

A computational DFT study of Imidazolium based Ionic liquids: binding energy calculation with different anions using Solvation Model

Kalyan Dhar¹, Jagannath Biswas², Ishmam Ibnul Arabi³, Md. Shariful Alam², Md. Mahbubur Rahman²

1 Department of TEX, Shyamoli Textile Engineering College, Dhaka, Bangladesh.
2 Department of TEX, Green University of Bangladesh (GUB), Dhaka, Bangladesh
3 Department of TEX, Port City International University, Chittagong, Bangladesh

*Corresponding author's email:
kalyankumar.dhar@polimi.it

Received: 17/05/2022
Accepted: 27/09/2022
Published: 13/07/2024

Data Availability: The data are available on request from the corresponding author.

Competing Interests: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DOI: 10.3329/gubjse.v9i1.74886

Copyright: © GUBJSE copyright related information.

Abstract

Basic knowledge of chemical events in the gaseous or liquid phase, as well as on surfaces, is required to determine the macroscopic process. The structure of ionic liquids were investigated using quantum chemistry. Cation and anion can bond together, according to the findings. Their binding and interaction energies reveal that they are produced by hydrogen bonds. The mechanism of a room temperature ionic liquid, such as [BMIM][Cl] (1-butyl-3-Methylimidazolium chloride) monomer, was studied using Density functional theory (DFT) computations using the modern continuum solvation model (IEFPCM-SMD). Ionic liquid [IL] contains both anions and cations, allowing for greater intermolecular interactions. By analyzing the relative minimum energy of [BMIM][Cl] in the presence and absence of water, we were able to establish the minimum energy structures and probable Cl anion binding sites in [BMIM][Cl] ionic liquid. We have found that all 1-butyl-3-methylimidazolium halide ILs investigated had trans conformations due to the butyl group's dihedral angles.

Keywords: Density functional calculations, absorption, ionic liquids, cation and anion, computational Protocol, anionic effect.

Highlights

- Computational DFT study identifies diverse interactions in imidazolium-based ionic liquids.
- Monoatomic anion-based ILs exhibit unique H-bonding contacts between cation and anion.
- Frequency analyses combined with DFT calculations enhance understanding of different ILs.
- Study provides insights into the structural stability and challenges of using [BMIM][Cl] commercially.

Acknowledgements

This research was supported by Technical University of Milan Research Grant (Basic Research Initiative FARB and for collaborative Research fellowship in 2018-2019). The author would like to thank to the CFA laboratory of the Politecnico di Milano, Italy, University of Liberal Arts Bangladesh, Green University and Shymoli Textile Engineering College. The author is also grateful to Professor Carlo Cavallotti for his constant support and encouragement.

1 Introduction

Ionic liquids (IL) are being studied as new liquid materials in addition to their potential to replace standard synthesis solvents [1], [2]. Many ILs are more fascinating than their typical application as a “green solvent,” according to recent discoveries. Since their finding, ILs have shown to be whole new materials with a variety of intriguing properties, many of which have yet to be explored. ILs are formed of molecular ions as opposed to the molecules that make up traditional solvents. Like any other ionic liquid, liquid ions produce ILs and molten salts when heated to room temperature or higher (less than 100 degrees Celsius). Additional interactions like H-bonding are found in ILs that are uncommon in traditional solvents [3], [4]. On the other hand, many types of forces alter the physical characteristics of various ILs. A detailed grasp of the structural elements of IL is necessary since the molecular structure of molecules in various phases determines the properties of any substance. Pyridium-based ILs have received less attention than imidazolium-based ILs in terms of biodegradability. Because of their propensity to conduct electricity, Pyrrolidinium ILs are more typically encountered in dye-sensitized solar cells and batteries [5]. It is important to note that the diffraction patterns of ILs based on imidazolium are quite similar in terms of intermediate-range ordering. For the sake of this piece, we'll concentrate on imidazolium cation-based ILs [BMIM][Cl] as they've received the most attention in the literature.

It has been shown that the physical characteristics of imidazolium cations are affected by small changes in the imidazolium cation, such as changes in the length of the alkyl chain. This is true for actual “designer solvents,” too. The density of IL, for instance, decreases as the length of the cation's alkyl chain increases. As the molecular weight of the cation falls, the anion's molecular weight increases. The anion's thermal stability rises with temperature and the number of atoms it contains, whereas its heat capacity rises with its size [6]. Anderson et al. [7] examined a number of imidazolium and pyridinium-based RTILs (room temperature ionic liquids) utilizing a linear free energy approach based on numerous solvation interactions with probing solute molecules. The data that this model produces can be utilized to compute significant chemical interactions and attributes. According to study, the anion has a greater effect on the hydrogen bond basicity of RTIL than the cation. It has been shown that RTILs may operate as both polar and non-polar solvents, depending on the presence of polar molecules in a process [8]. The probe-molecule and cation-anion interactions in ILs need to be extensively examined, thus researchers must also look at these interactions.

2 Methods and Materials

It has been shown that theoretical simulations can help us better comprehend the interactions that take place in ILs. [9] The electronic structure of a molecule (mainly in the ground state) and numerous thermodynamic properties of a molecule can be examined and computed using the Density Functional Theory (DFT), a quantum mechanical theory. If you know the function of another function, you can figure out the attribute of an electron system (electron density). In computational chemistry, DFT is now the most extensively used and versatile technique. The bulk of our work with DFT is devoted to structural analysis of ILs. Because most ILs are liquids at room temperature, conventional techniques such as single crystal x-ray diffraction are extremely difficult to use to investigate their structure (SCXRD). [10]

To examine the ionic pair with and without water, a simulation of ionic liquids was conducted. The minimal energy structures, interaction energies, and binding energies of complexes, as well as their intermolecular connections, were determined by density functional calculations. In quantum chemical calculations, the Becke gradient-corrected exchange function was used with the Lee-Yang-Parr functional for exchange and correlation. The B3LYP hybrid functional, which was designed by Becke, was used for this. [11] A new implicit PCM model was used to model the solvent in both water and vacuum (IEFPCM-SMD).

It's called the Polarizable Continuum Model, and it's used to figure out how the reaction fields in a certain place will change over time (IEFPCM). PCM is the same thing as IEFPCM. DFT found the minimum amount of energy and atomic charges needed to have an interaction. The 6-31+G(d,p) basis set was chosen because it was both correct and efficient to use. Because of a number of reasons, this set was chosen as the base (Dhar 2014). In this paper, we looked at gas and liquid phase architectures of ionic liquid [BMIM][Cl] ion pair (Cation and anion).

DFT calculations have also been proven to be quite useful in predicting the structure and interactions of a particular molecule, and this is also true. The same technique may be used to determine the magnetic moment, the dipole moment, and many other physical properties of molecules. It is feasible to determine the molecule's vibrational frequency and how its IR band shifts alter when it comes into touch with other substances using both infrared and Raman spectroscopy.

Chang et al. used DFT to show how the cation-anion interaction changes vibrational frequencies [12]. The IEFPCM was used to figure out the liquid phase structures and vibrational frequencies at 298 K and 1 atmosphere pressure.

The NBOs and ESPs of all the structures that were optimized were found at the B3LYP/6-31++ G(d,p) level. The SMD model found out how much energy was used for cavitation and not for polar energy. Molden 4.4 was used to make all of the graphics in this article and the accompanying material [13].

3 Results and Discussion

Understanding chemical bonds and intermolecular interactions is one of the most crucial chemistry concepts to master. According to their properties, chemical substances are often divided into categories. Ionic liquids (ILs) were first discovered in the early 1900s. In recent years, research on ILs has gotten a lot of attention due to their adaptability and low vapor pressure. Numerous applications are possible for them. Recognizing the intermolecular forces that are most crucial is a smart concept. Additionally, it's crucial to exercise caution while seeking for ILs' general characteristics because this desire for generality has given rise to several IL myths. Most of the time, the chemical composition of the particular material may be used to explain an ionic liquid's properties. They aren't always the same. As an example of imidazolium-based ionic liquids, we used 1-butyl-3-dimethylimidazolium chloride as a case study ([BMIM][Cl]).

The ionic liquid [BMIM][Cl] structures are discussed theoretically. Their preferred interaction sites also calculated. We discovered that RTIL anion have long-term stability compare to their cation. But may hurdles must be overcome before [BMIM][Cl] can be widely used commercially. As expected, the imidazolium ring is a planar pentagon, as demonstrated by the optimized structures. The trans conformations of all 1-butyl-3-methyl-imidazolium halide ILs under investigation were caused by the dihedral angles of the butyl group, as Table 1 shows. [BMIM][PF₆] was found to have the same issue as [BMIM]BF₄.

These computations have proved to be highly valuable in the description of the interactions that take place within a certain IL. The physical state of ILs varies substantially when the anion and cation are altered. BMIMCl [Bmim:1-butyl-3-methylimidazolium] is a liquid at room temperature. It was observed that DFT calculations accurately predicted the structures of these ILs, which we studied further in our next paper.

Additionally, in [BMIM][BF₄], [BMIM][PF₆], multiple H-bondings were observed between the cation and anion, whereas only one large H-bonding was found in [BMIM][Cl], which is agree to our study with other who study [BMIM][Cl] by using rotational isomerism analysis [14], [15].

Table 1. Binding energies from DFT simulations, implicit solvation method (b3lyp/6-31+g (d,p) (optimized ion pair cations and anions and their interaction energies)

Cation(+)	Anion(-) Position	Interaction energy (Kcal/mol)
1-butyl-3 methylimidazolium	Cl(Top)	-6.5
1-butyl-3 methylimidazolium	Cl(Ethyl side)	-3.1
1-butyl-3 methylimidazolium	PF ₆	-4.5
1-butyl-3 methylimidazolium	Cl(Methyl side)	-6.8
1-butyl-3 methylimidazolium	BF ₄	-3.1
Ethyl - methylimidazolium	Cl	-3.8
1,3 di methylimidazolium	Cl	-5.4
Hexa- methylimidazolium	Cl	-4.2
Tetra Methyl Ammonium	Cl	-7.8
Tetra Methyl Phosphonium	Cl	-7.1

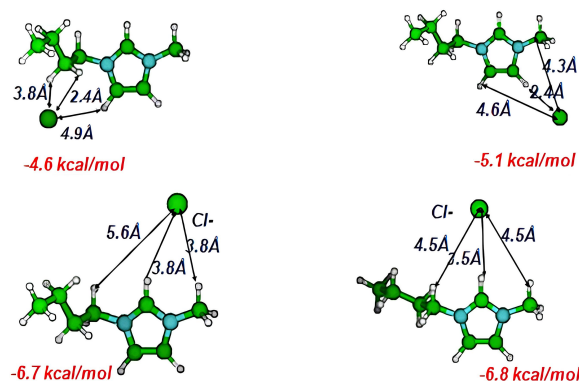


Fig 1. 1-butyl-3-methylimidazolium chloride (BMIMCl) ion pair analysis.

As stated earlier, we used DFT simulations to examine the interactions between the molecular structures of [BMIM][Cl] IL at the B3LYP/6-31G++ (d,p) level of computation is shown in Figure 1 as the optimally structured molecular structure. Their corresponding Binding energies also reported.

4 Conclusion

This study describes imidazolium-based ILs with anions ranging from straightforward monoatomic to intricate anions. All of the ILs were subjected to a comprehensive DFT computation at the B3LYP level in order to get completely optimized geometry. These calculations might advance our knowledge of a variety of interactions, including H-bonding interactions. In contrast to other ILs, such as [EMIM][BF₄], it was shown that monoatomic anion-based ILs (BMIMCl) exhibit multiple H-bonding contacts between the cation and anion. In addition, frequency analyses of different ILs were carried out in combination with DFT calculations to help the reader understand and interpret the results.

References

- [1] K. Dhar, "Mechanism of the absorption of co₂ in ionic liquid dimer," *Journal of the Asiatic Society of Bangladesh Science*, vol. 45, pp. 137–144, 2019.
- [2] D. Kalyan, "Theoretical study of the co₂ absorption in room temperature ionic liquids (rtil's)," *Politecnico di Milano PhD Thesis*, 2014.
- [3] K. Dhar and S. Fahim, "Investigation of the absorption of co₂ in ionic liquid," *Bangladesh Journal of Scientific Research*, vol. 29, no. 1, pp. 41–46, 2016.
- [4] K. Dhar and C. Cavallotti, "Investigation of the initial steps of the electrochemical reduction of co₂ on pt electrodes," *The Journal of Physical Chemistry A*, vol. 118, no. 38, pp. 8676–8688, 2014.
- [5] K. Dhar, "Dft study of the adsorption of co₂ on silver electrodes," *Journal of Bangladesh Chemical Society*, vol. 31, pp. 28–33, 2019.
- [6] K. Dhar, "Dft study of the absorption of co₂ , h₂ s in ionic liquids," Oct. 2022.
- [7] M. D. Joshi and J. L. Anderson, "Recent advances of ionic liquids in separation science and mass spectrometry," *Rsc Advances*, vol. 2, no. 13, pp. 5470–5484, 2012.
- [8] S. Beil, M. Markiewicz, C. S. Pereira, P. Stepnowski, J. Thöming, and S. Stolte, "Toward the proactive design of sustainable chemicals: Ionic liquids as a prime example," *Chemical Reviews*, vol. 121, no. 21, pp. 13132–13173, 2021.
- [9] F. Karadas, M. Atilhan, and S. Aparicio, "Review on the use of ionic liquids (ils) as alternative fluids for co₂ capture and natural gas sweetening," *Energy & Fuels*, vol. 24, no. 11, pp. 5817–5828, 2010.
- [10] J.-P. Zhang, P.-Q. Liao, H.-L. Zhou, R.-B. Lin, and X.-M. Chen, "Single-crystal x-ray diffraction studies on structural transformations of porous coordination polymers," *Chemical Society Reviews*, vol. 43, no. 16, pp. 5789–5814, 2014.
- [11] J. A. Pople, P. M. Gill, and B. G. Johnson, "Kohn—sham density-functional theory within a finite basis set," *Chemical physics letters*, vol. 199, no. 6, pp. 557–560, 1992.
- [12] K. Raghavachari, "Perspective on "density functional thermochemistry. iii. the role of exact exchange" becke ad (1993) j chem phys 98: 5648–52," *Theoretical Chemistry Accounts*, vol. 103, pp. 361–363, 2000.
- [13] G. Schaftenaar and J. H. Noordik, "Molden: A pre- and post-processing program for molecular and electronic structures," *Journal of computer-aided molecular design*, vol. 14, pp. 123–134, 2000.
- [14] D. Weijing, Z. Weihong, Z. Xiaodong, *et al.*, "The application of dft in catalysis and adsorption reaction system," *Energy Procedia*, vol. 152, pp. 997–1002, 2018.
- [15] S. Bana and R. Saini, "Experimental investigation on power output of different photovoltaic array configurations under uniform and partial shading scenarios," *Energy*, vol. 127, pp. 438–453, 2017.



Kalyan Kumar Dhar was born in Narail, Bangladesh in 1980. Currently, he is working as Assistant Professor at the department of Basic Science in Shyamoli Textile Engineering College (Affiliated College at University of Dhaka, Bangladesh). He completed his Ph.D. degree in Industrial Chemistry and Chemical Engineering at Politecnico di Milano, Italy in 2014. He completed his M.Sc in Materials Engineering at Politecnico di Milano, Milan, Italy in 2010 & B. Sc(Hons) at the department of Applied Chemistry & Chemical Engineering from University of Dhaka, Bangladesh. He published 8 research papers.



Jagannath Biswas was born in Magura, Bangladesh in 1969. Currently, he is working as Associate Professor at the department of Textile Engineering in Green University of Bangladesh. He completed his Ph.D. degree from Inha University, Incheon, South Korea in 2005. His research area was polymer synthesis and composites. He completed his M.Sc & B. Sc(Hons) at the department of Applied Chemistry & Chemical Engineering from University of Dhaka, Bangladesh. He published 20 research papers and more than 10 conference papers.

He completed his M.Sc & B. Sc(Hons) at the department of Applied Chemistry & Chemical Engineering from University of Dhaka, Bangladesh. He published 20 research papers and more than 10 conference papers.



Ishmam Ibnul Arabi was born in Chattogram, Bangladesh in 1995. He received the B.Sc(Hons) degree in chemistry from University of Chittagong in 2018 and completed his M.S with thesis in Organic Chemistry from the same institution. Prior to it, he completed his H.S.C from Govt. Hazi Muhammad

Mohsin College, Chattogram in 2013. His SSC was from Bakolia Govt. High School, Chattogram in 2011. Currently, he is working as Lecturer at the Department of Natural Science in Port City International University. Previously, he worked as a Lecturer at the Department of Textile Engineering in Green University of Bangladesh. Till now, he published 06 journal articles and 02 conference papers. His research interests include Organic Synthesis, Ionic Liquid synthesis and their application, drug design and computational analysis.



Md Shariful Alam is an Associate Professor in the Department of Textile Engineering at the Green University of Bangladesh, Dhaka. He received his Ph.D. degree in 2019 on Organic Synthetic Chemistry from the Myongji University, South Korea. Prior to this, he did his M.Phil. from BUET, Bangladesh in 2012. He completed M.Sc. and B.Sc. (Hons)

from the University of Rajshahi in 2002 and 2003 respectively. After completing M.Sc., he joined Green University of Bangladesh in 2008 as a lecturer. He has published 12 research papers in reputed national and international journals and conference. His research interest are Organic Synthesis, Environmental Chemistry, Computational Chemistry and Analytical Chemistry etc.



Md. Mahbubur Rahman was born in Narsingdi on 02 December 1988. At present, he is working as an Assistant Professor in the Department of Textile Engineering of Green University of Bangladesh. He received the degree M.Sc. in Textile Engineering from Dhaka University of

Engineering and Technology (DUET), Gazipur in 2022. He also completed his B. Sc in Textile Engineering from Primeasia University, Dhaka, Bangladesh, in 2010. His area of specialization was textile wet processing. He started his career as a production officer (Dyeing) in Wisteria Composite Mills Ltd, Gazipur in 2010.

He has published 23 research papers in reputed national and international journals and conferences. He is the Head, Institutional Quality Assurance Cell (IQAC) of the Department of Textile Engineering, Green University of Bangladesh. His research interests include application of natural dyes, technical textiles, smart textiles, effluent treatment plant (ETP), and environment friendly dyeing technology. Mr. Mahbubur Rahman was a recipient of the Gold Medal Award in the International Exhibition from Multimedia University (MMU) at the Research Innovation Commercialization & Entrepreneurship Showcase 2021. He also receives Silver Award from GUB Research Exhibition (GEX 2021) for the outstanding project work.