Recent advances in modeling green solvents

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Molecular modeling of environmentally benign solvents is essential for a microscopic understanding of interactions, processes and phenomena which contribute to their properties in bulk and at interfaces. Challenges in their modeling arise from their constitution – mixing of organic and inorganic components, their nano and possibly mesostructural order, and the quantum nature of interactions. This short review provides an overview of recent work on four categories of such solvents – room temperature ionic liquids, supercritical carbon dioxide, organic carbonates and deep eutectic solvents, with emphasis on their applications in electrochemistry and bio-molecular dissolution.

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Introduction

Green solvents encompass those which are non-toxic, non-volatile, recyclable and which do not involve a high energy cost of synthesis. Biodegradability is another desirable characteristic. Excluding water on which good reviews are available [1], green solvents of current interest include (a) room temperature ionic liquids (RTIL), (b) supercritical carbon dioxide, $scCO_2$ (c) organic carbonates and (d) deep eutectic solvents (DES). This review encompasses modeling studies carried out over the last two years. While some of the systems, particularly imidazolium or fluorine based ILs need not necessarily be 'green', they too have been included for the sake of completeness. A vast majority of literature on these systems are in electrochemistry or enzymatic catalysis domains. The systems are quite amenable to force field based molecular dynamics (MD) simulations. A schematic to derive effective force field parameters for green solvents is shown in Figure 1.

Room temperature ionic liquids

In terms of energy landscape characteristics, RTILs lie between molten sodium chloride and simple organic liquids such as dimethyl sulfoxide and toluene [3,4]. Even seemingly simple aqueous IL solutions can exhibit interesting properties [5]. While the density of [emim][OAc]/Water increases with increase in water content, those of [emim][Tfa] and [emim][BF$_4$] decrease [6]. Atomistic simulations show the presence of long hydrogen bonded (water-anion)$_n$ wires in [emim][OAc] solutions, making it nanostructured. Similar clusters when formed in [emim][Tfa] or in [emim][BF$_4$] disintegrate due to the large water clusters present in them.

In recent years, ionic liquids have emerged as competitive candidates in the field of gas capture [7,8], separation [9,10], and in nanoparticle dissolution [11]. Detailed MD simulations and quantum chemical calculations have revealed the role of cations and anions in the solvation of SO_2 in ionic liquids, while free energy calculations offer a microscopic rationale for the experimentally observed SO_2 solubility order for various anions in ionic liquids [12–14].

RTIL electrolytes

RTILs can act as alternatives to conventional electrolytes in lithium ion batteries, solar cells and fuel cells, due to their wider electrochemical window (ECW). The bounds of ECW of a RTIL are largely determined by the reduction and oxidation potentials of the cation and anion respectively. The minimum redox potentials among all possible reactions in an electrochemical cell needs to be considered and the sum of the reduction and oxidation potentials is the ECW. These potentials can be obtained from the corresponding free energy change for these reactions, which can be calculated via density functional theory (DFT). These quantities need to be determined not for the respective species in gas phase, but for the ones solvated in the IL medium.

While the thermodynamic cycle approach (see Figure 2) to calculate ECW is the most appropriate, single molecules treated via a polarizable continuum model (PCM) method can offer results of comparable quality with much less computational effort [15].

Lawson et al. [16] explored the calculation of ECW of ILs using *ab initio* MD (AIMD) simulations. However, as the ECW was calculated as just the difference between

Figure 1
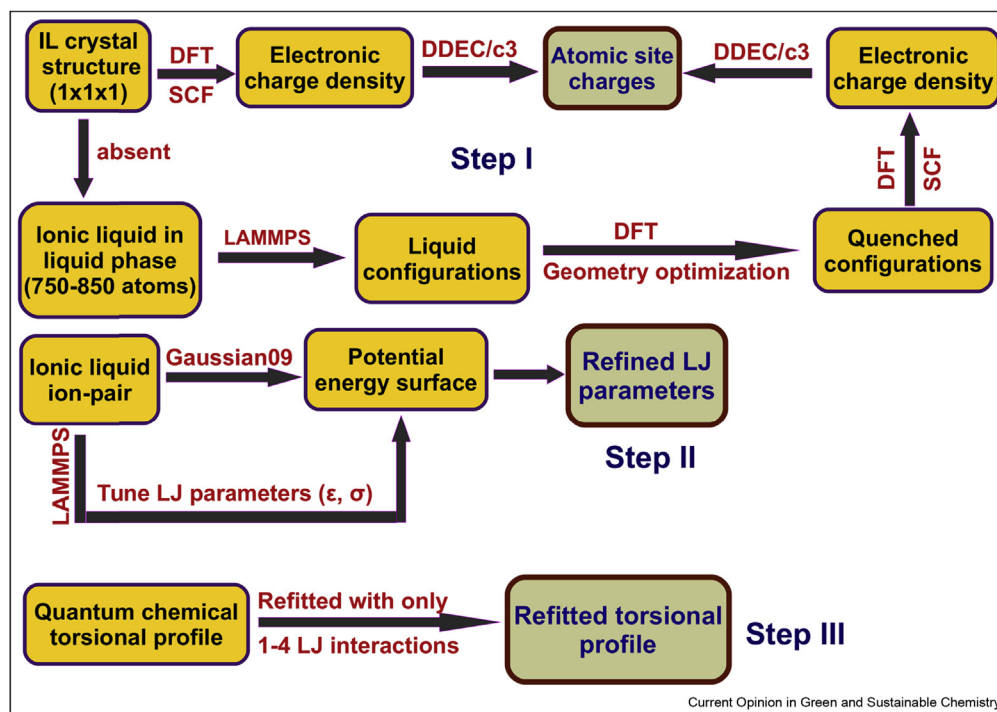
Refinement of potential parameters for 1-alkyl-3-methylimidazolium based room temperature ionic liquids. Site charges are derived through DDEC/c3 method from the condensed phase of ionic liquids to capture the electronic polarization and charge transfer effects in an effective manner. Intermolecular structure and dynamics, in particular, the collective quantities predicted by the refined force field, match experimental results quantitatively. For details, see Ref. [2].

ionization potential and electron affinity in the case of clusters and as the HOMO−LUMO gap for the liquids, the values were only in qualitative agreement with experimental data. Addition of dispersion corrections to the DFT paradigm and inclusion of a larger basis set, apart from the use of a thermodynamic cycle approach can improve the result obtained from computations.

Values of ECW calculated via the thermodynamic cycle method assuming implicit solvent fare much better than the bare HOMO−LUMO gap for comparison against experimental data. Banerjee et al. [17] showed that geometry relaxation of both product and reactant species followed by calculation of free energies is crucial for an accurate estimate of ECW.

Figure 2
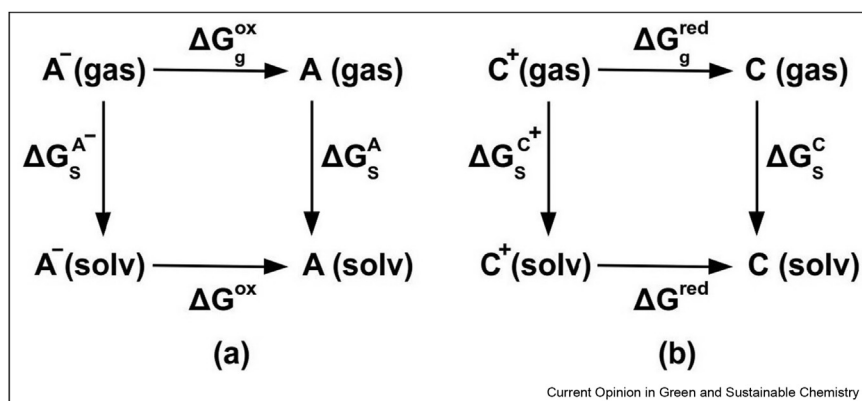
Thermodynamic cycles used to calculate free energy changes corresponding to the oxidation (a) and reduction (b) reactions. See Ref. [15] for the meaning of the labels.
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It is imperative that computations are employed to create a database of ECW of many ILs, including those of compounds which are yet to be synthesized, to be of utility to electrochemists.

Biological molecules in RTILs

Room temperature ionic liquids have been investigated for the long-time preservation of nucleic acids/bases at or near ambient conditions [18,19], for enzymatic catalysis at higher than ambient temperatures [20−23], cytotoxicity [24,25] and for biomass dissolution [26−32]. An excellent review summarizing both experimental and computational studies of the solvation, function and stability of biological systems in RTILs has appeared recently [33].

Imidazolium cations preferentially solvate the minor groove of DNA in aqueous RTIL solutions [18]. The consequent water depletion from the first solvation shell of DNA prevents hydrolytic reactions which denature DNA so as to hinder its long term storage. Unlike nucleic acids, nucleobases are poorly soluble in water, but are highly soluble in ILs. One drawback in the use of ILs though is that the resulting solution is quite viscous. Employing MD simulations, Senapati et al. [19] studied aqueous solutions of uracil and adenine with 1-ethyl-3-methylimidazolium acetate, [emim][OAc] at different concentrations of water which have much lower viscosities than pure IL. At low concentrations, water does not much perturb the IL/nucleobase network. With increasing concentrations, the anions of IL form hydrogen bonds with water in lieu of IL-nucleobase interactions. Thus, IL/water solutions offer high solubility for nucleobases and also possess low viscosity.

Chaban and coworkers [20] studied the behavior of f-Cage protein in aqueous solutions of three imidazolium based ionic liquids, in all of which amino acid based anions were employed. As expected, the addition of ILs reduced the conformational flexibility of the protein. A decrease in conformational flexibility can impair the function of proteins and enzymes, as it can reduce the number of states available during conformational selection.

The reaction of butyl alcohol with vinyl acetate to produce butyl acetate carried out in tert-butanol is catalyzed by the enzyme Candida antarctica lipase B (CALB). The structure, stability and catalytic activity of CALB in t-butanol, aqueous NaCl solution and in two different ionic liquids − [bmim][TfO] and [bmim][Cl] were investigated by MD simulations [21]. Enzymatic activity followed the order: [bmim][TfO] > t-butanol > [bmim][Cl], which was rationalized in terms of changes in the width of a solvent accessible channel in the enzyme.

In domains such as food preservation, the biocompatibility of ionic liquids is of important consideration. Thus, salts with cholinium cation and amino acid based anions are attractive alternatives to imidazolium based ones.

In general, biodiesel production reactions are carried out in aqueous-organic media and/or in presence of surfactants; currently, RTILs are being explored as alternative media. Thermomyces lanuginosus lipase (TLL), the catalyst for the production of biodiesel [22] showed solvent concentration-dependent optimal catalytic activity in an aqueous solution of cholinium amino acid IL. Classical MD simulations [23] show that 0.5 M concentration of IL in water is optimal (Figure 3) to facilitate the interfacial activation of the enzyme.

Imidazolium based ILs exhibit high toxicity with poor biodegradability. A recent study [24] combined both experiments and MD simulations to probe the cytotoxicity of ILs while that of Maginn et al. [25] studied the same problem through MD simulations. The effect of ILs on lipid bilayers was studied using fluorescence imaging and scattering techniques [24]. In particular cations with long alkyl tails insert themselves into the bilayers in a facile manner, distorting them. Addition of ILs increases the critical micelle concentration. Hydrophobic anions too exhibit a similar effect on lipid association. This behavior of ILs in such bilayers is reminiscent of ionic surfactants.

Cellulose dissolution ability of ionic liquids is determined by the formation of hydrogen bonds and van der Waals interactions between cellobiose and ionic liquids [31]. Atomistic molecular dynamics simulations and free energy calculations revealed the primary role of anions in cellobiose solvation and the profound stability of the anti−anti conformer of cellobiose in ionic liquids [32].

Supercritical carbon dioxide

Carbon dioxide is inexpensive, recyclable, and non-toxic. Supercritical carbon dioxide (scCO$_2$) can act as solvent for many organic reactions, in the extraction of natural products, for the dissolution of fluorous polymers and so on.

However, scCO$_2$ being non-polar with a low dielectric constant of less than 1.5, is unusable as a solvent for enzyme catalyzed reactions. Thus, osmolytes need to be employed to prevent the protein denaturation. The effect of proline, trehalose and trimethylamine-N-oxide (TMAO) on the stability and structure of chymotrypsin inhibitor 2 in scCO$_2$ was investigated through MD simulations [34]. While the first two osmolytes stabilize the native structure of the protein, TMAO (which is an

Figure 3
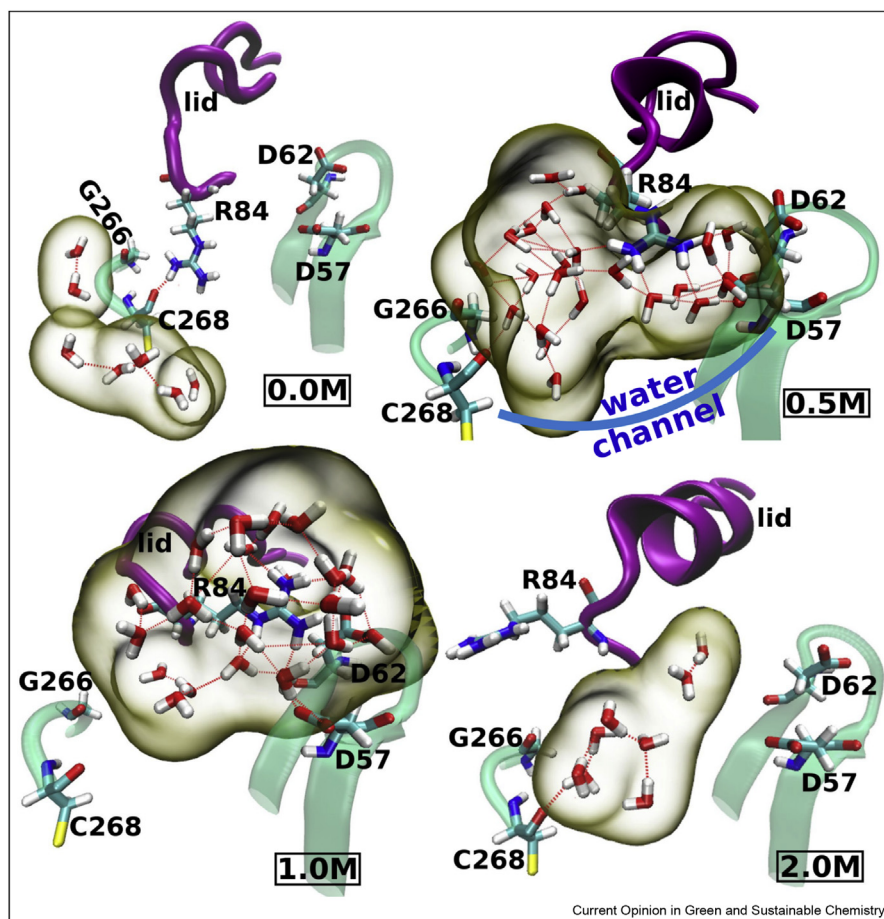
Arginine (Arg84) switch through water channel in the open form of TLL enzyme. Figure exhibits those water molecules which are within 10 Å of lid residue Arg84 and also can form water channel. Hydrogen bonds are represented by red dotted lines. Water molecules can form a channel between two regions – C268 and D57 only in the open 0.5 M IL system.
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osmolyte in aqueous solution) denatures it. Maginn et al. have carried out MD simulations to study the solubility of a medicinally important compound, Menadione in scCO$_2$ [35].

Traditionally, supramolecular complexes have been studied in either aqueous or non-polar organic solvents. Recently, Ruiz-Lopez et al. [36] studied a benzoic acid (BEA, substrate) complexed with peracetylated-beta-cyclodextrin (CD cavity) in scCO$_2$ using MD simulations. In scCO$_2$, the complex is stabilized by polar interactions between BEA and CD, whereas in water, it is stabilized by hydrophobic interactions. Such supramolecular host-guest interactions in this novel medium needs to be explored further.

Organic carbonates

Alkyl carbonates, in particular, dimethyl or ethylene or propylene carbonate are also green solvents with applications in electrochemistry and in extraction of natural products.

Organic carbonates are employed in lithium ion batteries for their ability to dissolve lithium salts. Rempe et al. [37] carried out extensive molecular simulations of lithium hexafluorophosphate dissolved in ethylene (EC) and propylene carbonate (PC) liquids. AIMD simulation was used as a benchmark to identify the most appropriate charge set for classical MD simulations. Lithium ion transference numbers, calculated from ion diffusion coefficients, ranged between 0.3 and 0.5 in the solvents, in good agreement with experiments. Scaled charge models provided quantitative agreement with experimental results relative to the full charge model, suggesting the extent of polarization and charge transfer in organic carbonates in the condensed phase.

Although dimethyl carbonate (DMC) itself is a good solvent for lithium salts, it crystallizes at 2 °C, rendering

it incapable for low temperature applications. Hence, it is typically mixed with EC to avoid crystallization. The electrochemical stability of EC-DMC mixtures was studied using quantum chemical methods [38]. Miller et al. performed extensive classical MD simulations of seven solutions of DMC-EC mixtures. Equilibrated configurations from MD simulations were considered for calculations of vertical ionization energy distributions. Accurate quantum chemical calculations on such large system sizes makes this work quite realistic. The work pointed to the influence of the high quadrupole moment of DMC in solvating lithium ions, despite its lower dipole moment than EC. While the cis–cis conformer of DMC is the most stable one, 0.1% of molecules are in the cis–trans state at ambient conditions [39]. The latter possesses a larger dipole moment of 4.5 D compared to a value of 0.32 D for the cis–cis one and thus could cluster together, an aspect that could be explored in future.

Several organic solvents including DMC have been studied for their ability to replace n-hexane in the extraction of carotenoids. Chemat et al. [40] employed a statistical thermodynamics model, COSMO-RS to rationalize the β-carotene extraction capabilities of DMC, cyclopentyl methyl ether and 2-methyltetrahydrofuran. MD simulations [41] of DMC-alkanol mixtures reveal the enrichment of alcohol at the solution-air interface, independent of the concentration of alkanol.

Deep eutectic solvents

Deep eutectic solvents (DES) are a binary mixture of organic compounds which are individually solids at ambient conditions but liquefy upon mixing due to the formation of intermolecular hydrogen bonds. DES are considered to be 'greener' than ILs due to the ease of synthesis. While 30 different eutectic combinations are known, a few among them are widely studied: 1:2 choline chloride/urea (reline), 1:2 choline chloride/ethylene glycol (ethaline) and 1:2 choline chloride/glycerol (glyceline) which are reviewed in Refs. [42,43].

Biswas and coworkers investigated orientational jumps of acetamide molecules and their relationship to the relaxation of hydrogen bonds in mixtures of acetamide with lithium salts [44]. The jump time distributions exhibited a power law dependence, suggesting dynamical heterogeneity [45]. The acetamide-lithium perchlorate mixture was also investigated by Kashyap et al. [46]. A pre-peak in the scattering structure factors whose intensity increased with the length of the alkyl chain on acetamide was observed, signifying nanoscale structural heterogeneities in these systems.

While standard force fields for the hydrogen bond donor (HBD) molecules in DES are available, attempts have been made to reparameterize better ones for the salt. A model for cholinium chloride [47] where the total ion charge is scaled by a factor 0.8 was able to predict all properties (diffusion coefficients, surface tension and isothermal compressibility), within 20% of experimental values. The charges were obtained from a bulk DFT calculation which makes this work superior. A similar charge spreading on the ions was also reported in the extensive *ab initio* MD simulations on reline [48].

Zahn [49] rationalized the liquidus range of reline via the presence of multiple hydrogen bond networks between all the constituents − chloride, cholinium and urea. Such multiple and similar interactions can lead to multiple minima in the free energy basin which will enhance the entropy of the liquid phase thus making it more stable than the crystal. Edler et al. [50] report the first neutron diffraction experiments of this DES which would be of much use to modelers.

Summary and outlook

Modeling studies of green solvents has seen enormous growth over the last decade. Both polarizable as well as effective charge based force fields have been developed which enable realistic MD simulations to be carried out on a routine basis, while quantum chemical calculations form the bedrock of theoretical work in this area.

Ionic liquids at charged solid surfaces with complex surface morphology (say, porous electrodes) is a domain that is of vital interest from an experimental point of view, but on which very few simulations have been carried out. The idea is to develop novel electrolytes which not only possess high energy density but also high power density [51] which demands fast relaxation processes and low viscosity. Can additives to IL reduce its viscosity and increase the power density without compromising energy density? What microscopic characteristics of the electrode pore surface determine the ion mobility near the pores? There is much scope for atomistic simulations to contribute in this regard. Significant contributions are also expected in modeling the microscopic structure, stability and dynamics of enzymes in green solvents.

In terms of methodology, most modeling reports on green solvents have confined themselves to studying phenomena at length scales of 0.1−10 nm. Coarse grained (CG) and mesoscale modeling methods must be specifically applied to these systems to probe phenomena at larger length scales [52]. While CG models have been developed for ionic liquids, those for DES have not yet been explored.

In summary, these are exciting times for modeling studies of environmentally benign solvents. The scope for offering microscopic insights into their role in novel

applications being studied experimentally, is vast. So also, are possibilities of coming up with predictions of new categories of compounds with specific properties.

Acknowledgments

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