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Experimental and Computational Evaluation of 1,2,4-Triazolium-Based Ionic Liquids for Carbon Dioxide Capture

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Abstract: Utilization of ionic liquids (ILs) for carbon dioxide (CO_2) capture is continuously growing, and further understanding of the factors that influence its solubility (notably for new ILs) is crucial. Herein, CO_2 absorption of two 1,2,4-triazolium-based ILs was compared with imidazolium-based Ils of different anions, namely bis(trifluoromethylsulfonyl)imide, tetrafluoroborate, and glycinate. The CO_2 absorption capacity was determined using an isochoric saturation method and compared with predicted solubility employing COnductor-like Screening Model for Real Solvents (COSMO-RS). To gain an understanding of the effects of cations and anions of the ILs on the CO_2 solubility, the molecular orbitals energy levels were calculated using TURBOMOLE. Triazolium-based ILs exhibit higher absorption capacity when compared to imidazolium-based ILs for the same anions. The results also showed that the anions' energy levels are more determinant towards solubility than the cations' energy levels, which can be explained by the higher tendency of CO_2 to accept electrons than to donate them.

Keywords: triazolium; CO_2 capture; ionic liquids; molecular interaction; COSMO-RS

1. Introduction

Carbon dioxide (CO_2) levels in the atmosphere are rising, posing a severe threat to the global climate [1–6]. Various techniques have been proposed to lower the greenhouse gas levels, like limiting industrial CO_2 emissions and lowering the use of fossil fuels [7–11]. CO_2 capture, utilization, and sequestration (CCUS) technologies are anticipated to provide an efficient industrial solution to reduce CO_2 emissions by 45% by 2050 [12–15]. The adoption of chemical processes such as adsorption, absorption, and membrane separation has been highlighted in much-reported research on carbon dioxide capture and storage technologies [13]. Moreover, technologies for low-temperature CO_2 capture, also known as cryogenic carbon capture (CCC), rely on phase changes to convert CO_2 from a gas to a liquid or solid [16]. The term "cryogenics" is mainly used to describe processes that take place at temperatures below 120 K, but frequently the term is used to describe low-temperature separation [17]. CCC has not gained much attraction due to the high cost and energy required for the process as well as the limited range of potential applications. However, many studies were performed to enhance the process [18] since it has many advantages, such as the ability to use it with a wide range of CO_2 concentrations and producing a high purity product without the use of hazardous chemicals.

Among these technologies, the most used is the absorption process with utilization of amine solvents such as monoethanolamine (MEA) and diethanolamine (DEA) [15].

Although primary and secondary amines have a high CO_2 absorption rate, they have a low absorption capacity. In addition, regeneration requires more energy due to the stability of the carbamate produced by the reaction, and high temperatures can cause several issues, such as the amine's oxidative degradation. While the bicarbonate product of tertiary amines is less stable and easier to regenerate, it also has a slower CO_2 reaction rate and less selectivity [19]. Thus, the major constraint on the amine absorption is the energy requirement due to the high enthalpy of the reaction, and the amine solvents are difficult to regenerate which results in the loss of the solvent, consequently increasing the cost of the process as well as equipment degradation due to corrosion [13]. Ionic liquids (ILs) have received attention as a potential substitute to amine solvents for CO_2 absorption and conversion media [20–26] due to their special characteristics, which include low vapor pressures, low heat capacities, liquid form over a large temperature range, and good thermal and chemical stability, as well as their corrosion inhibition properties [27–31]. Although ILs have lower CO_2 absorption capacity compared with MEA and less mass transfer due to high viscosity [32], ILs require low energy for regeneration as a result of the physical absorption mechanism. This is due to the low CO_2 sorption enthalpy (10–20 kJ/mol), which is just one-fourth of the energy used by conventional amine solutions [33]. Moreover, ILs are considered as designer solvents, which pave the way of improving CO_2 absorption capacity.

CO_2 solubility in ILs has since been the subject of a lot of research using both experimental and predictive methods [34–42]. The solubility of different gases, including carbon dioxide, was evaluated by Anthony et al. for different cations, namely imidazolium, pyrrolidinium, phosphonium, and ammonium [43]. They observed that CO_2 has strong interactions with the ILs mainly through the anions, and the maximum CO_2 solubility was found for ILs with bis(trifluoromethylsulfonyl)imide [TFSI] anion, regardless of the type of the cations. Comparably, Almantariotis et al. [44] investigated the CO_2 absorption performance using 1-alkyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ILs ([C_nMIM][eFAP] with n = 2, 4, 6). They noticed that for the same cations, the ILs containing the highly fluorinated anions [eFAP] reported better CO_2 solubility than the [TFSI]-based ILs. Several other studies also demonstrated that the inclusion of fluoroalkyl groups in ILs increases CO_2 absorption properties [43,44].

On the other hand, amino acid based ILs have also demonstrated high CO_2 solubility [45,46]. Nooraini and Mehrdad [45] correlated the CO_2 solubility in amino acid based ILs with the molecular interactions between the amino acid anions and CO_2. Through density functional theory (DFT) simulations, they found that the N atom of the amino acid is where substantial CO_2 sorption occurs. The influence of anions, namely [TFSI], [BF_4], [methide], [NO_3], [OTf], [DCA], and [PF_6] with alkylimidazolium as the cations, was investigated by Aki et al. [47], in which they demonstrated that the CO_2 solubility marginally rises with the length of the cation's alkyl chain because longer alkyl chains have bigger free volumes and are primarily dependent on anions. The maximum CO_2 solubility was recorded for anions containing fluoroalkyl groups, such as [TFSI] and [methide], which was explained by the increase of molar volumes [47].

Furthermore, to determine the potential of ILs for separating CO_2 and H_2S gases from natural gas as well as for separating the two gases from one another in gaseous streams that contain them, Safavi and Ghotbi [48] evaluated the solubility of CO_2 and hydrogen sulfide (H_2S) in a temperatures range from 303.15 to 353.15 K and pressures up to 2 MPa in 1-octyl-3-methylimidazolium hexafluorophosphate ([C_8MIM][PF_6]). They reported that the solubility of H_2S is around three times that of CO_2 in the specific ionic liquid under study. They also highlighted that the solubility of both gases increases with increasing pressure and decreases with rising temperature. Additionally, they investigated the impact of cation alkyl chain length on the solubility of CO_2 and H_2S by comparing the experimental results with previous reported study. They deduced that the solubility of CO_2 and H_2S in the ionic liquid increases as the cation alkyl chain length increases. In addition, the influence of the anion on gas solubility was evaluated by comparing the solubility of CO_2 and H_2S

in [C$_8$MIM][PF$_6$] and in [C$_8$MIM][TFSI]. They reported that both gasses CO$_2$ and H$_2$S are more soluble in the IL when [TFSI] is the anion.

Further understanding of the synergistic effects of the cations, anions, alkyl chain length, and functional groups towards the molecular interactions between CO$_2$ and ionic liquids is of high importance. Based on the frontier molecular orbital theory, the overlap between the donor's HOMO and the acceptor's LUMO can be used to gauge how intense the donor–acceptor interactions are [49,50]. Consequently, a study of the molecular orbital energy levels' effect on CO$_2$ capacity is therefore relevant. Moreover, since the carbon in carbon dioxide is partially positive while the oxygen is partially negative, then there is a possibility of acid/base interaction. Hence, in this study, CO$_2$ absorption capacity of a series of ionic liquids of different cations, anions, and alkyl chain lengths, namely two 1,2,4-triazolium-based ILs [BBT][BF$_4$] and [BBT][TFSI], were compared with five imidazolium-based ILs, namely [EMIM][TFSI], [BMIM][BF$_4$], [HMIM][TFSI], [EMIM][BF$_4$], and [BMIM][GLY]. The experimental CO$_2$ absorption capacity for each ILs was compared with predicted values obtained from COnductor-like Screening MOdel for Realistic Solvents (COSMO-RS). Density functional theory (DFT) calculations were performed using TURBOMOLE to investigate the impact of the molecular orbitals of the individual (cation and anions) pairs of the ionic liquids on CO$_2$ absorption. The molecular structures of the seven ILs are shown in Figure 1.
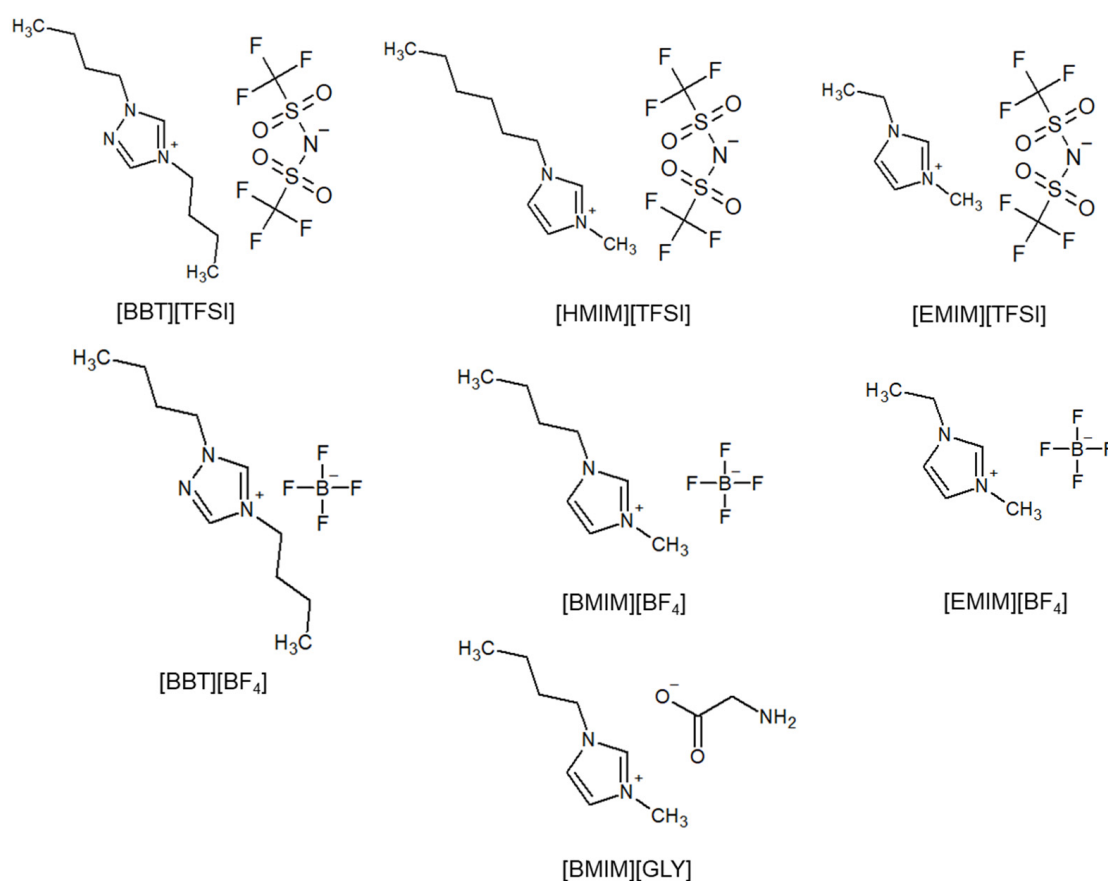

Figure 1. Molecular structures of ionic liquids used in this work.

2. Materials and Methods

2.1. Materials

In this work, the synthesis of [BBT][BF$_4$], [BBT][TFSI], [BMIM][BF$_4$], and [BMIM][GLY] was carried out in accordance with the procedures outlined in our earlier publication [51]. [EMIM][BF$_4$] (≥98.0%), [EMIM][TFSI] (≥97.0%), and [HMIM][TFSI] (≥98.0%) were procured from Sigma Aldrich.

2.2. Density Measurement

To aid in determination of number of moles of ILs, the density of all ILs was measured at 25 °C with an accuracy of 0.0001 g/cm^3 (Stabinger Viscometer SVM3000, Anton Paar). The molar volume of the ILs was determined via Equation (1),

$$V_m = \frac{M_w}{\rho} \tag{1}$$

where *Mw* is the molecular weight of IL in g/mol and ρ is the density of the IL in g/cm^3.

2.3. CO$_2$ Absorption Capacity in ILs

The isochoric saturation method to determine the CO$_2$ absorption capacity in the pure ILs was adapted from procedures reported in literature [52–56]. The experiments were carried out in a 15 mL capacity stainless steel high-pressure equilibrium cell (EC), as seen in Figure 2. A pressure gauge controller was attached to the system to maintain the required pressure (5 bar) and a water bath was used to maintain the cell at 25 °C.
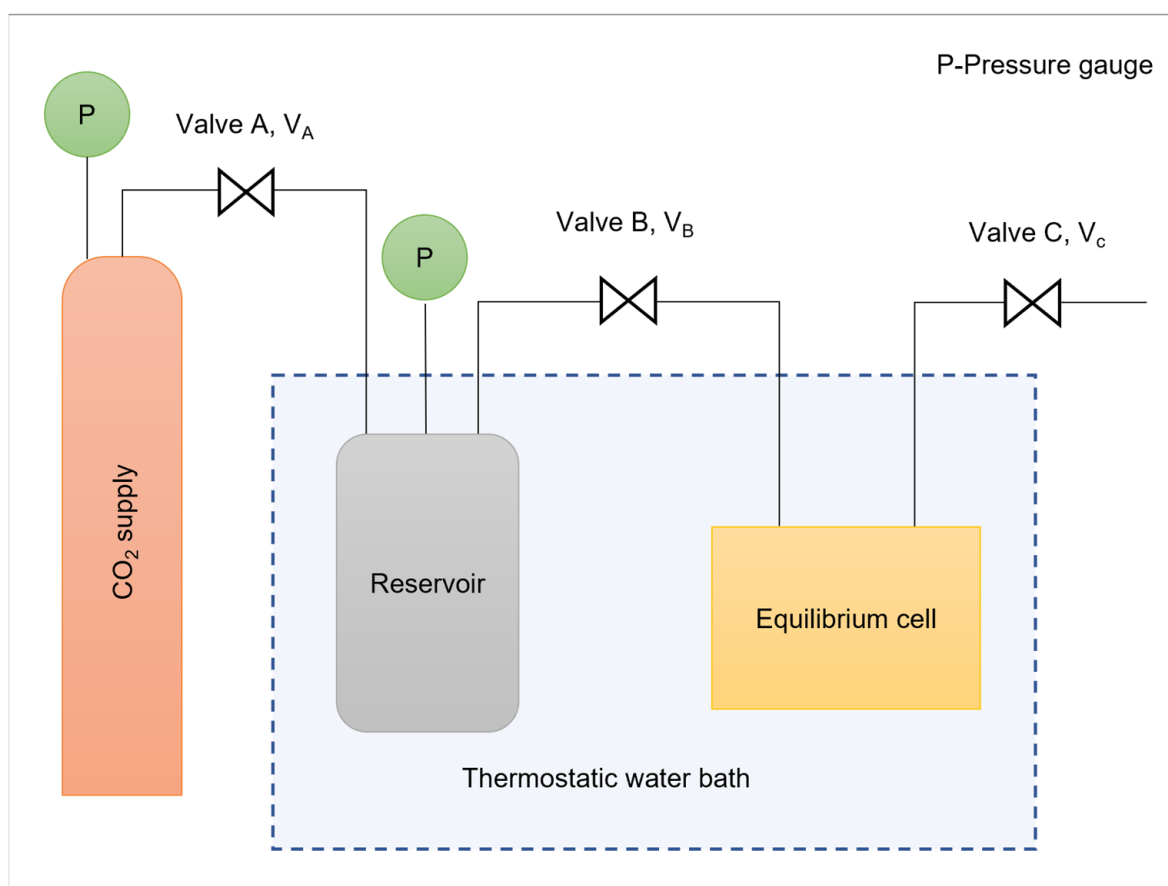

Figure 2. Schematic diagram of the isochoric saturation setup.

The IL was first loaded into the equilibrium cell during the experiment and degassed using a vacuum pump. The CO$_2$ gas was then supplied to the EC and the pressure inside the cell progressively dropped as the IL started to absorb CO$_2$. The pressure in the system was recorded every minute, and the system was given enough time to stabilize without any usage of stirrer. The time duration for reaching equilibrium varied between 160 and 200 min. The number of moles of CO$_2$ at the start was determined via Equation (2):

$$n^i_{CO_2} = \frac{P_i V_{res}}{Z^i_{CO_2} R T_i} \tag{2}$$

where $n_{CO_2}^i$ is the number of moles of CO_2 that were initially charged into EC, P_i is the initial pressure, V_{res} is the volume of the reservoir, $Z_{CO_2}^i$ is the compressibility factor at the starting temperature and pressure conditions, R is the universal gas constant, and T_i is the initial temperature.

Equation (3) was used to calculate the number of moles of CO_2 left inside the cell at equilibrium condition:

$$n_{CO_2}^{eq} = \frac{P_{eq}(V_{total} - V_s)}{Z_{CO2}^f RT_{eq}} \tag{3}$$

where $n_{CO_2}^{eq}$ is the number of moles of CO_2 molecules inside the system that is at equilibrium, P_{eq} is the pressure at equilibrium, V_{total} is the volume of the CO_2 absorption system from valve A (V_C) to valve C (V_C), V_s is the volume of the ILs, and $Z_{CO_2}^f$ is the compressibility factor at equilibrium conditions.

Equation (4) was used to calculate the number of moles of CO_2 absorbed $n_{CO_2}^{abs}$, and the mole ratio was used to express the solubility of CO_2 (x) using Equation (5):

$$n_{CO_2}^{abs} = n_{CO_2}^i - n_{CO_2}^{eq} \tag{4}$$

$$x = \frac{n_{CO_2}^{eq}}{\frac{w_{IL}}{M_{w\ of\ IL}}} \tag{5}$$

where w_{IL} is the weight of IL and $M_{w\ of\ IL}$ is the molecular weight of IL.

2.4. Computational Methods

The molecular orbitals (HOMO-LUMO) of the individual cations and anions of the ILs were generated using TmoleX simulation software (version 4.4.1), which is a graphical user-friendly interface for the quantum chemical program package (TURBOMOLE) [8]. First the geometry optimization was performed, followed by electronic structure computations with def-TZVP basis set. To create the input file, the functional BP86 was added under the DFT setting [57,58]. COSMO-RS was used to generate the sigma profile, sigma potential, and sigma surface for the selected structures and to calculate the predicted CO_2 capacity of various ILs [59–67]. The sigma profile (σ) provides the possibility of calculating the average screening charge density on the segments of molecule (X). For solvents consisting of many components X_i, with molar concentration x_i, the σ-profile was determined by the weighted sums of the Sigma profile (σ) of the components as per Equation (6).

$$p_i(\sigma) = \sum_i^N x_i \times p_i \tag{6}$$

The σ-profile and σ-potential were categorized into three main regions: hydrogen bond donor for $\sigma < -0.01$ e/Å^2, the non-polar region for $-0.01 < \sigma < +0.01$ e/Å^2, and hydrogen bond acceptor for $\sigma > +0.01$ e/Å^2. Sigma surface was used to provide visual representation for charge distribution on the structure surface. Color coding was used to determine the charge distribution of the molecule: green indicates neutral nature, yellow represents a partial negative charge, blue shows the positive charge region, and the negative charge region is represented by red. The activity coefficient at infinite dilution showed the degree of non-ideal behavior in the solvents, as in Equation (7):

$$\ln(\gamma_i) = (\mu_i^{S,\infty} - \mu_i^p)/RT \tag{7}$$

where $\mu_i^{S,\infty}$ and μ_i^p are chemical potentials of both solvent and pure compounds, respectively. The inverse activity coefficient of a solute i, obtained at infinite dilution of the solute in the IL solvent ($\gamma_i^{IL,\infty}$), was used to describe a solute's capacity solubility capacity C_i^{IL} in an IL solvent as in Equation (8).

$$C_i^{IL} = 1/\gamma_i^{IL,\infty} \tag{8}$$

The IL capacity C_i^{IL} thus corresponds to a non-iterative and unnormalized liquid solubility of solute *i* in the IL in mole fraction units [mol_i/mol_{IL}]. The IL stoichiometry scales the IL capacity calculated by COSMO-RS. On the other hand, the IL capacity can be defined in mass-based units as per Equation (9).

$$G_i^{IL} = MW_i / \left(MW_{IL}\ \gamma_i^{IL,\infty} \right) \tag{9}$$

The non-iterative and unnormalized mass-based liquid solubility of solute *i* in the IL is represented by the IL capacity with units [g_i/g_{IL}]. C_i^{IL} and G_i^{IL} are semi-quantitative relative measurements of how efficiently an IL solvent dissolves a certain solute *i*. Therefore, the IL capacity can be used to compare the solubility properties of several IL solvents for a specific solute [68]. The COSMO-RS theory is well illustrated elsewhere by the developer [69–71]. The sigma profile, sigma potential, and sigma surface are available in the supporting information.

3. Results and Discussions

3.1. Density and CO_2 Solubility of Different ILs

The density, the calculated molar volumes, and the maximum CO_2 absorption capacity of the selected ILs measured at 25 °C are shown in Table 1 and the CO_2 capacity of ILs vs. time depicted in Figure 3. The [TFSI]-based ILs with large anions exhibit the highest density and molar volumes compared to other types of anions. Interestingly, the triazolium-based ILs exhibit lower density than the imidazolium ILs for the same anions. This is favorable to allow more carbon dioxide to be absorbed in the ILs as the gas solubility is known to be dependent on the molar volume of the ILs where the CO_2 will occupy the free space between the ions [18,20,42].

Table 1. The density at 25 °C, the molar volume, and the maximum capacity values for different ILs.

Ionic Liquids	Density (g/cm³)	Molecular Weight, *MW* (g/mol)	Molar Volume (cm³/mol)	Maximum Capacity Values, *x*, (Mol (CO_2 abs)/Mol (IL))
[EMIM][BF₄]	1.280	197.97	154.63	0.0795
[BMIM][BF₄]	1.222	226.02	185.03	0.0972
[BMIM][GLY]	1.108	213.29	192.48	0.2150
[BBT][BF₄]	1.154	269.09	233.12	0.1553
[EMIM][TFSI]	1.517	391.3	257.96	0.1808
[HMIM][TFSI]	1.371	447.42	326.35	0.2335
[BBT][TFSI]	1.359	462.45	340.19	0.2523

From the results shown in Table 1 and Figure 3, it can be observed that the order of CO_2 capacity in ILs starting from the highest is [BBT][TFSI] > [HMIM][TFSI] > [BMIM][GLY] > [EMIM][TFSI] > [BBT][BF₄] > [BMIM][BF₄] > [EMIM][BF₄]. The triazolium-based ILs recorded high CO_2 absorption capacity compared to the imidazolium-based ILs, with the results of the latter consistent with other reported data [43,72–75]. It can be seen that the higher the molar volumes, the higher the absorption capacity, except for the case of [BMIM][GLY]. The absorption mechanism can be classified either by physisorption or chemisorption, with the latter being governed by a rate-limiting process but resulting in higher absorption capacity [76]. This can be seen in [BMIM][GLY], where a sharp increase of CO_2 absorption is observed until it stabilizes to its maximum capacity, which can be classified to follow the chemisorption process. On the other hand, in the case of physisorption, the CO_2 solubility depends on the fractional free volume of the ILs, which explains the good solubility of the large delocalized anions [TFSI] compared to [BF₄] [77]. Further investigations were performed to determine the factors that influence

the absorption types in ionic liquids, and parameters such as the type of cations, anions, and the alkyl chain length were taken into consideration.
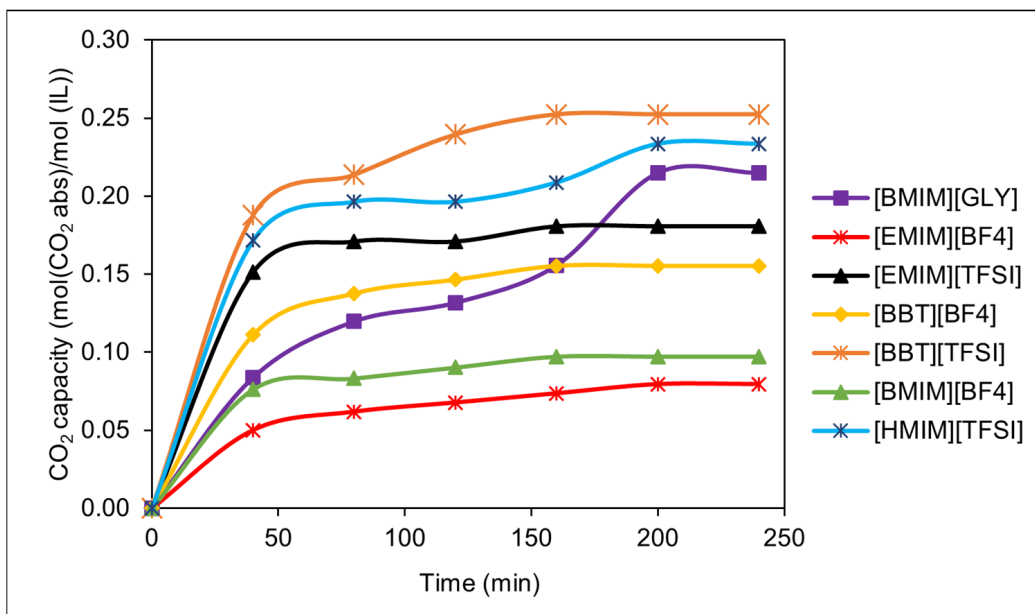

Figure 3. The amount of mole CO_2 absorbed/mole IL.

Figure 4 depicts the CO_2 capacity for different ILs through experimental and computational methods using COSMO-RS. By comparing the two methods, a linear regression (y = 11.381x + 0.9218) was obtained with R-squared value of 0.9374. It is noteworthy to highlight that the values from COSMO-RS are larger than the experimental results because COSMO-RS is a qualitative tool, and the capacity values are computed by employing the infinite dilution activity coefficients of the ILs. The COSMO-RS is therefore an effective tool for estimation of thermodynamic properties and reliable for prediction of gas solubility properties for new ionic liquids.
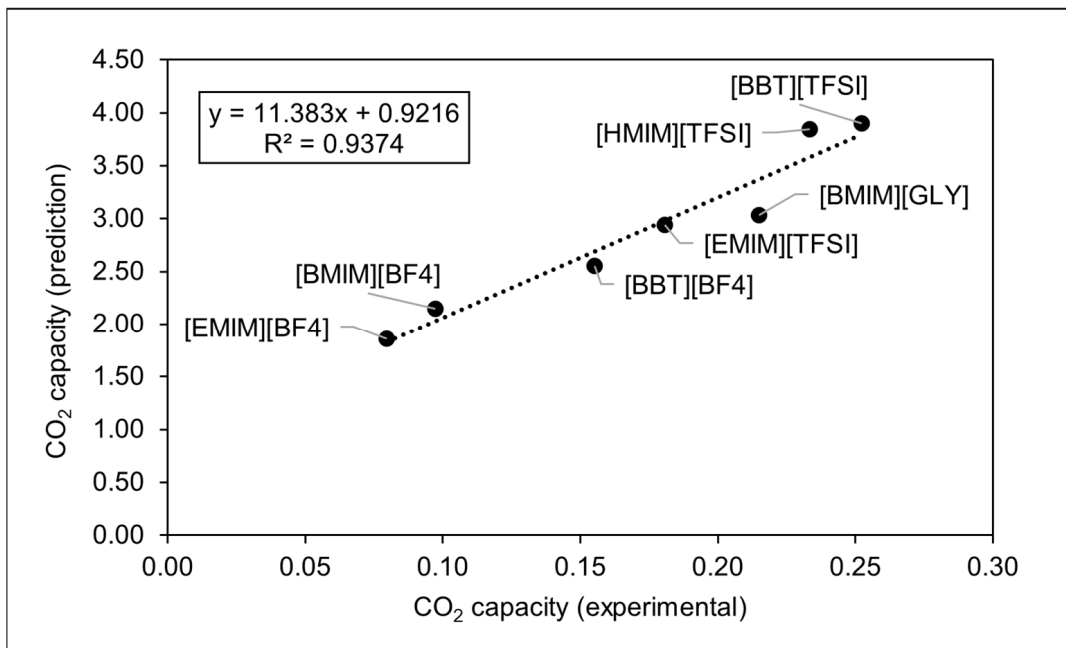

Figure 4. Quantitative comparison between experimental and computational CO_2 capacity.

3.2. Role of the Anions on the ILs' Capacity to Dissolve CO_2

To investigate the role of anions on CO_2 solubility in IL, a comparison of the CO_2 capacity values for [BBT][BF$_4$], [BBT][TFSI], [BMIM][BF$_4$], and [BMIM][GLY] was performed. It is apparent from Figure 3 that [BBT][BF$_4$] shows less capacity of CO_2 as compared to [BBT][TFSI], while [BMIM][GLY] has a higher CO_2 solubility than [BMIM][BF$_4$]. As reported by Aki et al., the solubility of CO_2 is not only determined by the acid/base interactions between CO_2 and the anions; they give the example of the basicity of [BF$_4$] which is reported experimentally higher than [TFSI], which eventually should show higher absorption capacity [47]. To understand this conflicting result, it is worth highlighting that there are three primary theories of acid–base, namely the Arrhenius theory (acid is a substance that produces H$^+$ ions in water and base is a substance that produces OH$^-$ ions in water), the Bronsted–Lowry theory (acid is a proton H$^+$ donor and a base is a proton H$^+$ acceptor), and lastly the Lewis acid–base theory (acid is an electron pair acceptor and base is an electron pair donor). The Lewis acid–base describes the bonding in quite different compounds, unlike the Bronsted acid–base concept, and thus can better explain the CO_2–ILs interaction [78]. Onofri et al. suggested that the glycinate anion reacted with CO_2 by two-step mechanisms involving an initial nucleophilic attack followed by a proton transfer process [76].

The interaction of the ionic liquids and the CO_2 can be further elucidated using the frontier molecular orbital theory [49,50]. We stipulated that the ionic liquids and CO_2 interaction can be explained by the donation of electrons from the HOMO level of the anions of the ionic liquids into the LUMO level of CO_2. Hence, to confirm this theory, the LUMO and the HOMO for the anions were calculated using Tmolex, as shown in Figure 5. Here, it can be observed that the [TFSI] anion has a higher HOMO value compared to the [BF$_4$] anion. It can be deduced that an increment in the HOMO values of anions increases the capacity of CO_2 in ILs. Alternately, the sigma profiles of [TFSI] and [BF$_4$] (cf. Figures S1 and S2) were evaluated to provide insight into the hydrogen bonding strength. The sigma profiles reveal that the [TFSI] anion is a greater hydrogen bond acceptor than [BF$_4$]. This results in a higher tendency for the [TFSI] anion to donate electrons compared to [BF$_4$].
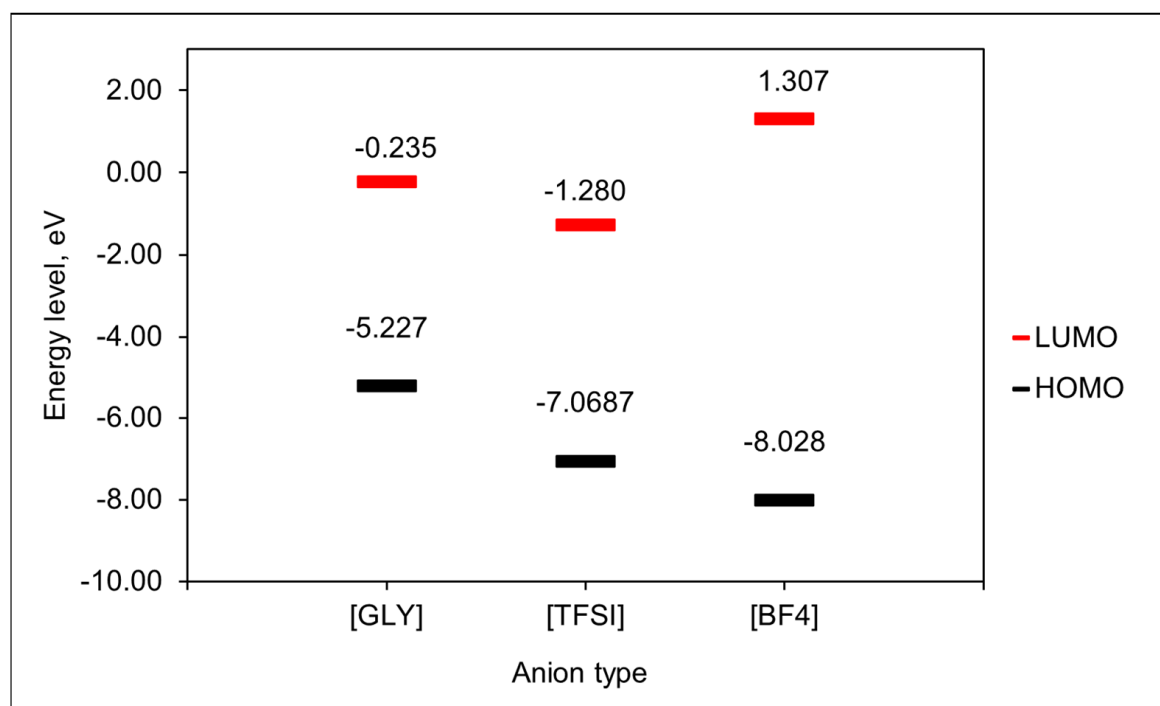

Figure 5. Values of HOMO-LUMO for [GLY], [BF$_4$], and [TFSI] anions.

Further comparison was made between [BMIM][BF$_4$] and [BMIM][GLY], whereby [BMIM][GLY] has shown a higher CO$_2$ solubility than [BMIM][BF$_4$]. From the HOMO–LUMO energy levels for anions, as shown in Figure 5, it can be observed that glycinate has a higher HOMO value. The results are also consistent with previous studies, which reported the order of CO$_2$ solubility starting from the highest is [BMIM][GLY] > [BMIM][TFSI] > [BMIM][BF$_4$] [43,73–75]. It can be noted that the order of CO$_2$ capacity is the same as the HOMO energy levels starting from the highest. It can be concluded that the anions that have higher HOMO energy levels show good CO$_2$ capacity since CO$_2$ in this case is considered as the Lewis acid and the anions are considered as the Lewis base, which means the gap between the HOMO of anion and the LUMO of CO$_2$ will be the lowest for the case of [BMIM][GLY]. This is also aligned with the sigma profiles and sigma potential, as shown in Figures S3 and S4, respectively, where [GLY] has a higher tendency to donate electrons compared to [BF$_4$]. Moreover, it can be noted that the good absorption in [BMIM][GLY] is due to the special characteristic of [GLY], which has a very high HOMO value as well as the terminal electronegatively charged which can be observed from the sigma surface in Figure S13. These two parameters could be the reason for the strong interaction that leads to chemisorption. Unlike other anions, such as [BF$_4$] which has relatively low HOMO values and also unlike [TFSI] which has a relatively high HOMO value, due to the big structure and the charge distribution as shown in the sigma surface in Figure S13, the interaction is not as strong which led to physisorption rather than by chemisorption.

3.3. Role of the Cations on the ILs' Capacity to Dissolve CO$_2$

On the other hand, to investigate the impact of cations on CO$_2$ absorption in ILs, the CO$_2$ capacity values for [BBT][BF$_4$], [BMIM][BF$_4$], and [EMIM][BF$_4$] are compared, while Figure 6 displays the HOMO–LUMO energy levels of the cations.
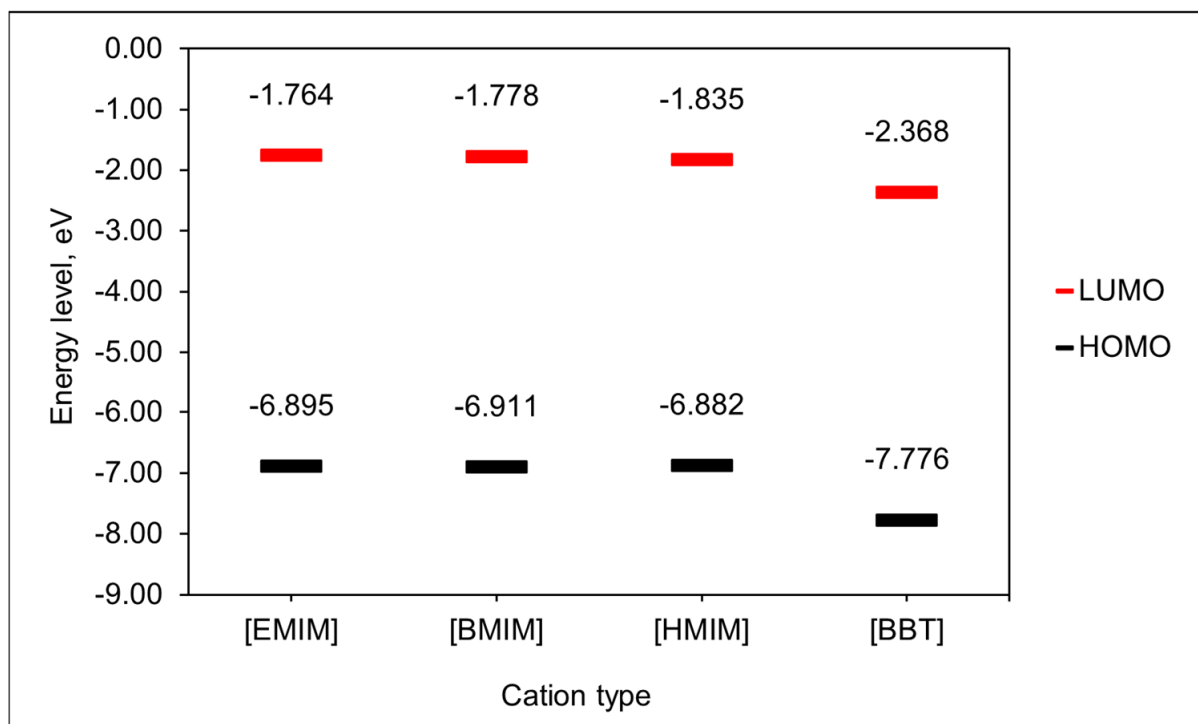

Figure 6. HOMO–LUMO energy levels for different cations.

The order of CO$_2$ capacity, starting from the highest, is [BBT][BF$_4$] > [BMIM][BF$_4$] > [EMIM][BF$_4$] as depicted in Figure 3. From Figure 6, the LUMO values of cations starting from the lowest is [BBT] < [BMIM] < [EMIM]. It can then be inferred that the cations with lower LUMO energy levels have higher CO$_2$ capacity. Furthermore, based on the sigma

profiles and sigma potentials in Figures S5 and S6, it can be noted that the [BBT] cation has a higher tendency to accept electrons, followed by [BMIM] and then [EMIM].

To further validate this assumption, another comparison between CO_2 capacity for [EMIM][TFSI], [HMIM][TFSI], and [BBT][TFSI] is carried out. From Figure 3, the order of CO_2 capacity starting from the highest is [BBT][TFSI] > [HMIM][TFSI] > [EMIM][TFSI]. A similar trend is observed in terms of LUMO energy levels of cations starting from the lowest, which is [BBT] < [HMIM] < [EMIM], as displayed in Figure 6.

From these results, we observed that the cations with lower LUMO values have higher CO_2 capacity. Kong et al. reported that CO_2 can act as an acid or base according to the surrounding condition [79]. In this case, CO_2 is considered a Lewis base, and the cations are considered a Lewis acid. The sigma profiles and sigma potentials (Figures S7 and S8) also confirm that the triazolium cation has a higher tendency to accept electrons, followed by [HMIM] and then [EMIM].

3.4. Effect of the Alkyl Chain Length on CO_2 Solubility of the ILs

To study the effect of cation's alkyl chain length on CO_2 solubility in ILs, and to further validate previously reported studies, CO_2 capacity values of [BMIM][BF$_4$] and [EMIM][BF$_4$] were evaluated. From Figure 3, it can be noted that more CO_2 can be dissolved in [BMIM][BF$_4$] of a higher alkyl chain as compared to [EMIM][BF$_4$]. Similarly, [BMIM] (C_4) has a slightly lower LUMO value as compared to [EMIM] (C_2), as shown in Figure 6. Their sigma profiles and sigma potentials (Figures S9 and S10) also show that [BMIM] has a slightly higher tendency to accept electrons compared to [EMIM].

Similarly, in another comparison between CO_2 capacity for [EMIM][TFSI] and [HMIM][TFSI] it can be noted that CO_2 is more soluble in [HMIM][TFSI] as compared to [EMIM][TFSI], which correlates with a lower LUMO energy level for [HMIM] (C_6) as compared to [EMIM] (C_2), as shown in Figure 6. From the sigma profiles and sigma potentials (Figures S11 and S12), it can be observed that [HMIM] has a higher tendency to accept electrons compared to [EMIM].

The results are aligned with other reported studies, whereby the CO_2 solubility marginally improves by the increase of the cation's alkyl chain length because the longer alkyl chains in ILs have a bigger free volume [47]. Based on our study, it is noteworthy to mention that the enhancement in CO_2 solubility when the alkyl chain length increases is due to the lower LUMO energy level of the cations that have a longer alkyl chain. Furthermore, by analyzing the experimental and theoretical CO_2 capacity of the ILs and the HOMO-LUMO energy levels, it can be deduced that the anions have more influence on the solubility compared to cations, thus the HOMO energy level of the anion is more determinant than the LUMO energy level of the cation. This can be described by the fact that CO_2 tends to receive electrons more often than to donate them. It can be concluded that to have good CO_2 solubility, it is recommended for the combination of ILs to use a cation of low LUMO energy level and an anion of high HOMO energy level.

4. Conclusions

In this study, the triazolium-based ionic liquids demonstrated higher solubility of CO_2 when compared with imidazolium-based ILs of different anions. As a result of our investigation into the CO_2 capacity of ILs using experimental and computational methods, we demonstrated that the increase of HOMO energy levels of the anions and the decrease of LUMO energy levels of the cations boost the CO_2's loading capacity in ILs. Moreover, it was also noted that the anion's HOMO energy level has a greater impact on solubility than the cation's LUMO energy level, which can be explained by the fact that CO_2 tends to receive electrons more often than to donate them. Furthermore, it was shown that as the length of the cation's alkyl chain increases, the cation's LUMO energy level decreases, thus increasing the CO_2 solubility. The results obtained can aid in selecting suitable combinations of cation–anion pairs of ILs for CO_2 absorption.

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