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Cycloaddition of carbon dioxide to butyl glycidyl ether using imidazolium salt ionic liquid as a catalyst

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Abstract−The catalytic performance of imidazolium salt ionic liquids in the cycloaddition of carbon dioxide to butyl glycidyl ether (BGE) was investigated. The catalytic activity was tested with different imidazolium salt ionic liquids at 60-140 °C under 0.62-2.17 MPa of CO_2 pressure. The imidazolium salt ionic liquid with the cation of bulkier alkyl chain length and with more nucleophilic anion showed higher conversion of BGE. High carbon dioxide pressure and high reaction temperature up to 140 °C was favorable for the high reactivity of the catalyst. The presence of zinc bromide co-catalyst enhanced the reactivity of the imidazolium salt ionic liquid. Kinetic studies with a semi-batch reactor revealed that the reaction could be considered as first order with respect to the concentration of BGE, and the activation energy was estimated as 22.6 and 22.8 kJ/mol for 1-ethyl-3-methylimidazolium chloride (EMImCl) and 1-butyl-3-methylimidazolium chloride (BMImCl), respectively.

Key words: Imidazolium Salt, Ionic Liquid, Butyl Glycidyl Ether, Carbon Dioxide

INTRODUCTION

Chemical fixation of carbon dioxide is a very attractive subject in view of resource utilization and environmental problems. Various chemical and biological methods to fix and utilize CO_2 are under study. Among them, the application of carbon dioxide as a monomer for the synthesis of various polymers has received much attention in recent years [1-3].

The synthesis of cyclic carbonate via cycloaddition of CO_2 to epoxide is one of the effective routes of CO_2 chemical fixation. Cyclic carbonates have found extensive use as excellent aprotic polar solvents, electrolytes in secondary batteries, precursors for polycarbonates and other polymeric materials, and intermediates in the production of pharmaceuticals and fine chemicals like dialkyl carbonates, glycols, carbamates, pyrimidines, purines, etc. [4].

The synthesis of cyclic carbonates from CO_2 and epoxides has been applied on industrial scale and a number of works on the catalyst development and the reaction mechanisms were reported in the literature [1-3,5]. Cycloadditions between epoxides and carbon dioxide using organic and inorganic compounds such as metal halides [6], onium halides [7], metal complexes [8-10] as catalysts generally occur at low rates unless high temperature, high carbon dioxide pressure, long reaction time and/or high catalyst/substrate ratios are used. However, activity, stability and recovery of catalysts still remain to be improved.

Ionic liquids are a kind of novel medium composed entirely of ions. Recently, significant progress has been made in the application of ionic liquids as alternative solvents and catalysts due to their negligible vapor pressure, excellent thermal stability and special characteristics in comparison with conventional organic and inorganic solvents [1].

Comprehensive information about this field may be found in the recent reviews by several authors [11-16]. These provide an excellent and essential source of the physical and chemical properties of ionic liquids and catalog a range of reactions that can be carried out in ionic liquids. The focus is on the catalytic applications of ionic liquids, in particular on the principles involved and analogies with catalytic reactions in conventional media. Many reactions catalyzed with ionic liquids and showing high performance have been reported [12,17-19]. In particular, ionic liquids based on imidazolium cations and chloroaluminate anions, such as 1-butyl-3-methylimidazolium aluminum chloride (BMImCl/$AlCl_3$), have attracted growing interest [20,21]. Recent studies reported that a number of imidazolium salt ionic liquids can serve as an effective catalyst for the cycloaddition of CO_2 to epoxides in the presence of certain metal halide as co-catalyst [22-30]. Immobilized ionic liquid on silica support were also used as heterogeneous catalyst for this reaction [31-35].

Although the extensive literature reported the cycloaddition of CO_2 to epoxides using imidazolium salt catalysts, there are very few works for the reaction of butyl glycidyl ether (BGE) and CO_2 using imidazolium salt ionic liquids as catalysts. In addition, kinetic study for this reaction has not been carried out.

In the present work, imidazolium salt ionic liquids of different alkyl groups and different anions were used to understand the catalytic role of the ionic liquids. The effects of reaction temperature, carbon dioxide pressure, and the presence of $ZnBr_2$ co-catalyst were also studied for the cycloaddition of carbon dioxide to BGE. Kinetic studies were also performed and activation energy of the reaction was estimated.

EXPERIMENTAL

BGE (purity: 95%) was purchased from Aldrich. Imidazolium salt ionic liquids based on 1-ethyl-3-methylimidazolium (EMIm), 1-butyl-3-methylimidazolium (BMIm), 1-hexyl-3-methylimidazo-

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lium (HMIm), 1-octyl-3-methylimidazolium (OMIm), with different anions such as Cl^-, Br^-, BF_4^-, were prepared according to the procedures reported previously [36]. The ionic liquids were dried and degassed under vacuum at 100 °C for 4 h prior to use.

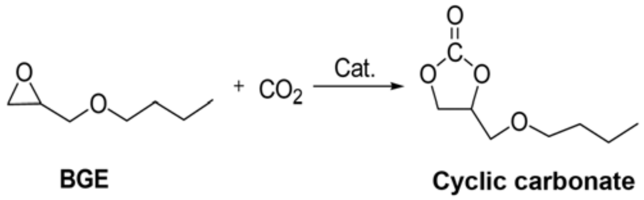
Experiments for the synthesis of cyclic carbonate from BGE and carbon dioxide were performed in a 50 mL stainless steel autoclave equipped with a magnetic stirrer. The reactor was charged with 40 mmol of BGE, 2 mmol of catalyst and then purged several times with CO_2. Then it was pressurized with CO_2 to a fixed pressure, heated to a desired temperature, and the reaction was started by stirring the reactant mixture. To determine the structure and the composition of the products, NMR spectra in deuteriochloroform at room temperature were measured with a NMR spectrometer (Burker AM-400) using tetramethylsilane as the standard, and IR spectra were measured by a React IR spectrometer (ASI Model 1000). The conversions of BGE were determined using a GC (HP 6890) with an FID.

RESULTS AND DISCUSSIONS

Cycloaddition of CO_2 to BGE leads to the formation of the cyclic carbonate shown in Scheme 1.

1. Identification of Cyclic Carbonate

The product of the reaction was analyzed by ^{1}H-NMR, and the characteristic peaks from ^{1}H-NMR analysis ($CDCl_3$) were as follows: 4.1-4.4 ppm (3H, cyclic -C*H*-O- and C*H*$_2$-O-), 3.4-3.8 ppm (2H, -C*H*$_2$-O-). The formation of cyclic carbonate was confirmed by IR analysis. The spectra showed absorption at 1,800 cm^{-1} (C=O of carbonate group) and the consumption of BGE was verified by the disappearance of the absorption at 910 cm^{-1} (C-O-C of epoxide ring). No peak was observed at 1,750 cm^{-1} (C=O of carbonate group), characteristic peak of polycarbonate.



Scheme 1. Synthesis of cyclic carbonate from BGE and carbon dioxide.

Table 1. Effects of the structure of imidazolium salt ionic liquid catalysts on the conversion of BGE

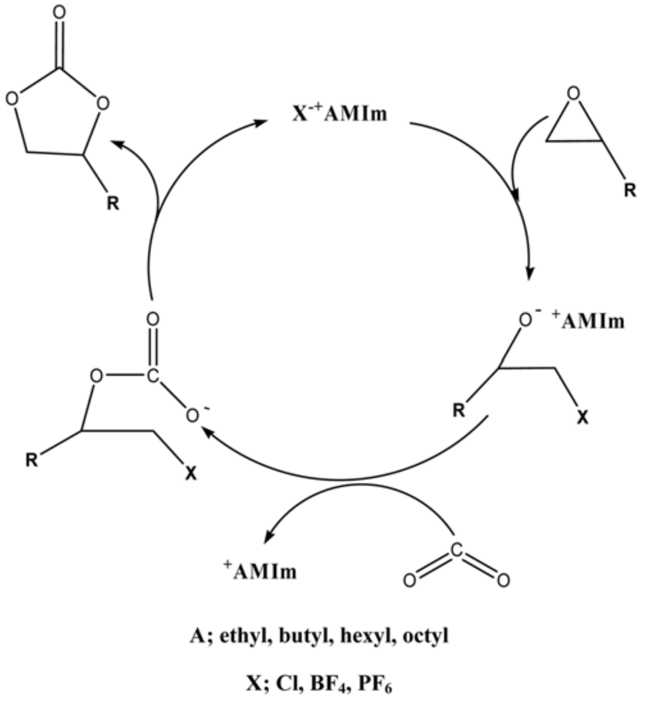
Run	Catalyst	Temp. (°C)	BGE conv. (%)
1	EMImCl	80	42.1
2	BMImCl	80	61.0
3	EMImCl	100	76.0
4	BMImCl	100	79.1
5	HMImCl	100	81.3
6	OMImCl	100	78.3
7	$EMImBF_4$	100	26.6
8	$BMImBF_4$	100	37.2
9	$HMImBF_4$	100	40.9
10	$OMImBF_4$	100	40.2
11	EMImBr	100	81.0

Reaction conditions: BGE=40 mmol, catalyst=2 mmol, time=6 h, pressure of CO_2 at 25 °C=1.13 MPa

2. Effects of Ionic Liquid Cation on the Cycloaddition Reaction

The catalytic activity of ionic liquid depends on the corresponding cation and counter anion of the catalyst. To understand the effects of cation structure for the reaction of BGE and CO_2, different imidazolium salt ionic liquids consisting of cations of $EMIm^+$, $BMIm^+$, $HMIm^+$, $OMIm^+$ were used at 100 °C. A little portion of reaction mixture was taken and analyzed to check the reactivity and selectivity. The conversions of BGE with catalysts of different alkyl chain length are summarized in Table 1. The selectivity of the cyclic carbonate was close to 100% in all the experiments.

The BGE conversion increased as the size of the cation of ionic liquids increased from $EMIm^+ < BMIm^+ < HMIm^+$. The rate-determining step of the epoxide - CO_2 reaction involves nucleophilic attack of the chloride anion to BGE as shown in Scheme 2 [37]. Bulky ionic liquids, having longer distance between cation and anion, may be considered to have higher anion activation ability. This explains why they are more effective in nucleophilic attack of the anion to the oxirane ring of BGE. The bulkiness of the alkyl imidazolium cation forces the chloride ion away from the cation, and this weaker electrostatic interaction would render the anion more nucleophilic [37]. Starks et al. [38] also reported that bulkier quaternary ammonium salt had higher anion activation ability due to the longer distance between cation and anion. For example, $(C_4H_9)N^+\cdots Br^-$ (d=62.8 nm) can have reactivity of four orders of magnitude higher than $Na^+\cdots Br^-$ (d=28.5 nm), although the difference in cation-anion interionic distances for the two ion pairs is only about 34.3 nm [38].



Scheme 2. Reaction steps for cyclic carbonate synthesis from BGE and CO_2 with imidazolium salt ionic liquid catalyst.

Table 2. Effect of temperature on the conversion of BGE

Run	Catalyst	Temp. (°C)	BGE conv. (%)
12	EMImCl	60	26.7
1	EMImCl	80	42.1
3	EMImCl	100	76.0
13	EMImCl	120	88.0
14	EMImCl	140	84.9
15	BMImCl	60	43.1
2	BMImCl	80	61.0
4	BMImCl	100	79.1
16	BMImCl	120	94.3
17	BMImCl	140	93.5

Reaction conditions: BGE=40 mmol, catalyst=2 mmol, time=6 h, pressure of CO_2 at 25 °C=1.13 MPa

Table 3. Effects of carbon dioxide pressure and zinc halide co-catalyst on the conversion of BGE

Run	Catalyst (mmol)	ZnX_2 (mmol)	Pressure (MPa)[a]	BGE conv. (%)
18	EMImCl (2)	-	Atmosphere	46.8
19	EMImCl (2)	-	0.62	65.5
3	EMImCl (2)	-	1.13	76.0
20	EMImCl (2)	-	2.17	91.4
21	BMImCl (1)	-	1.13	70.7
22	BMImCl (1)	$ZnBr_2$ (1)	1.13	85.6
23	BMImCl (1)	$ZnCl_2$ (1)	1.13	80.3
24	BMImCl (1)	ZnF_2 (1)	1.13	74.9

Reaction conditions: BGE=40 mmol, catalyst=2 mmol, T=100 °C, time=6 h

[a] Pressure of CO_2 at 25 °C

The increase in the solubilities of CO_2 in the mixture of BGE and ionic liquid with lengthening alkyl chain of the ionic liquid could also be a reason for the increase of BGE conversion. Kawanami et al. [39] also reported the increase of reactivity when the alkyl chain length increased for 1-alkyl-3-methylimidazolium tetrafluoroborate ($CxMImBF_4$) in the synthesis of propylene carbonate using a high pressure CO_2 - ionic liquid system. However, Table 1 shows that OMImCl and $OMIMBF_4$ had slightly lower conversion than HMImCl and $HMImBF_4$, respectively. This might be due to the steric hindrance of the bulky structure of the octyl group.

3. Effect of Counter Anion of Ionic Liquid

Ionic liquids with different anions (Cl^-, BF_4^-, Br^-) were also tested for the cycloaddition of CO_2 to BGE at 100 °C. The conversions of BGE with the catalyst of different anions are also summarized in Table 1. The conversion increased in the order $BF_4^- < Cl^- < Br^-$, which is consistent with the order of the nucleophilicity of the anions. More nucleophilic anion will attack the epoxide ring more easily to form a reaction intermediate shown in Scheme 2.

4. Effects of Reaction Temperature

Table 2 shows the effect of reaction temperature on the conversion of BGE after 6 h of reaction using EMImCl and BMImCl catalysts. The conversion of BGE increased as the temperature increased from 60 °C to 120 °C. However, the BGE conversion at 140 °C after 6 h of reaction shows a little decrease probably due to the decomposition of the cyclic carbonate to BGE and CO_2. Over the whole temperature range, more bulkier BMImCl showed higher BGE conversion than did EMImCl.

For the comparison of temperature dependence of imidazolium salt and quaternary salt catalysts, tetrabutylammonium chloride (TBAC) was also tested at the same reaction condition. At 80 °C, TBAC shows much higher activity than BMImCl. The better performance of tetralylammonium salt catalysts could be ascribed to the structural difference of the cation, which could influence the behavior of anions. Indeed, the bulkiness of the tetrahedral ammonium ion forces the chloride ion away from the cation, and this less electrostatic interaction renders these anions more nucleophilic [37]. However, at high temperature (140 °C) BMImCl shows higher conversion than TBAC. Quaternary ammonium salt is generally known to degrade over 140 °C [38]. Therefore, high operation temperature is another advantage of the imidazolium salt ionic liquid.

5. Effects of CO_2 Pressure and Co-catalyst

Table 3 lists the BGE conversion at 100 °C under different CO_2 pressure using EMImCl catalyst. The conversion increased as CO_2 pressure increased from atmosphere to 2.17 MPa. High CO_2 pressure could enhance the absorption of CO_2 in the solution of BGE and EMImCl. Zhang et al. [40] reported the increase of the solubility of CO_2 in $BMImPF_6$ with increasing the pressure of CO_2. It is also reported, in the CO_2/cyclohexne oxide coupling reaction catalyzed by chromium salen complexes, that high CO_2 pressure increased turnover number of the reaction [41].

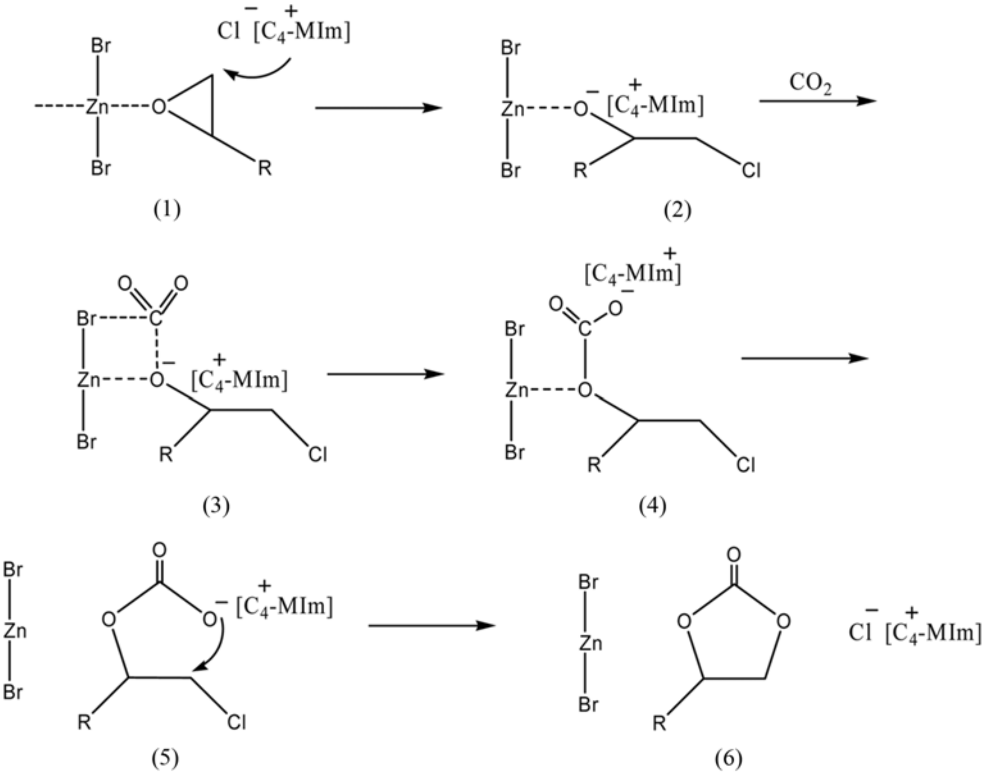
Table 3 also shows the effect of zinc halide co-catalyst on the cyclcoaddition of CO_2 to BGE with BMImCl catalyst. Zinc halide alone showed no activity for this reaction. All the mixtures of zinc halide with BMImCl showed an enhanced effect in BGE conversion compared to the BMImCl itself. The BGE conversion of the mixed catalyst increased in the sequence $ZnF_2 < ZnCl_2 < ZnBr_2$. The nucleophilicity of the halide anions is in the order $F^- < Cl^- < Br^-$. Therefore, more nucleophilic anion could increase the interaction of Br^- and carbon atom of CO_2.

The increased activity of BMImCl with $ZnBr_2$ may originate from the cooperative action of both the acidic site (Zn) for epoxide activation and basic site (Cl^- in BMImCl and/or Br^- in $ZnBr_2$) for CO_2 activation, as reported previously by Sun et al. [42] for the synthesis of styrene carbonate from styrene oxide and carbon dioxide. The role of $ZnBr_2$ co-catalyst on the cycloaddition of BGE and CO_2 can be explained by the mechanism proposed in Scheme 3. At initiation stage, BGE is coordinated with the Lewis acid site Zn to form the metal-epoxide complex. Then the Cl^- anion of the ionic liquid makes a nucleophilic attack on the less hindered carbon atom of the coordinated epoxide followed by ring opening. Next, CO_2 is coordinated to the complex through interactions with Br^- and O^-. Fuwei et al. [43] also reported an increase of the yield of propylene carbonate from propylene oxide and CO_2 with the use of $ZnBr_2$ co-catalyst.

6. Kinetic Studies in a Semi-batch Reactor

For the addition reaction of CO_2 to BGE using ionic liquid catalyst, the following elementary reaction rate equations can be proposed.

$$R + QX \underset{k_2}{\overset{k_1}{\rightleftarrows}} RQX^* \qquad (1)$$



Scheme 3. The reaction mechanism for the reaction of CO_2 and epoxide with [BMIm]Cl/$ZnBr_2$ mixed catalyst.

$$RQX^* + CO_2 \xrightarrow{k_3} P + QX \tag{2}$$

Where, R, P, QX and RQX* represent BGE, cyclic carbonate, catalyst and intermediate complex, respectively. k_1, k_2 and k_3 are reaction rate constants.

$$\frac{dP}{dt} = k_3[CO_2][RQX^*] \tag{3}$$

Assuming the reaction at pseudo-steady state, we obtain,

$$\frac{d[RQX^*]}{dt} = k_1[BGE][QX] - k_2[RQX^*] - k_3[CO_2][RQX^*] = 0 \tag{4}$$

$$[RQX^*] = \frac{k_1[R][QX]}{k_2 + k_3[CO_2]} \tag{5}$$

Substituting [RQX*] into Eq. (3) gives Eq. (6).

$$\frac{dP}{dt} = k_3\frac{k_1[BGE][CO_2][QX]}{k_2 + k_3[CO_2]} \tag{6}$$

When the reaction is carried out in a semi-batch reactor with a continuous supply of carbon dioxide, the concentration of CO_2 and catalyst can be assumed constant.

$$\frac{dP}{dt} = -\frac{dR}{dt} = k[BGE] \tag{7}$$

Integrating Eq. (7) yields

$$\ln([BGE]_0/[BGE]) = kt \tag{8}$$

From the slope of the linear plot of ln ($[BGE]_0$/[BGE]) versus time, one can estimate the pseudo first-order rate constant k.

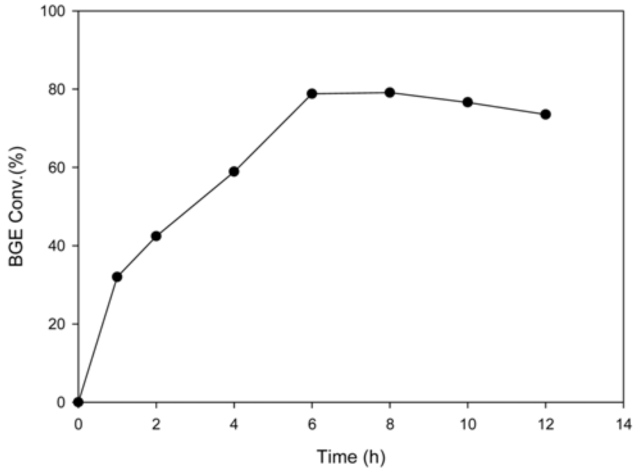


Fig. 1. Time variant conversion of BGE with EMImCl at 100 ℃ (BGE=40 mmol, catalyst=2 mmol, P_{CO2}=1.13 MPa).

Fig. 1 shows the variation of BGE conversion at 100 ℃ with EMImCl catalyst at 1.13 MPa of CO_2 pressure. The BGE conversion increased up to 6 h; then it decreased a little after long reaction time probably due to the decomposition of the cyclic carbonate. Therefore, the kinetic studies were carried out in a semi-batch reactor during the initial 1 h of reaction at 60-120 ℃. Fig. 2 is the plot of ln($[BGE]_0$/[BGE]) versus time. The data fit well to pseudo first order kinetics. The reaction rate constant k for 60, 80, 100, and 120 ℃ was 0.0024, 0.0041, 0.0068, and 0.0089 min^{-1}, respectively. From the Arrhenius plot shown in Fig. 3, the activation energy was estimated as 22.6 kJ/mol. Fig. 4 shows the plot of ln($[BGE]_0$/[BGE])

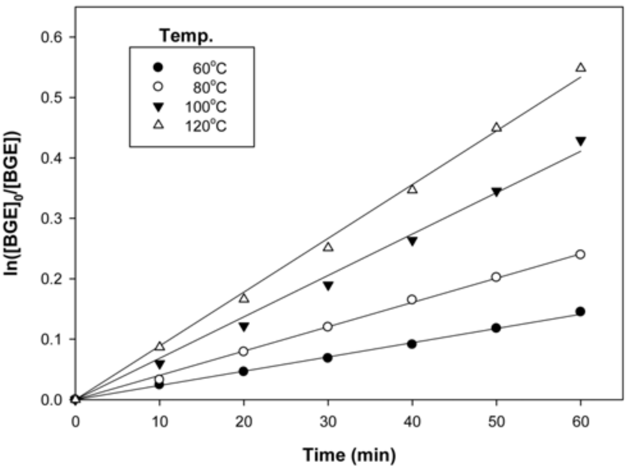


Fig. 2. First-order plot of ln($[BGE]_0$/[BGE]) versus reaction time at different temperature using EMImCl catalyst.

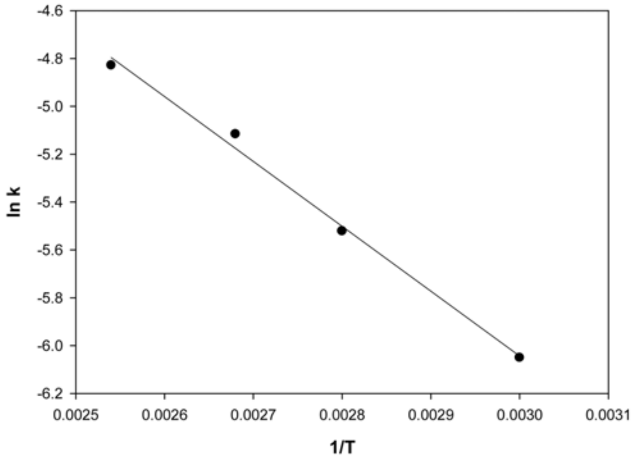


Fig. 3. Arrhenius plot for EMImCl catalyst.

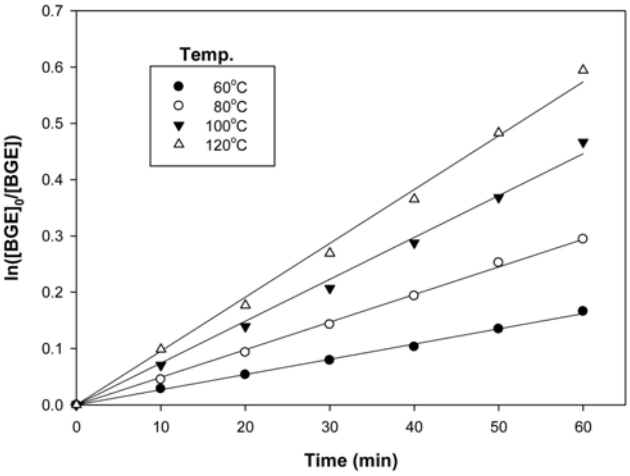


Fig. 4. First-order plot of ln($[BGE]_0$/[BGE]) versus reaction time at different temperature using BMImCl catalyst.

versus time for BMImCl catalyst. From Fig. 5, the activation energy for BMImCl catalyst was estimated as 26.8 kJ/mol.

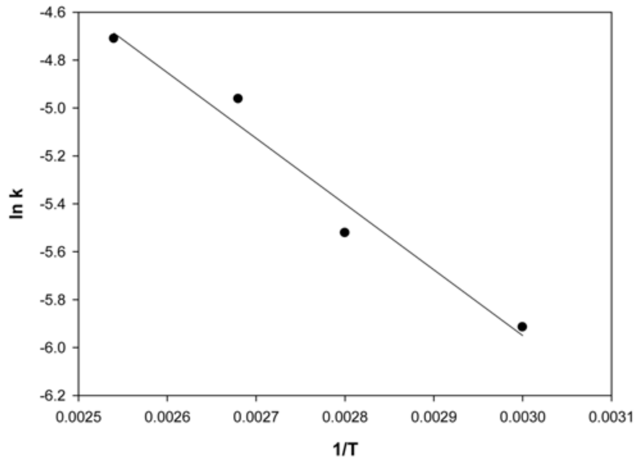


Fig. 5. Arrhenius plot for BMImCl catalyst.

CONCLUSIONS

Imidazolium salt ionic liquid showed good catalytic activity for the synthesis of cyclic carbonate from BGE and CO_2. The BGE conversion increased as the size of the cation of the imidazolium salt ionic liquids increased from $EMIm^+$<$BMIm^+$<$HMIm^+$. Ionic liquid having longer distances between cation and anion seems to exhibit higher activity in activating anions. The increase in the solubilities of CO_2 in the solution of BGE and ionic liquid with lengthening alkyl chain of the ionic liquid could also be a reason for the increase of BGE conversion. In the case of the counter anion of the ionic liquid, the order of the conversion increased $BF_4^-<Cl^-<Br^-$, which is consistent with the order of nucleophilicity of the anions. The zinc halide co-catalyst mixed with BMImCl showed an improved reactivity due to the cooperative action of both the acidic site (Zn) and basic site (X^-). The conversion of BGE increased in the sequence $ZnF_2<ZnCl_2<ZnBr_2$. High pressure also increased the BGE conversion because the solubility of CO_2 increased with increasing CO_2 pressure. The experimental data of semi-batch operation fitted well to the pseudo first-order reaction kinetics. From the Arrhenius plot, activation energy was estimated as 22.6 and 22.8 kJ/mol for EMImCl and BMImCl, respectively.

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