

Full Length Article

Kinetics, absorption and regeneration of biphasic solvent with ethylpiperidine for carbon dioxide absorption

D. Gómez-Díaz^{a,*}, M. Parajó^b, O. Richoux^c, M.D. La Rubia^d, A. Rumbo^e^a Departamento de Enxeñaría Química, Universidade de Santiago de Compostela, Spain^b Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS), Departamento de Química Física, Universidade de Santiago de Compostela, Spain^c Génie des Procédés Chimiques et Biochimiques, Université de Mons, Belgium^d Departamento de Ingeniería Química, Ambiental y de los Materiales Universidad de Jaén, Spain^e Departamento de Química Orgánica, Universidade de Santiago de Compostela, Spain

ARTICLE INFO

Keywords:

Gas-liquid-liquid

Absorption

Carbon dioxide

Switchable hydrophilicity solvent

ABSTRACT

The development of new solvents for carbon dioxide separation by chemical absorption has increased its importance during last years. Present work develops a series of studies using biphasic solvents (two liquid phases) in which amine is transferred from organic to aqueous phase during carbon dioxide chemical absorption. This type of solvents gets to reduce the amount of solvent that must be regenerated by stripping and this fact allows to reduce significantly the cost associated to this operation. The experimental results corresponding to the proposed solvent (based on the use of N-ethylpiperidine) have shown a suitable behavior when high ratios of organic phase/aqueous phase are used that allows to reduce the energy penalty. This behavior has been confirmed using bubbling and packed columns. Solvent regeneration studies showed suitable results avoiding losses in absorption rate and absorption capacity.

1. Introduction

Nowadays different alternative technologies have been proposed to be used in carbon dioxide separation or capture but this type of processes based on chemical absorption/desorption operations using solvents with amines are the base technology [1,2] though the high energetic requirements [3]. This undesirable characteristic of chemical absorption processes is mainly due to the high amount of energy [4] used in the solvent regeneration operation generally using stripping. In the last years one important aim has been the reduction in the energy penalty of the overall operation.

In order to decrease this important energy consume is necessary the development of new solvents that allow overcome the behavior of first (alkanolamines) and second (sterically hindered amines) generation solvents. The third generation solvents are centered on the use of organic liquid phases in order to take advantage of the lower heat capacity in comparison with water. Examples of new solvents included in this third generation are binding organic liquids [5] reducing the energy cost by avoiding to reach boiling temperature to regenerate the chemical solvent.

Other strategies included in the development of third generation solvents are centered on more complex solvents and specifically the use of biphasic and phase changing solvents. Some researchers have employed a blend of organic compounds that shows an homogeneous behavior at the beginning of absorption tests but an increase in carbon dioxide loading or a change in temperature causes the generation of an heterogeneous solvent (liquid–solid or liquid–liquid) [6–8]. The initial works in biphasic solvents were based on lipophilic amines in order to concentrate the absorbed carbon dioxide in one phase using for instance N,N-dimethylcyclohexylamine and dipropylamine or N-methylcyclohexylamine [9]. These studies are based on the DMXTM process for carbon dioxide separation that allow to reduce operation cost by the splitting of phases (rich and lean carbon dioxide streams) before solvent regeneration [10].

The aim of this strategy is to reduce the amount of solvent to be regenerated in the stripping section. In this type of solvents only one phase (aqueous one) is fed to regeneration section and it allows to reduce the amount of sensible heat [11] because the flow-rate is widely reduced. This fact and the higher loading of carbon dioxide in this part of the solvent allows to reach additional advantages related with the

* Corresponding author.

E-mail address: diego.gomez@usc.es (D. Gómez-Díaz).<https://doi.org/10.1016/j.fuel.2021.121020>

Received 25 January 2021; Received in revised form 4 May 2021; Accepted 7 May 2021

Available online 19 May 2021

0016-2361/© 2021 Elsevier Ltd. All rights reserved.

energy penalty associated to stripping operation [12].

Present research work tries to analyze the use of this type of heterogeneous solvents but employing switchable hydrophilicity solvents (SHS). These solvents show two liquid phases before carbon dioxide absorption and both liquid phases are present into the gas–liquid contactor during all absorption experiments. Switchable hydrophilicity solvents are chemical solvents based on amines with a tunable value of solubility in aqueous phase. The partial solubility of amines in water, instead of a negative effect, can be considered suitable characteristic in order to develop new carbon dioxide separation schemes. When carbon dioxide chemical absorption takes place the amine is continuously transferred between the liquid phases involved in the solvent. This behavior depends on the type of amine (primary, secondary or tertiary) used to formulate the solvent. This strategy tries to remove only the carbon dioxide-rich phase from the absorber to be treated in the stripping section. This fact allows to reduce significantly the amount of solvent that must be regenerated. A priori the reaction products can be concentrated in the aqueous phase where the amount of amine is low. This behavior avoids the presence of free-amine molecules in the stripping that reduces solvent degradation. The cost associated to utilities is also reduced in heat exchanger and stripping boiler due to the lower solvent flow-rate.

A previous initial work [13] analyzed the use of this type of solvents with a stirred tank contactor that allow a suitable dispersion of liquid phases and also the gas one. High interfacial areas (liquid–liquid and gas–liquid) were reached with this type of mechanical stirring. The results obtained for different amines were uneven but some of them were interesting and allow to consider ethylpiperidine as a possible amine to formulate this type of solvents.

This study is centered on the use of ethylpiperidine (EP) in different types of gas–liquid contactors commonly used at industrial level in order to evaluate the carbon dioxide separation behavior in contactors with a low degree of mixture between all phases. These studies will allow to evaluate this solvent to be consider as a suitable alternative to the commonly energy-intensive processes.

2. Materials and methods

2.1. Materials

Carbon dioxide was supplied by Praxair with a purity of 99.998% and used as feed stream without additional purification. The amines employed in present work were ethanolamine (MEA), methyldietanolamine (MDEA) and N-ethylpiperidine (EP) were supplied by Sigma-Aldrich (MEA and MDEA) and Alfa Aesar with purities of >99.5%, >99% and >99% respectively. Bi-distilled water was used to formulate the different solvents.

2.2. Ethylpiperidine – carbon dioxide chemical kinetics

In order to obtain the kinetic equation for the chemical reaction between N-ethylpiperidine and carbon dioxide, a stirred tank reactor working in batch with regard to both phases was employed. The stirred cell presented a planar interface area of 33.3 cm². The gas transfer in the liquid phase took place through this gas–liquid planar interface. Four baffles were placed in the internal wall of the reactor to improve the solution mixing and avoid the formation of vortex.

The gas phase, pure carbon dioxide, went through two humidifiers to be saturated in water to avoid water exchange between the gas phase and the liquid phase. Then, CO₂ was injected in the stirred tank before feeding the amine solvent in order to fill it firstly with a CO₂ atmosphere.

To determine the carbon dioxide absorption rate, a soap flowmeter was used. During solvent injection in the reactor, soap film was created into the flowmeter and its movement was followed during all the experiment. Due to the chemical absorption of CO₂ in the solvent, the film went down along the calibrated glass tube.

The magnetic stirring was launched when liquid addition was over. At the same time, experimental data were recorded by a software which provides the rate of the soap film in the flowmeter.

To maintain the temperature constant, water circulated continuously in all devices: into the humidifiers, the doubled-wall of the cell, the doubled-wall of the burette and the doubled-wall of the flowmeter. Water temperature was regulated by using a thermostat-cryostat (Selecta Frigiterm).

A stopped-flow spectrophotometer (Applied Photophysics) was used when reaction rate is high. A same quantity of water saturated in CO₂ and of aqueous solution of amine was injected separately with a syringe pump into the mixing chamber where the reactants were mixed. Then, the freshly blended mixture was pushed rapidly into the optical cell where the fast chemical reaction takes place. The absorbance of the ultraviolet light beam by the solution was measured by a detector during the reaction. The product formation was monitored by measuring the change in absorbance of the solution as a function of time. The dead time of the stopped-flow system (in milliseconds) corresponds to the age of the reaction mixture entering the optical cell. All parts of the equipment were thermostated and the temperature was controlled

2.3. Carbon dioxide absorption studies

Carbon dioxide absorption experiments were carried out using different column contactors: two bubble columns were employed. The first one with a cylindrical geometry (diameter = 3 cm and height = 30 cm) employs a liquid phase volume of 0.15 L. The gas phase was dispersed using a sintered glass plate. The second one was a square bubble column reactor (side length = 4 cm and height = 65 cm) using a liquid phase volume of 0.6 L. The gas stream was fed to the contactor through a five-hole sparger built in Teflon®. The carbon dioxide absorption rate was determined on the basis of the difference between inlet and outlet mass flow-rates. Two gas mass flowmeters (M-Series Alicat Scientific) regulated and measured the column inlet and outlet gas flow rate. The outlet CO₂ flow rate was recorded every 30 s by the Flow Vision SC software package (Alicat Scientific) which also controlled the flowmeters. The working regime was continuous in regard to the gaseous phase and discontinuous for the liquid phase.

Other type of studies were carried out using a packed column with geometrical characteristics of 3.5 cm of diameter, 50 cm of height and using glass Rachig rings as packing. The same equipment for control and measure de gas flow-rates (M-Series Alicat Scientific) were employed. The solvent was recirculated by a peristaltic pump (Selecta Percom N-M) with a flowrate of 150 mL·min⁻¹. This liquid flowrate was chosen to ensure a good wettability of packing. All absorption experiments were carried out at atmospheric pressure.

2.4. Solvent regeneration studies

The experimental procedure for solvent regeneration employs the stripping procedure and it consists on the use of a three-necked flask with a volume of 0.5 L, a heating mantle (Selecta Fibroman) and a temperature sensor (Selecta Sensoterm). After absorption experiment, the aqueous phase was separated using a separation funnel and this aqueous solution was introduced into the flask. A thermometer was used for monitoring the temperature and also two condensers were installed to prevent solvent evaporation. The bubble temperature was 81 °C, and regeneration was carried out until 87 °C was reached. After cooling 10 absorption/regeneration cycles were carried out in order to analyze the influence of aqueous phase regeneration upon absorption rate and carbon dioxide loading. The optimized time for regeneration was 15 min at boiling temperature.

3. Results and discussion

3.1. Carbon dioxide – EP kinetic behavior

The initial experiments carried out to analyze the chemical kinetic behavior of carbon dioxide and ethylpiperidine reaction have been performed using a stirring cell previously described in experimental section. The evolution of absorbed carbon dioxide throughout experiment time allows to calculate the data corresponding to absorption rate for each EP concentration in the liquid solvent (Fig. 1 shows these experimental data). In relation to the influence of amine concentration (C_B) upon absorption rate (N_A) is clear and causes a linear increase with EP concentration. These experiments were carried out using an homogeneous solvent (only aqueous phase) with EP concentrations lower than solubility. Only this type of solvent was considered because EP is a tertiary type amine and the reaction with carbon dioxide is only produced in the presence of water molecules [14]. The reaction mechanism in solvents with tertiary amines involves the reaction of carbon dioxide with water in the presence of the amine that is protonated. The kinetic experiments were carried out at different temperatures and an increase in this variable causes an enhancement of absorption rate, in agreement with previous studies of kinetic behavior of carbon dioxide chemical absorption with amines [15].

On the basis of experimental data and specifically in relation to the influence of amine concentration in the liquid solvent upon carbon dioxide absorption rate, the linear trend previously observed is in agreement with a fast or instantaneous absorption regime. This is a suitable characteristic for this type of solvents but the experimental set-up does not allow to obtain kinetic information because the overall process is controlled by the gas–liquid mass transfer. As previously commented this absorption regime with a fast chemical reaction is suitable for the process and also because a tertiary amine is used. This type of amine centers generally has a low reaction rate with carbon dioxide [16,17] in comparison with primary and secondary. It reduces the use of tertiary amines in the formulation of solvents. The high reaction rate of EP allows to take advantages of the suitable characteristics of tertiary amines in the overall process such as: high carbon dioxide loading, low degradation, low regeneration energy, etc [18,19].

In order to obtain the kinetic equation for the system $\text{CO}_2\text{-H}_2\text{O-EP}$ it is necessary implement other type of experimental procedure that allow

the study of fast reaction rates avoiding the influence of mass transfer processes. The experimental technique was based on the use of stopped-flow spectrophotometer using aqueous solutions of both reagents. This experimental procedure has been previously employed in different studies with suitable results [20].

The analysis of the experimental data of amine concentration through time to modelize the behavior of the carbon dioxide reaction with water and EP, the simplified equation suggested by Kadiwala et al [21] has been used (equation (1)).

$$r = k_o \cdot C_A = k_2 \cdot C_B \cdot C_A \quad (1)$$

where k_o is the observed constant, k_2 is the kinetic constant and C_A and C_B are the carbon dioxide and N-ethylpiperidine concentration respectively.

A first analysis of the experimental data allows to confirm a suitable fit of experimental data to the proposed equation (1) that has been confirmed in the posterior evaluation. Fig. 2 shows the value of the observed kinetic constant when the amine concentration in the liquid solvent is varied. A linear trend was observed and it fits with the definition of observed kinetic constant previously shown in equation (1). Then it is possible to calculate the value of the kinetic constant at the different experimental temperatures. This type of experimental data has been fitted with an Arrhenius type equation in order to modelize the influence of temperature upon the kinetics and allow to calculate the activation energy, reaching a value of $75.5 \text{ kJ} \cdot \text{mol}^{-1}$.

The kinetic results corresponding to the use of EP in the chemical absorption of carbon dioxide show interesting values because it allow to reach high reaction rate mainly in comparison with other tertiary amines commonly used as reference and also in industrial operations (see Table 1).

3.2. Carbon dioxide absorption in EP-based solvents

The experimental work in present study is centered on the basis of a previous study of our research team [13] that pointed out an enhancement in mass transfer rate under the presence of a second liquid phase (organic) in the gas absorber (stirred tank). New studies are carried out in present work in order to explain better the overall mechanism of carbon dioxide absorption with chemical reaction in this complex gas–liquid–liquid system. Also comparisons with well-established

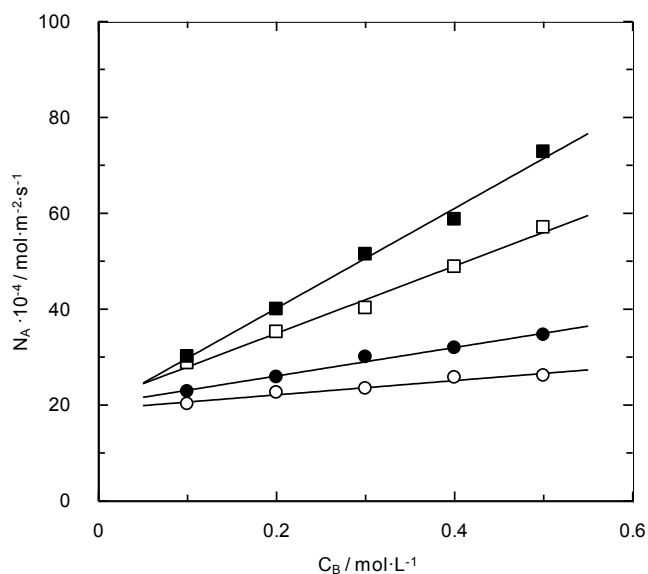


Fig. 1. Influence of amine concentration and temperature upon the absorption rate using a stirring cell for carbon dioxide – water – ethylpiperidine system. (○) $T = 15 \text{ }^\circ\text{C}$; (●) $T = 25 \text{ }^\circ\text{C}$; (□) $T = 35 \text{ }^\circ\text{C}$; (■) $T = 45 \text{ }^\circ\text{C}$.

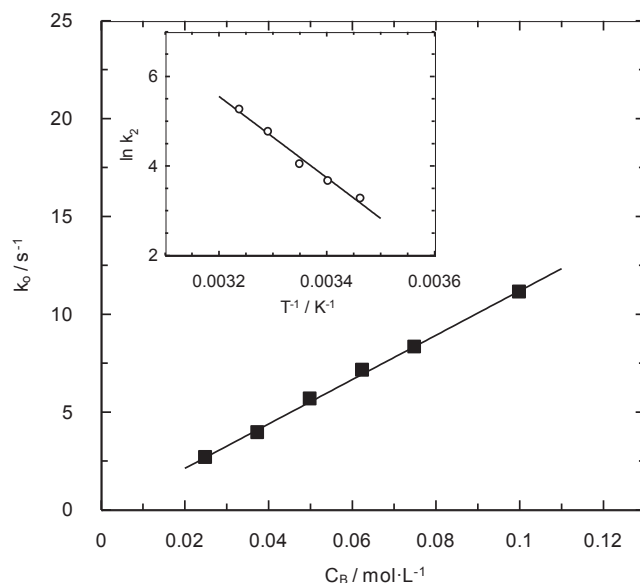

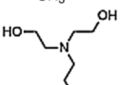
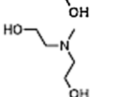


Fig. 2. Influence of EP concentration upon observed kinetic constant at $T = 25 \text{ }^\circ\text{C}$. Inner plot: influence of temperature upon the kinetic constant.

Table 1Kinetic constant corresponding to different tertiary amines at $T = 25^\circ\text{C}$.

Name	Structure	k_2 ($\text{m}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)
Ethylpiperidine		$5.65\cdot 10^{-2}$
Triethanolamine [22]		$1.66\cdot 10^{-3}$
N-methyldiethanolamine [22]		$3.20\cdot 10^{-3}$

solvents widely used in industry (aqueous solutions of monoethanolamine and methyldiethanolamine) allow to evaluate the behavior of the proposed solvent.

The previous study of Carrera et al [13] developed only a small amount of experiments with two liquid phases in the absorber (close to the amine solubility in water) and using a stirred tank contactor with mechanical agitation. This experimental device allowed to reach a suitable mixture between the three phases involved in the process. Present work has employed two different types of columns (bubble and packed) in order to analyze the possibility of the solvent use at industrial level.

The first part of experimental work related with overall mass transfer process accompanying with chemical reaction has been focused in the comparison of the solvent based on EP with other amine-based solvents. Figs. 3 and 4 show experimental data corresponding to the absorption curves using an aqueous solution of EP (homogeneous solvent) and an heterogeneous one (working upper the solubility value). These carbon dioxide absorption curves have been compared with the behavior showed by aqueous solutions of MEA and MDEA.

Fig. 3 shows the experimental results obtained using a small bubble column with a volume of 0.15 L. It is possible to observe that not very important differences in the absorption curves of homogeneous solvents are observed, but MEA-based solvent shows the best behavior with a high absorption rate at the beginning of the experiment. This behavior is in agreement with the reaction mechanism [23] that indicates the formation of carbamate at low carbon dioxide loadings with a high reaction

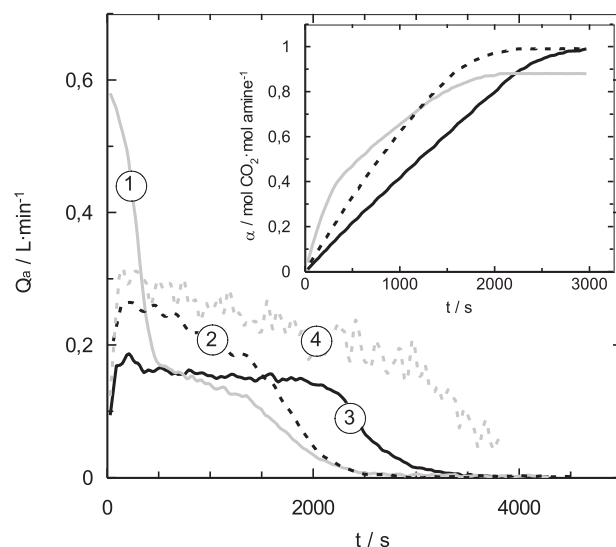


Fig. 4. Carbon dioxide absorption curves using a 0.6 L bubble column. $Q_G = 0.7 \text{ L}\cdot\text{min}^{-1}$. $C_B = 0.45 \text{ M}$. MEA (①), MDEA (②), EP (③). Heterogeneous solvent: 67% of organic phase (④).

rate. The difference in reaction rate of carbamate formation in comparison with the reaction of carbon dioxide with tertiary amines to produce carbonate or bicarbonate ion is very important [24]. For this reason the reaction rate is an important handicap for the use of tertiary amines in industrial processes. The analysis of carbon dioxide loading for each solvents allows to obtain values in agreement with literature [25]: values close to $1 \text{ mol CO}_2\cdot\text{mol amine}^{-1}$ for tertiary amines (EP and MDEA) and lower values of MEA aqueous solution due to the coexistence of carbamate and bicarbonate (from carbamate hydrolysis) in the reaction products.

When the solvent based on the use of EP is an heterogeneous solvent with the presence of an aqueous and an organic phase in the absorber (specifically a 17% of aqueous phase in volume) the experimental results included in Fig. 3 show an interesting behavior. In the first part of experiment the absorption rate was high reaching similar values than the solvent based in MEA, removing amounts of carbon dioxide close to 100% of the fed flow-rate. The experimental values for the EP heterogeneous solvent show certain dispersion in comparison with the homogeneous solvents due to a more irregular flow pattern in the bubble column, due to the presence of both liquid phases. Due to the presence of an excess of amine (in the organic phase) a relatively constant absorption rate was observed during a larger time than for MEA solvent. The heterogeneous solvent also shows a slow decrease in the trend though the amine concentration in the aqueous phase is maintained constant. This fact is due to the role played by the organic phase. An organic phase has higher carbon dioxide solubility and a shuttle effect [26,27] can be produced during the carbon dioxide absorption. Taking into account that during chemical absorption amine molecules are transferred to aqueous phase, the carbon dioxide previously absorbed in this phase is also transferred. This can increase the pathways for carbon dioxide absorption from gas to aqueous phase [13].

In order to confirm the experimental results showed in Fig. 3 the same type of experiments were carried out in a bubble column with a larger volume (0.6 L). This type of experiment allows to confirm the suitable behavior of EP heterogeneous solvent when the dimension of the gas-liquid contactor increases and the ideality in the flow pattern decreases. Fig. 4 shows the experimental results in this contactor and they show a similar behavior of homogeneous solvents than the previously ones discussed in Fig. 3 but the differences between them increases. The MEA-based solvent shows high absorption rate values at the beginning of experiment. In relation with tertiary amines MDEA-based solvent shows better results than EP homogeneous solvent during the

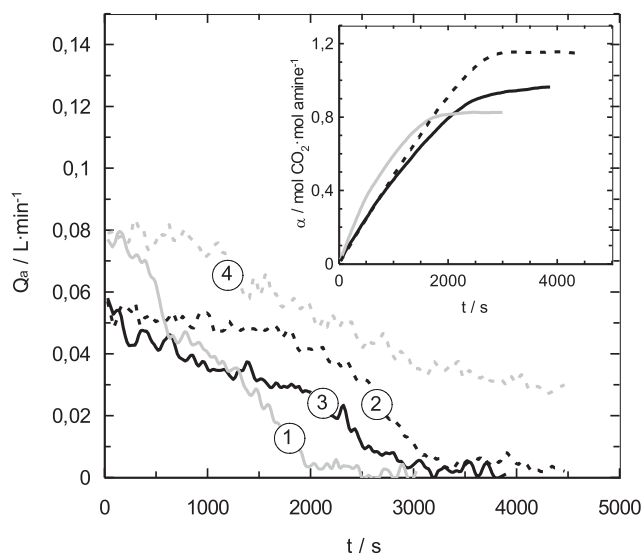


Fig. 3. Carbon dioxide absorption curves using a 0.15 L bubble column. $Q_G = 0.08 \text{ L}\cdot\text{min}^{-1}$. Homogeneous solvents: $C_B = 0.45 \text{ M}$. MEA (①), MDEA (②), EP (③). Heterogeneous solvent: 67% of organic phase (④).

experiment. With the small column at the beginning of experiment both solvents showed similar values. Attending to the use of de EP heterogeneous solvent better results than the other solvents based on tertiary amines are observed. These results confirm the good behavior of this solvent in comparison mainly with MDEA that is generally used in hydrogen purification operations. On the other hand in the first part of experiment (with low carbon dioxide loading) does not reach absorption rate values close to MEA solvent.

This fact can be produced by different reasons: (i) an increase in the volume of absorber increases the amount of both liquid phases (aqueous and organic) and when EP is consumed new amine molecules are solubilized in the aqueous phase. This phenomenon is produced through the liquid–liquid interface and the zone when carbon dioxide reaction with EP is produced can be situated far from the liquid–liquid interface and then the diffusion of amine molecules in the aqueous phase can be a limiting step. (ii) Another negative influence can be the effect of the ratio between both liquid phases. In Fig. 4 an heterogeneous solvent with a 50% in volume of each phase was employed. Perhaps the modification of liquid phases ratio can influence upon absorption rate, taking into account the previously commented carbon dioxide shuttle effect that can enhance mass transfer rate.

Then, on the basis of the experimental results obtained using different bubble columns (see Figs. 3 and 4) and the hypothesis formulated to explain the differences observed between both figures a study about the influence of aqueous/organic ratio upon carbon dioxide absorption curves was performed. Though shuttle effect can produce some type of influence when organic phases are present in the gas–liquid contactor, it is easy to think that an increase in the amount of aqueous phase in the absorber could have a positive effect. It is based on a higher amount of organic phase do not cause a higher concentration of EP in the aqueous phase, but a higher amount of aqueous phase increases the gas hold-up in this phase and it increases the gas–liquid (aqueous phase) interfacial area and it enhances mass transfer rate.

Several experiments were carried out modifying the aqueous phase/organic phase ratio (in volume) in a wide range in order to evaluate the influence of this operational variable. The experimental data corresponding to absorption curves are shown in Fig. 5. It is clearly observed that the behavior is opposite than the hypothesis previously formulated, because an increase in the organic phase enhances absorption rate increasing from 60% to ~100% under the experimental conditions employed in Fig. 5. The influence of organic phase presence observed in

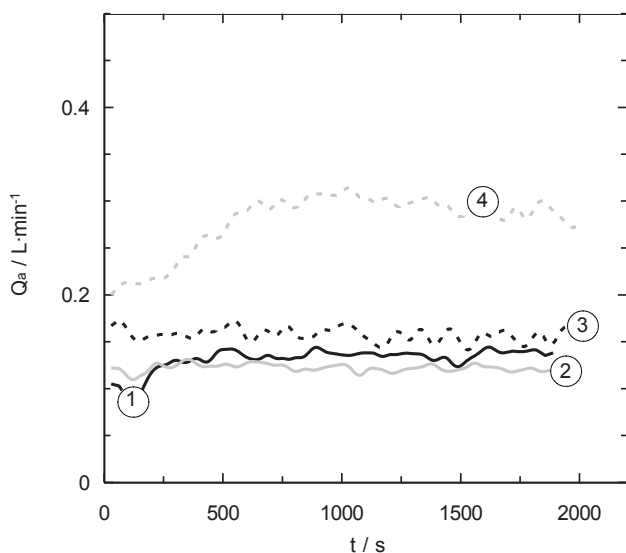


Fig. 5. Influence of aqueous phase/organic phase (AP/OP) ratio upon carbon dioxide absorption rate curves. $Q_G = 0.3 \text{ L} \cdot \text{min}^{-1}$. AP/OP = 83/17% (①); AP/OP = 67/33% (②); AP/OP = 50/50% (③); AP/OP = 33/67% (④).

the experiments allows to conclude that the phenomenon with the highest weight is the shuttle effect caused by the organic phase in the gas–liquid and liquid–liquid mass transfer processes. Fig. 6 shows an example of mass transfer mechanism proposed to explain this type of gas–liquid–liquid process for carbon dioxide removal.

The same type of experiments showed in Fig. 5 has been carried out using different gas flow-rates fed to bubble column. The experimental results corresponding to this study are included in the plots of Fig. 7. The main conclusions of these data is that a change in the carbon dioxide gas flow rate maintain the previously discussed influence of liquid phases ratio upon absorption rate. More specifically (left plot in Fig. 7) an increase in the amount of carbon dioxide fed to absorber causes a decrease in gas absorption (with a linear trend) but it is only due to a higher amount of carbon dioxide present in the absorber and using the same volume of solvent. The best results are always obtained for the experiments with the highest amount of organic phase.

In the right plot of Fig. 7 the removal percentage is shown versus the amount of organic phase in the solvent. This graph clearly shows that the influence of this variable does not show a linear trend. For compositions of organic phase lower than 50% the influence in the change of the ratio between liquid phases shows slight modifications and the separation of carbon dioxide is similar. Using a 50% of each phase in the bubble column and for the lowest gas flow-rate a clear improvement in carbon dioxide separation is observed, but a very important enhancement in carbon dioxide absorption is observed when the amount of organic phase reaches higher values than 50% in the bubble reactor. The enhancement is very important and it is observed with independence of the gas flow-rate employed in the experimental set-up.

After the study of the influence of liquid phases ratio under different experimental conditions, it is possible to conclude that the best behavior of this biphasic solvent is reached with low amounts of aqueous phase. This fact allows to simplify the experimental set-up and the use of bubble columns at industrial level can be a suitable option. A simplified scheme of the installation is shown in Fig. 8 to use this type of biphasic chemical solvent. The aqueous phase is placed in the bottom of the bubble column due to density value. The mixture between phases caused by the agitation of bubbles is low and the phases remain separated. It allows that the reaction products (ionic compounds) will be accumulated in the aqueous phase, also because the reaction takes place only in the aqueous phase by the use of a tertiary amine. The aqueous phase is easily removed from the absorbed from the bottom of the bubble column to be sent to solvent regeneration section. This operation configuration allows to reduce in a high percentage the amount of solvent that must be sent to regeneration (specifically a reduction close to 67%). On the basis of these explanations the reduction in the costs associated to the overall operation of carbon dioxide separation by chemical absorption can be considered high.

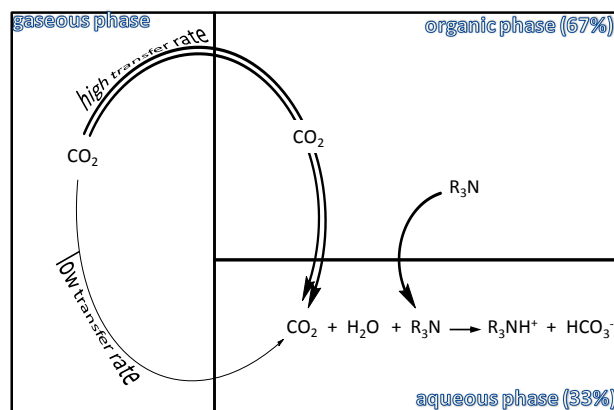


Fig. 6. Carbon dioxide chemical absorption pathway using the configuration of two liquid phases with N-ethylpiperidine as solvent.

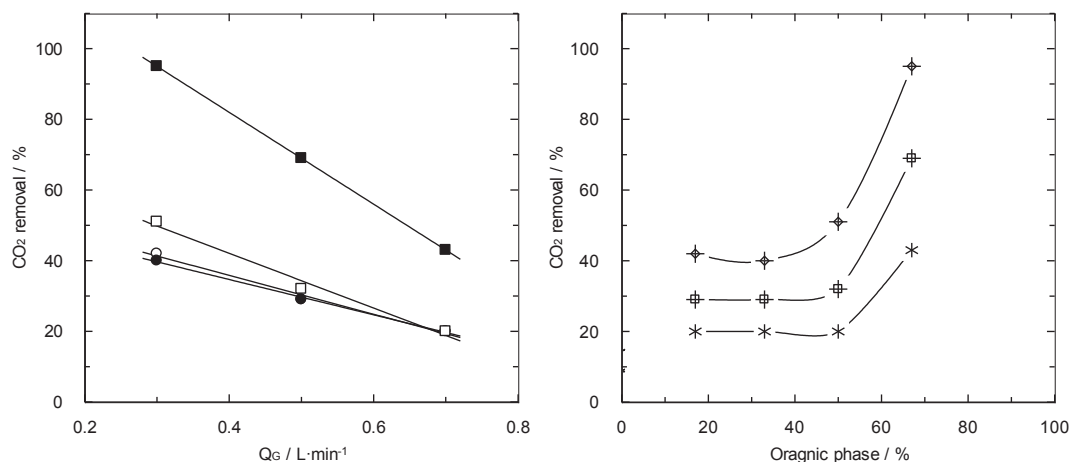


Fig. 7. Influence of gas flow-rate and the ratio between organic and aqueous phases upon the capacity for carbon dioxide absorption. Left plot: (○) OP = 17%; (●) OP = 33%; (□) OP = 50%; (■) OP = 67%. Right plot: (*) $Q_G = 0.3 \text{ L}\cdot\text{min}^{-1}$; (⊕) $Q_G = 0.3 \text{ L}\cdot\text{min}^{-1}$; (⊕) $Q_G = 0.3 \text{ L}\cdot\text{min}^{-1}$.

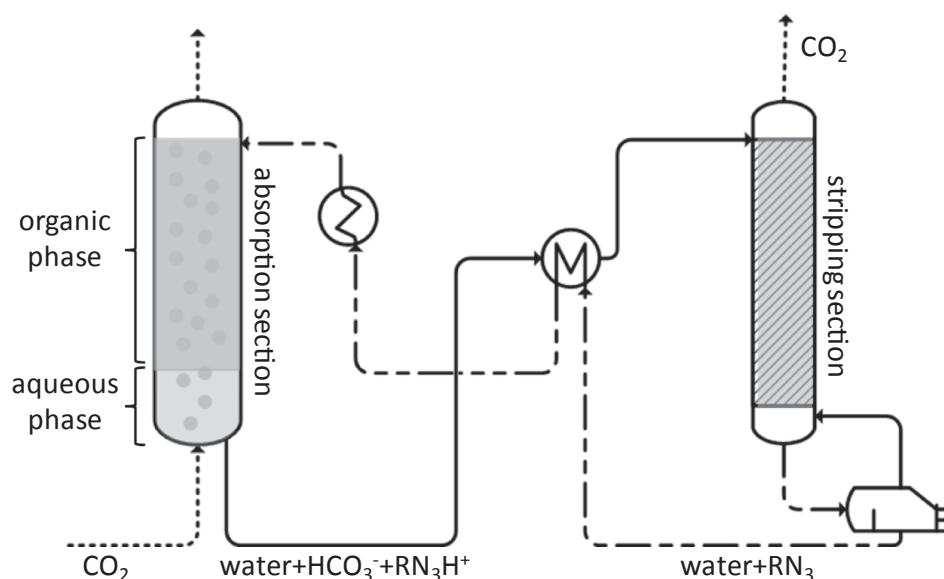


Fig. 8. Scheme corresponding to an industrial process using this type of biphasic solvent. (dotted line) gas phase; (solid line) aqueous phase; (dash-dotted line) organic + aqueous phases.

Solvent flow rate in the regeneration section is lower and then the size of stripping column, reboiler and condenser can be reduced.

The amount of energy needed to maintain the temperature (e. g. 40°C) of the solvent fed to the absorber is decreased significantly.

The boiling temperature of solvent is considerable lower than conventional processes and it reduces the energy employed in stripping reboiler.

In the scheme of Fig. 8 the presence of different phases in each stream is indicated because during the solvent regeneration operation by stripping, organic phase is generated due to the regeneration of amine (EP) because the reaction product is deprotonated. This type of configuration is simpler than other previously described in literature [28] involving the use of biphasic solvents (liquid–liquid or liquid–solid) because it avoids the presence of additional separation units in the outlet of the absorber.

Present research work proposes the use of a bubble column as gas–liquid contactor to carry out the carbon dioxide chemical absorption using biphasic solvent using EP but an additional study has been carried out using a packed column contactor because this type of absorber is commonly used at industrial level for gas–liquid absorptions. The

experimental procedure previously described in the experimental section, consists of the recirculation of the solvent after homogenization. Fig. 9 shows the experimental results of carbon dioxide absorption using the biphasic solvent with the highest organic phase ratio and using an aqueous solution of MEA (the most used solvent in industrial operations of CO_2 absorption).

The MEA-based solvent shows a complete carbon dioxide removal showing the suitable behavior of this solvent in this type of equipment. After a certain experiment time the amount of carbon dioxide absorbed in the liquid phase is reduced drastically because the concentration of MEA in the solvent decreases due to the chemical reaction.

In relation with the use of heterogeneous EP-based solvent the behavior is completely satisfactory. This solvent allows to remove a 96% average of the total amount of carbon dioxide fed to packed column. The drop in the absorption rate is produced in a time longer than the corresponding one for MEA solvent because the presence of EP in excess allow to maintain its concentration in the aqueous phase higher. Experiments with lower ratio of organic phase show a decrease in carbon dioxide absorption rate though the EP concentration in the aqueous remains constant. This behavior is in agreement with the previously

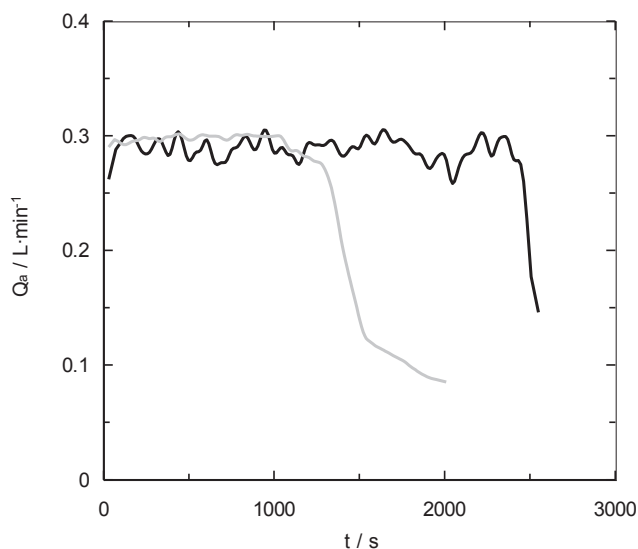


Fig. 9. Absorption of carbon dioxide using a packed column. $Q_G = 0.3 \text{ L}\cdot\text{min}^{-1}$. $Q_L = 0.15 \text{ L}\cdot\text{min}^{-1}$. MEA solvent (grey); EP heterogeneous solvent with AP/OP = 17/83% (black).

discussed results using a bubble column reactor and point out the high importance of the presence of the organic phase in the overall mechanism of carbon dioxide mass transfer from gas to aqueous phase.

3.3. Solvent regeneration

An important part of research studies focused on the development of new chemical solvents to be used in gas–liquid separation by chemical absorption is centered on solvent regeneration operation. Its importance is related with the important amount of energy that must be employed. The experimental procedure to carry out this type of studies has been deeply explained in the experimental section and consists in the development of absorption–regeneration cycles in order to evaluate losses in carbon dioxide separation capacities and rates produced by the regenerated solvent. The most commonly observed behaviors in this type of studies consist of an important lost in carbon dioxide loading after the first regeneration cycle [29,30]. This undesirable behavior can be due to different causes such as: (i) the value of the equilibrium constant that do not allow to recover the 100% of the amine present in the products and/or (ii) amine degradation by the high temperature or the high carbamate reactivity to produce undesirable products. Both phenomena implies the use of important values of solvent make-up to maintain the yield of the operation, increasing the operation cost.

Experiments carried out with the solvent developed in present work have shown the experimental results included in Fig. 10. This figure shows in one hand the carbon dioxide absorption curve during 20 min for some absorption experiments after different cycles of absorption/regeneration. The corresponding absorption curve of fresh solvent is also included (without any thermal treatment). The experimental data show a similar behavior for all the absorption curves with independence of the number of regenerations previously carried out. This behavior confirms the high stability of the chemical solvent without amine degradation.

Fig. 10 also includes an inner plot with the value corresponding to the regeneration degree that was calculated on the basis of carbon dioxide loading of each experiment (reached after 20 min) in comparison with the corresponding value obtained for fresh solvent. The calculated data allow to confirm that after several absorption/regeneration cycles the values of carbon dioxide loading remains practically constant and close to the behavior of fresh solvent.

On the basis of experimental data of absorption curves and regeneration degree it is possible to conclude that the heterogeneous solvent

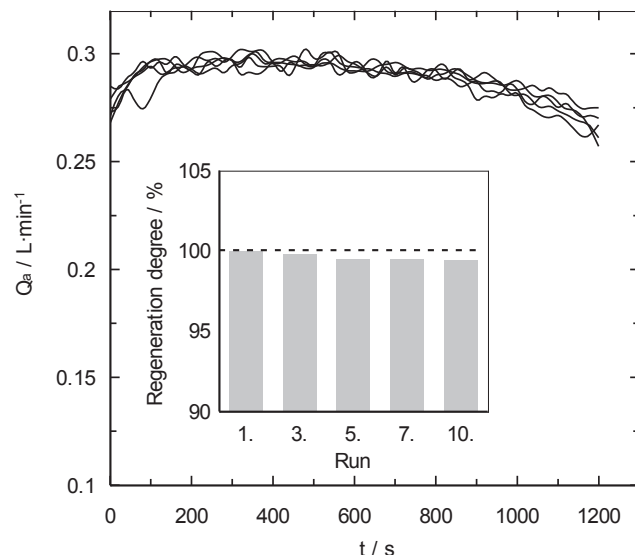


Fig. 10. Influence of regeneration upon absorption rate and regeneration degree calculated on the basis of carbon dioxide loading. AP/OP = 33/67%. $Q_G = 0.3 \text{ L}\cdot\text{min}^{-1}$.

maintains the absorption rate and loading despite regeneration treatments. Both characteristics are suitable for a chemical solvent to be used in carbon dioxide separation by chemical absorption. Previous results using MEA-based solvents have concluded an important decrease in the carbon dioxide loading after regeneration [31,32].

As previously commented in the experimental section, the solvent regeneration process was applied only for the aqueous phase due to the accumulation of reaction products in this part of the solvent. Then only the amine and reaction products included in the aqueous phase was treated with high temperatures. After the 20 min employed in these experiments the aqueous phase was always lower than 50% of the total liquid phase volume in the contactor. This fact and the temperature range employed during regeneration with a medium value of 85 °C, allows to reduce the cost associated to the energy in comparison with the conventional process.

An important part of the energetic requirements corresponding to the overall carbon dioxide separation process for chemical absorption is centered on heat exchangers and the boiler associated to the stripper (see Fig. 8). Then a decrease in the carbon dioxide rich solvent flow-rate (only aqueous phase with the reaction products) causes a decrease in the cost of the equipment (due to a decrease in size) and on the other hand in the flow-rate of utilities (boiler and cooler after the regeneration). The conventional one based for instance on the use of aqueous solutions of MEA or MDEA needs to feed the total solvent volume to the stripping section involving all the non converted amine.

4. Conclusions

Present work is focused on the use of ethylpiperidine in a chemical solvent for carbon dioxide separation and though this amine has a tertiary amino center, the kinetic studies show a fast reaction regime. This type of behavior is not commonly observed for tertiary amines and EP solvent reached significantly higher reaction rates than MDEA-based solvents. This type of reaction regime allows to consider EP solvent as a suitable candidate for its use for carbon dioxide separation by chemical absorption.

In relation with absorption studies, the heterogeneous solvent based on the use of EP shows better results than other tertiary amines using different types of columns contactors, and close to the absorption rate of solvents based on MEA that is a reference in this type of carbon dioxide separation.

The behavior of this solvent is enhanced with an increase in the amount of organic phase in the overall solvent that allows to reduce the amount of solvent that must be regenerated because the reaction products are concentrated in the aqueous phase. This fact reduces significantly the amount of energy needed (for instance sensible and stripping heat) to carry out the regeneration operation.

The experimental results of solvent (aqueous phase) regeneration show a high stability of the chemical solvent reaching values close to 100% of regeneration degree.

CRediT authorship contribution statement

D. Gómez-Díaz: Conceptualization, Methodology, Writing - original draft, Writing - review & editing, Supervision, Formal analysis. **M. Parajó:** Methodology, Formal analysis, Writing - review & editing. **O. Richoux:** Investigation, Writing - original draft, Formal analysis. **M.D. La Rubia:** Methodology, Formal analysis, Writing - review & editing. **A. Rumbo:** Methodology, Formal analysis, 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.

References

- [1] Vega F, Cano M, Camino S, Gallego LM, Portillo E, Navarrete B. Solvents for carbon dioxide capture. In: Karamé I, editor. Carbon dioxide chemistry, capture and oil recovery. London: IntechOpen; 2018. p. 141–63.
- [2] Li T, Keener TC. A review: desorption of CO₂ from rich solutions in chemical absorption processes. *Int J Greenhouse Gas Control* 2016;51:290–304.
- [3] Pinto DDD, Zaidy SHA, Hartono A, Svendsen HF. Evaluation of a phase change solvent for CO₂ capture: absorption and desorption tests. *Int J Greenhouse Gas Control* 2014;28:318–27.
- [4] Singh P, Versteeg GF. Structure and activity relationships for CO₂ regeneration from aqueous amine-based absorbents. *Process Saf Environ Prot* 2008;86:347–59.
- [5] Ozturk MC, Yuksel-Orhan O, Alper E. Kinetics of carbon dioxide binding by 1,1,3,3-tetramethylguanidine in 1-hexanol. *Int J Greenhouse Gas Control* 2014;26:76–82.
- [6] Wang L, Yu S, Li Q, Zhang Y, An S, Zhang S. Performance of sulfolane/DETA hybrids for CO₂ absorption: phase splitting behavior, kinetics and thermodynamics. *Appl Energy* 2018;228:568–76.
- [7] Zhuang Q, Clements B, Dai JY, Carrigan L. Ten years of research on phase separation absorbents for carbon capture: achievements and next steps. *Int J Greenhouse Gas Control* 2016;52:449–60.
- [8] Raksajati A, Ho MT, Wiley DE. Reducing the cost of CO₂ capture from flue gases using phase change solvent absorption. *Energy Procedia* 2014;63:2280–8.
- [9] Zhang J, Qiao Y, Wang W, Misch R, Hussain K, Agar DW. Development of an energy-efficient CO₂ capture process using thermomorphic biphasic solvents. *Energy Procedia* 2013;37:1254–61.
- [10] Raynal L, Alix P, Bouillon PA, Gomez A, le Febvre de Nailly M, Jacquin M, Kittel J, di Lella A, Mouglin P, Trapy J. The DMXTM process: an original solution for lowering the cost of post-combustion carbon capture. *Energy Procedia* 2011;4:779–86.
- [11] Barzagli F, Mani F, Peruzzini M. Novel water-free biphasic absorbents for efficient CO₂ capture. *Int J Greenhouse Gas Control* 2017;60:100–9.
- [12] Zhang S, Shen Y, Wang L, Chen J, Lu Y. Phase change solvents for post-combustion CO₂ capture: principle, advances, and challenges. *App Energy* 2019;239:876–97.
- [13] Carrera M, Gómez-Díaz D, Navaza JM. Switchable hydrophilicity solvents for carbon dioxide chemical absorption. *J Ind. Eng Chem* 2018;59:304–9.
- [14] Versteeg GF, van Swaaij W. On the kinetics between CO₂ and alkanolamines both in aqueous and non-aqueous solutions-II. Tertiary amines. *Chem Eng Sci* 1988;43:587–91.
- [15] López AB, Pacheco R, La Rubia MD, Sánchez A, Sánchez S, Camacho F. Kinetics of the absorption of pure CO₂ by mixtures of diisopropanolamine and triethanolamine in aqueous solution. *Int J Chem Kin* 2017;49:398–408.
- [16] García-Abuín A, Gómez-Díaz D, Navaza JM, Rumbo A. CO₂ capture by pyrrolidine: reaction mechanism and mass transfer. *AIChE J* 2014;60:1098–106.
- [17] Xu S, Wang YW, Otto FD, Mather AE. Kinetics of the reaction of carbon dioxide with 2-amino-2-methyl-1-propanol solutions. *Chem Eng Sci* 1996;51:841–50.
- [18] Tong D, Trusler JPM, Maitland GC, Gibbins J, Fennell PS. Solubility of carbon dioxide in aqueous solution of monoethanolamine or 2-amino-2-methyl-1-propanol: experimental measurements and modeling. *Int J Greenhouse Gas Control* 2012;6:37–47.
- [19] Mac Dowell N, Shah N. Identification of the cost-optimal degree of CO₂ capture: an optimisation study using dynamic process models. *Int J Greenhouse Gas Control* 2013;13:44–58.
- [20] Yuksel-Orhan O, Alper E. Kinetics of reaction between CO₂ and ionic liquid-carbon dioxide binding organic liquid hybrid systems: analysis of gas-liquid absorption and stopped flow experiments. *Chem Eng Sci* 2017;170:36–47.
- [21] Kadiwala S, Rayer AV, Henni A. Kinetics of carbon dioxide (CO₂) with ethylenediamine, 3-amino-1-propanol in methanol and ethanol, and with 1-dimethylamino-2-propanol and 3-dimethylamino-1-propanol in water using stopped-flow technique. *Chem Eng J* 2012;179:262–71.
- [22] da Silva EF, Svendsen HF. Computational chemistry study of reactions, equilibrium and kinetics of chemical CO₂ absorption. *Int J Greenhouse Gas Control* 2007;1:151–7.
- [23] Fan GJ, Wee AGH, Idem R, Tontiwachwuthikul P. NMR studies of amine species in MEA-CO₂-H₂O system: modification of the model of vapor-liquid equilibrium (VLE). *Ind Eng Chem Res* 2009;48:2717–20.
- [24] Galindo P, Schaffer A, Brechtel K, Unterberger S, Scheffknecht G. Experimental research on the performance of CO₂-loaded solutions of MEA and DEA at regeneration conditions. *Fuel* 2012;101:2–8.
- [25] García-Abuín A, Gómez-Díaz D, López AB, Navaza JM, Rumbo A. NMR characterization of carbon dioxide chemical absorption with monoethanolamine, diethanolamine, and triethanolamine. *Ind Eng Chem Res* 2013;52:13432–8.
- [26] Dumont E, Andres Y, Le Cloirec P. Effect of organic solvents on oxygen mass transfer in multiphase systems: application to bioreactors in environmental protection. *Biochem Eng J* 2006;30:245–52.
- [27] da Silva TL, Calado V, Silva N, Mendes RL, Alves SS, Vasconcelos JMT, et al. Effects of hydrocarbon additions on gas-liquid mass transfer coefficients in biphasic bioreactors. *Biotechnol Bioprocess Eng* 2006;11:245–50.
- [28] Sánchez-Fernández E, Heffernan K, van der Ham L, Linders MJG, Goetheer ELV, Vlucht CJH. Precipitating amino acid solvents for CO₂ capture. Opportunities to reduce costs in post combustion capture. *Energy Procedia* 2014;63:727–38.
- [29] Li J, You C, Chen L, Ye Y, Qi Z, Sundmacher K. Dynamics of CO₂ absorption and desorption processes in alkanolamine with cosolvent polyethylene glycol. *Ind Eng Chem Res* 2012;51:12081–8.
- [30] Schaffer A, Brechtel K, Scheffknecht G. Comparative study on differently concentrated aqueous solutions of MEA and TETA for CO₂ capture from flue gases. *Fuel* 2012;101:148–53.
- [31] Du Y, Wang Y, Rochelle GT. Piperazine/4-hydroxy-1-methylpiperidine for CO₂ capture. *Chem Eng J* 2017;307:258–63.
- [32] Gao H, Liang Z, Liao H, Idem RO. Thermal degradation of aqueous DEEA solution at stripper conditions for post-combustion CO₂ capture. *Chem Eng Sci* 2015;135:330–42.