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CO_2 capture by task specific ionic liquids (TSILs) and polymerized ionic liquids (PILs and AAPILs)

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ABSTRACT

In the present study, new ionic liquids (ILs) such as task specific ionic liquids (TSILs), polymerized ionic liquids (PILs), and amino acid-based polymerized ionic liquids (AAPILs) were synthesized and their efficiency for capturing CO_2 was studied. Nitrile imidazolium-based TSILs with different alkyl chain length and different anion ([DDS], [TFMS], [SBA], [BS], [DOSS]), PILs consisting of [VBTMA], [VBTEA] and [METMA] cations and $[BF_4]$,[Cl], $[NO_3]$, $[PF_6]$ and [TFMS] anions and AAPILs incorporating [VBTMA] as cation and [Arg], [Pro] as anions were synthesized. The results showed that the CO_2 sorption increases as alkyl chain length increased and $[C_2CNDim]$[DOSS] gave the highest CO_2 sorption among the TSILs, which reach up to 0.55 mol fraction at 10 bar, 298 K. In polymerized ionic liquids the CO_2 sorption capacity increases in polymeric forms than monomeric forms. To enhance the efficiency of PILs for adsorbing CO_2, AAPILs have been studied. The results showed that the AAPILs are capable of capturing CO_2 more than TSILs and PILs as they have functionalized amine tethered at the anion. The result of CO_2 sorption showed that even at low pressure (P_{eq} 0.7 bar) and 298 K, the AAPILs [VBTMA][Arg] and [VBTMA][Pro] absorbed 0.530 and 0.38 mol fractions of CO_2.

1. Introduction

The emissions of greenhouse gases which resulted to the global warming have received widespread attention. CO_2 contributes more than 60% to global warming, where the concentration is now closed to 400 ppm which is higher than preindustrial level of 300 ppm. There are several CO_2 capture technologies such as chemical absorption, physical adsorption and membrane separation that have been studied. Among the current CO_2 capture technologies, chemical absorption by alkanolamines or their mixtures such as monoethanolamine (MEA), diethanolamine (DEA) and *n*-methyldiethanolamine (MDEA) are one of the effective methods for the CO_2 uptake. However, there were some serious drawbacks such as corrosion of amines, limitation of the concentration of amines in solution, and the degradation of amines in high temperature during regeneration process. Thus, this would seriously influence the development of green processing and environmental impact [1–7].

The development of a solution which could absorb high CO_2 which minimizes these disadvantages is highly recommended. Ionic liquids (ILs), organic salt with melting point below 100 °C are an attractive replacement to alkanolamines because they have negligible vapor pressure, high thermal stability, designable structure and wide liquids temperature range [8]. This makes ILs the best candidate to substitute organic solvents for capturing CO_2 [9]. ILs are liquid that contains cations (organic) and anions (organic or inorganic) which are liquid over a wide temperature range with low melting point (below 100 °C). ILs can be designed by an appropriate combination of various cations (quaternary ammonium, imidazolium, pyridinium, phosphonium ions and etc.) and various anions ($[Cl]^-$, $[Br]^-$, $[PF_6]^-$, $[BF_4]^-$, $[Tf_2N]^-$, etc.) [10].

There are numerous studies on the thermal stability of ILs [11–15]. Cao et al. have investigated thermal stability on 66 of ILs by using TGA method [11]. The investigations showed that anion type plays the major role than the cation while cation modification has the least effect. By varying the anions, it has a close relationship with anion coordinating nature, nucleophilicity and hydrophilicity. The thermal stability increased by using shorter alkyl chain, greater substituent number and by replacing the C2-H with a methyl group. The functionalization such as allyl-functionalization would decrease the thermal stability. By studying the functionalized ILs, Liu et al. have studied the thermal stability and decomposition mechanism of amine-functionalized ILs [12]. It showed that amine-functionalized ILs were found to reduce the thermal stability of [aEMMIM]$[BF_4]$ compared to their non-functionalized counterpart. This is due to the tether of amine NH_2 to the imidazolium cation that makes the nearby carbon atom more positively charged hence easier to be attacked by the F from the anion.

ILs also are promising candidates as absorbents for CO_2 removal because of their high thermal stability, negligible vapor pressure and tunable physicochemical properties [16]. Many research groups have carried out research on solubility of CO_2 in ILs [17–21]. Brennecke

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et al. were the first to report on carbon dioxide solubility in imidazolium and pyridinium ionic liquids. They found out that ILs that contain fluoroalkyl chains on either cation or anion improves CO_2 solubility when compared to less fluorinated ILs. These fluorinated ILs have high stability and low reactivity and thus give them many excellent properties [22–25]. However, they are poorly biodegradable and persistent in the environment and thus are less environmentally benign [23]. The anion plays a key role in determining CO_2 solubility in ILs and through physical adsorption with CO_2, less energy is needed for the regeneration of ILs. The enthalpy required is about 20 kJ/mol to release the physically adsorbed CO_2 in regeneration step, which is only a quarter of the energy consumed in amine-based method [6].

Bates et al. have designed a mechanism of TSILs-amine functionalized with CO_2. The reaction mechanism results in a maximum of 0.5 mol of CO_2 being captured with 1 mol of ILs. (1:2 mechanism) [26]. Goodrich et al. suggested that 1:1 (CO_2: IL) mol ratio can be achieved when amine is tethered in anion instead of cation called amino acids ionic liquids (AAILs) [27]. Therefore AAILs have an advantage since amino acids act as anion. Since $[AA]^-$ have a structure of $[H_2N\text{–}CHR\text{–}COO^-]$, it can represented as $R^-\ NH_2$.

$$CO_2 + R^-NH_2 \leftrightarrow R^-N^+H_2COO^- \tag{1}$$

$$R^-N^+H_2COO^- + R^-NH_2 \leftrightarrow R^-NHCOO^- + R^-NH_3^+. \tag{2}$$

The theoretical calculations showed that dianion formed in the second Eq. (2) is chemically unstable therefore the reaction would expect to terminate at Eq. (1) upon addition of CO_2 to AAILs.

Polymerized ionic liquids (PILs) also have attracted recent attention on CO_2 absorption due to their higher CO_2 absorption exhibited by PILs compared to the monomeric ILs [28–32]. PILs can be prepared by polymerization of the monomer or co-polymerization of the monomer with ILs species being in repeating units indicating that PILs have higher CO_2 absorption compared to the monomer [33]. Therefore, PILs would have larger volume which in turn will theoretically trap a large amount of CO_2.

In amino acid-based polymerized ionic liquids (AAPILs), the CO_2 sorption increased and by using functionalized-amine anion, (amino acids), the AAPILs showed higher absorption due to the chemical reaction of amine and CO_2 to form carbamate group.

2. Experimental procedure

2.1. Chemicals

Imidazole, acrylonitrile, 1-bromohexane, 1-bromooctane, 1-bromodecane, 1-chlorohexane, 1-chlorooctane, 1-chlorotetradecane, sodium dioctylsulfosuccinate, sodium dodecylsulfate, sodiumbenzenesulfonate, 3-sulfobenzoic acid sodium salt and lithium trifluoromethanesulfonate 98–99%, 1-chlorobutane, anhydrous methanol, anhydrous ethylacetate, acetone, anhydrous diethyl ether 98–99%, α-(Vinylbenzyl)trimethylammonium chloride 99%, ([VBTMA][Cl]), dimethylformamide (DMF) 99.89%, anhydrous acetonitrile 99.8%, sodium trifluoromethanesulfonate 98%, triethylamine 99.5%, [2-(methacryloyloxy)ethyl]trimethylammonium chloride 75 wt.% in H_2O, ([METMA][Cl]) and sodium methyl sulfate 98%, sodium nitrate 99%, anhydrous sodium acetate 99% and diethylamine 99.5%, 2,6-di-tert-butyl-4-methylphenol (DBMP) 99%, 4-vinylbenzyl chloride 90%, Amberlite IRA 402 (OH form), arginine and proline were purchased from Aldrich. 1-Bromobutane 98% purity was purchased from Merck. Azobisisobutyronitrile (AIBN) 98% was purchased from R&M. Purified gases supplied by MOX-Linde Gases Sdn. Bhd were used for the CO_2 solubilities measurement. The grades of gases used are carbon dioxide 99.99% minimum (moisture <10 ppm, hydrocarbon <1 ppm) and methane, nitrogen, and helium with 99.99% purity. Amberlite IRA 402 (OH form), arginine and proline were purchased from Aldrich. All the chemicals were used without any purification.

2.2. Experimental procedure of task specific ionic liquids (TSILs)

2.2.1. Synthesis of 1-alkyl-3-propanenitrile imidazolium bromide, [C_2CN $C_n$im][Br]

1-Alkyl-3-propanenitrile imidazolium bromide ILs were synthesized by following the method shown in Fig. 1.

Imidazole (0.5 mol) was mixed with methanol and acrylonitrile (0.6 mol) and refluxed under nitrogen atmosphere at 50–55 °C for 10 h. The volatile materials were removed from the mixture under *vacuo* at 70 °C. The viscous liquid left was propanenitrile imidazole. Then, nitrile functionalized IL was synthesized by direct quartenization reaction of the propanenitrile imidazole with 1-bromobutane (0.5 mol). The resulting compound was cooled to room temperature and washed with ethyl acetate and kept in vacuo at 80 °C.

Similar procedure was repeated for the synthesis of 1-hexyl-3-propanenitrile imidazolium bromide, [C_2CN Him][Br], 1-octyl-3-propanenitrile imidazolium bromide, [C_2CN Oim][Br] and 1-decyl-3-propanenitrile imidazolium bromide, [C_2CN Dim][Br] by replacing 1-bromobutane with 1-bromohexane, 1-bromooctane and 1-bromodecane, respectively.

2.2.2. Synthesis of [C_2CN $C_n$im][DOSS]

1-Alkyl-3-propanenitrile imidazolium dioctylsulfosuccinate, [C_2CN $C_n$im][DOSS] was synthesized by mixing [C_2CN $C_n$im][Br] (0.03 mol) and sodium dioctylsulfosuccinate (0.03 mol) in 50 ml acetone. The mixture was stirred at room temperature for 48 h. The solid precipitate formed was separated and the solvent removed in vacuo.

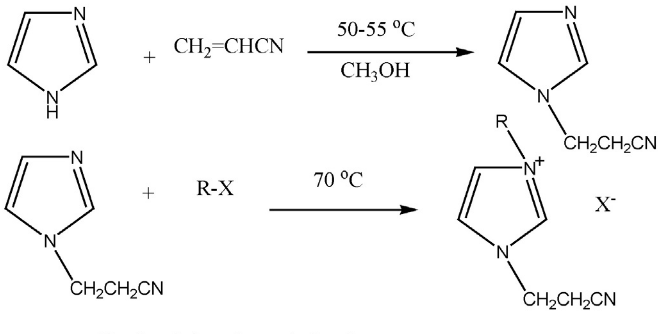
2.2.3. Synthesis of [C_2CN $C_n$im][DDS], [C_2CN $C_n$im][SBA], [C_2CN $C_n$im][BS] and [C_2CN $C_n$im][TFMS]

1-Alkyl-3-propanenitrile imidazolium dodecylsulfate, [C_2CN $C_n$im][DDS] was synthesized by mixing [C_2CN $C_n$im][Br] (0.04 mol) and sodium dodecyl sulfate (0.04 mol) in 40 ml hot deionized water (60 °C). The mixture was stirred at room temperature for 48 h. The solid precipitate formed was separated and the solvent removed by vacuum. Similar procedure was applied to [C_2CN $C_n$im][SBA], [C_2CN $C_n$im][BS] and [C_2CN $C_n$im][TFMS] by using equimolar of sodium sulfobenzoic acids, sodium benzenesulfonate and lithium trifluoromethanesulfonate, respectively.

2.3. Experimental procedure of poly(ionic liquid)s, (PILs)

2.3.1. Synthesis of vinylbenzyltriethylammonium chloride, [VBTEA][Cl]

4-Vinylbenzyl chloride (0.16 mol), triethylamine (0.168 mol) and DBMP (0.4 g) were mixed and stirred at 50 °C for two days under N_2



R = butyl, hexyl, octyl, decyl
X = Br, Cl

Fig. 1. Synthesis route of the RTILs [C_2CN $C_n$im][X].

atmosphere. The formed solid vinylbenzyl triethylammonium chloride [VBTEA][Cl] was washed with diethyl ether, filtered and dried under vacuum.

2.3.2. Synthesis of poly[VBTMA][BF_4], poly[VBTMA][PF_6], poly[VBTMA][TFMS] and poly[VBTMA][NO_3]

Poly[VBTMA][BF_4], Poly[VBTMA][PF_6], Poly[VBTMA][TFMS] and Poly[VBTMA][NO_3] were prepared in two steps. In the first step, metathesis reactions of the [VBTMA][Cl] with sodium tetrafluoroborate, sodium hexafluorophosphate, sodium trifluoromethanesulfonate and sodium nitrate were performed to prepare [VBTMA][BF_4], [VBTMA][PF_6], [VBTMA][TFMS] and [VBTMA][NO_3] respectively. In the second step, [VBTMA][BF_4], [VBTMA][PF_6], [VBTMA][TFMS] and [VBTMA][NO_3] were polymerized by mixing 10 g from each with AIBN (100 mg) and DMF (20 ml) at 60 °C for 6 h. Similar procedure was applied to synthesize Poly[VBTEA]][NO_3] and Poly[METMA][NO_3].

2.4. Synthesis of amino acid-based polymerized ionic liquids (AAPILs)

Two amino acid ionic liquids (AAILs); [VBTMA][Arg] and [VBTMA][Pro] were synthesized according to the following method. In the first step, [VBTMA][Cl], was dissolved in deionized water and underwent anion exchange by subjecting it to a Amberlite IRA 402 (OH form) resin in a column. The resulting [VBTMA][OH] was tested for the presence of chloride by using $AgNO_3$. In the second step, The [VBTMA][OH] was neutralized with an equimolar of arginine [Arg] and proline [Pro] to synthesize [VBTMA][Arg] and [VBTMA][Pro] respectively. The mixtures were stirred at room temperature for 12 h then the water was evaporated by using rotary evaporator at 50 °C with under reduced pressure. The excess of amino acids were precipitated by adding proportions of acetonitrile and methanol in 7:3 ratio. The products ([VBTMA][Arg] and [VBTMA][Pro]) were dried by using rotary evaporator and followed by vacuum oven. In polymerization process, the monomer ([VBTMA][Arg]) (10 g), AIBN (100 mg) and methanol (20 ml) were mixed at 60 °C for 6 h to form poly[VBTMA][Arg]. Similar procedure was repeated for the polymerization of [VBTMA][Pro].

2.5. Characterization of ionic liquids

All the ionic liquids (TSILs) and polymerized ionic liquids (PILs and AAPILs) were characterized by using ^{1}H NMR Bruker Avance 400 (9.4 Tesla magnet), 400 MHz.

The CO_2 sorption measurement was performed by using Magnetic Suspension Balance (MSB), Rubotherm GmbH (Germany) rated at 500 bar and 500 °C. The MSB consists of a sorption chamber where the sample is exposed to a gas at the desired temperature and pressure, and a microbalance with accuracy up to five decimals of a gram. An electromagnet is connected to the microbalance and adjusted to keep the permanent magnet in suspension. The microbalance measures a weight which is proportional to the electromagnetic force that keeps the rod-rod basket assembly in suspension. A heating circulator (Julabo, model F25ME) is used to control the temperature of the sorption chamber with an accuracy of ± 0.5 °C.

FTIR spectra before and after CO_2 sorption were recorded using FTIR Shimadzu in the mid region of 4000–600 cm^{-1} using Diamond Attenuated Total Reflactance (D-ATR) measurement mode.

3. Results and discussion

3.1. ^{1}H NMR

The ^{1}H NMR for all TSILs, PILs and AAPILs are provided at supplementary information (ESI-1). These ^{1}H NMR results confirm the structure of ionic liquids synthesized.

3.2. CO_2 solubility in TSILs

The CO_2 solubility in ILs depends primarily on the strength of interaction of CO_2 with the anion. Five ILs with same cation ([C_2CN Him]) and five different anions ([DOSS], [DDS], [TFMS], [SBA] and [BS]) were used to study the effect of their anions on CO_2 solubility.

3.2.1. Effects of the anions on CO_2 solubility in TSILs

Fig. 2 shows the CO_2 solubility at 10 bar, 298 K with [C_2CN Him] as cation and [DOSS], [DDS], [TFMS], [SBA] and [BS] as anion.

The results showed that the CO_2 solubility depends on the anion type as reported in literature [34]. From Fig. 2, it can be seen that ILs with [C_2CN Him][DOSS] have higher affinity for CO_2 with 0.443 mol fraction compared with the ILs incorporating [DDS], [TFMS], [SBA] and [BS] as anions with 0.281, 0.340, 0.306 and 0.263 mol fraction, respectively. The carbonyl and sulfonyl functionalities, long alkyl chains and branched alkyl chains in [DOSS] lead to good CO_2 solubility [35]. Another major factor is the molar free volume of ILs which exerted a more pronounced effect besides the anion basicity. The larger the molecular size of anion, the larger the free volume in which CO_2 can occupy [36].

The relatively high solubility of CO_2 in the [TFMS] compared to the [DDS], [SBA] and [BS] may be due to the greater interactions between CO_2 and the fluoroalkyl substitutents in [TFMS] anion [37,38]. There are basically two interactions between CO_2 and anion which are an acid–base interaction between CO_2 and anion and also CO_2 and fluorine in anion in ILs [39]. The fluorinated compounds have a high stability and low reactivity which gives them many excellent properties, but these also led them to being poorly biodegradable and persistent in environment [40]. The high solubility of CO_2 in ILs with [SBA] anion compared to [DDS] and [BS] anions is associated with the presence of carbonyl functionality. This enhances a molecule's CO_2 philicity and led to good CO_2 solubility of CO_2 [41]. Moreover, the relatively high solubility capacity of CO_2 in [DDS] compared to [BS] anion is due to the long alkyl chain of [DDS], which results in the increases of *van der* Waals-type interactions between the gas and the liquids.

3.2.2. Effects of cations on CO_2 solubility in TSILs

The influence of ILs cation on CO_2 solubility was studied by comparing the CO_2 solubility with a similar anion, [DOSS] and difference of alkyl chain length from butyl to decyl. Fig. 3 shows the CO_2 solubility at temperature 298 K, 10 bar.

From Fig. 3, it can be seen that the CO_2 solubility increases as the alkyl chain length increases; [C_2CN Bim] (0.412 mol fraction) < [C_2CN Him] (0.443 mol fraction) < [C_2CN Oim] (0.502 mol fraction) < [C_2CN Dim] (0.548 mol fraction). As expected, CO_2 is more soluble in ILs with long alkyl chain. The alkyl groups also increases the dispersion force of the cation for better interaction with CO_2 [42]. The increasing trend for CO_2 solubility in the [C_2CN Bim][DOSS], [C_2CN Him][DOSS], [C_2CN

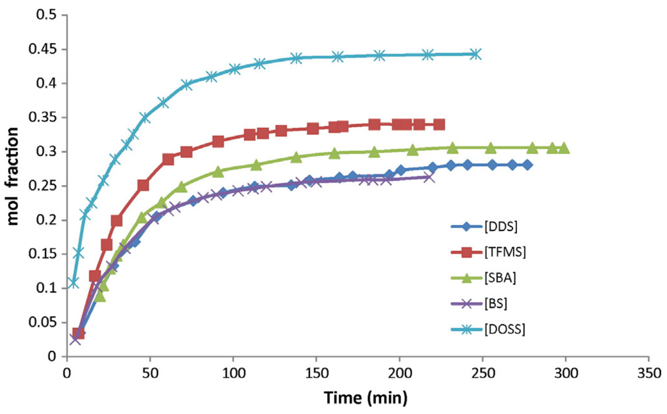


Fig. 2. Effect of anion on CO_2 solubility with [C_2CN Him] as cation.

Oim][DOSS] and [C_2CN Dim][DOSS] may be due to the increase of the molar volume and the presence of the CN group in the side chain of the ILs. This is because the presence of the CN group would change the architecture of the hydrogen bonding network of these ILs. The differences in the alkyl chain affects the hydrogen bond interaction between the C-2 of the imidazolium cation, the remaining H atoms on the cation and the anions [43].

However, these TSILs often suffer the problem of having high viscosity. On the other hand, polymerized ionic liquids (PILs) have recently attracted attention for CO_2 absorption due to its solid form and exhibiting higher CO_2 sorption compared to the monomeric ILs [28–33]. The properties of PILs also can be customized by varying the combination of polycation-anion pair [44].

3.3. CO_2 solubility in poly ionic liquids (PILs)

3.3.1. Effects of polymerization on PILs

Fig. 4 shows the solubility of CO_2 by [VBTMA][Cl] monomer and its polymer poly[VBTMA][Cl] at 10 bar, 298 K.

From Fig. 4, it can be concluded that the polymerization increased the sorption capacity. The polymer, poly[VBTMA][Cl] showed CO_2 solubility at 0.188 mol fraction higher than the monomer, [VBTMA][Cl] at only 0.07 mol fraction.

3.3.2. Effects of cations with CO_2 in PILs

The type of cation for PILs with [NO_3] showed a significant effect on sorption capacity. Fig. 5 shows the CO_2 sorption for different cations with [NO_3] as anion at 10 bar, 298 K.

The results showed that the sorption trend is in the order of poly[VBTMA][NO_3] 0.177 mol fraction > poly[VBTEA][NO_3] 0.133 mol fraction > poly[METMA][NO_3] 0.066 mol fraction. This is agreed by Tang et al. where the [VBTMA] cation shows higher CO_2 sorption than [VBTEA] and [METMA] cation [45]. The result shows that, polycation with longer alkyl side chain may pose a stearic hindrance that hinders CO_2 sorption thus results in a decrease of microvoid volume with fewer interaction between CO_2 and cation [44]. Therefore, long alkyl substituents on the cation and cross-linking would decrease the CO_2 sorption capacity [45]. This explains the highest sorption rate of poly[VBTMA][NO_3] compared to poly[VBTEA][NO_3]. The difference between [VBTMA] and [METMA] is the structure of backbone. PILs with [VBTMA] have vinylbenzyl backbone and this would enhance the sorption rate and CO_2 capacity compared to methacryloyloxyethtyl backbone poly ionic liquids [44].

This trend was agreeable at low pressure (592.3 mmHg, 22 °C) as reported by Tang et al. where poly[VBTMA][BF_4] shows higher CO_2 sorption with 10.2 mol% follows with poly[VBTEA][BF_4] (4.85 mol%) and poly[VBTBA][BF_4] with 3.1 mol% [46].

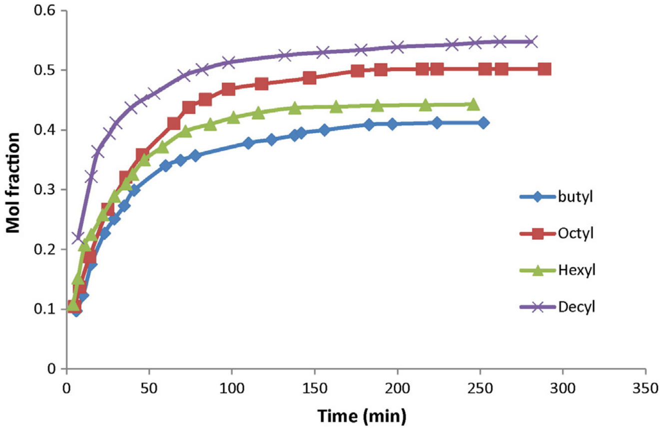


Fig. 3. Effects of cations in ILs on CO_2 solubility with [C_2CNC_nim] cation (butyl,octyl, hexyl, decyl) and [DOSS] as anion.

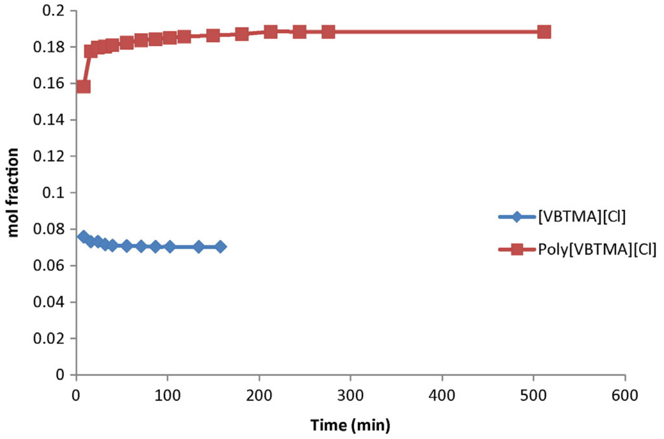


Fig. 4. CO_2 solubility for [VBTMA][Cl] and poly[VBTMA][Cl] at 10 bar, 298 K.

3.3.3. Effect of anions with CO_2 in PILs

Fig. 6 shows the CO_2 sorption on different of anion with [VBTMA] as cation at 10 bar, 298 K. The anions studied were [Cl], [BF_4], [NO_3], [PF_6] and [TFMS].

From Fig. 6 can be seen that poly[VBTMA][BF_4] shows the highest CO_2 sorption capacity with 0.209 mol fraction. The sorption capacity is in the order of poly[VBTMA][BF_4] (0.209 mol fraction) > poly[VBTMA][Cl] (0.188 mol fraction) > poly[VBTMA][PF_6] (0.180 mol fraction) > poly[VBTMA][NO_3] (0.177 mol fraction) > poly[VBTMA][TFMS] (0.164 mol fraction). Contrary to RTILs, in PILs the presence of fluorine atom in anion is not a decisive factor to enhance the CO_2 sorption which explains the lower of CO_2 sorption in PF_6 and TFMS anions. This is agreed by Tang et al. that poly[VBTMA][Tf_2N] (2.85 mol%) had a sorption capacity much lower than [BF_4] and [PF_6] anions and similar to non-fluorinated PILs which is poly[VBTMA][Sac] with 2.67 mol% [46]. This indicates that in PILs, fluorine atom is not a decisive factor for CO_2 sorption. The bulky anion on [TFMS], may decrease the spare volume and would prevent CO_2 penetration towards the polycation which is responsible for CO_2 capture [44].

From these results, it can be concluded that by polymerizing the ionic liquids, the CO_2 sorption increases than in monomeric forms. However, this PILs CO_2 solubility results are much lower than in reported TSILs. Therefore, we synthesized amino acid-based polymerized ionic liquids (AAPILs) where it has amine tethered in the anions, so the chemisorptions of CO_2 can be achieved.

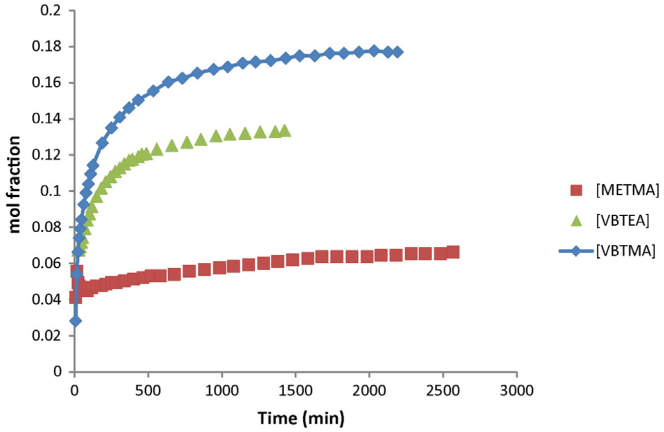


Fig. 5. CO_2 sorption for different poly cations with [NO_3] as anion at 10 bar.

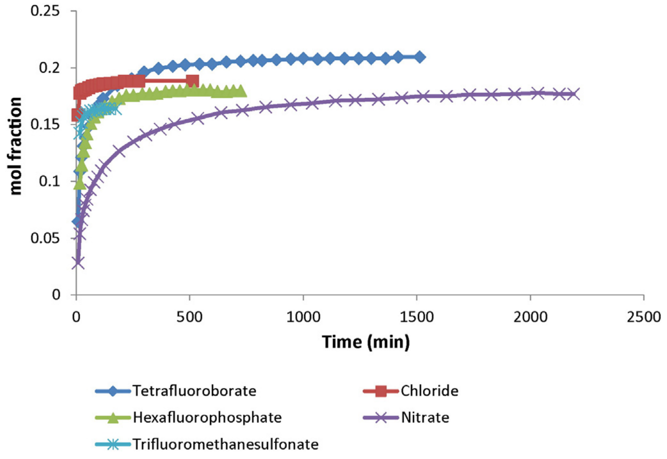


Fig. 6. CO_2 sorption on different anions and poly [VBTMA] as cation.

3.4. CO_2 solubility in amino acid-based polymerized ionic liquids (AAPILs)

In AAPILs, the anion used was amino acids where it has functionalized amine tethered at the anion. Fig. 7 shows the CO_2 sorption of the monomer, amino acids ionic liquids (AAILs) and the polymer, amino acid-based polymerized ionic liquids (AAPILs). The CO_2 sorption was carried out in low pressure (P_{eq} 0.7 bar) at 298 K. From these results, it can be observed that poly[VBTMA][Arg] gave higher CO_2 sorption at 0.530 mol fraction compared to poly[VBTMA][pro] at 0.380 mol fraction. These AAPILs also showed higher CO_2 sorption compared with the monomers, [VBTMA][Arg], 0.454 mol fraction and [VBTMA][Pro], 0.274 mol fraction. This indicates that polymerization increases the CO_2 sorption of the monomer [47]. Arginine, [Arg] shows higher CO_2 sorption than proline, [Pro] anion. This is mainly because of arginine, [Arg], comprises of two primary amines and two secondary amines. Thus, the accessibility of CO_2 to react with one or more of these four amine sites is an advantage compared to the [Pro] anion; has one secondary amine in a ring [48].

These results are similar with those reported in the literature that AAILs with more than one amine site have shown higher CO_2 absorption capacity than the AAILs with only one primary amine group. Sistla et al. reported that [bmim][Arg] has shown higher CO_2 sorption with 0.62 mol/mol due to the availability of more accessible amine groups [48]. Saravanamurugan et al. reported that [N_{66614}][Arg] shows higher CO_2 sorption with 1.0 mol CO_2/mol ILs with arginine containing several additions of amine groups [16]. Xue et al. have synthesized dual amine ILs, [aemmim][Tau], where the amine tethered to the cation and anion. The absorption capacity of CO_2 reaches 0.9 mol CO_2 per mol ILs at 303 K, 1 bar [49]. The absorption mechanism shows chemical process and it confirms by NMR and FTIR. This CO_2 can easily desorb at higher temperature and under vacuum therefore, it can be reuse.

These results support the idea that the CO_2 sorptions of PILs were affected by anion types. From these results, we have showed that AAPILs with polymerized amino acids-anion showed much higher CO_2 sorption compared to other PILs.

3.4.1. Effect of pressure

The CO_2 sorption for poly[VBTMA][Arg] was measured in the range 0.7 to 10 bar in 25 °C. Fig. 8 shows the effect of pressure on CO_2 sorption to poly[VBTMA][Arg].

The plot indicates that the CO_2 absorption increases with increasing pressure. At 7.7 bar, the CO_2 absorbed was 0.742 mol ratio which, was higher compared to 0.530 mol ratio at 0.7 bar. It can be seen that the CO_2 molar uptake increases continuously with increasing pressure under studied conditions. At low pressure, a large uptake of CO_2 can be expected to be due to the chemical absorption process and the further increase at higher pressure is in part because of physical adsorption [27]. This is especially relevant at high pressures whereas they reach their absorption limits at low pressure. This is agreed by Chen et al. where there are both physical and chemical interactions between amine-functionalized ionic liquids with CO_2 [50]. In general, this arginate AAPILs might have an absorption capacity as high as 2 mol CO_2/mol ILs if all of the amine nitrogens are active towards CO_2. This shows how the absorption performances of AAILs merge the characteristics of physical solvents with the attractive features of chemical solvents [51]. The time required in high pressure for the system to attain equilibrium increases because of the chemical complexation by forming carbamate species as well with physical adsorption on poly[VBTMA][Arg].

3.4.2. Characterization of AAPILs after CO_2 sorption

The characterization of poly[VBTMA][Arg] after CO_2 absorption can be characterized by using FTIR before and after CO_2 absorption as shown in Fig. 9. The reaction CO_2 and amine shows a broad peak in the range 3280–3350 cm^{-1} which corresponds to –NH in secondary amides that resulted from CO_2 reacting with NH_2. New peak with high intensity at 1639 cm^{-1} indicate the carbamate species. The reaction of CO_2 and NH_2 was confirmed in poly[VBTMA][Arg]. The increasing of intensity after CO_2 sorption also can be seen. This confirmed that the chemical and physical sorption occurred in poly[VBTMA][Arg].

4. Conclusion

The development of ionic liquids for CO_2 sorptions have been studied from TSILs followed with PILs and AAPILs. Poly[VBTMA][Arg]

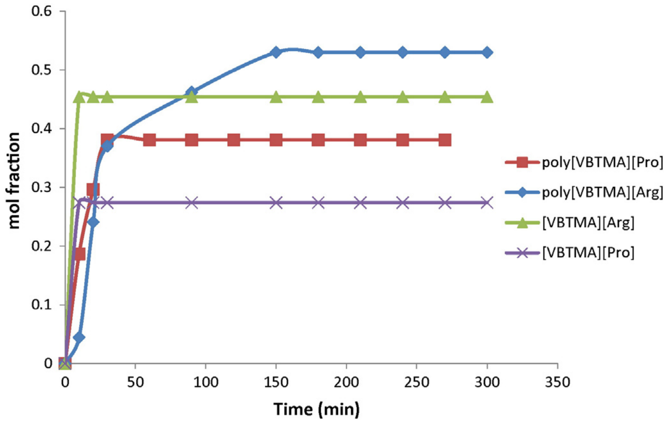


Fig. 7. CO_2 sorption of AAPILs and AAILs in 0.7 bar, 298 K.

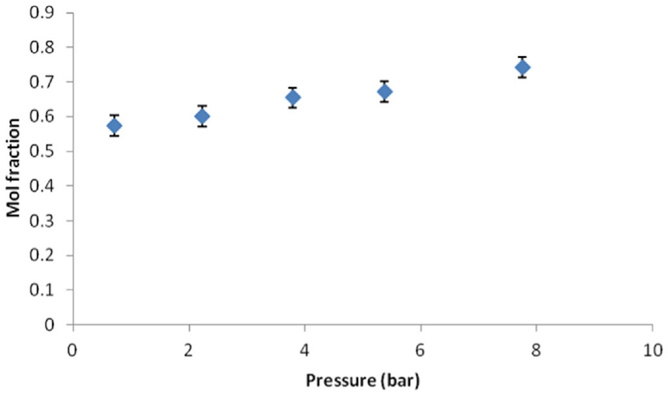


Fig. 8. CO_2 sorption of poly[VBTMA][Arg] with increasing pressure.

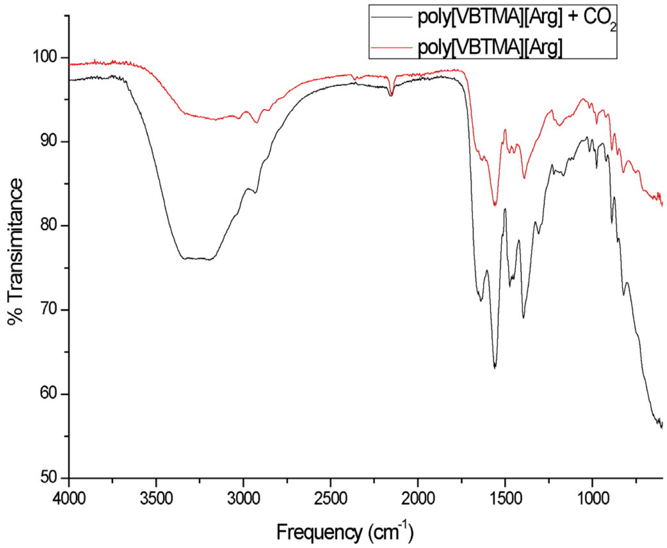


Fig. 9. FTIR spectrum before and after CO_2 sorption on poly[VBTMA][Arg].

showed higher CO_2 sorption with 0.530 mol fraction in 0.7 bar, because the structure [Arg] has greater numbers of amines to react with CO_2. By comparing the data on the best TSILs, PILs and AAPILs synthesized, at 10 bar [C_2CNDim][DOSS] gave the CO_2 sorption up to 0.55 mol fraction. For PILs, Poly[VBTMA][BF_4] with 0.209 mol fraction and for AAPILs, poly[VBTMA][Arg] gave the highest CO_2 sorption at 0.742 mol fraction. This is confirmed that by polymerized the ionic liquids and with anions-amine functionalized would enhances the CO_2 sorption.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.molliq.2016.02.046.

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