Recent Advances in Molecular Simulations of Ionic Liquid-Ionic Liquid Mixtures

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Abstract

The research in the field of ionic liquids has exploded in the last two decades enabled by the availability of a large number of cations, anions, and pendant groups on the ions. In recent years, mixing of two ionic liquids constituted either by two anions or cations has been gaining momentum as this is a simple yet powerful approach to generating new ionic liquids with tailor-made properties. In this article, we review publications from 2017 and 2018 reporting molecular simulations of binary ionic liquids.

Introduction

Ionic liquids can be thought of as non-aqueous electrolytes composed entirely of low charge-density cations and anions. Low vapor pressure and considerable freedom to select the type of cations and anions to modulate the properties of the resulting ionic liquids have been major drivers for extensive research in this field. Recently, the approach of mixing two ionic liquids to manipulate thermophysical,[1–6] physicochemical,[7–11] phase equilibria,[9,12–24] and mechanical[25] properties of ionic liquids has gained considerable attention. For a thorough review of ionic liquid mixtures, the reader is referred to the articles by Rogers and co-workers[26] and Welton and co-worikers.[27] In this mini-review, we highlight papers published in this domain during the last few years with a particular focus on molecular simulation methodology to investigate such mixtures. A listing of the molecular simulations studies conducted prior to 2017 is also included in the bibliography.[28–40]

Bulk Properties and Structure of Binary Ionic Liquids

Kapoor and Shah carried out molecular dynamics (MD) simulations on two ionic liquid mixtures containing the common cation 1-*n*-butyl-3-methylimidazolium $[C_4mim]^+$. One mixture was formed by pairing chloride (Cl^-) and methylsulfate $[MeSO_4]^-$ while the second mixture contained Cl^- and bis(trifluoromethanesulfonyl)imide $[NTf_2]^-$.[41]The primary objective of the study was to assess the influence of mixing two anions with different hydrogen bonding ability on thermophysical and structural properties of the ionic liquid mixtures. The authors reported that the combination of a weakly hydrogen bonding anion such as $[NTf_2]^-$ with a strongly interacting anion Cl^- leads to the appearance of structural arrangements not found in the pure ionic liquids. For example, $[NTf_2]^-$ is displaced from the plane of the imdiazolium ring by Cl^-. Such dramatic rearrangements were not noted for the mixture composed of Cl^- and $[MeSO_4]^-$ (Figure 1). Kapoor and Shah conducted MD simulations of 11 ionic liquid mixtures: $[C_4mim]Cl$ combined with $[C_4mim]$ acetate $[CH_3COO]^-$, $[C_4mim]$ trifluoroacetate $[CF_3COO]^-$, and $[C_4mim]$ trifluoromethanesulfonate $[CF_3SO_3]^-$, $[C_4mim][CH_3COO]$ and $[C_4mim][CF_3COO]$, $[C_4mim][CH_3COO]$ and $[C_4mim][CF_3SO_3]$, 1-ethyl-3-methylimidazolium $[C_2mim]^+$ in combination with Cl^- and $[MeSO_4]^-$, $[C_2mim]Cl$ and $[C_2mim][NTf_2]$, 1-*n*-hexyl-3-methylimidazolium $[C_6mim]^+$ in mixed with Cl^- and $[MeSO_4]^-$, $[C_6mim]Cl$ and $[C_6mim][NTf_2]$, 1-*n*-octyl-3-methylimidazolium $[C_8mim]^+$ with the anions Cl^- and $[MeSO_4]^-$, $[C_8mim]Cl$ and $[C_8mim][NTf_2]$. The primary conclusion of the study was that these ionic liquid mixtures exhibited nearly ideal mixing behavior (linear combining rule) for properties such as the molar volume, self-diffusion coefficient, and ionic conductivity with the exception of a few ionic liquid mixtures.[42] In a study involving the ionic liquid mixtures $[C_4mim]Cl$ and $[C_4mim][CF_3SO_3]$ for $[C_4mim]Cl$ mole fractions of 0.000, 0.192, 0.303, and 0.402,[43] Kirchner and co-workers noted that the height of the first peak in the radial distribution functions (RDFs) between the most acidic hydrogen H2 and either O or Cl decrease as the concentration of Cl^- increases. It was also observed that the number of $[CF_3SO_3]^-$ anions decreased more rapidly than the corresponding increase in the Cl^- coordination number in line with the other studies reporting that the stronger hydrogen bonding ability anion preferentially interacts with the H2 position displacing the weaker hydrogen bonding anion. The authors also analyzed the dynamics in these mixtures using the reactive flux method, which enabled them to extract the lifetime data data for the dissociation and association of the cations and anions. The lifetimes were found to increase as Cl^- is added to $[C_4mim][CF_3SO_3]$ except at the lowest Cl^- concentration. The observation is puzzling as the experimentally determined viscosity of these mixtures increase over the entire composition range.

Lepre et al. carried out experimental and molecular dynamics investigations of the ionic liquid mixture $[C_4mim][CH_3COO]$ and $[C_4mim]$ tricyanomethanide $[C(CN)_3]$. Similar to the studies reported above, the authors concluded, from spatial distribution function analysis, that the strong hydrogen capability anion ($[CH_3COO]^-$) preferentially occupied the position in the plane of the imidazolium ring, while $[C(CN)_3]^-$ tended to be more diffuse with positions located below and above the ring.[44]

Voroshylova, Pereira, Cordeiro, and co-workers applied MD simulations at 303 K to elucidate structures of binary ionic liquid mixtures comprised of the common cation $[C_4mim]^+$.[45*] Three anion pairs were considered: $[NTf_2]^-$ and hexafluorophosphate $[PF_6]^-$, $[NTf_2]^-$ and tris(perfluoroethyl)trifluorphosphate $[eFAP]^-$, $[NTf_2]^-$ and $[eFAP]^-$. The findings indicated, as before, that the anion with lower charge density is outcompeted from associating with the acidic hydrogen sites on the cation. The excess molar volumes for the ionic liquid mixture $[C_4mim][PF_6]$ + $[C_4mim][NTf_2]$ were found to be positive but small (less than 1 cc/mol). On the other hand, the other two mixtures displayed rather large and negative deviation (maximum deviation -4 cc/mol for $[C_4mim][PF_6]$ + $[C_4mim][eFAP]$ and -7 cc/mol for $[C_4mim][eFAP]$ + $[C_4mim][NTf_2]$) from ideality. The self-diffusion coefficients in these mixtures point to an interesting behavior. In the mixture $C_4mim][PF_6]$ + $[C_4mim][eFAP]$, the diffusion of smaller $[PF_6]^-$ is lower than that of the bulkier $[eFAP]^-$ when $[PF_6]^-$ is the

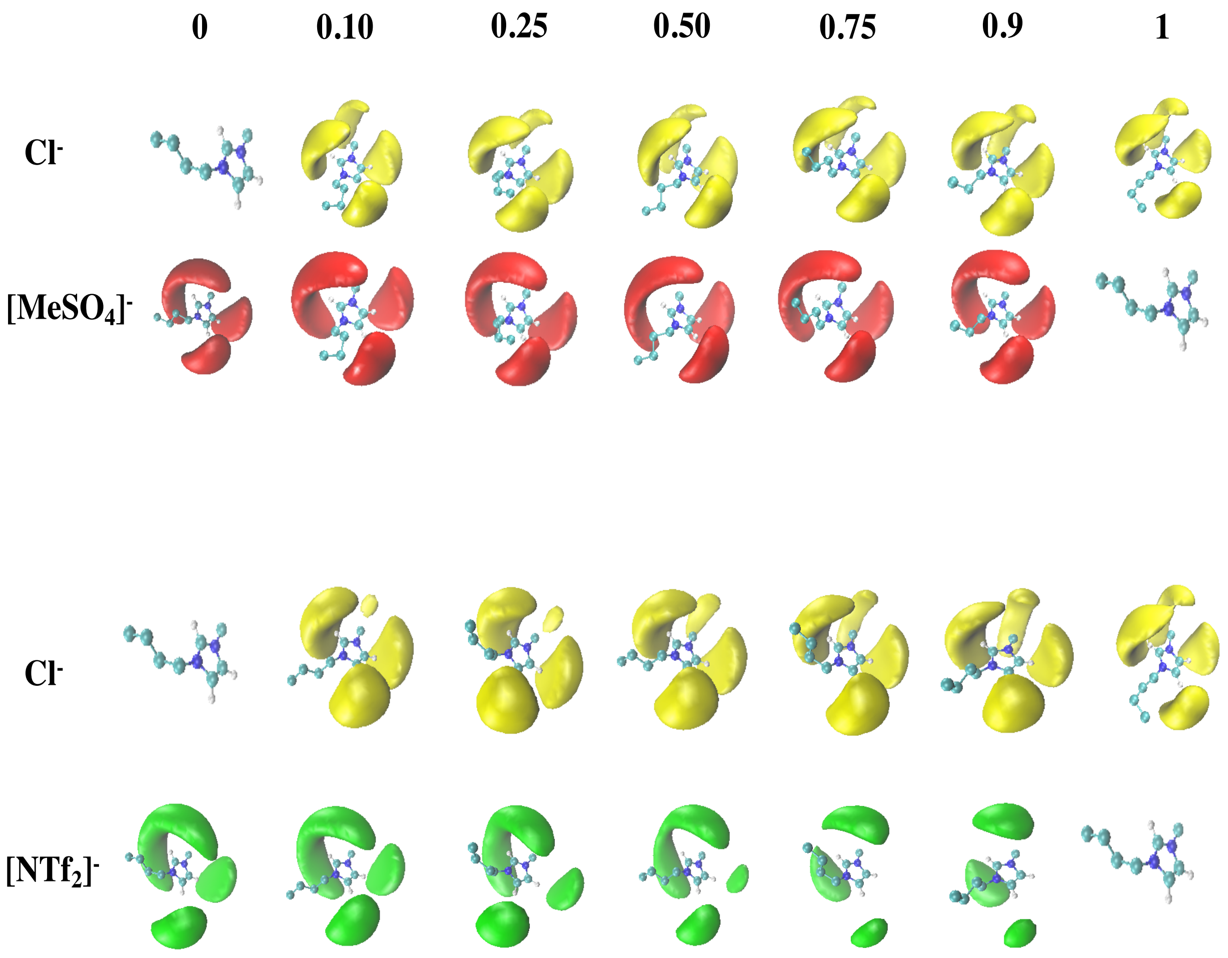

Figure 1: Spatial distribution functions (SDFs) of anions (Cl^-, $[MeSO_4]^-$, and $[NTf_2]^-$ around the cation $[C_4mim]^+$. Isosurface density is 2.5 times the bulk density. (Legends - Cl : $MeSO_4/NTf_2$ :: 10 : 90). Color coding: Cl^- in yellow and $[MeSO_4]^-$ in red and $[NTf_2]^-$ in green. Atoms: C in cyan, N in blue, and H in white. It is clear that hydrogens attached to the imidazolium rings are the most favorable binding sites. Reprinted with permission from Kapoor, U. and Shah, J. K. "Preferential Ionic Interactions and Microscopic Structural Changes Drive Nonideality in Binary Ionic Liquid Mixtures as Revealed from Molecular Simulations", Industrial and Engineering Chemistry Research, 55, 13132-13146 (2016). Copyright 2016 American Chemical Society.

lean component. The trend reverses at high $[PF_6]^-$ concentrations. Similar results were reported for the $[C_4mim][eFAP]$ + $[C_4mim][NTf_2]$ mixtures. The authors attributed the findings to the formation of nano-segregated domains by $[eFAP]^-$.

Docampo-Alvarez et al.[46] studied mixture of alkylammonium protic ionic liquids and alkylimidazolium aprotic ionic liquid by means of MD simulations at 298 K and 1 atm over the entire composition range. The authors investigated mixtures of $[C_2mim][BF_4]$ with ethyl-, propyl-, and butylammonium nitrate ([EAN], [PAN[, [BAN], respectively) in addition to the mixture of $[C_4mim][BF_4]$ and [EAN]. Experiments and MD results indicated that the excess molar volumes were close to those predicted using ideal mixing. For the excess enthalpy, the ionic liquid mixtures $[C_2mim][BF_4]$ + [EAN] and $[C_4mim][BF_4]$ + [EAN] displayed small negative deviation from ideality with minimum occurring in the vicinity of equimolar composition. Contrarily, the other two mixtures showed larger deviation from ideality with minimum located near the pure protic ionic liquid composition, indicating substantial changes in the structure of [PAN] and [BAN] upon the addition of $[C_2mim][BF_4]$. Through structural analyses, the authors concluded that the different behavior for protic ionic liquids with longer alkyl chains is due to $[BF_4]^-$ occupying the positions near the tail of the protic alkyl chains disrupting ionic coordination in the pure ionic liquids and inducing structural changes.

Herrera et al.[47] performed MD simulations on ionic liquid mixtures formed by mixing $[C_2mim]$ glycine [GLY] + $[C_2mim]$ alanine [ALA] , $[C_2mim]$[GLY] + $[C_2mim]$ serine [SER], $[C_2mim]$[GLY] + $[C_2mim]$ phenylalanine [PALA]. The authors also considered more complex mixtures: tetraanionic $[C_2mim][GLY]_{0.25}[ALA]_{0.25}[SER]_{0.25}[PALA]_{0.25}$ and tricationic $[C_2mim]_{0.33}$ cholinium $[CH]_{0.33}$ methylpiperazinium $[MP]_{0.33}$[GLY], $[C_2mim]_{0.33}[CH]_{0.33}$ $[MP]_{0.33}$[ALA], $C_2mim]_{0.33}[CH]_{0.33}$ $[MP]_{0.33}$[SER], and $C_2mim]_{0.33}[CH]_{0.33}$ $[MP]_{0.33}$[PALA]. The excess molar volumes computed for the binary mixtures displayed small deviations from ideality. The structural features of all the ionic liquid mixtures were analyzed in terms of RDFs between the center-of-mass of the cation and anion, which revealed that there is no preferential coordination of either the anions around the cations for mixtures with more than one anion or those containing multiple cations. The authors concluded that the near ideal behavior for these mixtures arises due to the preservation of the primary interaction involving the anion carboxylate group and the hydrogen bonding sites in the cation.

Thus far, molecular simulations of binary ionic liquid mixtures have been conducted keeping the charge of the constituting ions fixed, either ± 1 or some fraction of the unity, typically ± 0.8. Recently, Licence and co-workers[48,49] have shown, on the basis of that the electronic environment of the ions in binary ionic liquid mixtures can be tuned by varying the composition of such mixtures. To capture this effect, Balasubramanian and co-workers generated snapshots of binary ionic liquid mixtures consisting of [C_4mim]Cl and [C_4mim] tetrafluoroborate [BF_4], from which the authors derived atomic site charges using DFT calculations. The authors concluded that the average charge of the cation in this mixture follows a linear trend with the anion composition. It was also reported in this study that the average charge of the cation is inversely related to the fraction of the more basis anions present in the first coordination shell.[50]

Interfacial Structure of Binary Ionic Liquid Mixtures

Very few studies have appeared in literature that probe the interfacial behavior of ionic liquid mixtures using MD simulation.[51–53] Zhang et al.[54*] performed angle-resolved X-ray photoemission spectroscopy measurements and molecular simulations to study the interface of the binary ionic liquid mixture [C_2mim][CH_3COO] and [C_2mim][NTf_2] at a volumetric ratio of 9:1. Remarkable agreement between the experiments and molecular simulation results was obtained in that it was revealed that there is a significant enhancement of $[NTf_2]^-$ at the interface relative to its overall composition. On the contrary, there was a depletion in concentration of the anion $[CH_3COO]^-$. As expected the alkyl groups from the ionic liquid $[C_2mim][CH_3COO]$ were found to point toward the vacuum. Similarly, the -CF_3 groups belonging to $[NTf_2]^-$ were observed to occupy the outer layer while the nitrogen atom was located deeper in the liquid. Bruce et al.,[53] on the other hand, carried out a detailed investigation of the bulk and ionic liquid-vacuum interface of ionic liquid mixtures formed from different cations: $[C_2mim]^+$ and 1-*n*-dodecyl-3-methylimidazolium $[C_{12}mim]^+$ combined with $[NTf_2]^-$ as the anion over the whole composition range using a variety of experimental (small-angle X-ray, neutron scattering, reactive atom scattering-laser-induced fluorescence) and MD simulations. Physical properties such as viscosity, conductivity, and density measurements provided the first clue of the non-ideal mixing in these mixtures hinting at a strong coupling between the structure and dynamics with the composition. Results from the MD simulations suggested that $[C_{12}mim]^+$ exists as small aggregates due to the nanosegregation of the long non-plolar chain from the polar domain dispersed in the $[C_2mim][NTf_2]$. With the rise in the $[C_{12}mim]^+$ concentration, the size of the aggregates increases until the alkyl chain of the larger cation percolates through the system resulting in the formation of a bicontinous morphology. The ionic liquid-vacuum interface was found to be enhanced by the more non-polar $[C_{12}mim]^+$ cation even when its concentration is low similar to the observation reported in the Zhang et al. work.[54]

Binary Ionic Liquid Mixtures with a Solute

In addition to various binary ionic liquid mixtures, ternary mixtures composed of two ionic liquids and another species have also recently appeared in the literature. One example is that of a recent MD study employing free energy calculations[55] in which Kapoor and Shah investigated the influence of the non-native structures in the ionic liquid mixtures of $[C_4mim]Cl$ + $[C_4mim][NTf_2]$ and native structures for $[C_4mim]Cl$ + $[C_4mim][MeSO_4]$ on the Henry's constant of CO_2 and mechanism of CO_2 absorption in the ionic liquid mixtures. It was revealed that the CO_2 Henry's constants could be determined using the ideal mixing behavior; however, the mechanism of CO_2 solubility is different from that in the corresponding pure ionic liquids ([C_4mim]Cl and [C_4mim][NTf_2]); the increased interaction of [NTf_2]$^-$ with CO_2, due to the rearrangement of [NTf_2]$^-$, was the primary reason for the solubility of CO_2 in the [C_4mim]Cl + [C_4mim][NTf_2] ionic liquid mixtures. On the other hand, the absence of non-native structures in [C_4mim]Cl + [C_4mim][$MeSO_4$] ionic liquid mixtures resulted in no such preferential interactions of CO_2 with the anion (Figures 2 and 3).

Padua, Gomes, and co-workers carried out CO_2 absorption measurements in the ionic liquid mixture [C_4mim][CH_3COO] and [C_4mim][$C(CN)_3$] along with the determination of Henry's

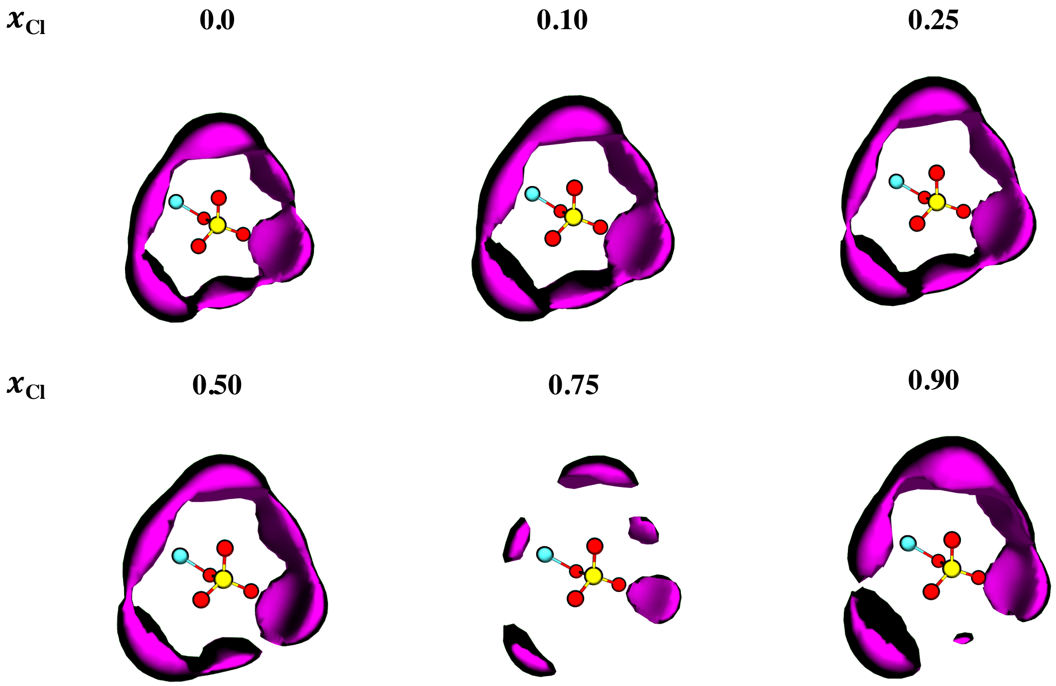

Figure 2: Spatial distribution functions of CO_2 around the [$MeSO_4$]$^-$ anion in [C_4mim]Cl + [C_4mim][$MeSO_4$] mixture system. Isosurface density is 1.7 times the bulk density. The top row, x_{Cl}, represents the Cl^- concentration. Color coding: CO_2 in purple. Atoms: S yellow, O red and C cyan. Reprinted with permission from Kapoor, U. and Shah, J. K. "Molecular Origins of Apparent Ideal CO_2 Solubilities in Binary Ionic Liquid Mixtures", Journal of Physical Chemistry B, 122, 9763-9774 (2018). Copyright 2016 American Chemical Society.

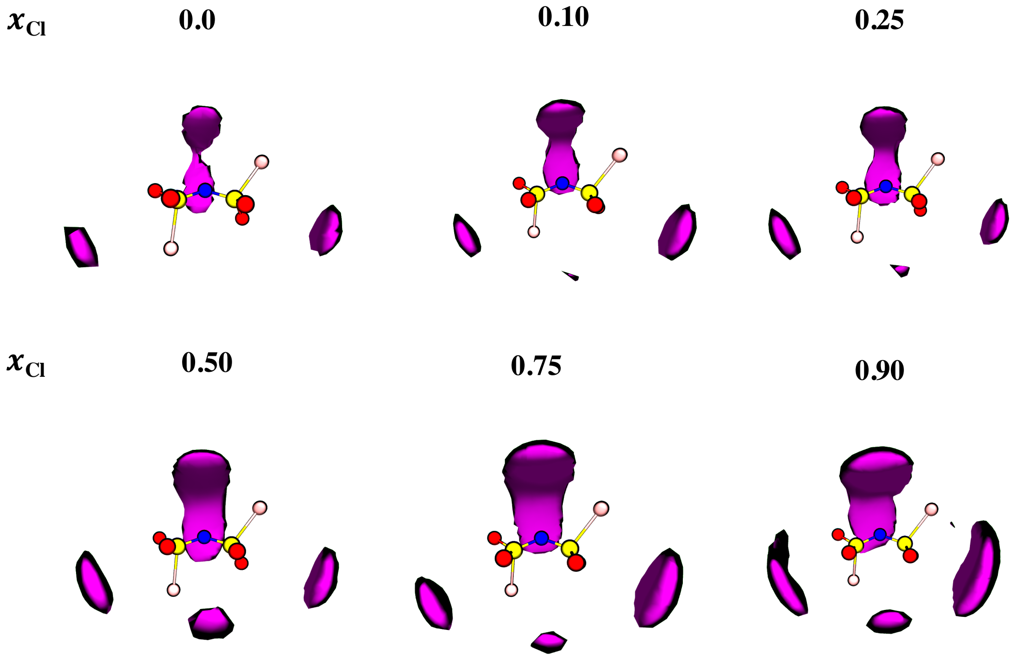

Figure 3: Spatial distribution functions of CO_2 molecules around the $[NTf_2]^-$ anion in $[C_4mim]Cl$ + $[C_4mim]NTf_2]$ mixture system. Isosurface density is 2.0 times the bulk density. The top row, x_{Cl}, represents the Cl^- concentration. Color coding: CO_2 in purple. Atoms: S yellow, O red, N blue and CF3 orange.Reprinted with permission from Kapoor, U. and Shah, J. K. "Molecular Origins of Apparent Ideal CO_2 Solubilities in Binary Ionic Liquid Mixtures", Journal of Physical Chemistry B, 122, 9763-9774 (2018). Copyright 2016 American Chemical Society.

constants of CO_2 using molecular simulations.[56] The authors also reported structural features as deduced from RDFs and spatial distribution functions. It was observed that the underlying ionic liquid structure resembles those observed for pure ionic liquids. It was also found that CO_2 interacts preferentially with the oxygen atoms in $[CH_3COO]^-$ and nitrogen atoms in $[C(CN)_3]^-$; the cation is increasingly involved in binding with CO_2 as the concentration of $[C(CN)_3]^-$ increases. The computed Henry's constants revealed that the physical absorption of CO_2 increases with increase in the concentrations of the $[C(CN)_3]^-$ anion, the observation was used by the authors to explain the increase in self-diffusion coefficients upon CO_2 absorption. Another example is that of Li^+ solvation in the 1:9 volumetric mixture of *n*-methyl-*n*-propylpyrrolidinium [PYR13][NTf_2] and [C_2mim] dicyanamide [DCA] studied with Raman spectroscopy and MD simulations by Maginn, Gurkan, and co-workers.[57] Both experiment and simulations suggest that the first solvation shell of Li^+ is primarily occupied by the smaller and more abundant $[DCA]^-$, which binds Li^+ predominately through either of the terminal nitrogen atoms. Whereas, $[NTf_2]^-$ coordinates Li^+ ion in monodentate or bindendate mode and is capable of bridging multiple Li^+ ions. The findings underscore that the solvation structure of Li^+ can be manipulated by using anions differing in their coordinating ability.

Maginn, Shiflett, and co-workers examined the ability of water to induce phase separation in equimolar mixtures of ionic liquids [C_2mim][NTf_2] + [C_2mim]Cl and [C_2mim][CH_3COO] + [C_2mim]Cl at varying concentrations of water.[58] The results from experiments and MD simulations were consistent that the ionic liquid mixture [C_2mim][CH_3COO] + [C_2mim]Cl comprised of two hydrophilic anions remained as a homogeneous phase at all water concentrations. On the other hand, phase separation could be induced in the mixture [C_2mim][NTf_2] + [C_2mim]Cl containing anions with widely different hydrophilicity with [C_2mim]Cl and water forming the water-rich phase while water-lean phase was comprised of mostly [C_2mim][NTf_2]. Additionally, experimentally observed color change from pale green to amber in the [C_2mim][CH_3COO]

+ $[C_2mim]Cl$ mixture at a certain water concentration was correlated to a dramatic change in the spatial distribution of Cl^- from predominantly around to less acidic hydrogen atoms to the most acidic hydrogen atom as the water concentration increases. Macchieraldo et al. performed *ab initio* MD of the binary ionic liquid mixture constituted by $[C_4mim]Cl$ and $[C_4mim][BF_4]$ in the molar ratio 10:22 and the same mixture containing 36 wt% water.[59] The choice of AIMD approach over the classical simulation methodology was motivated in order to account for the charge transfer and polarization. The RDF analysis indicated that the mole fraction of the anions surrounding a cation reflects the corresponding bulk molar ratio. The presence of water, however, tilts this balance in favor of the $[BF_4]^-$ anion such that its mole fraction is enhanced in the first coordination sphere of a cation. Thus, the addition of water leads to "solubilization" of the Cl^- anion, while the ionic liquid network is preserved through the coordination of the cation with $[BF_4]^-$

Outlook

A number of research articles have appeared in the literature over the last couple of years investigating binary ionic liquid mixtures by means of molecular simulations. Almost exclusively, these studies have been carried out using atomistic molecular dynamics simulation methods with the primary objective of elucidating the structure and dynamics of ionic liquid-ionic liquid mixtures and computing thermodynamic properties such as excess molar volumes, which can be compared with experimental observations. A trend is emerging with respect to the structure of imidazolium-based binary ionic liquid mixtures formed by combining two anions that the stronger hydrogen bonding anion preferentially participates in the hydrogen bonding with the most acidic hydrogen in the imidazolium ring displacing the weakly coordinating anion to the positions above and below the plane of the imidazolium ring. On the other hand, when the hydrogen bonding ability of the anions are similar, the distribution of anions around a cation resembles those observed for the pure ionic liquids. Only one study has probed the impact of such (non)ideality in the local structure on the phase equilbria properties of solutes. We urge the research community to contribute to this unexplored field in the binary ionic liquid mixture domain. Monte Carlo simulation techniques implemented in the open-source software packages such as Cassandra,[60] and RASPA[61] are ideally suited to perform such calculations. We also note that the imidazolium-based ionic liquids continue to dominate the binary ionic liquid mixture simulations. It is likely that highly nonideal systems will be encountered when properties of the ions being blended are vastly different such as hydrogen bonding ability, van der Waals interactions, π-π interactions of lack thereof. Thus, the mixtures consisting of cations from different classes of ionic liquids need to be scrutinized. There is also a considerable room to delve into reciprocal ionic liquid mixtures obtained by two ionic liquids not sharing any either the cation or the anion.

We believe that the force field development for binary ionic liquid mixtures will continue to play a significant role as the coordination shells of ions contain multiple ions with differing degrees of charge transfer ability. With the continuous rise in the computational power and accessibility of software packages supporting implementation of polarizable models, we expect researchers to embrace this crucial aspect in accurately modeling ionic liquid mixtures. Our mini-review of the status of the molecular simulations of binary ionic liquid mixtures clearly suggests to us that there are a number of opportunities for the simulation community to contribute to exploiting this simple yet very powerful approach to expand the range of ionic liquids and further tailor properties of ionic liquids for a given application and we hope and expect that the simulation community, in collaboration with experimentalists, will exploit these opportunities and further the ionic liquid research in the coming years.

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bonding ability of the anions forming an ionic liquid mixture plays a crucial role in generating molecular structures in ionic liquid mixtures that may or may not differ from those encountered in pure ionic liquids. The authors draw this conclusion by considering the cation $[C_4mim]^+$ with two anions Cl^-– and $[MeSO_4]^-$– small difference in the hydrogen bonding ability vs. Cl^-– and $[NTf_2]^-$– two anions differing greatly in terms of their propensity to bind to the acidic hydrogen in the cation. Molecular dynamics simulations suggest that the former leads to the formation of native structures while the latter combination produces non–native structures.

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