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Molecular simulation on carbon dioxide fixation routes towards synthesis of precursors for innovative urethanes

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Abstract

Classical molecular dynamics were carried out in order to obtain insights into proper conditions to perform chemical fixation of carbon dioxide (CO_2) with epoxide molecules into cyclic carbonates. Two different molecules containing epoxide groups were investigated: 1,2–Epoxybutane (EB), called linear aliphatic epoxide molecule, and 3-Ethyl-7-oxabicyclo(4.1.0)heptane (EC), called cycloaliphatic epoxide molecule. The reaction systems involving carbon dioxide additionally were catalyzed by tetraethylammonium bromide (TEAB). The dynamics of the molecular groups were studied by taking into account known reaction mechanisms to investigate whether the optimal reaction conditions were observed.
Radial distribution functions and self-diffusion coefficients were calculated and revealed that in case of the systems with cycloaliphatic epoxide groups as reagent the CO_2 molecules were located far away from the agglomerate formed by the dispersed tetraethylammonium bromide catalyst and epoxide groups (EC), and they do not present enough mobility to overcome the long distances to react. Additionally, it was observed that, in the case of the linear aliphatic epoxide groups (EB), the dynamics of the groups tends to facilitate the reaction mechanisms by presenting a considerable amount of available CO_2 molecules in the neighborhood of the epoxy rings. Thus, via the Molecular Dynamics insights, the systems containing linear aliphatic epoxide groups presented a much more accessible condition for the subsequent reaction steps of the carbon dioxide fixation to occur as compared to systems containing cycloaliphatic epoxide groups. The simulation results are in agreement with the experimental findings, which showed via infrared spectroscopy the successful conversion of epoxy rings from linear aliphatic epoxide molecules into five-membered cyclic carbonates after reacting with carbon dioxide.

Keywords: Carbon dioxide fixation; Molecular dynamics; Reaction conditions

Background

Environmental issues and sustainability appeal have a strong impact on the development of novel chemistry approaches in order to synthesize materials via eco-friendly routes. Among the worldwide current environmental and economic concerns is the need to reduce the carbon dioxide (CO_2) released to the atmosphere by a wide range of human activities such as burning of fossil fuels, mineral extraction, bio-ethanol production, etc. [1-3]. A further impact of environmental requests is on the search for

alternative chemical routes for polymeric materials industry [3], as for instance for the synthesis of polyurethanes (PUs). PUs are very versatile materials and present an extremely strong bonding, consequently PUs are vastly used in applications such as plastics, and used matrices for fiber-reinforced polymers or as adhesives [4,5]. Furthermore, PUs are applied in marine, transportation, automotive, furniture and food packaging industries or coatings on many different materials due to the improvement of properties like appearance and life time. However, the usual synthesis of PUs relies on isocyanate reactions, i.e. involving toxic compounds. K.R. Aguiar et al. [6] have shown an alternative route to tackle the challenges of reducing CO_2 emissions and simultaneously forming urethanes based material via green routes instead of using isocyanates. In that work, the authors presented an efficient environmentally friendly synthesis of a bis(cyclic carbonate) poly (dimethylsiloxane) (CCPDMS) derivative via CO_2 addition to yield precursor materials for the synthesis of innovative urethanes. Basically, the work profits from the ability of the catalyzed CO_2 fixation using epoxides as reactants to produce cyclic carbonates [6]. The resulting CCPDMS can be applied to synthesize urethanes. Furthermore, K. R. Aguiar et al. presented the feasibility of reacting CCPDMS and (di)amines in solvent-free conditions. Although the route from the CO_2 fixation with epoxides to the final urethanes synthesis is achieved by K. R. de Aguiar and co-authors, the yield of the CO_2 fixation is strongly dependent on the accessible reaction steps, the appropriate conditions and chemical structures of the components. The understanding of those phenomena is extremely relevant. Several experimental and theoretical efforts [7-9] were performed in this direction, including the investigation of the reaction process, the design of the catalyst [10-13] and of the appropriate substituents at three-membered epoxide rings to form the desired products. Computer simulations represent powerful tools to support the experimentalists towards the development of novel materials. Via computational modelling, several features can be studied such as system dynamics or reaction mechanisms at short and large time and length scales [14-17]. Via density functional theory (DFT), J-Q. Wang and co-authors elucidated the reaction mechanisms for the CO_2 fixation of ethylene oxide (EO) and of propylene oxide (PO) catalyzed by quaternary ammonium salts [7], identifying main three steps: (i) A nucleophilic attack of the bromide ion to the less hydrogenated carbon of the epoxide group occurs, forming a β-haloalkoxide anion; (ii) the new anion reacts with the CO_2 molecule, generating a carbonate ion; (iii) in order to form the cyclic carbonate, the bromide acts as a leaving group regenerating the catalyst and obtaining the cyclic carbonate product. Furthermore, the intermediate and transition states were calculated, and aspects that influence the design of the catalysts were presented, such as the chain length of substituents at the epoxide group and the type of catalyst anion. In spite of the fact that calculations are scaled for short lengths and times, the quantum based methods, such as the DFT, provided important information on the mechanisms and the parameters which influence the reaction processes.

This study reports a molecular dynamics (MD) investigation to gain insights into the dynamical behavior of the molecular systems and its influence on the formation of the aspired products. Via classical MD calculations, no reactions are carried out. Nevertheless, the dynamics of a large scale system of reagents can be accessed. By MD simulations, it is feasible to know whether the system presents the optimal conditions required for the subsequent reaction steps to occur considering the reported steps of the reaction mechanism [7,18]. The computer simulations intend to support the

understanding of the experimental findings, regarding the reaction to form molecules based on cyclic carbonates. Two different molecules containing epoxide groups were investigated; the 1,2 – Epoxybutane (EB) which is a linear aliphatic epoxide, and 3- Ethyl-7- oxabicyclo(4.1.0)heptane (EC) which is a cycloaliphatic epoxide; as catalyst tetraethylammonium bromide (TEAB) was used. In addition, the present work reports experimental results on the CO_2 fixation with epoxides. The experimental part also considered two different epoxide groups used as reagents: as a linear aliphatic epoxide the diglycidylether-terminated poly(dimethylsiloxane) (PDMS), and a cycloaliphatic epoxide the poly[dimethylsiloxane-co-(2-(3,4-epoxycyclohexyl)ethyl)methylsiloxane] (CPDMS), and TEAB as catalyst.

In the next section, the computational and experimental methods and materials are detailed explained. In the sequence, the results and discussion section is dedicated to present the radial distribution functions and diffusion coefficients calculated using the produced MD trajectories; furthermore the experimental findings are presented. Finally, the main conclusions are summarized.

Methods

For the computational part, classical Molecular Dynamics (MD) simulations were performed using the software packages MAPS© (Materials and Processes Simulation Platform) [19] and LAMMPS© (Large-scale Atomic/Molecular Massively Parallel Simulator) [20,21]. The simulation cells were composed by three different molecule groups: epoxide groups, CO_2 molecules, and the catalyst groups. As epoxide groups, a linear aliphatic epoxide the 1,2 – Epoxybutane (EB) and a cycloaliphatic epoxide the 3-Ethyl-7-oxabicyclo (4.1.0)heptane (EC) were investigated. The catalyst used in both cases was a dispersed tetraethylammonium bromide (TEAB) unit. The simulation cells were created using the Amorphous builder tool of MAPS©. The overview of molecular groups and their stoichiometry considered in the simulation boxes are presented in the Table 1. Regarding the computational parameters, all the systems were fully atomistically modelled and periodic boundary conditions were applied and the polymer consistent force field (pcff) used.

For each system, a geometry optimization (steepest descent and conjugated gradient, in cascade) was performed. Afterwards, a 1 ns equilibration run was carried out composed of a 500 ps run in the canonical ensemble (NVT) followed by a 500 ps run in the isothermal–isobaric ensemble (NPT) with an isotropic pressure coupling using a Nosé–Hoover thermostat. For both systems CS1-EB and CS2-EC, the temperature was 298 K and the pressure 11.0 bar. For the CS1-EB system the 500 ps NVT equilibration run had an initial density of 0.5 g/cm^3. For the CS2-EC the 1 ns equilibration run was done as follows: a total of 500 ps NVT run in 3 steps (200, 200 and 100 ps), followed

Table 1 Computational systems considered and their respective stoichiometry

Computational system 1 CS1-EB	Stoichiometry			Total number of atoms in Computational Cell
	EB	CO_2	TEAB	
	100	50	1	2960
Computational system 2 CS2-EC	Stoichiometry			Total number of atoms in Computational Cell
	EC	CO_2	TEAB	
	100	50	1	4960

Table 2 Experimental systems considered and the respective quantities used

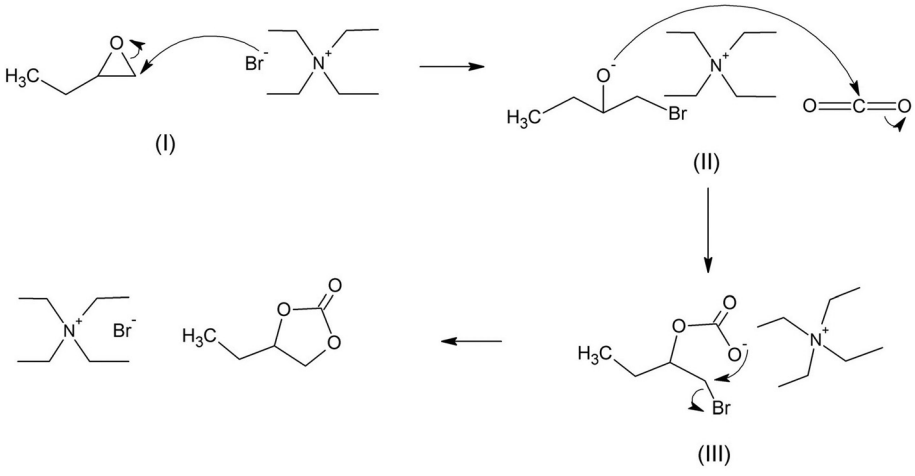
Experimental System 1 ES1-PDMS	Reagents			
	PDMS	CO_2	TEAB	EG
	12.4 mmol	excess	1% w	40 mL
Experimental System 2 ES2-CPDMS	Reactants			
	CPDMS	CO_2	TEAB	EG
	12.4 mmol	charged in reactor	1% w or 2% w	40 mL

by a 500 ps NPT run. After proper equilibration for both systems a 1 ns production run was carried out using NPT at 298 K and 11.0 bar, the trajectories were collected each 1 ps for analyses.

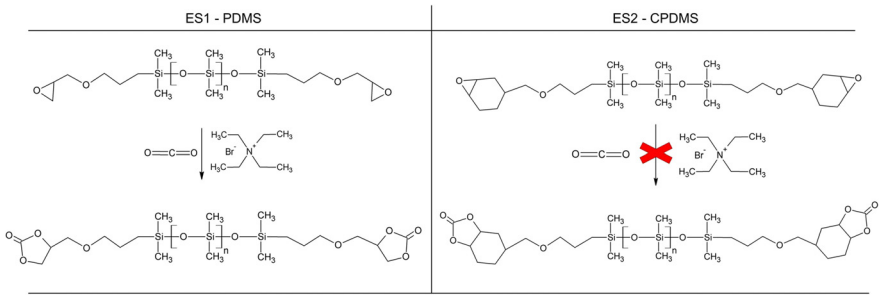
For the experimental part, two different systems were investigated, formed by epoxide groups, CO_2 molecules, catalyst and additionally a solvent. The difference in the experimental reagent systems was in the chemistry of the epoxide groups, since a linear aliphatic epoxide the diglycidylether-terminated poly(dimethylsiloxane) (PDMS), and a cycloaliphatic epoxide the poly[dimethylsiloxane-co-(2-(3,4-epoxycyclohexyl)ethyl) methylsiloxane] (CPDMS) were used. As catalyst and solvent, the TEAB and the 2-ethoxyethanol (EG) were used respectively. The two experimental systems are listed in Table 2 considering the molecular groups and their respective quantities used for the experiment. The optimal reaction conditions were determined by "trial and error" method varying pressure, temperature and time. The reagents and catalyst were dissolved in the EG solvent and transferred to the reactor cup. The system was closed and filled with CO_2, following the experimental procedure published by Aguiar and co-authors [6]. The formation of reaction products for the two different epoxide systems was followed by infrared spectroscopy (FTIR).

Results and discussion

The discussion of the results will take into account the reaction mechanism and the resulting reaction steps reported in literature [7,18]. A general concept of the reaction mechanism is sketched in Scheme 1, presenting three main reaction steps: (I) the catalyst approaching the epoxy ring where the bromide anion Br^- will attack the C atom



Scheme 1 Reaction mechanisms of CO_2 fixation with epoxide to form cyclic carbonates.



Scheme 2 Expected reaction of CO_2 with diepoxide yielding cyclic carbonate based molecules. Left: Experimental System 1 (ES1 - PDMS). Right: Experimental System 2 (ES2 - CPDMS).

forming the intermediate specie (II) the CO_2 fixation takes place (III) and the cyclic carbonate is formed.

Regarding the experimental part, the Scheme 2 presents the CO_2 addition to the diepoxide yielding cyclic carbonate molecules for the two experimental systems studied.

Figure 1 presents infrared spectroscopy results for both experimental systems. The upper spectra for ES1 show the formation of cyclic carbonate as seen by the C = O band (ES1-CCPDMS); the results are as obtained by K. Aguiar et al. [6]. Nevertheless, for the ES2 the aspired reactions did not occur since no cyclic carbonate was formed as shown by the absence of the C = O peak in the ES2-CCPDMS.

The experimental results revealed the success of obtaining cyclic carbonate molecules when using as reagent the linear aliphatic epoxide (PDMS), while the use of the cycloaliphatic epoxide (CPDMS) as reagent did not yield the expected products in the conditions investigated.

The MD calculations provided the access to a 1 ns dynamics of the systems in intervals of 1 ps between the frames. Although the classical MD method as applied does not allow considering chemical reactions, the access to the dynamics permits obtaining insights by revealing the development of the reaction regions and groups

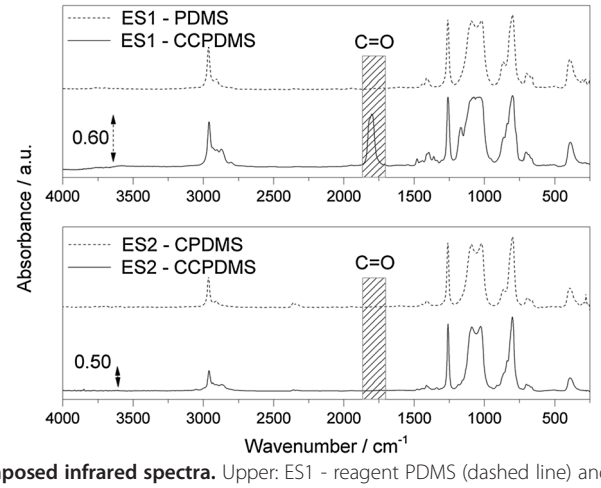


Figure 1 Superimposed infrared spectra. Upper: ES1 - reagent PDMS (dashed line) and product CCPDMS (solid line). Bottom: ES2 - reagent CPDMS (dashed line) and reaction mixture without indicating formation of a product CCPDMS (solid line).

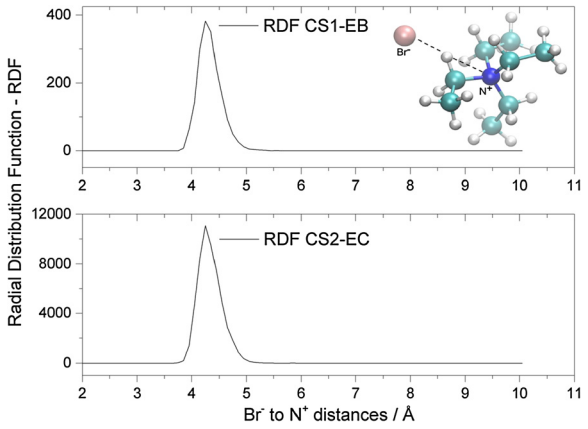


Figure 2 RDF for the distances between the Br^- and ammonium$^+$ within the TEAB catalyst molecules for the both simulation systems CS1 and CS2. Upper: CS1-EB, the inset contains the illustration of the atom groups of the TEAB molecule for which the RDF was calculated. Bottom: CS2-EC.

during a certain time interval. Analyses of the radial distribution function (RDF) provide the information on the distances where groups of atom pairs which are of interest for the reaction can be found together first. The RDF calculations take into account the volume available to the system and the total number of particles or atoms, i.e. the density, as well as the number of available atoms of the type for which the RDF is calculated. Considering the difference in the system densities, the RDF analyzes presented intend to provide the distances where the first pairs are found (in RDF plot the x-axis), while the values found for the RDF (in RDF plot the y-axis) for the different systems are not comparable due to the different available volume. To select for which pairs the RDF were to be collected advantageously, the reaction steps (I), (II) and (III) within the mechanism of Scheme 1 were taken into account. Thus, the first pairs investigated were concerning reaction step (I) to evaluate the distances between catalyst cation ($(H_5C_2)_4$ N^+) and anion (Br^-) for both simulation systems CS1 and CS2. Figure 2 presents the RDF for the Br^- and ammonium$^+$ within the

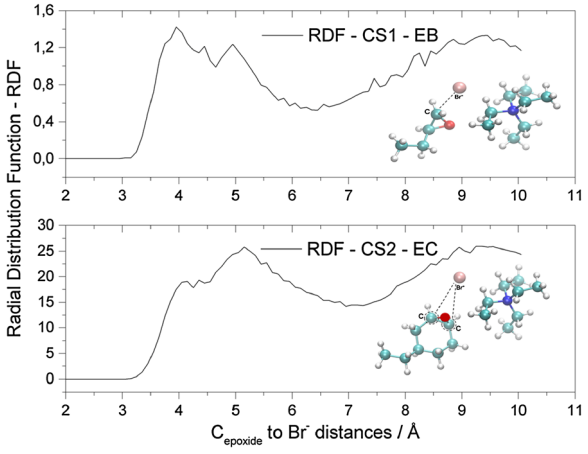


Figure 3 RDF for the distances between the Br^- of the TEAB catalyst molecules and one C atom of the epoxide molecules for both simulation systems. Upper: CS1. Bottom: CS2. The atoms among which the RDF is taken are illustrated in the inset sketch.

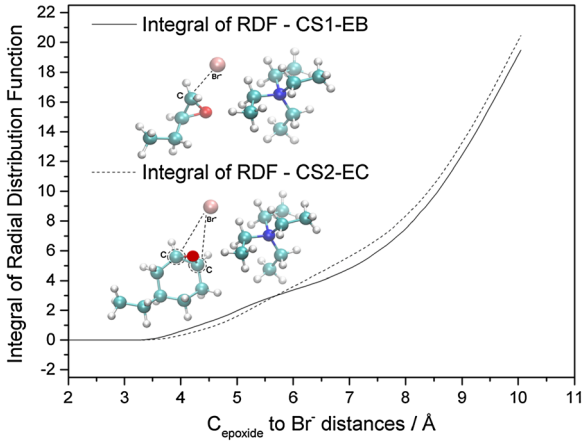


Figure 4 Integral of the RDF for pairs of Br^- of the TEAB catalyst molecules and the C atoms from the epoxide molecules for both simulation systems. Full line is the CS1. Dashed line is the CS2. The atoms considered in the pairs for which the integral of the RDF is taken are illustrated in the inset sketch.

TEAB catalyst moieties. The peak in the RDF appears in both cases at a distance of 4.25 Å, and no difference among the reaction systems regarding step (I) of the reaction mechanism can be seen by evaluating the interatomic distances within the catalyst. This finding might indicate that, considering the dynamics, the whole catalyst anion-cation pair is diffusing together inside the simulation box, and no anion-cation dissociation is clearly presented during the dynamics. The value 4.25 Å may be expected for the anion-cation distance within the undissociated TEAB catalyst [22,23].

Following the reaction mechanism, the next RDF analyzed considered the step when the epoxide group is to be attacked by the bromide ion. Thus, the RDF is calculated for the distances between the Br^- from the TEAB moieties and the carbon atoms of the epoxide rings to be attacked. The distances considered are sketched in the molecules drawn in the inset in Figure 3. The upper RDF is for the system CS1, and the bottom one shows the findings for the system CS2. The CS2 has two possible carbon atoms in

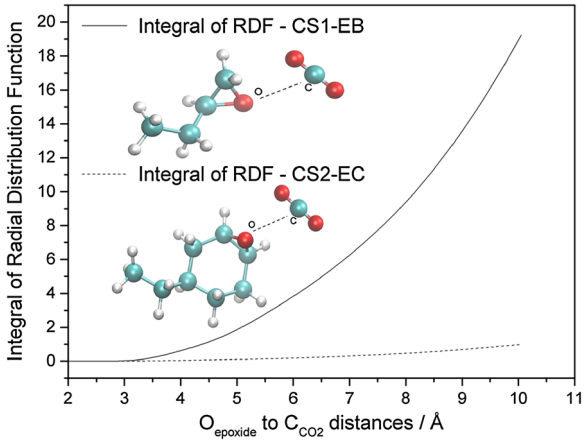


Figure 5 Integral of the RDF for the pairs formed by the C atom in a CO_2 molecule and the O atom from the opened epoxide ring. Full line is the CS1. Dashed line is the CS2. The atoms considered in the pairs for which the integral of the RDF is taken are illustrated in the inset sketch.

the epoxide ($C_{epoxide}$) rings where the bromide could attack. The different density of the systems and also the different amount of available atoms within the simulation cell volume results in the distinct range of ordinate values of the RDF plot. Nevertheless, the profile of the RDF for Br^- and $C_{epoxide}$ does not reveal any relevant difference between CS1 or CS2 which might indicate that CS1 and CS2 would have different accessibilities for reacting considering the reaction step (I).

The estimative of the amount of pairs found at a certain distance can be taken from the integral over the RDF curve. The integral of the RDF of Figure 3 is presented in Figure 4 normalized with relation to the number of available pairs. Comparing the integral for both systems, no pronounced difference in the available number of Br^- and $C_{epoxide}$ pairs in the first peak neighborhood is observed. Then, regarding the reaction step (I), both systems CS1 and CS2 are in comparable condition for the reaction to occur when only the dynamics is analyzed.

In the next reaction step, i.e. step II of Scheme 1, a CO_2 molecule would approach an intermediate complex formed by the attack of the Br^- on the epoxide groups, i.e. in the next reaction step the base for an irreversible CO_2 fixation would be laid. To evaluate the availability of atom pairs for the reaction step II to take place, the integral of the RDF between the C atom from a CO_2 molecule and the O atom from the former epoxide ring were calculated for both systems and are presented in Figure 5. From the integral (Figure 5) and, from the system dynamics accessed by the classical MD technique, it is observed that the number of available pairs of C_{CO2} and $O_{epoxide}$ for the CS1-EB systems is much higher in comparison to the CS2-EC. CS2-EC showed almost no CO_2 molecules close to the O atoms of the epoxide groups even when considering distances of up to 10 Å.

For the reaction step II to take place, the CO_2 molecules will have to approach considerably to the epoxide groups. As the results displayed in Figure 5 indicate, this seems to be much more difficult in the case of the CS2-EC than in case of CS1-EB. In the system CS2-EC the catalyst and the epoxide groups cluster together, and CO_2 molecules result to be excluded from these aggregates, far away from the aspired reaction sites.

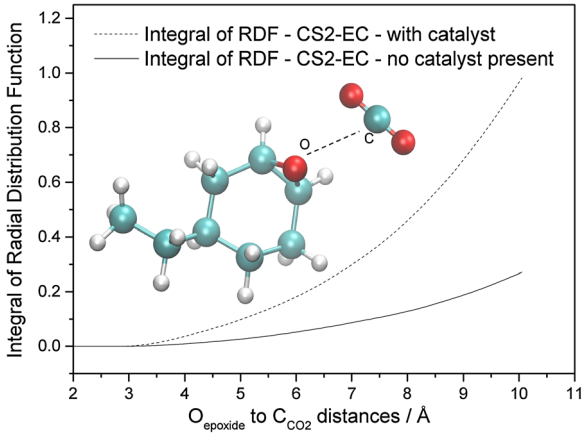


Figure 6 Integral of the RDF for the pairs formed by the C atom in a CO_2 molecule and the O atom from the opened epoxide ring for system CS2-EC with and without considering catalyst. Dashed line is the original CS2-EC with catalyst. Full line is the CS2-EC without the presence of catalyst molecules. The atoms considered in the pairs for which the integral of the RDF is taken are illustrated in the inset sketch.

Table 3 Self-diffusion coefficients for each molecular group for both computational systems CS1-EB and CS2-EC

	Molecular group	Diffusion D (10^{-5} cm^2 s^{-1})
Computational System 1 CS1 - EB	EB	2.70
	CO_2	2.25
	TEAB	2.32
Computational System 2 CS2 - EC	EC	6.65
	CO_2	6.64
	TEAB	6.37

The access for CO_2 molecules by transport through the clusters formed by the epoxide groups and catalyst results to be limited. This finding provides a qualitative description of a non-optimal scenario for the reactions in case of the CS2-EC systems, since the transport of CO_2 reagent towards the catalyst region appears to be hindered in this case.

Moreover, an additional system was investigated in order to evaluate if the cluster formation is influenced by the effect of the catalyst groups within the CS2-EC. Therefore, a system containing cycloaliphatic epoxide molecules, CO_2 reagents and excluding the catalyst was investigated considering the same stoichiometry and conditions applied for the CS2-EC. It was observed that even when the catalyst is not present the clustering of the cycloaliphatic epoxide molecules occurs, and the CO_2 molecules are located even further away of the epoxy rings as shown in the RDF integral in Figure 6. Thus, the catalyst in the conditions investigated influences slightly in the arrangement of CO_2 molecules in relation to the clustering formed by the cycloaliphatic epoxide groups; however the amount of the CO_2 available in the neighborhood of the epoxide reaction centers is extremely low.

Self-diffusion coefficients were calculated to complement the analyses by estimating the mobility of the groups. Basically, the self-diffusion supports to evaluate whether the CO_2 and epoxide molecules would have enough mobility to approach each other. The self-diffusion coefficients for each molecular group for each system were calculated using the Einstein relation [24,25] for 200 ps trajectories. The obtained values are presented in the Table 3. The self-diffusion coefficients for the CS2–EC system are slightly higher than the ones for the CS1-EB system; however they are in the same order of magnitude. Based on this similar order of self-diffusion values, the groups in both systems seem to have comparable mobility within the simulation box.

Combining the analyses of the integral of the RDFs (Figure 5) and the dynamics accessed (Table 3), the CO_2 molecules in CS2-EC have to travel much longer distances to be able to approach opened epoxide rings. Besides, there would be limitations caused by the stronger steric effect in the EC molecules compared to the EB ones. Those outcomes seem to hinder the reagents of the systems CS2-EC to proceed with the reaction steps within the mechanism for the CO_2 fixation and formation of further cyclic carbonate based molecules. The effect of agglomeration and the resulting hindrance is mirrored in the observed experimental results which indicated a much faster and more effective CO_2 fixation in case of linear aliphatic epoxide molecules as reagents as compared to cycloaliphatic epoxides.

Conclusions

The CO_2 fixation with epoxides to form cyclic carbonate based molecules was investigated via computational and experimental work. In both experimental and computational part, two different epoxide groups were considered: a linear aliphatic epoxide and a cycloaliphatic epoxide. Experimentally, only the systems considering the linear aliphatic epoxide as reagent have successfully produced the cyclic carbonate based product as revealed by the infrared spectroscopy (FTIR). The dynamics of model systems were accessed by classical MD simulations in order to investigate the conditions for the reactions steps to occur, taking into account a reaction mechanism reported in the literature. The analyses of the computational data were performed by radial distribution functions and self-diffusion coefficients calculations. It was observed for the system containing the linear aliphatic epoxide as reagent a large amount of CO_2 available in the neighborhood of the epoxide reaction centers. Moreover, in the systems containing cycloaliphatic epoxide, the CO_2 groups are located very far away of the epoxy rings and did not present enough mobility to overcome the long distances to react. In summary, the computational study of the dynamics showed a preferable condition for reactions to occur in the systems containing linear aliphatic epoxide as reagent when compared to cycloaliphatic containing systems; the results are in agreement with the experimental output.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

Authors VCB, LTC, JOJ, WLC contributed to the computational studies and all calculations, including choice of the computational parameters (WLC, JOJ), validations, interpretation and discussion; and drafted the manuscript. Authors KRA, UPRF, PLMN and KR contributed to the experimental part including interpretation and discussions. KR and PLMN contributed in discussing aspects of the catalysed insertion of carbon dioxide in strained O-C bonds and in drafting the manuscript. All authors read and approved the final manuscript.

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