Understanding SO\textsubscript{2} Capture by Ionic Liquids

Anirban Mondal and Sundaram Balasubramanian\textsuperscript{*}

Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560 064, India

ABSTRACT: Ionic liquids have generated interest for efficient SO\textsubscript{2} absorption due to their low vapor pressure and versatility. In this work, a systematic investigation of the structure, thermodynamics, and dynamics of SO\textsubscript{2} absorption by ionic liquids has been carried out through quantum chemical calculations and molecular dynamics (MD) simulations. MP2 level calculations of several ion pairs complexed with SO\textsubscript{2} reveal its preferential interaction with the anion. Results of condensed phase MD simulations of SO\textsubscript{2}–IL mixtures manifested the essential role of both cations and anions in the solvation of SO\textsubscript{2}, where the solute is surrounded by the “cage” formed by the cations (primarily its alkyl tail) through dispersion interactions. These structural effects of gas absorption are substantiated by calculated Gibbs free energy of solvation; the dissolution is demonstrated to be enthalpy driven. The entropic loss of SO\textsubscript{2} absorption in ionic liquids with a larger anion such as [NTf\textsubscript{2}]\textsuperscript{−} has been quantified and has been attributed to the conformational restriction of the anion imposed by its interaction with SO\textsubscript{2}. SO\textsubscript{2} loading IL decreases its shear viscosity and enhances the electrical conductivity. This systematic study provides a molecular level understanding which can aid the design of task-specific ILs as electrolytes for efficient SO\textsubscript{2} absorption.

INTRODUCTION

Sulfur dioxide (SO\textsubscript{2}), a dominant air pollutant, is released into the atmosphere through the combustion of fossil fuels for energy conversion. For instance, the gas emission from coal plants contains 0.3–5% of SO\textsubscript{2}. It is extremely important to control and minimize this outflow, as it is harmful to environment and causes health hazards.\textsuperscript{1}

Another important aspect concerning SO\textsubscript{2} is its use as a component in lithium–sulfur dioxide (Li–SO\textsubscript{2}) batteries.\textsuperscript{2} Li–SO\textsubscript{2} system is a class of primary battery which is longer-lasting than alkaline ones, metal-air batteries etc., with high energy density, wherein the inexpensive SO\textsubscript{2} can be used as the active cathode material.\textsuperscript{3} Also, Li–SO\textsubscript{2} battery has some inherent advantages in contrast to other primary batteries, such as alkaline batteries,\textsuperscript{4} and metal-air batteries.\textsuperscript{5} For instance, Li–SO\textsubscript{2} battery has a high energy density (up to 330 Wh kg\textsuperscript{−1}, i.e., 2–4 times higher than those of alkaline batteries) and good discharge performance with working voltage around 3.0 V.\textsuperscript{2}

These unique characteristics have made Li–SO\textsubscript{2} batteries to be useful for applications requiring long service life which is beyond the reach of conventional primary batteries.

In spite of these positive attributes, safety issues associated with Li–SO\textsubscript{2} batteries restrict its applications;\textsuperscript{3} the cell is comprised of liquefied SO\textsubscript{2} under pressure, and this constrains the upper limit of pressure that it can resist without leaking toxic SO\textsubscript{2} being 3.4 atm at 294 K.\textsuperscript{2} Moreover, the electrolyte, acetonitrile being used in a Li–SO\textsubscript{2} battery is volatile in nature and can lead to an uncontrolled increase in pressure, resulting in the risk of fire. A great deal of effort has focused on the search for electrolyte solvents which have low vapor pressure, and are less reactive too.\textsuperscript{6,7}

In light of these facts, there is general interest to develop new materials for the efficient, reversible, and economical capture of SO\textsubscript{2} which can also function as electrolytes. Traditional technologies developed over the years for flue-gas desulfurization (FGD) includes limestone scrubbing, ammonia scrubbing, and absorption by organic solvents.\textsuperscript{8,9} As an alternative, ionic liquids (ILs) have manifested their efficacy as better absorbents for acidic gases such as SO\textsubscript{2},\textsuperscript{10–13} and CO\textsubscript{2},\textsuperscript{14–18} owing to their properties such as low vapor pressure, high thermal and chemical stability, wide liquid temperature range, nonflammability, and tunable properties.\textsuperscript{19–21} Three types of interactions such as physical, chemical or hybrid (physical and chemical), play important roles in the solubility of SO\textsubscript{2} in ILs.\textsuperscript{12,16,23–24} However, an effective capture of SO\textsubscript{2} from flue gases entails chemical absorption because of low partial pressure in flue gases.\textsuperscript{25} Han et al. demonstrated the first example of SO\textsubscript{2} capture by chemisorption in a functionalized IL, namely, tetramethylguanidinium lactate ([TMG][L]).\textsuperscript{26} Subsequently, several other functionalized ILs were explored for effective SO\textsubscript{2} capture, including hydroxyl ammonium ILs,\textsuperscript{26} imidazolium ILs,\textsuperscript{22,23,27–29} TMG-based ILs,\textsuperscript{12} phenolate-based ILs,\textsuperscript{30} and supported ionic liquid membranes (SILMs).\textsuperscript{31–35} In general, the chemisorption of SO\textsubscript{2} is based on strong interactions between SO\textsubscript{2} with the electronegative oxygen atom or nitrogen atom in the anion.\textsuperscript{24,34,35} Recently, a new strategy was developed for improving SO\textsubscript{2} capture through multiple-site...
The observed trend of SO2 solubility in ionic liquids from experimental measurements is not entirely conclusive. Jiang et al. reported the solubility of SO2 in imidazolium based ILs in the order [BMIM][BF4] > [BMIM][NTf2] > [BMIM][PF6] at 298 K and 1 bar. In another study, the order in SO2 solubility in [BMIM]+ based ILs was seen to be [OAc]− > [NTf2]− > [BF4]− > [PF6]−. In a recent work, Dai and co-workers reported the SO2 solubility in imidazolium ILs in the following order, [SCN]− > [Cl]− > [NTf2]− at 296 K and 1 atm.

Molecular simulations are frequently employed to understand microscopic interactions. In recent years, several molecular simulation studies to understand gas absorption in ILs have been undertaken. Maginn et al. investigated the structure and dynamics of 1-butyl-3-methylimidazolium bromide ([BMI][Br]) IL on addition of SO2 using MD simulations and Raman spectroscopy. Wick and co-workers employed a polarizable force field to examine the binding of CO2 and SO2 at the air/liquid interface of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]-[BF4]). A minimum in free energy was observed at the interface. The nature of interactions between acidic gases at the interface of ILs was further studied using Gibbs free energy of solvation by many research groups.

As mentioned above, most studies have focused on interactions in CO2−IL mixtures, while only a few have been devoted to SO2−IL mixtures. Furthermore, a systematic study of interactions of SO2 at IL interface and its anion dependence is lacking. Needless to state, a fundamental understanding of interactions between ILs and SO2 is extremely important for the further design of new ILs for SO2 absorption. The present work is aimed in this direction and examines the anion dependence of SO2 capture in eight ionic liquids using MD simulations and quantum chemical calculations. On the basis of the solvation free energy and binding energies of SO2 in ILs, we find the IL with the thiocyanate anion to be the most suited for SO2 absorption.

**COMPUTATIONAL DETAILS**

ILs, all having 1-butyl-3-methylimidazolium ([BMIM]+) as the cation, and the following anions, chloride ([Cl]−), nitrate ([NO3]−), tetrafluoroborate ([BF4]−), hexafluorophosphate ([PF6]−), triflate ([CF3SO3]−), bis(trifluoromethanesulfonyl)imide ([NTf2]−), acetate ([OAc]−), and thiocyanate ([SCN]−) were studied. These are displayed in Figure 1. The atom labeling in [BMIM]+ cation is shown in Figure 2. Three different approaches were utilized to study SO2−IL interactions: (i) quantum chemical (QM) calculations, (ii) classical molecular dynamics (MD) simulations, and (iii) free energy (FE) calculations based on point ii.

**QM Calculations.** Systems, each of isolated IL ion pair, SO2 molecule, and SO2−IL complex (one SO2 molecule and one IL ion pair) were geometry optimized at MP2/aug-cc-pVQZ level of theory. Five different initial conditions were constructed using Gaussian software, wherein the SO2 molecule was kept near H1, H3, or H4 sites. Optimized minima on the potential energy surface were confirmed via frequency analysis. Binding energy (BE) was estimated as the energy difference between the complex and the sum of the energy of components.
The initial configurations were generated with the program Packmol.\textsuperscript{52} Experimental observations suggest that SO\textsubscript{2} is soluble in all ILs studied here up to at least 0.5 mol fraction at 298 K. Thus, the simulations of bulk solutions were performed in a cubic box containing 256 cations, 256 anions, and 128 SO\textsubscript{2} molecules to obtain a molar ratio of 0.5. Simulations were carried out at 298 K in order to compare the results against reported experimental properties (although [BMIM][Cl] is solid at 298 K, the simulations for SO\textsubscript{2} loaded [BMIM][Cl] system was also performed at 298 K for the sake of comparison). All the systems were equilibrated in the NPT ensemble for 10 ns duration. It was followed by another 5 ns equilibration in the NVT ensemble. Finally, a 48 ns production run was generated in the NVT ensemble. The simulated box dimensions for all SO\textsubscript{2}−IL mixtures are tabulated in Table S1 of Supporting Information. For purpose of comparison, a separate simulation was performed with CO\textsubscript{2} loaded ionic liquid system at 298 K. The systems were visualized in VMD.\textsuperscript{76}

Transport properties such as self-diffusion coefficient, shear viscosity and electrical conductivity were calculated using equilibrium Green−Kubo relations discussed earlier.\textsuperscript{50,77}

Free Energy Calculations. All the FE simulations were carried out employing the colvars module\textsuperscript{68} as implemented in LAMMPS.\textsuperscript{68} The solvation free energy (SFE) can be defined as the energy required to bring one SO\textsubscript{2} molecule into bulk IL from the gas phase. A simulation cell containing 256 ion pairs was equilibrated in the NPT ensemble at 298 K for 8 ns ([BMIM][Cl] at 353 K, as it is a solid at room temperature). To create a liquid−vapor interface, the cell length along z-axis was stretched to 200 Å, and then the system was further equilibrated in the NVT ensemble for 2 ns. This was followed by FE calculations in the NVT ensemble. Colvar style “distance Z” was employed in determining the free energy profile using the adaptive biasing force (ABF) method.\textsuperscript{79} The distance between the center of mass (COM) of IL molecules and the center of mass of SO\textsubscript{2} molecule was used to define the reaction coordinate (RC) (see Figure S1 of the Supporting Information). Four nonoverlapping windows along the Z direction were created to divide the whole reaction coordinate, spanning from 0 to 50 Å. The first and last window represents SO\textsubscript{2} to be completely submerged in bulk IL and completely in gas phase, respectively. ABF forces were applied every 500 steps with a bin width of 0.1 Å. In each window, an average sampling ratio of 5 between the highest and lowest point was achieved, after running for at least 40 ns.

## RESULTS AND DISCUSSION

Quantum Chemical Analysis. The computed binding energies (BE) at MP2/aug-cc-pVDZ level of theory for SO\textsubscript{2}−IL complexes are tabulated in Table 1. Aparicio et al. investigated the interaction strength in a pool of SO\textsubscript{2}−IL systems by decomposing the total BE into cation−anion, SO\textsubscript{2}−cation, and SO\textsubscript{2}−anion contributions.\textsuperscript{51} They observed SO\textsubscript{2}−anion interactions to be the major contribution to total BE for SO\textsubscript{2}−IL systems. In our calculations, BE varies between $-31.38$ kJ/mol ([BMIM][NTf\textsubscript{2}]) and $-82.19$ kJ/mol ([BMIM][SCN]) (see Table 1).

Table 1. BSSE Corrected Binding Energies (BE) of SO\textsubscript{2}−Ion Pair Systems at the MP2/aug-cc-pVDZ Level of Theory

<table>
<thead>
<tr>
<th>SO\textsubscript{2}−IL system</th>
<th>BE (kJ mol\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM][SCN]</td>
<td>$-82.19$</td>
</tr>
<tr>
<td>[BMIM][Cl]</td>
<td>$-72.17$</td>
</tr>
<tr>
<td>[BMIM][OAc]</td>
<td>$-59.12$</td>
</tr>
<tr>
<td>[BMIM][CF\textsubscript{3}SO\textsubscript{2}]</td>
<td>$-57.78$</td>
</tr>
<tr>
<td>[BMIM][NO\textsubscript{3}]</td>
<td>$-54.68$</td>
</tr>
<tr>
<td>[BMIM][BF\textsubscript{4}]</td>
<td>$-49.51$</td>
</tr>
<tr>
<td>[BMIM][PF\textsubscript{6}]</td>
<td>$-40.05$</td>
</tr>
<tr>
<td>[BMIM][NTf\textsubscript{2}]</td>
<td>$-31.38$</td>
</tr>
</tbody>
</table>

Table 1)

Among the systems studied, there appears to be more than one approach for the SO\textsubscript{2} molecule to interact with the IL cations. Anions such as [Cl]− or [SCN]− prefer to be located above the imidazolium ring plane whereas SO\textsubscript{2} interacts along the C\textsubscript{1} site on cation. However, anions like [BF\textsubscript{4}]−, [NO\textsubscript{3}]−, and [TFO]−, interact along the most acidic site on cation (C\textsubscript{D}) and SO\textsubscript{2} prefers to stay above the ring plane, interacting with H\textsubscript{3} hydrogens. In the acetate system, both the anion as well as SO\textsubscript{2} prefer to be in the same plane as that of the imidazolium ring; while acetate anion shows very strong interaction with the acidic proton (H\textsubscript{a}), SO\textsubscript{2} interacts with H\textsubscript{3} sites. But, in systems such as [PF\textsubscript{6}]− and [TFSO\textsubscript{2}]−, SO\textsubscript{2} and the anion are located on either side of the imidazolium ring, resulting in minimal SO\textsubscript{2}−anion interaction among all SO\textsubscript{2}−IL system examined here. The same can be seen in the BE values for SO\textsubscript{2}−IL system having either [PF\textsubscript{6}]− or [TFSO\textsubscript{2}]−. The minimum energy structures of SO\textsubscript{2}−IL complexes are displayed in Figure 3 and Figure S2 of Supporting Information.

Charge transfer between SO\textsubscript{2} and IL has been reported earlier,\textsuperscript{51} which can be used to understand the gas absorption capacity. The charge transfer between the ion pair and SO\textsubscript{2} molecule is calculated as the difference in total charge on SO\textsubscript{2} molecule in the isolated state and in the SO\textsubscript{2}−IL complex and the same is tabulated in Table S2 of Supporting Information. In all the systems studied here, the total charge on SO\textsubscript{2} molecule is negative; this implies that charge is transferred to the SO\textsubscript{2} molecule from the ion pair. A linear relationship between the BE and charge transfer in these complexes is observed (Figure 4). The trend in observed experimental solubility\textsuperscript{2,31,41} ties with that of the BE and points to the enthalpic nature of SO\textsubscript{2} solvation in ILs.

Liquid Structure. To obtain an insight into the effect of SO\textsubscript{2} on the structure of ILs, we compared cation−anion and anion−H\textsubscript{a} radial distribution functions (RDFs) in the pure IL and in SO\textsubscript{2} loaded ILs (see Figure S3 of the Supporting Information). No significant changes were observed in these pair correlation functions upon SO\textsubscript{2} inclusion, which is consistent with previous MD simulations of SO\textsubscript{2} loaded ILs.\textsuperscript{56,57,80} SO\textsubscript{2} solvation in ILs was further investigated through RDFs between the center of mass (COM) of the ions and that of SO\textsubscript{2} and the same are shown in Figure S4a of the Supporting Information and Figure 5. Anions interact with the solute better than cations do. Within its first coordination sphere, the SO\textsubscript{2} molecule is surrounded by around 1.5 anions and 5.5 cations (see Table S3 of the Supporting Information). The presence of such high cation to anion ratio (which was also seen in many instances for CO\textsubscript{2} solvation in ILs,\textsuperscript{51,82} as well as for SO\textsubscript{2} solvation in [EMIM][SCN] from an ab initio MD study\textsuperscript{57}) suggests a possible formation of “cation cage” around SO\textsubscript{2}. Thus, it is worth investigating in more detail the role of contributing sites and compare them against results for CO\textsubscript{2} solvation by ILs.

We have examined various site−site RDFs to unveil the role of specific interactions in SO\textsubscript{2} solvation and these are displayed in Figure 6 and Figure S4b of the Supporting Information. The cation hydrogen atoms, e.g., H\textsubscript{a} and H\textsubscript{3} possess a stronger...
interaction with SO$_2$ (than HA as is evident from the well-defined and sharp peak around 2.6−2.7 Å in Figure 6). The coordination numbers (integrated RDFs up to 3.5 Å) suggest that SO$_2$ molecule is surrounded by more H$_1$ atoms (1.65) than HB atoms (0.75), which is consistent with the preference seen in gas phase quantum chemical calculations. Interestingly, the acidic hydrogen (HA) atom having a strong interaction with anion (see Figure S3 of Supporting Information), also shows notable contact with SO$_2$, indicated by a sharp rise at short distance of 2.2 Å in Figure S4b, but its peak height is lower than that with either the HB or H$_1$ (Figure 6). It is followed by a small hump at around 4.2 Å and broad peak around 6 Å. On the contrary, the interaction of CO$_2$ with IL cation is primarily driven by the dispersion between solute and alkyl side chain, as no such direct contact between oxygen of CO$_2$ and the acidic hydrogen atom (H$_A$) on imidazolium ring was observed in a simulation of CO$_2$−IL solution (Figure S5 of Supporting Information) and in previous reports as well.$^{81,82}$ Thus, the considerably higher solubility of SO$_2$ than CO$_2$ in ILs might be a consequence of the crucial contrast in their structure of the solvation shell.

Spatial distribution functions (SDFs) were examined to validate these structural correlations. Figure 7 displays the computed SDFs of the anion and SO$_2$ molecule around the center of ring of the imidazolium cation, at isosurface values of 0.006 and 0.003 Å$^{-3}$, respectively. It is evident from Figure 7 that there is a hole in the density map of SO$_2$ exactly on top of the HA atom. Instead, the density map of SO$_2$ is condensed around sites such as HB and H$_1$, indicating binding preferences for SO$_2$ with these sites. Anions show stronger binding toward the most acidic hydrogen atom (HA) located on the cation ring.
(see anion density map in Figure 7) than the neutral SO$_2$ molecules do. Consequently, SO$_2$ interacts with the other hydrogen atoms on cation, i.e., H$_6$ and H$_1$. These observations are in agreement with the RDF analysis and gas phase quantum chemical calculations. Spatial distributions of cation ring center and of SO$_2$ molecule around the center of mass of the anion are displayed in Figure 8. Although both cation and SO$_2$ share the same space around the anion, the latter interacts from a shorter distance than the former. A similar phenomenon was also observed in their respective radial distribution functions (see Figure S6 of Supporting Information). The more electron rich centers in anion e.g. oxygens of [OAc]$^-$, [NO$_3$]$^-$, [TFO]$^-$, etc. are more preferred over the other sites by the cation and SO$_2$.

In order to quantify the arrangement of the anion and SO$_2$ around the cation ring plane, combined distribution functions (CDFs) were calculated.$^{83,84}$ Figure 9 shows the same for [BMIM][Cl]–SO$_2$ (see Figure S7 of Supporting Information for such data for other ILs). As described earlier, the acidic hydrogen atom H$_A$ exhibits pronounced interaction with the anion rather than with the SO$_2$ molecule. Figure 9a and c indicate that the probability for anions to be located closer to this acidic hydrogen and more linear to the C$_6$–H$_A$ bond is higher than that for SO$_2$. Similar conclusions can be drawn for other anions as shown in Figure S7 of Supporting Information.

The CDFs depicting the coordination at acidic hydrogen atom reveal that the anion interacts directly toward the H$_A$ atom (in-plane arrangement) and this directionality is most intense in [BMIM][Cl] and least in [BMIM][TFSO]. This trend can be justified based on the reduced acceptor probability due to larger charge delocalization in anions such as [PF$_6$]$^-$, [TFSO]$^-$ etc. However, the orientation of SO$_2$ molecule toward the acidic hydrogen atom is independent of the anion. It is evident from Figure 9b,d (also Figure S7 of Supporting Information) that the anion is likely to be present on-top of the imidazolium ring too at short distances when compared to that of SO$_2$ distribution. These observations further substantiate the fact that SO$_2$ is
more likely to be found near the methyl hydrogen atoms (H$_1$) which was also seen in RDF analysis and gas phase DFT calculations.

**Thermodynamics of SO$_2$ Absorption.** The potential of mean force (PMF) for bringing the solute, SO$_2$, from its vapor phase into the bulk IL was calculated. The free energy profiles for SO$_2$ solvation in various ILs consisting [BMIM]$^+$ as the common cation combined with different anions are displayed in Figure 10. Solvation free energy (SFE) is the difference in the free energies between the vapor phase and the solvated state of the solute in the IL. The SFE profiles become zero around 42 Å in most ILs, except in [BMIM][Cl]. This is due to the smaller thickness of the [BMIM][Cl] liquid slab (see Figure S8 of Supporting Information). As the SO$_2$ approaches the liquid region, the PMF displays a monotonic decay and it becomes most negative at the air–IL interface. The PMF increases in value in the bulk region, before converging to a constant value.

Similar kinds of PMF profiles were observed in earlier gas absorption studies in ILs. The occurrence of the minimum near the air–IL interface in the SO$_2$ PMF clearly reveals a preference for the solute to be at the interface. Further, Figure 11 presents the PMF along with the number density profile of various sites on cation and anion in [BMIM][NO$_3$] (see Figure S9 of Supporting Information for other ILs). It is evident that the minimum in SO$_2$ PMF coincides with the maximum in C$_1$ number density at the interface, which confirms the preferable interaction of SO$_2$ with H$_1$ atoms over other sites of the cation. The cation alkyl chain is oriented normal to the liquid–vapor interface, which can enhance the gas solubility through dispersion interaction with SO$_2$ (also seen from the bulk liquid structure).

In a liquid system which is in equilibrium with its vapor phase, the change in potential energy across the vapor–liquid interface is presumed to be the same as the enthalpy change. Thus, the relative solubility of SO$_2$ in different ILs can be understood in terms of enthalpy and entropy contributions. The trend in SFE determined using an empirical force field can be correlated to the binding energy of one ion pair with a SO$_2$ molecule (computed at MP2/aug-cc-pVDZ level of theory) and a linear correlation is displayed in Figure 12. This observation suggests that the SO$_2$ solvation in ILs is largely enthalpy driven. In addition, the energetic and entropic contributions to SFE were determined through two additional simulations. In one, a solute SO$_2$ molecule was kept 40 Å away from the bulk IL region, i.e., clearly in the vapor phase. The other one contained the SO$_2$ molecule submerged inside the bulk IL. The simulation box dimensions, temperature etc. were kept the same as in those described in the Free Energy Calculation section. Both the systems were equilibrated in the NVT ensemble for 8 ns duration (see Figure S10 of the Supporting Information).

The difference in potential energy between these two equilibrated systems was taken as the enthalpy change ($\Delta U$) for SO$_2$ solvation. The entropy contribution to the dissolution process is obtained as the difference between the solvation free energy and the potential energy and the same is tabulated in Table 2. In most of the ILs, the change in entropy with respect to the energy difference is moderate. However, in the case of [BMIM][NTf$_2$], the relative entropy contribution is much higher than in rest of the ILs, resulting in it becoming a poor solvent for SO$_2$ solvation. Further investigation suggests that the addition of solute SO$_2$ in the bulk ILs stretches the cation marginally (see Figure S11 of Supporting Information). For the smaller anions such as [SCN]$^-$, [OAc]$^-$, [CF$_3$SO$_3$]$^-$, [BF$_4$]$^-$, [PF$_6$]$^-$ etc. there is no conformational change and thus
no change in geometry, upon addition of SO2. However, [NTf2]− being larger in size, can be rotationally excited and thus have different conformational preferences with and without SO2. Figure 13 displays the distribution of distances between the terminal fluorine atoms in [NTf2]− anion in pure [BMIM][NTf2] and in 50% SO2 loaded [BMIM][NTf2] mixture.

![Figure 13](image-url)

**Figure 13.** Distribution of distance between the terminal fluorine atoms of [NTf2]− anion in pure [BMIM][NTf2] and in 50% SO2 loaded [BMIM][NTf2] mixture.

Table 2. Changes in Free Energy (ΔG = G_gaq − G_sol), Enthalpy (ΔU = U_gaq − U_sol), and Entropy (TΔS = S_gaq − S_sol) for SO2 Solvation in Various ILs

<table>
<thead>
<tr>
<th>IL</th>
<th>ΔG (kJ/mol)</th>
<th>ΔU (kJ/mol)</th>
<th>TΔS (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SCN]−</td>
<td>−12.84</td>
<td>−53.68</td>
<td>−40.84</td>
</tr>
<tr>
<td>[Cl]−</td>
<td>−12.38</td>
<td>−89.41</td>
<td>−77.03</td>
</tr>
<tr>
<td>[OAc]−</td>
<td>−11.84</td>
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<td>−63.51</td>
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<tr>
<td>[CF3SO3]−</td>
<td>−11.55</td>
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<td>−23.68</td>
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<tr>
<td>[BF4]−</td>
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<td>[NO3]−</td>
<td>−10.50</td>
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<tr>
<td>[NTf2]−</td>
<td>0.502</td>
<td>−43.89</td>
<td>−44.39</td>
</tr>
</tbody>
</table>

“ΔS is a derived quantity from ΔG and ΔU. [BMIM]+ is the cation.

Table 3. Henry’s Law Constant (K_H) of SO2 in Studied ILs at 298 K and P = 1 atm

<table>
<thead>
<tr>
<th>IL</th>
<th>K_H (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM][SCN]</td>
<td>0.77</td>
</tr>
<tr>
<td>[BMIM][Cl]</td>
<td>1.01</td>
</tr>
<tr>
<td>[BMIM][OAc]</td>
<td>1.08</td>
</tr>
<tr>
<td>[BMIM][CF3SO3]</td>
<td>1.21</td>
</tr>
<tr>
<td>[BMIM][BF4]</td>
<td>1.49</td>
</tr>
<tr>
<td>[BMIM][NO3]</td>
<td>2.08</td>
</tr>
<tr>
<td>[BMIM][PF6]</td>
<td>2.80</td>
</tr>
<tr>
<td>[BMIM][NTf2]</td>
<td>5.72</td>
</tr>
</tbody>
</table>

“The temperature is 353 K.

Thus, [BMIM][SCN] is the most preferred solvent for SO2 capture, while [BMIM][NTf2] fares the worst. It is interesting to note that the solubility of SO2 is more in ILs with smaller molar volumes.55 Enthalpic contributions as captured through gas phase calculations and bulk MD simulations largely determine SO2 solubility in ILs. These observations are important in further design of functional ionic liquids for SO2 capture.

**Dynamics in SO2–IL Mixtures.** Ion self-diffusion coefficients in pure IL and SO2–IL mixtures are computed from mean square displacement (see Figure S12 of the Supporting Information) and are compared in Table 4. Ionic diffusion in SO2–IL mixture is higher than in pure ILs, which was also seen in previous MD simulations.53,56,58,61 Likewise, shear viscosity and ionic conductivity are affected by the dissolution of SO2 in ILs. Computed viscosity and electrical conductivity are presented in Table 5. In accordance with both experimental and simulation results,5,13,53,56,58 the dissolution of SO2 reduces the viscosity and enhances the electrical conductivity of the liquid. The transport coefficient values obtained from Green–Kubo relations for ILs [BMIM][NTf2] and [BMIM][SCN] showed adequate agreement with experimental measurements.
Table 5. Shear Viscosity, $\eta$ (mPa·s) and Electrical Conductivity, $\sigma$ (S·m$^{-1}$) in Pure IL and SO$_2$–IL Mixtures at 298 K

<table>
<thead>
<tr>
<th>IL</th>
<th>$\eta$ pure</th>
<th>$\eta$ mix</th>
<th>$\sigma$ pure</th>
<th>$\sigma$ mix</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM][SCN]</td>
<td>35.20</td>
<td>14.05</td>
<td>0.62</td>
<td>1.34</td>
</tr>
<tr>
<td>[BMIM][OAc]</td>
<td>191.5</td>
<td>62.19</td>
<td>0.07</td>
<td>0.31</td>
</tr>
<tr>
<td>[BMIM][CF$_3$SO$_3$]</td>
<td>65.00</td>
<td>32.21</td>
<td>0.25</td>
<td>0.66</td>
</tr>
<tr>
<td>[BMIM][BF$_4$]</td>
<td>71.00</td>
<td>26.39</td>
<td>0.42</td>
<td>1.06</td>
</tr>
<tr>
<td>[BMIM][NO$_3$]</td>
<td>129.0</td>
<td>50.38</td>
<td>0.31</td>
<td>0.76</td>
</tr>
<tr>
<td>[BMIM][PF$_6$]</td>
<td>185.0</td>
<td>72.19</td>
<td>0.17</td>
<td>0.51</td>
</tr>
<tr>
<td>[BMIM][NTE]</td>
<td>42.00</td>
<td>18.27</td>
<td>0.29</td>
<td>0.79</td>
</tr>
</tbody>
</table>

*The temperature is 300 K.*

available at low SO$_2$ loading.$^2$ Although SO$_2$ has been reported to be reactive with some ionic liquids,$^{20,28}$ its effect on the IL viscosity is unknown. However, the viscosity of ionic liquids increases drastically upon chemisorption of CO$_2$.$^{57,58}$ In the present work, we assume the physisorption of SO$_2$ in ILs and thus the viscosity of the solution decreases with respect to the neat IL.

**CONCLUSIONS**

A microscopic understanding behind the solvation of SO$_2$ is important to obtain in order to interpret its solubilities in different ionic liquids. In this contribution, we have employed molecular dynamics simulations and *ab initio* calculations to provide a detailed understanding of the dissolution of SO$_2$ in ionic liquids and consequent changes in their structure and transport coefficients.

Gas phase quantum chemical calculation results indicated the propensity of both the cation and anion to interact with the SO$_2$ molecule. Strong charge transfer interaction between the anion and SO$_2$ molecule was also observed. A linear correlation between the binding energy of SO$_2$ with the ion pair and the net charge transfer (primarily from the anion to the SO$_2$ molecule) evidenced the anion–SO$_2$ interaction as the major contribution in SO$_2$ capture in ILs. Binding energy values ranged from $-31.38$ kJ/mol ($\text{[BMIM][NTf}_2\text{]}$) to $-82.19$ kJ/mol ($\text{[BMIM][SCN]}$). Thus, $\text{[SCN]{−}}$ emerged as the best anion to provide high SO$_2$ capture efficiency.$^2$

Condensed phase MD simulations of SO$_2$–IL mixtures revealed the significant role of both cations and anions in the SO$_2$ dissolution process. SO$_2$ molecule was found to be surrounded by the cations through dispersion interaction, mainly with the alkyl group which leads to the formation of a “cage cage” around SO$_2$. On the other hand, less than a pair of anions were present within the first coordination shell of the solute. Thus, SO$_2$ shares favorable interactions with both the cation and the anion. The dynamical consequences of the dissolution of SO$_2$ in IL are the significant decrease in the shear viscosity and a resultant increase in diffusion coefficient and electrical conductivity.

The free energy profiles for SO$_2$ dissolution obtained from MD simulations demonstrate the preference for the solute to be located at the IL-vapor interface relative to the bulk liquid; the same can be rationalized from the richness of the cation alkyl groups at the interface. A nearly linear relationship between the solvation free energy and the gas phase binding energy of SO$_2$ with the ions is observed which points to the enthalpic nature of SO$_2$ dissolution in ILs. Thus, a good solvent for SO$_2$ capture must possess good hydrogen bond donor ability in the cation and a strong interaction with the anion. The calculated solubility order, based on the Henry’s law constant of SO$_2$ in various ILs, indicates [BMIM][SCN] to be the best solvent for SO$_2$ dissolution, which was also reported earlier experimentally.$^2$

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.6b02553.

Charge transfer in IL–SO$_2$ complexes, reaction coordinate for SFE calculations, minimum energy structures of IL–SO$_2$ complexes, RDFs, CDFs, coordination numbers, mass density profiles, potential energy of SO$_2$ in ILs, and MSDs (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

*S.(B.) E-mail: bala@jncasr.ac.in. Telephone: +91 (80) 2208 2808. Fax: +91 (80) 2208 2766.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We thank DST for support. SB thanks Sheikh Saqr Laboratory, JNCASR for a senior fellowship. We thank the Centre for the Development of Advanced Computing, Bangalore, where a part of the computations were carried out.

**REFERENCES**


