

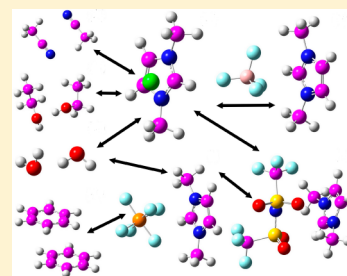
Ionic and Molecular Liquids: Working Together for Robust Engineering

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ABSTRACT: Because of their outstanding versatility, room-temperature ionic liquids (RTILs) are utilized in an ever increasing number of novel and fascinating applications, making them the Holy Grail of modern materials science. In this Perspective, we address the fundamental research and prospective applications of RTILs in combination with molecular liquids, concentrating on three significant areas: (1) the use of molecular liquids to decrease the viscosity of RTILs; (2) the role of RTIL micelle formation in water and organic solvents; and (3) the ability of RTILs to adsorb pollutant gases. Current achievements are examined, and future directions for the potential uses of RTILs are outlined.



Although room-temperature ionic liquids (RTILs) were first reported as early as 1914, they have only achieved recognition for their outstanding utility during the past decade. This large class of compounds includes approximately one million¹ currently synthesized substances and potential candidates. Today, RTILs are defined as semiorganic salts that are liquid at and below 300 K under atmospheric pressure. The salts combine an organic cation with an organic or inorganic anion. Various RTILs are able to exist in liquid form within a wide range of temperatures, with the most remarkable one existing as a liquid at 177 K.² Besides the fact that these compounds are able to remain in a liquid form at extreme temperatures, most of them exhibit relatively high ionic conductivity, excellent thermal and electrochemical stability, large heat capacity, cohesive energy density, nonflammability, and often negligible vapor pressure. As a result, most RTILs present low hazard levels and are benign for humans.^{3–8} However, probably the most remarkable feature of ionic liquids is their tunability. For instance, when one considers conventional solvents such as water, alcohols, nitriles, ethers, dialkylsulphoxides, and hydrocarbons, there is a limited opportunity to alter their properties other than by adding aliphatic groups and introducing halogen substituents. On the contrary, RTILs are an amazing scaffold for combinatorial design, allowing for the formation of hundreds of cationic and anionic species. Therefore, nearly every property from the dielectric constant of the medium to the aggregation state at a given condition can be tuned, and a particular RTIL can, in principle, be designed for each particular application.

To date, many excellent reviews have been published, covering topics such as manifold properties and applications of RTILs, including energy storage, nanotechnology/nanomaterials, organic synthesis, biocatalysis, biosensing, extraction, and so on.^{9–23} In this Perspective, we do not intend to provide a comprehensive review covering all aspects of RTILs, but will focus exclusively on the ever-growing applications, in which the

robust combination of the properties of both ionic and molecular liquids is necessary and/or desirable.

Electrolytes. In the case of energy storage applications, which employ RTILs owing to their nontoxicity, nonflammability, and wide electrochemical potential windows, the ionic conductivity of RTILs is an issue. Electrolyte conductivity is an integral measure of the available charge carriers (ions) and their mobility (diffusion). An electrochemist may intuitively expect RTILs to possess extremely high conductivities, since they comprise exclusively charged particles. Most RTILs exhibit lower conductivity than traditional concentrated aqueous electrolytes, in which inorganic ions are combined with an organic solvent or water molecules. This feature of RTILs can be attributed to the significant degree of ion pairing (more generally, ion aggregation) and reduced mobility due to strong electrostatic forces, large molecular mass, and the sometimes bulky shape of the compounds. The relationship of the RTILs' conductivity with temperature typically demonstrates a linear Arrhenius behavior near 298 K. When the temperature approaches the glass transition temperature for the RTIL, a significant deviation from the linear behavior is reached.^{24,25} This temperature range is best described by the empirical Vogel–Tamman–Fulcher equation.

The classic Walden rule predicts that the product of viscosity and molar conductivity at any temperature should remain constant. Therefore, theoretically, we can substantially increase the conductivity of RTILs by simply decreasing their viscosity. While RTILs are more viscous^{26,27} than most of the commonly used molecular solvents such as water, acetonitrile (ACN), alcohols, dichloromethane, benzene, and toluene, adding these viscous solvents to RTILs results in a drastic overall viscosity decrease.^{28–40} For instance, the addition of as little as 20 mol %

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of a cosolvent reduces the viscosity of $[C_4C_1MIM][BF_4]$ by 50%. However, it has been found that the presence of the chloride anion in RTILs systematically increases the viscosity of RTILs.^{33,41} This likely occurs due to the large electron density of this particular anion, as compared to other anions of RTILs. Lopes and co-workers⁴² reported the viscosity of pure 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, μ ($[BMIM][TFSI]$) to be 50.4 cP at 298.15 K, while even a 16 mol % admixture of methanol decreased the viscosity down to 35.8 cP (Figure 1). Large molar fractions of methanol allowed

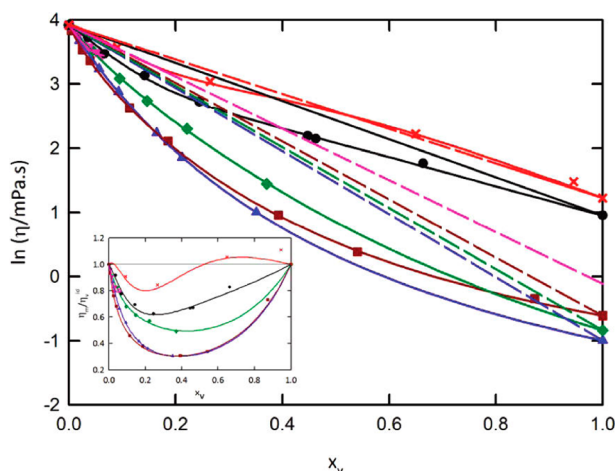


Figure 1. Logarithm of the viscosity, η_{mol} , and real-to-ideal ratio (inset) of mixtures of $[C_4C_1IM][TFSI]$ with a molecular component as a function of composition, expressed in molecular component molar fraction at 298 K: ACN (blue triangles); methanol (red squares); dichloromethane (green diamonds); water (purple triangles); 1-butanol (black circles); *t*-butanol (red X's). Reproduced with permission from ref 42. Copyright 2011 American Chemical Society.

for viscosity decrease down to values as small as 1 cP (i.e., 50 times). The conductivity maximum of the $[C_4C_1MIM][TFSI]$ /methanol system (2.58 S m^{-1}) is reached at $x_m(\text{MeOH}) = 88\%$, representing a very significant dilution. It should, however, be emphasized that since the molecular masses of MeOH and $[C_4C_1MIM][TFSI]$ differ from each other significantly, the corresponding mass fraction of the ions present is not so small. The position of the conductivity maximum varies substantially for other alcohols. For instance, the maximum of 0.677 S m^{-1} for *n*-butanol is reached at $x(n\text{-BuOH}) = 52\%$, whereas *t*-butanol reaches its maximum of 0.520 S m^{-1} at $x(t\text{-BuOH}) = 60\%$.^{28,43} On the basis of atomistic-precision computer simulations, Chaban and co-workers found that a conductivity increase in RTILs is correlated with the intrinsic mobility of the molecular cosolvent and depends poorly on ion mobility in neat RTILs.^{28,43} Thus, there exists the promising possibility of using very bulky cations, such as 1-decyl-3-methylimidazolium, $[C_{10}C_1IM]$, as efficient charge carriers in combination with a low-viscous aprotic cosolvent, such as ACN or acetone. As an illustration, the conductivity of pure $[C_{10}C_1IM][BF_4]$ is 0.029 S m^{-1} at 283 K, but increases to 1.8 S m^{-1} at $x_m([C_{10}C_1IM][BF_4]) = 10\%$ in ACN. This observation motivates one to probe solvents with high self-diffusion: foremost, nontoxic volatile liquids and electrochemically stable gases. A variety of existing RTILs possessing unique electronic structures provide numerous possible combinations with solvents that can exhibit desirable relationships between cohesive energy, viscosity, conductivity, and phase transition points. The toxicity of the

mixtures of RTILs in nonaqueous solvents has been recently assessed based on their volatility. It was found that the inherent volatility of ACN can be, to certain extent, decreased due to strongly favorable interactions with the cations and anions of the imidazolium-based RTILs.^{29,44} From our standpoint, more comprehensive studies in this area are needed and are of pressing concern and importance.

A conductivity increase in RTILs is correlated with the intrinsic mobility of the molecular cosolvent.

Most experimental and computer simulation studies to date have been devoted to RTIL/water mixtures, and their scope is expanding continually. The properties of these mixtures studied range from structure and dynamics to phase separation, interface structure, and molecular aggregation. Because of their large dipole moment, water molecules are strongly attracted to RTIL ions, but these interactions can be adjusted by altering the concentration of the RTIL. The first study indicating this phenomenon was published in 2003, when Hanke and Lynden-Bell^{45,46} reported a molecular dynamics (MD) investigation of the local structure and dynamics of $[C_1C_1IM][Cl]$ and $[C_1C_1IM][PF_6]$ in mixtures with water. Feng and Voth uncovered the role of alkyl chain length and anion nature on the transport properties in the RTIL/water mixtures.⁴⁷ Mendez-Morales and co-workers analyzed radial distribution functions, coordination numbers, hydrogen bonding, and mean-squared displacements in several aqueous solutions of imidazolium-based RTILs.^{48–50} Raju et al. studied the collective structure of an aqueous solution of $[C_4C_1IM][PF_6]$. They found that in dilute aqueous solution, anions diffused faster than cations, in contrast to the situation in pure RTIL, where cations diffused faster.⁵¹ Margulis et al. investigated the impact of small water admixtures on the very similar imidazolium-based RTIL, $[C_6C_1IM][PF_6]$, and found water to be preferentially coordinated by $[PF_6]$ particles;⁵² given that many reports characterized $[PF_6]$ as a hydrophobic particle, this observation is noteworthy. As a result of electrostatic water-driven screening, the translational and rotational dynamics of RTILs are boosted. Claumont and Wipff studied the solvation of the ions uranyl and europium from nuclear waste in dry and humid hexafluorophosphate containing solutions (1:1 RTIL/water).^{53,54} In dry solution, both uranyl and europium coordinate the anion, but in humid solution they are coordinated by water exclusively. Furthermore, the solubility in humid RTILs was found to be significantly larger. Dai et al. demonstrated that cation extraction by 18-crown-6 to RTILs was more efficient than traditional methods of extraction. The solvation of 18-crown-6 and its complexes with K^+ , Cs^+ , and Sr^+ in $[C_4C_1IM][PF_6]$ and its humid modification suggest a principal difference between these two systems. Similarly, while anions coordinate with 18-crown-6 in dry RTIL, they are mainly coordinated with water in humid RTIL.⁵⁵

An unusual phenomenon observed in RTIL/water concentrated systems is the presence of solitary water, standing as small water clusters surrounded predominantly by ions. NMR, IR, electrochemical, thermodynamic, and volumetric measurements have been recently reported for solitary water. NMR has been used for determining liquid structures based on the nuclear Overhauser enhancement and chemical shift, for

deriving diffusion coefficients using pulsed-gradient spin-echo pulse sequences, for unveiling rotational dynamics by spin-relaxation time measurements, and for determining the kinetics of chemical reactions involving water. Cammarata et al. recorded the IR spectrum of wet RTILs exposed to atmospheric conditions, considering the high hygroscopicity of the selected RTILs.⁵⁶ At very low water fractions, a molecule of water is bound to two anions via weak hydrogen bonds. This conclusion was arrived at based on the relationship between the frequencies of the two stretching bands. An interesting illustration of water reactivity differences between RTILs was contributed by Hardacre et al. In particular, PCl_3 was found to be stable in wet RTILs,⁵⁷ whereas even negligible amounts of water in molecular solvents resulted in an immediate hydrolysis of the compound.

Welton et al. suggested that the choice of the anion of the RTIL greatly affected the states of the solitary water and also predetermined its solubility. It was found that the extent of hydrogen bonding increased for the following anions as such: $[\text{PF}_6]^- < [\text{BF}_4]^- < [(\text{CF}_3\text{SO}_2)_2]^- < [\text{CF}_3\text{SO}_3]^- < [\text{NO}_3]^-$.⁵⁶ Here, anion–water binding is promoted by the abundant electron density on the oxygens, while the fluorine-containing derivatives are less efficient hydrophiles and are therefore not able to interact to water. We hypothesize that for large hydrophobic anions, such as PF_6^- , practically nonexistent water–anion interactions are unable to overwhelm water–water interactions at any reasonable temperature; therefore, an aprotic solvent is required to efficiently dissolve these RTILs. A comprehensive ab initio or density functional theory study of the correlation between electron density on the most electronegative sites of the cation/anion and solvation behavior in binary systems is still lacking. Yasaka and co-workers reported a rotational dynamics comparison study of heavy water in a hydrophilic RTIL, $[\text{C}_4\text{C}_1\text{IM}][\text{Cl}]$, versus a hydrophobic RTIL, $[\text{C}_4\text{C}_1\text{IM}][\text{PF}_6]$, by examining NMR relaxation times of both solutions.⁵⁸ The Debye-type relaxation mechanism was assumed for this study. Unlike the case with $[\text{PF}_6]^-$, the chloride anion was found to greatly retard the rotation of water molecules. Viscosity differences between these RTILs are not sufficient to explain differences in rotational dynamics. The authors claim that water/chloride hydrogen bonding is of key importance in strongly solvating the RTILs.

There are several RTILs with hydrophobic cations and anions that possess very limited solubility, among them are the widely known $[\text{C}_4\text{C}_1\text{IM}][\text{PF}_6]$ and tris(tetradecyl)-hexaphosphonium chloride. They tend to create biphasic systems,⁵⁹ which are of primary interest for creating highly efficient reaction and purification media. The phase behavior of biphasic systems is very sensitive to temperature and to the particular structure of the ions. As such, the reactant and the catalyst can be separated into distinct RTIL and water phases by adjusting the temperature after the reaction is finished. Depending on the density variations and interfacial tension, emulsions can also be prepared. In the following section, we address lyophobic and lyophilic phases of RTILs in water and organic solvents in more detail.

Micellization. Many RTILs are amphiphilic,^{60–63} where pronounced hydrophilic moieties neighbor lipophilic fragments. De facto, amphiphilicity predetermines their surface activity and self-organization potential.^{64–67} This is true for the following families of RTILs: dialkylimidazoliums, alkylpyridiniums, dialkylpyridiniums, alkylphosphoniums, and alkylammoniums. The surface activity and self-organization of RTILs can be

exploited in numerous applications, such as liquid extraction,⁶⁸ liquid chromatography, micellar capillary electrophoresis, in sol–gel synthesis,⁶⁹ nanoscale synthesis,⁷⁰ and drug delivery.^{71,72}

Ionic aggregates can be identified most directly by atomistic computer simulations, but other methods for their identification include surface tension, heat capacity, NMR, conductivity, and light scattering experiments. Simultaneous use of these techniques within a single system allows for a more comprehensive characterization of the process by determining the critical aggregation concentration (CAC), aggregation number, and concentration of free ions. However, determining the molecular structure of the aggregates is often not possible with currently available experimental methods. Therefore, MD and Monte Carlo computer simulation tools are an invaluable source of information (Figure 2),⁷³ where experimental results

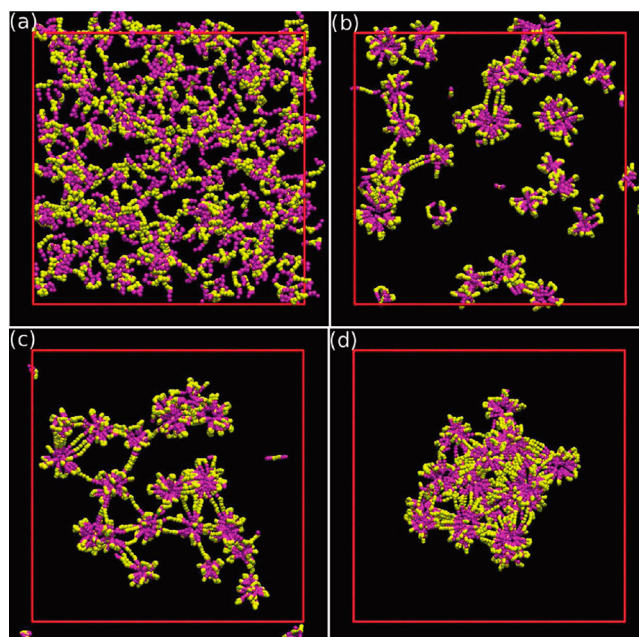


Figure 2. Snapshots of a dilute bulk system (400 ion pairs of 1,5-bis(3-decylimidazolium-1-yl)pentane bromide and 240 000 water molecules) at various stages of aggregation: after (a) 1 ns; (b) 16 ns; (c) 110 ns, and (d) 1 000 ns. Polar and nonpolar groups are shown in yellow and magenta, respectively. Water and anions are not displayed for clarity. Courtesy of Michael Klein. Copyright 2013 American Chemical Society.

are lacking. Aggregate formation of hydrophobic cations was reported by Jiang and co-workers for various water fractions in mixtures with $[\text{C}_8\text{C}_1\text{IM}][\text{NO}_3]$.⁷⁴ They found that when the water content increased, the head-anion polar network was broken, whereas the tail–tail spatial correlations were enhanced.

Recent MD simulations of $[\text{C}_n\text{C}_1\text{IM}]$ -based compounds suggested that they formed domains of two types. Due to electrostatic interactions, positively charged imidazole rings and anions generate three-dimensional polar networks, while lyophobic moieties are aggregated, with van der Waals interactions prevailing. The processes of self-organization of RTILs in aqueous solutions have attracted significant attention in recent years.^{75–80} Upon the addition of water, long-tailed RTILs form liquid-crystalline ionic gels within a particular range of concentrations. The MD simulations of $[\text{C}_8\text{C}_1\text{IM}]$ -

[NO₃]/water mixtures revealed that when the water concentration increased, the polar network in RTILs was destroyed, and the impact of the RTIL–water interactions was drastically increased.^{81–83} On the other hand, in concentrated solutions, micelles are formed. Attention has also been brought to classical surfactants in RTILs,^{84–86} RTILs/classical-surfactant mixed solutions in different solvents, and RTIL-containing microemulsions and dispersions; a novel promising reaction media arising from this area of focus is the surfactant–RTIL–supercritical CO₂ mixture.⁸⁷

An analysis of the literature suggests that micelles can be created in aqueous solutions of RTILs, provided that the latter contain more than eight methylene groups. For RTILs with shorter tails, there is no definite CAC, although a certain level of aggregation at high concentrations can be observed even for [C₄C₁IM]–containing RTILs. Imidazolium-based RTILs in water behave as a typical cationic surfactant with their micellization regularities bearing similarities to that of [N_{1,1,1,N}]-based RTILs. A leading contributing factor in the micellization of imidazolium-based RTILs is usually ascribed to the presence of the C(2)–H site of the cationic ring.⁸⁸ Recently, the methyl group of [C_nC₁IM] was substituted by longer alkyl groups, and the micellization of a new compound was achieved.⁸⁹

The incorporation of carbazole substituents into the imidazole ring also facilitates micellization. According to Dong et al.,⁹⁰ the CAC of [carbazoleC_nC₁IM][Br] is lower than that of [C_nC₁IM][Br]. The presence of large hydrophilic substituents was considered using S-3-hexadecyl-1-(1-hydroxypropan-2-yl)-imidazolium bromide.⁹¹ While the CAC changed only marginally, from 0.56 to 0.51 mM at 298 K, the average aggregation number decreased.

Generally, micellization properties of RTILs can be tuned in the same way as for classical surfactants. The CAC for [C_nMIM][Cl] exceeds that of [C_nMIM][Br].^{92,93} A similar relationship was found for alkylpyridinium and alkyltrimethylammonium, depending on the presence of either a chloride or bromide. It is likely that bromide is more weakly solvated due to its larger size, which allows for a more energetically favorable adsorption on the aggregate surface.

As temperature increases, the CAC initially decreases and then it starts rising; this minimum is typically observed near room temperature. There are two principal reasons explaining this trend. First, as the temperature increases, the degree of hydration of the polar group of the surfactant is reduced, so aggregation is promoted. Second, water structuring is also reduced with an increase in temperature, so entropy loss occurs when alkyl groups from the aqueous medium orient toward the micelle core, which is also the main driving force of the aggregation process. At lower temperatures, the first factor dominates. After the minimum is reached, the second factor becomes dominant. Another empirical correlation is that the more hydrophobic the RTIL, the lower temperature minimum it exhibits.

Addition of inorganic salts is a robust tool to tune the aggregation behavior of RTILs in concentrated solutions.⁹⁴ It leads to CAC decreases, micelle ionization decreases, ion–ionic binding increases, and aggregation number alteration. These effects have been recently reported for aqueous [C₁₀C₁IM][Cl] solutions with a small admixture of potassium salts.⁹⁵

The data on the micellization of RTILs in nonaqueous solvents and nonaqueous solvent/water mixtures are available to a markedly lesser extent. However, interest in this field will

hopefully be increasing, as these potential investigations could be of great importance for such problems as extraction, catalysis, organic synthesis, and chromatography. Pino and co-workers reported a very encouraging study on the influence of alcohols and ACN on the aggregation and adsorption of [C₁₆C₄IM][Br] and [C₁₂C₁₂IM][Br] solutions in water.⁸⁹ They found that when the fraction of the organic cosolvent is increased, the CAC also increases and the adsorption efficacy decreases.

The aggregation of RTILs in solutions is a critical factor in determining their ionic conductivity. Conversely, measurements of ionic conductivity provide valuable information about the degree of clusterization of RTILs in solution. Feng et al.⁹⁶ studied the aggregation of [C₁₂C₁IM][Br] in a number of organic solvents, including ethylene glycol (EG), formamide (FA), dimethyl sulfoxide (DMSO), and ACN. It was found that the CAC of [C₁₂C₁IM][Br] gradually increased from DMSO to ACN to FA. The authors correlated this relationship with the solvophobic effect and the hydrogen bonding between the anion and molecular solvent. Notably, the aggregation of RTIL was not observed in EG. Singh⁹⁷ recently indicated that [C₈C₁IM][BF₄] created aggregates in EG, while [C₄C₁IM] octyl sulfate did not aggregate, despite their seemingly similar physical and chemical properties.

The ability of amphiphilic molecules to exhibit self-organization in RTILs, which results in the formation of micelles, microemulsions, liquid crystals, vesicles, and gels, will be very important for the application of microheterogeneous systems, such as reaction and extraction media. These molecular aggregates are often able to solubilize insoluble substances. However, the microstructure of these surfactants in RTILs must be studied more comprehensively. We hypothesize that nonionic surfactants would exhibit a better potential for self-aggregation in RTILs, as compared to ionic ones. A noteworthy study has been recently presented by Inoue et al.,⁹⁸ who revealed the temperature dependence of the CAC for polyoxyethylenealkyl ethers in [C₄C₁IM][BF₄]. According to this study, at lower temperatures, micellization was determined by the entropic factor, while at higher temperatures it was determined by the enthalpic factor.

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Gas Dissolution. Not only do ionic liquids eliminate the hazards originating from volatile organic solvents,⁴⁴ they can also be used for gas storage and as reversible adsorbents for pollutant gases.^{99–102} Obtaining reliable solubility of various gases in RTILs is required for the design and operation of many emerging devices. Therefore, a number of studies focusing on this area have been conducted recently. These investigations included studies on optimal pressure and temperature, chemical structural patterns; determining gas solubility and gas pair selectivity, capturing carbon dioxide and supporting RTIL

membranes, tailoring imidazolium-based RTILs through grafting of functional groups, and the calculation of solubility parameters using group contribution theory.¹⁸ An excellent review of these topics was provided by Anderson et al., in which a summary was provided for enhancing CO₂ solubility that included both physisorption and chemisorption mechanisms.^{103,104} In turn, Vega et al. provided a comprehensive overview of solubility trends for selected compounds, such as CO₂, H₂, and BF₃ in RTILs.¹⁰⁵

Not only do ionic liquids eliminate the hazards originating from volatile organic solvents, they can also be used for gas storage and as reversible adsorbents for pollutant gases.

Shiflett and co-workers have made significant contributions to the field of carbon dioxide dissolution in RTILs and gas separation using RTILs.^{53,55,59,74,101,106–109} For instance, H₂S and CO₂ can be efficiently separated using [C₄C₁IM][PF₆] and [C₄C₁IM][C₁SO₄].^{55,74} The chemical and physical factors responsible for increased adsorption of CO₂ by various RTILs have been thoroughly addressed in refs 53, 108, and 109.

It would be expected that the mass, spatial structure, and flexibility of the positively charged moiety of the cation imposes a greater influence on the polar gas solubility than would alkyl tail groups. Methylation at the C(2)-position of the imidazole ring decreases the molar Gibbs free energy of cavity formation and gas-RTIL interactions, but increases the molar volume of the solvent. Methylation promotes solubility of the gases, exhibiting relatively weak interactions with the RTILs. For instance, Dyson et al. reported that the solubility of molecular hydrogen increased upon C(2)-methylation of [C₄C₁IM][TFSI].¹¹⁰ However, this same strategy decreases the affinity of RTILs to CO₂, which has a solubility that relies primarily on

the attraction of its negatively charged oxygens to the positively charged imidazole ring. Anderson reported the solubilities of CO₂ and SO₂ to be greater in [C₆C₁IM][TFSI] than in [C₆-3-C₁Py][TFSI],¹¹¹ because of the favorable interactions between these gases and the C(2)-H site of the imidazole ring. For reference, the partial molar enthalpies of CO₂ dissolution in these two RTILs are –12.1 and –11.4 kJ mol^{–1}.¹⁰⁴ [C₄C₁IM][TFSI] and [C₆C₁IM][TFSI] show a worse solubilization ability for methane, ethane, ethylene, and O₂ than that of [C₆-3-MePy][TFSI].

In a number of studies, it has been found that the low-pressure solubility of CO₂, H₂, and C₂H₆ was greater in [C₂C₁IM][TFSI] than [P_{1,4}][TFSI], as measured at 300–345 K.^{110,112} The presence of the pyrrolidinium cation increases the solubility of these gases. This can be explained by the flexibility of the head rings of the [P_{1,4}]⁺ cation; since a variety of conformations are possible for the cation, it likely increases the free volume in ionic domains and facilitates spontaneous cavity formation (Figure 3).¹¹³ It has become evident that elongation of the cation chain has a negligible impact on the ionic domains and is unable to promote solubility of CO₂ and other gases with nonzero electric moments. Indeed, there are multiple studies reporting insignificant solubility increases of CO₂ and SO₂ with alkyl chain length. In particular, [C₄C₁IM][BF₄], [C₆C₁IM][BF₄], [C₈C₁IM][BF₄], [C₂C₁IM][TFSI], [C₄C₁IM][TFSI], [C₆C₁IM][TFSI], [C₈C₁IM][TFSI], [C₁₀C₁IM][TFSI], [C₂C₁IM][PF₆], [C₄C₁IM][PF₆], [C₆C₁IM][PF₆] were considered.^{103,114–118} If the size of the anion is increased, it weakens gas-anion interactions and, hence, results in lower solubility. Carvalho et al. found that CO₂ solubility was lower in [C₄C₁IM][MeCOO] than [C₄C₁IM][TFA] at low pressures,¹¹⁹ although Coulombic forces showed just the opposite trend; the free energy appears larger in the case of [C₄C₁IM][MeCOO]. Knowing that there exists a specific affinity of CO₂ to the fluorinated carbons, we can now understand why the experimental solubility increases for COO[–]. The number of sites responsible for specific

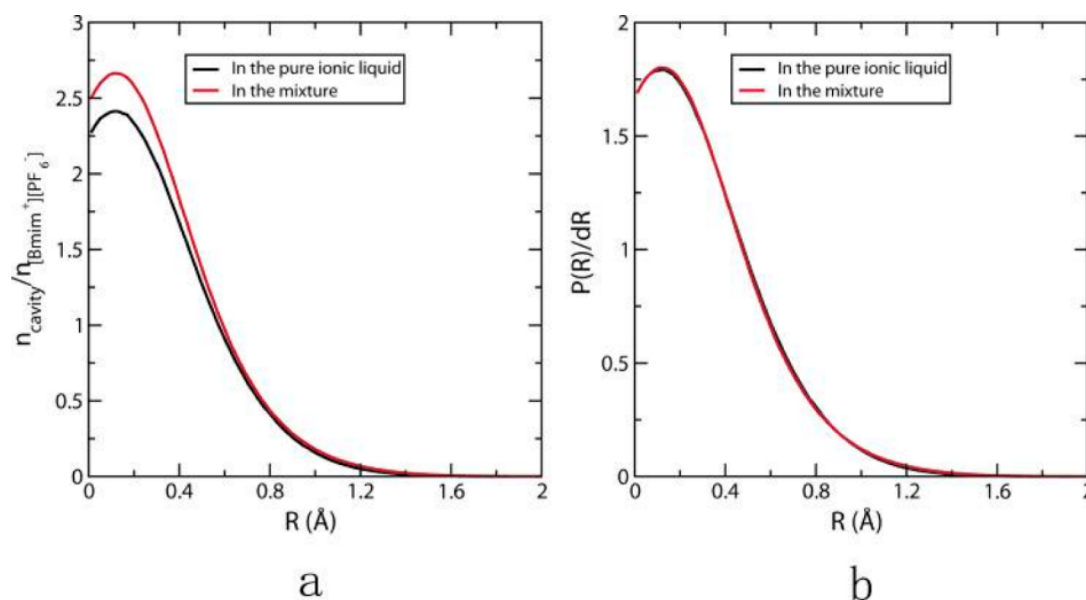


Figure 3. Average number of cavities per ionic liquid molecule [C₄C₁IM][PF₆] with certain radius versus the radius in the pure IL (black line) and in the RTIL/CO₂ mixture (red line). (b) Distribution of radii of all spherical cavities in the neat RTIL (black line) and in the RTIL/CO₂ mixture (red line) generated by Voronoi analysis. Courtesy of Claudio Margulis, ref 113. Copyright 2005 American Chemical Society.

interactions decreases with pressure. At a given high pressure, all sites become saturated, preventing any further CO₂ capture.

To recapitulate, in combination with water and organic solvents, RTILs are versatile agents in many areas of science and technology, including electrochemistry, micelle formation, phase separation, and pollutant gas dissolution. The most thoroughly investigated families of RTILs are imidazolium- and pyridinium-based, in combination with water, lower molecular weight alcohols, acetone, and ACN. There are still hundreds of uninvestigated molecular-ionic systems, some of which appear very promising. A comprehensive examination of these systems using a self-consistent experimental or computational method is of urgent importance. In this Perspective, we emphasized the most notable current breakthroughs and proposed future avenues for further integration of RTILs in modern materials science.

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Author Contributions

The manuscript has been written though the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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