

Computational Screening of the Physical Properties of Water-in-Salt Electrolytes

Trinidad Mendez-Morales,^{†,‡,¶} Zhujie Li,^{†,‡,¶} and Mathieu Salanne^{*,†,‡,¶,§}

[†]*Maison de la Simulation CEA, CNRS, Université Paris-Sud, UVSQ, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France*

[‡]*Sorbonne Université, CNRS, Physico-Chimie des Électrolytes et Nanosystèmes Interfaciaux, F-75005 Paris, France*

[¶]*Réseau sur le Stockage Electrochimique de l'Énergie (RS2E), FR CNRS 3459, Amiens, France*

[§]*Institut Universitaire de France (IUF), 75231 Paris Cedex 05, France*

E-mail: mathieu.salanne@sorbonne-universite.fr

Abstract

Water-in-salts form a new family of electrolytes with properties distinct from the ones of conventional aqueous systems and ionic liquids. They are currently investigated for Li-ion batteries and supercapacitors applications, but to date most of the focus was put on the system based on the LiTFSI salt. Here we study the structure and the dynamics of a series of water-in-salts with different anions. They have a similar parent structure but they vary systematically through their symmetric/asymmetric feature and the length of the fluorocarbonated chains. The simulations allow to determine their tendency to nanosegregate, as well as their transport properties (viscosity, ionic conductivity, diffusion coefficients) and the amount of free water, providing useful data for potential applications in energy storage devices.

Lithium-ion batteries (LIBs) involve organic electrolytes, which allows them to reach high voltages and thus increases the energy density of the devices.¹ However, some concerns remain associated with their cost, safety and environmental impact.^{2,3} Aqueous electrolytes can be an alternative to solve these problems, but the use of water as solvent results in a much narrower electrochemical stability window.^{4,5} Recently, a new class of water-in-salt (WiS) electrolytes was reported by Suo *et al.*⁶ to expand the electrochemical stability window up to nearly 3 V by using aqueous solutions of lithium bis[(trifluoromethyl)sulfonyl]imide (LiTFSI) with a molality of 21 m (mol/kg). In such superconcentrated electrolytes the increased stability window is due to several effects:⁷ Firstly, water molecules display a specific speciation, since most of them belong to the lithium ion solvation shells, thus leading to low fractions of free water molecules. This reduces the concentration of water at the positive interface, which mainly contains TFSI⁻ anions.^{6,8} However, the main reason for the extended voltage window is the formation of a solid electrolyte interface (SEI) layer that mainly consists of LiF as a result of the electrochemical decomposition of the TFSI anion.⁹⁻¹¹ Although most of the studies of WiS electrolytes were performed using the LiTFSI salt,¹²⁻¹⁶ the WiS concept was extended to other metallic ions such as potassium,¹⁷ sodium¹⁸⁻²⁰ and zinc-based²¹ electrolytes.

In parallel, the chemistry of Li-ion based WiS electrolyte family was also explored further. For example, since the concentration of LiTFSI in the WiS electrolyte is limited by the solubility limit, it was proposed to mix them with other salts to increase further the electrochemical stability window.^{22,23} On the contrary, the WiS electrolytes form biphasic systems when they are mixed with simpler solutions such as highly concentrated aqueous LiCl,²⁴ which was exploited to develop a dual battery involving lithium ions together with halogen conversion-intercalation.²⁵ A mixture of lithium and potassium acetate-based WiS was also recently proposed as a greener and lower-cost alternative to TFSI-based systems,²⁶ showing further the versatility of this family of electrolytes.

In practice, it could be possible to develop WiS electrolytes with a large number of

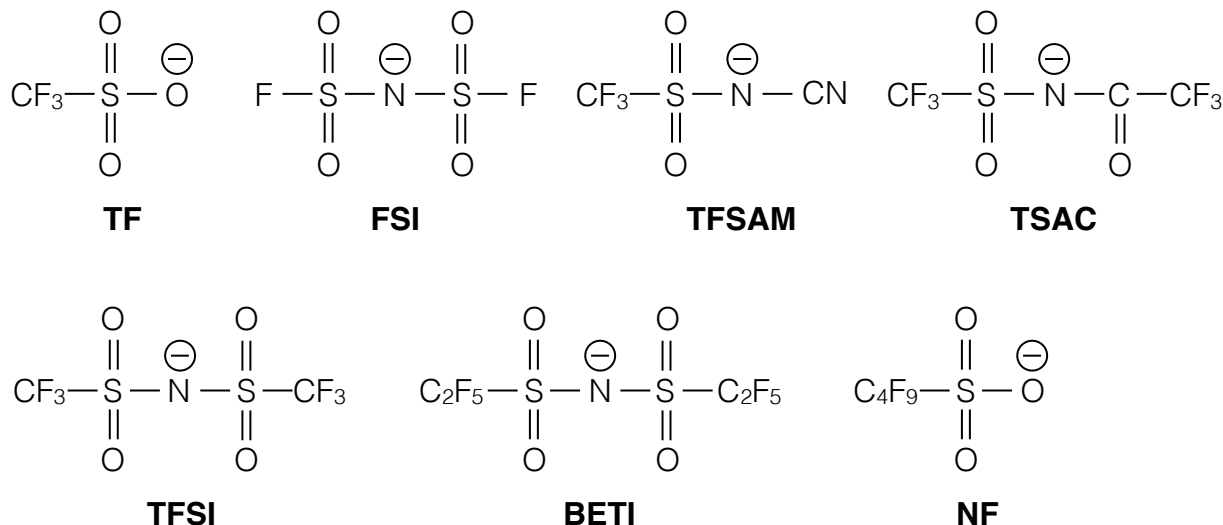


Figure 1: Chemical formulae of the various anions investigated in this work. The full names of the molecules are trifluoromethanesulfonate (TF), bis(fluorosulfonyl)imide (FSI), 2,2,2-trifluoromethylsulfonyl-N-cyanoamide (TFSAM), 2,2,2-trifluoro-N-(trifluoromethylsulfonyl) acetamide (TSAC), bis[(trifluoromethylsulfonyl)imide (TFSI), bis[(pentafluoroethylsulfonyl)imide (BETI) and nonafluorobutanesulfonate (NF).

different anions. Here we show that molecular dynamics (MD) simulations provide a convenient framework for studying their physical properties. We studied seven different anions, including five which were imide-based, namely bis[(trifluoromethylsulfonyl)imide (TFSI), bis(fluorosulfonyl)imide (FSI), bis[(pentafluoroethylsulfonyl)imide (BETI), 2,2,2-trifluoromethylsulfonyl-N-cyanoamide (TFSAM) and 2,2,2-trifluoro-N-(trifluoromethylsulfonyl) acetamide (TSAC), and two sulfonate anions, trifluoromethanesulfonate (TF) and nonafluorobutanesulfonate (NF). Their chemical formulae are provided on Figure 1. The same force field is used for all the ions²⁷ in order to ensure systematic comparisons of their properties. We first study the structure at a large molality of 15 mol kg⁻¹. One of the systems shows a tendency to phase separation, so that we discard it from the other analysis. We then compare the conductivity, the viscosity of the liquids as well as the individual diffusion coefficients of all the species. Comparing these transport properties allows to rank the various anionic species for applications. Finally, we determine the amount of “free” water in the various systems since this quantity is known to influence the reactivity at the electrochemical interface.

Among all the mixtures considered in this article, the only one for which there is available experimental data concerning the solubility limit is LiTFSI-H₂O, whose value was reported to be a molality of 31.3 m at 303.15 K.¹⁵ Accurately computing solubilities is very challenging in molecular dynamics,²⁸ so that we decided to analyze the medium/long range structure as a proxy to determine the relative miscibility of the systems. To do this, partial structure factors were computed using the formalism proposed by Faber and Ziman,²⁹ in which the structure factor is represented by the correlations between the different chemical species α and β :

$$S_{\alpha\beta}(q) = 1 + 4\pi\rho \int_0^\infty dr \frac{\sin(qr)}{qr} r^2 (g_{\alpha\beta}(r) - 1) \quad (1)$$

where $g_{\alpha\beta}(r)$ are the partial radial distribution functions and ρ is the number density of the system.

Figure 2 shows the partial structure factors of (a) S-S and (b) O(H₂O)-O(H₂O) atoms in the different mixtures. A demixing effect indicated by the peak at $q \rightarrow 0$ in the system based on the NF-anion can be seen. This is also shown by a snapshot of the simulation box included in Figure 2, in which we can clearly observe a segregated distribution of the liquid into (c) apolar (composed of the CF₂- and CF₃-groups of the NF-anion) and (d) polar (consisting of lithium atoms, water molecules and the negatively charged SO₃-group of the NF-anion) domains. That is, we can conclude that LiNF solubility in water is not high enough to satisfy the WiS condition and it will not be included in our analysis hereinafter. All the other simulated WiS show similar structures, *i.e.* the formation of nano-heterogeneities¹² at medium range as can be seen from the presence of intense peaks at q values ranging from 0.95 to 1.5 Å⁻¹ and from 0.7 to 0.9 Å⁻¹ for the S-S and the O-O partial structure factors, respectively.

The use of WiS as electrolytes in energy storage devices will then be a compromise between a high concentration to extend the electrochemical stability window and a good ionic conductivity that guarantees acceptable power density.^{15,16,30} Thus, the tailored design

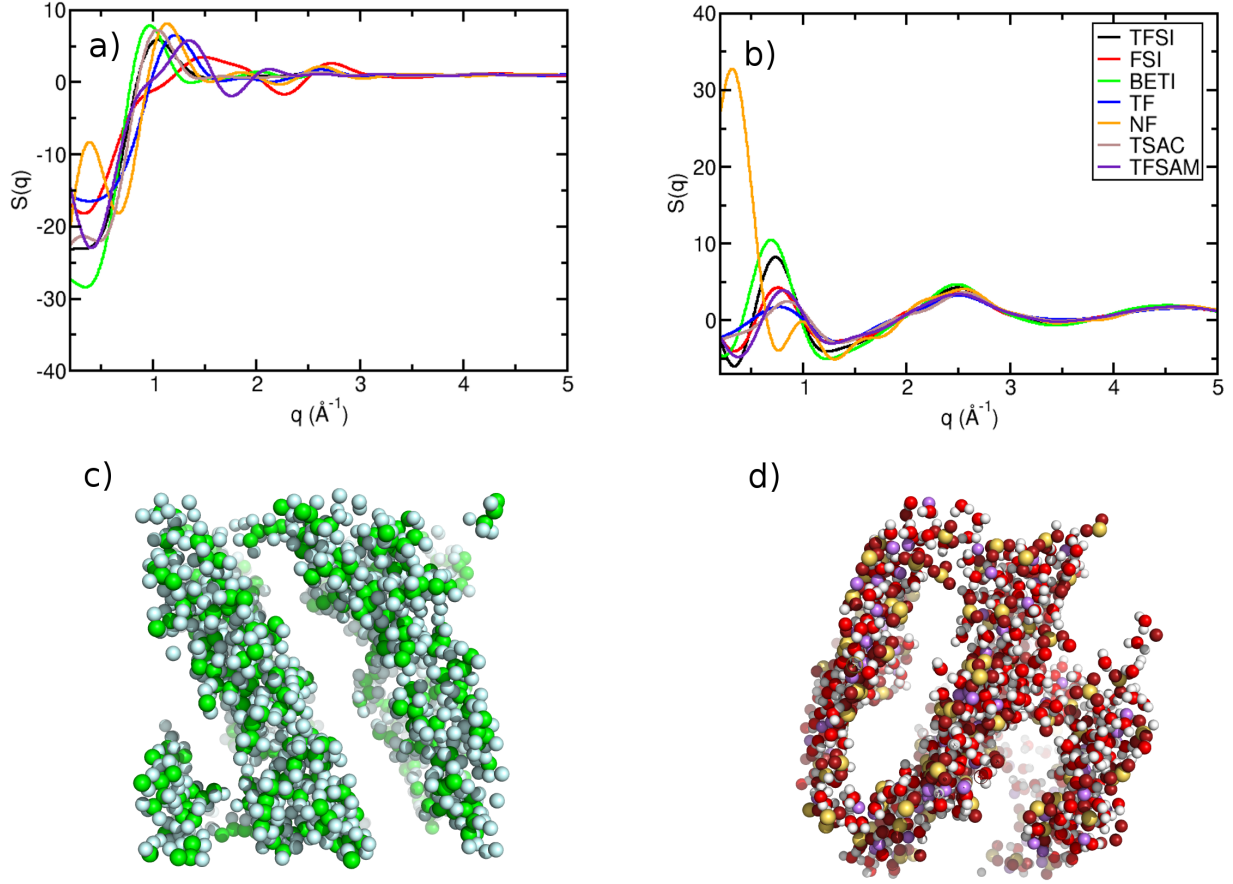


Figure 2: Partial structure factors of (a) S-S and (b) O(H₂O)-O(H₂O) atoms from MD simulations at 298.15 K for all the different mixtures. Snapshots of the simulation box that shows a segregation of the LiNF-H₂O system into (c) apolar (composed of C and F atoms, in green and light blue, respectively) and (d) polar (consisting of lithium atoms in violet, H₂O molecules in white and light red, and S and O atoms, in yellow and dark red, respectively) domains.

of superconcentrated aqueous electrolyte systems requires a deep understanding of the ion transport mechanism, and several reports suggested a fast Li ion transport through water-rich domains.^{12,13} The two key collective transport quantities are the electrical conductivity and the viscosity. The former can be calculated in molecular dynamics simulations using

$$\sigma = \frac{e^2}{k_B T V} \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\sum_i q_i \Delta_i(t)|^2 \rangle \quad (2)$$

where e is the elementary charge, V is the volume of the simulation cell, T is the temperature,

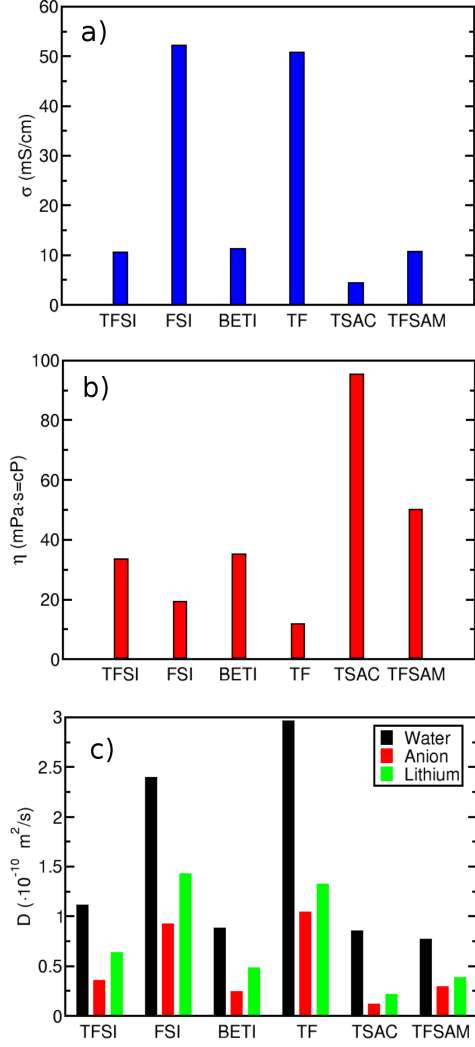


Figure 3: Comparison of the transport properties of the WiS electrolytes at room temperature. (a) ionic conductivity; (b) viscosity; (c) diffusion coefficients.

k_B is the Boltzmann constant and $\Delta_i(t) = \vec{r}_i(t) - \vec{r}_i(0)$ is the displacement of the ion i , which carries a charge q_i , over a time interval t (brackets $\langle \dots \rangle$ indicate an ensemble average). This expression includes the contribution not only of the self-terms of each ion but also the complex effect of cross-correlations due to the correlated motion of ions. The electrical conductivities obtained using Eq.(2) are included in Figure 3a.

The shear viscosity of the electrolytes was computed within the Green-Kubo (GK) formalism³¹ by integration of the stress-tensor correlation function

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle \Pi_{\alpha\beta}(0) \Pi_{\alpha\beta}(t) \rangle dt \quad (3)$$

where $\Pi_{\alpha\beta}$ represents any of the five independent components of the stress tensor, Π_{xy} , Π_{xz} , Π_{yz} , Π_{xx-yy} , $\Pi_{2zz-xx-yy}$. The values obtained for the viscosity of each system, that is, the value of the plateau at which the running integral in Eq.(3) converges after a certain time, are shown in Figure 3b.

The simulations predict a LiTFSI-H₂O viscosity in good agreement with experimental data (≈ 33 cP instead of 22 cP³²), while they underestimate the ionic conductivity by a factor 2,^{6,15,32} which corresponds to typical error for the prediction of transport properties in electrolytes by non-polarizable molecular dynamics.³³ Although the use of a different parameterization for the partial charges and Lennard-Jones parameters of the anion could improve the situation,³² the present parameters were chosen in order to keep consistency between all the different anions studied and to compare them without introducing any bias.

When comparing the various liquids, we observe that they can be separated between three groups. Firstly, the superconcentrated LiFSI-H₂O and LiTF-H₂O mixtures have low viscosities and high ionic conductivities. In particular, the latter (~ 50 mS/cm in both cases) is greater than the values observed in typical non-aqueous electrolytes used in commercial Li-ion batteries³⁴ and supercapacitors.³⁵ Then we observe that the LiBETI-H₂O mixture shows similar performances as the reference TFSI system. The LiTFSAM-H₂O has a larger viscosity but a similar conductivity as those two, so it can be put in the same group. Finally, the system involving the TSAC anions shows significantly poorer performances than all the others, with a viscosity reaching ~ 100 cP and a low ionic conductivity. It is worth noting that the variations between anions cannot easily be explained using their relative size/weights since for example TFSAM and FSI have relatively similar sizes, as well as TFSI and TSAC, while BETI has the largest fluorocarbonated chains. Nevertheless, if we split them between the symmetric (FSI, TFSI and BETI by order of increasing size) and asymmetric (TF, TFSAM and TSAC) ones, we observe a trend for the viscosity to increase

with the anion size. Based on this observation, the best transport properties seem to arise for small symmetric anions.

In order to analyze further the individual dynamics of the liquids, the self-diffusion coefficient of the species i can be calculated from the long-time limit of the mean-squared displacement (MSD) using

$$D_i = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\Delta_i(t)|^2 \rangle \quad (4)$$

Note that a correction due to the use of periodic boundary conditions must be added.³⁶ Figure 3c shows the values obtained for H₂O molecules, lithium cations and the various anions. In agreement with previous works,^{12,32} it can be seen that water molecules are the most mobile species, followed by lithium cations and anions. This corresponds to an opposite behaviour with respect to the dynamics of the ions in typical ionic liquid electrolytes, where anions generally diffuse faster than cations.^{12,30,37}

The individual dynamics provide further points of comparison between the various electrolytes. The main difference with respect to the analysis of the collective transport properties is that the diffusivity of water molecules in the TSAC-based system is similar to the cases of TFSI, BETI and TFSAM. This points towards a predominant role of the low diffusivity of the anions in the high viscosity of the system. We also observe that the lithium ion dynamics is enhanced in LiTFSI-H₂O with respect to BETI and TFSAM-based systems, which points towards a better performance of the former in Li-ion batteries applications despite the similar conductivities of the systems.

Unlike in ionic liquid/water systems, where the interaction between H₂O molecules and anions is generally stronger than with the cations,³⁸ in WiS electrolytes they are strongly attracted by the lithium ions.⁶ At infinite dilution the first solvation shell of Li⁺ is made of four water molecules. At the molality studied here, the ratio H₂O/Li is smaller than four. As a consequence the first solvation shell of lithium cations includes both water and anions. It was previously reported that as the concentration of the mixture increases the coordination

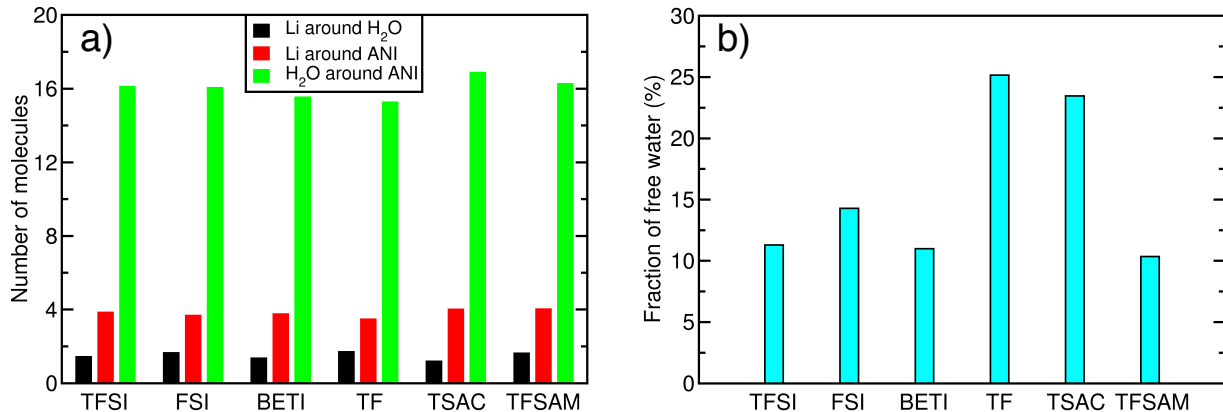


Figure 4: a) Neighbour count around the reference subset from Voronoi analysis for the different mixtures. b) Fraction of free water not bound to any Li cation obtained for the different mixtures.

environment is expected to change from solvent-separated ion pairs to a majority of contact ion pairs and even ionic aggregates.^{12,18,39} In the present work, we employed the trajectory analysis program TRAVIS⁴⁰ to analyze the formation of domains in these electrolytes, whose methodology is based on Voronoi tessellation.^{41,42} The subsets were defined so as to match the three types of molecules in the mixtures, and two subsets were considered to be neighbours if they share at least a common face. This approach provided us with valuable information on the neighborhood of the reference subset, and the results are included in Figure 4a. We can observe that the choice of the anion does not have a remarkable impact on the number of molecules neighbouring a reference one, so that the WiS studied here have qualitatively similar structures.

Nevertheless, the small variations observed for the coordination of the Li ions by the water molecules may lead to substantial changes in the concentration of “free” water molecules at such molalities. A water molecule is considered to be free when it is not coordinated to any lithium ion, but it is worth noting that in WiS they remain partly coordinated to other water molecules through an extended hydrogen-bond network, which will affect their reactivity as well.⁴³ The amount of free water molecules is shown in Figure 4b. We observe that it is significantly higher in the TF and the TSAC-based systems. This probably

affects significantly the electrochemical window because non-coordinated water molecules can adsorb more easily on the positive electrode than the lithium-coordinated ones (due to the Coulombic repulsion of the Li^+ ions). At the negative electrode it is also expected that the formation of the protective SEI will be more difficult for these salts.

In conclusion, we have studied through extended molecular dynamics simulations a series of WiS electrolytes where the nature of the anion was systematically changed. The same force field was used for all the simulations and the molality was kept fixed at 15 m in order to allow for representative comparisons. By analyzing the structure factors, we observed that the NF anion has a strong tendency to demix from the aqueous phase due to its highly hydrophobic fluorinated chain. All the other anions have structural features typical of water-in-salts, namely the formation of nanoheterogeneities with two type of domains, the first ones containing mostly the anions and the second ones made of solvated lithium ions linked through the hydrogen-bond network of the water molecules.

In a second step, by computing the transport properties we have identified that they do not vary in a systematic way with the size or the molecular weight of the anion. For a given ion size, the use of symmetric anions leads to a lower viscosity and increased ionic conductivities and diffusion coefficients. The TF and FSI display higher diffusion coefficients, followed by the TFSI, BETI and TFSAM-based systems. Finally, the TSAC has a poor viscosity and should therefore be avoided in electrochemical systems.

Finally, we have looked at the speciation of the systems, we have observed that the TF-based system has a relatively high amount of free water molecules, which may affect its electrochemical window. Nevertheless, future work should address more specifically the reactivity of the molecules since the mechanisms that have been identified for TFSI may not be adequate for all the other anions. This will require the use of density functional theory-based simulations in order to allow the formation/break of chemical bonds.

Simulation details

MD simulations of WiS electrolytes were carried out using the LAMMPS package.⁴⁴ All cubic simulation boxes contained 473 water molecules and 128 salt ion pairs that were randomly distributed using Packmol.⁴⁵ The SPC/E water model was used in these simulations,⁴⁶ whereas the parameterization of the anions was made in the framework of the CL&P⁴⁷ force field for ionic liquids, for which we employed the set of parameters reported in Ref. 27. Lithium cations were modelled as a single site whose Lennard-Jones (LJ) parameters are $\epsilon = 6.25$ kcal/mol and $\sigma = 1.25992$ Å. It must be noted that the charges of both ions were uniformly scaled by a factor of 0.8 so as to accelerate the dynamics of the mixtures, which was shown necessary to have good agreement with the experimental results in LiTFSI WiS.³²

In order to reach proper density, each system was firstly equilibrated at 298.15 K and 1 bar for 4 ns in the NpT ensemble by using Nosé-Hoover thermostat and barostat^{48–50} with relaxation times of 10 and 500 femtoseconds, respectively. Then we performed a second equilibration of 60 ns within an NVT ensemble, followed by a production run of around 90 ns (with a time step $dt = 1$ fs) that was used to obtain structural and dynamic information about the systems.

Acknowledgments

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