Importance of the Ion-Pair Lifetime in Polymer Electrolytes

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ABSTRACT: Ion pairing is commonly considered as a culprit for the reduced ionic conductivity in polymer electrolyte systems. However, this simple thermodynamic picture should not be taken literally, as ion pairing is a dynamical phenomenon. Here we construct molecular dynamics simulations. It is found that there exist two distinct regimes where solvent-separated ion pairs (SSIPs). In addition, it implies that rendering a distinction between contact ion pairs (CIPs) and polarity plays a critical role in the formation of ion pairs, temperature \( T \) deviations of the ionic conductivity from the Nernst relation cannot solely be attributed to the formation of ion pairs.

One common approach to define an ion pair is to use Bjerrum’s criterion, in which the distance \( r_{\text{ss}} \) is smaller than the effective range of \( -q_i q_j/2\varepsilon \) (half of the Bjerrum length) with \( \varepsilon \) as the dielectric constant of the solution, \( q_i \) and \( q_j \) being the ionic charges, the Boltzmann constant \( k_B \) and the temperature \( T \). Bjerrum’s criterion suggests that the solvent polarity plays a critical role in the formation of ion pairs, rendering a distinction between contact ion pairs (CIPs) and solvent-separated ion pairs (SSIPs). In addition, it implies that the formation of pairs of equal ionic species is unlikely to occur due to the electrostatic repulsion but that the possibility of forming triplets or larger aggregates, for example, an anion–cation–anion cluster, cannot be excluded.\(^{8,9}\)

The idea that ion pairing affects the ionic conductivity was introduced early on by Arrhenius, who ascribed the decrease of the equivalent conductivity at a higher concentration to the formation of charge-neutral ion pairs.\(^{10}\) This idea has been put forward using the molar conductivity ratio \( \Lambda_{\text{EIS}}/\Lambda_{\text{NMR}} \) measured by electrochemical impedance spectroscopy (EIS) and pulse-field gradient NMR to quantify the ionicity (the degree of dissociativity), particularly for ionic liquids and polymer electrolytes.\(^{11,12}\) Nevertheless, it has been realized that deviations of the ionic conductivity from the Nernst–Einstein relation cannot solely be attributed to the formation of ion pairs,\(^{14,15}\) where other factors such as the hydrodynamic interactions manifested via viscosity can play an important role.\(^{17}\)

To describe the effect of ion pairing on the ionic conductivity, one needs an observable that can be accessed both theoretically and experimentally. The key quantity used here is the cation–anion distinct conductivity \( \sigma_{\text{d}} \) from liquid-state theory.\(^{18,19}\)

\[
\sigma_{\text{d}} = \lim_{t \to \infty} \frac{1}{3 k_B T \Omega} \sum_{i, j} \langle q_{i+} q_{j-} \Delta r_{i+}(t) \cdot \Delta r_{j-}(t) \rangle
\]

where \( \Omega \) is the volume of the system, and \( \Delta r(t) \) is the displacement vector of each ion at time \( t \). Note that \( \sigma_{\text{d}} \) is experimentally measurable and related directly to the Onsager transport coefficient \( \Omega_{\text{ss}} \).\(^{8,9}\)

Somewhat unexpectedly, \( \sigma_{\text{d}} \) is often found positive (instead of negative as in Arrhenius’ picture) in different types of electrolyte systems, spanning categories from aqueous electrolyte solutions to polymer ionic liquids.\(^{15,17,23-27}\) This suggests that the existence of ion pairs, as evidenced by a number of spectroscopic experiments, does not necessarily imply a negative contribution to the measured ionic conductivity but can instead contribute to an increase in the transport of ions. Therefore, understanding the ion pairing effect on polymer electrolytes is crucial, as their application in energy storage systems is largely limited by a low ionic conductivity.\(^{31-33}\)

The crucial point to this conundrum lies in the fact that Bjerrum’s convention is a thermodynamic criterion, while the ionic conductivity is a dynamical property. Therefore, the lifetime of charge-neutral ion pairs needs to be considered.

Supporting Information

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explicitly when discussing the contribution of ion pairing to the ionic conductivity, in addition to the distance criterion due to the thermodynamic stability. In other words, an ion pair should be "long-lived enough to be a recognizable kinetic entity."\textsuperscript{34}

Theoretically, the lifetime of ion pairs $\tau_{+−}$ can be extracted from the normalized time correlation function of the cation−anion pairs in molecular dynamics (MD) simulations\textsuperscript{35}

$$P(s) = \frac{\sum_i^n \sum_j^n (\theta(r_c - r_{ij}(0))) f(r_{ij}; s)}{\sum_i^n \sum_j^n (\theta(r_c - r_{ij}(0)))}$$

where $f(r_{ij}; s)$ is a window function to detect whether a cation−anion pair lies within the cutoff $r_c$ for a given period $s$.

The first approach is to use the product of the Heaviside functions $\theta(x)$ defined by a time series of pairwise distances $r_{ij}$ between a cation−anion pair, as follows.\textsuperscript{36}

$$f_{PT}(r_{ij}; s) = \prod_{i\leq j} \theta(r_c - r_{ij}(t))$$

However, the persistence time (PT) from this procedure clearly neglects recrossing events, for example, reactions passing over the transition state but returning to the reactant afterward, which has been discussed extensively for hydrogen-bond dynamics.\textsuperscript{35,37} Here, we used the stable states picture (SSP) of chemical reactions proposed by Laage and Hynes, which remedies this problem.\textsuperscript{38} Then $f(r_{ij}; s)$ in SSP is given as

$$f_{SSP}(r_{ij}; s) = \prod_{i\leq j} \theta(r_{c,prod} - r_{ij}(t))$$

where $r_{c,prod}$ is the product SSP boundary, which corresponds to the cation−anion distance at the half height of the second peak in the radial distribution function (RDF). Then, $r_c$ in eq 2 should be replaced by the reactant SSP boundary $r_{c,react}$ which is at the first maximum of the cation−anion RDF.

To investigate the relation between $\sigma_{+−}$ and $\tau_{+−}$ in polymer electrolyte systems, we constructed simulation boxes consisting of 200 poly(ethylene oxide) (PEO) polymer chains each with 25 ethylene oxide (EO) repeating units and 400 bis-(trifluoromethane)sulfonimide lithium salt (LiTFSI) ([Li\textsuperscript{+}]/[EO] concentration = 0.08). As indicated by Bjerrum’s criterion, the solvent polarity strongly modulates the ion pairing. This motivated us to apply the charge scaling method\textsuperscript{39} to PEO molecules to change the degree of ion pairing. General AMBER force field (GAFF)\textsuperscript{40} parameters were used for describing bonding and nonbonding interactions in PEO and LiTFSI, and all MD simulations were performed using GROMACS 2018.1.\textsuperscript{41} All systems were properly equilibrated to make sure that the simulation length is larger than the Rouse time of the polymer. Details for the system setup and MD simulations can be found in the Supporting Information Section A.1.

Before discussing our main result, it is necessary to check how structural and transport properties change when we tweak...
the handle of the solvent polarity. Here, the solvent polarity is described by the dielectric constant of the system $\varepsilon_P$, which was computed for each polymer electrolyte system (see Section A.2 in the Supporting Information for details).

The RDFs of Li–N(TFSI) are plotted in Figure 1a, where peaks in the Li–N(TFSI) RDF increase significantly when $\varepsilon_P$ becomes smaller. This is a sign of formation of ion pairs, which is also evinced in Figure 2. Accordingly, there is an optimal value in the total Green–Kubo conductivity $\sigma_{\text{GK}}$ when the solvent polarity is modulated as seen in Figure 1b. Both of these results support our previous observations of the effect of solvent polarity on the Li$^+$ transportation in PEO-LiTFSI systems$^{42}$ and agree with other recent studies of polymer electrolyte systems.$^{43,44}$

Figure 1c,d, however, demonstrates novel phenomena. The lifetime of ion pairs increases when $\varepsilon_P$ is either high or low, and it reaches a minimum at the intermediate value of $\varepsilon_P$ (see Section A.3 in the Supporting Information for further details of calculations of the lifetime of ion pairs and a comparison of outcomes from eq 3 and eq 4). Inspecting Figure 1b,c, one may attempt to relate the opposite trend shown in the total ionic conductivity $\sigma_{\text{GK}}$ to that of $\tau_{\text{ff}}$. However, the lifetime increases much more rapidly at a lower dielectric constant regime ($\varepsilon_P < 2.3$) compared to that at a higher dielectric constant regime ($\varepsilon_P > 3$). This suggests there are different types of ion pairs in polymer electrolyte systems under investigation here. Looking at the cation–anion distinct conductivity $\sigma_{\text{d, pair}}^\text{d}$ one can clearly see that it goes from positive to negative when $\varepsilon_P$ becomes smaller. (Note that $\sigma_{\text{d, pair}}^\text{d} > 0$ corresponds to anticorrelated cation–anion movements for the sign convention used in this work.) In particular, the rapid decrement in $\sigma_{\text{d, pair}}^\text{d}$ at lower $\varepsilon_P$ seems in accord with the rapid increment in $\tau_{\text{ff}}$. These observations also point to the direction that these two key properties of ion pairs, namely, $\sigma_{\text{d, pair}}^\text{d}$ and $\tau_{\text{ff}}$, must be closely related. This leads to our main result shown in Figure 3. What we find is that there exist two distinct regimes: $\sigma_{\text{d, pair}}^\text{d}$ scales with $1/\tau_{\text{ff}}$ (for higher values of $\varepsilon_P$), and $\sigma_{\text{d, nonpairing}}^\text{d}$ scales with $\tau_{\text{ff}}$ (for lower values of $\varepsilon_P$). Moreover, the transition between these two regimes shows a combined feature. Therefore, the general scaling relation we propose for polymer electrolyte systems is

$$\sigma_{\text{d, pair}}^\text{d} = \frac{A}{\tau_{\text{ff}}} + B \cdot \tau_{\text{ff}}$$

where both $A$ and $B$ are system-dependent coefficients.

The result of this decomposition is shown in Figure 1d. The $\sigma_{\text{d, pair}}^\text{d}$ remains zero until a lower value of $\varepsilon_P$. This agrees with the appearance of longer-lived ion pairs as seen in Figure 1c. More interestingly, in the presence of longer-lived ion pairs, the $\sigma_{\text{d, pair}}^\text{d}$ is negative, but the $\sigma_{\text{d, nonpairing}}^\text{d}$ is positive instead. To understand why, we made a toy model of a NaCl solution where all Na–Cl are paired up with holonomic constraints. Details for the system setup and MD simulations can be found in Section B of the Supporting Information.

Mean square charge displacements (MSCD, i.e., quantities inside the square bracket in eq 1 and eq 6) of this toy model are shown in Figure 4, for the total ionic conductivity $\sigma_{\text{GK}}$ self-conductivities ($\sigma_{\text{d, cation}}$ and $\sigma_{\text{d, anion}}$), and the sum of cation–cation and anion–anion distinct conductivities ($\sigma_{\text{d, cation}} + \sigma_{\text{d, anion}}$) as well as $\sigma_{\text{d, pair}}^\text{d}$ and $\sigma_{\text{d, nonpairing}}^\text{d}$. Since all Na–Cl ion pairs are permanent by construction, the total ionic conductivity as the sum of all these individual contributions mentioned above must be zero (i.e., the slope of the MSCD “total” is zero), as evinced in Figure 4. Moreover, self-conductivities ($\sigma_{\text{d, cation}}$ and $\sigma_{\text{d, anion}}$)
natural and its relationship with other static and dynamical properties in electrolyte systems.

[ASSOCIATED CONTENT]

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c02474. Descriptions of the setup and MD simulations of PEO-LiTFSI systems and NaCl solution with permanent ion pairs (PDF)

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Notes

The authors declare no competing financial interest.

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