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Theoretical Description of Ionic Liquids

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12.1 Introduction

Ionic liquids (ILs) are a novel family of solvents that has piqued the curiosity of both business and academics. These liquids are intriguing from an academic standpoint as they are versatile solvents that can be customized to address issues with diverse properties and conflicting behavior patterns, which we are still in the process of

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comprehending completely. Fascinating discoveries about the physical features of ILs continue to appear in recent reviews [1–4]. Furthermore, some ILs can develop vastly complicated H-bond structures, adding another layer of complexity to the issue. The major competitive advantage for advanced materials is their ability to tune their material characteristics with varying chemical frameworks of their component ions and the fact that they can be used as greener alternatives to more hazardous organic solvents.

It is worth noting that ILs do not simply match the traditional definition of molecular fluids, and explaining many of their unique qualities has necessitated a microscopic examination of their physical constitution. ILs are substances entirely made up of ions [5–7] and have a melting point of less than 100 °C, making them liquid in normal conditions. However, defining the liquid phase – particularly complex liquids like ILs – remains difficult [8]. While quantum chemistry (QC) methods may be used to obtain features of such materials in the gaseous state, single-molecule methods of this sort do not sufficiently capture most aspects of the liquid state, primarily because they disregard temperature and surroundings as well as dynamics.

ILs present a unique set of problems for theoretical chemistry. Due to their elevated viscosity, ILs must be considered over a wide simulation timeframe. Additionally, the analysis must include a dependable electrical structure to acquire accurate results, owing to the significant significance of intermolecular interaction [9]. Regrettably, the theoretical methods necessary are only practical for medium-sized structures. These methods have the required electrical and structural flexibility for an effective ab initio description of intermolecular interactions. Additionally, dispersion forces complicate selecting a suitable strategy for ILs. Nonetheless, well-chosen theoretical approaches can provide forecasts for ILs and validate and explore numerous experimental discoveries [10].

Simple models based on continuum theories can often produce superior results, although molecular dynamics (MD) simulations are still the preferred method for condensed-matter research [11, 12]. Large samples may be catered for, including a model-inherent dynamical description. Scientists can address several molecules with this technology, which uses periodic boundary settings to simulate signals around the center cell, overcoming issues caused by surface impacts. Despite the reality that MD is gradually approaching the capabilities of modern supercomputers, it is still not a feasible option for studying dynamical characteristics. The reason for this limitation is twofold: the significant computational expense involved and the exceedingly high viscosity of most ILs. These necessitating simulation timeframes are still impractical for evaluating dynamical features like self-diffusion ratios. For the theoretical conclusions to be reliable, the classical force field must be chosen carefully [13–15]. Even though the force fields have been tested against a variety of experimental parameters, their flexibility with other systems that were not actually linked in the verification phase can be problematic [16, 17]. Due to the plethora of molecular variations conceivable with ILs, the use of any force field must be empirically confirmed, even though it has been successfully utilized previously.

We are confident that this chapter will not only provide information on how to use an interpretation tool to forecast experimental amounts of IL but will also offer additional information on recent experimental quantities and allow us to observe

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numerous factors that IL experiments cannot. As a result, in this chapter, we will outline and discuss current advances in theoretical simulations of ILs and potential future prospects. We will go through some of the challenges with theoretical simulations of ILs in particular. We will also go over general theoretical methodologies and the nuances of applying them to ILs.

12.2 Ionic Liquid Dynamics

With improved modeling tools and force fields, atomistic MD simulations have become valuable for gaining molecular scale knowledge of structure-property correlations and the virtual development of advanced materials [18]. MD simulations have uncovered numerous details regarding the dynamic characteristics of ILs, such as viscosity, self-diffusivity, electrical conductivity, and thermal conductivity.

ILs have evolved from simple liquids, catalysts, isolation media, or electrolytes to task-specific, programmable molecular machines with specialized features. A comprehensive understanding of these features and structure-property correlations is required to adequately harness their capabilities, explore future paths in IL-based research, and appropriately deploy suitable implementations. In this section, we present and discuss the existing data on a wide range of IL systems' physicochemical properties (self-diffusion and viscosity).

12.2.1 Self-Diffusion

Self-diffusion is a basic molecular feature that provides quantifiable data on ion mobility in a liquid and may be readily estimated over a sufficiently lengthy simulation period. An equation for diffusion coefficient can be formulated in terms of the Stokes–Einstein equation [17] for a special instance of Brownian particle diffusion in a viscous fluid:

$$D_{\mathrm{s}} = \frac{k \times T}{6 \times \pi \times \eta \times R_{\mathrm{H}}} \tag{12.1}$$

where k denotes the viscosity and R_{H} denotes the particle's hydrodynamic radius. This equation has been effectively used to explain glycoprotein diffusion in diluting liquids. Equation (12.1) can be adjusted in some circumstances where the molecule form is clearly quasi by inserting an experimental actor (c) accountable for the divergence of the particle's self-diffusion action, as stated by Eq. (12.2):

$$D_{\mathrm{s}} = \frac{k \times T}{c \times \pi \times \eta \times R_{\mathrm{H}}} \tag{12.2}$$

The type of an IL's cation and anion and parameters, such as temperature and pressure, impact its diffusion properties. To explore the dynamics of $[C_4\mathrm{mim}][PF_6]$, Hu and Margulis [18] employed MD simulations for 3 ns at 400 and 500 K and for 9 ns at 300 K. The non-Gaussian parameter $\alpha(t)$ led to the highest at roughly 2.5 ns at 300 K, and slightly over 100 ps at 400 K, in keeping with Del Popolo and Voth's results that these liquids have continuous variability. They also discovered that, whereas most ions have slow movements, a tiny proportion of ions move rapidly; these fast-moving ions travel 200 times faster than less mobile ions. The behavior of

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aromatic hydrocarbons at the liquid–liquid interface and the alkylation efficiency of IL/benzene have been investigated using MD simulations and experimental research. The acid–hydrocarbon interfacial layer was shown to be the richest in benzene due to the larger interfacial area. The vertical self-diffusion of isobutane was calculated using the survival rate. It was discovered that benzene's interface properties improved isobutane diffusion in the interfacial layer. The accumulation of benzene molecules in the acid–hydrocarbon interfacial layer, which buffered the acid content of anions in that location, was the fundamental reason for the improved butane alkylation efficiency [19].

MD simulations were utilized by Blanco-Diaz et al. to examine the effects of different chain lengths on the density, self-diffusion coefficient, and viscosity of $[C_n\text{mim}][TF_2N]$ ILs. With increasing chain length, density and self-diffusion rates were reduced [20]. Using nuclear magnetic resonance (NMR) fast-field-cycling (FFC) relaxometry, Overbeck et al. calculated the self-diffusion ratios and rotational correlation durations of the anions and cations in triethylammonium-based PILs. At room temperature, the diffusion coefficients of the cations were found to be in the order of 6×10^{-11} m^2 s^1 and nearly 50% greater than those of the anions [21]. The diffusion ratios of both ions in PILs contrasted with those found in pulsed-field gradient (PFG) NMR investigations and those calculated using a unified dispersal power law. The Stokes–Einstein and Stokes–Einstein–Debye relationships were employed to link the diffusion coefficients and correlation durations with the high viscosity [21].

ILs/graphene oxide (GO) membranes have recently been suggested as a potential replacement for CO_2 capture. Nevertheless, no apparent link exists between ILs/GO microstructure and CO_2 separation efficiency [22]. MD simulation was used to investigate the dynamic characteristics and relationships for CO_2/CH_4 in three imidazole compounds ([Bmim][PF_6], ([Bmim][BF_4], and ([Bmim][TF_2N]) contained between two GO plates with varying layer distances. The increased solubility and diffusion selectivity of CO_2/CH_4 in the ILs/GO membrane can be attributed to the stronger affinity of CO_2 ions and the faster mobility of CO_2 compared to CH_4. Furthermore, it was discovered that lowering layer distance increased solubility selectivity while decreasing diffusion selectivity. However, because solubility specificity was found to be the most important factor, the ideal layer spacing was determined to be 2 nm. Low-viscosity ILs were also advantageous in improving diffusion selectivity [22].

12.2.2 Viscosity

Shear viscosity is a second property allowing reliable MD simulation confirmation. To calculate the viscosity, the off-diagonal variables of the stress tensor can be auto-correlated and averaged

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{xz}(0) P_{xz}(t) \rangle \, \mathrm{d}t \tag{12.3}$$

where P_{xz} represents the stress tensor's off-diagonal component. While Eq. (12.3) is technically valid, the integral's infinite-time limit indicates that the simulation is lengthy enough to sample all important motions. In addition, the integral's signal-to-noise ratio must be adequate throughout this duration. The dynamics of

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ILs are clearly more complicated than those of "simple" liquids, as they include numerous timeframes and various forms of mobility. Because of the intricate dynamical behavior, simple notions of the relationship with diffusion rate, viscosity, and conductance may not be relevant in several cases.

Increasing the duration of molecular simulations was investigated using the time-temperature superposition (TTS) approach [23]. The IL exhibited a Newtonian plateau in shear viscosity at low flow rates, followed by shear-thinning behavior at high flow rates. The IL displayed characteristics of a viscous liquid at high and low frequencies, whereas at high frequencies and low temperatures, it exhibited viscoelastic properties akin to those of an elastic substance. This work highlights TTS's intriguing capacity to bridge the enormous temporal gap between simulations and experiments, allowing molecular simulations to reliably forecast rheological property values at a frequency of practical importance [23].

Ntum and Silpizi investigated the out-of-equilibrium characteristics of [BMIM][BF_4] enclosed between metal surfaces using MD simulations. They were particularly interested in learning how the shear flow affects the interfacial characteristics. They discovered the system does not act like the ideal linear Couette flow. The section of fluid closest to the shearing slabs was discovered to behave as a chaotic, thick wall that stretched to a few nanometers under the examined conditions [24]. The observed viscosity of the ILs 1-ethyl-3-methyl-imidazolium tetrafluoroborate ([EMIM][BF_4]) and 1-butyl-3-methyl-imidazolium tetrafluoroborate ([BMIM][BF_4]) as a factor of the shear rate was determined using non-equilibrium molecular dynamics (NEMD) simulations at pressures of 0.101, 507, and 1013 MPa [25]. A comparable investigation was also carried out for benzene as a comparative. It was found that the IL's zero shear viscosity and relaxation time were strongly influenced by pressure. At high pressure, shear thinning commenced at lower shear rates, coinciding with the thinning of the initial coordination shell of anions surrounding cations. At high shear rates, both the imidazolium ring and benzene selectively retain a lateral flow direction, and this impact is amplified at increased pressure [25].

A burgeoning amount of research is being conducted to investigate the self-diffusivities and viscosities of various ILs. Furthermore, additional macroscopic mobility characteristics, such as electrical and thermal conductivities, have also been investigated, albeit far less commonly. Although it is hard to assess all previous work thoroughly, a fair sample of latest projects will indicate the reliability that can be achieved along with some of the difficulties that these calculations can present. With respect to transport properties, imidazolium-based ILs are still the most widely investigated based on molecular simulations.

12.3 Theoretical Advances in Force Fields and Electronic Structures

The task of selecting, developing, or modifying force fields for MD computations is complex and necessitates meticulous verification of the results against current experimental measurements. To construct a force field, one can pick from a variety

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of frameworks: the "atomistic" scale and the electrostatic method are two popular options. There are two primary possibilities for electrostatic interactions (which are obviously critical for the depiction of ILs): fixed partial charges and polarizable formulations [17]. Partial charges must be known properly to do accurate MD simulations of these ionic systems [26–28]. Their quantities can greatly impact the structural and dynamical features of ILs that are computed [29, 30].

The impact of thermostat selection and fundamental variables like Drude particle masses and force constants on ILs' stationary and nonstationary features was investigated [31]. The enormous computational effort required for polarizable MD simulations of ILs was reduced by employing a graphics processing unit (GPU)-enhanced CHARMM algorithm to speed up the calculations. This study demonstrated how to speedily and effectively apply polarizable MD simulation for complex and viscous processes, such as the simulation of ILs. The influence of hydrogen bonding on the structural features of the IL $[C_4C1_{im}][Br]$ was investigated using MD simulations with various model charge systems. These findings correspond to experimental observations [30]. Based on the extent of the modification, the hydrogen bonding capability, indicated by differing molecular partial charges on the most acidic hydrogen atom and its connected carbon atom, affects the morphology and kinetics significantly [30].

New OPLS force field parameters were established for imidazolium-based ILs, yielding precise dynamic behavior, thermoelectric characteristics, and valid intermolecular interactions between cations and anions. The OPLS-VSIL offers an empirically based collection of partial charges for [RMIM] with a unique configuration that integrates a virtual site particle dividing the nitrogen atoms to unload negative electrical charge to the ring's interior plane [31]. The following equation [32] can express nonpolarizable OPLS force fields:

$$V_{\text{nonpolar}} = V_{\text{bonded}} + V_{\text{nonbonded}} = \sum_{ij} kij\left(r_{ij} - r_{ij}^0\right)^2 + \sum_{ijk} a_{ijk}\left(\theta_{ij} - \theta_{ij}^0\right)^2 + \sum_{ijkl}\sum_{n=1}^{3}\frac{1}{2}V_n\cos(n\emptyset_{ijkl}) + \sum_{ij}4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \quad (12.4)$$

The first term represents the linked sets' periodic vibrational energy, and the second represents the bending energy. The third term is associated with 1–4 torsion connections, while the final two terms represent the Lennard-Jones (LJ) short-range term and the electrostatic binding energies. The last two terms are referred to as nonbonded connections.

A structure-based coarse-grained force field (CGFF) has been designed to simulate imidazolium-based ILs with acceptable transferability across varied chain lengths. The structure and pressure produced from coarse-grained (CG) models match with all-atom MD simulations at different thermodynamic conditions for varying alkyl chain lengths. It was also discovered that the CG model's dynamical features, such as diffusion, maintain the heavy cation's quicker dynamics compared to the anion. The methods for reproducing thermodynamic properties and treating lengthy Coulombic connections presented here can be applied to other soft-matter systems [33].

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The nonpolarizable force field of ILs can be modified through the use of a self-consistent methodology combining MD simulation and first-principles computation based on the order-N density functional theory (DFT). In imidazolium, pyrrolidinium, and ammonium-rich ILs, the efficiency of nonpolarizable force fields computed with the MD-DFT method was examined [34]. The efficient DFT charge was found to increase the flow of ILs, electrical properties, and kinematic precision. This is due to decreased ion couplings, and the overly slow movements detected with a fitted model have been well adjusted through MD and DFT repetition. The collection of nonpolarizable force fields produced using the MD-DFT self-consistent system was more accurate in describing the flow behavior of ILs. The accuracy of ab initio MD simulations has also been studied. These electronic structural techniques use Kohn-Sham density functional theory (KS-DFT) [35, 36]. In the literature, substantial variations between B_3LYP estimates and experimental data have been observed [29]. One inaccuracy could be due to the failure of standard density functionals to describe dispersion forces [37]. Due to interactions, such as the agglomeration of alkyl chains leading to nanoscale partition [38] or the grouping of imidazolium cations [39], they are thus inaccurately portrayed. As a result, the KS-reliability DFT in these IL systems has been evaluated for both standard density functionals and recently developed dispersal-adjusted approaches [40]. It has been demonstrated that omitting dispersion forces in ab initio MD simulations results in unrealistically quicker anions than cations diffusion, which contradicts experimental evidence [41].

Nonetheless, given the importance of inductive forces [42, 43], the issue emerges as to whether the possible system scale of ab initio MD simulations is adequate for the agreement of electronic characteristics. It has been demonstrated in collaboration with the Holm, Berger, and Delle Site teams that when eight ion sets are considered under regular boundary conditions, electronic parameters such as the dipole moment agree [44, 45]. As a result, dispersion-adjusted KS-DFT methods, particularly ab initio MD approaches, are a good fit for IL systems. Szabadi and colleagues examined three polarizable MD force fields with an ab initio path for a 1-butyl-3-methylimidazolium tetrafluoroborate and chloride IL system, assessing their ability to describe both steady-state and transient phenomena. [46]. Radial distribution patterns accord qualitatively in most circumstances; nevertheless, the high polarization of chloride in MD directions leads to inherently unknowable findings. The good accordance between dipolar dispersion indicates the importance of explicit polarizability in MD simulations. The agreement between experimental and theoretical infrared spectra also highlights the similarities between classical and ab initio dynamics in the low-wavenumber region.

12.4 Mixtures in Ionic Liquids

12.4.1 Ionic Liquids and Interfaces

Many essential macroscopic features, such as solubility, liquid crystallization degree, oxygen content, and so on, are influenced by interfacial structure. Furthermore, the properties and shape of the liquid–vapor interface influence many critical aspects of

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liquids, particularly chemical processes that are mediated primarily by species near the surface. Understanding the nature and structure of IL interfaces is also crucial to determining chemical species' movement across them [47]. Whenever an interface develops, particles at the interface have fewer interactions, and changes in molecular alignment, volume, or concentration can sometimes decrease the energy state of a surface. Two well-known instances are surface deposition in liquids and the coordination of water droplets along the gas–liquid surface, where the dipole moments are located [48]. IL interfaces exhibit a significant impact on local composition, which may be proven using simulations and investigated using a variety of experimental methods. Many research studies have employed simulation to study the interface morphology of ILs with various inorganic anions [49, 50].

MD simulations utilizing bis(trifluoromethylsulfonyl)imide (NTf_2) as the anion have been used to investigate the effect of imidazolium cation alkyl chain uniformity on the morphology and characteristics of the IL–vapor interface [51]. The electric potential gap between the gas and liquid states was found to be positive and significantly reduced as the alkyl group length increased.

In interfacial studies and electrochemistry, ILs have theoretical and practical applications. Unfortunately, analyzing their behavior near a surface is difficult due to strong Coulomb contacts and huge and uneven ionic sizes, which influence both their morphology and kinetics. Voegtle et al. reported a mixed experimental and theoretical investigation that used a vibrational sensor particle, 4-mercaptobenzonitrile, placed at the interface between a metal and a range of ILs, to identify the situation better. They also used MD simulations of these surfaces to learn more about the ionic structures that created the observed forces. They discovered that partial complexation of smaller anions into the probe layer caused a stiffer packing of ionic levels near the surface, which caused the connection. The total lateral ion packing density at the surface was decreased by greater anions, which lowered the net charge per unit area and explained the lower measured fields [52]. Gomez-Gonzalez and colleagues ran MD simulations of mixes of a model protic IL, ethylammonium nitrate, with lithium or magnesium nitrate ($LiNO_3$/$Mg[NO_3]_2$) contained in two graphene layers. They used ab initio DFT to study the morphology of the mixture with Li salt interlayer, and the performance was compared to that obtained from classical MD simulations. They discovered that the charge of the salt cation in these combinations seemed to be primarily influenced by its location near the interface. With a lower ion charge density, the cation was able to traverse fewer miles to the sheets, both in aprotic and protic solutions [53].

The immediate environment near IL ions is isotropic, as shown by simulations [54–56]. Because the ions' electron concentrations are deformed during their contact, they may not be properly represented as solid bodies in such a system. It is essential to characterize these contacts using a completely electrically polarizable force field [47]. CL&Pol polarizable force field was developed recently by Goloviznina et al. as a comprehensive yet expandable and transportable model that can describe solutions, mixes, and material interfaces and is not too hard to apply to other systems [47]. The polarizable model reflects the modification of the charged particle of the ion in a more practically precise way once the electric field is turned on through

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intermolecular contacts. For the polarizable model, the force field is as follows:

$$V_{\text{polar}} = V_{\text{nonpolar}} - \sum_i \mu_i \times \varepsilon_i^0 - \sum_i \sum_{j>1} \mu_i \times \mu_j \times T_{ij} + \sum_i \frac{\mu_i \times \mu_j}{2\alpha_i^2} \tag{12.5}$$

where the first term reflects Eq. (12.1), the second term indicates charge–dipole interactions, the third term describes dipole-dipole interactions, and the last term is the energy needed to design the dipole.

The surface and interfacial behavior of three newly synthesized fatty acid ionic liquids (FAILs), namely methyltrioctylammonium octanoate ($[N_{8881}][C_{8:0}]$), methyltrioctylammonium laurate ($[N_{8881}][C_{12:0}]$), and methyltrioctylammonium palmitate ($[N_{8881}][C_{16:0}]$), was studied and analyzed [57]. The bond energy of $[N_{8881}][C_{8:0}]$ (28.961 kcal/mol) was discovered to be higher than that of $[N_{8881}][C_{16:0}]$ (−22.942), which could explain their differing surface activity. Furthermore, at elevated temperature (80 °C) and high-salinity (100 000 mg/l) conditions, the oil/water surface tension was found to be reduced to a significant value (4.9×10^{-3} and 1.7×10^{-2} mN/m), implying that FAILs could be a perfect choice for enhanced oil recovery (EOR) using emulsifiers with good temperature and saline tolerance levels [57].

12.4.2 Ionic Liquids and Water

Organic solvents have been replaced with ILs, which are said to be more environmentally friendly. Water is added to diminish their troublingly high viscosity and cut their exorbitant price. As a result, it is critical to comprehend the various effects of water on IL characteristics. Koishi conducted MD simulations for several anions in $[C_4mim]$ IL–water blends [58]. He examined the impact of wettability and anion size on the morphologies and dynamics of IL–water blends using four different ionic species: NO_3, BF_4, PF_6, and NTf_2. Because of the high anion–water interaction in NO_3 and BF_4 systems, the influence of water–anion–water structures linked by hydrogen bonds was significant. The peak levels of the radial distributions in PF_6 and NTf_2 systems were also found to be affected by the formation of water droplets [58].

At a charged interface, water in room-temperature ionic liquids (RTILs) can greatly impact their interfacial characteristics. Although the interfaces between RTILs and mica substrates have a complex topology, the impact of water activity on these surfaces has been rarely studied, especially given that RTILs are always connected with water due to their hydrophilic nature. MD simulations were used to study the impact of surface ions, water concentration, and ILs' wettability (hydrophobic and hydrophilic nature) on the structure at the RTILs-mica surface [59]. The study found that denser water was deposited on the mica layer as the water content increased. Because of the RTIL hydrophobicity and ion size, more water is collected at the interface with the aquaphobic $[Emim][TFS_I]$ than with the aquaphilic $[Emim][BF_4]$ [59]. To explain the microstructure and dynamic features of the isopiestic systems, MD simulation studies were recently conducted on certain ternary mixtures of $[C_2MIM]Br + [C_6MIM]Br + H_2O$ systems [60]. The results showed that the hydrophilicity of the examined ILs diminishes as the side alkyl

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chain size of the cation rises. The findings also revealed that raising the surface charge of the anion boosts the anion's interface with the water molecules [60].

$[C_6mim][PF_6]$ and water combinations were simulated using MD [61]. Water was observed to be strongly connected with the anions, and their availability improved both the translational and rotational dynamics of the ILs. The rapid mobility generated by contact with water was inferred to be the source of the experimentally measured reduction in viscosity [61]. It was also discovered that the spectral analysis of Coumarin-153 is red-shifted, which is attributed to the prevalence of water, which is consistent with the findings. Using MD simulations, Zhou et al. investigated two types of ILs: ([Bmim][PF_6]) and ([Bmim][NTf_2]) [62]. They looked into how water molecules could distribute into the IL after being absorbed from the vapor phase. Agglomeration was detected as the water content increased. Despite the fact that the amount of absorbed water grew noticeably, the level of available water and small clusters in the ILs did not alter much and remained constant. Because of their hydrophobic nature, [Bmim][PF_6] was found to have more available water and tiny clusters than [Bmim][NTf_2].

Zhou and colleagues utilized MD simulations to explore the impact of impurities on the viscosities of three different ILs, namely [Bmim][BF_4], [Bmim][Tf_2N]], and [Bmim][Ac], and investigated the dependence of their viscosities on temperature and water content. The study was motivated by the observation that even small amounts of impurities can significantly affect the viscosity of ILs. The viscosities were investigated using NEMD simulation, and it was discovered that viscosities changed in distinct ways. For example, viscosities for [Bmim][BF_4] and [Bmim][Tf_2N] fall rapidly during the first phase, then steadily decline with additional water addition. The viscosities of [Bmim][Ac] nevertheless rise in the first phase and thereafter drop [63]. It has been proven that the viscosity of ILs can be considerably altered by adding water. The excess chemical potentials μ_A of a series of molecules dissolved in the IL $[C_1mim][C_l]$ were computed to highlight the effect of water on viscosity further [16]:

$$\mu_A - \mu_A^{\text{ideal}} + \mu_A^{XS} \tag{12.6}$$

where μ_A^{ideal} denotes substance A's ideal gas chemical potential with the same number density as in a solution. The chemical potential could be calculated using the thermodynamic integration method:

$$\mu_A - \mu_B = \int_0^1 \left(\frac{\partial H(\lambda)}{\partial(\lambda)} \right)_\lambda d\lambda \tag{12.7}$$

where $H(\lambda)$ is the solvent interaction energy of a hybrid molecule similar to molecule A at $\lambda = 0$ and molecule B at $\lambda = 1$.

The MD simulation was recently used to explore the mechanism of water molecule adsorption by a carbon-based substrate in the presence of NaCl impurities [64]. The findings revealed that as the defects in atomic structures increase, the rate of water molecule adsorption by the porous carbon matrix drops, disrupting the process. The adsorption process of disrupting atoms by the porous carbon matrix also increased when aberrations in atomic structures increased. Finally, by running this simulation

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and examining the influence of contaminants on water absorption by porous carbon structures, it was discovered that an efficient water treatment procedure might be devised, one of humanity's most pressing concerns [64].

12.5 Applications of Ionic Liquids in Chemical Processes

12.5.1 Preamble

ILs have attracted significant attention in chemical processes due to their unique properties, such as nonvolatility, high thermal stability, and tunable physicochemical properties [65]. These properties make ILs a promising alternative to traditional organic solvents and offer many opportunities for their use in various chemical processes [66]. ILs can be used as reaction media, catalysts, separation agents, and electrolytes in chemical reactions, including organic synthesis, catalysis, extraction, and electrochemistry [67]. This subsection will cover recent applications of ILs in chemical processes, emphasizing their benefits compared to traditional solvents and their potential role in sustainable and eco-friendly chemistry.

12.5.2 Separation and Purification

ILs have shown great potential as separation and purification agents due to their ability to dissolve and extract a wide range of compounds, including polar and nonpolar species. Moreover, the unique physicochemical properties of ILs, such as their high thermal stability, low volatility, and tunable solubility, make them attractive alternatives to traditional solvents in separation and purification processes. This subsection will discuss some recent applications of ILs in separation and purification processes, highlighting their advantages and limitations.

One of the most promising applications of ILs in separation and purification is extracting natural products, such as essential oils, alkaloids, and flavonoids. ILs effectively extract these compounds from plant material, offering advantages over traditional organic solvents regarding selectivity, efficiency, and environmental impact [68]. IL-based extraction processes have also been applied to recover value-added compounds from waste streams, such as phenolic compounds from lignocellulosic biomass [69].

ILs have also been used to separate a wide range of chemicals, including organic acids, aromatics, and carbohydrates, from complex mixtures. The selectivity and efficiency of ILs in these separations depend on the choice of IL, their physicochemical properties, and the operating conditions (e.g. temperature, pressure, and extraction time). ILs have also been applied in separating rare earth elements, offering advantages over traditional solvent extraction methods in terms of selectivity, efficiency, and environmental impact [70].

12.5.3 Reaction Media in Chemical and Biochemical Catalysis

Due to their environmentally friendly physicochemical characteristics, such as their near-zero relative volatility, high electrical conductivity, high polarity and thermal

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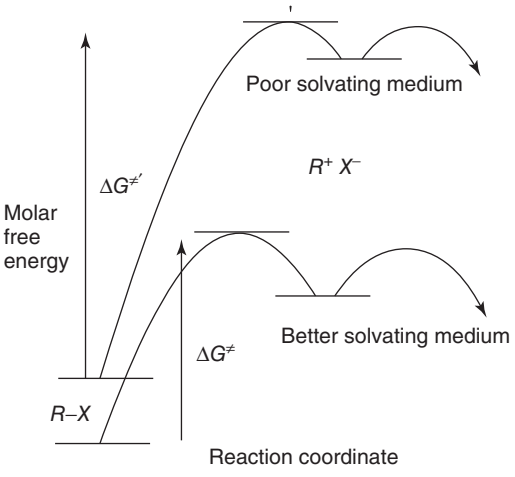

Figure 12.1 Effect ionic liquids on the reactivity of a chemical reaction.

stability, and many other properties, which have been treated in different sections of this chapter, ILs are becoming more significant and have proven to be extremely useful as a suitable media for some chemical processes, thereby substituting some previously known solvents and catalysts. Some examples of reaction media for bioconversions are water, organic solvents, supercritical fluids, two-phase systems, and emulsions.

However, some of the challenges observed in over 85 million organic and inorganic conventional substances registered by CAS are their low volatility, poor miscibility, and other non-friendly properties, which pose complications during chemical reactions. Particularly in organic reactions, water is not a suitable solvent due to its high boiling point. Other conventional solvents are highly volatile in biocatalysis reactions and might threaten the environment. But in contrast, ILs are widely used for organic and inorganic processes, including new processes for pollution reduction. This makes them preferred and highly sought after since other conventional substances pollute the environment and eventually pose major health risks. Due to this fact alone, ILs are quickly being adopted as new technologies for extracting, separating, transforming, and eliminating chemicals [71].

ILs have been commonly used as extraction media in gas–liquid or liquid–liquid equilibria and as reaction media in other non-equilibrium chemical reactions. This is major because of the impact they have on the reactions. For example, Figure 12.1 is a schematic diagram by [71] explaining briefly how ILs may influence chemical reactivity when used as solvents in a chemical reaction. Generally, when reaction rates approach diffusion control, the selectivity of a process decreases as the reactivity increases [71]. And it can be seen from the illustration that ILs tend to actively reduce the free energy of both the initial state (IS) and intermediate stage (TS). In the process, energy is generated, whose magnitude depends on the differential stabilization of IS and TS.

The role of ILs as extraction media has already been discussed in other chapters of this book, but they also have broad applications as reaction media in many different

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processes. For example, they are more cost-effective when used as enzymes in the enzymatic transesterification process. According to Nawshad et al. [72], although the enzymatic transesterification method has several advantages over chemical methods, such as its mild reaction conditions, flexibility in enzyme selection for different substrates, reusability of enzymes, and reduced water requirements resulting in lower waste treatment, the process faces challenges due to the limitations of conventional enzymes. For example, the poor miscibility of solvents like methanol with fats and oils when performing the transesterification reaction forces the process to be conducted in heterogeneous systems involving complicated liquid–liquid interfaces. This produces more waste and also increases costs.

The use of IL as a catalyst in the separation of biodiesel was also referenced in the study. The unique ability of ILs to selectively dissolve various organic, inorganic, and organometallic materials due to their high polarity proved useful in the separation process. While several processes utilizing ionic liquids have yet to be implemented commercially due to ongoing research into their properties, it has been demonstrated that ionic liquids substantially benefit various chemical processes. For instance, in the production of alkoxyphenolphospines, their inclusion significantly diminishes the required amount of reactants, resulting in a considerable enhancement of production capacity [72].

Other applications of ILs are in enzymatic esterification in microreactor devices and special esterification in ionic liquid in integrated systems.

12.6 Future Developments

It is obvious from the preceding discussion that molecular simulations are becoming more important in aiding the development of theoretical knowledge of ILs. In addition to predicting IL properties, MD simulations are often used to help explicate the framework of ILs, such as structure and polarity.

Despite all of the tremendous development, a number of issues persist. For a considerably greater spectrum of materials, reliable force fields must be constructed and confirmed. Many force fields, particularly for imidazolium-based ILs, have been published. Force-field characteristics are still unavailable for several cation and anion types, and many proposed force fields have not undergone thorough validation. In addition to validating established force fields, the development of new force fields for various cation and anion categories is necessary. Developing new force fields is arduous and tedious, yet it is necessary if molecular simulations are to be employed to drive the creation of novel ILs. The use of molecular simulations will dwindle until new force fields are developed that allow for the investigation of a wide variety of probable ILs.

The methods used to run simulations are another key area where improvements can be made. As previously stated, one of the most challenging parts of modeling ILs is that their dynamics are typically slow, making conformational sampling problematic. The difficulty is particularly challenging in MD simulations with predictable trajectories. There is a need to find a method that allows for rapid

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simulations and an extended timescale, allowing for the simulation of complex systems for longer durations.

12.7 Conclusion

The study of ILs is a rapidly evolving field with exciting potential for a wide range of applications. ILs have distinct characteristics such as high solubility, a wide temperature range, and low vapor pressure, making them a desirable alternative to conventional solvents in different industries. Although the development of reliable force fields and slow dynamics in simulations pose challenges, significant advancements have been made in comprehending the molecular-level behavior of these novel substances.

In particular, advances in molecular simulations have provided valuable insights into the structure, dynamics, and properties of ILs. These theoretical models have helped predict ILs' behavior in different conditions and design new ILs with specific properties. Furthermore, research into the application of ILs in separation and purification, catalysis, and electrochemistry has shown promising results, highlighting the potential of these materials to drive sustainable and environmentally friendly chemical processes.

Looking ahead, further research into the behavior of ILs at the molecular level will be crucial in enabling their widespread use in industry. Developing new force fields and methods to overcome the slow dynamics of simulations will be necessary. Additionally, interdisciplinary collaboration between researchers in different areas will be necessary to fully realize ILs' potential in various applications. Overall, studying ILs presents an exciting opportunity for researchers to address some of the major challenges faced by the chemical industry and develop sustainable solutions for the future.

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