Comparing ion transport in ionic liquids and polymerized ionic liquids

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Polymerized ionic liquids (polyILs) combine the unique properties of ionic liquids (ILs) with macromolecular polymers. But anion diffusivities in polyILs can be three orders of magnitude lower than that in ILs. Endeavors to improve ion transport in polyILs urgently need in-depth insights of ion transport in polyILs. As such the work we compared ion transport in poly(1-butyl-3-vinylimidazolium-tetrafluoroborate) (poly ([BVIM]-[BF4])) polyIL and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]-[BF4]) IL. The diffusivities of ions in the polyIL and IL were measured and computed. According to the results of the molecular dynamics simulations performed, in the IL the coupling motion between an anion and the ions around determines the ion diffusivities, and the ion association lifetime gives the time scale of ion transport. But in the polyIL, the hopping of an anion among cages composed of cationic branch chains determines the diffusivity, and the associated anion transport time scale is the trap time, which is the time when an anion is caught inside a cage, not the ion association lifetime, as Mogurampelly et al. regarded. The calculation results of average displacements (ADs) of the polyIL chains show that, besides free volume fraction, average amplitudes of the oscillation of chains and chain translation speed lead to various diffusivities at various temperatures.

Polymerized ionic liquids (polyILs) integrate the unique properties of ionic liquids (ILs) with macromolecular polymers. PolyILs are attractive candidates for potential applications in energy storage and electrochemical devices, e.g. supercapacitors and batteries. Using these materials can avoid some disadvantages of liquid electrolytes, such as flammability, and furthermore utilize the polymeric nature of polyILs to produce materials with different shape, e.g. thin films.

But the anion diffusivities in polyILs can be three orders of magnitude lower than that in ILs. Researches are being performed to promote anion transport in polyILs, but such endeavors necessarily need in-depth insights of mechanisms of anion transport in polyILs. Zhang and Maginn proposed that in ILs, the ion transport mechanism is the structural relaxation of ion association, but researchers have uncertainty and discrepancy in the ion transport mechanism in polyILs. Some researchers observed that ion transport in polyILs is related to the segmental dynamics of polyILs, but some other researchers reported a decoupling between ionic conductivity and structural dynamics in polyILs. Mogurampelly et al. proposed that electrostatic interactions between anions and branch chains of polyILs and how anions move along polyIL chains are the key factors that influence the magnitude of ion diffusivities. They used the lifetime of ion pairs, the continuous ion pairing time, to determine the anion transport time scale in polyILs, but we did not think it is correct. The work shows that the associated anion transport time scale is the trap time, which is the time when an anion is caught inside a cage, not the lifetime of ion pairs. So we obtained totally novel results. Wrong theories would give totally misleading guidance to researches of other researchers, causing large waste of money and labor, both manual and mental. As a result our work is essential and important.

These three groups, MacFarlane and Forsyth, Shaplov and Gerbaldi, Mecerreyes and Brandell, had done experimental researches to explore solid-state electrolytes for batteries, focusing on application research. Gerbaldi et al. and Ahmad and Deepa developed composite materials containing IL used for batteries or electrochromic devices. But none above from a molecular level analyzed the mechanisms that lead to the differences between the conductivity between solid and liquid electrolytes. Such researches are essential, as they can be very important guidance for experimental researches. If we only develop another solid electrolyte and do not theoretical exploration from a molecular level, then such research will surely lack novelty.

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In this work we did a novel research. From a molecular level, we compared the mechanisms of ion transport in poly(1-butyl-3-vinylimidazolium-tetrafluoroborate) (poly([BVIM]−[BF₄] )) polymerized ionic liquid (polyIL) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]−[BF₄] ) ionic liquid (IL): The relationship between ion transport and structure dynamics in the polyIL and the IL was clarified.

We employed both experimental methods and molecular dynamics (MD) method to determine ion diffusivities. The anion diffusivities were determined experimentally with broadband dielectric spectroscopy (BDS)²⁸⁻³³ and pulsed field gradient nuclear magnetic resonance (PFG-NMR)³⁴⁻³⁶.

The MD methods are extensively applied in scientific researches to obtain in-depth knowledge behind phenomena from a molecular level³⁷⁻⁴¹. In the research, MD simulations were carried out to simulate ion transport in the polyIL and IL.

Experimental and computational methods

Experimental methods to measure diffusivities.

To determine anion diffusion coefficients in the polyIL and IL, pulsed field gradient (PFG) NMR ⁴²⁻⁴⁴ and broadband dielectric spectroscopy (BDS) for lower temperature⁴⁸ were employed.

The PFG is a short, timed pulse with spatial-dependent field intensity. A PFG is identified with four parameters: axis, strength, shape, and duration. Gradient enhanced NMR is a method for obtaining high resolution nuclear magnetic resonance spectra. PFG NMR techniques are employed widely for studies of diffusion via diffusion ordered nuclear magnetic resonance spectroscopy ⁴²⁻⁴⁴.

BDS is a very powerful experimental tool for understanding molecular level dynamics in ILs and PolyILs ⁴⁶⁻⁴⁹. This technique allows the dielectric response to be measured over 12 decades of frequency at different temperatures, below as well as above its glass transition temperature, giving valuable insight into molecular mobility of polyILs ⁵⁰.

BDS measures the complex dielectric function and the complex conductivity function. The real part of the complex conductivity function in ionic liquids is characterized by the intermediate frequency regime by a plateau, the value of which directly yields the dc conductivity, σₚ. At lower frequencies, the real part of the complex conductivity function decreases from σₚ due to electrode polarization. The diffusion coefficient can be determined from BDS spectra by a combination of the Einstein and Smoluchowski equations⁴⁵. The DC conductivity σₚ is given by

\[
\sigma_0 = N q \mu = n q^2 D = \frac{n q^2 l_{jump}^2 \times \omega_c}{kT} \frac{1}{2}
\]

where \( n \) denotes the effective number density (given by \( N \gamma (T) \), where \( \gamma (T) \) is the fraction of mobile charge carriers at a given temperature \( T \) and \( N \) is the total number density of charge carriers available in the material), \( \mu \) is the mobility of charge carriers, \( q \) is the elementary electric charge, \( D \) is the diffusion coefficient, \( k \) is the Boltzmann constant, \( l_{jump} \) (0.5–1 nm) is the displacement anions travel in one jump and \( \omega_c \) is the characteristic (diffusion) rate.

Preparation of the polyIL.

The IL, [BMIM]−[BF₄] , was purchased from IOLITEC Ionic Liquids Technologies, Inc. and samples were used as received. By mixing 1-vinylimidazole (68.0 g, 0.722 mol) and excess bromobutane (168.8 g, 0.940 mol) in methanol (60 mL) at 75 °C for 3 days, 1-butyl-3-vinylimidazolium bromide ([BVIM]−[Br]) was prepared. [BVIM]−[Br] was dried under vacuum at 55 °C and remaining bromoethane. Free radical polymerization was initiated by azobisisobutyronitrile (AIBN) (0.294 g, 1.78 mmol) in a vessel (72 mL) solution at 65 °C and carried out for 15 h. Then poly([BVIM]−[Br]) was diazoylated against water for 4 days and finally a powder was obtained from freeze-drying (80% yield). A ¹H NMR measurement in D₂O was performed to confirm that the no [BVIM]−[Br] component remains. Poly([BVIM]−[BF₄] ) was treated with the counterion conversion method. An aqueous solution including 1.50 equiv of NaBF₄ was slowly titrated into aqueous poly([BVIM]−[Br]) solution and mixed for at least 2 days at room temperature. The obtained preparation of poly([BVIM]−[BF₄] ) was washed with water until the eluent remained clear with the addition of an aqueous solution of AgNO₃. The purity of poly([BVIM]−[BF₄] ) was confirmed using elemental analysis.

Differential scanning calorimeter (DSC) technique was used to measure the glass transition temperature of the prepared polyIL at a heating and cooling rate of 10 K/min. The midpoint of the total heat flow curve in the thermal transition region was taken as the transition temperature. The obtained glass transition temperature of the prepared polyIL is 414 K. Differential scanning calorimeter (DSC) technique was also used to measure the melting temperature of the IL and the result is 202 K.

Molecular dynamics (MD) simulation.

Figure 1 presents the optimized structures of [BF₄]−, [BMIM]+ and poly([BVIM]+) achieved with QC calculation. Like Tamai et al., the polyIL chain was modeled as H([BMIM]−[BF₄]), 3, H 31 repeating units being adopted. The methyl and ethyl groups of [BMIM]+ and poly([BVIM]+) were treated as united units (a methyl group was regarded as an individual unit in a whole; a ethyl group is regarded as being composed of two individual units, a methyl unit and a methylene unit), while all the other atoms were treated as single units. According to our experience, treating all atoms of methyl or ethyl groups individually only increase the computation cost and relaxation difficulty of the system, while has no contribution to simulation results improvement. Atoms of [BF₄]− were treated individually. The simulation cell of the IL has 31 polyIL chains. We applied the AMBER/OPLS force field ⁵²⁻⁵³ for parameters of bond, angle, dihedral, electrostatic and van der Waals (VDW) interactions among the units. We computed the electrostatic interaction and VDW interaction with Ewald sum algorithm and Lennard-Jones equation, respectively ⁵⁵. The Lorentz-Berthelot mixing rule was applied to compute the interactions between various types of units.
VDW and electrostatic interactions are among those that matter most for MD simulation. Table 1 shows the VDW potential parameter and charge values for the units of the polyIL and IL. The charges of B and F are correlated according to quantum chemical (QC) calculation results with the technique proposed by Singh and Kollman and their VDW energy parameters were fitted through least square fit of the interaction potentials computed with QC method between two anions having different distance.

### Potential parameters and control parameters of molecular dynamics (MD) simulation

Figure 1 shows the geometries of $[\text{BF}_4]^{-}$, $[\text{BMIM}]^{+}$ and poly([BVIM]$^+$). The bond and angle interactions were calculated with harmonic potential equation while dihedral interaction was estimated with OPLS dihedral angle potential equation (Eq. (3)). The electrostatic interactions were estimated using Ewald sum algorithm, while the VDW interactions were computed using Lennard-Jones equation.

$$U(r) = U_{\text{bonds}}(r) + U_{\text{ambonds}}(r)$$

$$U_{\text{bonds}}(r) = \sum_{\text{bonds}} k_r (r - r_0)^2 + \sum_{\text{angles}} k_{\theta} (\theta - \theta_0)^2 + \sum_{\text{dihedrals}} \left[A_0 + \frac{1}{2} A_1 (1 + \cos \phi) + A_2 (1 - \cos 2\phi) + A_3 (1 + \cos 3\phi)\right]$$

As in MD simulation, VDW and electrostatic interactions are among those that matter most, Table 1 shows the VDW potential parameters and charge values for units of the polyIL and IL.

The IL and the polyIL densities at 300 K, 1.21 g/cm$^3$ and 1.31 g/cm$^3$, respectively, were employed to calculate the sizes of the simulation cells at 300 K. The simulation cells of the IL and the polyIL contains 310 $[\text{BMIM}][\text{BF}_4]$ ion pairs and 10 polyIL chains, respectively. For the simulation of anion transport in the IL, the cell size is 4.00 nm
The DLPOLY55 software system was used. Under condition of constant pressure and temperature, the Verlet algorithm was used, in purpose of solving equations of motion with the time step of 2.5 fs. To obtain a reasonable starting configuration of the IL and polyIL systems, energy minimization was done first, using the steepest descent algorithm. Subsequently the structure was relaxed by a 5 ns MD equilibration run in the NPT ensemble. The weak coupling technique was used to adjust the temperature and pressure with relaxation times of 0.1 ps and 0.5 ps, respectively. After the equilibration run, production runs were performed in the NVT ensemble. In this ensemble the averaged kinetic energy $E_{\text{kinetic}}(T)$, the molecules was held constant. The temperature was set to 300 K to do simulation at the temperature first, the pressure was set to 1 bar, the VDW potentials cut off distance was set to 1.0 nm and the electrostatic potential cut off distance was set to 1.2 nm. To do simulation at other temperatures, equilibrium runs in the NPT hoover ensemble at those temperatures were performed again, after which production runs in the NVT ensemble at those temperatures were performed.

MD production run time was estimated based on Eq. (4):

$$\sqrt{\frac{l_{\text{jump}}^2}{6 \times D}}$$

where $l_{\text{jump}}$ (~0.5–1 nm) is the jump length, the displacement an anion can make in one single jump. MD production run time is at least several times of the time Eq. (4) gives so anions have enough time to complete at least several jumps (5–10) and long enough trajectories can be obtained. Besides, the time should be also long enough for anions to reach the Fickian diffusion regime. Only in the Fickian diffusive regime can diffusivities be calculated through the slope of MSDs versus time plot.

**Quantum chemical (QC) calculations.** QC calculations were performed for $[\text{BMIM}]^+$, $[\text{BF}_4^-]$, $[\text{BMIM}]^- [\text{BF}_4^-]$ and $\text{H}[\text{BMIM}][\text{BF}_4]$ with Gaussian 09 program package. The density functional theory (DFT) level of calculation was done, using the B3LYP functional with the standard 6–31++G(2d,p) basis set. Vibrational frequencies calculation was performed to verify that the optimized structures are globally optimal. The optimized structures were used to build the models for MD simulations.

The results of QC optimization structures for an ion pair are presented in Fig. 2. The structures of $[\text{BMIM}]^+$ and $[\text{BMIM}]^-$ in Fig. 1 only differ slightly from that in Fig. 2. Such minor differences would have no influence on MD simulation results. The interaction potential between ion pair is $-37.04 \text{ kcal/mol}$. The ion association interactions give the IL brilliant properties, e.g. high viscosity, low vapor pressure and good thermal and chemical stability.

**Diffusivity calculation.** The mean squared displacements (MSD) which were averaged on various time origins were applied to calculate anion diffusivities according to Eq. (5):

$$D = \lim_{\Delta t \to \infty} \frac{\langle [R(t_0 + \Delta t) - R(t_0)]^2 \rangle_{t_0}}{6 \times \Delta t}$$

where $R(t)$ represents the anion location at $t$ and $\langle ... \rangle$ stands for an average of moving time and the average is calculated with respect to $t_0$.

The logarithmic plot of MSD versus time was plotted to determine if the diffusion was in the Fickian diffusive regime. The MSD were averaged over different time origin. Then diffusivities were calculated through the slope of the plot of MSD versus time. The slope was obtained through a least square fit of the plot. Long time of production run was done to ensure ion transport trajectories are long enough. The diffusivities obtained are the average of all the ions. The sampling size is very large. All these ensure the accuracy of the calculated diffusivities and repeated simulations show that the relative standard deviation (RSD) (standard deviation as a percentage of average diffusivity) in the calculated diffusivities is smaller than 5%.

For $\Delta t$, the average displacement (AD) of a chain is estimated according to Eq. (6).
Results and discussion

Figure 3 shows the snapshots of the inside of the simulation cells of the IL and the polyIL. It is observed that in the polyIL, the cations are connected together by chains, so small or large cavities among cations are formed and anions are constrained inside these cavities before they get chances to jump to cavities nearby. On the contrary, in the IL, the cations are not linked, so they can move freely as anions do.

Figure 4 shows the diffusivities of anions of the polyIL and IL at various temperatures obtained via experiments and MD simulations. The values obtained via both methods are in agreement. At the same temperatures, anions in the polyIL have diffusivities 3 orders of magnitude lower than that of anions in the IL. In the calculated diffusivities the relative standard deviation (RSD) is smaller than 5%.

To clarify the underlying mechanisms, the exploration of the three diffusion regimes of anion transport, ballistic regime, the subdiffusive regime and Fickian diffusive regime, especially the subdiffusive regime is necessary. As presented in Fig. 5(a), in the ballistic regime, the subdiffusive regime and the Fickian diffusive regime, MSDs are proportional to $t^2$, $t^{0.5}$ and $t$, respectively.

The logarithmic plots of MSD versus time for anion transport in the polyIL and IL at 300 K are presented in Fig. 5(b), which shows the three diffusion regimes above. The ballistic regime is shorter than the other two regimes ($t < 2.0$ ps). Compared to the IL, the polyIL has short ballistic regime. In the ballistic regime, anions fly freely, having no bounces with other ions. Hence the results show that in the polyIL, the average cavity size is smaller than that in the IL and an anion is constrained more stringently in the polyIL than in the IL.

The subdiffusive regime is longer than the ballistic regime according to Fig. 5. The subdiffusive regime of the polyIL is longer than the IL. The hindrance influence of surrounding units on anions lead to the subdiffusion phenomena, so studying the subdiffusive regime is essential for clarify the mechanisms behind.

Different models for anomalous diffusion models, e.g. random walk on a fractal (RWF), fractional Langevin equation (FLE) and continuous time random walk (CTRW) have been presented. A rather good example of where anomalous CTRW have been successfully used to model a physical process is DNA gel electrophoresis, as presented in Fig. 6(a). In the process, an electric field is applied to force DNA molecules through a porous gel. The rate at which molecules pass through the gel is determined by their mobility, which is a function of size and charge. For small sections of DNA, separation can be achieved successfully. But large molecules are often trapped in the gel, causing a long waiting time between displacements. The work of Weiss shows that this process can be described successfully by subdiffusive CTRW model, with finite drift and zero variance in the step size, but a diverging mean waiting time $\psi(\tau) \sim \tau^{-1-\alpha}$ ($1 < \alpha < 2$).

In contrast, FLE is a Gaussian process in which anomalous diffusion comes about via statistical correlations between successive steps. Such FLE processes are widely associated with modeling of stochastic transport in viscoelastic environments. FLE equations can be postulated but may also arise as an effective description of more complex multiparticle Markovian dynamics.
Figure 6(b) shows an example of the FLE process, the subdiffusion of fullerene in molten polymers, which is incurred by the coupling between the motions of fullerene molecules and the molten polymers or fullerene molecules nearby. RWF model can describe the effect of geometric constraints arising in complex geometries, is not space-filling, and displays non-Gaussian propagators. Figure 6(c) shows one example of the RWF process, where penetrants can only "walk" along certain passages. When gas penetrants diffuse in polymers, like poly (4-methyl-2-pentyne) (PMP), such processes are observed as well, as presented in Fig. 6(d). From Fig. 6(d), it is observed that there are small vacancies among the long chains of PMP, penetrants, like methane and n-butane can only diffuse among vacancies through passages connecting these vacancies. Figure 6(e) shows the snapshot of the PMP-gas system after the penetrants are placed in the vacuum portion at the left and right sides and the simulation production run has been performed for 2 ns. Most of the n-butane molecules penetrate deeply into the bulk, whereas most of the methane molecules placed at the same time as n-butane molecules only wander around the interface.

Figure 4. The diffusivities of the anions of the polyIL and IL at various temperatures.

Figure 5. (a) The scheme of three diffusion regimes. (b) The logarithm plot of MSD versus time for the anion transport in the IL and polyIL.
Therefore larger molecules have larger displacements, contrary to the example in Fig. 6(a), an anomalous CTRW process, where smaller DNA molecules travel longer distance.

Processes that can be described by the CTRW model have random penetrant jump time and penetrant jump length. In the research, motion of anions is not in a random way, but is influenced by cavities nearby and chain oscillation. As a result, we cannot apply the CTRW model to describe the subdiffusive behavior of anions in the research. Furthermore, processes describable by the FLE model are Gaussian, while that describable by the RWF model are non-Gaussian.

The minimal excursion ratio (MME) method, given by Meroz and Sokolov, was used to determine if a transport process is non-Gaussian or Gaussian:

\[
MME = \frac{\langle R(t_0 + \Delta t) - R(t_0)^2 \rangle_{t_0}}{\langle R(t_0 + \Delta t) - R(t_0)^2 \rangle_{t_0}}
\]

(7)

where \( R(t) \) is the position of gas molecules at \( t \), \( \langle \ldots \rangle \) denotes a moving time average and the sub-index \( t_0 \) indicates the average it taken with respect to \( t_0 \).

From Fig. 7, the MME ratio is approaching one for anion transport in the IL while that for anion transport in the polyIL is not tending to one. Hence the subdiffusive behavior of anions in the IL is Gaussian while that in the polyIL is non-Gaussian. The FLE model and the RWF model should be applied to explain the subdiffusion phenomena in the IL and the polyIL, respectively.

According to the FLE model, in the IL the coupling between the motions of an anion and the ions nearby causes the subdiffusive behavior of the anion. The same explanation is given by the scaling theory, which explains that relaxation processes of the ions lead to subdiffusive phenomena and when the motions of an anion and the ions around complete coupling, the relaxation processes cease. For such type of subdiffusion phenomena, the ion association lifetime gives the time scale.

According to the RWF model, the trap of anions in cages consisting of chains lead to the subdiffusive behavior of anions in the polyIL. Cages in the polyIL are stable and anions can be caught for long time. The associated anion transport time scale is hence the trap time, the time when an anion is caught inside a cage, not the ion association lifetime. The following equation can be applied to give an estimate of the trap time:

\[
t = \frac{l_{\text{jump}}^2}{6 \times D}
\]

(8)

where \( l_{\text{jump}} \) (~0.5–1 nm) is the jump length, the displacement an anion can make in one single jump.
From Fig. 5, longer subdiffusive regime is observed for the polyIL than the IL. As presented above, it is because of the anion trap in the stable cages, which consist of polyIL chains. On the contrary, there are no such cages in the IL because cations are free to move and not constrained by the main chains. The motion of main and cationic branch chains that compose cages need to be investigated in order to get the detailed knowledge of the cages.

Figure 8 shows the trajectory Scheme of an anion in [BMIM]-[BF_4] for a time interval of 2.5 ns and in poly([B-VIM]-[BF_4]) for a time interval of 550 ns. It is observed that the anion in the IL have remarkably higher diffusivity than that in poly([B-VIM]-[BF_4]) according to Eq. (5). Therefore, poly([B-VIM]-[BF_4]) made a jump from a cage to another cage and the trajectories in the two cages are distinct.

Figure 9(a) is the plot showing the ADs of the polyIL chain units versus time intervals. The ADs increase sharply to a stair value in short time intervals (~3.5 ps). It is known polymer chains swing around their balance locations rapidly. The stair value is an estimate of the average swing amplitudes. The ADs of chains are composed of the swing and the translation portions. The ADs nearly remain constant, after reaching a stair value, so the speed of the chain translation is tiny. The rates of the chain translation are around 0.00161, 0.00188, 0.00219 and 0.00251 Å/ps corresponding to 300 K, 400 K and 500 K, respectively. With the translation rate and the average swing amplitude shown in Fig. 9(a), ADs for any time intervals may be estimated. The promotion of both the average swing amplitude and the chain translation rate is observed with the increase of temperatures.

The free volume fraction (FVF) of a polymer also affects the magnitude of diffusivities. In order to shun the FVF effects, for 400 K and 500 K we set the volume of the simulation cells the same. According to the simulation results, the calculated diffusivities of anions and the average swing amplitudes of the polyIL chains at 500 K are larger than that at 400 K. As a result, the average swing amplitude the polyIL chains is doing contributions to the various diffusivities at various temperatures. Anions will be caught in cages and the anion diffusivity will be null if the polyIL chains remain static. With the promotion of the average swing amplitude, anions achieve more chances to jump to cages nearby and the diffusivities get promotion accordingly.

With the increase of temperatures, the increase of both the average swing amplitude and the chain translation rate is observed. The cages are composed of branch and main chains. Higher chain swing amplitudes cause more opportunities in the same time periods for the emergence of large enough holes in the cages which anions can pass. Due to the promotion of the FVF of the polyIL with temperatures, larger spaces between the chains emerge. These factors mentioned above take effects, leading to increased opportunities for an anion to flee from a cage and jump to a cage around.

An anion should overcome the electrostatic and VDW interactions with the units of the chains composing the cage, in order to flee from a cage. When the anion approaches the cage wall, if there are no VDW interactions, the attractive electrostatic interactions between the anion and cationic branch chains that the anion is getting closer will become higher; the anion can hence flee from the cage when it makes the first try. Therefore electrostatic interactions alone cannot catch an anion inside a cage. When the anion approaches the cage wall, the repulsive VDW interactions between the anion and cage units that the anion is getting closer get higher, larger that the corresponding electrostatic interactions. The anion is pushed back to the cage inside. Hence it is VDW interactions that have the largest contribution in trapping anions. From Eq. (4), the length of the trap time determines the time scales underlying ion transport. As a result VDW interactions exert a more important influence on anion diffusivities than electrostatic interactions, including ion association interactions. Analyzing only electrostatic interactions between ions cannot give the correct ion transport mechanisms. On the contrary, such analysis can only give wrong and misleading mechanisms, as Mogurampelly et al. did. We cannot deny that ion associations affect anion diffusivities, but VDW interactions exert the most important influence, as presented above.

Mogurampelly et al. proposed that if the cation-anion distance is below a benchmark value an ion pair is established and if the distance is above that value the ion pair is separated. They applied the continuous ion pairing time, the time interval when the ion pair remains paired continuously, to describe the time scales underlying ion transport.

Anions moves up and down, left and right rapidly inside cages composed of chains of the polyIL. Therefore at one moment an anion may be closer than a benchmark value to a cationic branch chain, but after a while the distance between the anion and cationic branch chain can be larger than that value. Then with time going on, the distance can vary to values larger or smaller than that value. However, in the whole process, the anion is inside
the cage, i.e. whether the distance between the ion pair is larger or smaller than the benchmark value making no fundamental differences. Hence to use the continuous ion pairing time above to estimate the anion transport time scale is totally wrong. Definitely the trap time of an anion inside a cage should be applied instead. So we obtained totally novel results. Our work is essential and important, as wrong theories would give totally misleading guidance to researches of other researchers, causing large manual and mental waste of money and labor.

The diffusivities and trap times of anions in the polyIL at various temperatures are shown in Fig. 10. The trap times in the figure are the averaged trap times of all the anions. The promotion in diffusivities is observed with the increase of temperatures. Diffusivities go down with the increase of trap times and are inversely proportional to trap times, matching Eq. (4). The trap times decrease with temperatures. This can be explained by higher temperatures causing higher chain swing amplitudes, larger chain translation rate and larger spaces between chains and anions obtaining more hopping opportunities to flee from the cage.

**Conclusions**

In conclusion, in the work we explored and compared the mechanisms and time scales of ion transport in the polyIL and the IL. In the IL the coupling between the motions of an anion the ions nearby cause the subdiffusive behavior of the anion, while in the polyIL, the trap of anions in cages consisting of chains lead to the subdiffusive behavior of anions.

Mogurampelly et al. stated that electrostatic interactions between anions and branch chains of polyILs and how anions move along polyIL chains are the key factors that influence the magnitude of ion diffusivities. They used the lifetime of ion pairs, the continuous ion pairing time, to determine the anion transport time scale in polyILs, but we did not think it is correct. The work shows that the associated anion transport time scale is the trap time, which is the time when an anion is caught inside a cage, not the lifetime of ion pairs. So we obtained totally novel results. Our work is essential and important, as wrong theories would give totally misleading guidance to researches of other researchers, causing large manual and mental waste of money and labor.

Higher temperature bring about higher chain swing amplitudes, leading to more opportunities in the same time periods for the emergence of large enough holes in the cages which anions can pass. Due to the promotion
of the FVF of the polyIL with temperatures, larger spaces between the chains emerge. These factors mentioned above take effects, leading to increased opportunities for an anion to flee from a cage and hop to a cage around.

In the polyIL, VDW interactions exert a more important influence on anion diffusivities than electrostatic interactions, including ion association interactions.

The diffusivities go down with the increase of trap times and are inversely proportional to trap times. The trap times decrease with temperatures. This can be explained by higher temperatures causing higher chain swing amplitudes, larger chain translation rate and larger spaces between chains, so anions obtaining more hopping opportunities to flee from the cage.

**Data availability**
The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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**Figure 9.** (a) The ADs of polyIL chain units for various time intervals. (b) The average oscillation amplitudes of the main and branch chains of the polyIL as a function of temperatures.

**Figure 10.** The anion diffusivities and trap times in the polyIL at different temperatures.
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**Author contributions**

W.-C.X. and Q.Y. contributed equally. W.-C.X. and Q.Y. did simulation work, wrote the manuscript and part of experiment work. S.–L.Z. did experiment work.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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