



Universal and low energy-demanding platform to produce propylene carbonate from CO₂ using hydrophilic ionic liquids

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ABSTRACT

Ionic liquids (ILs) have been extensively proposed as efficient catalysts to promote CO₂ cycloaddition reaction to epoxides for producing cyclic carbonates. Recently, liquid-liquid extraction with water as an enhancer approach to regenerate ILs and to purify the product was proposed, since it reduces energy consumption and enhances the neat catalytic activity of the IL due to hydroxyl groups of water. In this work, a comprehensive sample of homogeneous IL catalysts proposed in the literature is experimentally evaluated both in the catalytic step and in its separation by liquid-liquid extraction with water, to demonstrate the universality of the proposed reaction-separation proposal for hydrophilic ILs. Then the complete processes for CO₂ conversion to propylene carbonate were modelled using Aspen Plus to compare the catalyst/product separation efficiency and the specific energy consumption using liquid-liquid extraction and distillation-based platforms. The energy consumption is significantly lower using liquid-liquid platform (1.1–1.3 kWh/kg_{PC}) than distillation one (2.4–3.1 kWh/kg_{PC}). It is concluded that hydrophilic ionic liquids, as those formed by [EtOHmim]⁺ cation and halide anions, are promising catalysts since they allow: (i) reducing the process energy consumption due to their high catalytic activity and (ii) full catalyst recovering, even at high catalyst loadings, by improving the water extractive properties for IL separation from PC.

1. Introduction

In recent years, anthropogenic carbon dioxide emissions have increased significantly, causing the concentration of CO₂ in the atmosphere to rise to 412.5 ppm by 2020 [1]. In this context, technologies such as Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU) have been developed in recent years with the aim of removing carbon dioxide from the atmosphere or from a process output stream and thus avoiding the increase in atmospheric CO₂ levels. The main difference is that in CCS, the captured CO₂ is stored in long-term reserves (subsoil, ocean floor or mineral carbonates) [2], while in CCU the captured CO₂ is directly used in an application (enhanced oil recovery, refrigerant, carbonation of beverages, etc.), or as a raw material in other processes, in order to obtain value-added products. Some of the products that can be obtained from CO₂ are methanol, formic acid, urea, organic and inorganic carbonates, polymers, fuels, etc. [3], which renders CCU as a more sustainable alternative than CCS, promoting circular economy.

Among the products resulting from CO₂ valorization, cyclic carbonates have proven their interesting purposes in the chemical industry, since their properties can be modulated to meet the requirements of different contemporary separations [4,5]. Moreover, they can be used as battery electrolytes or as substitutes for other toxic and more volatile compounds such as N,N-dimethylformamide, 1,4-dioxane, N,N-dimethylacetamide or tetrahydrofuran [6]. They can be easily converted into polymers such as polycarbonates or polyurethanes, which enables their application in the pharmaceutical [7] and biomedical field [8], as well as in electrolyte formulation for batteries or coatings [9]. The production of these cyclic carbonates can be carried out by reacting CO₂ and epoxides in the presence of a catalyst to minimize the reaction energy barriers [10]. Said catalysts are primarily based on metal complexes, metal organic frameworks, or functional polymers, although new generation compounds have also been proposed such as ionic liquids (ILs) or eutectic solvents [11,12].

ILs stand out as potential homogeneous catalysts due to their low volatility and high thermal and chemical stability, in addition to their

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designer-solvents capacity, implying that combinations of cations and anions that allow a chemical absorption of CO₂ or an easy separation from the reaction medium can be selected [13,14]. ILs have been previously tested in the synthesis of different linear and cyclic carbonates, such as dimethyl carbonate [15,16] or propylene carbonate [17,18], portraying good results. Different kind of ionic liquids have been used as catalysts in these reactions [15], for instance amino-acid based ILs [19] or aprotic heterocyclic anion-based ILs [20]. However, equally to other homogeneous catalysts, they face a need in the improvement of the separation from the reaction product, as well as the pursuit for milder reaction conditions [21].

Given the partial solubility in water of some cyclic carbonates, such as propylene carbonate [22], the use of water as extracting solvent for the separation of the IL from the cyclic carbonate -in a low-energy demanding liquid-liquid extraction (LLE)- has been developed [23]. Water was selected instead of other solvents because of its low boiling point compared to cyclic carbonates, which facilitates its separation in a distillation, and because of its low cost, negligible environmental impact and affinity with certain hydrophilic ILs [24,25]. This is the case of ILs based on imidazolium cations, in which by properly selecting the cation and the anion, the solubility of the IL in water and the solubility of water in the IL can be modified [26].

Recently, the possibility of using hydrogen bond donor compounds (HBD) as solvents in various organic synthesis reactions to improve the reactivity and selectivity of catalysts has been demonstrated, allowing to carry them out under milder conditions [27]. Specifically, in the cycloaddition of CO₂ to epoxides, Alassmy and Pescarmona (2019) [24] verified that, even though water requires a higher molar loading than other HBDs, the same improvement in conversion can be achieved, in addition to being a cheaper and more environmentally friendly compound than other solvents, becoming one of the most suitable alternatives. Also, several other studies in the literature conclude that these cycloaddition reactions catalyzed by ILs exhibit an improvement when carried out in the presence of water [23,28,29]. This is because water can form hydrogen bonds with the cations and the epoxide, which reduces the energy barrier of the transition states [30]. Recently, our group demonstrated that the presence of water in the reaction system to produce propylene carbonate from propylene oxide using an hydrophilic amino acid-based IL not only permits the efficient separation of the catalyst by means of liquid-liquid extraction, but also improves the catalytic performance of the IL catalyst [23].

In this work, the compatibility of water with several hydrophilic ILs -presenting remarkable different structures- in CO₂ cycloaddition reaction to propylene oxide (PO) and in catalyst/product separation by liquid-liquid extraction is both computationally and experimentally investigated. These selected ILs are based on imidazolium cations, covering different alkyl chain lengths or substituents in the case of the cation, with different halide or amino acid-based anions. In addition, the selected reaction product is propylene carbonate (PC), since it is a carbonate of conventional use, well studied in the bibliography for different applications [4,31,32]. Furthermore, it presents an intermediate solubility in water in comparison to other similar carbonates [9,33,34], which renders conservative results that open the possibility of improvement of the proposed platform in the case of exploring a more hydrophobic product.

The main objective is analyzing the influence that different ILs have on both the catalysis of CO₂ cycloaddition to epoxides in presence of water and on the product separation by LLE, as well as on the overall energy consumption of the propylene carbonate production process. For this purpose, first a preliminary computational analysis based on COSMO/Aspen methodology is performed to evaluate the extractive properties of studied ILs. Then, liquid-liquid equilibrium measurements are carried out in order to develop the reliable design of catalyst-product separation process based on liquid-liquid extraction. Then, the compatibility of water in reaction media is analyzed by catalytic tests of CO₂ cycloaddition to propylene oxide using the selected ILs. Finally,

obtained results are used to model the process of PC production using the proposed water-based platform for the studied ILs by means of COSMO/Aspen simulations. The role of IL in process efficiency is then analyzed in terms of product recovery/purity and energy consumption.

2. Experimental and computational details

2.1. Materials

The main properties of the compounds that were experimentally employed are collected in Table 1. The ILs were outgassed prior to their use as catalysts or solutes in liquid-liquid equilibria experiments at 60 °C and 10⁻³ bar during 24 h.

2.2. Molecular simulation and Aspen database creation

Propylene carbonate and ILs electronic structures (collected in Table S1 of [Supplementary Material](#)) were calculated using Turbomole 7.3 software [37], using a molecular model of ion-pair to describe the ionic liquids [38]. The geometries were optimized through B88-P86 method (Becke 1988) exchange functional and the Perdew 86 correlation functional method with TZVP (Triple Zeta Valence Polarized) basis set in gas phase and using the continuum solvation method COSMO [39]. Minimum level of energy of these geometries was ensured by means of vibrational frequencies calculations. The resulting *.cosmo files were entered into COSMOtherm v.19 software to calculate the IL main properties, namely molecular weight, density, boiling point, COSMO volume and σ -profile. This software employs COSMO-RS method (Conductor-like Screening Model for Real Solvents) for thermodynamic calculations. Then, the ILs were added as pseudocomponents to Aspen Plus v12 simulator following a multiscale COSMO-based/Aspen Plus methodology previously reported elsewhere for systems involving ILs among others [4,23,40,41]. The name and structure of the ILs are collected in Table S1 of [Supplementary Material](#). The rest of compounds involved in Aspen Plus calculations were available in Aspen Plus conventional databases.

2.3. Liquid-liquid equilibria predictions by COSMO/Aspen and experimental measurements

First, a literature search was carried out on the different ILs that have been used to produce propylene carbonate from CO₂ and propylene oxide. With all these, an Aspen Plus database was created and used to predict the ternary liquid-liquid equilibria of {propylene carbonate + water + IL}. The COSMO-SAC property method (code 2) based on the COSMO-RS model by Klamt (1995) [40] was selected for all the Aspen Plus calculations. A 100 kmol/h stream of a mixture of PC and 0.5% mol of IL (F) and a second stream of pure water (S) were fed to a DECANTER unit operating at ambient conditions (1 bar and 25 °C), setting an S/F of 0.5. The partition coefficient (K_{IL} ; eq. (1)) and selectivity ($S_{IL/PC}$; eq. (2)) of the mixture were calculated with the data obtained.

$$K_{IL} = \frac{x_{IL}^E}{x_{IL}^R} \quad (1)$$

$$S_{IL/PC} = \frac{K_{IL}}{K_{PC}} = \frac{\frac{x_{IL}^E}{x_{IL}^R}}{\frac{x_{PC}^E}{x_{PC}^R}} \quad (2)$$

where x_{IL}^i and x_{PC}^i denote the IL and the PC molar fraction, respectively, in the extract (E, solvent-rich) or the raffinate (R, carbonate-rich) phase.

To experimentally analyze the extractive properties of the systems containing the different ILs and to validate COSMO-SAC predictions, the liquid-liquid equilibria of mixtures containing PC, purified water and the various ILs were measured in different concentrations ranging from approximately 0.1% mol to 1.4% mol of IL. Different IL:PC molar

Table 1
Chemicals: properties and specifications.

Compound	Alias	CAS	Molecular Weight (g/mol)	Density (g/cm ³)	Provider
1-butyl-3-methylimidazolium bromide	[bmim][Br]	85100-77-2	219.12	1.30 [35]	Sigma-Aldrich
1-(2-Hydroxyethyl)-3-methylimidazolium chloride	[EtOHmim][Cl]	65039-09-0	162.62	1.27 ^b	Sigma-Aldrich
1-butyl-2,3-dimethylimidazolium chloride	[bmim][Cl]	98892-75-2	188.70	1.08 ^b	Sigma-Aldrich
1-butyl-3-methylimidazolium chloride	[bmim][Cl]	79917-90-1	174.67	1.11 [36]	Green Solutions
1-methyl-3-octylimidazolium chloride	[omim][Cl]	64697-40-1	230.78	1.01 [36]	Sigma-Aldrich
1-butyl-3-methylimidazolium prolinat	[bmim][PRO]	N/A	253.34	1.08 [19]	IoLiTec
1-butyl-3-methylimidazolium methioninat	[bmim][MET]	N/A	287.42	1.10 [19]	IoLiTec
1-butyl-3-methylimidazolium glycinate	[bmim][GLY]	N/A	213.28	1.06 [19]	IoLiTec
CO ₂	-	124-38-9	44.01	1.9·10 ⁻³	Praxair Inc.
Propylene carbonate	PC	108-32-7	102.09	1.20 [19]	Sigma-Aldrich
Propylene oxide	PO	75-56-9	58.08	0.83 [19]	Sigma-Aldrich
Purified water ^a	-	7732-18-5	18.02	1.00	

^aPurified water (Type I) was obtained from an Automatic purification system (Wasserlab) ^bCalculated with COSMO-RS method.

proportions, up to 4% mole of IL, were studied in order to analyze the effect of increasing the IL content in the feed. These molar proportions were selected since they are common reaction conditions when using ionic liquids as catalysts. The measurable highest IL:PC proportion allowing phase immiscibility is thus fixed in 4% mole. In order to completely achieve phase separation and systematize the procedure, the mixtures were centrifuged in a Serie Digicen 21 centrifuge. Afterwards, 20 μ L of each phase were dissolved in 0.5 mL of deuterium oxide (D₂O) and analyzed by Nuclear Magnetic Resonance (NMR) in a Bruker Varian Unity 500 to determine IL and propylene carbonate concentrations. Water concentration was quantified using an Agilent 7820A gas chromatograph to avoid the uncertainty related to NMR. Then, the IL distribution ratio (K_{IL} ; eq. (1)) was calculated. Following the same approach stated before, IL distribution ratios derived from COSMO-SAC predictions were calculated mimicking the experimental tests for a 0.5% mol of IL and were compared to the experimental results for *ad hoc* validation.

2.4. Catalytic tests: Water effect on PO conversion to PC

For the catalytic reaction, 439 mmol of PO and 2.2 mmol of IL were mixed and added to a Berghof BR-100 high-pressure stirred reactor. In the case of reactions in the presence of water, 43.9 mmol of purified water were also added to the reactor. Then, an initial pressure of 5 bar of CO₂ was fed to the reactor until the temperature set point (120 °C) was reached. The temperature was kept constant during the selected reaction time (10 h) and a continuous flow of CO₂ was fed at 20 bar in order to ensure the presence of propylene oxide in the liquid phase. Once the reaction is finished, the product selectivity to PC is measured by 1H NMR in a Bruker Varian Unity 500 and the conversion is determined by evaporating the remaining propylene oxide and water and then

calculating the difference between the initial and final masses, which includes the IL since its high boiling point avoids its removal. Triplicate runs were done for each reaction, finding that standard deviation in conversion calculations with the stirred reactor was never higher than 3% for the reactions without water and 5% for the reactions in presence of water.

2.5. Process modelling of the water-mediated strategy to produce PC from CO₂ conversion using IL catalyst

The process was simulated in Aspen Plus v12 following the diagram shown in Fig. 1. First, PO and the IL are pressurized and heated to the reaction conditions (20 bar and 120 °C) in P-100 and E-100. Then, they are fed to the reactor (R-100) as well as CO₂, which is already at 20 bar. The reactor model employed is RStoic, in which the conversion of PO obtained in the experimental tests in presence of water is fixed. The liquid stream that exits the reactor is conducted to a 1 bar flash vessel to separate most of the CO₂. Then, the resulting liquid stream enters a 10 theoretical equilibrium stages stripping column (D-100) modeled as a RADFRAC rigorous distillation, with a partial condenser. The reboiler temperature in D-100 is set at a maximum of 120 °C to ensure the IL thermal stability, which implies working in vacuum conditions. Said stripping column is designed to recover 99.5% mol of PO in the distillate stream, which is mixed with the vapor stream leaving the reactor and subsequent flash; then it is recycled back to the reactor after reconditioning in C-100 and E-101. The outlet stream from the bottom of D-100 is a liquid stream which contains mainly propylene carbonate and it is cooled down to 25 °C in E-102; then, it enters an extraction column (S-100) set as EXTRACT model of Aspen Plus with 4 stages. Water is fed to said extraction column in a different S/F ratio depending on the IL, with the aim of ensuring a 10:1 PO:water molar ratio in the reactor

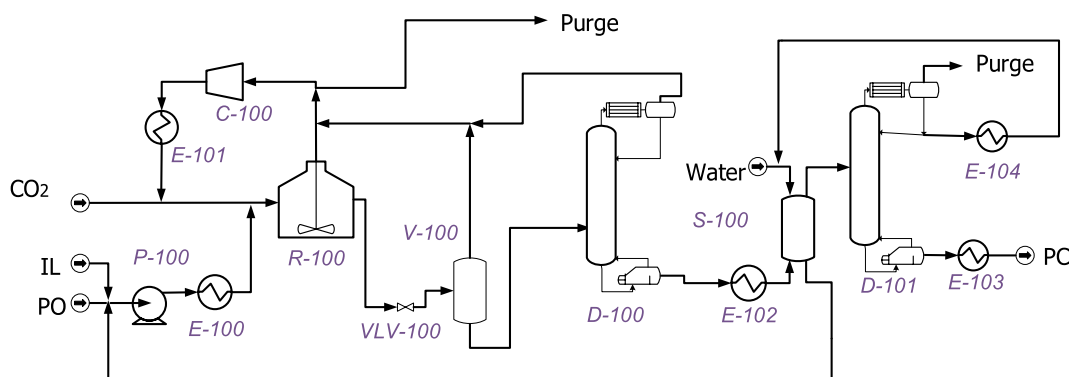


Fig. 1. Process flow diagram for the water-mediated separation strategy.

(mimicking experimental conditions). The bottom stream leaving S-100 contains mainly water and IL, hence it is recycled back to the conditioning (P-100 and E-100). On the other hand, the top stream from S-100 contains mainly PC product and water, consequently it is fed to a distillation column (D-101, modeled as RADFRAC with 30 theoretical equilibrium stages and a partial condenser). There, 99.9% of PC product is recovered in the bottom stream with a 99.9% mass purity, whereas the top stream contains the residual water which is recycled back to the extraction column after being cooled to 25 °C in E-104. Finally, PC stream is also cooled to 25 °C in E-103. The main specifications for this process can be found in Table 2. The operating conditions of the process are based on those of another article [23] in order to suit the different ILs without interfering with their performance.

2.6. Process modelling of the reference process to produce PC from CO₂ conversion using IL catalyst

For comparison purposes, a reference process was modeled in which the separation of the catalyst and the product is carried out by vacuum rectification, as it is commonly proposed in bibliography [23]. As can be seen in Fig. 2, the conditioning, reaction and recovery of PC and CO₂ are identical to the LLE-based process (Fig. 1). However, in the case of the rectification process, instead of the S-100 extraction unit, a rectification unit (D-101), column model RADFRAC with 10 stages, a total condenser and a reflux ratio of 5, is used to recover 99.9% of PC with a mass purity of 99.9% as distillate stream. Since this rectification column works in vacuum conditions to maintain a reboiler temperature lower than 120 °C, the recovered PC is then conditioned to 1 bar and 25 °C in P-101 and E-103. On the other hand, the bottom stream of D-101 is composed mainly of IL and traces of PC, therefore it is mixed with the fresh IL make-up stream to be recycled. Table 2 collects the main specifications for this benchmark process.

3. Results and discussion

3.1. Screening of conventional ILs in the catalyst/product separation by liquid-liquid extraction using water as extracting agent

Conventional hydrophilic ILs (>30) used as catalyst in cycloaddition reaction of CO₂ to PO to form PC were identified and modelled, creating an IL database collected in Table S1. Most of the ILs used in the literature that could be miscible with water are those created by combining halides and amino acids with cations of different nature. After validating the COSMO/Aspen predictions on the {PC + water} system as function of temperature (Figure S1 in Supplementary Material), the extractive properties of water to separate IL from PC were systematically tested for all potential systems in which a hybrid IL/water reaction media could be created. Predicted IL distribution ratio and IL/PC selectivity are graphically presented in Fig. 3. As seen, all studied {PC + IL + water} systems move into great IL/PC selectivity ranges (from 10 to 10000) and mostly favorable IL distribution ratios (from 1 to 100). Therefore, extractive

properties reveal that the use of hydrophilic IL and water, when evaluating the IL extraction from PC, displays a universal and effective separation platform. It should be emphasized that, attending to COSMO/Aspen predictions, the IL nature plays a main role, being easily separated those IL with more polar structure and hydrophilic character. Because of that, a representative IL collection (8) is selected to further evaluate not only the separation platform but also the whole CO₂ conversion process. In order to provide main keys, the ILs previously collected in Table 1 are experimentally tested in this work to deeply evaluate their extractive properties and catalytic activity to produce PC. The IL structure set as benchmark is [bmim][Cl], since chloride anion is one of the most active anions in the literature and imidazolium rings with short alkyl groups, namely butyl and methyl, enhance halide-based ILs solubility [26]. Moreover, the anion role was evaluated for other halides (bromide) and for most sustainable amino acids (methionate, glycinate and proline). Regarding the cation structure, several chloride-based ILs have been tested, covering the impact of its hydrophilicity with the next permutes: i) the change of butyl substituent by a hydroxyethyl group; ii) an additional methyl group; iii) the change of butyl substituent by an octyl one.

3.2. Liquid-liquid equilibria {PC + IL + water}: Experimental and computational analysis

The liquid-liquid equilibria of {water + IL + PC} ternary systems were experimentally determined at 25 °C and 1 atm. Figure S2 in Supplementary Material shows the measured ¹H NMR spectra of the two immiscible phases for a 1.4% mol of IL in the case of [EtOHmim][Cl] and [bmim][Cl], and a 0.7% mol of IL in the case of [omim][Cl] (highest achievable concentration for biphasic system). The part referring to some peaks associated with the cation and PC (used as reference for the integrals) of these same spectra for [EtOHmim][Cl] and [bmim][Cl] are shown in Fig. 4.

It is found that the IL splits differently in the two immiscible phases as function of its nature: [EtOHmim][Cl] displays a high hydrophilicity which is noticeable by the IL absence in the PC-rich phase and the high IL:PC proportion in the water-rich phase, while [bmim][Cl] is also mainly attracted to the water-rich phase, but not as favorably as [EtOHmim][Cl], since [bmim][Cl] is still present in the PC-rich phase. On the other hand, [omim][Cl] shows a higher hydrophobicity, being more concentrated in the propylene carbonate-rich phase than to the water-rich phase, as can be seen in Figure S2 in Supplementary Material. This is also confirmed in Figure S3 in the Supplementary Material, where the experimental distribution ratios of the studied ILs and are presented as a function of the IL concentration, showing that [bmim][Cl] distribution ratios move from 12 to 6, while in the case of [omim][Cl] $K_{IL} < 1$ for every IL concentration. Excluding the latter [omim][Cl] case, which was selected as control IL, the IL favorably concentrates in the aqueous phase for all ILs studied here, particularly at low IL concentration, expecting negligible losses in the PC-rich phase even in a single equilibrium step. This means that low IL concentration enhances compatibility of this platform for almost all IL partially soluble with water

Table 2
Processes specifications.

Equipment Case	D-100		D-101		S-100
	Reference Distillation	Water-based LLE	Reference Distillation	Water-based LLE	Water-based LLE
N° stages	10	10	10	30	4
Feed stage	5	5	5	15	F 1 /S 4
Reflux ratio	2	2	5	5	-
Pressure (bar)	0.02–0.03	0.30–0.47	0.001	1.00	1.00
Maximum temperature (°C)	120	120	120	240	25
Specifications	99.5%mol PO recovery	99.5%mol PO recovery	99.9% PC mass purity and recovery	99.9% PC mass purity and recovery	-

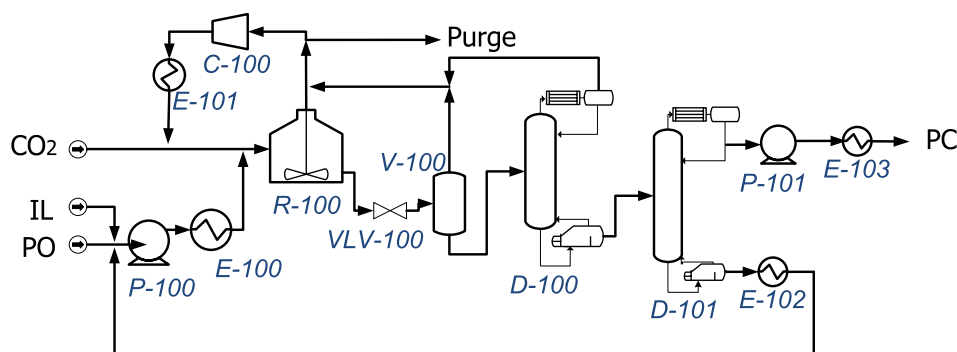


Fig. 2. Process flow diagram for the reference process.

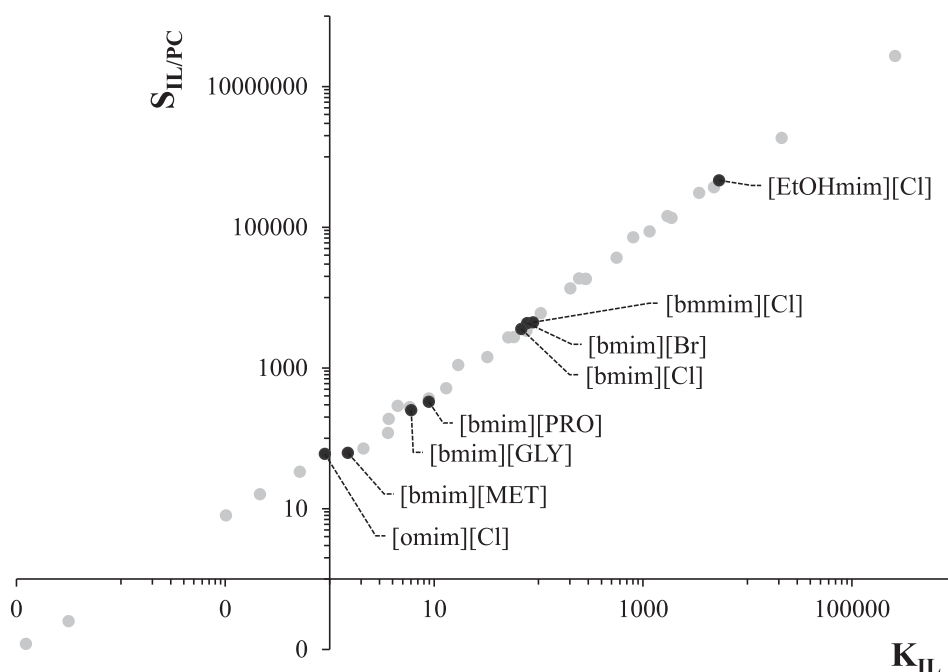


Fig. 3. IL nature impact on extractive properties in {PC + IL + water} benchmark ternary system predicted by COSMO/Aspen.

reported in the literature. Experimental [EtOHmim][Cl] distribution ratios were not calculated since the IL concentration in the PC-rich phase is below the detection limit in some cases. It was found that for a molar content of IL higher than 5% mole, the extractive properties of the systems become more unfavorable due to the higher content of IL in the carbonate-rich phase, as was the case of [omim][Cl] even for lower IL: PC proportions. Nevertheless, due to the high hydrophilicity of [EtOHmim][Cl], a 30% mole IL:PC molar proportion (7% IL content including water) can be reached maintaining the same exceptionally favorable extractive properties.

Confirming COSMO/Aspen predictions in Fig. 3, the change of chloride anion by amino acids does decrease extractive properties for catalyst recovery from PC. In addition, regarding cation effect, the alkyl chain length and the polarity and number of substituents are keys to enhance extractive properties, which follow the next expected trend: [EtOHmim]⁺ > [bmim]⁺ > [omim]⁺. Therefore, the use of [EtOHmim][Cl] is suggested when moderate to high catalyst loading is envisioned (i.e. to reduce reactor cost), whereas the use of water-based separation platform in most studied hydrophilic ILs would be more efficient at low catalyst concentrations (<2%). In contrast, the recovery of [omim][Cl] by means of this strategy is considered unfeasible, pointing that long alkyl chain substituents are not allowed in the separation step.

Fig. 5 compares experimental and computational (COSMO/Aspen predictions) LLE ternary diagrams of the studied {water + IL + PC} systems, containing [bmim][Cl] and [EtOHmim][Cl] ILs. In addition, experimental and computational ternary diagrams for the rest of the studied mixtures are collected in Figure S4 in Supplementary Material. As shown, slight deviations are observed in the description of both phases, probably due to the low IL content. However, because of the low experimental IL content in the carbonate-rich phase, these differences will not imply a noticeable impact in the amount of solvent required for IL recovery even impacting moderately in extractive properties values. Therefore, COSMO/Aspen approach properly describes main insights on the LLE of said ternary systems, revealing itself as an affordable model to evaluate the IL performance at process scale at preliminary conceptual design stage. Therefore, COSMO/Aspen approach properly describes main insights on the LLE of said ternary systems, revealing itself as an affordable model to evaluate the IL performance at process scale at preliminary conceptual design stage.

3.3. Compatibility of water as reaction media in CO₂ conversion to PC for selected IL catalyst

Prior to evaluate the IL role at process scale, the water impact on reaction extents must be covered, in order to properly describe reaction

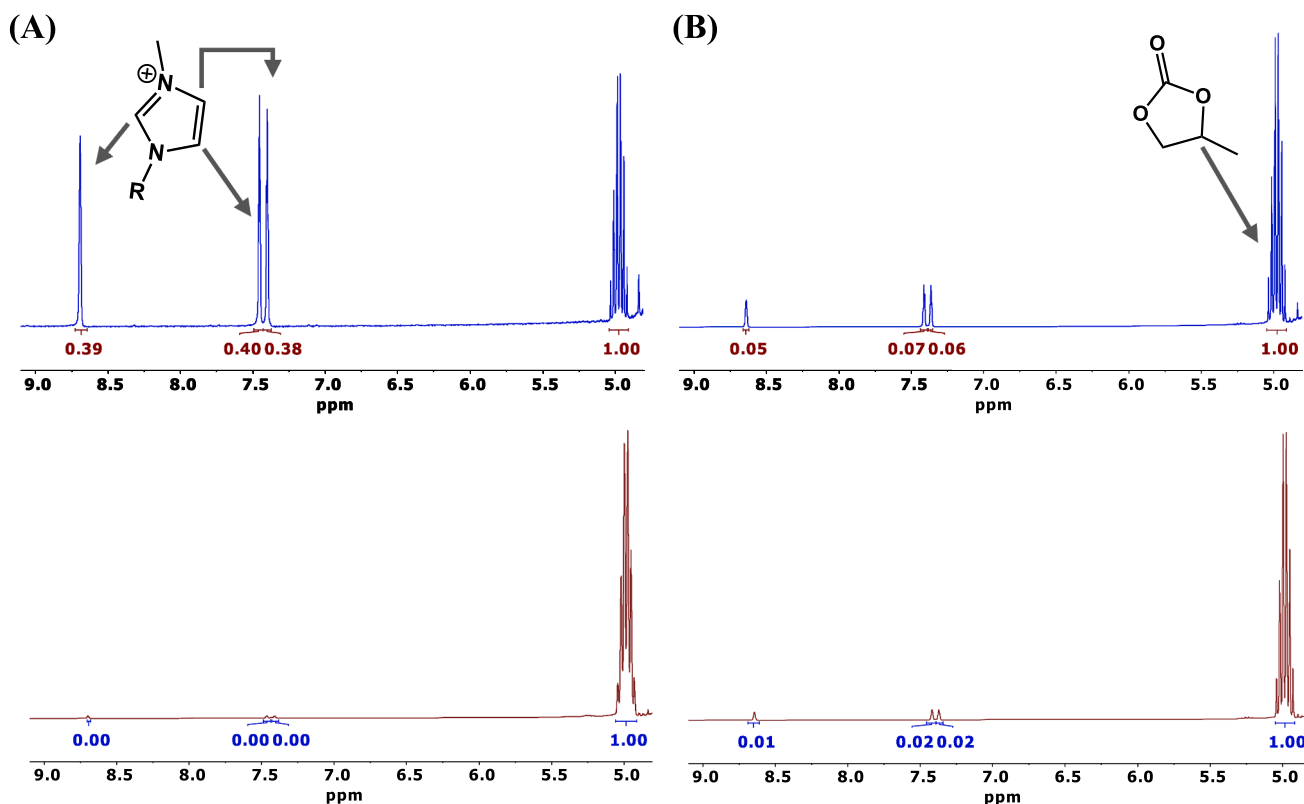


Fig. 4. ¹H NMR spectra of the resulting water-rich phase (blue line; top) and PC-rich phase (red line; bottom), from the ternary equilibria involving water, PC [EtOHmim][Cl] (A) or [bmim][Cl] (B). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

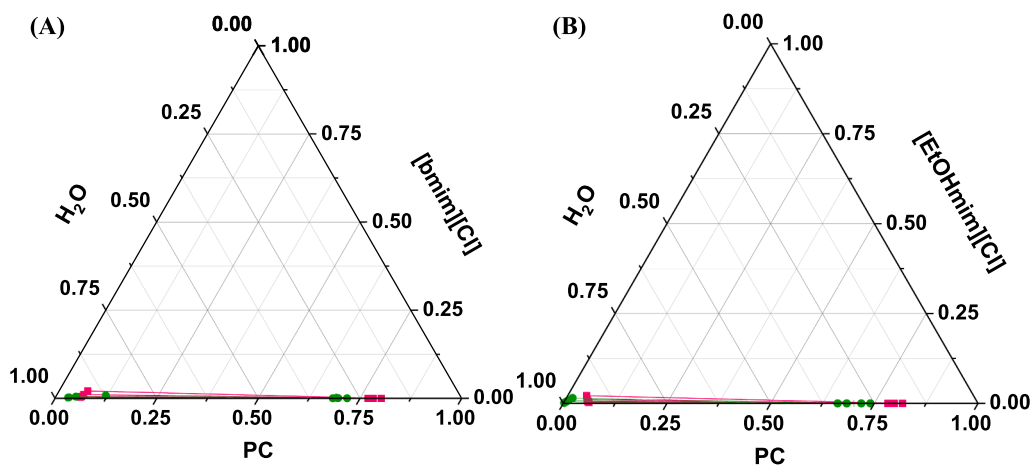


Fig. 5. Experimental (green; dots) and computational (pink; squares) ternary diagrams of the {water + PC + [bmim][Cl]} (A) and {water + PC + [EtOHmim][Cl]} (B) mixtures. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

step within reaction/separation platform based on IL/water hybrid systems. With the aim of comparing all studied catalysts, Fig. 6 shows the conversion results of the CO₂ cycloaddition to PO in presence of the neat IL (PO:IL 200:1 mol) and in presence of the IL (PO:IL 200:1 mol) and water (PO:water 10:1 mol). As seen, the conversion relies on the anion nature, finding that halides are more active than the amino acid-based anions. The role of the cation, within the selected species, remains negligible.

Regarding the water role, it is obtained that PO conversion catalyzed by ILs occurs in absence and presence of water. In the case of the less active amino acid-based ILs, water enhances the catalytic activity, in good agreement with previous results, whereas the water presence

slightly decreases the PO conversion for halide-based ILs at the same reaction conditions. Literature works discuss a favorable role of the IL/water pair for a wide number of species [24,30]. However, these studies advised that the kinetic improvement turns in a slight depression of the equilibrium conversion [28]. At this time, an additional experiment for a shorter time (1.5 h against the previous 10 h) using an IL containing a halide anion ([bmim][Br]) was carried out, the results of which are shown in Figure S5 in Supplementary material. As shown, the conversion in the presence of water is higher than the conversion for the neat IL. It therefore follows that water improves conversion for times preceding reaching equilibrium conversion but imposes a small negative impact at the equilibrium. By contrast and favorably, water promotes

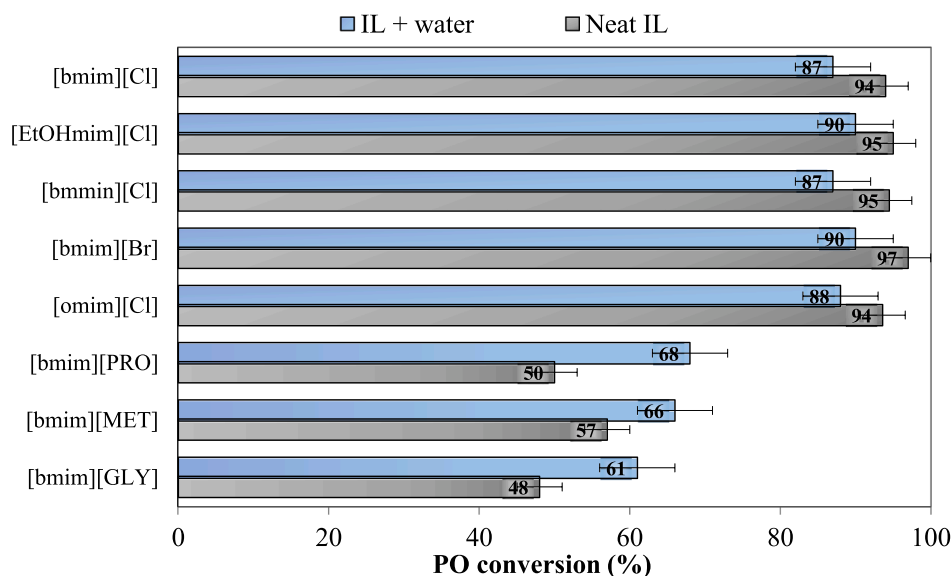


Fig. 6. PO conversion with or without water as reaction media for selected ILs for 10 h. Blue represents reactions in the presence of water, while grey represents reactions in the absence of water. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

catalytic activity of amino-acid-based solvents because competitive times are far from their equilibrium conversion. Therefore, the use of water can be considered as a tool to narrow down the catalytic activity gap between conventional and amino acid-based ILs. In any case, for both kind of ILs, water promotes a feasible liquid-liquid equilibria systems to regenerate the catalyst, describing also an enhanced or compatible reaction step.

3.4. Evaluation of the water-mediated close-cycle CO₂ conversion process to produce PC using IL catalysts

All selected ILs were tested at process scale following flowsheet discussed in the methodology section (Figs. 1 and 2). From these simulations, IL recovery in extraction column (S-100) is calculated and shown in Fig. 7 against the IL distribution ratio. As seen, the drawbacks in terms of IL total recovery are noticed for the two ILs with lower values

of K_{IL} , as cases with intermediate hydrophilicity that are compatible with the platform but offer results of less interest. For the rest of the ILs, the recovery is complete regardless of the value of K_{IL} . In fact, it should be noted that water consumption is almost independent of the extractive properties of the ILs in current operating conditions, since the required mass S/F values range from 0.053 to 0.059 for all studied cases.

Selecting two representative ILs with the least and most favorable conversions and extractive properties among those ILs that meet the requirement of full IL recovery ([bmim][GLY]: 6 K_{IL} , 250 $S_{IL/PC}$; 61% conversion; [bmim][Br]: 78 K_{IL} , 4340 $S_{IL/PC}$; 90% conversion), the specific energy consumption of the reference and water-based process are collected in Fig. 8. As seen, using LLE extraction as IL recovery and PC purification step enables to drastically reduce energy consumption independently from the IL nature and effectiveness in the catalytic step. In addition, the required energy in the process decreases using [bmim][Br] instead of [bmim][GLY]. Since the S/F ratio is nearly the same in

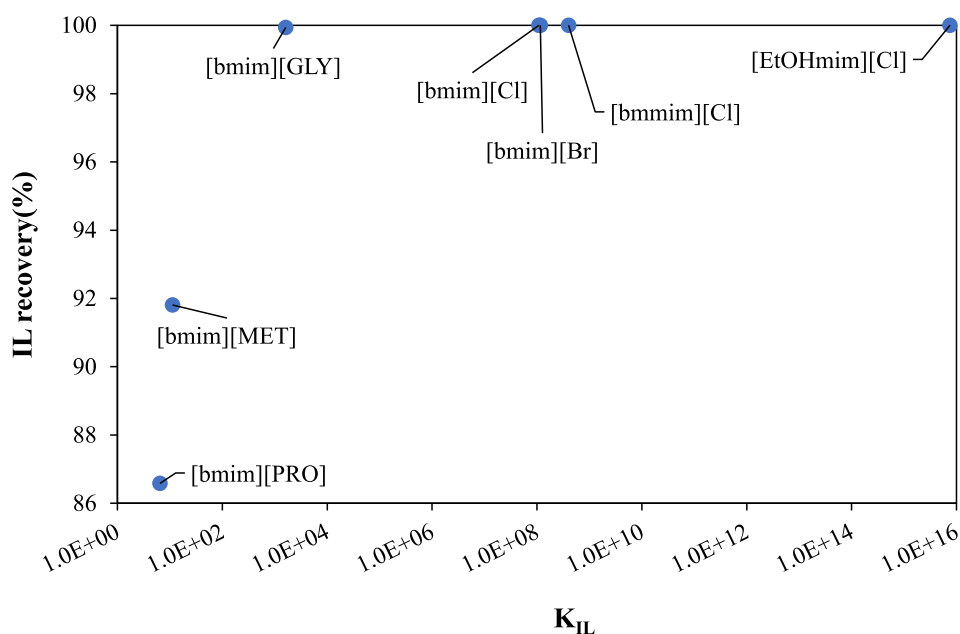


Fig. 7. IL recovery in as a function of computational IL distribution ratio for an extractor with 4 stages.

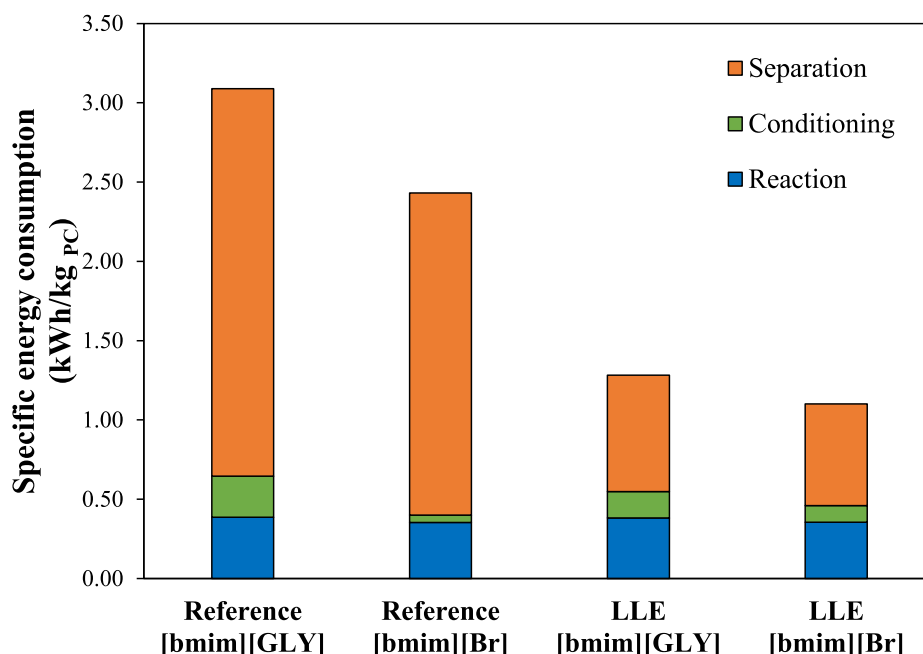


Fig. 8. Specific energy consumption comparison between reference process (rectification) and water-mediated strategy (LLE) for [bmim][GLY] and [bmim][Br] as representative amino acid and halide anion ILs, respectively.

both cases, this result is related to catalyst activity: higher conversion implies lower energy consumption in the separation of unconverted reactants and their conditioning, being this impact less accentuated in the LLE-based process (Fig. 8). It should be noted that the processes' energy consumption could be modified by increasing the S/F ratio, as this may allow eliminating vacuum conditions in D-100 as was previously demonstrated [23], and as shown in Figure S6 in Supplementary Material. However, in this study the S/F ratio is the required to mimic experimental conditions in the reactor.

Afterwards, Fig. 9 displays specific energy consumption as a function of the PO conversion for the water-mediated strategy, confirming that, there is a clear relationship between process energy consumption and conversion, since the energy demands related to the PO and CO₂ separation after the reaction step is the most energy-demanding step. The energy demands related to the final drying of the propylene carbonate

(D-101 in Fig. 1) are almost constant for all cases since it only depends on the water solubility in PC, which is independent from the IL nature when it is fully recovered. In addition, as shown in Figure S7 in Supplementary Material, the ILs with higher catalytic activity require the use of a more competitive refrigerant, under similar vacuum conditions. This suggests that, at current operating conditions, the conversion is the optimization key of the proposed platform, with extractive properties being a variable of secondary significance.

Since water slightly decreases conversion in the case of the halide anions, it could be considered that drying the IL before feeding it back to the reactor could improve energy consumption of the process. Nevertheless, it has been observed that water smooths the reboiler requirements in the PO and CO₂ separation (D-100), therefore, drying the IL before feeding it back to the reactor would impose a negative impact. D-100 would demand higher boiling temperatures or vacuum. In order

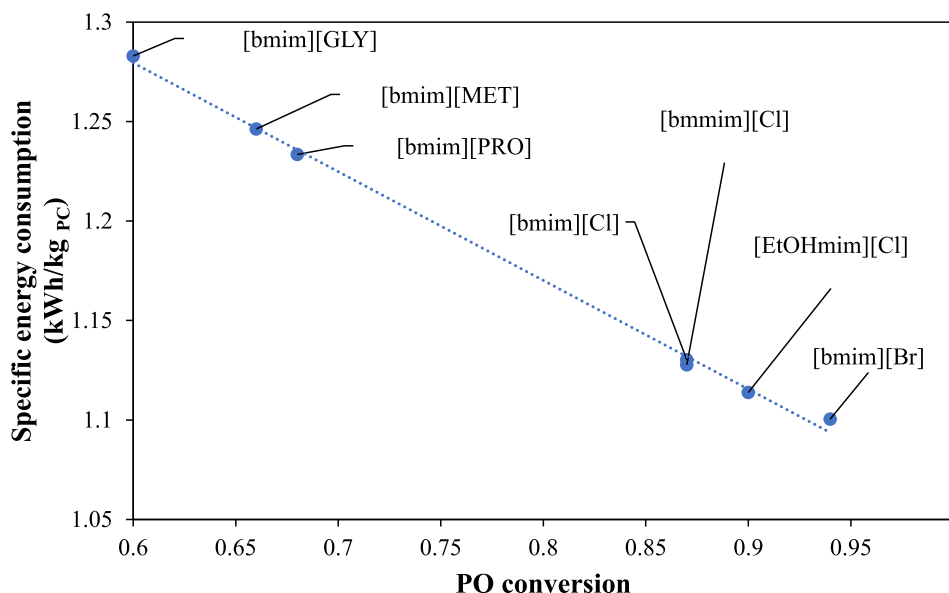


Fig. 9. Correlation between specific energy consumption and propylene oxide conversion for the selected ILs.

to increase the reactor conversion, there are different strategies that may be evaluated, from increasing reactor volume to selecting ILs with higher catalytic activity or higher solubility in reaction media (allowing increasing the amount of IL present in the reactor). In any case, the proposed water-based separation strategy can be considered universally applicable to the use of hydrophilic IL catalysts in the production of PC by CO₂ cycloaddition to PO, requiring significantly lower energy consumption than distillation-based benchmark process.

4. Conclusions

In this work, computational and experimental research has been done in order to demonstrate the universal character of using hydrophilic IL/water mixtures as CO₂ conversion platform to produce PC. Preliminary, COSMO/Aspen simulations have been used to scan the liquid-liquid equilibria of ILs with water from PC matrix and selecting representative species. Experimental studies of both catalytic and liquid-liquid extraction operations have been done in order to demonstrate the compatibility of water as reaction media and extracting solvent, respectively. Finally, COSMO/Aspen methodology has been used to model the whole processes in order to obtain PC with standard purity and energy consumption.

First, extractive properties predicted by COSMO/Aspen for more than 40 ILs have demonstrated that many catalysts proposed in the literature are compatible in the envisioned separation of the IL and propylene carbonate by liquid-liquid extraction with water. Second, experimental evidence support the separation platform proposal, extending its use for a wide range of hydrophilic ILs. Water is compatible with the catalytic activity of the ILs, enhancing kinetics of all ILs selected, with a slight depression of the conversion at equilibrium conditions, whereas experimental distribution ratios of the IL in water/PC systems clearly point out the total recovery of ILs by liquid-liquid extraction. Regarding catalytic activity, halide anions (87–97% PO conversion) are superior to amino acid ones (48–68% PO conversion), whereas cation role is almost negligible. Referring to liquid-liquid equilibria, polar and short alkyl chain substituents promote hydrophilicity and, thus, maximize IL distribution ratios. Most of the studied ILs allow for a complete recovery in the simulated process, portraying [EtOHmim][Cl] the highest distribution ratio ($7 \cdot 10^{15}$). Also, [EtOHmim][Cl] ternary equilibrium was experimentally proved to support greater concentrations of IL while maintaining the extractive properties, which would allow for higher catalyst loading in the reactor. Finally, COSMO/Aspen process simulations indicated that the reaction/separation platform proposed systematically reduces energy consumption in a 50–60%, independently from the IL, respect to distillation-based process, being [EtOHmim][Cl] and [bmim][Br] the ILs with higher catalytic activity and lowest energy consumption. Now, an adequate IL design and selection can be envisioned, focused on IL catalytic activity and extractive properties, the latter a crucial aspect to reduce energy consumption. This new design scheme allows (i) reducing the process energy consumption by increasing its catalytic activity and (ii) full catalyst recovering and reutilization by improving the water extractive properties for IL separation from PC, concluding that the hydrophilic [EtOHmim] cation and halide anions are the best combination.

CRedit authorship contribution statement

Elisa Hernández: Data curation, Formal analysis, Investigation, Writing – original draft. **Rubén Santiago:** Formal analysis, Investigation, Writing – original draft. **Alejandro Belinchón:** Data curation, Formal analysis, Investigation, Writing – review & editing. **Gema Maria Vaquerizo:** Data curation, Formal analysis, Investigation, Writing – review & editing. **Cristian Moya:** Formal analysis, Investigation, Writing – review & editing. **Pablo Navarro:** Conceptualization, Formal analysis, Investigation, Writing – review & editing. **José Palomar:** Investigation, Funding acquisition, Project administration, Resources,

Software, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2022.121273>.

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