

Simulation Based Insight into Solvation Properties of Ferric Chloride Based Eutectic Solvent

Farouq S. Mjalli*, Dhawal Shah

Petroleum and Chemical Engineering Department, Sultan Qaboos University, 123, Oman
farouqsm@yahoo.com

Our experiments on desulfurization of liquid fuels reveals suitability of novel type I deep eutectic solvents (DES) as potential solvents for thiophenic compounds. While the results are intriguing, molecular interactions leading to the solubility remains unclear. We herein, perform Molecular Dynamics (MD) simulations on tetrabutylphosphonium bromide/ferric chloride (TBP.Br-Fe.Cl₃), a DES which showed higher affinity to thiophenic compounds. Simulations on the DES itself shows a preference of chloride ion by TBP over the bromide ion, forming a TBP.Cl.Br complex structure, which possibly explains the freezing point depression associated with formation of the DES. MD analysis of the DES in the presence of thiophene and dibenzothiophene (DBT) shows strong interactions between sulphur-based central ring of these compounds with the TBP ion. Further work need to be done on optimizing these results for possible extraction of sulfur-based solutes from liquid fuels.

1. Introduction

Fossil liquid fuels contain a variety of sulfuric compounds in different forms. The content of these compounds may vary depending on the type of fuel as well as the separation and purification technologies involved in the fuel production processes. The existence of such thiophenic-based compounds result in the release of sulfur oxides in the burned fuels from engines and industrial complexes. This consequently negatively affects the natural ecosystems and degrades industrial equipment. In a global effort for a remedial solution, the international community adopted stringent regulations aimed at producing ultralow sulfur content fuels. In this context, new technologies are being under continuous research for the deep desulfurization of fuels. Among these technologies, extractive desulfurization (EDS) show great promise in this sector. These separation methods, in contrast to the widely spread hydrodesulfurization (HDS), are employed at mild operating conditions and without the utilization of hydrogen and expensive catalyst (Nie et al. 2007).

The practical implementation of EDS depends heavily on the efficiency of the used solvent, its cost, recyclability and environmental friendliness. Recently, ionic liquids (ILs) and their analogues (usually termed Deep Eutectic Solvents, DES) have shown great potential as possible solvents for sulfuric compounds (Kulkarni and Afonso 2010). The literature list of publications in this theme is increasing rapidly (Gao et al. 2008). Having many of the favorable properties of ILs, DES are considered as cheaper alternatives with better environmental footprint (Ru and Konig 2012). One class of DES that show effective desulfurization efficiency is the one made by mixing a quaternary ammonium or phosphonium salt with a metal halide. Gano et al. (2014), reported a novel type of DES based on anhydrous ZnCl₂ or FeCl₃ for the removal of refractory-sulfur containing compounds namely: thiophene (TH) and dibenzothiophene (DBT) from simulated diesel fuel. Their solubility studies revealed that FeCl₃ based DESs were capable of dissolving all thiophene and more than 90 wt% of DBT in the fuel. These are very encouraging results as compared to the best desulfurization efficiencies attained by ILs that does not exceed a sulfur removal efficiency of 80% (Gano et al. 2014).

While many desulfurization studies were performed using strict experimental methods, no study has been attempted to conduct such investigations using computational methods. Atomistic simulations have the merit

of providing a fundamental understanding and insight in the extraction process on a molecular level. They are also useful in facilitating simulation of the process under extreme operating conditions that cannot be attained with conventional experimental ones (Argyris et al. 2011). More importantly, these computational methods help in exploring new solvent systems and screen optimum ones among many alternatives in the most economical way (Jayaraman 2009). However, they are not intended to replace experiments but to complement them and optimize their application.

In this study, a molecular level approach is implemented to study this extraction process aiming to understand the interactions between the DES constituents as well as that between the DES from one side and sulfuric compounds in the other side. The study sheds the light on the factors affecting the freezing point depression associated with the formation of the DES. In addition, the mutual solubilities of the sulfuric compounds are investigated and proper reasoning for the type of attraction forces is proposed. This work can be extended to include more types of DES and optimize the sulfur solubility in these solvents.

2. Simulation Details

All atom molecular dynamics simulations were performed using Gromacs 4.6.5 package on 1:2 and 1:1.5 mixtures of ferric chloride (FeCl_3) and tetrabutylphosphonium bromide (TBPBr), at which the mixture was reported to form a DES (Gano et al. 2014). Thiophene (TP) and dibenzothiophene (DBT) were used as typical representatives for the sulfuric compounds and their interactions with the DESs were analyzed. Optimized coordinates and forcefield parameters for all the molecules were generated from Automated Topology Builder (ATB) and Repository 2.1 (Malde et al. 2011). Bonded and van der Waals parameters were taken from the Gromos54A7 parameter set. Parameters for the ferric ions (Lin et al. 1994) and bromide ions are not available in the gromos set and hence were taken from the literature (Jorgensen et al. 1996), where they have been optimized (Mujika et al. 2012). All the simulations were started with a low density simulation box of $20 \times 20 \times 20 \text{ nm}^3$ to ensure efficient equilibration. The number of TBPBr molecules was set to 400 in all the simulation box and the number of salt (FeCl_3) was adjusted to obtain the desired ratio in the DESs. The solubility of DBT was studied in the DES at the solubility limits (Gano et al. 2014) and 485 molecules of DBT molecules were used accordingly. Although thiophene (TP) is complete soluble in the DES, 485 molecules of TP were used to ensure a comparable basis with the DBT.

After the initial configuration was obtained, energy minimization was performed with the steepest descent method. After minimization, the system was subjected to NVT-equilibration followed by NPT-equilibration for 0.2 ns each at 343 K and 1 bar. The resulting configuration was further used for a 10 ns production run, of which only last 2 ns were used for analysis. Long production runs are essential for simulating DES because of their sluggish dynamics (Perkins et al. 2013). LINCS constraint algorithm was used for all the bonds. A cut-off of 1.5 nm was used for the short-range Coulomb and Lennard-Jones interactions. Long-range electrostatic interactions were calculated using Particle Mesh Ewald summation method with a grid spacing of 0.16 nm with a fourth-order interpolation. Temperature of the system was kept constant at 343 K with the modified Berendsen coupling method and pressure was kept constant at 1 bar with Parrinello-Rahman coupling method. Periodic boundary conditions were implemented in all the simulations. Analysis of the trajectories were using Visual Molecular Dynamics (VMD) and gromacs tools.

3. Results and Discussions

The research begin with an in-depth analysis of the molecular interactions of the DES, however, a lot depends on the choice of the forcefield parameters. The suitability of the forcefield parameters for ionic liquids and DESs is generally decided by comparing thermo-physical properties obtained from experiments to those computed by the simulations. While TBPBr/ FeCl_3 based DESs are promising in their deep-desulfurization applications, there is a dearth of experimental data on its thermo-physical properties. To establish the suitability of our choice of the forcefield, we, hence compute and compare only density and volume expansivity of the DESs. Although the comparison of these two properties is not enough, they are often used to justify the forcefield (Sun et al. 2013).

Figure 1 shows density of the DES at a ratio of 1:2 and 1:1.5 as computed from our simulations in comparison with our previous experimental findings at different temperatures. In particular, the density of the DES at 1:2 ratio is obtained to be $1.101 \pm 0.0054 \text{ g/cm}^3$ at 343 K which is in close agreement with those reported for experiments, 1.160 g/cm^3 .

Volumetric thermal expansion (α), given by the equation 1, is commonly used to quantify temperature dependence of density.

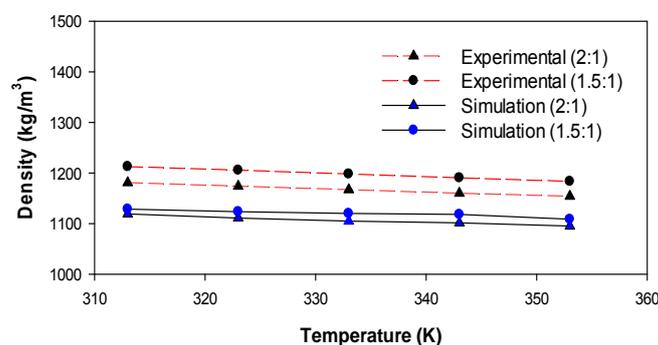


Figure 1: Dependence of TBPBr:FeCl₃ DESs density on temperature at two mole fractions as obtained from our simulations (solid lines) and experiments (dashed lines).

$$\alpha = -\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (1)$$

where V is the molar volume and T is the temperature of the system. The experimental value of the volumetric thermal expansion coefficient was reported to be $5.82 \times 10^{-4} \text{ K}^{-1}$, which is comparable to the value of $5.20 \times 10^{-4} \text{ K}^{-1}$ calculated from the simulations. Likewise, the density data for the DES at 1:1.5 ratio is close to the reported values, thereby supporting our choice of the forcefield parameters.

The interactions within DES was originally reported in terms of the hole theory, i.e., the movement of constituting ions is limited by the free volume available, and henceforth analyzing their physical properties such as their depression in freezing point, viscosity, and conductivity based on the available free volume (Abbott et al. 2004). More recent works have focused on the molecular interactions and formation of hydrogen bonds between the components (Shah and Mjalli 2014) of the DES. However, metal halide based DESs, as we consider in this study, are different as there is no hydrogen bond formation. The freezing point depression associated with the formation of such DES is usually explained in terms of exchange of ions between species and/or formation of complex structure. For example, it was reported (Abbott et al. 2007) that in choline chloride (ChCl)/ZnCl₂ DES, the ionic species undergo the following equilibrium reaction: $\text{ZnCl}_2 + \text{ChCl} \leftrightarrow \text{Ch}^+ + \text{ZnCl}_3^-$. The strong Lewis basicity of the chloride anion and acidity of ZnCl₂ shifts the reaction to the right forming more of ZnCl₃⁻. The authors suggests that the formation of the new ionic species affects the intermolecular interactions thereby causing a depression in the freezing point and formation of DES.

In order to explore the molecular interactions and possible complexation in phosphonium based DES, we further study radial distribution functions between different components. For simplicity, discussions about the interactions in DES are limited to at a ratio of 1:2. Similar results were also observed for a 1:1.5 ratio, and henceforth not discussed further. Figure 2a presents rdfs and coordination number between the phosphonium atom in the TBP ion with other ions. The results show a preference of both, chloride and bromide ions by TBP. While the height of first peak of bromide ion is 2.8, it is 2.4 for chloride ion and the peak position of chloride ion is closer than bromide. A second shoulder peak occurs nearby with a height of 1.9 for chloride ion indicating interactions of the ion in two different orientations with TBP.

Figure 2b shows cumulative coordination numbers around the TBP ions as calculated from the rdfs. The first coordination shell contains 1.55 chloride ion as compared to 1.33 bromide ion, showing a preference of chloride over bromide ion by TPB ion. Furthermore, ferric ion is away from TBP ion suggesting that it does not participate in any complex formation. Taken together, the results indicate a formation of new [TBP.Br][Cl]⁻ ion, which we propose is the reason for the formation of the DES, as described above. In order to explain this further, we also simulate pure TBPBr (refer to figure 4), where the first coordination number of TBP ion around another TBP ion was observed to be 4.4, whereas in the DES we found the number to be 3.4, indicating a decrease in the intermolecular interactions between TBP ions in the DES. The decrease in interactions combined with a formation of a cross-species complex leads to a depression in the melting point of the DES.

Next we discuss the solubility of thiophenic compounds in the DES. As noted above, we take thiophene and dibenzothiophene as representative molecules and perform a simulation on 485 thiophenic molecules in the DES. Figure 3a shows various rdfs with respect to sulfur atom of DBT.

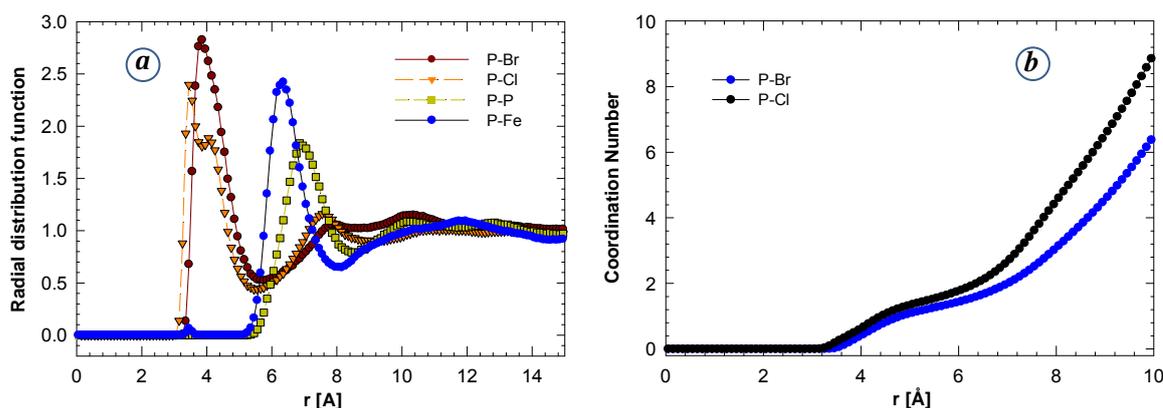


Figure 2: Radial distribution functions and coordination number between different ions to the phosphonium in the TBP ion at 343 K and 1 bar in 1:2 DES.

Amongst all the ions present in the mixture, the closest interaction of DBT is with TBP ion, with a peak of 1.07 at distance of 0.5 nm from the sulfur atom. All other ions, i.e., Br, Cl, and Fe have a distance of their first peak beyond 0.8 nm as shown in the figure. The results, in particular for the ferric ions, are contrasting, as some of the previous studies have focused on the Fe-S interactions to explain the DBT solubility. Ko et al. (2008), for example, have performed preliminary quantum based studies on [EMIm] and FeCl_3 based ionic liquid complexes at B3LYP level of the theory. They report formation of highly favorable Fe-S bond with a bond length of 0.26 nm and a [EMIm] FeCl_4 -DBT- FeCl_3 type of complex formation. However, in our study we do not observe any Fe ions in the vicinity (~ 0.4 nm) of S atom of DBT, which we believe is due to a relatively stronger DBT-TBP interactions.

Furthermore, we also observe a strong interaction between DBT molecules as shown from S-S rdf, which reflects the π - π interactions between the benzene rings of DBT molecules. Figure 3a also shows a frame from the simulation, wherein we present a typical distribution of molecules within 0.5 nm of a DBT molecule (shown in red). Other DBT and TBP molecules are shown in green and grey color, respectively. There are no Fe, Cl or Br ions in the snapshot, as discussed above from the rdfs.

Similar analysis was also done with thiophene and is presented in figure 3b. Unlike DBT, TP is completely soluble in the DES and we herein compare the rdfs between DBT and TP. The S-S rdf has higher peak indicating stronger interactions between thiophene as compared to DBT. However, in comparison, S-phosphonium rdf also has a slightly higher peak. More importantly, unlike DBT, the smaller ions, i.e., Fe, Cl, and Br ions do interact with TP with distances much closer than DBT. We propose that these favorable interactions with the smaller ions might lead to complete solubilization of TP in the DES.

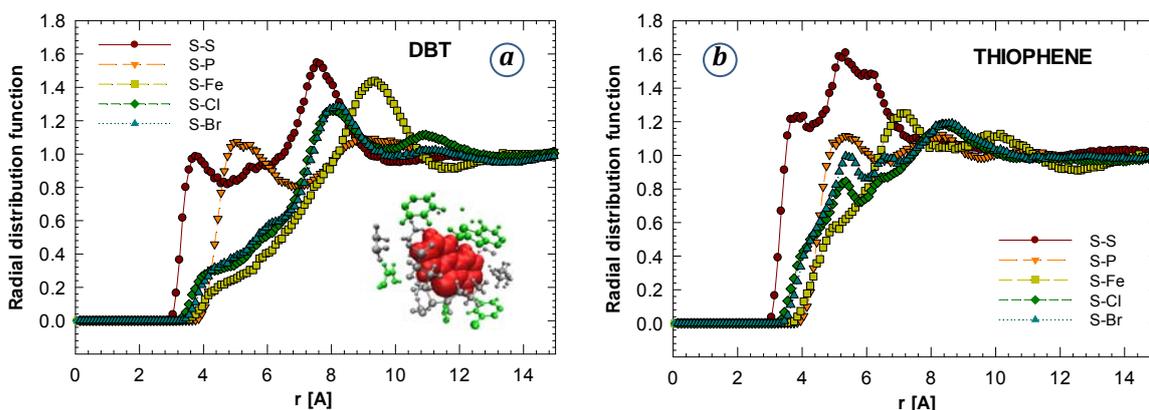


Figure 3: Radial distribution functions between the sulfur in the DBT and thiophene with other species at 343 K and 1 bar in 1:2 DES.

Based on the above results we observed the favorable interactions between the DES and the sulfur-based compounds and inferred about their solubility. Conversely, we also studied the effect of these sulfur-based compounds on the DES structure. Figure 4 compares the rdfs between the phosphorous atoms of TBP ions in pure TBPBr, in DES, and in the presence of DBT, and TP. Although all the initial peaks are close enough in terms of distance of their occurrence, the peak height is maximum in the presence of DBT. First coordination number in the case for pure TBPBr is 4.4 and for the DES is 3.4. However, in the presence of thiophenic compounds, the coordination number decreases to 2.5 and 2.2 in the case of TP and DBT indicating a gradual disruption in the structure of the DES.

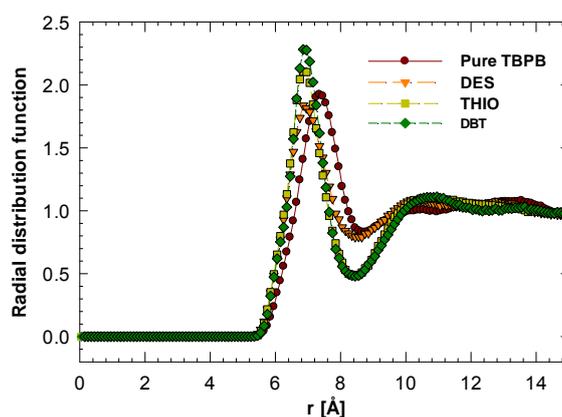


Figure 4: Radial distribution functions between the phosphonium in TBP at 343 K and 1 bar in pure TBPBr, in DES, and in the presence of DBT and TP.

4. Conclusion

Molecular dynamics simulations reveal the predominant interactions in $\text{FeCl}_3/\text{TBPBr}$ based DES. A transfer of chloride ion occurs to the TBP ion in the mixture, which we propose lead to the formation of the DES. Further, the solubility of DBT and TP were studied in the DES. Simulation reveals a preference to TBP by the thiophenic compounds, and exclusion of Fe, Cl, and Br. In contrast to the previous reports, which focused on Fe-S interactions to explain the solubility of thiophenic compounds, we here did not observe any possible Fe-S interaction. The outcome of these results may help to establish and design of suitable FeCl_3 -based DES as solvents for deep desulfurization of liquid fuel, however, further similar studies in the presence of fuels are still required.

Acknowledgements

The authors appreciate the financial support of The Research Council and Sultan Qaboos University, Muscat Oman, under the project RC/ENG/PCED/12/02.

References

- Abbott, A. P., J. C. Barron, K. S. Ryder, and D. Wilson. 2007. Eutectic-Based Ionic Liquids with Metal-Containing Anions and Cations. *Chemistry – A European Journal* 13:6495-6501.
- Abbott, A. P., D. Boothby, G. Capper, D. L. Davies, and R. K. Rasheed. 2004. Deep Eutectic Solvents Formed between Choline Chloride and Carboxylic Acids: Versatile Alternatives to Ionic Liquids. *Journal of the American Chemical Society* 126:9142-9147.
- Argyris, D., T. A. Ho, D. V. Papavassiliou, and A. Striolo. 2011. Equilibrium and transport properties of aqueous electrolytes within narrow slit-shaped pores: From molecular dynamics results to nanofluidics devices. Pages 1363-1368 *Chemical Engineering Transactions*.
- Gano, Z. S., F. S. Mjalli, T. Al-Wahaibi, Y. Al-Wahaibi, and I. M. AlNashef. 2014. Solubility of Thiophene and Dibenzothiophene in Anhydrous FeCl_3 - and ZnCl_2 -Based Deep Eutectic Solvents. *Industrial & Engineering Chemistry Research* 53:6815-6823.
- Gao, H., M. Luo, J. Xing, Y. Wu, Y. Li, W. Li, Q. Liu, and H. Liu. 2008. Desulfurization of Fuel by Extraction with Pyridinium-Based Ionic Liquids. *Industrial & Engineering Chemistry Research* 47:8384-8388.
- Jayaraman, S. 2009. Computing thermodynamic and transport properties of room temperature ionic liquids and molten salts from atomistic simulations. Notre Dame, Indiana, US.

- Jorgensen, W. L., D. S. Maxwell, and J. Tirado-Rives. 1996. Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. *Journal of the American Chemical Society* 118:11225-11236.
- Ko, N. H., J. S. Lee, E. S. Huh, H. Lee, K. D. Jung, H. S. Kim, and M. Cheong. 2008. Extractive Desulfurization Using Fe-Containing Ionic Liquids. *Energy & Fuels* 22:1687-1690.
- Kulkarni, P. S. and C. A. M. Afonso. 2010. Deep desulfurization of diesel fuel using ionic liquids: current status and future challenges. *Green Chemistry* 12:1139-1149.
- Lin, W., W. J. Welsh, and W. R. Harris. 1994. Molecular Mechanics Studies of Model Iron(III) Transferrin Complexes in vacuo and in Aqueous Solution. *Inorganic Chemistry* 33:884-890.
- Malde, A. K., L. Zuo, M. Breeze, M. Stroet, D. Poger, P. C. Nair, C. Oostenbrink, and A. E. Mark. 2011. An Automated Force Field Topology Builder (ATB) and Repository: Version 1.0. *Journal of Chemical Theory and Computation* 7:4026-4037.
- Mujika, J. I., B. Escibano, E. Akhmatkaya, J. M. Ugalde, and X. Lopez. 2012. Molecular Dynamics Simulations of Iron- and Aluminum-Loaded Serum Transferrin: Protonation of Tyr188 Is Necessary To Prompt Metal Release. *Biochemistry* 51:7017-7027.
- Nie, Y., C.-X. Li, and Z.-H. Wang. 2007. Extractive Desulfurization of Fuel Oil Using Alkylimidazole and Its Mixture with Dialkylphosphate Ionic Liquids. *Industrial & Engineering Chemistry Research* 46:5108-5112.
- Perkins, S. L., P. Painter, and C. M. Colina. 2013. Molecular Dynamic Simulations and Vibrational Analysis of an Ionic Liquid Analogue. *The Journal of Physical Chemistry B* 117:10250-10260.
- Ru and B. Konig. 2012. Low melting mixtures in organic synthesis - an alternative to ionic liquids? *Green Chemistry* 14:2969-2982.
- Shah, D. and F. S. Mjalli. 2014. Effect of water on the thermo-physical properties of Reline: An experimental and molecular simulation based approach. *Physical Chemistry Chemical Physics* 16:23900-23907.
- Sun, H., Y. Li, X. Wu, and G. Li. 2013. Theoretical study on the structures and properties of mixtures of urea and choline chloride. *Journal of Molecular Modeling* 19:2433-2441.