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# Synthesis of glycerol carbonate from glycerol and dimethyl carbonate in basic ionic liquids*

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*Abstract*: Glycerol carbonate is a key multifunctional compound used as solvent, additive, and building block in alternative chlorine-free processes. Here, we report the synthesis of glycerol carbonate from renewable materials (glycerol and dimethyl carbonate, DMC) using basic ionic liquids (ILs) as catalysts. After process optimization, it has been possible to isolate pure glycerol carbonate in quantitative yield using a three-fold excess of DMC and ca. 15 % of IL. The IL could be reused at least four times without any significant reduction in the conversion yield.

*Keywords*: catalysis; green chemistry; ionic liquids.

## INTRODUCTION

Chlorine is the main link in many of the world's most famous environmental poisons: dioxin, DDT, chlorinated solvents, PCBs and the ozone destroyers, CFCs, and HCFCs. Most chlorine is combined with petrochemicals to produce organochlorine products, including plastics, pesticides, solvents, reagents, and building blocks (epichloridrin is one of the most widely used chemicals). Many more are produced by accident like the unintentional by-products of manufacturing processes and other uses of chlorine. The development of alternative chemical processes using chlorine-free compounds (building blocks, reagents, and solvents) represents, therefore, a valid approach for chlorine pollution reduction.

Among the chemicals derived from glycerol, glycerol carbonate, a stable colorless liquid, represents an important high added-value derivative that shows low toxicity, good biodegradability, and highly boiling point. For these important properties, it finds several applications in different industrial sectors, especially as a polar high-boiling solvent or intermediate in organic syntheses (i.e., synthesis of polycarbonates and other polymeric materials in the plastics field [1] as well as of very valuable intermediates such as glycidol [2], which is employed in textile, plastics, pharmaceutical, and cosmetics industries), as a precursor in biomedical applications and as a protection group in carbohydrate chemistry. It is also used as a component in membranes for gas separation, instead of ethylene and propylene carbonates [3], in the synthesis of polyurethanes [4] and in the production of surfactants [5]. As a chemical intermediate, it reacts readily with alcohols, phenols, and carboxylic acids with loss of $CO_2$ as well as with aliphatic amine with carbon dioxide recovery. Finally, glycerol carbonate and its derivatives can be used as electrolytes and solvents in lithium ion batteries, and it is considered to be a green substitute for important petro-derivative compounds (ethylene carbonate or propylene carbonate) [6].

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The research of new synthetic approaches to obtain pure glycerol carbonate through sustainable procedures represents an important aim that can favor the large-scale application of this important chemical. Traditionally, cyclic carbonates have been prepared by reaction of glycols with phosgene [7,8], but owing to the high toxicity and corrosive nature of phosgene, alternative routes such as transesterification reaction [9] of dialkyl or alkylene carbonates to obtain cyclic carbonates have been explored. The transesterification between glycerol and ethylene carbonate is generally performed using an alkaline base [10]. Recently, it has been reported that the use of sodium bicarbonate and ethylene carbonate, at 130 °C, yielded 81 % of glycerol carbonate [11] after 30 min. But other catalysts, such as CaO, $K_2CO_3$, and imidazolium-2-carboxylate, have also been used under different reaction conditions to produce glycerol carbonate. In particular, $K_2CO_3$ or CaO have been used as an efficient catalyst to produce glycerol carbonate from glycerol and dimethyl carbonate (DMC), obtaining a quantitative amount of the expected product [12]. The use of DMC can be considered an increase in the sustainability of the process; DMC can be manufactured by environmentally safe industrial methods (potentially from $CO_2$ and renewable resources), avoiding the formation of the high-boiling ethylene glycol. However, the proposed $K_2CO_3$- or CaO-catalyzed process always requires the final neutralization step (phosphoric acid, sulfuric acid, benzenesulfonic acid, etc. must be added to the system to neutralize the catalyst), which produces relevant amounts of salts as by-products. Attempts to avoid the neutralization step and reduce waste formation have been carried out by using solid catalysts [13]. Unfortunately, under heterogeneous conditions the catalyst deactivation, normally observed in the recycling experiments, dramatically decreases the glycerol carbonate yield. Recently, also the approach to use a biocatalyst has been investigated. Kim et al. [14] in the year 2007 reported the use of *Candida antarctica* (CALB, Novozyme®435) lipase as the first example in which an enzymatic catalyst was used for the synthesis of glycerol carbonate, whereas, more recently, Lee et al. [15] have reported on the use of glycerol-coated silica gel in the transesterification reaction in DMC by immobilized lipase (Novozyme 435).

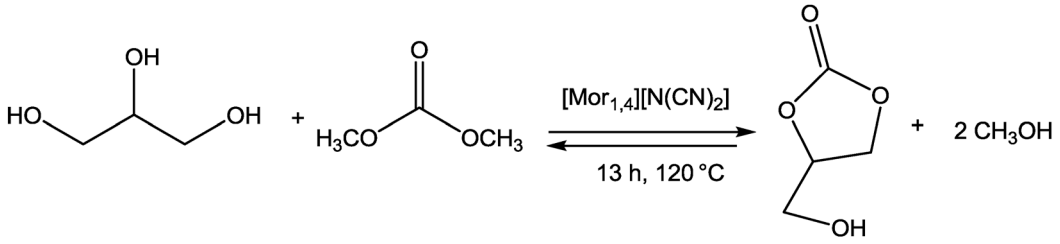
On the other hand, alternative pathways to produce glycerol carbonate have been investigated such as the direct reaction of glycerol with $CO_2$ or carbon monoxide and oxygen, in the presence of Cu(I) as catalyst [16], the reaction of glycerol and ethylene carbonate in supercritical $CO_2$, in the presence of zeolites [17], and the use of urea as source of the carbonate group, a process which was a patent [18,19] in the year 2002, and it has been more recently performed [20] also under catalytic conditions.

Here, we report on the possibility to use ionic liquids (ILs), alternative solvents constituted exclusively by ions that are liquid at room temperature, as cosolvents and catalysts in the synthesis of glycerol carbonate through transesterification process between glycerol and DMC. To this aim, several neutral or basic ILs were synthesized, and their ability to act as catalysts has been related to their hydrogen bond acceptor ability (basicity). Nevertheless, the sustainability of the process in terms of product recovery and IL recyclability has been evaluated.

## RESULTS AND DISCUSSION

To test the ability of ILs to act as catalysts in the transesterification of DMC with glycerol, preliminary experiments were carried out using *N*-methyl-*N*-butylmorpholinium dicyanamide, $[Mor_{1,4}][N(CN)_2]$, as solvent and catalyst (Scheme 1).




**Scheme 1** Formation of glycerol carbonate using ILs.

Since the reaction of glycerol with DMC is an equilibrium process, for which it has been shown that an increase in temperature determines an increase in the related equilibrium constant and normally an excess of DMC is necessary to obtain high yields, reactions were carried out at 120 °C using a molar ratio glycerol:DMC:IL of 1:3:0.15. A practically complete conversion was obtained after 13 h. On the other hand, as expected the use of an equimolar amount of DMC drastically reduced the product yield, whereas higher temperatures (140 °C) produced a rapid darkening of the reaction mixture. However, since we could not exclude that similar results could be obtained at lower temperatures or in a shorter time the same reaction was carried out at 40, 60, 80, and 120 °C and analyzed at different times (Fig. 1).

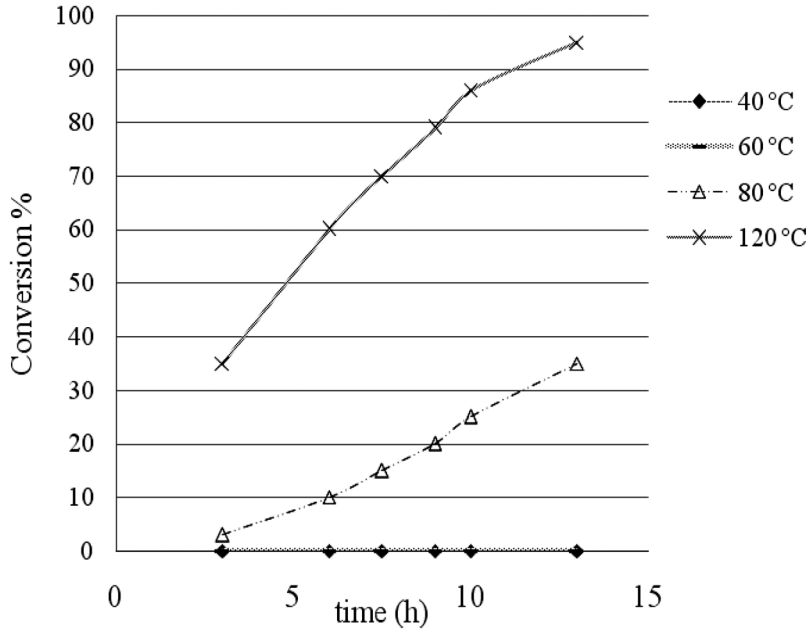



**Fig. 1** Behavior of conversion with temperature.

The crude reaction mixtures were analyzed directly and after removal of the more volatile compounds (DMC and methanol) at reduced pressure by $^{13}C$ NMR. The entity of conversion was evaluated on the basis of the peaks at 77.43 and 72.79 ppm related to the CH carbons of the product and reagent, respectively (Fig. 2).

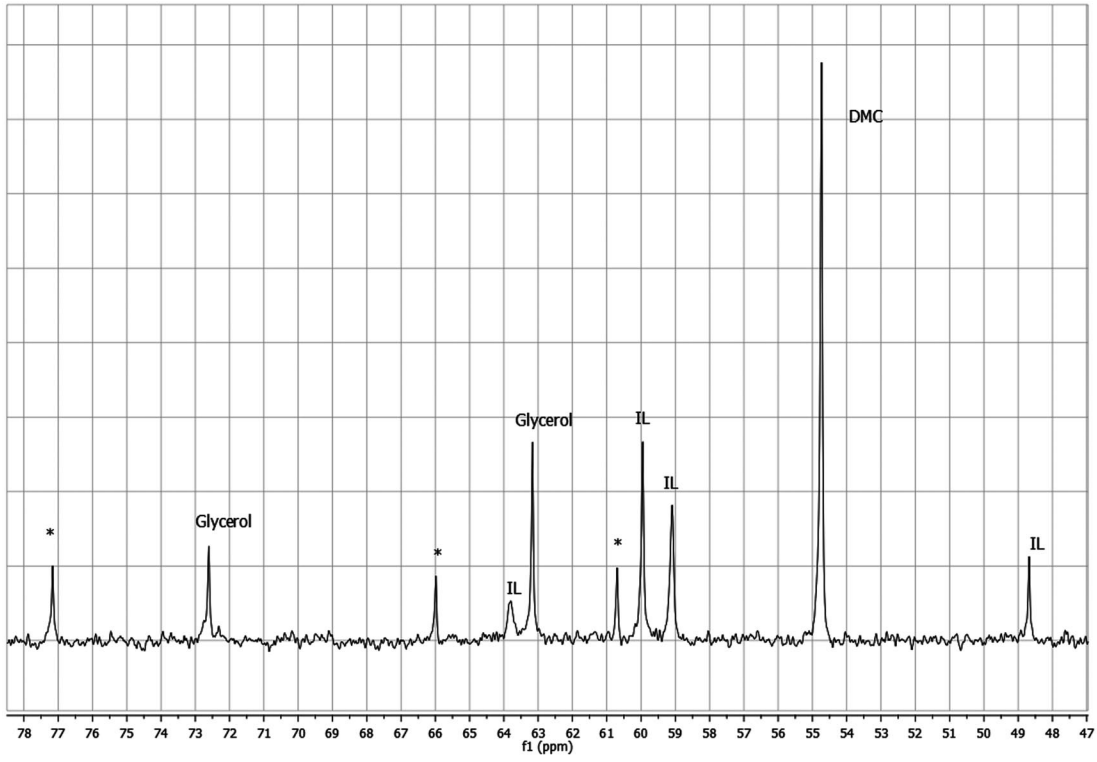



**Fig. 2** $^{13}$C NMR spectrum of the reaction mixture in DMSO-$d_6$ (between 46 and 79 ppm) after 5 h using [$Mor_{1,4}$][$N(CN)_2$] as catalyst. The mixture is essentially formed by four species, i.e., glycerol, glycerol carbonate (*), DMC, and IL.

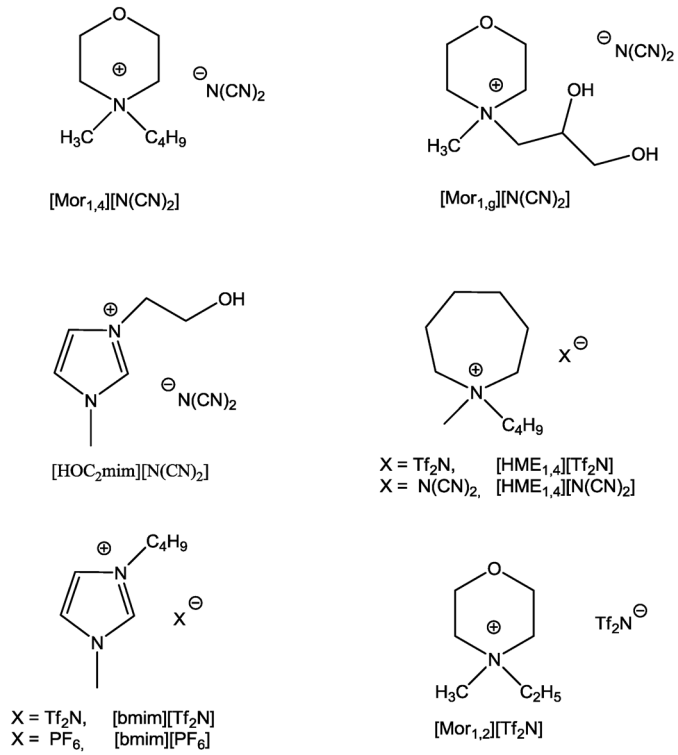
Subsequently, the catalytic ability of this IL was compared with those of the other ILs (both neutral and basic) performing a series of reactions under identical conditions (120 °C, 13 h) using a molar ratio of glycerol:DMC as 1:3 and the amount of IL that is reported in Table 1. In particular, four basic dicyanamide-based ILs (*N*-methyl-*N*-butylmorpholinium dicyanamide, [$Mor_{1,4}$][$N(CN)_2$], *N*-methyl-*N*-glycerylmorpholinium dicyanamide, [$Mor_{1,g}$][$N(CN)_2$], 1-methyl-3-(2-hydroxylethyl)imidazolium dicyanamide, [$HOC_2$mim][$N(CN)_2$], *N*-methyl-*N*-butylazepanium dicyanamide, [$HME_{1,4}$][$N(CN)_2$]) and four neutral ILs having as counteranion bistriflimide or hexafluorophosphate (*N*-methyl-*N*-butylazepanium bistriflimide, [$HME_{1,4}$][$Tf_2N$], 1-methyl-3-butylimidazolium bistriflimide, [bmim][$Tf_2N$], 1-methyl-3-butylimidazolium hexafluorophosphate, [bmim][$PF_6$], and *N*-methyl-*N*-ethylmorpholinium bistriflimide, [$Mor_{1,2}$][$Tf_2N$] have been tested (Scheme 2).

**Table 1** Various catalysts showing their respective conversions at 120 °C.

| ILs | Molar ratio[a] | Conversion % |
|---|---|---|
| $[Mor_{1,4}][N(CN)_2]$ | 0.17 | 95 |
| $[Mor_{1,g}][N(CN)_2]$ | 0.16 | 90 |
| $[HME_{1,4}][N(CN)_2]$ | 0.16 | 45 |
| $[HOC_2mim][N(CN)_2]$ | 0.20 | 95 |
| $[HOC_2mim][N(CN)_2]$ | 0.40 | 100 |
| $[Mor_{1,2}][Tf_2N]$ | 0.20 | 0 |
| $[bmim][Tf_2N]$ | 0.18 | 0 |
| $[bmim][PF_6]$ | 0.13 | 0 |
| $[HME_{1,4}][Tf_2N]$ | 0.20 | 0 |
| $[mmPyrr][MeOCO_2]$ | 0.10 | 100 |

[a]Molar ratio with respect to glycerol.



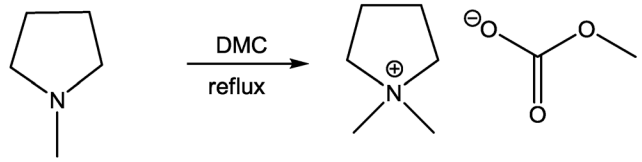

**Scheme 2** Investigated ILs.

Practically, no reaction occurred in the presence of neutral ILs, whereas dicyanamide-based salts were able to give higher conversions and selectivities; the glycerol carbonate was the sole product formed in the presence of these catalysts.

The exception was represented by $[HME_{1,4}][N(CN)_2]$. In the presence of this IL the reaction proceeded with the same product selectivity, but a significant lower conversion was obtained under comparable conditions. This behavior may be attributed to the peculiar solvent properties of this class of ILs. The association of the dialkylazepanium cation to dicyanamide gives liquid salts characterized by

a higher hydrogen bond donor ability and a lower hydrogen bond acceptor ability compared to other dicyanamides based on alicyclic cations, at least when these properties are determined on the basis of the Kamlet–Taft parameters [21]. Nevertheless, it is noteworthy that the presence of hydroxyl groups on the cation did not affect the catalytic activity and the NMR analysis of the reaction mixtures showed that the dihydroxyl-functionalized ILs do not compete significantly with the glycerol in the reaction with DMC. On the basis of these results, considering that IL anion basicity appears fundamental to obtain higher conversions, we decided to test another basic salt, namely, *N*,*N*-dimethylpyrrolidinium methylcarbonate ([mmPyrr][$MeCO_3$]), which can be easily obtained by the reaction of the corresponding tertiary amine, *N*-methylpyrrolidine, with an excess of DMC under reflux (Scheme 3) and is characterized by a high basicity [22,23].




**Scheme 3** Synthesis of *N*,*N*-dimethylpyrrolidinium methylcarbonate.

In the presence of [mmPyrr][$MeCO_3$], a complete conversion was obtained in 9 h just by using a 0.1 molar ratio. However, NMR analysis of the reaction mixture evidenced the formation besides the expected glycerol carbonate of several by-products. Despite its activity, this IL appeared unable to compete with the dicyanamide-based ILs as catalyst in this kind of reaction in terms of selectivity.

Therefore, since it is well known that product recovery and IL recycle are two important aspects for the development of sustainable processes in ILs, we tried to optimize the isolation step of glycerol carbonate, using [$Mor_{1,4}$][$N(CN)_2$] as catalyst. Reactions were carried out under the previously described conditions. Attempts to separate glycerol carbonate from the IL, after removal of DMC by distillation, by extraction with a molecular solvent immiscible with [$Mor_{1,4}$][$N(CN)_2$], such as diethyl ether, failed owing to the low solubility of glycerol carbonate in these solvents. A recovery around 50 % was obtained only by using relevant amounts of diethyl ether. However, it was possible to increase the efficiency of the process by adsorbing the reaction mixture on a small silica gel column. In this case, pure glycerol carbonate was recovered in quantitative yield using a moderate amount of ethyl acetate. Nevertheless, from the silica gel the pure IL could be collected by elution with methanol. After removal of the solvents, the recovered [$Mor_{1,4}$][$N(CN)_2$] was used to test the recyclability of the systems. At least four recycles were performed without any significant reduction in the conversion yield (Table 2).

**Table 2** Recycle of IL [$Mor_{1,4}$][$N(CN)_2$] at 120 °C for 13 h.

| No. of the cycle | Conversion |
|---|---|
| 1st cycle | 95 |
| 2nd cycle | 92 |
| 3rd cycle | 97 |
| 4th cycle | 95 |

## CONCLUSIONS

On the basis of the reported results, we can state that the basic ILs can be used as an appropriate catalyst for the transesterification of DMC with glycerol. In particular, dicyanamide-based ILs appear to be

suitable catalysts for this reaction. In the presence of $[Mor_{1,4}][N(CN)_2]$ (17 % molar ratio), it is possible to obtain a practically complete conversion of glycerol in glycerol carbonate in 13 h by working at 120 °C. Under comparable conditions, no reaction was observed in the case of neutral ILs like $[bmim][Tf_2N]$ and $[bmim][PF_6]$, whereas $[mmPyrr][MeOCO_2]$ gives relevant amounts of by-products. Product recovery and IL recycle can be performed through adsorption of the reaction mixture on silica gel.

## EXPERIMENTAL SECTION

### Materials and methods

Glycerol and DMC were obtained from Sigma-Aldrich and were used as present. $[Mor_{1,4}][N(CN)_2]$, $[bmim][Tf_2N]$, $[bmim][PF_6]$, $[Mor_{1,2}][Tf_2N]$, $[Mor_{1,g}][N(CN)_2]$, $[HME_{1,4}][N(CN)_2]$, $[HME_{1,4}][Tf_2N]$, $[HOC_2mim][N(CN)_2]$ and $[mmPyrr][MeOCO_2]$ were prepared as previously reported [21,22] and checked by NMR and ESI-MS.

### Synthesis of glycerol carbonate

To a mixture of glycerol (1.26 g, 13.7 mmol) and DMC (41 mmol) the selected IL (2–0.5 g, 1.4–5 mmol) was added and the biphasic system was heated at 120 °C. The transesterification reaction progress was monitored by NMR, however, the formation of a sole phase could be taken as the end point of the reaction. The product recovery was carried out by adsorption of the reaction mixture on a small silica gel (3 g) column (Φ 0.5 cm) using ethyl acetate (100 ml) as eluent. After product removal, IL was collected using methanol (100 ml) and reused after solvent evaporation at reduced pressure. Isolated glycerol carbonate presented IR and NMR spectra in agreement with the literature data.

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