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Chemical fixation of CO_2: the influence of linear amphiphilic anions on surface active ionic liquids (SAILs) as catalysts for synthesis of cyclic carbonates under solvent-free conditions

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Abstract

Carbon dioxide (CO_2) conversion is an efficient option to mitigate environmental impacts caused by CO_2 high concentration in the atmosphere. In this work are described catalytic activities of surface active ionic liquids (SAILs) composed of well-known cations 1-butyl-3-methylimidazolium ([bmim$^+$]) and tetra-*n*-butylammonium ([TBA$^+$]) and long alkyl chain anions: lauryl sulfate ([$C_{12}SO_4^-$]), lauryl ether sulfate ([$C_{12}ESO_4^-$]), lauryl benzene sulfonate ([$C_{12}BSO_3^-$]) and lauroyl sarcosinate ([$C_{12}SAR^-$]) for cyclic carbonate synthesis. Results evidenced that [TBA$^+$] is more active as a catalyst due to its higher molecular volume increasing the cation–anion distance and weakening the electrostatic interaction resulting in a more electrophilic cation. The [TBA][$C_{12}BSO_3$] SAIL presented better catalytic activity for styrene carbonate (SC) synthesis, reaching 81.4% of conversion and 87.0% of selectivity as well as the high recycle capacity and possible application as catalyst for the syntheses of different cyclic carbonates: glycidyl isopropyl ether carbonate (GC) and epichlorohydrin carbonate (EC).

Keywords Carbon dioxide · Catalysis · Cycloaddition · Ionic liquid · Cyclic carbonate

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Introduction

Greenhouse gas (GHG) concentration in the atmosphere is increasing due to anthropogenic source emissions. CO_2 is a greenhouse gas with important environmental impact [1, 2]. Approximately 116 million tons of CO_2 are used annually for value-added products production, 94% of which are used only for urea production [3]. However, this CO_2 use is still insignificant (~0.1%) [4]. In this way, research development involving CO_2 conversion is a current issue and of paramount importance for climate change mitigation [5, 6].

Cyclic carbonates are used in numerous industrial sectors such as aprotic polar solvents, monomers for polycarbonate synthesis and electrolytes for batteries [7–9]. CO_2 reaction with epoxide forming cyclic carbonates has been extensively studied using different catalysts [10–16].

Surface active ionic liquids (SAILs) contain significantly long hydrophobic chains in the cation (C_6 to C_{16}), in the anion (up to C_{20}) or both [17, 18]. The most reported cations to form SAILs are imidazolium, pyridinium and quaternary ammonium. Anions are usually derived from anionic surfactants and SAILs performance depends both on the cation and the anion [19–21]. Although several studies have been performed with SAILs in several scientific segments (micelle formation, facilitating microemulsions and liquid crystals preparation) [22–24], these are poorly investigated in catalysis context [25, 26].

In a previous work, we described SAILs use for cycloaddition of CO_2 in propylene epoxide (PC) [26]. The literature describes the use of solvent in styrene carbonates (SC) synthesis [27]. On the other hand, additional solvent in SC synthesis is not required when SAILs are used as catalysts. In addition, SAILs are derived from low cost and abundant surfactants. SAILs utilization as catalysts is still little explored. For this reason, a more detailed study of cycloaddition is proposed.

In this work, we describe the use of imidazolium ([bmim$^+$]) and tetrabutylammonium ([TBA$^+$]) cations based SAILs combined with different anions derived from the surfactants: sodium lauryl sulfate ([$C_{12}SO_4^-$]), sodium lauryl ether sulfate ([$C_{12}ESO_4^-$]), sodium lauryl benzene sulfonate ([$C_{12}BSO_3^-$]) and sodium lauroyl sarcosinate ([$C_{12}SAR^-$]) as catalysts for CO_2 cycloaddition to styrene oxide (SO) in order to produce styrene carbonate (SC). We also tested recycling capacity and the possibility of using these SAILs in other cyclic carbonates production: glycidyl isopropyl ether carbonate (GC) and epichlorohydrin carbonate (EC).

Methodology

The synthesis of 1-butyl-3-methylimidazolium lauryl sulfate ([bmim][$C_{12}SO_4$]; yield = 47%), 1-butyl-3-methylimidazolium lauryl ether sulfate ([bmim][$C_{12}ESO_4$]; yield = 76%), 1-butyl-3-methylimidazolium lauryl benzene sulfonate

([bmim][$C_{12}BSO_3$]; yield = 81%), 1-butyl-3-methylimidazolium lauroyl sarcosinate ([bmim][$C_{12}SAR$]; yield = 63%), tetra-*n*-butylammonium lauryl sulfate ([TBA][$C_{12}SO_4$]; yield = 87%), tetra-*n*-butylammonium lauryl ether sulfate ([TBA][$C_{12}ESO_4$]; yield = 90%), tetra-*n*-butylammonium lauryl benzene sulfonate ([TBA][$C_{12}BSO_3$]; yield = 92%) and tetra-*n*-butylammonium lauroyl sarcosinate ([TBA][$C_{12}SAR$]; yield = 79%) was performed with an equimolar mixture of [bmim][Cl] or [TBA][Br] and the sodium salt of the anion of interest was dissolved in sufficient volume of water to dissolve the salts and kept at 333 K for 18 h. Water was removed from the reaction mixture after completion of reaction in vacuum in the same temperature. The product was dissolved with dichloromethane and washed with water several times. The dichloromethane was removed with vacuum at room temperature and the remaining product is the pure ionic liquid which is stored under inert atmosphere.

Characterization of synthesized SAILs are presented in supplementary material.

Cycloaddition reaction

Styrene carbonate (SC) syntheses from CO_2 and styrene oxide (SO) were carried out in presence of surface active ionic liquids (SAILs) used as catalyst. These compounds were tested in presence of metallic halide ($ZnBr_2$) as cocatalyst. All cycloaddition reactions were performed in a stainless steel autoclave of 120 cm^3 equipped with magnetic stirring. For a typical reaction, 50 mmol of styrene oxide, 0.5 mmol of SAIL and 0.125 mmol of cocatalyst ($ZnBr_2$) were used. All reactions were performed using catalyst content of 1 mol% relative to epoxide.

The syntheses were performed without any additional solvent. Autoclave was pressurized with CO_2 and heated to the desired working temperature. After the completion of the reaction, the reactor was cooled to room temperature and slowly depressurized.

Catalyst separation from SC was performed by a simple distillation under inert atmosphere (N_2). To determine the conversion and selectivity of CO_2 cycloaddition reaction, the resulting liquid mixtures were analyzed using a gas chromatograph Shimadzu CG-2014 equipped with a flame ionization detector (FID) and a 100% dimethyl polysiloxane column (30 m × 0.53 mm ID) using acetophenone as internal standard and diethyl ether as solvent.

The [TBA][$C_{12}SO_4$] was chosen for reaction parameter (temperature, time and pressure) determination because it showed better catalytic results in the propylene carbonate (PC) synthesis as previously reported [26].

The best catalyst was reused for 5 times without any catalyst or cocatalyst addition. The procedure used to separate the catalytic system [SAIL + $ZnBr_2$] from SC was the same used in all syntheses, a simple distillation in inert atmosphere.

For the other cycloaddition reactions (GC and EC), the assays were performed in the same way, also using the [TBA][$C_{12}SO_4$] to determine the optimum reaction parameters.

Determination of nucleophilicities

The geometries of ions were optimized using the steepest descent algorithm with an energy threshold of 10^{-4} Hartree. The hybrid density functional Becke-3-Lee–Yang–Parr (B3LYP) was employed [28, 29]. The wave functions of the simulated ions were constructed from the atom-centered split-valence triple-zeta polarized basis set $6\text{-}311 + G^*$. Diffuse functions were deliberately supplemented to allow for high-quality reproduction of the electron density on organic anions. All electrons of the simulated ions were treated explicitly. The wave function convergence criterion was set to 10^{-7} Hartree. Hirshfeld charges localized on the oxygen atoms of the head groups were used as a measure of respective nucleophilicities [30]. The reported quantum mechanical calculations were conducted in US GAMESS 2014 [31].

Results and discussion

Influence of reaction parameters

We first performed reaction parameters (temperature, pressure and time) optimization for SC formation reaction from styrene oxide and CO_2 (Fig. 1). The detailing of these reactions (entries 1–10) are presented in Table 1.

Temperature optimization (Fig. 1b) was performed varying temperature from 333 to 373 K (4.0 MPa of CO_2 pressure and 4 h). As the reaction temperature increases progressively, styrene oxide conversion increased with selectivity loss in SC at 373 K. The best results (entry 2: 74.5% of conversion and 87.8% of selectivity) were obtained at 353 K of temperature and are in agreement with literature [32]. It was evidenced that the ideal temperature for the styrene oxide cycloaddition is 353 K using $[TBA][C_{12}SO_4]$ as catalysts [33–35]. The selectivity decrease with increasing
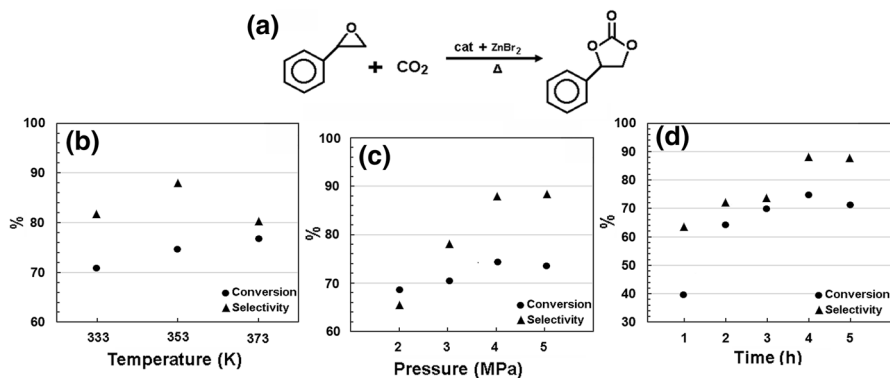

Fig. 1 The reaction scheme (**a**), the effect of temperature (**b**), pressure (**c**) and time (**d**) on the SC synthesis using $[TBA][C_{12}SO_4]$ as catalyst. Reaction conditions: styrene oxide 50 mmol, catalyst 0.5 mmol, 0.125 mmol of $ZnBr_2$

Table 1 Effect of reaction parameters using [TBA][$C_{12}SO_4$] as catalyst for the cycloaddition of CO_2 to form SC*

Entry	Time (h)	Temperature (K)	Pressure (MPa)	Conversion (%)	Selectivity (%)
1	4	333	4.0	70.6	81.6
2	4	353	4.0	74.5	87.8
3	4	373	4.0	76.7	80.1
4	4	353	2.0	68.7	65.4
5	4	353	3.0	70.4	78.1
6	4	353	5.0	73.3	88.1
7	1	353	4.0	39.4	63.2
8	2	353	4.0	64.2	71.7
9	3	353	4.0	69.8	73.1
10	5	353	4.0	71.5	86.9

*Reaction conditions: styrene oxide 50 mmol, catalyst 0.5 mmol and 0.125 mmol of $ZnBr_2$

temperature is related to product formation derived from styrene carbonate hydrolysis as diols [36, 37].

The CO_2 pressure (Fig. 1c) was varied from 2.0 to 5.0 MPa (353 K and 4 h). The best result (entry 2: 74.5% conversion and 87.8% selectivity) was obtained at 4.0 MPa of pressure. This result improvement in relation to selectivity is proportional to pressure increase (2.0 MPa < 3.0 MPa < 4.0 MPa < 5.0 MPa). In relation to conversion, there is an ideal pressure around 4.0 MPa. This tendency was already described in SC synthesis and attributed to epoxide dissolution by CO_2 excess [34].

Finally, time (Fig. 1d) was varied from 1 to 5 h (4.0 MPa of CO_2 and 353 K). Increasing the time from 1 to 4 h significantly increases conversion and selectivity. Previous studies demonstrate that styrene oxide conversion increased up to 4 h of reaction [34]. In agreement with literature when time was increased to 5 h a decrease in conversion and a slight decrease in selectivity were noticed. The results evidenced that under these conditions 4 h is the ideal reaction time.

Nucleophilicities of the anions

Organic anions constituting SAILs get attached to the reactant to saturate one of the dangling bonds of epoxide's carbon and get liberated from the product to give rise to the cyclic carbonate moiety (Fig. 2). Therefore, the nucleophilicity of the anion is its most important descriptor that determines catalytic activity of the SAIL. In terms of electronic density, nucleophilicity is numerically equal to electronic charge on the atom participating in the reaction. More positive charge (electron-poor site) indicates smaller nucleophilicity, whilst more negative charge (electron-rich site) indicates larger nucleophilicity. In principle, nucleophilicity depends both on electronic structure of an ion and on its chemical environment. In the herein reported simulations, we neglected an effect of the cation, since they act separately. Indeed, the head group of the anion is covalently bound to an emerging carbonate moiety, whereas the cation does not directly participate at this stage. The obtained nucleophilicities
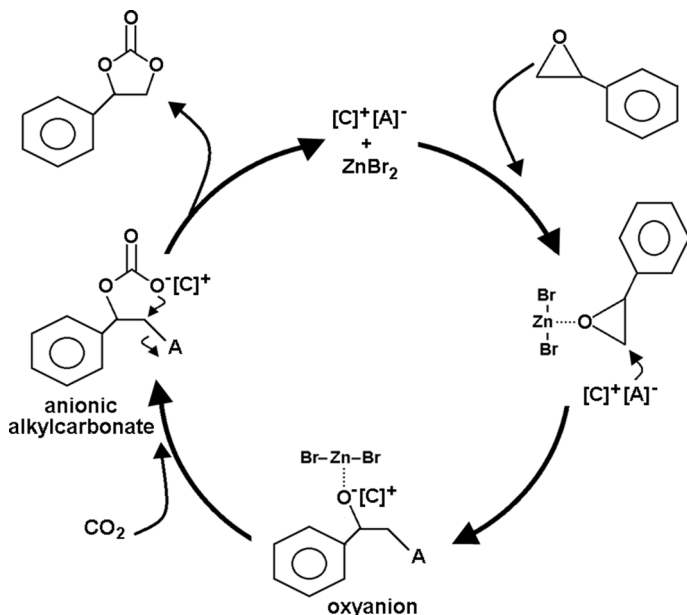
Fig. 2 Proposed mechanism for the synthesis of styrene carbonate from styrene oxide and CO_2

of the anions are quite similar. Nonetheless, modest differences can be observed: $[C_{12}SAR^-]$ $(-0.45) > [C_{12}BSO_3^-]$ $(-0.43) > [C_{12}SO_4^-]$ $(-0.41) = [C_{12}ESO_4^-]$ (-0.41). In the sulfur containing anions, an effect of the groups (hydrocarbon, methoxy, benzyl) in the attached chain is insignificant and nucleophilicity is primarily determined by the structure of the head group. A somewhat larger nucleophilicity of the head group of $[C_{12}SAR^-]$ is in line with chemical expectations considering its structure. Although $[C_{12}SAR^-]$ is the strongest nucleophile among the probed anions, it is also an attractive target for polar molecules such as those of water vapor.

The SAIL effect

Table 2 presents the results of SAILs catalytic performances for cycloaddition of CO_2 to styrene oxide. In the beginning of the study catalytic performances of two cations were compared [bmim⁺] (entries 11–14) and [TBA⁺] (entries 4, 15–24). As we can see, [TBA⁺] presented better catalytic activity for all anions. The higher molecular volume of [TBA⁺] increases the cation–anion distance making the electrostatic interaction weaker, promoting a more electrophilic cation compared to [bmim⁺] [38]. There is evidence that higher temperatures generate a degradation product of [TBA⁺], called trialkylammonium [39], providing basic sites resulting in a more effective catalyst.

Analyzing $[C_{12}SO_4^-]$ anion one observes that [bmim][$C_{12}SO_4$] (entry 11) presents the lowest catalytic activity. This result is possibly related to the high amount of water (1.43%) imprisoned in SAIL structure, comparing to other

Table 2 Catalytic performances of SAILs for the cycloaddition of CO_2 to form SC

Entry	SAIL	Structure SAIL	Conversion (%)	Selectivity (%)
11	[bmim][$C_{12}SO_4$]		25.4	77.4
12	[bmim][$C_{12}ESO_4$]		73.6	80.5
13	[bmim][$C_{12}BSO_3$]		79.2	81.3
14	[bmim][$C_{12}SAR$]		83.4	46.9
2	[TBA][$C_{12}SO_4$]		74.5	87.8
15	[TBA][$C_{12}SO_4$]**		Trace	–
16	***	–	–	–
17	[TBA][$C_{12}ESO_4$]		76.3	85.6
18	[TBA][$C_{12}BSO_3$]		81.4	87.0
19	[TBA][$C_{12}BSO_3$]1x		85.3	87.9
20	[TBA][$C_{12}BSO_3$]2x		82.1	83.5
21	[TBA][$C_{12}BSO_3$]3x		81.4	81.1
22	[TBA][$C_{12}BSO_3$]4x		78.3	80.9
23	[TBA][$C_{12}BSO_3$]5x		74.1	80.1
24	[TBA][$C_{12}SAR$]		87.9	44.1

Reaction conditions: SO 50 mmol, catalyst 0.5 mmol, 0.125 mmol of $ZnBr_2$, T = 353 K, initial CO_2 pressure 4.0 MPa and $t = 4$ h

**Reaction without cocatalyst $ZnBr_2$

***Reaction only $ZnBr_2$

SAILs, which present significantly lower moisture content [26]. Water can deactivate the catalyst decreasing conversion [37]. Yet, water can compete with CO_2 in SO interaction or even hydrolyzing the SC forming undesirable by-products, usually diols [36]. This water interference is no longer perceived in the single hydrophobic SAIL [20, 26] ([TBA][$C_{12}SO_4$], entry 2) presenting 74.5% of conversion and 87.8% of selectivity, quite satisfactory results.

In a previous study $[TBA][C_{12}SO_4]$ was described as the best catalytic system for propylene carbonate (PC) synthesis compared to other SAILs [26]. Even if the reaction mechanism for PC synthesis is close to that of SC synthesis, a different behavior was observed concerning the catalyst activity. Styrene oxide is a far bulkier molecule than propylene oxide, so a stereo impediment was already expected. Despite the similar mechanism, a catalyst to promote the geometric fit is needed.

The addition of an ether functional group to the anion, $[bmim][C_{12}ESO_4]$ (entry 12) and $[TBA][C_{12}ESO_4]$ (entry 17), in both cations improved the conversion when compared to the anion without this group ($[C_{12}SO_4^-]$). This result is very pronounced in the cation $[bmim^+]$. The organic functional group "ether" is a group with polar affinities; it may be that any moisture contained in the medium is interacting with this group, avoiding the interaction with catalyst active sites. The $[TBA][C_{12}SO_4]$ (entry 2) and $[TBA][C_{12}ESO_4]$ (entry 17) evidenced the similar catalytic activity. We see that, from the theoretical computational study, taking into account only the anion, the nucleophilicities values of the $[C_{12}SO_4^-]$ and $[C_{12}ESO_4^-]$ are practically the same (-0.41), corroborating with the activity presented in the catalytic tests.

The anion $[C_{12}BSO_3^-]$ presented the best results when combined with both cations $[bmim^+]$ and $[TBA^+]$. SAIL $[TBA][C_{12}BSO_3]$ (entries 18–23) was the one with the best catalytic activity. This behavior is related to the anion containing an aromatic ring. The substrate being a styrene oxide, producing styrene carbonate (both containing aromatic ring in the structure) and the anion of the catalyst in question being aromatic ($[C_{12}BSO_3^-]$), an interaction between these aromatic rings may be occurring during the catalytic cycle. Aromatic rings π–π stacking increase the formed oxyanion stabilization (see Fig. 2) not displacing electronic charge contained in the structure, facilitating interaction with CO_2. This anion has higher nucleophilicity (-0.43) as compared to $[C_{12}SO_4^-]$ and $[C_{12}ESO_4^-]$, also justifying a better catalytic activity.

The anion $[C_{12}SAR^-]$ presents some peculiarities justifying its behavior of high conversion and low selectivity (entries 14 and 24). Among all tested SAILs containing $[bmim^+]$ as cation, $[bmim][C_{12}SAR]$ was the catalyst that presented the highest conversion (83.4%) and lower selectivity (46.9%). The same was observed with $[TBA^+]$ cation where $[TBA][C_{12}SAR]$ presented the highest conversion result (87.9%) and lower selectivity (44.1%). The higher conversion results when compared to other tested anions are justified by the higher nucleophilicity of this anion (-0.45). Another fact that deserves attention, justifying the low selectivity, is the presence of resonance in the anion amide group. This displacement of electrons between oxygen and nitrogen (amide group) can cause an early anion release in the anionic alkylcarbonate step (see Fig. 2). Yet, a bonding of this anion in the epoxide to a place other than the carboxylate can occur favoring other species formation in addition to styrene carbonate.

That reaction (CO_2 cycloaddition to SO to produce SC) is not spontaneous, therefore no product was detected when the reaction was performed without a catalytic system (catalyst/cocatalyst). When only the SAIL was used (entry 15) or only the cocatalyst was used (entry 16), there is no significant conversion to SC [10, 26].

The presence of a Lewis acid as a cocatalyst ($ZnBr_2$) is essential for SAILs activity [40, 41]. The $ZnBr_2$ interact with the oxygen atom of the epoxide, so that the basic anion of SAIL carries out the attack on the least impeded carbon atom of the epoxy ring. Fig. 2 presents a possible mechanism for the cyclic carbonate synthesis. The CO_2 carbon atom interacts with the anionic species producing an anionic alkyl-carbonate. The latter is converted into the cyclic carbonate by intermolecular cyclic elimination and finally the SAIL is regenerated.

For industrial application, it is desired that catalyst stay active for several cycles of use. To evaluate the SAILs stability we performed several catalytic cycles using the system with highest catalytic activity ([TBA][$C_{12}BSO_3$]) (Table 2, entries 19–23). Fig. 3 presents the behavior of SAIL during recycle tests. In the first recycle (entry 19), one observed an increase in conversion (from 81.4 to 85.3%) and selectivity (from 87.0 to 87.9%). This catalytic activity increase in the first recycle is not rare, since after the first reaction any possible impurities have been washed away from the catalytic system [13, 35]. Residual moisture removal of the catalyst is also possible. Therefore, the [TBA][$C_{12}BSO_3$] maintains significant activity after 3 replicates with good reproducibility. From recycle 4, there is little gradual activity loss.

Application to other cyclic carbonates

It is very usual in most current publications, the use of the best catalytic system for propylene oxide and styrene oxide cycloaddition to obtain other cyclic carbonates [42–46]. A few works study further the formation reaction of glycidyl isopropyl ether carbonate (GC) and epichlorohydrin carbonate (EC) [9, 47], often not describing optimization study of reactional parameters. Here we studied the best reaction conditions for glycidyl isopropyl ether carbonate (GC) (Table 3, entries 25–32) and epichlorohydrin carbonate (EC) (Table 4, entries 34–41). The [TBA][$C_{12}SO_4$] was elected as catalyst. Fig. 4 shows the results of Tables 3 and 4.

It is important to mention that without $ZnBr_2$ as cocatalyst, there is no significant conversion of GC and EC. Temperature optimization (entries 25-27 for GC—Fig. 4b) (entries 24–36 for EC—Fig. 4f) was performed varying temperature from 383 to 403 K. The progressive increase of the reaction temperature significantly increased the conversion of GC and EC. In addition, a loss of selectivity at 403 K

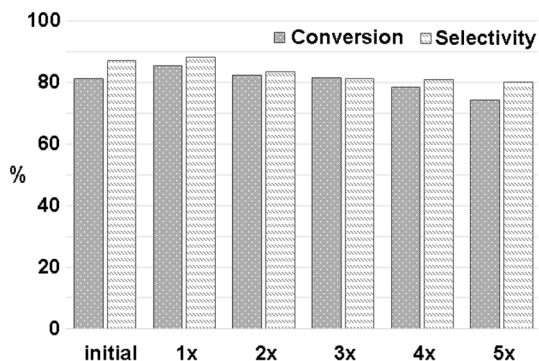
Fig. 3 SC recycling experiments of [TBA][$C_{12}BSO_3$]

Table 3 Effect of the reaction parameters using [TBA][$C_{12}SO_4$] as catalyst and performances of the best SAILs ([TBA][$C_{12}BSO_3$]) for the cycloaddition of CO_2 to form GC

Entry	SAIL	Time (h)	Temperature (K)	Pressure (MPa)	Conversion (%)	Selectivity (%)
25	[TBA][$C_{12}SO_4$]	3	383	3.0	80.1	92.9
26	[TBA][$C_{12}SO_4$]	3	393	3.0	86.5	92.6
27	[TBA][$C_{12}SO_4$]	3	403	3.0	87.7	90.4
28	[TBA][$C_{12}SO_4$]	3	393	2.0	81.2	88.6
29	[TBA][$C_{12}SO_4$]	3	393	4.0	84.0	81.5
30	[TBA][$C_{12}SO_4$]	1	393	3.0	64.2	71.0
31	[TBA][$C_{12}SO_4$]	2	393	3.0	77.3	89.4
32	[TBA][$C_{12}SO_4$]	4	393	3.0	87.1	92.4
33	[TBA][$C_{12}BSO_3$]	3	393	3.0	87.2	84.6

Reaction conditions: glycidyl isopropyl ether 50 mmol, catalyst 0.5 mmol and 0.125 mmol of $ZnBr_2$

Table 4 Effect of the reaction parameters using [TBA][$C_{12}SO_4$] as catalyst and performances of the best SAILs ([TBA][$C_{12}BSO_3$]) for the cycloaddition of CO_2 to form EC

Entry	SAIL	Time (h)	Temperature (K)	Pressure (MPa)	Conversion (%)	Selectivity (%)
34	[TBA][$C_{12}SO_4$]	2	383	3.0	86.3	93.4
35	[TBA][$C_{12}SO_4$]	2	393	3.0	92.1	94.7
36	[TBA][$C_{12}SO_4$]	2	403	3.0	96.8	84.3
37	[TBA][$C_{12}SO_4$]	2	393	2.0	84.6	89.8
38	[TBA][$C_{12}SO_4$]	2	393	4.0	92.0	91.7
39	[TBA][$C_{12}SO_4$]	1	393	3.0	53.3	74.2
40	[TBA][$C_{12}SO_4$]	3	393	3.0	92.4	93.9
41	[TBA][$C_{12}SO_4$]	4	393	3.0	90.7	91.1
42	[TBA][$C_{12}BSO_3$]	2	393	3.0	81.5	93.5

Reaction conditions: epichlorohydrin 50 mmol, catalyst 0.5 mmol and 0.125 mmol of $ZnBr_2$

for GC and a marked loss of selectivity for the EC were observed. Selectivity loss for EC with increasing temperature is probably due to decomposition of the product into 1-chloroethane-1,2-diol [37, 48].

The influence of pressure in selectivity and conversion (entries 26, 28–29 for GC—Fig. 4c) (entries 35, 37–38 for EC—Fig. 4g) was evaluated from 2.0 to 4.0 MPa. An increase in conversion and selectivity up to 3.0 MPa was observed for both carbonates. For pressure values superior to 3.0 MPa a decrease in both conversion and selectivity was observed, being more pronounced in GC. This behavior is due to an ideal stoichiometric rate of epoxide/CO_2, so that one does not inhibit the role of the other and/or the CO_2 acts as an epoxide diluent [48].
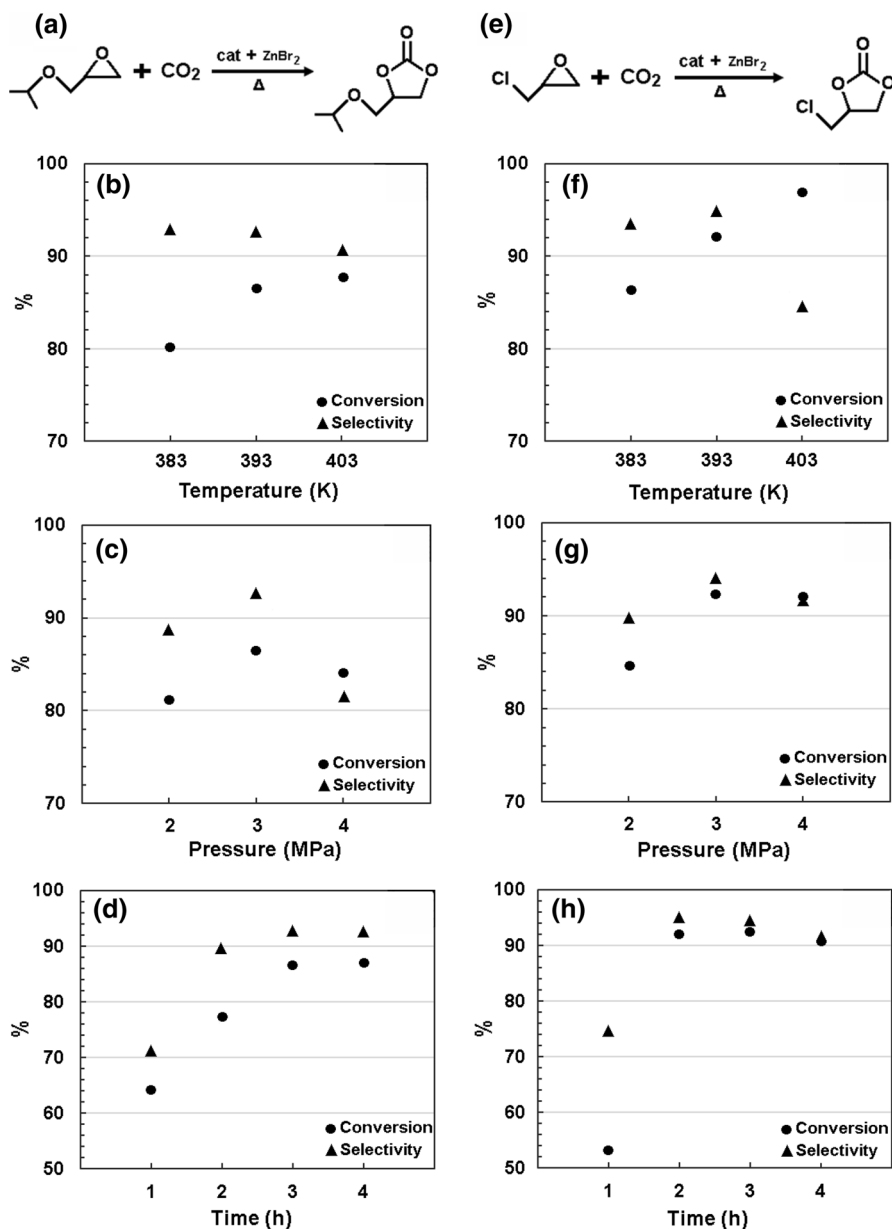
Fig. 4 The reaction scheme on the GC synthesis (**a**): the effect of temperature (**b**), pressure (**c**) time (**d**); and the reaction scheme on the EC synthesis (**e**): the effect of temperature (**f**), pressure (**g**), time (**h**) both using [TBA][$C_{12}SO_4$] as catalyst and $ZnBr_2$ as cocatalyst

Finally, time influence in selectivity and conversion (entries 35, 39–41 for GC—Fig. 4d) (entries 35, 39–41 for EC—Fig. 4h) was performed varying from 1 to 4 h of reaction time. Increasing the time up to 3 h significantly increases the conversion

and selectivity to GC. For EC the increases in conversion and selectivity was observed up to 2 h. Increasing the reaction time does not improve selectivity and conversion since the reaction was already at equilibrium and product decomposition could occur in longer times (entry 41) [9, 38, 48].

The presence of functional groups in the starting epoxide, such as ether in glycidyl isopropyl ether (entries 26 and 33) and chlorine in epichlorohydrin (entries 35 and 42) resulted in higher conversions and selectivities when compared to SC, both for [TBA][$C_{12}SO_4$] (entry 2) and [TBA][$C_{12}BSO_3$] (entry 18) because of the less significant steric hindrance.

After these studies, an ideal condition was determined for glycidyl isopropyl ether carbonate (GC) synthesis, being: 393 K of temperature, 3 h and 3.0 MPa of initial pressure of CO_2. For the epichlorohydrin carbonate (EC) it was: 393 K of temperature, 2 h and 3.0 MPa of initial pressure of CO_2. The use of the best catalytic system elected previously, [TBA][$C_{12}BSO_3$] was evaluated obtaining interesting results for GC (Table 3, entry 33; selectivity 84.6% and conversion 87.2%) and EC (Table 4, entry 42; selectivity 93.5% and conversion 81.5%) syntheses.

Conclusion

Several SAILs were used as catalysts in the CO_2 cycloaddition to styrene oxide and showed catalytic efficiency. The best reaction condition for the synthesis of styrene carbonate (SC) was 353 K of temperature, 4 h of time at 4.0 MPa of pressure when using the [TBA][$C_{12}SO_4$] as catalyst. The [TBA][$C_{12}BSO_3$] was the SAIL that presented better catalytic activity, reaching 81.4% of conversion and 87.0% of selectivity and these results increasing after the first recycle. The best reaction condition when using the [TBA][$C_{12}SO_4$] as catalyst for glycidyl isopropyl ether carbonate (GC) synthesis was 393 K of temperature, 3 h of time at 3.0 MPa of pressure and for the synthesis of epichlorohydrin carbonate (EC) was 393 K of temperature, 2 h of time at 3.0 MPa of pressure. Both GC and EC, the use of [TBA][$C_{12}BSO_3$] as catalyst shows satisfactory activity.

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