the anions in all cases, despite their larger volumes and masses, in agreement with previous results reported in the literature.^{30,41,64} Moreover, all the self-diffusion coefficients of pure ILs reported in this work are around 2 orders of magnitude lower than that of pure water at 298.15 K and 1 atm, 2.6×10^{-9} m²/s,^{68,74,80} and pure alcohols.

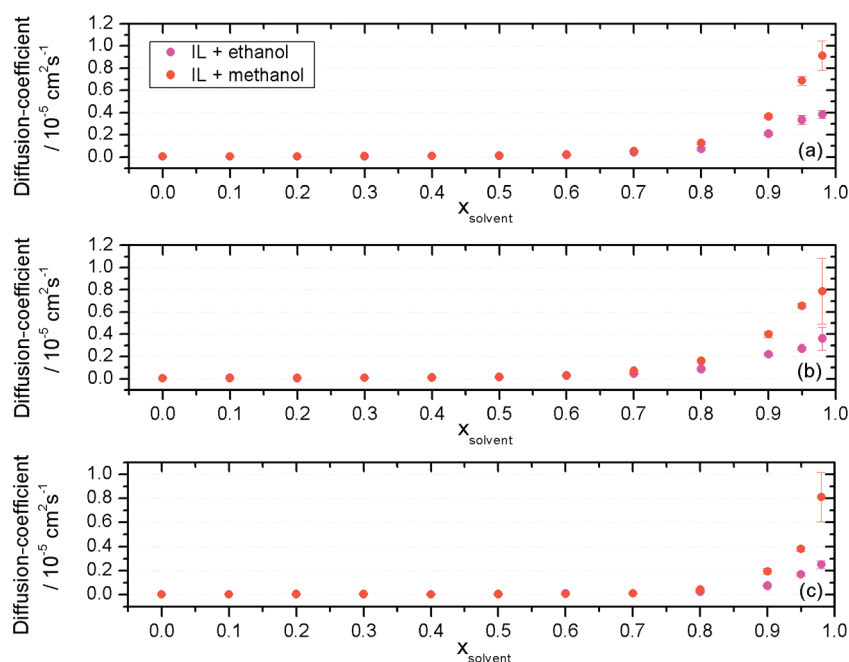


Figure 4. Concentration dependence of the self-diffusion coefficients of cations in (a) [HMIM][PF₆] + alcohol, (b) [HMIM][BF₄] + alcohol, and (c) [HMIM][Cl] + alcohol mixtures, calculated by the Einstein relation.

Figures 2–4 provide some further insight into the effect of the anion nature, the size of the alcohols, and solvent concentration on self-diffusion coefficients of the mixtures of imidazolium-based ILs with alcohols. In Figure 2 we represent self-diffusion coefficients of an alcohol molecule in all the analyzed IL + alcohol mixtures as a function of alcohol molar fraction. In all cases, self-diffusion coefficients of alcohol molecules increase with an increasing amount of alcohol, this increase being more gradual in mixtures with [HMIM][PF₆] and [HMIM][BF₄] over alcohol molar fractions of $x_{\text{alcohol}} = 0.7$ and of $x_{\text{alcohol}} = 0.9$ in mixtures with [HMIM][Cl]. Moreover, diffusion of methanol molecules in all the studied mixtures is higher than diffusion of ethanol molecules in IL + ethanol mixtures at the same concentration, probably due to their smaller sizes and weights. Figure 2 also illustrates that the diffusion of both alcohols is faster in mixtures of IL with polyatomic anions than in mixtures of the chlorinated IL over the whole concentration range, which shows that alcohol molecules interact more strongly with chloride than with polyatomic ions, as we reported in our previous work.⁸² These results are in good agreement with the ones previously published by Jahangiri et al.⁵⁷ for mixtures of methanol with [EMIM][PF₆] and [EMIM][Cl] and by Raabe and Köhler⁸¹ for mixtures of ethanol and 1-propanol with [AMIM][Cl]. In addition, the self-diffusion coefficients for both ethanol and methanol molecules follow the same trend as those found in our previous work⁸⁰ for water molecules; however, their values are smaller than those of water over the entire miscibility range studied since significant interactions similar to the ones observed between water molecules were not found between alcohol molecules.⁸² Furthermore, two different regimes can be distinguished: (i) at low alcohol concentrations self-diffusion coefficients of alcohol molecules increase slowly, pointing to a possible glassy state of the system and showing that no continuous solvent region is formed in the bulk mixture up to very high alcohol concentrations, and (ii) at low IL concentrations self-diffusion coefficients of alcohol molecules increase rapidly due to the

percolation of alcohol regions in the mixture. Similar behavior was reported in previous experimental⁵³ and computational studies with water and alcohols.^{57,75–77,80,81}

Figures 3 and 4 illustrate the self-diffusion coefficients of anions and cations, respectively, as a function of alcohol concentration. In general, the trend of these components is the same as the one observed for alcohol molecules, the diffusion of ions being very slow until the molar fraction of alcohol is greater than $x_{\text{alcohol}} = 0.8$, a concentration after which the diffusion of both species increases considerably. However, the values of the self-diffusion coefficients of anions and cations are very similar, with the diffusion of cations slightly faster than that of anions in the corresponding mixture, in spite of the smaller size of the latter ones. This supports the notion that, in these systems, the interaction between alcohol molecules and anions (above all with chloride) is stronger than that with cations.⁸² Figure 3 shows that, although chloride is smaller than hexafluorophosphate, the former anion has a slower diffusion than the polyatomic one, which is due to the highly solvophobic character of PF₆[−] and the existence of a stronger interaction between alcohol molecules and Cl[−].⁸² Finally, it can be seen that the effect of solvent concentration and of anion nature on the self-diffusion coefficient is more notable for alcohol molecules than for any of the ions.

Thus, from the analysis of self-diffusion coefficients we can conclude that self-diffusivities of all components of the mixtures decrease rapidly with increasing amounts of IL. Moreover, both alcohols interact strongly with the anion of the IL, which has an important role in the structural and dynamical properties, and this interaction is stronger with the halogen anion than with the polyatomic ones, confirming previously reported results.⁸²

With the aim of getting further insight into the influence of the amount of alcohol on the dynamics of ILs, Figure 5(a) shows the MSD of both cation and anion as a function of time in pure [HMIM][PF₆] and the MSD of PF₆[−] in mixtures with an alcohol

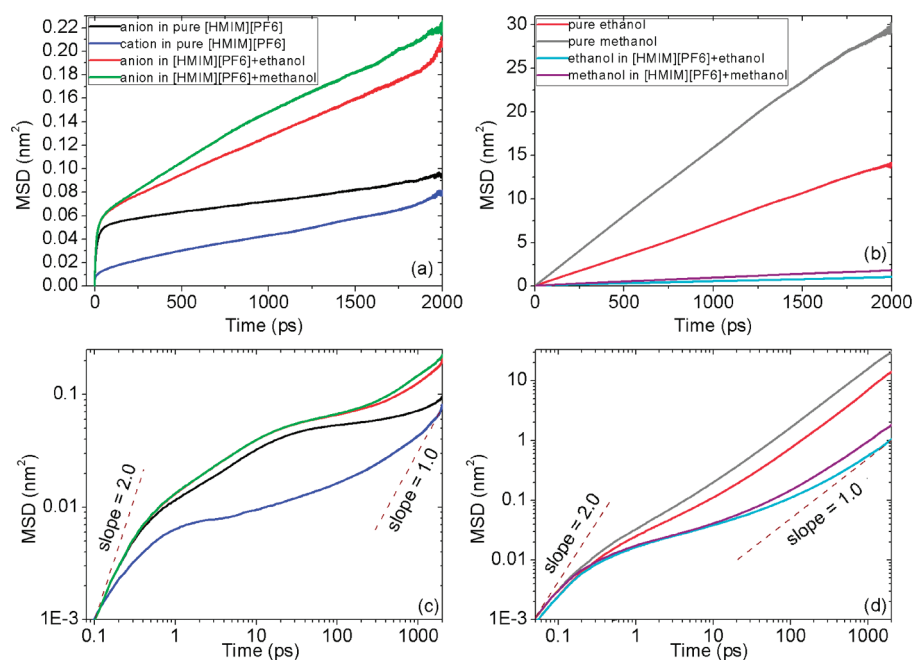


Figure 5. Time dependence of the MSDs of (a) cation and anion in pure [HMIM][PF₆] and in mixtures with an alcohol concentration of $x_{\text{alcohol}} = 0.5$ and (b) pure alcohols and both methanol and ethanol in mixtures with [HMIM][PF₆] at $x_{\text{alcohol}} = 0.5$. Parts (c) and (d) are the log–log plots of the MSDs of (a) and (b), respectively. Dashed lines of slope 1 and 2 have been included to identify the ballistic and diffusive regimes.

concentration of $x_{\text{alcohol}} = 0.5$. Likewise, in Figure 5(b) we represent the MSD of pure alcohols and both methanol and ethanol in mixtures with [HMIM][PF₆] at a solvent concentration of $x_{\text{alcohol}} = 0.5$. The results for HMIM⁺ and PF₆[−] included in Figure 5(a) are very similar to each other, with a faster diffusion of the anion at short times. However, after a few picoseconds both species diffuse approximately in the same proportion, which shows that the diffusion of these molecules is correlated and that they do not move separately.

Figures 5(c) and 5(d) show the logarithmic plots of Figures 5(a) and 5(b), respectively. If we compare the MSDs of pure ILs with those of pure alcohols or pure water,⁹⁹ it can be seen that ILs exhibit complex and slow dynamics, as we expected from the fact that the self-diffusion coefficients reported in Table 1 for pure ILs are around 2 orders of magnitude smaller than those of pure water or alcohols at the same temperature. In Figures 5(a) and (b) it seems that the dynamics reaches a diffusive regime after a few picoseconds, since then MSDs appear to have a linear dependence with time. However, Figures 5(c) and (d) prove that the situation is somehow more complex, and we can observe the existence of three different regimes that can be characterized by means of the dependence of the MSD with time. This can be measured as

$$\langle \Delta |\vec{r}(t)|^2 \rangle = \frac{1}{N} \left\langle \sum_{i=1}^N |\vec{r}_i(t) - \vec{r}_i(0)|^2 \right\rangle \propto t^\beta \quad (2)$$

where the sum extends over all the molecules present and β describes the type of motion of the molecules of the system. As we have seen, self-diffusion coefficients of pure ILs are on the order of 10^{-11} m²/s, which implies that ILs have very slow dynamics. For this reason, it is of fundamental importance to ensure that the system has reached the diffusive regime during the simulations to get correct values of the self-diffusion coefficient, which as can be seen is a long-time quantity. For this

purpose

$$\beta(t) = \frac{d \log(\Delta |\vec{r}(t)|^2)}{d \log(t)} \quad (3)$$

can be used to analyze the regime in which the system is. First, a ballistic behavior of the ions dominates at short times, so that $\beta = 2$. Then, at long times the molecules of the system exhibit a diffusive motion, and this Gaussian diffusion implies $\beta = 1$. Finally, a very long subdiffusive regime is found at intermediate times, this non-Gaussian dynamics (for which $\beta < 1$) being characteristic of glass formers in the supercooled region.⁶³ Many research groups have reported that, in these systems, true diffusive motion only appears over large time scales, which are usually on the order of nanoseconds.^{30,60–63} Looking at the log–log plot of the MSD of PF₆[−] represented in Figure 5(c), it can be seen that the transition from a ballistic regime to the subdiffusive one takes place at similar times in pure [HMIM][PF₆] and in its mixtures with alcohols. However, the diffusive regime is reached at lower times when alcohol is added to the system. Thus, the subdiffusive regime at intermediate times is progressively narrowed by the addition of alcohol to the mixture, as also detected in water.⁸⁰ On the other hand, as can be seen in Figure 5(d), motion of alcohol molecules in mixtures with ILs is very different from that in pure alcohols at room temperature. In this latter case, the subdiffusive regime at intermediate times is almost absent, while in mixtures with IL it extends from about 0.2 ps up to hundreds or thousands of picoseconds.

This behavior can be further described by defining the characteristic times of ballistic (τ_b) and diffusive (τ_d) regimes defined as the times corresponding to the beginning and the end of the intermediate subdiffusive plateau that can be approximated as the intersection of the straight line defining the plateau and the two lines corresponding to the ballistic and diffusive regime themselves, in the same way that we reported in our previous

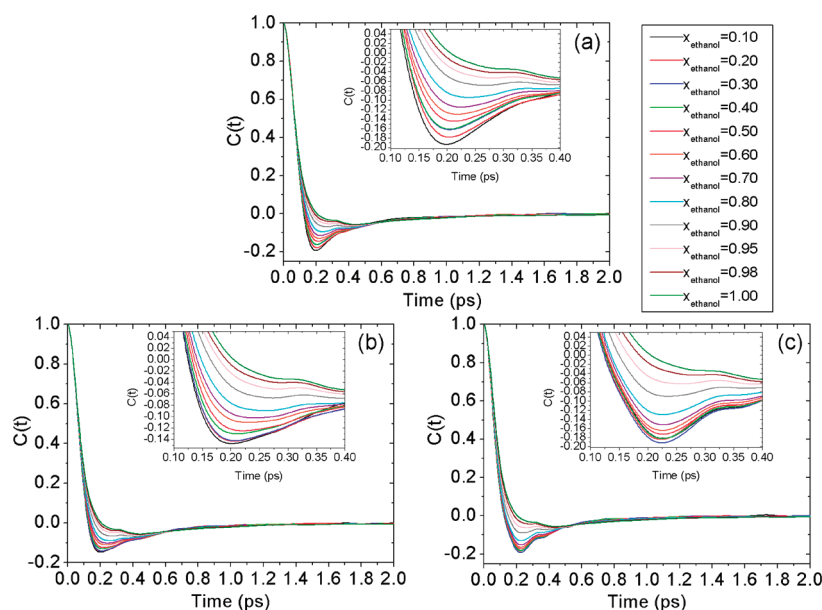


Figure 6. Concentration dependence of the VACFs of ethanol molecules in mixtures with (a) [HMIM][PF₆], (b) [HMIM][BF₄], and (c) [HMIM][Cl].

work for IL + water mixtures.⁸⁰ The end of the ballistic regime essentially coincides with the collision time. The calculated collision times increase monotonically with increasing alcohol concentration, much more rapidly above a solvent concentration of 80%. This behavior is due to the fact that the interactions present in an IL are stronger than the ones that exist in alcohols, so the greater the number of alcohol molecules in the mixture, the longer collision times are. In addition, diffusive times gradually decrease with increasing the amount of alcohol in all cases, so the addition of alcohol causes a faster transition to the diffusive regime. Moreover, it must be noticed that the subdiffusive regime at intermediate times extends over thousands of picoseconds, since τ_d is around 4 orders of magnitude greater than τ_b . Finally, let us point out that collision and diffusive times are shorter and larger, respectively, for the halogen anion than for the polyatomic ones, in agreement with our previous observations for the interaction between anions and alcohol molecules and therefore for the clusterization of alcohols in mixtures with ILs. These observations show a greater clusterization of alcohol molecules in the presence of hexafluorophosphate, which implies that the motion of alcohol molecules is more similar to that in pure alcohol.

A different way of characterizing single-particle dynamics in this kind of system is through the center-of-mass VACFs. In general, a VACF can be defined as

$$C(t) = \langle \vec{v}(t) \cdot \vec{v}(0) \rangle \quad (4)$$

where the vector $\vec{v}(t) = \sum_j m_j \vec{v}_j / \sum_j m_j$ is the velocity of the center-of-mass of the molecule and the scalar product is calculated in the laboratory frame. As far as we know, this is the first time that computational results are reported for this magnitude in alcohol + IL mixtures. In Figures 6 and 7, concentration dependence of normalized VACFs of ethanol and methanol molecules, respectively, are shown. The VACFs of both pure ethanol and methanol are in good agreement with the MD results reported previously by Saiz et al.¹⁰⁰ for liquid ethanol and by Haughney et al.⁹⁷ for

liquid methanol. The $C(t)$ functions of both pure alcohols exhibit a secondary maximum at approximately 0.3 ps, which is more marked for pure methanol. The same behavior was found in pure water,⁸⁰ with this secondary maximum placed at shorter times (around 0.15 ps). $C(t)$ decays in a subpicosecond scale, and the first zero of the VACFs, which indicates the mean collision time of alcohol molecules, increases with the addition of alcohol to the mixture in all cases until the value of pure alcohols (around 0.21 ps for ethanol and 0.28 ps for methanol due to the “cage effect”) is reached. Moreover, at the same amount of alcohol, the mean collision time is somewhat longer in mixtures with [HMIM][PF₆] than that in mixtures with [HMIM][Cl] since alcohol molecules seem to be homogeneously placed in the structure of the chlorinated IL⁸² and alcohol motion in bulk cavities of mixtures with solvophobic ILs is more similar to that in pure alcohols. Collision times manifest the same trend as in our previous studies of IL + water mixtures.⁸⁰ On the other hand, correlations are rapidly and monotonically weakened in all the studied systems, so within 0.6 ps correlations are no longer present for alcohol molecules. Furthermore, there is no evidence of long-time tails in these mixtures. Finally, the oscillatory behavior of the VACFs found in [HMIM][Cl] + water mixtures,⁸⁰ which indicates a “rattling” motion of the molecules inside the cages formed by their heavier neighbors and is related to the diffusive regime in MSD,⁶⁹ is not registered in mixtures of this chlorinated IL with alcohols.

CONCLUSIONS

We performed MD simulations for mixtures of three imidazolium-based ILs, [HMIM][PF₆], [HMIM][BF₄], and [HMIM][Cl], with methanol and ethanol, and we investigated several dynamical properties of the system. Specifically, we analyzed the effect of the anion hydrophobicity degree, of the length of the molecular chain of the alcohol, and of alcohol concentration on the evolution of the dynamics of the mixtures. Furthermore, we analyzed self-diffusion coefficients of the species present in the mixtures, MSDs (with an additional study of both ballistic and diffusive regimes), and VACFs of alcohol molecules.

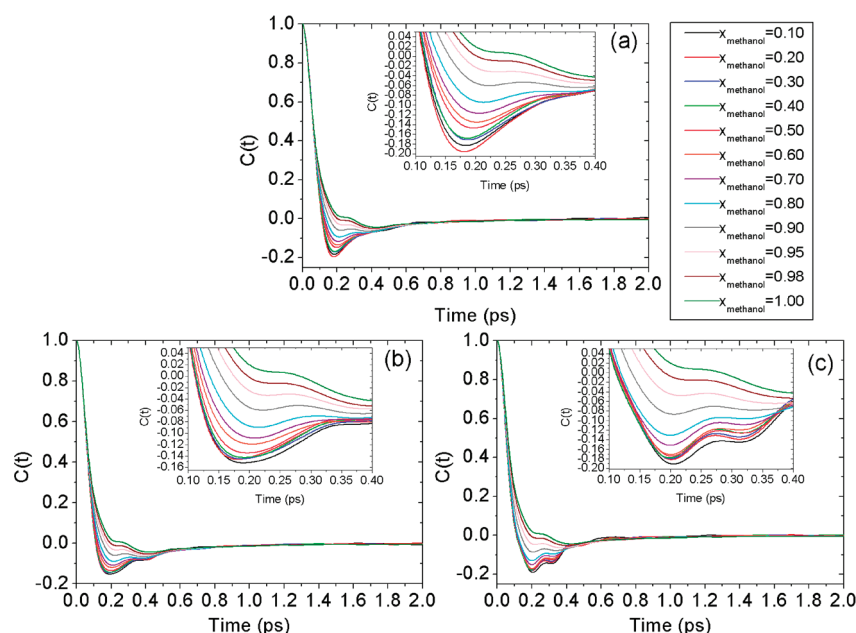


Figure 7. Concentration dependence of the VACFs of methanol in mixtures with (a) [HMIM][PF₆], (b) [HMIM][BF₄], and (c) [HMIM][Cl].

Self-diffusion coefficients were computed from the slopes of the center-of-mass MSDs of the corresponding molecule, using data between 200 and 1800 ps. To check the accuracy of the force field employed we computed the self-diffusion coefficients of both ions in pure ILs and of pure alcohols and compared them with previously reported values. Our self-diffusion coefficients for pure liquids were found to be in good agreement with the experimental and computational values available in the literature, and self-diffusivities of the ions were around 2 orders of magnitude smaller than those of pure alcohols or pure water at room temperature. Moreover, cations have a faster diffusion than their counterions, in spite of being heavier and larger. In mixtures with both alcohols, self-diffusion coefficients increase with increasing concentrations of alcohol, and two different regimes can be observed for this magnitude: (i) at high IL concentrations self-diffusion coefficients of alcohol molecules increase very slowly, which is associated to a possible glassy state of the system, and (ii) at low IL concentrations self-diffusion coefficients of alcohol molecules show a rapid increase with the amount of alcohol, which is related to percolation of alcohol regions (especially in mixtures with [HMIM][PF₆]), thus breaking the IL polar network. Faster diffusion was observed for PF₆[−] than for the halogen anion in mixtures with both alcohols due to the higher hydrophobicity degree of hexafluorophosphate and the stronger interactions between alcohol molecules and chloride.

The analysis of the MSDs of these liquids and their mixtures confirms that the dynamics of these systems is very slow and complex. From the representations of the MSDs of the center-of-mass of the alcohols we observed three different time scales. At very short times the ballistic motion is characterized by the quadratic dependence of the MSD with the time, while at long times (after the alcohol molecules have undergone many collisions in the bulk) the behavior becomes diffusive and the dependence of MSD with time becomes linear. The subdiffusive regime observed at intermediate times within a time scale of several thousands of picosecondss is associated with the slow structural relaxation of the studied mixtures, and this non-Markovian

dynamics exhibits a power-law dependence of the MSD with time with an exponent smaller than unity. This intermediate plateau was found to be narrower as the concentration of alcohol increases, until the faster dynamics of pure alcohols is reached. Moreover, the diffusive regime is reached at larger times in mixtures with the chlorinated IL since the motion of alcohol molecules is more similar to that in pure alcohol when the highly solvophobic hexafluorophosphate is present in the mixture.

Finally, the analysis of the VACFs of alcohol molecules revealed that the correlations are rapidly and monotonically weakened in all cases and that the mean collision time increases with the addition of alcohol to the mixture. These collision times were shown to be longer for the more hydrophobic ILs, as determined by the clusterization degree of alcohols in mixtures with these ILs, which shows the dominant role of the anion on the dynamical properties of IL + solvent mixtures.

AUTHOR INFORMATION

Corresponding Author

*E-mail: luismiguel.varela@usc.es.

ACKNOWLEDGMENT

The authors thank the financial support of Xunta de Galicia through the research projects with references 10-PXI-103-294 PR and 10-PXIB-206-294 PR. Moreover, this work was funded by the Spanish Ministry of Science and Innovation (Grant No. FIS2008-04894/FIS). All these research projects are partially supported by FEDER. J. Carrete and T. Méndez-Morales thank the Spanish ministry of Education for their FPU grants. Facilities provided by the Galician Supercomputing Centre (CESGA) are also acknowledged.

REFERENCES

- (1) Wilkes, J. S. *Green Chem.* **2002**, *4*, 73–80.
- (2) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D. *Green Chem.* **2001**, *3*, 156–164.

- (3) Hagiwara, R.; Ito, I. *J. Fluorine Chem.* **2000**, *105*, 221–227.
- (4) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH Verlag GmbH Co. KGaA: Weinheim, Germany, 2003.
- (5) Heintz, A. J. *Chem. Thermodyn.* **2005**, *37*, 525–535.
- (6) Earle, M. J.; Esperança, J. M. S. S.; Gilea, M. A.; Canongia-Lopes, J. N.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. *Nature (London, U.K.)* **2006**, *439*, 831–834.
- (7) Rogers, R. D.; Seddon, K. R. *Science* **2003**, *302*, 792–793.
- (8) Fannin, A. A.; King, L. A.; Levisky, J. A.; Wilkes, J. S. *J. Phys. Chem.* **1984**, *88*, 2609–2614.
- (9) Wakai, C.; Oleinikova, A.; Ott, M.; Weingärtner, H. *J. Phys. Chem. B* **2005**, *109*, 17028–17030.
- (10) Earle, M. J.; Seddon, K. R. *Pure Appl. Chem.* **2000**, *72*, 1391–1398.
- (11) Hussey, C. L. *Pure Appl. Chem.* **1988**, *60*, 1763–1772.
- (12) Bonhôte, P.; Dias, A.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 1168–1178.
- (13) Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2083.
- (14) Rogers, R. D.; Seddon, K. R. *Ionic Liquids, Industrial Applications to Green Chemistry*; ACS Symposium Series, 818; American Chemical Society: Washington DC, 2002.
- (15) Rogers, R. D.; Seddon, K. R. *Ionic Liquids as Green Solvents: Progress and Prospects*; ACS Symposium Series, 856; American Chemical Society: Washington DC, 2003.
- (16) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772–3789.
- (17) Holbrey, J. D.; Seddon, K. R. *Clean Prod. Proc* **1999**, *1*, 223–236.
- (18) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H. *J. Am. Chem. Soc.* **2002**, *124*, 926–927.
- (19) Lu, W.; Fadeev, A. G.; Qi, B.; Smela, E.; Mattes, B. R.; Ding, J.; Spinks, G. M.; Mazurkiewicz, J.; Zhou, D.; Wallace *Science* **2002**, *297*, 983–987.
- (20) Liu, W.; Ye, C.; Gong, Q.; Wang, H.; Wang, P. *Tribol. Lett.* **2002**, *13*, 81–85.
- (21) Xu, W.; Angell, C. A. *Science* **2003**, *302*, 422–425.
- (22) Seki, S.; Kobayashi, Y.; Miyashiro, H.; Ohno, Y.; Usami, A.; Mita, Y.; Watanabe, M.; Terada, N. *Chem. Commun.* **2006**, *2006*, 544–545.
- (23) Anderson, J. L.; Armstrong, D. W.; Wei, G. *Anal. Chem.* **2006**, *78*, 2892–2902.
- (24) Fabregat-Santiago, F.; Bisquert, J.; Palomares, E.; Otero, L.; Kuang, D.; Zakeeruddin, S. M.; Grätzel, M. *J. Phys. Chem. C* **2007**, *111*, 6550–6560.
- (25) Han, X.; Armstrong, D. W. *Acc. Chem. Res.* **2007**, *40*, 1079–1086.
- (26) MacFarlane, D. R.; Meakin, P.; Sun, J.; Amini, N.; Forsyth, M. *J. Phys. Chem. B* **1999**, *103*, 4164–4170.
- (27) Sun, J.; Forsyth, M.; MacFarlane, D. R. *J. Phys. Chem. B* **1998**, *102*, 8858–8864.
- (28) Carmichael, A. J.; Seddon, K. R. *J. Phys. Org. Chem.* **2000**, *13*, 591–595.
- (29) Wilkes, J. S. *J. Mol. Catal. A: Chem.* **2004**, *214*, 11–17.
- (30) Cadena, C.; Zhao, Q.; Snurr, R. Q.; Maginn, E. J. *J. Phys. Chem. B* **2006**, *110*, 2821–2832.
- (31) Wu, X.; Liu, Z.; Huang, S.; Wang, W. *Phys. Chem. Chem. Phys.* **2005**, *7*, 2771–2779.
- (32) Price, W. S. *Concepts Magn. Reson.* **1997**, *9*, 299–336.
- (33) Price, W. S. *Concepts Magn. Reson.* **1998**, *10*, 197–237.
- (34) Marquardt, E.; Grober, N.; Richter, J. *Opt. Eng.* **1997**, *36*, 2857–2862.
- (35) Marquardt, E.; Richter, J. *Opt. Eng.* **1998**, *37*, 1514–1519.
- (36) Umecky, T.; Kanakubo, M.; Ikushima, Y. *Fluid Phase Equilib.* **2005**, *228–229*, 329–333.
- (37) Every, H. A.; Bishop, A. G.; MacFarlane, D. R.; Orädd, G.; Forsyth, M. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1758–1765.
- (38) Noda, A.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2001**, *105*, 4603–4610.
- (39) Jin, H.; O'Hare, B.; Dong, J.; Arzhantsev, S.; Baker, G. A.; Wishart, J. F.; Benesi, A. J.; Maroncelli, M. *J. Phys. Chem. B* **2008**, *112*, 81–92.
- (40) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2004**, *108*, 16593–16600.
- (41) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Tsuzuki, S.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2006**, *110*, 2833–2839.
- (42) Umecky, T.; Kanakubo, M.; Ikushima, Y. *J. Mol. Liq.* **2005**, *119*, 77–81.
- (43) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2005**, *109*, 6103–6110.
- (44) Bara, J. E.; Carlisle, T. K.; Gabriel, C. J.; Camper, D.; Finotello, A.; Gin, D. L.; Noble, R. D. *Ind. Eng. Chem. Res.* **2009**, *48*, 2739–2751.
- (45) Morgan, D.; Ferguson, L.; Scovazzo, P. *Ind. Eng. Chem. Res.* **2005**, *44*, 4815–4823.
- (46) Shiflett, M. B.; Yokozeki, A. *Ind. Eng. Chem. Res.* **2005**, *44*, 4453–4464.
- (47) Shiflett, M. B.; Harmer, M. A.; Junk, C. P.; Yokozeki, A. *Fluid Phase Equilib.* **2006**, *242*, 220–232.
- (48) Iacob, C.; Sangoro, J. R.; Papadopoulos, P.; Schubert, T.; Naumov, S.; Valiullin, R.; Kärger, J.; Kremer, F. *Phys. Chem. Chem. Phys.* **2010**, *12*, 13798–13803.
- (49) Lovell, C. S.; Walker, A.; Damion, R. A.; Radhi, A.; Tanner, S. F.; Budtova, T.; Ries, M. E. *Biomacromolecules* **2010**, *11*, 2927–2935.
- (50) Sarraute, S.; Costa Gomes, M. F.; Pádua, A. A. H. *J. Chem. Eng. Data* **2009**, *54*, 2389–2394.
- (51) Wong, C.; Soriano, A. N.; Li, M. *Fluid Phase Equilib.* **2008**, *271*, 43–52.
- (52) Nieto de Castro, C. A.; Langa, E.; Morais, A. L.; Lopes, M. L. M.; Lourenço, M. J. V.; Santos, F. J. V.; Santos, M. S. C. S.; Canongia-Lopes, J. N.; Veiga, H. I. M.; Macatrac, M. *Fluid Phase Equilib.* **2010**, *294*, 157–179.
- (53) Menjoge, A.; Dixon, J.; Brennecke, J. F.; Maginn, E. J.; Vasenkov, S. *J. Phys. Chem. B* **2009**, *113*, 6353–6359.
- (54) Heintz, A.; Lehmann, J. K.; Schmidt, E.; Wandschneider, A. *J. Solution Chem.* **2009**, *38*, 1079–1083.
- (55) Richter, J.; Leuchter, A.; Grober, N. *J. Mol. Liq.* **2003**, *103–104*, 359–370.
- (56) Su, W. C.; Chou, C. H.; Wong, D. S. H.; Li, M. H. *Fluid Phase Equilib.* **2007**, *252*, 74–78.
- (57) Jahangiri, S.; Taghikhani, M.; Behnejad, H.; Ahmadi, S. *J. Mol. Phys.* **2008**, *8*, 1015–1023.
- (58) Huang, X.; Margulis, C. J.; Li, Y.; Berne, B. J. *J. Am. Chem. Soc.* **2005**, *127*, 17842–17851.
- (59) Hu, Z.; Margulis, C. J. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 831–836.
- (60) Kelkar, M. S.; Maginn, E. J. *J. Phys. Chem. B* **2007**, *111*, 4867–4876.
- (61) Kelkar, M. S.; Shi, W.; Maginn, E. J. *Ind. Eng. Chem. Res.* **2008**, *47*, 9115–9126.
- (62) Liu, Z.; Chen, T.; Bell, A.; Smit, B. *J. Phys. Chem. B* **2010**, *114*, 4572–4582.
- (63) Del Pópolo, M. G.; Voth, G. A. *J. Phys. Chem. B* **2004**, *108*, 1744–1752.
- (64) Borodin, O.; Smith, G. D. *J. Phys. Chem. B* **2006**, *110*, 11481–11490.
- (65) Margulis, C. J.; Stern, H. A.; Berne, B. J. *J. Phys. Chem. B* **2002**, *106*, 12017–12021.
- (66) Margulis, C. J. *Mol. Phys.* **2004**, *102*, 829–838.
- (67) Micaelo, N. M.; Baptista, A. M.; Soares, C. M. *J. Phys. Chem. B* **2006**, *110*, 14444–14451.
- (68) Morrow, T. I.; Maginn, E. J. *J. Phys. Chem. B* **2002**, *106*, 12807–12813.
- (69) Urahata, S. M.; Ribeiro, M. C. C. *J. Chem. Phys.* **2005**, *122*, 024511(1)–024511(9).
- (70) Yan, T.; Burnham, C. J.; Del Pópolo, M. G.; Voth, G. A. *J. Phys. Chem. B* **2004**, *108*, 11877–11881.
- (71) Liu, Z.; Huang, S.; Wang, W. *J. Phys. Chem. B* **2004**, *108*, 12978–12989.
- (72) Andrade, J.; Böes, E. S.; Stassen, H. *J. Phys. Chem. B* **2002**, *106*, 13344–13351.

- (73) Prado, C. E. R.; Freitas, L. C. G. *J. Mol. Struct. (Theochem.)* **2007**, *847*, 93–100.
- (74) Liu, Z.; Wu, X.; Wang, W. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1096–1104.
- (75) Hanke, C. G.; Lynden-Bell, R. M. *J. Phys. Chem. B* **2003**, *107*, 10873–10878.
- (76) Jiang, W.; Wang, Y.; Voth, G. A. *J. Phys. Chem. B* **2007**, *111*, 4812–4818.
- (77) Feng, S.; Voth, G. A. *Fluid Phase Equilib.* **2010**, *294*, 148–156.
- (78) Annappureddy, H. V. R.; Hu, Z.; Xia, J.; Margulis, C. J. *J. Phys. Chem. B* **2008**, *112*, 1770–1776.
- (79) Liu, X.; Vlugt, T. J. H.; Bardow, A. *J. Phys. Chem. B* **2011**, *115*, 8506–8517.
- (80) Méndez-Morales, T.; Carrete, J.; Cabeza, O.; Gallego, L. J.; Varela, L. M. *J. Phys. Chem. B* **2011**, *115*, 6995–7008.
- (81) Raabe, G.; Köhler, J. *J. Chem. Phys.* **2008**, *129*, 144503(1)–144503(8).
- (82) Méndez-Morales, T.; Carrete, J.; Cabeza, O.; Gallego, L. J.; Varela, L. M. *J. Phys. Chem. B* **2011**, *115*, 11170–11182.
- (83) Spoel, D. V. D.; Lindahl, E.; Hess, B.; Buuren, A. R. V.; Apol, E.; Meulenhoff, P. J.; Tieleman, D. P.; Sijbers, A. L. T. M.; Feenstra, K. A.; Drunen et al. *GROMACS User Manual version 4.0*; <http://www.gromacs.org>, 2005.
- (84) Pereiro, A. B.; Rodríguez, A. J. *Chem. Thermodyn.* **2007**, *39*, 978–989.
- (85) Gómez, E.; Calvar, N.; Domínguez, I.; Domínguez, A. *Phys. Chem. Liq.* **2006**, *44*, 409–417.
- (86) Rilo, E.; Pico, J.; García-Garabal, S.; Varela, L. M.; Cabeza, O. *Fluid Phase Equilib.* **2009**, *285*, 83–89.
- (87) Jorgensen, W. L. *J. Phys. Chem.* **1986**, *90*, 1276–1284.
- (88) Darden, T.; York, D.; Pedersen, L. J. *J. Chem. Phys.* **1993**, *98*, 10089–10094.
- (89) Hess, B.; Bekker, H.; Berendsen, H. J. C.; Fraaije, J. G. E. M. *J. Comput. Chem.* **1997**, *18*, 1463–1472.
- (90) Hess, B. *J. Chem. Theory Comput.* **2007**, *4*, 116–122.
- (91) Bussi, G.; Donadio, D.; Parrinello, M. *J. Chem. Phys.* **2007**, *126*, 014101(1)–014101(7).
- (92) Parrinello, M.; Rahman, A. *J. Appl. Phys.* **1981**, *52*, 7182–7190.
- (93) Einstein, A. *Ann. Phys.* **1905**, *17*, 549–560.
- (94) Frenkel, D.; Smit, B. *Understanding Molecular Simulation*; Academic Press: New York, 1996.
- (95) Karger, N.; Vardag, T.; Lüdemann, H.-D. *J. Chem. Phys.* **1990**, *93*, 3437–3444.
- (96) Martí, J.; Padró, J. A.; Guàrdia, E. *J. Mol. Liq.* **1995**, *64*, 1–12.
- (97) Haughney, M.; Ferrario, M.; McDonald, I. R. *J. Phys. Chem.* **1987**, *91*, 4934–4940.
- (98) Guevara-Carrion, G.; Nieto-Draghi, C.; Vrabec, J.; Hasse, H. *J. Phys. Chem. B* **2008**, *112*, 16664–16674.
- (99) Stern, H.; Rittner, F.; Berne, B. J.; Friesner, R. A. *J. Chem. Phys.* **2001**, *115*, 2237–2251.
- (100) Saiz, L.; Padró, J. A.; Guàrdia, E. *J. Phys. Chem. B* **1997**, *101*, 78–86.