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Insights into solvation and dynamics behaviors of lithium salt in organic- and ionic liquids-based electrolytes

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\textbf{ABSTRACT:}

The new-generation lithium-ion batteries use ionic liquids (ILs) as electrolyte solution, greatly enhancing the safety and energy storage capacity of battery. Fundamental molecular insights are useful for understanding the advantages of high conductivity of ILs solvent electrolytes over organic solvent ones. In this work, we computationally studied two organic solvents (DMC and DEC) and four ILs solvents ([C\textsubscript{n}mim][BF\textsubscript{4}] and [C\textsubscript{n}mim][TFSI] (n=2, 4)) to examine the physicochemical properties of the high concentration electrolytes. As expected, the ILs solvent electrolytes exhibit higher density and viscosity, larger self-diffusion coefficient and conductivity than the organics solvent electrolytes. Further, the microstructures of the lithium salt LiTFSI in various solvent electrolytes were investigated to explore the effect of the organic and ILs solvents on the ionic associations of the ions Li\textsuperscript{+} and TFSI\textsuperscript{−}. The structural analysis of LiTFSI revealed that the organic solvents restrict the free motion of the ions, reducing the conductivity of the electrolytes. The [BF\textsubscript{4}]\textsuperscript{−}-type ILs electrolytes have higher conductivity than the [TFSI]-type ILs electrolytes, especially the [C\textsubscript{4}mim][BF\textsubscript{4}] with the highest conductivity among the ILs-based electrolytes. More importantly, the dissolution of LiTFSI in the ILs solvents is an anion-driven process was proved.

\textbf{KEYWORDS:} Electrolyte Solvation, Imidazole-based Ionic liquids, Dissolution Behavior, Physicochemical Properties

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1. Introduction

Lithium-based battery, as opposed to traditional alkaline battery, has emerged as a novel rechargeable energy storage device due to its high charge density and low self-discharge.\textsuperscript{1,2} Technically, lithium-ion battery utilizes the transportations of lithium ions from the negative electrode to the positive electrode in organic solvent electrolytes to achieve the charging/discharge process.\textsuperscript{3,4} Lithium bis(trifluoromethylsulfonyl) imide (LiTFSI), a most commonly-used lithium salt, takes advantage of its two unique sulfonyl groups to effectively disperse the negative charges on the anions so as to yield more free Li\textsuperscript{+} cations for charge transport, thus exhibiting higher ionic conductivities than other lithium salts, such as LiClO\textsubscript{4}, LiPF\textsubscript{6}, in both liquid and solid polymer electrolytes.\textsuperscript{5}

Thus far, most of studies on the development of high-performance lithium-ion battery still involve the use of organic solvent electrolytes, such as propylene carbonate, diethyl carbonate, and dimethyl carbonate. Peng et al.\textsuperscript{5} utilized multinuclear magnetic resonance to study the solvation behaviors of two lithium salts, viz. lithium hexafluorophosphate (LiPF\textsubscript{6}) and lithium tetrafluoroborate (LiBF\textsubscript{4}), in the mixed electrolytes of ethylene carbonate/dimethyl carbonate, and they found that low solvent polarity favors ion aggregations in both LiPF\textsubscript{6} and LiBF\textsubscript{4} electrolytes.\textsuperscript{6} Fulfer et al.\textsuperscript{6} investigated the structure and dynamics of electrolytes composed of LiPF\textsubscript{6} in various linear organic carbonates using a combination of linear and two dimensional infrared spectroscopies. Their experimental results indicated that all the linear carbonates can form tetrahedral solvation shells around the ion Li\textsuperscript{+}, thereby strengthening the interactions between Li\textsuperscript{+} and the carbonate group (-CO).\textsuperscript{7} Heckmann et al. added LiPF\textsubscript{6} and LiTFSI into dimethyl carbonate, diethyl carbonate or ethyl methyl carbonate to produce high-concentration electrolytes for dual-ion batteries and dual-graphite batteries. They demonstrated that the use of the newly-formulated electrolytes enables a highly reversible cycling stability for the lithium-ion batteries, thus providing high specific discharge capacities.\textsuperscript{8} However, the uses of organic solvent electrolyte in the lithium-ion battery exist two flaws: (i) the inevitable chemical reactions within the electrolyte decrease battery lifetime and (ii) the high inflammability of organic substances increases the risk of fire or explosion. Therefore, developing safe and sustainable novel electrolytes for the lithium-ion battery is a crucial challenge in current energy storage industry.

Ionic liquids (ILs), an environmentally-friendly green solvent, is an alternative to traditional organic solvent in battery manufacturing industry, because of its unique physicochemical properties, such as high thermal stability, negligible vapor pressure (i.e., neither flammable nor volatile), and high ionic conductivity.\textsuperscript{9,10} The IL is a molten salt in the liquid state at room temperature, which exists a large number of free cations/anions and short-lived ion pairs. Generally, when using the ILs as solvent to dissolve lithium salt, the free IL ions are easy to associate with the Li\textsuperscript{+} through ionic coupling interactions. The formation of ion association increases ionic strength, thereby improving the electrical conductivity of solutions. Hu et al.\textsuperscript{11} developed a novel polymeric ionic liquid-based gel electrolyte and then characterized several important property parameters, such as thermal stability, ionic conductivity, and electrochemical stability. They found that this polymeric electrolyte film exhibits high polymer
segmental mobility, a large number of charge carriers as well as high mobility. To develop novel high-safety lithium-ion battery, Yang et al. improved the electrolyte by mixing pyrrolidinium-based ionic liquid with organic additive and LiTFSI. Their work indicated when the content of ionic liquid in the mixed electrolyte is 65 vol%, the LiFePO₄/Li cells produced by the mixed electrolyte showed a good cycle performance at room temperature, delivering high reversible capacities in the range of 152-157 mAhg⁻¹ at 0.1 C. Borodin et al. conducted computational studies on the transportations of the ions Li⁺ in the ILs-based electrolytes. They simulated the self-diffusion of Li⁺ in ionic liquids, N-methyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl) imide ([mppy][TFSI]) and N,N-dimethyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide ([mmpy][TFSI]), and found that the ion self-diffusion coefficients follow the order Li⁺ < TFSI⁻ < mmpy⁺ or mppy⁺.

To enhance the electrochemical performance of lithium-ion battery, it is necessary to examine the solvation behaviors of lithium salt in varied electrolyte solutions. Fundamental molecular insights are useful for understanding the advantages of novel ILs solvent electrolytes over traditional organic solvent electrolytes. However, few studies were conducted to provide a systematic comparison of the organic- and IL-based electrolytes, especially in high concentration of lithium salt solution. Further, a detailed discussion regarding “how the cation/anion moieties in ILs affect the physicochemical properties of the ILs-based electrolytes” is lacked in other studies. Understanding the effect of IL cation/anion moieties on the dissolution of Li salt in the electrolytes is useful in improving the ionic conductivities of ILs-based electrolytes. In this work, we conducted atomistic molecular dynamics (MD) simulations to examine the solvation behaviors of LiTFSI in two organic solvent electrolytes (viz. dimethyl carbonate (DMC) and diethyl carbonate (DEC)) and four 1-alkyl-3-methyl imidazole ILs solvent electrolytes (viz. [C₃mim][BF₄] and [C₄mim][TFSI] (n=2,4)). The physicochemical properties of the electrolyte solutions, such as density, viscosity, self-diffusion coefficient, and conductivity, were calculated to compare the organic and ILs solvent electrolytes. The microstructures of LiTFSI were analyzed further in various solvent electrolytes by evaluating the radial distribution function (g(r)) and ionic coordination number (N) to explore the correlations between structural and physical properties at a micro-scale level.

2. Simulation Method and Model

All the atomistic MD simulations in this work were conducted for the lithium salt LiTFSI with a concentration of 2 mol/L when got solvated in the organic solvents of dimethyl carbonate (DMC) and diethyl carbonate (DEC), and the ionic liquids of [C₃mim][BF₄] and [C₄mim][TFSI] (n=2,4), at 298K and 313K, respectively. The general Amber force field (GAFF) was used to describe the atom types for DMC, DEC. The validity of the GAFF to describe pure organic electrolyte solvents, for instance DMC, DEC and ethylene carbonate (EC), was studied by Zhang et al.; an average deviation between the computed and experimentally-measured liquid density is within 3%. An optimized all atom force field improved by Liu et al. based on the AMBER force field was used to
describe \([\text{C}_2\text{mim}]^+, [\text{BF}_4^-], [\text{TFSI}^-]\), which accurately characterized the density, diffusion coefficient, and conductivity of ILs in their simulation study. The partial charges of these organic solvents and ILs were obtained by following the restrained electrostatic potential (RESP) procedure.\(^\text{18}\) To accurately capture the thermodynamic and transport properties of ILs in this work, scaled down the atomic partial charges by a charge scaling factor of 0.8 to alleviate the problem associated with overestimating the electrostatic interactions between ions due to polarization effects.\(^\text{19,20}\) Using the reduced partial charges and the polarizable force field, Schmollngruber et al.\(^\text{21}\) simulated and compared the diffusion coefficient and the electrical conductivity of ILs, and found that their results are comparable in the two approaches.

To keep a consistent salt concentration in our simulations, 40 ion pairs \(\text{Li}^+\)-TFSI\(^-\) were placed in a periodic boundary box containing 135 DMC or 94 DEC for organic solvents, and 75 \([\text{C}_2\text{mim}][\text{BF}_4]\) or 61 \([\text{C}_4\text{mim}][\text{BF}_4]\) or 45 \([\text{C}_2\text{mim}][\text{TFSI}]\) or 39 \([\text{C}_4\text{mim}][\text{TFSI}]\) for ILs, respectively (Figure 1). The initial configurations of the simulated models were constructed by using Packmol package.\(^\text{22}\) All the MD simulations were carried out in the Gromacs software.\(^\text{23}\) Details of the simulation procedure are given as follows. Each simulation system is relaxed in the canonical (NVT) ensemble for the first 5ns and then in the isothermal-isobaric (NPT) ensemble for the next 5ns. Production simulation is carried out for 30ns in the NPT ensemble and for 10 ns in the microcanonical (NVE) ensemble to achieve the configurational equilibria. The Verlet algorithm with a time step of 1.0 fs is employed to integrate Newton’s equations of motion. The van der Waals interaction is treated with the Lennard-Jones potential and the electrostatic interaction is evaluated using the Particle Mesh Ewald (PME) technique. During the simulation, the trajectories are recorded at every 0.1ps for further post-analysis.

**Figure 1.** Structures of the ions and solvent molecules involved in our MD simulations: (a) lithium (\(\text{Li}^+\)); (b) [bis(trifluoromethanesulfonyl)imide] (TFSI\(^-\)); (c) dimethyl carbonate (DMC); (d) diethyl carbonate (DEC); (e) 1-ethyl-3-methylimidazolium ([\(\text{C}_2\text{mim}]^+\)); (f) 1-butyl-3-methylimidazolium ([\(\text{C}_4\text{mim}]^+\)); (g) tetrafluoroborate ([\(\text{BF}_4^-\)].
3. Results and Discussions

3.1 Physicochemical properties

3.1.1 Density

Aqueous electrolyte solutions with high density offer battery a more powerful energy. In this work, the average bulk density \( \rho \) of the electrolyte solutions was calculated in 30ns NPT ensemble equilibration simulations using the equation (1)

\[
\langle \rho \rangle = \frac{\sum n_i M_i}{\langle V \rangle}
\]

(1)

Where \( n_i \) is the amount of substance of component i, \( \langle V \rangle \) is the volume, \( M_i \) is the molar mass of component i.

The densities of both the LiTFSI-organic solvent and LiTFSI-ILs solvent electrolytes at 298K and 313K (Table 1) were firstly calculated. Meanwhile, the experimentally-measured densities of these pure solvents are given in Table 1. Obviously, the addition of the lithium salt LiTFSI to the electrolytes causes the increase of density due to their strong mutual interactions between Li\(^+\) and TFSI\(^-\) (The ion-ion interactions will be discussed in detail at a molecular level later). This observation has been reported in other studies of ILs/Li\(^+\) mixtures. By comparing the organic solvents DMC and DEC with the ILs solvents \([C_{n}mim][TFSI]\) and \([C_{n}mim][BF_4]\) in Table 1, it is seen that the computed density of the LiTFSI-ILs solvent electrolytes is higher than that of the LiTFSI-organic solvent electrolytes at each temperature. Additionally, it is found that for a common anion ([BF_4\(^-\) or [TFSI\(^-\)]), \([C_{2}mim]\)-type ILs solvent electrolytes have higher density than \([C_{n}mim]\)-type electrolytes, while for a common cation ([C_2mim]+ or [C_4mim]+), [TFSI]-type ILs solvent electrolytes have higher density than [BF_4]-type ILs solvent electrolytes. As the temperature increases from 298K to 313K, the densities of both the LiTFSI-organic solvent and LiTFSI-ILs solvent electrolytes experience a notable decrease, which is in accordance with Yang’s experimental observation.

<table>
<thead>
<tr>
<th>Temperature(K)</th>
<th>DMC</th>
<th>DEC</th>
<th>[C_2mim][TFSI]</th>
<th>[C_2mim][BF_4]</th>
<th>[C_4mim][TFSI]</th>
<th>[C_4mim][BF_4]</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1.471(1.07(^a))</td>
<td>1.373(0.98(^b))</td>
<td>1.743(1.52(^c))</td>
<td>1.538(1.28(^c))</td>
<td>1.672(1.42(^c))</td>
<td>1.429(1.19(^c))</td>
</tr>
<tr>
<td>313</td>
<td>1.448</td>
<td>1.361</td>
<td>1.708</td>
<td>1.534</td>
<td>1.599</td>
<td>1.383</td>
</tr>
</tbody>
</table>

\(^a\)Densities of these pure solvents at 298K are provided in parentheses.

(a) Tojo et al. experiment (ref.\(^{27}\)), (b) Shukla et al. experiment (ref.\(^{28}\)), (c) Zhang et al. experiment (ref.\(^{29}\)).

3.1.2 Viscosity
The electrolyte with moderate viscosity can effectively prevent the solvents from evaporation, thereby reducing environmental pollution and increasing energy storage capacity of battery. In this work, the zero-shear viscosity was calculated in 30ns NPT ensemble equilibration simulations using the Green-Kubo (GK) formula:

\[ \eta = \frac{V}{10K_BT} \int_0^\infty \langle \sum_{xy} P_{xy}(0)P_{xy}(t) \rangle dt \]  

where \( V \) is the volume of the system, \( T \) is the temperature, \( K_B \) is the Boltzmann constant, and \( P_{xy} \) refers to an independent component of stress in the \( x-y \) direction.

The calculated viscosity of the six electrolyte systems was given in Table 2. It is seen that the four LiTFSI-ILs solvent electrolytes, viz. \([C_{2mim}][TFSI] \), \([C_{2mim}][BF_4] \), \([C_{4mim}][TFSI] \) and \([C_{4mim}][BF_4] \), have higher viscosity than the two LiTFSI-organic solvent electrolytes, viz. DMC and DEC, at 298K and 313K. Additionally, for the ILs solvent electrolytes with the common anion (\([BF_4]^- \) or \([TFSI]^- \) ), we observed that the viscosity of \([C_{2mim}]^- \)-type electrolytes is a little higher than \([C_{4mim}]^- \)-type electrolytes, indicating that the viscosity of the \([C_nmim]^- \)-type ILs solvent electrolytes is affected by the chain length \( n \) of cyclic carbonate. As the temperature increases, both the organic and ILs solvent electrolytes encounter a decrease in viscosity.

Table 2. Viscosity (unit: kg/m·s) for the LiTFSI-organic and LiTFSI-ILs solvent electrolytes.

<table>
<thead>
<tr>
<th>Temperature(K)</th>
<th>DMC</th>
<th>DEC</th>
<th>([C_{2mim}][TFSI] )</th>
<th>([C_{2mim}][BF_4] )</th>
<th>([C_{4mim}][TFSI] )</th>
<th>([C_{4mim}][BF_4] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.396</td>
<td>0.949</td>
<td>1.924</td>
<td>1.554</td>
<td>1.035</td>
<td>1.537</td>
</tr>
<tr>
<td>313</td>
<td>0.116</td>
<td>0.663</td>
<td>1.491</td>
<td>1.154</td>
<td>0.836</td>
<td>0.802</td>
</tr>
</tbody>
</table>

3.1.3 Self-diffusion coefficient

A high rate of self-diffusion of ions can enhance the conductivity of electrolyte for lithium-ion battery. Therefore, according to the Einstein equation, we calculated the self-diffusion coefficient (D) of the \( Li^+ \) and TFSI-ions in the organic and ILs solvent electrolytes, which is a function of the mean square displacement (MSD) of ions in solution, as given in equation (3):

\[ D = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \langle \sum_{i=1}^{N} [\vec{r}_i^2(t) - \vec{r}_i^2(0)] \rangle \]  

where \( \vec{r}_i(t) \) indicates the positional vector of the center of mass of the \( i \)-th ion at a given time \( t \). In this work, we calculated the MSDs of \( Li^+ \) and TFSI- in solution over the time interval (t) from 2ns to 6ns, as an example of the LiTFSI-DMC and LiTFSI-[C_{2mim}][BF_4] electrolytes at 298K (Figure 2). Through linearly fitting the slope of the MSD-t plots, we can obtain the self-difffusivity coefficients of \( Li^+ \) and TFSI- in the electrolytes, as listed in Table 3.
As compared to the organic solvents DMC and DEC, the ILs solvents allow the Li\(^+\) and TFSI\(^-\) ions move more freely in the electrolytes, as evidenced by the self-diffusion coefficients in Table 3. As a matter of fact, it occurs on many ILs, including, but not limited to, [C\(_n\)mim][TFSI] and [C\(_n\)mim][BF\(_4\)].\(^{31,32}\) Ray et al. point out that the mobility of Li\(^+\) in solution is proportional to the strength of the interionic interactions within the electrolytes.\(^{33}\) In our work, stronger cation-anion coupling interactions were observed in the ionic-type solvents rather than in the molecular-type solvents, increasing the ionic strength of the ILs electrolytes. Therefore, ionic association facilitates the mobility of cation/anion in the ILs electrolytes. (Detailed discussions can be seen later in the text).

No matter what the solvents are, the arising temperature increases the kinetic energy of systems, eventually resulting in the increase of self-diffusion of ions. Further, our simulation results revealed that Li\(^+\) and TFSI\(^-\) have higher diffusion rates in the [C\(_n\)mim]-type electrolyte than in the [C\(_2\)mim]-type electrolyte, which differs from the results of density and viscosity studies. Among all the organic and ILs solvents, the [C\(_4\)mim][BF\(_4\)] was found to be the best solvent, facilitating the transport of Li\(^+\) and TFSI\(^-\) in solution. Since stronger coordination with the surrounding solvent molecules, the cation Li\(^+\) exhibits lower rate of diffusion in the electrolytes than the anion TFSI\(^-\) (The solvation behaviors of Li\(^+\) and TFSI\(^-\) will be discussed in detail later in the text).

![Figure 2](image)

**Figure 2.** The plots of mean square displacement (MSD) of Li\(^+\) and TFSI\(^-\) vs. simulation time (\(t\)) in the solvents DMC and [C\(_2\)mim][BF\(_4\)] at 298K.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>LiTFSI-DMC</th>
<th>LiTFSI-DEC</th>
<th>LiTFSI-[C(_4)mim][BF(_4)]</th>
<th>LiTFSI-[C(_2)mim][TFSI]</th>
<th>LiTFSI-[C(_4)mim][BF(_4)]</th>
<th>LiTFSI-[C(_4)mim][TFSI]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li(^+)</td>
<td>TFSI(^-)</td>
<td>Li(^+) TFSI(^-)</td>
<td>Li(^+) TFSI(^-)</td>
<td>Li(^+) TFSI(^-)</td>
<td>Li(^+) TFSI(^-)</td>
</tr>
</tbody>
</table>

**Table 3.** Self-diffusion coefficients (unit: 10\(^{-12}\) m\(^2\)/s) of the lithium salt LiTFSI in the organic and ILs solvent electrolytes.
298  0.24  0.44  0.17  0.25  1.43  3.01  1.75  3.84  5.83  6.57  5.62  6.24
313  0.55  0.81  0.19  0.28  2.17  4.94  2.08  4.18  6.24  6.65  6.74  6.83

1

3.1.4 Conductivity

High-performance electrochemical device requires its electrolyte having a high ionic conductivity. To compare the organic and ILs solvents, we examined the total conductivity of the cation Li+ and the anion TFSI- in the six electrolytes using the equation (4):

$$\sigma = \lim_{t \to \infty} \frac{1}{6tV R_b} \sum_{j=1}^{N} ([R_i(t) - R_i(0)]q_i) \cdot ([R_j(t) - R_j(0)]q_j)$$  (4),

where N is the number of ions in the electrolyte, V is the volume, $k_b$ is the Boltzmann’s constant, T is the temperature, $q_x$ ($x = i,j$) indicates the charge of the $x^{th}$ ion, and $R_x(t)$ ($x = i,j$) is the position of the $x^{th}$ ion at a given time t. The angle bracket $<...>$ denotes an ensemble average and the sum $\Sigma$ runs over all the ions in the electrolyte. According to the difference of ionic species and correlations, we could divide the total conductivity ($\sigma_{tot}$) into five distinct sub-terms$^{34,35}$, viz. cation-self ($\sigma_{cat}^s$), anion-self ($\sigma_{an}^s$), cation-distinct ($\sigma_{cat}^d$), anion-distinct ($\sigma_{an}^d$), and cation/anion-distinct ($\sigma_{cat,an}^d$), which $\sigma_{cat}^s$ and $\sigma_{an}^s$ are conductivity types for self (uncorrelated) ions, while $\sigma_{cat}^d$, $\sigma_{an}^d$ and $\sigma_{cat,an}^d$ are conductivity types for distinct (correlated) ions. The $\sigma_{cat}^d$ and $\sigma_{an}^d$ describe the correlations between two distinct cations and between two distinct anions, respectively; while the $\sigma_{cat,an}^d$ describes the correlations between one cation and one anion. These five conductivity types, which are general expressions derived from linear response and conservation laws, can be applied for any binary ILs of symmetric and asymmetric charge. Details on the calculations of the five sub-terms are given in Supporting Information, and the results of the five conductivity types for the organic and ILs solvent systems are shown in Table S1 and Table S2, respectively.

We calculated the total conductivity ($\sigma_{tot}$) of the six electrolytes at 298K, as listed in Figure 3(a). Simulation results revealed that the four ILs solvents exhibit a notable higher ionic conductivity than the two organic solvents, implying that ionic-type solvents have higher conductivity than molecular-type solvents. It is also seen that the conductivity of the two [C₅mim]⁺-type electrolytes is 5.593 S/m and 5.075 S/m, which is a little higher than the two [C₃mim]-type electrolytes of 4.265 S/m and 2.748 S/m. The [C₅mim][BF₄] with the highest conductivity among the electrolytes is considered to be the best solvent to dissolve LiTFSI. A number of high-conductivity ILs-based electrolytes have been reported in other experimental work. Rosol et al.$^{36}$ experimentally measured the conductivity of LiTFSI in the 1-butyl-3-methylimidazolium thiocyanate ([C₅mim][SCN]) electrolyte, showing a high conductivity 3 S/m at the salt concentration [LiTFSI] = 0.4 mol/L. Zygadlo-Monikowska et al.$^{37}$ examined a class of imidazolium ILs with short polyoxyethylene chain ([Im nEO]⁺[X]; where n=0, 3, 7, 20 and X=Cl, BF₄, N(CF₃SO₂)₂), and found that the electrolytes produced by these imidazolium ILs are good solvents for lithium
salts, such as LiBF₄ and LiN(CF₃SO₂)₂. Especially for the [BuMeIm 3EO][BF₄] electrolyte, a low viscosity and high conductivity can be achieved even at high salt concentration of LiBF₄ and LiN(CF₃SO₂)₂ in solution. Kalaga et al. studied the solvation of LiTFSI in the electrolyte of 1-methyl 1-propylpiperidinium bis(trifluoromethylsulfonyl)imide. They revealed that as the salt concentration [LiTFSI] increases from 0.2 M to 1.0 M, this kind of ionic liquid electrolyte has a notable increase in conductivity. Chagnes et al. used the mixture of γ-Butyrolactone and 1-butyl 3-methyl-imidazolium tetrafluoroborate (BmimBF₄) (ratio: 3/2, v/v) as electrolyte to solvate LiBF₄. Their experiment indicates that as the temperature arises, this mixture exhibits a higher conductivity in solution, even up to 9.5 S/m at 25 °C. The aforementioned experimental observations reflect a common fact that ionic conductivity depends on the unique molecular structure of the ILs, and on the temperature and salt concentration applied, which qualitatively agree to our simulation results. Figure 3 shows each individual contribution of the five sub-terms to the total conductivity of the LiTFSI-organic and LiTFSI-ILs solvent electrolytes, respectively. The uncorrelated conductivity types σ⁺⁻ and σ⁻⁺ of the cations Li⁺ and the anions TFSI⁻ that are positive values for both organic and ILs solvents, contribute positively to the total conductivity of the electrolyte. The correlated conductivity types σ⁺⁺ and σ⁻⁻ of the same ionic species are close to zero for the [C₂mim]-type electrolytes, making little contribution to the total conductivity; while the σ⁺⁺ and σ⁻⁻ for the [C₄mim]-type electrolytes are unfavorable to the total conductivity due to the negative values. Since the correlated conductivity type σ⁺⁻ for the distinct ionic species is almost zero for all the six electrolytes, we, therefore, neglect the contribution between the cations and anions.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>DMC</th>
<th>DEC</th>
<th>[C₂mim][BF₄]</th>
<th>[C₂mim][TFSI]</th>
<th>[C₄mim][BF₄]</th>
<th>[C₄mim][TFSI]</th>
</tr>
</thead>
<tbody>
<tr>
<td>σₜₜot (S/m)</td>
<td>2.191</td>
<td>1.572</td>
<td>4.265</td>
<td>2.748</td>
<td>5.593</td>
<td>5.075</td>
</tr>
</tbody>
</table>

Figure 3. (a) Results of the total conductivity σₜₜot (S/m) of the six electrolytes at 298K. (b) Results of the five conductivity types, viz. σ⁺⁺, σ⁻⁻, σ⁺⁻, σ⁻⁺ and σ⁺⁻, for (b) the two organic solvent systems and (c) the four ionic liquids solvent systems at 298K.
3.2 Microstructural analysis

Radial Distribution Function (RDF)\(^\text{40}\) provides a molecular insight into exploring the correlations between structural and physical properties at a micro-scale level. We investigated the RDF, \(g(r)\), for center of mass of the ions in the six electrolytes:

\[
g(r) = \frac{\langle \sum_{ij} \delta(r-r_{ij}) \rangle}{N\rho} \tag{5}
\]

where \(N\) is the number of particles, \(\rho\) is the number density, \(r_{ij}\) is the spatial distance of the particles \(i\) and \(j\), and \(<…>\) indicates an ensemble average.

The coordination number \((N)\)\(^\text{25}\) is identified by integrating the site-site RDF along the radial direction. The coordination number \(N_{(i-j)}\) of the particle \(i\), herein, is defined to be the number of the molecule \(j\) surrounding the particle \(i\) in its first solvation shell, as calculated in equation (6):

\[
N_{(i-j)} = 4\pi \rho_j \int_{0}^{r^*} g_{ij}(r)r^2 dr \tag{6}
\]

where \(r^*\) is the first minimum in the \(g(r)\) plot, \(r\) is the distance and \(\rho_j\) is the density of particle \(j\).

In this section, the effect of solvents on the density distributions of cations and anions was examined firstly to explore the ionic association tendency of \(\text{Li}^+\) and \(\text{TFSI}^-\) in various solvent electrolytes. Later, the electrolyte solvation of the cation \(\text{Li}^+\) was discussed in the organic and ILs solvents to reveal the solution interactions between solute and solvent.

3.2.1 The effect of solvents on the density distributions of cations and anions

The RDF of the lithium salt \(\text{LiTFSI}\) in various solvent electrolytes at 298K were shown in Figure 4 to study the effect of solvents on the density distributions of the cation \(\text{Li}^+\) and the anion \(\text{TFSI}^-\). It is clear to see that regardless of the solvents (Figure 4) and temperatures (Figure S1), the primary peak in the \(g(r)\) plots of the \(\text{Li}^+\)-TFSI always appear at the position of around 0.2 nm, indicating that the \(\text{Li}^+\) and \(\text{TFSI}^-\) have a strong coordination in the electrolytes and the structural stability is affected less by the temperature. Seo et al.\(^\text{41}\) systematically studied the ionic association of lithium salts in electrolyte, and reported that the changes of temperature slightly affect the coordination structure of \(\text{Li}^+\) and \(\text{TFSI}^-\), which is in accordance with our simulation results. Followed by the primary peak, there are another two secondary peaks in the \(g(r)\) plots of the \(\text{Li}^+\)-TFSI, which exist at 0.32nm and 0.42nm, respectively. Seo et al.\(^\text{41}\) considered that the cis-trans isomerism of \(\text{TFSI}^-\) is the main cause for the two secondary peaks. However, in their study, they did not clarify a question how the cis-trans isomerism of \(\text{TFSI}^-\)
affects the presence of the two secondary peaks in the \( g(r) \) plots of the \( \text{Li}^+\text{TFSI}^- \). By analyzing our MD simulations, we found that more cis-TFSI appear at the peak position of 0.32nm, while more trans-TFSI at 0.42nm (Figure 4a).

Further, we investigated the interactions of the cation \( \text{Li}^+ \) with the oxygen (O) and nitrogen (N) atoms within the anion TFSI to shed light on the coordination mechanism of the ions \( \text{Li}^+ \) and TFSI in the electrolytes. Take the LiTFSI-DMC electrolyte system as an example (Figure 5), where the density distributions of the \( \text{Li}^+\text{O(TFSI)} \) and \( \text{Li}^+\text{N(TFSI)} \) were demonstrated. The computed coordination numbers \( (N) \) of \( \text{Li}^+\text{O(TFSI)} \) and \( \text{Li}^+\text{N(TFSI)} \) are \( N_{(\text{Li-O})}=2.5 \) and \( N_{(\text{Li-N})}=0.7 \), implying that each cation \( \text{Li}^+ \) preferentially coordinates with the O(TFSI) atoms, not the more electronegative N(TFSI) atom in the electrolytes. The same conclusions were drawn by Li et al.\textsuperscript{42} in their simulation study of the LiTFSI-acetamide electrolyte.

The interactions of the cations \( \text{Li}^+ \) in various solvent electrolytes can be examined by plotting the \( \text{Li}^+\text{Li}^+ \) RDF (Figure 4). Strong interaction between \( \text{Li}^+ \) promotes the fast ion transport in electrolytes, thereby improving the performance of Li-ion battery. As observed in Figure 4, the \( g(r) \) plots of the \( \text{Li}^+\text{Li}^+ \) of the four ILs-type electrolytes exhibit a larger peak value and a closer peak location than those of the two organic solvent electrolytes, implying that the cations \( \text{Li}^+ \) have stronger mutual interactions in the ILs solvents than in the organic solvents. We computed the coordination numbers \( (N_{(\text{Li-Li})}) \) of the \( \text{Li}^+\text{Li}^+ \) in the two organic solvents and the four ILs solvents: \( N_{(\text{Li-Li})}=1.4 \) for DMC, \( N_{(\text{Li-Li})}=1.5 \) for DEC, \( N_{(\text{Li-Li})}=2.1 \) for [C\text{\textsubscript{2}}\text{mim}][BF\text{\textsubscript{4}}], \( N_{(\text{Li-Li})}=1.9 \) for [C\text{\textsubscript{2}}\text{mim}][TFSI], \( N_{(\text{Li-Li})}=2.7 \) for [C\text{\textsubscript{4}}\text{mim}][BF\text{\textsubscript{4}}], and \( N_{(\text{Li-Li})}=1.7 \) for [C\text{\textsubscript{4}}\text{mim}][TFSI]. Obviously, the strengths of the \( \text{Li}^+\text{Li}^+ \) interactions in the six electrolytes follow the order: [C\text{\textsubscript{4}}\text{mim}][BF\text{\textsubscript{4}}] > [C\text{\textsubscript{2}}\text{mim}][BF\text{\textsubscript{4}}] > [C\text{\textsubscript{4}}\text{mim}][TFSI] > [C\text{\textsubscript{2}}\text{mim}][TFSI] > DEC > DMC. Additionally, we calculated the average positions of the primary peak in the \( g(r) \) plots of the \( \text{Li}^+\text{Li}^+ \): 0.46nm for the ILs solvents and 0.51nm for the organic solvents, which is in consistency with the observations in the LiTFSI crystal by Nowinski et al.\textsuperscript{43}

The \( g(r) \) plots of the TFSI-TFSI in Figure 4 indicated a variety of association behaviors of the anions TFSI when dissolved in the organic and ILs solvents. Obviously, the ILs solvents (Figure 4c-f)) rather than the organic solvents (Figure 4a,b) can facilitate the ionic association of TFSI, resulting in a notable peak at around 0.13nm in the \( g(r) \) plot of the TFSI-TFSI, especially for [C\text{\textsubscript{2}}\text{mim}][BF\text{\textsubscript{4}}] (Figure 4c) and [C\text{\textsubscript{4}}\text{mim}][BF\text{\textsubscript{4}}] (Figure 4e). Due to the presence of the anion [BF\text{\textsubscript{4}}]\textsuperscript{-} in the [C\text{\textsubscript{4}}\text{mim}][BF\text{\textsubscript{4}}] solvents, the anion TFSI\textsuperscript{-} of the lithium salt (LiTFSI) is repelled to self-aggregate into a cluster, causing a highly-protruding peak at the position of 0.13nm (Figure 4c,e). However, in the [C\text{\textsubscript{4}}\text{mim}][TFSI] solvents, the anion TFSI\textsuperscript{-} of the lithium salt (LiTFSI) is distributed uniformly in the electrolytes and simultaneously interacts with other ions TFSI\textsuperscript{-} and Li\textsuperscript{+}, resulting in two sizeable peaks at around 0.13nm and 0.20nm (Figure 4d,f). Additionally, we can observe that the position of the primary peak in the \( g(r) \) plot of the TFSI-TFSI shifts forward from 0.18nm in the organic solvents (Figure 4a,b) to 0.13nm in the ILs solvents (Figure 4c-f). The mobility of ions in solution depends on ionic strength. In the organic- and IL-based electrolytes, the ionic strength is a function of the coordination number \( (N) \) of ion-ion. A small value of \( N_{(\text{TFSI-TFSI})} \) indicates a low mobility of the anion TFSI\textsuperscript{-} in the solvents. We computed the \( N_{(\text{TFSI-TFSI})} \) in the organic

(11)
and ILs solvents: $N_{(TFSI-TFSI)}=1.31$ for DMC, $N_{(TFSI-TFSI)}=1.38$ for DEC, $N_{(TFSI-TFSI)}=1.83$ for \([\text{C}_2\text{mim}][\text{BF}_4]\), $N_{(TFSI-TFSI)}=1.55$ for \([\text{C}_2\text{mim}][\text{TFSI}]\), $N_{(TFSI-TFSI)}=1.87$ for \([\text{C}_4\text{mim}][\text{BF}_4]\), and $N_{(TFSI-TFSI)}=1.57$ for \([\text{C}_4\text{mim}][\text{TFSI}]\). By comparing the values of $N_{(TFSI-TFSI)}$, we found that the ionic strength of the anions TFSI$^{-}$ in the organic solvents is weaker than that in the ILs solvents, indicating that the free motion of the anions TFSI$^{-}$ is restricted in the organic solvents. This observation about the structural distribution of TFSI$^{-}$ proves our previous calculations in Table 3: lower the self-diffusion coefficients of TFSI$^{-}$ in the organic solvents as compared to in the ILs solvents.
**Figure 4.** Radial distribution function of the lithium salt LiTFSI at 298K in the organic solvents (a) DMC and (b) DEC, and the ILs solvents (c) [C₂mim][BF₄], (d) [C₂mim][TFSI], (e) [C₄mim][BF₄] and (f) [C₄mim][TFSI].
Figure 5. (a) Simulation snapshot of the cation Li\(^+\) (purple sphere) surrounded by the anion TFSI\(^-\) in the first solvation shell for the LiTFSI-DMC electrolyte at 298K. (b) Site-site radial distribution function \((g(r))\) and coordination number \((N)\) of Li\(^+\)-O(TFSI\(^-\)) (red trace) and Li\(^+\)-N(TFSI\(^-\)) (blue trace) in the LiTFSI-DMC electrolyte.

3.2.2 The electrolyte solvation of lithium salt in the organic and ILs solvents

Figure 6(a) presents the spatial correlations of the cation Li\(^+\) with the two organic solvent molecules DMC and DEC at 298K. It is clear to see that there are two peaks existing in the \(g(r)\) plots of both the Li\(^+\)-organic solvents: one is at 0.2nm and the other is at 0.4nm, which signifies that the organic solvents DMC and DEC form a two-layer solvation shell to wrap the cation Li\(^+\). A small value of \(N_{(Li-Li)}\) indicates a low mobility of the cation Li\(^+\) in the electrolytes. As stated above, the values of \(N_{(Li-Li)}\) in the DMC and DEC solvents are 1.4 and 1.5, respectively. Also, we computed the coordination numbers \((N)\) of the Li\(^+\)-DMC and Li\(^+\)-DEC: \(N_{(Li-DMC)}=2.4\) and \(N_{(Li-DEC)}=2.5\). It is found that the \(N_{(Li-Li)}\) is smaller than the \(N_{(Li-organic\ solvent)}\) in both the DMC or DEC solvents, indicating that the organic molecules hinder the free motions of Li\(^+\) in the electrolytes. It is the main reason why the diffusion rates of the lithium salt (LiTFSI) are slow in the organic solvent (Table 3).

Figures 6(b,c) present the spatial correlations of the cation Li\(^+\) in LiTFSI with the cations ([C\(_2\)mim]\(^+\) and [C\(_4\)mim]\(^+\)) and anions ([BF\(_4\)]\(^-\) and [TFSI]\(^-\)) of the four ILs solvents at 298K. For both the [BF\(_4\)]-type and [TFSI]-type ILs solvents, only a small peak takes place at a relatively-far position of about 0.7nm in the \(g(r)\) plots of the Li\(^+\)-cation(ILs) (Figure 6b), indicating a weak interaction between Li\(^+\) and the ILs cations [C\(_2\)mim]\(^+\) and [C\(_4\)mim]\(^+\).
In contrast, a strong interaction between Li$^+$ and the ILs anions [BF$_4$]$^-$ and [TFSI]$^-$ is observed in both the [C$_2$mim]-type and [C$_4$mim]-type ILs solvents, as evidenced by a protruding peak occurring at 0.2nm (Figure 6c). Also, we found that the peak values in the $g(r)$ plots of the Li$^+$-[BF$_4$]$^-$ reach up to 10 or more, which are higher than that of around 6.5 in the $g(r)$ plots of the Li$^+$-[TFSI]$^-$ (Figure 6c). It reflects a fact that it is easier to disperse the ions Li$^+$(LiTFSI) into the [BF$_4$]-type ILs solvents, rather than into the [TFSI]-type ILs solvents. Our hypothesis about the reason is that the anion [BF$_4$]$^-$ exhibits a higher polarity than the [TFSI]$^-$, leading to a stronger coordination with the ions Li$^+$(LiTFSI). Thus, it is reasonable to believe that the dissolution of LiTFSI in ILs solvents is an anion-driven process.

To avoid simulation errors resulting from a small electrolyte system with 40 ion pairs of Li$^+$-TFSI, we examined a large electrolyte system including 200 LiTFSI and organic/ILs solvent molecules. The 674 DMC, 469 DEC, 371 [C$_2$mim][BF$_4$], 221 [C$_4$mim][BF$_4$], 304 [C$_2$mim][TFSI], and 194 [C$_4$mim][TFSI] were added separately to solvate the 200 LiTFSI to maintain a same concentration of 2 mol/L. Following the above computational procedure, we calculated the density, viscosity, and conductivity of both the LiTFSI-organics and LiTFSI-ILs solvent electrolytes, as listed in Table S3. The spatial correlations of the cation Li$^+$ with the DMC and DEC, the cations ([C$_2$mim]$^+$ and [C$_4$mim]$^+$), and the anions ([BF$_4$]$^-$ and [TFSI]$^-$) were shown in Figure S2. In observation of Tables (1, 2 and S1) and Figures (6 and S2), we found that the two systems of 40 and 200 LiTFSI exhibit the same physicochemical properties and microstructures of the electrolytes, proving the reliability of our simulation results.

### 4. Conclusions

Ionic liquids that are used as electrolytes in battery manufacturing industry enhance the safety, energy storage capacity, cycling life of lithium-ion battery. Fundamental molecular insights are useful for understanding the advantages of novel ILs solvent electrolytes over traditional organic solvent electrolytes. In this work, atomistic
MD simulations were employed to investigate the solvation behaviors of the lithium salt LiTFSI in two organic solvent (DMC and DEC) and four ILs solvent ([C₆mim][BF₄] and [C₈mim][TFSI], n=2,4) electrolytes.

We firstly calculated the physicochemical properties of both the organic and ILs solvent electrolytes. Simulation results revealed that the LiTFSI-ILs solvent electrolytes have higher density and viscosity, larger self-diffusion coefficient and conductivity than the LiTFSI-organic solvent electrolytes, indicating that the ILs-based electrolytes exhibit stronger energy power, lower solvent evaporation, and faster ion transport than the organics-based electrolytes. Later, we examined the effect of the organic and ILs solvents on the ionic associations of the ions Li⁺ and TFSI⁻ by evaluating the radial distribution function (g(r)) and ionic coordination number (Nᵢ). For both the organic and ILs solvent electrolytes, the cation Li⁺ has strong interactions with the anion TFSI⁻ through coordinating with the O(TFSI) atom, not the more electronegative N(TFSI) atom. The cis-trans isomerism of TFSI⁻ was observed to appear near Li⁺ at the positions of 0.32nm and 0.42nm, respectively. By calculating the coordination number N(Li⁺) of the Li⁺-Li⁺, we found that the [BF₄]-type ILs have a fastest ion transport, followed by the [TFSI]-type ILs, DEC, and DMC. The organic solvents restrict the free motion of the anion TFSI⁻, resulting in a low conductivity for the organics-based electrolytes, while the ILs solvents facilitate the ionic association of the TFSI⁻-TFSI⁻, causing a high conductivity for the ILs-based electrolytes. Additionally, we realized that the dissolution of LiTFSI in ILs solvents is an anion-driven process. The presence of high-polarity anion like [BF₄]⁻ in the solution promotes the coordination with the ion Li⁺(LiTFSI), improving the electrolyte solvation of the lithium salt.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgment

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References


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Table Captions

Table 1. Density (unit: g/cm$^3$) for the LiTFSI-organic and LiTFSI-ILs solvent electrolytes.

Table 2. Viscosity (unit: kg/m·s) for the LiTFSI-organic and LiTFSI-ILs solvent electrolytes.

Table 3. Self-diffusion coefficients (unit: 10$^{-12}$ m$^2$/s) of the lithium salt LiTFSI in the organic and ILs solvent electrolytes.
Table 1. Density (unit: g/cm$^3$) for the LiTFSI-organic and LiTFSI-ILs solvent electrolytes$^\circ$.

<table>
<thead>
<tr>
<th>Temperature(K)</th>
<th>DMC</th>
<th>DEC</th>
<th>[C$_2$mim][TFSI]</th>
<th>[C$_2$mim][BF$_4$]</th>
<th>[C$_4$mim][TFSI]</th>
<th>[C$_4$mim][BF$_4$]</th>
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<td>298</td>
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<td>1.743(1.52$^a$)</td>
<td>1.538(1.28$^a$)</td>
<td>1.672(1.42$^a$)</td>
<td>1.429(1.19$^a$)</td>
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<td>1.361</td>
<td>1.708</td>
<td>1.534</td>
<td>1.599</td>
<td>1.383</td>
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</table>

$^\circ$Densities of these pure solvents at 298K are provided in parentheses.

(a) Tojo et al. experiment (ref. 27). (b) Shukla et al. experiment (ref. 28). (c) Zhang et al. experiment (ref. 29).

Table 2. Viscosity (unit: kg/m·s) for the LiTFSI-organic and LiTFSI-ILs solvent electrolytes.

<table>
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<tr>
<th>Temperature(K)</th>
<th>DMC</th>
<th>DEC</th>
<th>[C$_2$mim][TFSI]</th>
<th>[C$_2$mim][BF$_4$]</th>
<th>[C$_4$mim][TFSI]</th>
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Table 3. Self-diffusion coefficients (unit: 10$^{-12}$ m$^2$/s) of the lithium salt LiTFSI in the organic and ILs solvent electrolytes.

<table>
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<tr>
<th>T(K)</th>
<th>LiTFSI-DMC</th>
<th>LiTFSI-DEC</th>
<th>LiTFSI-[C$_2$mim][BF$_4$]</th>
<th>LiTFSI-[C$_2$mim][TFSI]</th>
<th>LiTFSI-[C$_4$mim][BF$_4$]</th>
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<td>4.94</td>
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Figure Captions

Figure 1. Structures of the ions and solvent molecules involved in our MD simulations: (a) lithium (Li$^+$); (b) [bis(trifluoromethanesulfonyl)imide] (TFSI$^-$); (c) dimethyl carbonate (DMC); (d) diethyl carbonate (DEC); (e) 1-ethyl-3-methylimidazolium ([C$_2$ mim]$^+$); (f) 1-butyl-3-methylimidazolium ([C$_4$ mim]$^+$); (g) tetrafluoroborate ([BF$_4$$^-$.]

Figure 2. The plots of mean square displacement (MSD) of Li$^+$ and TFSI$^-$ vs. simulation time ($t$) in the solvents DMC and [C$_2$mim][BF$_4$] at 298K.

Figure 3. (a) Results of the total conductivity $\sigma_{\text{tot}}$ (S/m) of the six electrolytes at 298K. (b) Results of the five conductivity types, viz. $\sigma_{\text{cat}}^c$, $\sigma_{\text{an}}^c$, $\sigma_{\text{cat}}^d$, $\sigma_{\text{an}}^d$, and $\sigma_{\text{cat,an}}^d$, for (b) the two organic solvent systems and (c) the four ionic liquids solvent systems at 298K.

Figure 4. Radial distribution function of the lithium salt LiTFSI at 298K in the organic solvents (a) DMC and (b) DEC, and the ILs solvents (c) [C$_2$mim][BF$_4$], (d) [C$_2$mim][TFSI], (e) [C$_4$mim][BF$_4$] and (f) [C$_4$mim][TFSI].

Figure 5. (a) Simulation snapshot of the cation Li$^+$ (purple sphere) surrounded by the anion TFSI$^-$ in the first solvation shell for the LiTFSI-DMC electrolyte at 298K. (b) Site-site radial distribution function ($g(r)$) and coordination number ($N$) of Li$^+$-O(TFSI$^-$) (red trace) and Li$^+$-N(TFSI$^-$) (blue trace) in the LiTFSI-DMC electrolyte.

Figure 6. Composite graph of the radial distribution functions representing the spatial correlations of the cation Li$^+$ with (a) the two organic solvent molecules, and with the (b) cations and (c) anions of the four ILs solvents at 298K.
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Figure 2. The plots of mean square displacement (MSD) of Li⁺ and TFSI⁻ vs. simulation time (t) in the solvents DMC and [C₂mim][BF₄] at 298K.
<table>
<thead>
<tr>
<th>Solvent</th>
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<th>DEC</th>
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<th>[C$_2$ mim][TFSI]</th>
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**Figure 3.** (a) Results of the total conductivity $\sigma_{\text{tot}}$ (S/m) of the six electrolytes at 298K. (b) Results of the five conductivity types, viz. $\sigma_{\text{cat}}^c$, $\sigma_{\text{an}}^c$, $\sigma_{\text{cat}}^d$, $\sigma_{\text{an}}^d$ and $\sigma_{\text{cat,an}}^d$, for (b) the two organic solvent systems and (c) the four ionic liquids solvent systems at 298K.
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