Absorption of carbon dioxide in aqueous solutions of imidazolium ionic liquids with carboxylate anions

Stefan Baj[*,**], **Tomasz Krawczyk**[*,†], **Aleksandra Dąbrowska**[*], **Agnieszka Siewniak**[*], and **Aleksander Sobolewski**[**]

*Department of Chemical Organic Technology and Petrochemistry, Faculty of Chemistry,
Silesian University of Technology, Krzywoustego 4, 44-100 Gliwice, Poland
**Institute for Chemical Processing of Coal, Zabrze, Poland

Abstract−The solubility of carbon dioxide at atmospheric pressure in aqueous mixtures of 1,3-alkyl substituted imidazolium ionic liquids (ILs) containing carboxylic anions was studied. The ILs showed increased solubility of CO_2 with decreasing water concentration. The relationship between the CO_2 concentration in solution and the mole fraction of water in the ILs describes a sigmoidal curve. The regression constants of a logistic function were used to quantitatively assess the absorbent capacity and the effect of water on CO_2 absorption. ILs containing the most basic anions, such as pivalate, propionate and acetate, had the best properties. It was observed that the impact of water on absorption primarily depended on the cation structure. The best absorption performance was observed for 1,3-dibutylimidazolium pivalate and 1-butyl-3-methyl imidazolium acetate.

Keywords: Absorption, Carbon Dioxide, Carboxylate Ionic Liquids, Solubility, Water Content
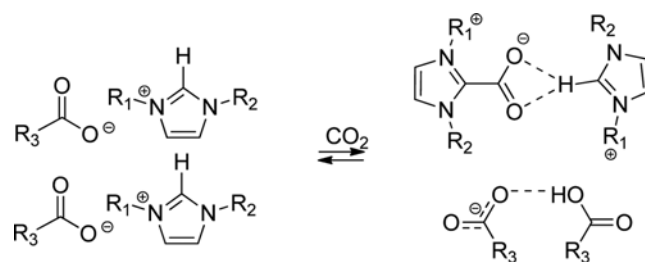
INTRODUCTION

Since the ratification of the Kyoto Protocol in 1997, which was aimed at reduction of the greenhouse gas emissions, a number of research teams have undertaken investigations into new and economical ways of mitigating human-induced interference with the atmosphere. The main goal of the Kyoto Protocol was the reduction of CO_2 emissions [1]. At its current stage of evolution, civilization is largely dependent on fossil fuels, and a possible means of achieving the goal of the Kyoto Protocol is the separation of CO_2 from flue gas followed by underground or deep-ocean storage (CCS) [2,3]. The most cost-intensive stage of this solution is the separation of CO_2, which can be conducted using an available amine gas processes [4]. This technology has been well known for over a century, but it is expected that its application for carbon capture and storage in a conventional coal-fired power plant would lead to a 14-38% reduction of the electricity output [4,5]. This reduction is a major economic incentive, which has triggered the emergence of a number of alternatives, such as new solvents, membranes and adsorbent-based technologies [6]. Some of the most promising modern solvents for CO_2 capture are ionic liquids [7,8]. They offer good thermal stability, low heat capacity, tunable properties and high CO_2 uptake [9]. However, the high viscosity and the relatively high production cost are still among the factors limiting the wider use of this industrial practice [10].

Absorption of CO_2 by ILs is governed by either chemical or physical processes [11]. A number of different mechanisms have been proposed for chemisorption. The most obvious is a reaction between the NH_2 group of a functionalized IL and the formation of the corresponding carbamate, which implies a 1 : 2 molar ratio of CO_2 to amine [12]. The quantity may be altered to a more favorable 1 : 1 stoichiometry when the amine is tethered to the anion close to the charge center [13]. Another possible mechanism involves formation of hydrogen-bonded complexes in carboxylate functionalized ionic liquids in the presence of water [14]. Other authors postulated bicarbonate formation in alkylammonium acetate and its water complexes [15]. A more unusual reaction involving the formation of an O-C bond was suggested for dry (i.e., 2.1 ppm of water) ether functionalized ILs [16-18].

For imidazolium ILs containing basic anions of carboxylic acids, the absorption of CO_2 occurs due to the formation of a C-C bond between CO_2 and the C2 carbon of the imidazolium ring. Such ILs are able to absorb CO_2 up to 1 mol per 2 moles of IL at atmospheric pressure. The mechanism, which has been confirmed by an X-ray structure [19] of the solid products isolated from a reaction between CO_2 and an IL, is shown in Scheme 1.

An attractive feature of this type of IL is the low heat of CO_2 absorption (approximately $-30 \text{ kJ mol}^{-1} CO_2$), which is less than half that observed for aqueous amine absorbents [20]. Simulations have

†To whom correspondence should be addressed.
E-mail: tomasz.krawczyk@polsl.pl

Scheme 1. Mechanism of CO_2 absorption in imidazolium ILs.

implied that the low heat of CO_2 absorption allows for reducing the operating costs of an industrial absorption installation, but increased investment costs are involved [21]. The anion basicity is the most important structural property of the imidazolium ILs that affects their absorption capacity. The best results were obtained for pivalate and acetate [22]. This class of ILs is water-soluble; therefore their high viscosity can be lowered by dilution. The presence of water has also a positive impact on mass transfer properties of ILs, yet it is detrimental to the cost of absorbent regeneration [23] and to the absorption capacity [24].

The aim of this study was to establish a possible IL structure with a high absorption capacity that would be minimally affected by the presence of water.

EXPERIMENTAL

1. Reagents and Materials

The commercial chemicals required for the synthesis of ILs were reagent grade (95-99%) and were used without further purification. The ILs 1-butyl-3-methylimidazolium acetate (95%) and 1-butyl-3-methylimidazolium trifluoroacetate (96%) were purchased from Sigma-Aldrich (Steinheim, Switzerland). Other ILs were prepared by using two standard procedures: an anion exchange between 1-butyl-3-methyl imidazolium chloride and sodium salt of various carboxylic acids [25], and a one-pot synthesis using the reaction between glyoxal, formaldehyde, amine and carboxylic acid to yield 1,3-dialkyl imidazolium carboxylic ILs [26]. The products of this reaction were sufficiently pure and required no further treatment, as confirmed by ^1H and ^{13}C NMR data. The samples were dried for two weeks in a desiccator. The water content was measured by a Karl Fischer method.

2. Measurement of CO_2 Solubility in Binary IL-water Systems

To measure the CO_2 solubility, a portion of IL (1 g) was weighted into a 5 mL round bottom two-neck flask (1). The flask was placed in an oil bath (2) to maintain constant temperature (25 °C) and connected with the remainder of the apparatus. The gas burette was filled with ethylene glycol. Prior to each measurement, CO_2 was bubbled through the vessel (3) to saturate the glycol with CO_2, because of the non-zero solubility of CO_2 in ethylene glycol. The lack of CO_2 absorption or desorption from ethylene glycol as well as the tightness of apparatus were confirmed by checking the liquid level stability in the burette (4). Before measurements were made, the flask was evacuated by a vacuum pump and then filled with CO_2 at atmospheric pressure by switching the valve (5). While stirring with a magnetic stirrer (6), the CO_2 consumption was measured as a function of time until the equilibrium of the CO_2-IL reaction was reached. Then, portions of H_2O were injected into the flask with a syringe (7). Typically, 15 portions were added. The weight of each portion of water was calculated based on the weight of the syringe before and after the injection. Each portion of water caused the desorption of a certain volume of CO_2. The measurements were repeated at least twice using separate samples of the IL. The accuracy of the CO_2 volume measurement was 0.1 mL. The uncertainty of the CO_2 concentrations calculated in binary IL-water systems was 0.01-0.05 mol dm^{-3}. Statistical evaluation of the results and nonlinear regression was performed with STATISTICA 10 software.

The concentration of absorbed CO_2 in the solutions was calculated assuming a constant density of 1 g cm^{-3} for all liquids.

RESULTS AND DISCUSSION

The mechanism of CO_2 absorption by imidazolium ILs containing carboxylate anions (Scheme 1) implies the possibility of stoichiometric absorption of 1 mol of CO_2 per 2 moles of IL. However, that value was not recorded for any IL of this class. With the decrease of basicity of carboxylic anions, the absorption capacity decreases [22]. Additionally, the cation structure was suggested to be a contributing factor [27]. The impact of the water content was investigated by other researchers, but no attempts were made to establish a quantitative relationship between the structure of ILs and the effect exerted by water on absorption [24].

The absorption capacities of various imidazolium ILs were measured and the effect of the presence of water was investigated for a broad range of concentrations regarding the amount of CO_2 that could be absorbed by aqueous solutions of ILs, focusing on 1-butyl-3-methyl and 1,3-symmetrically substituted imidazolium ILs with carboxylic anions. The pK_b of the carboxylic acids employed varied between 8.97 (pivalic) and 13.48 (trifluoroacetic). The alkyl chain length was investigated over a range of 1 to 8 carbon atoms. An attempt to synthesize ILs bearing aromatic substituents in imidazolium ring yielded solid products at room temperature, but these were not suitable as absorbents.

The measurements were performed by absorbing CO_2 in a sample of an IL (1 g) using a gasometric apparatus (Fig. 1). After attaining equilibrium, portions of water were added and the volume of the CO_2 released was recorded. The results were plotted as the amount of CO_2 absorbed as a function of water content. Representative sets of data are shown in Fig. 2.
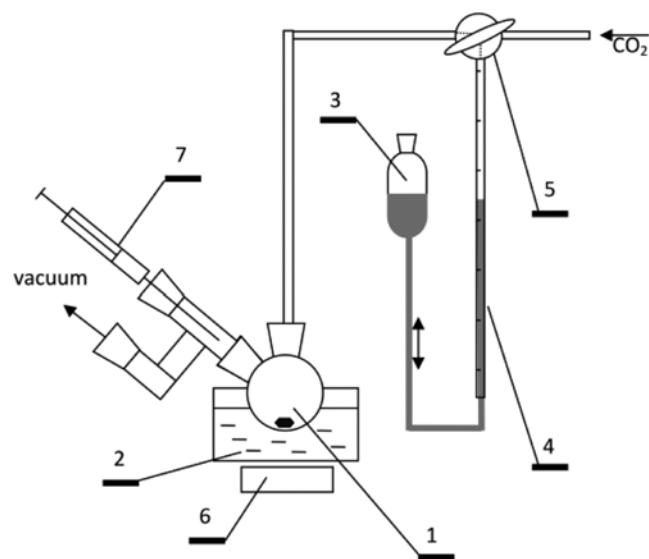

Fig. 1. Schematic diagram of a gasometric apparatus.
1. Flask with stirring rod
2. Oil bath (25 °C)
3. Vessel with ethylene glycol
4. Glass burette (50 mL)
5. Valve
6. Magnetic stirrer
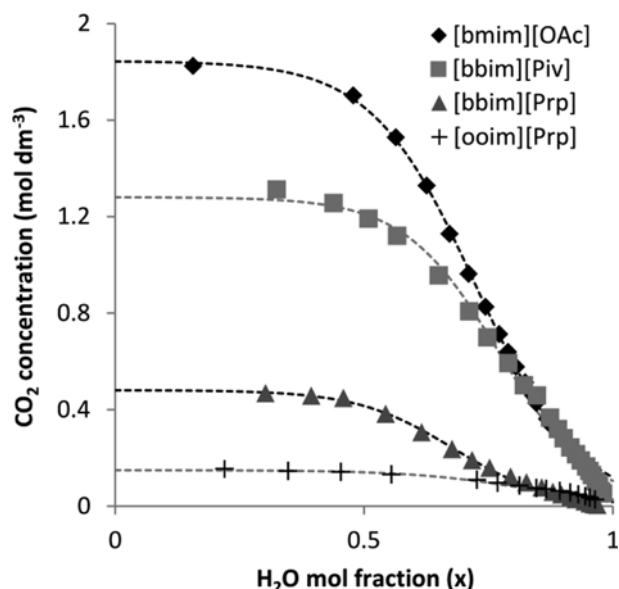7. Syringe with water

Fig. 2. Absorption capacity of binary mixtures of imidazolium ILs with water. Dashed lines correspond to Eq. (1).

It is clear that the absorption capacity varied between ILs, but the relationship between the water content in the absorbent and the CO_2 concentration in the liquid phase followed the same trend for all samples. A logistic function (Eq. (1)) fitted the data well (x represents the mole fraction of water). For all systems, the R^2 values were 0.998 or higher. The values predicted usually showed a 1-5% discrepancy against the actual data. Higher deviations were observed in the region of high water concentrations (x>0.9).

$$[CO_2] = \frac{z}{1 + be^{a(x-1)}} \qquad (1)$$

The physical sense of experimental coefficient z is the absorption capacity of pure IL in molar concentration units. The dimensionless coefficients b and a describe the impact of water on absorption. Essentially, with an increase of b, the effect of water is more detrimental, but the converse is true for the coefficient a. To compare the ILs, the b to a ratio was used as a good descriptor of the

effect of water. All results are summarized in Table 1.

The experimentally determined CO_2 capacity of ILs, expressed as moles of CO_2 per moles of IL, is linearly correlated with z. In terms of moles dm^{-3} of CO_2, the best results were obtained for [bmim][OAc], while [bbim][Piv] delivered better results when molar ratios of CO_2 to IL were compared. A high absorption capacity is only displayed by those ILs that contain anions of pK_b less than 10. Nevertheless, this does not guarantee good absorption, and some ILs containing acetate or propionate anions had a low absorption capacity. The impact of the cation structure was not straightforward. Cations containing only methyl or octyl groups were not suitable. The best results were obtained for cations of moderate size, especially those with different substituents at positions 1 and 3. Similar differences for a larger cation were found for 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium acetates [28]. It is likely that this effect is a consequence of the probability of a C-C bond formation between CO_2 and C2 carbon of the imidazolium ring. The impact of the cation structure was studied by other researchers with DFT calculations, and they showed that the absorption energy may vary as much as threefold for 1-*n*-butyl-3-methyl and 1-*tert*-butyl-3-methyl imidazolium acetates [27]. These results imply that 1-butyl-3-methyl substitution is better than the 1,3-dibutyl variant. Nevertheless, the effect can be offset by the anion basicity. This may be a consequence of an absorption mechanism in which two imidazolium rings participate in the coordination of one CO_2 molecule, while the displaced proton is coordinated by two anions. If the cations are sterically hindered, then the coordination is weaker. For small cations, such as [mmim], a stronger interaction between the anion and the cation might inhibit the absorption process.

Previously published data suggest a similar structure-absorption relationship. To the best of our knowledge, other experimental data for CO_2 absorption are available for [bmim][TFA], [bmim][Prp] and [bmim][OAc] [28]. Similar capacities as those studied in this paper were reported, and a considerably lower capacity of [bmim][Prp] was recorded, yet the relative order was unchanged, most likely as a consequence of a different water content in the samples or the presence of various impurities, such as small excess of free carboxylic acid. Other compounds discussed in this paper are either new ([ooim][Prp], [bbim][Piv], [bbim][Prp]), or no relevant

Table 1. Quantitative description of CO_2 absorption in the ILs investigated and their basic properties

IL	z (mol dm^{-3})	a	b	Water effect (b/a)	pK_b	MW	Maximal capacity (mol CO_2 mol IL^{-1})
[bmim][OAc]	1.84	11	18	1.6	9.25	198.3	0.37
[bbim][Piv]	1.31	11	12	1.1	8.97	282.4	0.40
[bmim][Prp]	1.03	14	23	1.6	9.25	212.3	0.23
[mmim][Prp]	0.61	11	47	4.3	9.13	170.2	0.10
[mmim][OAc]	0.58	10	40	3.9	9.25	156.2	0.08
[bmim][For]	0.54	9	26	3.0	10.25	184.2	0.10
[bbim][OAc]	0.50	14	50	3.5	9.25	240.3	0.12
[bbim][Prp]	0.47	11	25	2.3	9.13	254.4	0.12
[ooim][Prp]	0.15	9	4	0.5	9.13	366.6	0.06
[bbim][Lac]	0.14	9	15	1.6	10.15	270.4	0.04
[bmim][TFA]	0.08	7	14	2.1	13.48	252.2	0.02
[bmim][Slc]	0.05	6	16	2.4	11.03	276.3	0.01

data are available.

Studies on a larger number of imidazolium ILs containing carboxylic anions [22,28-30] have demonstrated that aromatic, dicarboxylic or formate anions are not suitable as an IL building block for CO_2 absorption, whereas phenolate [30], pivalate, levulinate, propionate, acetate or isobutyrate [28] showed better performance. These data confirm that the pK_a of the anion is a major factor affecting the absorption of CO_2, and they are consistent with the observations made by the authors for a different set of compounds.

An interesting feature of the absorption process was observed when the first derivative of the relationship between the water concentration and the CO_2 concentration was calculated. At a low water content, the capacity change rate increases, reaches a minimum and then decreases. The inflection point is approximately at 0.5-0.7 molar fraction of water (Fig. 4).

The foregoing suggests that the absorption mechanism may differ between both concentration ranges. As determined by other authors using X-ray data [19], CO_2 reacts with water and IL leading to the formation of bicarbonate (Scheme 2). For ILs with a low absorption capacity, such as [ooim][Prp], the effect is negligible. In those cases, it is likely that absorption proceeds according to Scheme 2 over the entire concentration range or that physical absorption substantially contributes to the observed capacity.

The results obtained in this study imply that the formation of bicarbonate becomes dominant when water concentration is higher
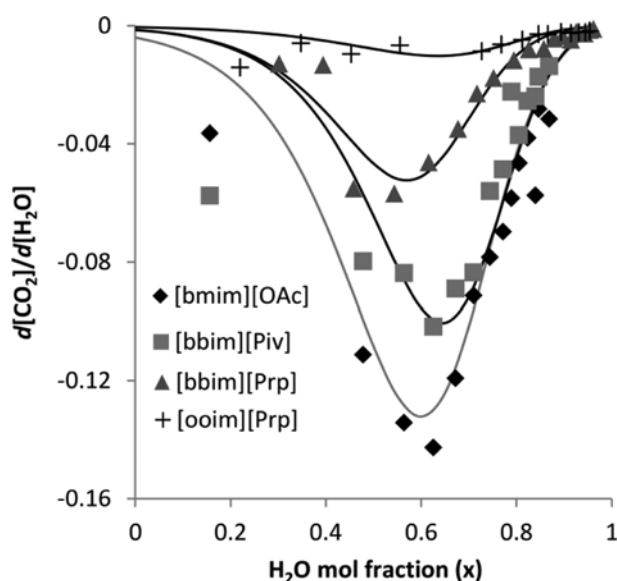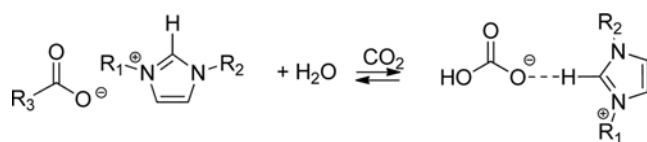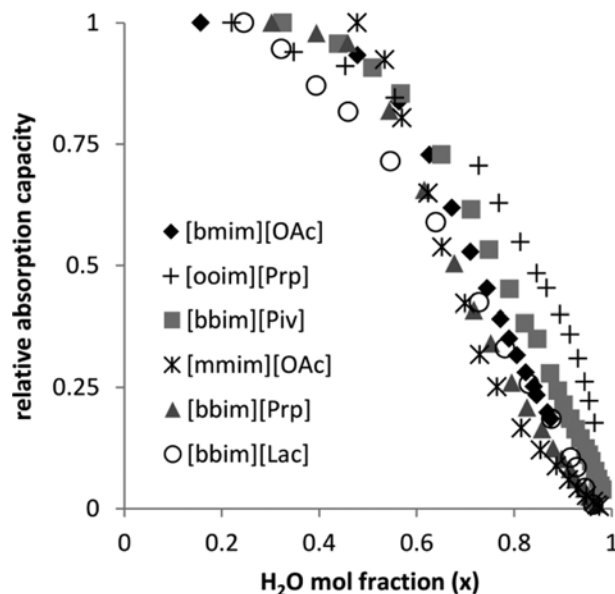

Fig. 3. Effect of water on relative absorption capacity of aqueous solutions of imidazolium ILs.

than the concentration of IL. With further addition of water, the chemisorption capacity is diminished, most likely as a consequence of the competition between water and CO_2 for solvation sites [28].

In all cases, the presence of water negatively affected the absorption capacity of the ILs. The differences between the ILs were relatively high and depended on the molar fraction of water. This fact is illustrated in Fig. 3.

The impact of water quantified in terms of the b and a ratio mainly depended on the cation molecular weight, as it decreased in the following order: [mmim]>[bbim], [bmim]>[ooim].

The ILs studied can be divided into four categories depending on their CO_2 absorption capacity (z>1 or z<1) and the effect of water on their capacity (b/a>2.5 or b/a<2.5). There were no high-capacity ILs which would be largely affected by water. Because both empirical constants were apparently not correlated with each other, it was possible to select an IL characterized by properties suitable in terms of the overall CO_2 absorption capacity that was less affected by water. In the case analyzed, [bbim][Piv] displayed the best performance.

CONCLUSIONS

The most important factor limiting the absorption capacity of imidazolium ILs was the anion basicity. This effect was particularly apparent when pK_b was higher than 10 units, as all the best performing ILs fell within this region. The highest capacities were noticed for pivalate, propionate and acetate, which were the most basic. The cation structure also exerted an important impact on the absorption capacity. The 1-butyl-3-methyl substituted ILs (acetates and propionates) performed better than 1,3-dibutyl analogs. It is likely that this effect may be offset to a certain extent by the anion basicity. The water sensitivity of the absorbents studied was most likely a consequence of the CO_2 absorption mechanism, particularly because

Fig. 4. First derivative of the relationship between water concentration and CO_2 concentration. Solid lines correspond to results obtained from Eq. (1).

Scheme 2. Alternative mechanism of CO_2 absorption by imidazolium ILs in the presence of water.

ILs that only displayed physical absorption or absorption by means of bicarbonate formation were less affected. Therefore, the ILs which primarily absorb by means of the imidazolium ring carboxylation are likely to be equally affected by the presence of water, but the differences in viscosity and MW can be considered during the structure optimization.

Whether the arrangement of cations and anions at the molecular level has any impact on the CO_2 absorption is interesting. If so, then certain combinations of alkyl groups in the imidazolium ring and the anion structure may yield better results than those discussed in this paper. Further research should be focused on acetate and pivalate anions and cations containing 1-5 carbon atoms as substituents of the imidazolium ring.

ACKNOWLEDGEMENT

NOMENCLATURE

a   : empirical parameter of Eq. (1)
b   : empirical parameter of Eq. (1)
x   : mol fraction of water
z   : empirical parameter of Eq. (1)

Abbreviation

[bbim][Lac]   : 1,3-dibutylimidazolium lactate
[bbim][OAc]   : 1,3-dibutylimidazolium acetate
[bbim][Piv]   : 1,3-dibutylimidazolium pivalate
[bbim][Prp]   : 1,3-dibutylimidazolium propionate
[bmim][TFA]   : 1-butyl-3-methylimidazolium trifluoroacetate
[bmim][For]   : 1-butyl-3-methylimidazolium formate
[bmim][OAc]   : 1-butyl-3-methylimidazolium acetate
[bmim][OAc]   : 1-butyl-3-methylimidazolium acetate
[bmim][Prp]   : 1-butyl-3-methylimidazolium propionate
[bmim][Slc]   : 1-butyl-3-methylimidazolium salicylate
[mmim][OAc]   : 1,3-dimethylimidazolium acetate
[mmim][Prp]   : 1,3-dimethylimidazolium propionate
[ooim][Prp]   : 1-butyl-3-methylimidazolium propionate
CCS   : carbon capture and storage
DFT   : density functional theory
IL   : ionic liquid

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