A New Approach to CO_2 Capture and Conversion Using Imidazolium Based-Ionic Liquids as Sorbent and Catalyst

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Embora tecnologias de captura e armazenamento de carbono (CCS) estejam recebendo grande atenção para a mitigação do efeito estufa, ainda existem muitas desvantagens, tais como o aumento dos custos e gastos de energia associados à sua implementação. No entanto, o uso de CO_2 como bloco de construção C1 em síntese orgânica pode ser muito atraente para o desenho de processos ecológicos. Neste trabalho, foram estudados a sorção de CO_2 e atividades catalíticas de alguns líquidos iônicos (ILs) base imidazólio para síntese de carbonato cíclico. O trabalho demonstra que a presença de um grupo nucleófilo no sistema catalítico pode melhorar seu desempenho, através da utilização de um IL com ânion halogenado ou por mistura de co-catalisador halogenado com ILs. A última abordagem permitiu a obtenção de um sistema de captura de CO_2 eficaz, constituída por IL fluorado mais $ZnBr_2$ que realiza a síntese de carbonato cíclico com 90% de rendimento e 82% de seletividade.

Although the carbon capture and storage (CCS) technologies are receiving great attention for mitigation of greenhouse gas effect, the increasing costs and energy penalties associated to its implementation are still major drawbacks. However, the use of CO_2 as a C1 building block in organic synthesis can be very attractive for the design of environmentally friendly processes. In this work, we have studied both the CO_2 sorption and catalytic activities of some imidazolium based ionic liquids (ILs) for cyclic carbonate synthesis. The work demonstrates that the presence of a nucleophilic group in the catalytic system can enhance its performance by the use of an IL with a halide anion or by mixing a halide co-catalyst with ILs. The latter approach allowed to obtain an effective system for CO_2 capture constituted by a fluorinated IL plus $ZnBr_2$ that performs cyclic carbonate synthesis with 90% yield and 82% of selectivity.

Keywords: ionic liquids, CO_2 capture, cyclic carbonate

Introduction

The increase of CO_2 concentration in the atmosphere and, consequently, the intensification of global warming are posing major problems to the environment. Actions aiming to reduce this gas amounts in the atmosphere are imperative.[1-5] Among the possibilities, are the CO_2 capture and geological storage and CO_2 capture and subsequent conversion in products with higher added value.

The chemical transformation of CO_2 is one of the most interesting options for CO_2 mitigation. The synthesis of cyclic carbonates appears as an interesting and effective solution. These compounds are versatile, widely used in chemical industry as polar aprotic solvents and raw materials for the production of a broad range of products.[4,6-9] However, CO_2 is a thermodynamically stable compound and the development of an effective and selective catalytic system is crucial. A catalytic system that could performe cyclic carbonates syntheses under mild conditions still remains as major challenge allied to the difficulties faced for catalyst separation and recycle.[8,9]

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To our beloved master who taught us more than science

In order to overcome these operational difficulties, various conversions of CO_2 to cyclic carbonates using ionic liquids (ILs) as catalysts have been reported in literature.[6,9-12] Ionic liquids are very versatile compounds. They are more environmentally friendly when compared to conventional organic solvents exhibiting the possibility of the catalyst separation and recycling.[6,13-16]

Peng and Deng[10] reported the synthesis of propylene carbonate from CO_2 using the ILs [bpy][BF_4], [bmim][BF_4], [bmim][Cl] and [bmim][PF_6] and demonstrated that the catalytic activity of an ionic liquid depends on the nature of the cation and the anion. For the anions, the activity decreased in the order bmim$^+$ > bpy$^+$ and BF_4^- > Cl$^-$ > PF_6^-. The effect of the cation and the anion were also investigated by Yang *et al.*[9] using IL based on cations C_4DABCO$^+$, C_8DABCO$^+$, HDBU$^+$, HTBD$^+$ or HHMTA$^+$ and anions OH$^-$, Cl$^-$, Br$^-$, BF_4^-, PF_6^-, Tf_2N^- and AcO$^-$. The results showed that the catalytic effect decreases in the order HDBU$^+$ > HTBD$^+$ ~ OMIM$^+$ > C4DABCO$^+$ ~ C8DABCO$^+$ > BMIM$^+$ > HHMTA$^+$. The anion OH$^-$ presented the best result and Cl$^-$ and Br$^-$ showed good performance as well. The acetate anion bound to the cation HDBU also showed catalytic activity comparable to that of Cl$^-$, but its thermal stability was not ideal. The anions Tf_2N^-, PF_6^-, and BF_4^- were not effective.

The effect of alkyl chain length was studied by Kawanami *et al.*,[6] in the 1-alkyl-3-methylimidazolium through variations of the alkyl chain length from C_2 to C_8. The results indicated that the increase of the side alkyl chain in the cation has large effect on the catalyst performance since the yield has been improved with the increasing of the alkyl chain length. This result can be attributed to the increasing solubility of both the epoxide and the CO_2 in the ionic liquid. Further studies showed that the combination of ionic liquids and metallic compounds has proven to be effective, increasing the catalytic activity of ILs in the synthesis of cyclic.[11,15]

Regarding CO_2 capture, the imidazolium cations allied to fluoroalkyl anions stand as very effective systems for CO_2 absorption.[17,18] Nevertheless, in relation to the reaction of CO_2 conversion in cyclic carbonates, the results reported in the literature are contradictory in respect to the activity of ionic liquids combined to fluoroalkyl anions.

This study aims to investigate the ionic liquids behavior in both catalytic activity in propylene carbonate syntheses as well as the CO_2 absorption capacity. The reaction conditions as temperature, pressure, reaction time, effect of IL cation and anion as well as the addition of metallic compounds to reaction media and the catalyst recycling were also investigated.

Experimental

Chemicals

Acetone (Vetec, 99.5%), acetonitrile (Vetec, 99.5%), toluene (Merck, 99.9%), carbon dioxide (99.998%, Air Liquid), 1-chlorobutane (Acros Organics, 99%), dichloromethane (Vetec, 99.5%), 3,3-dimethylchlorobutane (Alfa Aesar, 97%), lithium(I) bis(trifluoromethanesulfonyl) imide - $LiTf_2N$ (Aldrich, 99%), 1-methylimidazole - $C_4H_6N_2$ (Aldrich, 99%), magnesium sulfate - $MgSO_4$ (Acros Organics, 97%), sodium tetrafluoroborate - $NaBF_4$ (Acros Organics, 98%), sodium hexafluorophosphate - $NaPF_6$ (Alfa Aesar, 99%), propylene oxide - C_3H_6O (Aldrich, 99%), zinc chloride - $ZnCl_2$ (Nuclear, 97%), zinc bromide - $ZnBr_2$ (Sigma-Aldrich, 98%).

Ionic liquids syntheses

The ionic liquids 1-butyl-3-methylimidazolium chloride [bmim][Cl], 1-butyl-3-methylimidazolium tetrafluoroborato [bmim][BF_4], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][Tf_2N] and 1-dimethylbutyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [dmbmim][Tf_2N] were synthesized following procedures well described in literature.[19-21]

The ionic liquids were characterized by Fourier transform infrared spectroscopy (FTIR), using a Perkin-Elmer spectrophotometer model Spectrum 100 FT-IR with full attenuated reflectance accessory (ATR), as well as by proton nuclear magnetic resonance (^{1}H-NMR) on a Varian Spectrophotometer, model VNMRS 300 MHz, using DMSO-d_6 as solvent and glass tubes of 5 mm in diameter and are in accordance with the literature.

Cycloaddition reaction

The syntheses of propylene carbonate (PC) from CO_2 and propylene oxide (PO) were carried out in the presence of imidazolium cation-based ILs combined to different anions Cl$^-$, BF_4^- and Tf_2N^-. These compounds were tested in the presence of metallic halides ($ZnCl_2$ or $ZnBr_2$). The use of IL [dmbmim][Tf_2N] was also evaluated.

All cycloaddition reactions were performed in a stainless steel autoclave of 120 cm^3 equipped with magnetic stirring. For a typical reaction, it was used 100 mmol of propylene oxide, 0.625 mmol of metal salts ($ZnCl_2$ or $ZnBr_2$) and/or 2.5 mmol of ionic liquid. The syntheses were performed without any additional solvent. The autoclave was pressurized with CO_2 and heated to the desired working

temperature. After the reaction completion, the reactor was cooled to room temperature and slowly depressurized.

The separation of the catalyst from propylene carbonate was performed by a simple distillation under inert atmosphere (N_2). In the reactions carried out in the presence of metal salts, a filtration step was performed before the distillation process. The resulting liquid mixtures were analyzed using a gas-chromatograph Shimadzu GC-14B equipped with a flame ionization detector (FID) and a DB-5HT column (15 m × 0.32 mm × 0.10 μm) using acetophenone as internal standard and dimethyl ether as solvent.

CO_2 absorption measurements

The CO_2 sorption of the samples were gravimetrically assessed in a magnetic suspension balance (MSB), (Rubotherm Prazisionsmesstechnik GmbH, 35 MPa and 673.15 K) equipped with a single sinker device for absorbate density determination and thermostatized with an oil bath (Julabo F25 ± 273.16 K). The apparatus details are well described in literature.[22,23] When compared to other gravimetrical sorption methods, the MSB device has the advantage of allowing high pressure sorption measurements since the sample can be potted into a closed chamber coupled to an external accurate balance (accuracy of ± 10 μg). The samples (0.06 to 0.09 g) were weighed and transferred to the MSB sample container and the system was subjected to a 10^{-7} MPa vacuum at the temperature of the sorption measurement, 298.15 K, for 24 h. For all tests, constant weight was achieved in this time. The CO_2 was admitted into the MSB pressure chamber till the desired pressure, 0.1-3 MPa in this study, pressure gauges with an accuracy of 0.01 bar. The solubility of CO_2 in the ILs pressure was measured 3 to 4 h until there was no more weight variation for CO_2 sorption. At this step of solubility of CO_2 in the ILs, the weight reading from the microbalance at pressure P and temperature T is recorded as w_t (P,T). After each sorption test, CO_2 desorption were performed and all the samples returned to its original weight at the end. The mass of dissolved CO_2 in the ILs (w_g), was calculated using the equation 1.

$$W_g = [W_t(P,T) - W_{sc}(P,T) + \rho(P,T) \cdot (V_{sc}(T) + V_s(T))] - W_s(vac,T) \qquad (1)$$

where $W_t(P,T)$ is the weight of the sample container, $\rho(P,T)$ CO_2 density, directly measured with the MSB coupled single-sinker device, being not necessary the application of any state equation to calculate the CO_2 sorption values. $V_{sc}(T)$ is the volume of the sample container, determined

from a buoyancy experiment when no sample is charged into the sample container, $V_s(T)$ is the original volume of the sample, and $W_s(vac,T)$ is the weight of the sample under vacuum. The term $\rho(P,T) \cdot (V_{sc}(T) + V_s(T))$, represents the buoyancy force. The results of CO_2 sorption were expressed in molar fraction.

Results and Discussion

Effect of IL and co-catalyst

Aiming to evaluate the influence of the anion in the syntheses of propylene carbonate (PC) from CO_2 and propylene oxide (PO), cycloaddition reactions were carried out in the presence of ionic liquids (ILs) based on imidazolium cation combined to Cl^-, BF_4^- and Tf_2N^- anions.

The first choice for assessing the ILs catalytic activity for CO_2 conversion reactions were [bmim][Tf_2N] and [bmim][BF_4], since these compounds are reported in the literature as good solvents for carbon dioxide.[17,24] The results depicted in Table 1 show that these ILs exhibited extremely low activities in the cyclic carbonates syntheses. Despite the good ability for CO_2 absorption presented by Tf_2N^- and BF_4^- anions their catalytic activities were not satisfactory (entry 1 and 7).

On the other hand, the IL [bmim][Cl] presented an interesting catalytic performance presenting an yield of 84% and 90% of selectivity in PC and a turnover frequency (TOF) of 5 h^{-1} (entry 6) as seen in Table 1. This behavior is probably due to its good nucleophilic character.[9] These results demonstrate that the activity of ILs is strongly influenced by the nature of the anion and are in accordance with the results described by Yang *et al.*[9] in relation to the anions behavior. The low catalytic activity for Tf_2N^- and BF_4^- anions can be directly linked to the structural volume of the anions and their low nucleophilicity indicating that the best ILs for CO_2 capture are not necessarily the best catalysts for CO_2 transformation. However, the combination of these ILs with metallic compounds contributed to an increase on the catalytic activity.

The results of the combination of metal compounds to [bmim][Tf_2N] and [bmim][BF_4] revealed that the addition of $ZnBr_2$ contributed to an increase in catalytic activity for both ILs (entry 3-4; 9, Table1), indicating that the presence of Lewis acidic compounds as cocatalysts greatly enhances the activity of ionic liquid for the cyclic carbonate syntheses.[25] With the exception of [bmim][Cl], the catalytic activities of ionic liquids were quite influenced by the nature of halide bonded to zinc atoms. The reactivity was found to be in the order $ZnBr_2 > ZnCl_2$ as seen in Table 1, suggesting the importance of the nucleophilicity of halide counterions.

Table 1. Catalysts screening for cycloaddition reaction

entry	Catalyst	Cocatalyst	Yield / %	Selectivity / %	TON	TOF / (h⁻¹)
1	[bmim][Tf₂N]	–	Trace	–	–	–
2	[dmbmim][Tf₂N]	–	Trace	–	–	–
3	[bmim][Tf₂N]	ZnCl₂	19	60	4.56	0.760
4	[bmim][Tf₂N]	ZnBr₂	90	82	29.5	4.92
5	[dmbmim][Tf₂N]	ZnBr₂	Trace	–	–	–
6	[bmim][Cl]	–	84	90	30.2	5.04
7	[bmim][BF₄]	–	Trace	–	–	–
8	[bmim][Cl]	ZnBr₂	86	90	30.9	5.16
9	[bmim][BF₄]	ZnBr₂	34	91	12.4	2.06
10	[bmim][Tf₂N] + [bmim][Cl]	ZnBr₂	67	84	22.5	3.75
11	–	ZnCl₂	0	–	–	–
12	–	ZnBr₂	0	–	–	–

Reaction conditions: PO 100 mmol, catalyst 2.5 mmol, cocatalyst 0.625 mmol, initial CO₂ pressure 4.0 MPa, t = 6 h, T = 383.15 K, TON = mmol of products/mmol of catalyst. TOF = TON/time.

For example, when [bmim][Tf₂N] was used as catalyst, the addition of ZnCl₂ the yield of the carbonation reaction was 19% and the selectivity 60%. When ZnBr₂ was added, the yield increased to 90% and the selectivity to 82%.

This behavior is probably due to the high reactivity of Zn(II) combined with the nucleophilicity of bromide,[7,26] which has favored the propylene oxide ring-opening. Although the activity of ZnBr₂ containing systems is higher than those with ZnCl₂, the latter is commonly chosen as the cocatalyst for the coupling of carbon dioxide with epoxides because it is the cheapest Zn(II) salt and has satisfactory activity.[7] However, when bmimCl was used as catalyst, the metallic halides contribution were not significant (entry 8). In this case the yield, selectivity and activity remained almost constant.

We also performed cycloaddition reactions only with the metals compounds without IL. No activity was observed with ZnCl₂ (entry 11) or ZnBr₂ (entry 12) according to previous studies.[7,11,25]

The effect of the branching in the alkyl chain of imidazolium cation was also evaluated. The IL [dmbmim][Tf₂N] alone, as well as its combination with ZnBr₂, presented low activities in the PC syntheses (entry 2 and 5, Table1). It was expected that the branching on the alkyl lateral chain would increase the CO₂ solubility resulting in a higher activity. The alkyl side branching increases the free volume and consequently improves the CO₂ solubility in the ionic liquid.[17] Probably, the steric hindering caused by the branching in the alkyl side chain interfered with the approach of the substrate/catalyst, difficulting the reaction.

Aiming to increase the catalytic activity, an equimolar mixture of the catalytic ILs [bmim][Tf₂N] + [bmim][Cl] and the metallic compound ZnBr₂ has been evaluated

(entry 10). However, the yield of this system was lower than that attained separately for each IL in the presence of ZnBr₂ (entry 4-8).

One of the acceptable mechanisms for the cycloaddition of CO₂ to epoxide catalysed by IL involves a nucleophilic attack of the IL anion to the less hindered carbon atom of the epoxide ring. In the next step, an oxy anion species is formed. The carbon atom of the CO₂ interacts with the anion species producing an anion alkylcarbonate converted to the cyclic carbonate by intermolecular cyclic elimination.[15]

In our work, we concluded that the Tf₂N⁻ and BF₄⁻ containing ILs need a metal halide, a Lewis acid to interact with the oxygen of the epoxide atom allowing the IL basic anion to perform the attack to the less hindered atom of the epoxide ring, see Scheme 1a. This could be assigned to the non-nucleophilic natures of the Tf₂N⁻ and BF₄⁻ anions.[27] When [bmim][Cl] is used as catalyst, probably the attack of the epoxide is performed by the Cl⁻ in the less hindered carbon atom, in the first step of the reaction, see Scheme 1b.

As we can see in Table 1, the IL [bmim][Tf₂N] combined with ZnBr₂ showed the best yield (90%) (entry 4). Thus, it has been selected for the evaluation of temperature; pressure, reaction time as well as the behavior of this system in recycle.

Effect of temperature

The selectivity, yield and activities values obtained at different temperatures are shown in Table 2. It is evidenced that the increase in temperature from 373.15 K to 383.15 K resulted in a significant increase in the yield (entry 13-4), and after 383.15 K the increasing of the temperature decreases the yield (entry 4-16).
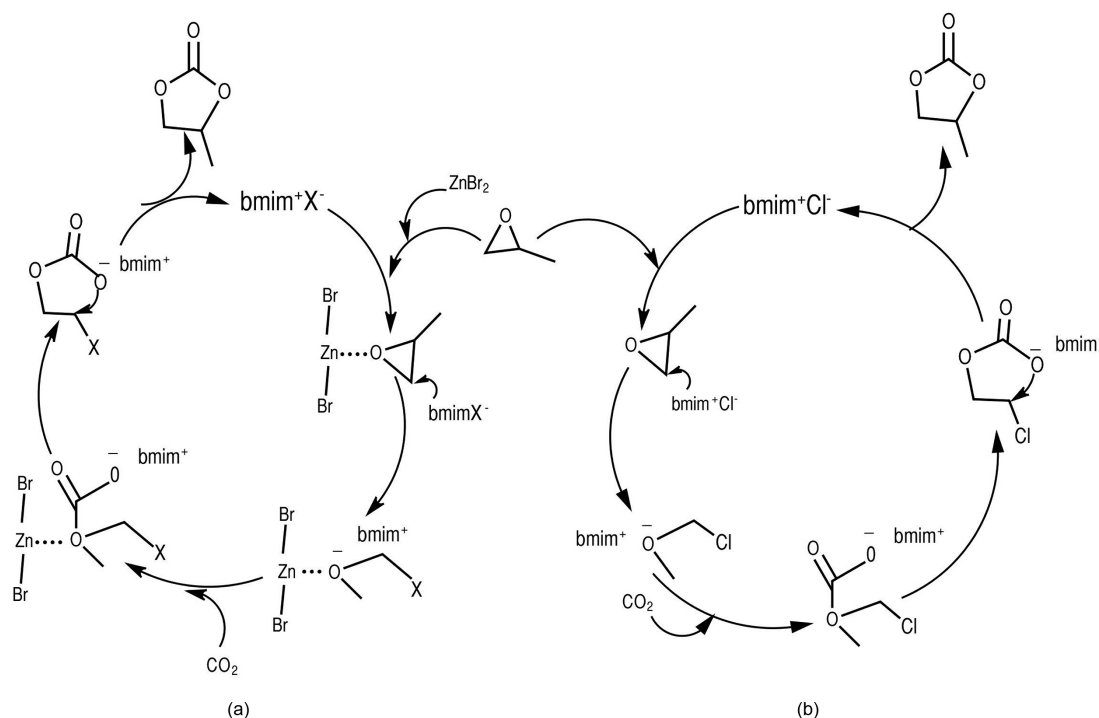
Scheme 1. Proposed mechanism for the synthesis of propylene carbonate from propylene oxide and CO_2 using different ionic liquids: (a) IL combined to the anions Tf_2N^- and BF_4^- and (b) [bmim][Cl].

Table 2. Temperature effect in the PC synthesis using [bmim][Tf_2N] and $ZnBr_2$ as catalyst

entry	Temperature / K	Yield / %	Selectivity / %	TON	TOF / h^{-1}
13	373.15	65	96	24.9	4.16
4	383.15	90	82	29.5	4.92
14	393.15	75	68	20.4	3.40
15	403.15	68	94	25.6	4.26
16	413.15	64	86	22.0	3.67

Reaction conditions: PO 100 mmol, catalyst 2.5 mmol, 0.625 mmol of $ZnBr_2$, initial CO_2 pressure 4.0 MPa, t = 6 h. TON = mmol of products/ mmol of catalyst. TOF = TON/time.

It is possible that the yield decreasing is associated with the reduction in the PC selectivity in higher temperature, resulting in side reactions such as PO isomerization and PC polymerization.[28]

Influence of CO_2 pressure

Pressure affects cyclic carbonate synthesis, and the optimal pressure occurs at around the CO_2 critical pressure.[12] From the results shown in Table 3, it can be seen that our results showed a different behavior. The results shown in Table 3 are in accordance to the literature, evidencing that an insufficient or excessive amount of CO_2 results in relatively low conversions, i.e.,

there is an ideal molar ratio of propylene oxide and CO_2 to obtain a high conversion. A higher CO_2 pressure can retard the interaction between epoxide and the catalyst. On the other side, it can be highlighted a significantly improve in the carbonate selectivity with the pressure augmentation.[9,10]

Table 3. CO_2 effect pressure in the PC synthesis using bmimTf_2N +$ZnBr_2$ as catalyst

entry	CO_2 pressure / MPa	Yield / %	Selectivity / %	TON	TOF / h^{-1}
17	2.5	84	53	17.8	2.97
4	4.0	90	82	29.5	4.92
18	5.0	52	95	19.8	3.30

Reaction conditions: PO 100 mmol, catalyst 2.5 mmol, 0.625 mmol of $ZnBr_2$, T = 383.15 K, t = 6 h. TON = mmol of products/mmol of catalyst. TOF = TON/time.

Influence of the reaction time

The influence of the reaction time on the propylene carbonate synthesis is presented in the Table 4. It was observed that the reaction time reduction from 6 up to 2 h (entry 4-19), provided a decreases in yield, curiously the increase in reaction time from 6 to 8 h (entry 4-21) decreases the yield. The reaction time of 6 h was ideal for this the system.

Table 4. Influence of the reaction time in PC synthesis using bmimTf$_2$N+ZnBr$_2$ as catalyst

entry	Reaction time / h	Yield / %	Selectivity / %	TON	TOF / h^{-1}
19	2	31	89	11.0	5.52
20	4	55	96	21.1	5.28
4	6	90	82	29.5	4.92
21	8	74	77	22.8	2.85

Reaction conditions: PO 100 mmol, catalyst 2.5 mmol, 0.625 mmol ZnBr$_2$, initial CO$_2$ pressure 4.0 MPa, T = 383.15 K. TON = mmol of products/ mmol of catalyst. TOF = TON/time.

Recycling

To investigate the reuse effect in the catalyst system ([bmim][Tf$_2$N] and ZnBr$_2$) the recycling experiment was conducted at the best conditions achieved (4.0 MPa, 383.15 K and 6 h). The procedure adopted for the separation of the catalytic system and propylene carbonate was the same used for all syntheses and described in experimental section. This procedure was repeated four times. The catalytic activity was not maintained even for only four recycle reactions. This behavior is probably due to the loss of the metallic compound (ZnBr$_2$) in the PC separation operation, decreasing the catalytic activity.[7]

Aiming to study the ZnBr$_2$ loss in PC recycle, reactions were carried out in the same conditions of the recycle reactions presented before. After the PC separation step the ZnBr$_2$ was re-added (0.625 mmol) and the reaction performed. With the addition of the ZnBr$_2$ after each reaction the yield increased 17% when compared to the reaction without the addition of the metal halide and remained almost constant. These results evidenced that the loss of the ZnBr$_2$ is probably occurring as described in literature.[7]

In order to improve the separation process and also study the influence of the increase of IL concentration in the reaction medium, a reaction with 100 mmol of PO, 28 mmol of [bmim][Tf$_2$N], 0.625 mmol de ZnBr$_2$, in the same reaction conditions (383.15 K, 6 h and 4 MPa of CO$_2$) was performed. The yield, selectivity and activity were the same obtained with 2.5 mmol of IL. The increment of IL content in the reaction medium, in this case, does not facilitate the PC separation. These results evidenced that the catalytic conversion of propylene oxide and CO$_2$ in PC works with catalytic quantities of IL but for integration of CO$_2$ capture and transformations process it is possible to use a higher IL volume and maintain the same yield.

CO$_2$ solubility

The results shown for PC syntheses using ILs as catalysts evidenced the importance of the anion. For CO$_2$ capture also the anion plays a major role. In order to combine the CO$_2$ capture and conversion, it is important to find a system that can act both as a solvent for CO$_2$ separation and as a catalyst for CO$_2$ transformation. In Figure 1 it can be seen the different CO$_2$ absorption capacity for the ILs that proved to perform also the role as a catalyst for propylene carbonate syntheses.
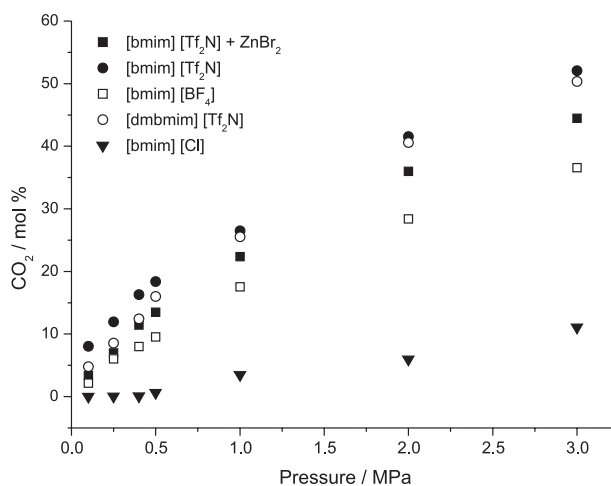
Figure 1. CO$_2$ solubility in different ionic liquids at 298.15 K.

As it can be seen from Figure 1, the use of [bmim][Cl]$^-$ for CO$_2$ capture is not a good option, despite of this IL act as a good catalyst for PC synthesis. The CO$_2$ sorption at 0.5 MPa is near 0 mol% stead for the combination of [bmim][Tf$_2$N] and ZnBr$_2$ it is approximately 14 mol%. The fluoroalkyl anions allied to imidazolium cations present a relatively high CO$_2$ solubility and have been described in the literature for CO$_2$ absorption process.[17] The use of these compounds for PC syntheses needs the addition of a metallic compound in order to achieve an acceptable yield. It must be mentioned that the best conditions for CO$_2$ capture and chemical conversion are distinct. Nevertheless, the results presented in Figure 1 evidenced that the CO$_2$ solubility in a solvent combining [bmim][Tf$_2$N] and ZnBr$_2$ can be a good option for CO$_2$ capture and conversion of this molecule in a PC adding value to this chemical.

Conclusions

The results showed that the best ILs for capturing CO$_2$ are not necessarily the best catalysts for CO$_2$ conversion. The activities of the ILs in both processes are strongly influenced by the nature of the anion. While the solubility

of CO_2 is improved by fluorinated anions in catalysis for CO_2 conversion, the activity is favored by a higher nucleophilicity of the anion. Our results evidenced that the combination of imidazolium-based ILs/fluoroalkyl anions and a metal halide compound is a good approach for combining the CO_2 capture and conversion. In catalytic conversion of CO_2 to carbonates, the temperature, pressure and reaction time showed to play an important role in the conversion and selectivity. The best result was obtained with the catalytic system [bmim][Tf_2N]/$ZnBr_2$ at 4.0 MPa of pressure, 383.15 K of temperature and 6 h of reaction time.

Acknowledgements

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