

EXPERIMENTAL ASSESSMENT OF CO₂ ABSORPTION RATES FOR AQUEOUS SOLUTIONS OF HEXYLAMINE, DIMETHYLCYCLOHEXYLAMINE AND THEIR BLENDS

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Abstract: Highly emissive fossil origin CO₂ systems are mainly combustion based. Presenting considerable investment costs and potential leaks into the environment as drawbacks, conventional amine solvent based processes remain the most mature technological option for CO₂ capture. In the regeneration step of solvents, the energy consumed in these processes is provided by steam at temperatures ranging from 120 °C till 140 °C. In order to avoid this level of temperature that fosters amine degradation, a novel series of thermomorphic solvents are studied. These solvents aim at minimizing energy consumption while improving CO₂ capture and potentially replacing the consumption of steam by using waste heat. This paper presents the selection of lipophilic amine based solvents and compares the performance of hexylamine 3M aqueous solutions and the mixture of dimethylcyclohexylamine/hexylamine in aqueous solutions at different compositions. Both absorption and regeneration rates for the selected lipophilic mixtures show outstanding results compared to the benchmark solvent monoethanolamine (MEA). Absorption of CO₂ was performed in a Lewis cell for temperatures 20, 30 and 40 °C. Results obtained show the impact of amine blends on the kinetics of absorption and enable novel solvents to be suggested for low energy carbon capture processes. Data collected enables apparent kinetic constants for each of the blends to be calculated. Hexylamine and dimethylcyclohexylamine aqueous blends have demonstrated higher capability to absorb CO₂ at high rates. In fact, the kinetics remain similar to those of hexylamine aqueous solvents, while the regeneration tests show a rate increase induced by the dimethylcyclohexylamine.

Keywords: *absorption rate, CO₂ captures, kinetics, lipophilic amines, thermomorphic solvents*

INTRODUCTION

As early as 1931, Bottoms [1] was the first to study the high capacity of absorption of acid gases by amines, in particular monoethanolamine (MEA). Since the first findings, aqueous MEA solvent has become the reference for CO₂ removal, the MEA solvent at 5M is referred to as MEA Benchmark. Work on amines carried out in-house, both experimentally [2] and modeling [3] confirms such results. Alkanolamine aqueous solutions became the most widely used solvents in gas treatment processes; these amines require a regeneration temperature of about 120 °C.

Depending on the nitrogen atom position in the amine molecule, amines are categorized into primary, secondary and tertiary. Primary and secondary amines reaction kinetics is higher than tertiary amines that, on the other hand, have higher absorption capacity and require lower solvent stripping energy than primary and secondary amines. Amine selection for treatment of a given gas depends on the equipment (investment and operating) costs, but essentially, on the content and kind of acid gases to be removed. In most of the cases, these are CO₂ and H₂S. The regeneration step of amines requires a high energy supply at the level of the regeneration column (stripper). The use of a mixture of amines has been reported to be advantageous with respect to cost reduction, while corrosion of equipment is reduced, as stated by Amann and Bouallou [4].

According to Zhang *et al.* [5], conventional aqueous amine solvents have yielded only modest impact on regeneration energy reduction with an unsatisfactory CO₂ absorption capacity. Biphasic solvents, however, show the potential for regeneration energy reduction of 30 - 35 % compared to the MEA benchmark [6, 7]. Biphasic solvents are divided into demixing solvents and thermomorphic solvents. The demixing solvents separate into two liquid phases after the absorption of CO₂ without any heat supply. One of these liquid phases is rich in CO₂ and is further introduced into the stripping column (regenerator) while the other, poor in CO₂, would be returned to the absorber without regeneration. A decanter between the absorption column and the stripper is needed in the CO₂ capture unit to biphasic separation to take place. Energy savings originate due to the reduced flow of the solvent stream to be regenerated. Moreover, the high concentration of CO₂ in the fraction to be regenerated enables slightly lower temperatures in the stripping operation, as first mentioned by Agar *et al.* [8]. Assessing the best combination of biphasic aqueous amines and the higher improvements compared to performances of MEA Benchmark 30 % have been the focus of several research works throughout the world. Arshad *et al.* [9] carried out a study concerning 3-(methylamino) propylamine (MAPA) and 2-(diethylamino) ethanol (DEEA) at 5M DEEA 2M MAPA mixtures. This study illustrated the relevance of the demixing amines and their potential for real savings on regeneration heat needed.

A second study by Xu *et al.* [10] has shown that a mixture of 1, 4-butanediamine (BDA) and 2-(diethylamino)-ethanol (DEEA) with a composition of 2M BDA and 4M DEEA would provide a greater CO₂ absorption capacity, the separation after absorption is attributed to the limited solubility of DEEA in the reaction products of BDA with CO₂ and the rapid kinetics. On the other hand, biphasic thermomorphic solvents, which will be further studied in this article, are characterized by a limited solubility in water. Stirring the mixture at temperatures of 30 - 40 °C allows the formation of an homogeneous medium. When heat is supplied (increase of temperature) to the biphasic amines, a separation into two liquid phases and a gaseous phase occurs: a

lower aqueous phase rich in CO₂ and an organic upper phase rich in amines and the CO₂ released occur. This has been thoroughly explained by Tan [11].

The lower critical solution temperature (LCST) of the loaded solvent, above which there is liquid-liquid separation, is around 70 - 90 °C depending on the amine. Consequently, partial regeneration of the solvent is carried out at temperatures beyond the LCST and lower than temperatures that would lead to amine losses by evaporation. The main advantage of low regeneration temperatures is that it renders possible to use the residual heat to regenerate the solvent [12]. CO₂ absorption by these biphasic solvents has the following advantages:

- high motive force during regeneration via liquid-liquid separation;
- absence of precipitation phenomena related to both low amine concentrations (10 to 15 % by mass) and to the low regeneration temperature which inhibits the formation of amine degradation by-products.

Activating amines and adding regeneration promoters has also been considered for lipophilic aqueous amine solvents. However, little information about such blends is available in open documentation. The blend methylcyclohexylamine (MCA) and dimethylcyclohexylamine (DMCA) was examined in proportions of 1 : 1 respectively in a solvent with a concentration of 3M amine. Although improvements were observed on absorption and regeneration compared to the MEA Benchmark, oxidation problems were opposed [11, 12]. The dimethylcyclohexylamine and dipropylamine blend was also examined in a 3M solution at 1 : 3. Both blends performed well, however, dipropylamine reported precipitation problems [11, 13]. The 2,6 dimethylpiperidine solution was also tested at 3M concentration. It showed 60 % better overall performance than the conventional MEA Benchmark, but showed problems of degradation and volatility occurred [14]. More recently, Mehassouel *et al.* [15] investigated kinetics of CO₂ absorption into mixed methyl-diethanolamine (MDEA) and hexylamine (HxA) solutions. Their experimental results showed that adding a small amount of hexylamine enhances the kinetics of CO₂ absorption and that the kinetics of CO₂ absorption with aqueous MDEA 37 wt % + HxA 3 wt % is pseudo first order regime with reduced activation energy compared to that of MDEA 40 wt %. Similar results were observed by Mukherjee *et al.* [16] with benzylamines. They also simulated the absorption / regeneration system using Aspen Plus™ software for the treatment of gas streams from cement plant in a post-combustion process. The analysis of their results established that blended solvent MDEA 37 wt % + HxA 3 wt % gives lower energy consumption than that of MDEA 40 wt %.

Theory of CO₂ absorption with amine solvents: mechanism and kinetics

The kinetics of reaction between the amines and the different acid gases has a considerable effect on the absorption rate and the size of the equipment to remove acid gases. Versteeg *et al.* [17] stated that the reaction of hydrogen sulfide with amines is very fast since there is only one phase of proton exchange. As regards CO₂, the reaction kinetics of amines strongly varies (slow, fast, instantaneous) depending on amines considered. Nowadays, reaction mechanisms explaining CO₂ absorption by amine aqueous solvents are very diverse and there is no single agreed mechanism to describe this phenomenon [18]. Reaction mechanisms differ depending on the nature of the amine and some have shown more compatibility with the experimental results. As a

general rule, primary and secondary amines react in similar way, while tertiary amines react with a different mechanism.

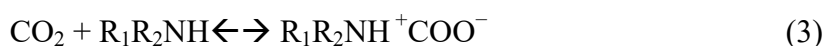
Primary and secondary amines

Kinetics are described for MEA as a reaction of second order [19]. However, other amines performing CO₂ absorption, like the case of the diethanolamine (DEA) show that the reaction is experimentally determined of third order. Versteeg and van Swaaij [20] have shown that the so-called Zwitterion mechanism introduced initially by Caplow in 1968 is the most representative, especially since it takes into account the order of the reaction which varies according to the amine used. The mechanism of the Zwitterion states that the capture of CO₂ passes through the formation of the element Zwitterion of limited lifespan, and which is then consumed according to the following equations:

For primary amines



For secondary amines



This Zwitterion undergoes a deprotonation by the base B according to equation 1 (and also 3), the base B can be OH⁻ ion, water or the amine itself.

Tertiary amines

Tertiary amines (containing three radicals R₁, R₂, and R₃) serve as a catalyst during the formation of carbohydrates (bicarbonates), according to reaction 5, but cannot react directly with CO₂. This has been demonstrated experimentally when using non-aqueous tertiary amines and measuring the absorbed amount of CO₂. It was found that this amount was equivalent to the CO₂ solubilized in the solution.



Thermomorphic amines screening

Zhang *et al.* [21] have carried out a selective study in order to determine the best performing thermomorphic aqueous solvents. Involving more than 32 thermomorphic amines, Tan [11] also carried out a similar study. The main criteria considered are the following:

1. Volatility: low vapor pressure in order to avoid solvent loss during regeneration.
2. Phase change temperatures: the solvent must have low LCST (30 - 40 °C) to ensure an absorption process in a homogenous liquid. Once loaded, solvent must have phase separation at temperatures between 60 °C and 90 °C.
3. Absorption capacity: It must be higher than MEA Benchmark.
4. Regeneration capacity higher than 90 % at temperatures preferable between 80 °C and 90 °C.
5. Negligible precipitation phenomenon: Undesired stable elements (stable nitrogenated salts) that lead to clogging risks and energy consumption increase while regenerating the solvent.

6. Kinetics: The solvent shall show fast absorption kinetics in order to reduce the size of industrial absorption columns.

Studies on lipophilic amines have concluded that no amine can perfectly match the six criteria. Thus, within the aim of satisfying the criteria stated above, particular effort is focused on blended lipophilic amines in aqueous solutions. Based on reaction kinetics, primary and secondary amines are considered as activators of the absorption. Based on the energy needs for regenerating the solvents, tertiary amines are considered as regeneration promoters [5].

For this study, 28 thermomorph amines (Table 1) were thoroughly studied in order to select the better fits to serve as a preliminary list of candidate amines for aqueous solvent blends.

Table 1. List of thermomorph amines and their types [5, 11, 21]

Amine	Type	Amine	Type
Cyclohexylamine	Primary	<i>N</i> -Methylcyclohexylamine (MCA)	Secondary
Cycloheptylamine	Primary	<i>N</i> -Sec-butyl- <i>n</i> -propylamine	Secondary
Cyclooctylamine	Primary	Tetramethylpiperidine	Secondary
Heptylamine	Primary	Dimethylbutylamine	Tertiary
Hexylamine (HxA)	Primary	Diethylcyclohexylamine	Tertiary
Octylamine	Primary	Di-isopropyl-methylamine	Tertiary
Dibutylamine	Secondary	Di-isopropyl-ethylamine	Tertiary
Dicyclohexylamine (DMCA)	Secondary	Dimethylcyclohexylamine (DMCA)	Tertiary
Diisobutylamine	Secondary	Dimethyloctylamine	Tertiary
Dipropylamine (DPA)	Secondary	Ethylpiperidine (EPD)	Tertiary
Di-sec-butylamine	Secondary	Methylpiperidine	Tertiary
2,6-Dimethylpiperidine (2,6-DMPD)	Secondary	Tributylamine	Tertiary
<i>N</i> -Ethylbutylamine	Secondary	Triethylamine	Tertiary
Isopropylcyclohexylamine	Secondary	Tripropylamine	Tertiary

From the previous table, a first shortlisting of amines is carried out by excluding those with Normal Boiling Point (NBP) higher than 85 °C. The reason is that vapor pressure would be high at high temperatures and leads to potential losses of amines by transfer to the gaseous phase exiting to other operating units. The amines excluded based on the above-mentioned criterion are *N*-ethylbutylamine (NBP = 109 °C), di-isopropyl-methylamine (NBP = 95 °C), triethylamine (NBP = 89 °C) and dimethylbutylamine (NBP = 93 °C).

Phase change temperature

Amine-water LCST shall be within the range of ambient temperature and slightly higher, at concentrations of 3M [21]. Information about the LCST of the amines in Table 1 is collected. Some examples of solubility diagrams are presented in Figure 1. It can be observed that LCST of heptylamine, ethylpiperidine, 2,6-DMPD, MCA, DMCA and octylamine stands within the range of 20 °C (ambient) and 40 °C, which renders

them the possibility to be shortlisted as potential lipophilic amines to be used on CO₂ capture.

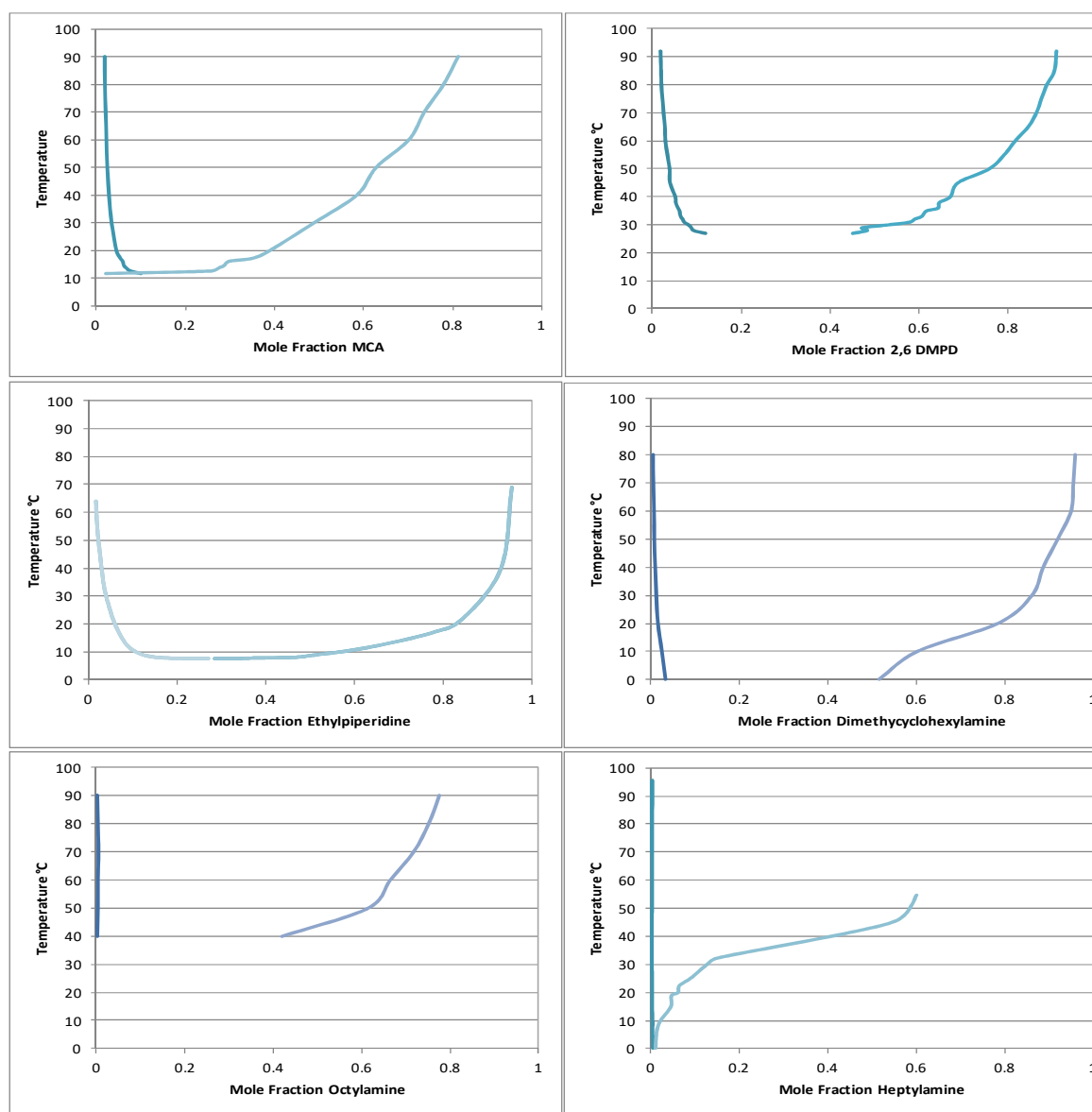


Figure 1. Solubility diagrams of lipophilic amine-aqueous systems (based on Stephenson [22], Góral et al. [23])

Kinetics of reaction

In the particular case of some lipophilic primary and secondary amines, a faster reaction rate than MEA Benchmark can be observed. Among the amines listed, those showing higher reaction kinetics are hexylamine (HxA), cycloheptylamine, dipropylamine (DPA), diisopropylamine, *N*-sec-butyl-*n*-propylamine and the 2,6 DMPD. In some other cases, kinetics have shown a slower reaction rate compared to MEA Benchmark and lead amines in this case (diisopropylamine and dicyclohexylamine) to be excluded from this study. Figure 2 shows the comparison of absorption kinetics in amines of CO₂.

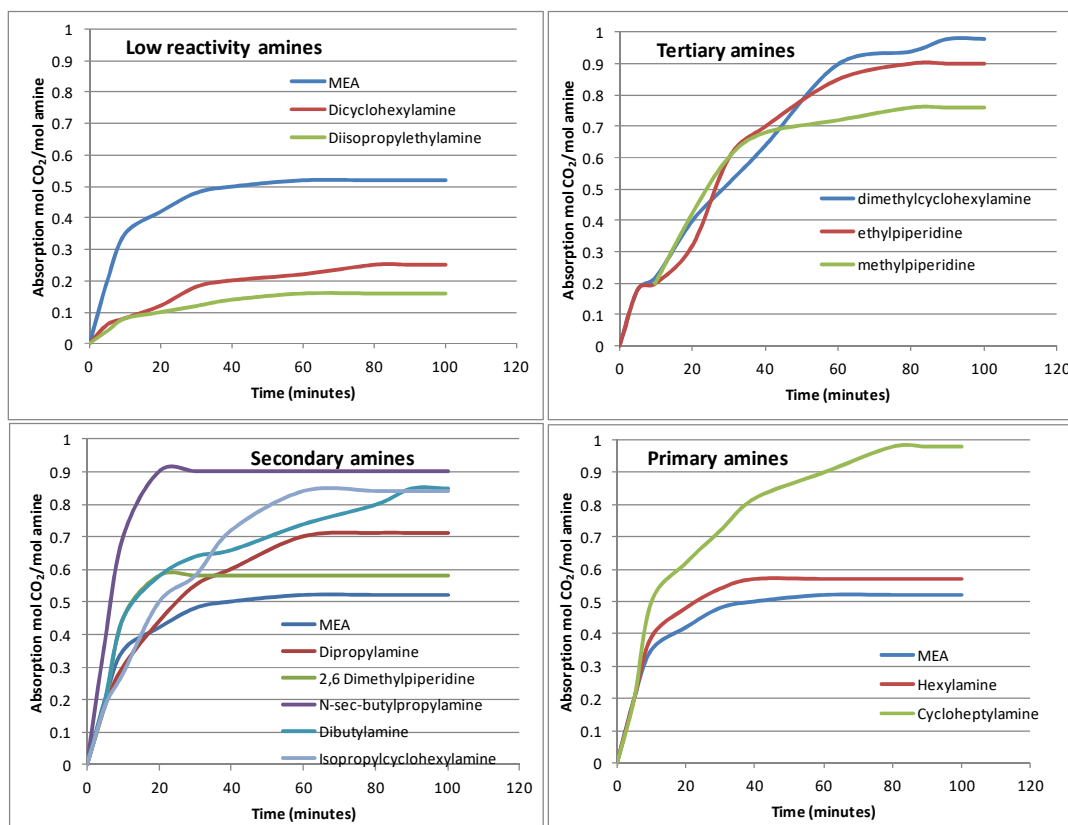


Figure 2. Reaction kinetics of CO₂ in MEA [24] and in lipophilic amines (based on Zhang *et al.* [12] and Zhang *et al.* [25])

Absorption capacity

Energy consumed for the regeneration of solvent depends on the quantity of CO₂ absorbed by the amine [26]. Energy of absorption and quantity of gas absorbed are two variables to be considered for optimizing the capture process. Absorption capacity shall be as high as possible, while energy of absorption shall be the lowest. Zhang *et al.* [21] studied the absorption capacity of lipophilic amines and found that their capacity is frequently higher than MEA Benchmark (0.5 mol CO₂/mol amine):

- Hexylamine 0.75
- Cycloheptylamine 0.90
- Dipropylamine 1.2
- 2,6 Dimethylpiperidine 1.2
- Dimethylcyclohexylamine 0.9
- Ethylpiperidine 0.9.

Lipophilic amines excluded from this work are those with lower absorption capacities (tripropylamine, *N,N*-diisopropylethylamine and tributylamine).

Regeneration conditions

Regeneration temperature targeted ranges between 70 °C to 90 °C. At this temperature, 90 % of the loaded CO₂ shall be released and little must be amine losses and degradations. As previously mentioned, degradation is mainly related to stable salt formation that cumulate in equipment, such as reboilers, and reduces efficiency of the absorption process. The economic standard to assess viability of CO₂ capture by a lipophilic solvent is a maximum degradation rate of 2.2 %, which is 0.5 % higher than the accepted degradation rate for MEA Benchmark. Figure 3 presents information related to the degradation of lipophilic amines at 120 °C. In contrast, MCA and DMCA show the highest degradation and the closest values to MEA Benchmark, respectively. Other amines, such as dibutylamine, cyclo-octylamine, cyclohexylamine, ethylbutylamine, isopropylcyclohexylamine and dipropylamine have shown degradation at a temperature of 90 °C.

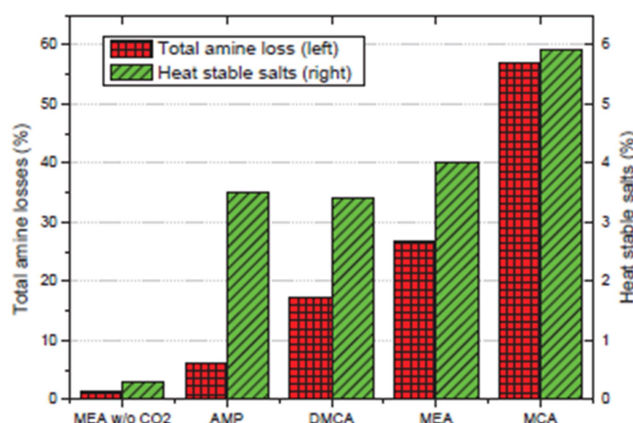


Figure 3. Degradation (salt formation) and losses for MEA, DMCA, MCA and AMP amines after 6 months of use [12]

Moreover, amine losses due to evaporation are studied by considering the Liquid-Vapor equilibria of amine-water mixtures at 3M. Particular attention is paid to positive azeotropic points that may lead to lower boiling points than pure compounds (Figure 4). Zhang *et al.* [25] concluded that DMCA and ethylpiperidine (EPD) are the most adequate amines to be considered for the capture of carbon dioxide. Regeneration at temperatures close to 80 °C enables 90 % of CO₂ to be released and little degradation is reached. The main drawback of these amines is their slow reaction rate, which has been discussed in Zhang *et al.* [25] work. The slow reaction rate of these amines led the same authors to work with amine blends [21].

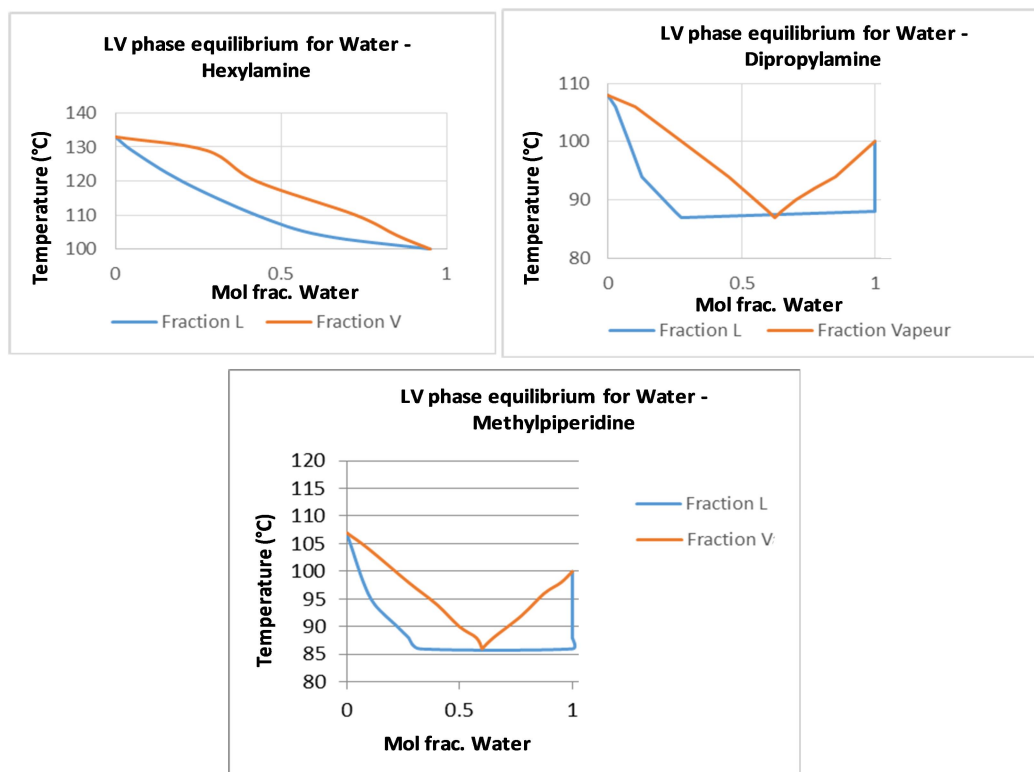


Figure 4. Liquid-Vapor phase diagrams for hexylamine, dipropylamine and methylpiperidine aqueous solutions

Blends of amines

It is reported that MCA/DMCA aqueous solutions, 1 : 1 respective amine ratio, absorb and regenerate better than MEA Benchmark solvents, however, oxidation of amines degrade the solvent [11, 12]. Similar degradation phenomena are observed for DMCA/DPA [5, 11].

Choice of amines for aqueous/amine blends

Accounting for the absorption kinetics, absorption capacity, ease of regeneration and lower volatility, as well as data lacking, the thermomorphic amines hence selected for this work are listed in Table 2.

Table 2. Selected thermomorphic amines

Category	Amine	Acronym	Type
Activator	Hexylamine	HxA	Primary
Regeneration promoter	<i>N,N</i> -dimethylcyclohexylamine	DMCA	Tertiary

It should be noted that Ye *et al.* [27] have already studied the mixture HxA and DMCA, but as a demixing solvent which was expected to present a phase separation at 30 - 40 °C. However, this mixture has never been examined as a thermomorphic solvent which would exhibit a phase change at temperatures in the region of 70 - 90 °C.

Ethylpiperidine / DMCA has been studied as thermomorphing amine and data are available, hence repeating the kinetic study on these amines would be redundant.

EXPERIMENTAL

Aqueous amine blends preparation

All the solutions have been prepared with deionized water. DMCA was from Sigma ALDRICH with 98 % mass purity, HxA was from ACROS ORGANICS with 98 % mass purity, CO₂ was provided by Air Liquid with a certified purity of 99.99 vol. %. Solvents considered for experimentation are prepared at 3M concentration (3 mol·L⁻¹). Four samples were tested: 3M HxA, 3M DMCA, and 2 amine blends of HxA/DMCA mixture at different proportions (1 : 2, 2 : 1) adding up to 3M of total amine concentration in the aqueous solvent.

Lewis cell

The experimental apparatus [28] used to carry out kinetics measurements is a thermostated Lewis type reactor with flat horizontal gas-liquid interface (15.34 ± 0.05) 10^{-4} m². The temperature is controlled by circulating a thermostatic fluid through the glass double jacket. The reactor is closed at both ends by two metallic flanges. The liquid and gas phases are agitated respectively by a $4.25 \cdot 10^{-2}$ m diameter six-bladed Rushton turbine and $4 \cdot 10^{-2}$ m diameter propeller; they are driven magnetically by adjustable speed motor. On the upper flange is connected a DRUCK pressure transducer working in the range 0 to 250 kPa, it is thermostated at temperature higher than the experiment temperature to avoid liquid condensation in its measuring chamber. A tube is settled through the upper flange it allows either to degas the cell or to connect the cell to a reserve of CO₂ gas. The lower flange is provided with a temperature probe, and a non-rotating stem valve. Four vertical baffles are placed inside the cell, in order to avoid the formation of a vortex. The pressure transducer is calibrated within ± 42 Pa against a pressure calibration device. The temperature in the reactor is known within 0.020 K it is calibrated against a 25 Ω platinum probe from LYON ALEMANT LOUYOT. The temperature probe and the pressure transducer are connected to a unit of data acquisition connected to a computer. CO₂ absorption is followed by recording the absolute pressure drop through a DRUCK pressure transducer as a function of time.

Test protocol

Prior to the absorption tests, the saturating pressure of the mixture at different temperatures should be determined, to avoid biased pressure values. Measurements of the saturating vapor pressure of each solvent as a function of given temperature values were carried out. The partial pressure of the solvent at regeneration temperatures is considered in the calculations of partial pressure of the CO₂ during the regeneration tests.

The absorption tests were carried out at three temperatures (20, 30, 40 °C). The aim is to determine the absorption rate and the Arrhenius law for the kinetic constant. The heat

exchanger linked to the cell is set at the desired temperature and the system is left for sufficient period of time until the thermal equilibrium is reached. The solvent is then introduced through the cell's syringe and stirred till it reaches homogeneity. The CO₂ is then introduced to the system for the absorption to start. This operating procedure was validated by several authors when evaluating kinetics of absorption [2, 5].

RESULTS AND DISCUSSION

Absorption experiments

Solvents showed Liquid-Liquid phase separation between amine and water at room temperature. After stirring, an emulsion is formed by the effect of intermolecular hydrogen bonds as commented in previous sections. After CO₂ absorption, the amine-water mixture becomes miscible (Figure 5). A two-liquid phase separation and preliminary desorption of CO₂ (gas bubbles) are visible at temperatures around 70 °C. This phenomenon is in agreement with Zhang *et al.* [5] and Zhang *et al.* [12].

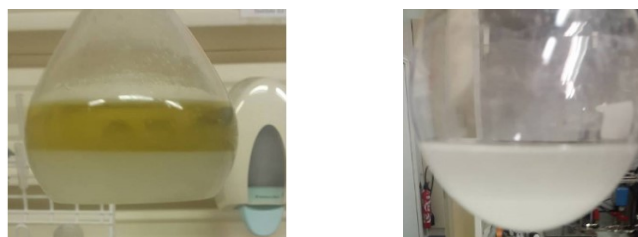


Figure 5. Amine blends before and after agitation

Data collected enables calculations for maximum load capacity of the mixture and the kinetics of absorption and regeneration. The solvent composed of HxA and water exhibited very rapid absorption rate (143 seconds). The DMCA and water solvent takes about 5000 seconds to fully absorb the CO₂. The mixture of DMCA and HxA at 3M concentration and 1 : 2 proportions almost resumed the same kinetics of CO₂ absorption by HxA with a more improved absorption capacity and a return to equilibrium at 181 seconds. The blend of DMCA and HxA at 3M concentration and proportions 2 : 1 respectively also showed an absorption rate close to that of hexylamine alone (234 seconds), with a rapid return to thermodynamic equilibrium. Taking into account that the initial pressures in the cell, before CO₂ injection, and the quantities of CO₂ injected at each test are different normalized pressure values are considered to properly compare all experiments.

Regeneration of solvents

The Lewis cell stands no more than 3 bars, hence, carrying out the regeneration in the cell is complicated. Hence, barely loaded amines solutions are considered so that the regeneration would take place without damaging the cell. It is not intended to determine the maximum regeneration rate of the solvents studied, but to obtain indicators for the best conditions for regeneration of lipophilic solvents.

Figure 6 illustrates the partial pressure of the CO₂ released. Total pressure in the cell results from this partial pressure of CO₂, and vapor pressure of the solvent initially measured. The regeneration of HxA was carried out at 80 °C; however for DMCA it was sufficient to bring it to a temperature of 70 °C.

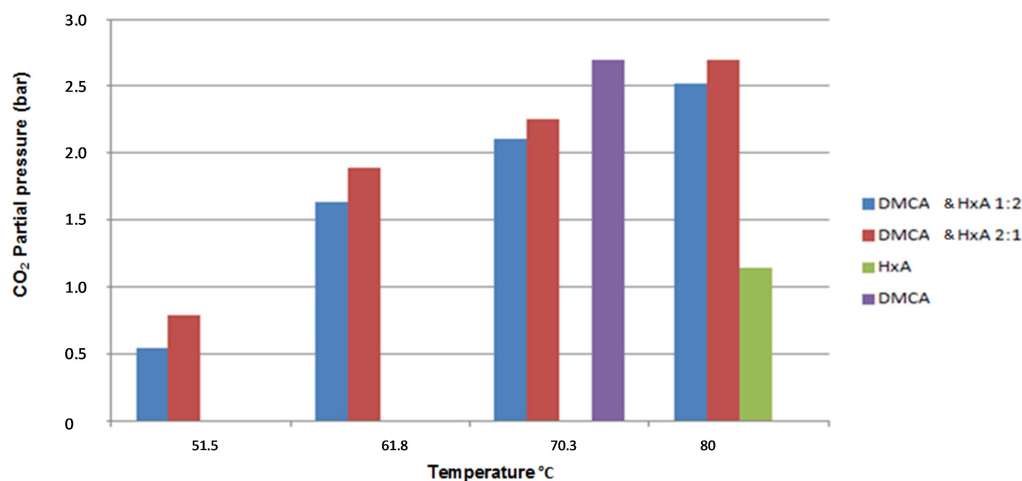


Figure 6. Regeneration temperatures and partial pressure of CO₂ for the tested thermomorphic solvents

The blend of DMCA and HxA at 3M concentration and 1 : 2 ratios respectively also showed better regeneration than HxA, and a phase change was observed at a temperature of 80 °C. As for DMCA and HxA blend at 3M concentration and proportions of 2 : 1 respectively, the regeneration achieved at 80 °C was similar to that of the DMCA at 70 °C, and the phase change appeared at a temperature of 76 °C.

Absorption kinetics

Qualitative comparison of CO₂ enhanced absorption

Versteeg and Oyeveaar [29] have been one of the first works to address the kinetics of CO₂ absorption by amines. In fact while modeling CO₂ absorption, the CO₂ is considered to behave as an ideal gas, and that it is totally consumed by the chemical reaction. It is also considered that the resistance of the gas-side transfer is negligible, since the gas phase only contains pure CO₂. These assumptions have been verified for other work under the same conditions [30].

Experimental data acquisition consists on collecting pressure vs. time values within a time of 1 - 2 seconds and generates a spike in the total pressure values (Figure 7). Pressure decreases as the gas is absorbed by the solvent until equilibrium is again reached.

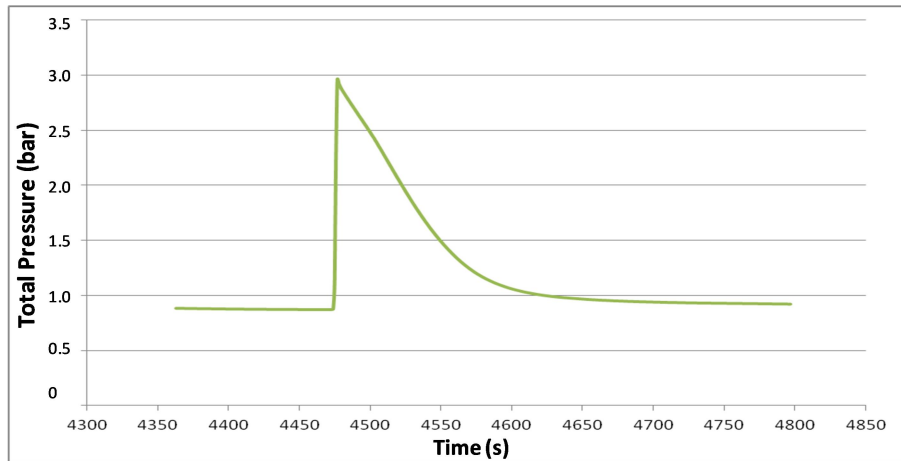


Figure 7. Pressure vs. Time data acquisition of CO₂ absorption by HxA

Absorption data collected at 20 °C for the lipophilic solvents studied are presented in Figure 8. The highest absorption rate is shown by water-HxA, while the lowest rate is shown by water-DMCA. This corresponds to the intrinsic nature of amines as DMCA is a tertiary amine promoter of regeneration and HxA is an absorption activator. Which is outstanding, is that high absorption rate for 1 : 2 and 2 : 2 blends of DMCA/HxA importantly differs from water-DMCA solvents.

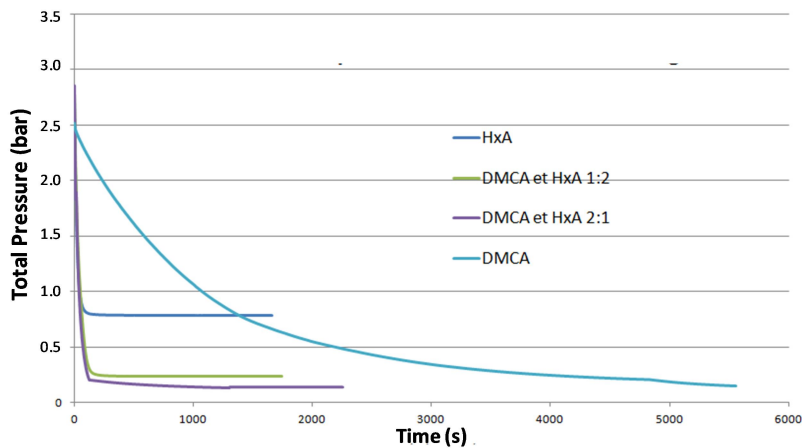


Figure 8. Absorption data collected at 20 °C for the lipophilic solvents studied

From all data collected at 20, 30 and 40 °C, apparent absorption kinetic constants are calculated. In the case of mass transfer with reaction, an enhancement factor E is introduced to assess the difference when non-reactive mass transfer takes place [31]. E is expressed by (Equation 6).

$$E = \frac{\phi}{k_L (C_{CO_2, int} - C_{CO_2, mix})} \quad (6)$$

The concentration in the liquid bulk ($C_{CO_2, mix}$) can be neglected as it is constant and close to zero during the experiment.

The CO₂ flux transferred to the amine aqueous solvent is expressed as follows [31, 32]:

$$\Phi \times A = -\frac{dn(CO_2)}{dt} = \frac{-V_g}{RT} \left(\frac{dP_{CO_2}}{dt} \right) \quad (7)$$

Equations (6) and (7) yield the following equation:

$$k_L E (C_{CO_2, int}) A = \frac{-V_g}{RT} \left(\frac{dP_{CO_2}}{dt} \right) \quad (8)$$

Henry's law is considered in order to determine the CO_2 concentration at the interface:

$$C_{CO_2, int} = \frac{P_{CO_2}}{H_{CO_2}} = \frac{P_T - P_I}{H_{CO_2}} \quad (9)$$

Hence,

$$\ln \left(\frac{P_T - P_I}{P_{T,0} - P_I} \right) = \frac{-K_L \times E \times A \times RT}{V_g H_{CO_2}} (t - t_0) \quad (10)$$

$$\ln \left(\frac{P_T - P_I}{P_{T,0} - P_I} \right) = -\beta (t - t_0) \quad (11)$$

The slope β makes it possible to quantify the enhancement of absorption phenomena, and is directly linked to the kinetics, as it is in fact an acceleration factor. In Figure 9 are compared the performances of each mixture. Steepness of the slope provides the degree of acceleration of the mass transfer due to the reaction kinetics.

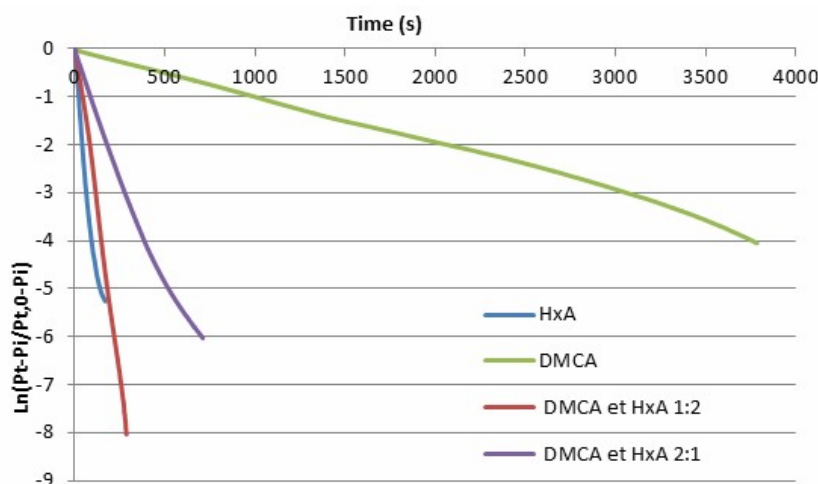


Figure 9. Determination of the β coefficient values for the studied thermomorphic solvents

The most pronounced enhancement corresponds to the fastest kinetics and belongs to the HxA, while the slowest reaction kinetics is observed in the case of DMCA. The blends of different proportions of HxA and DMCA show enhancement phenomena on the absorption of CO_2 step. This is due to the promoter effect of HxA that leads to high reaction kinetics. Results highlight the potential of the solvent resulting from the blend of DMCA and HxA, as it potentially allows rapid kinetics, size reduction on equipments, high absorption capacity and low energy requirements for regeneration. Data collected is used to obtain the apparent constants and it is clear that the mixtures of the two solvents have kinetics very close to that of HxA alone. Thus the HxA, even at

small proportions, has a major impact on the activation of the solvent. The DMCA/HxA blend at 1 : 2 proportions appears to be the most promising solvent, since its kinetics is approximately as rapid as the HxA solvent, while its regenerative capacities at 80 °C were as good as the DMCA solvent.

Calculation of apparent kinetic constants

Apparent kinetic constants would enable the modeling of these new blends and simulation of full processes via softwares, such as Aspen Plus. In fact, these simulation softwares don't take into account the particularity of lipophilic amines, and handle them the same way as classic amines.

In order to calculate the apparent kinetic constant, the determination of density and cinematic viscosity was performed experimentally. The slope β values obtained for each CO₂ injection enable calculations for apparent kinetic constants for each mixture for 3 temperatures and thus determining their corresponding Arrhenius law. The determination of the apparent constant k_{app} needs calculating the coefficient of Hatta (Ha) as can be observed in (Equations 12 and 13).

$$k_{app} = \frac{k_{obs}}{[Amine]^n} \quad (12)$$

$$Ha = \sqrt{\frac{D_{CO2} \times k_{obs}}{k_L^2}} \quad (13)$$

Based on the enhancement factor E value, the Hatta coefficient Ha is obtained by iteration on (Equation 18).

$$E = \frac{Ha}{Tanh(Ha)} \quad (14)$$

From Equation 19 it can be observed that β obtained experimentally, as stated by Equation 15, allows E to be calculated.

$$\beta = \frac{K_L \times E \times A \times RT}{V_g H_{CO2}} \quad (15)$$

The diffusion coefficient D_{CO2} , dynamic viscosity μ , and density ρ values are considered for the calculations of the liquid-side transfer coefficient k_L through the Reynolds (Re), Schmidt (Sc) and Sherwood (Sh) numbers according to the (Equations 16, 17, 18).

$$Re = \frac{\rho N D_{ag}^2}{\mu} \quad (16)$$

$$Sc = \frac{\mu}{\rho D_{CO2}} \quad (17)$$

$$Sh = 0.352 \times Re^{0.618} \times Sc^{0.434} \quad (18)$$

The correlation (18) between dimensionless numbers [31] was developed for a Lewis cell identical to ours. It is therefore possible to finally calculate the apparent kinetic constants and eventually determine the transfer coefficient liquid side k_L according to the Equation 19 (Figure 10).

$$Sh = \frac{k_L d_{cellule}}{D_{CO_2}} \quad (19)$$

As for the Henry coefficient, it is calculated by the methods given by Al-Ghawas *et al.* [33], based on the temperature of tests and the % w of amines in the aqueous solvent. The diffusion coefficient of CO₂ in the solvent referred to as D_{CO_2} was calculated according to the correlation given by Frank *et al.* [34] based on CO₂ diffusivity in water and in the amine which were collected from the data published by Bharatiya *et al.* [35].

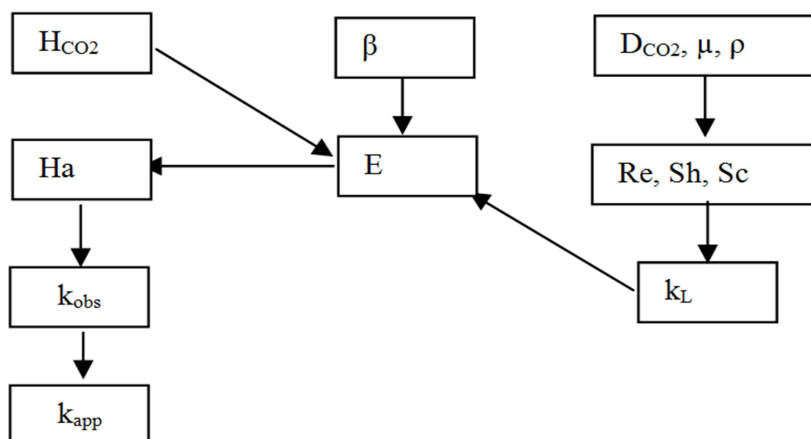


Figure 10. Calculation method for apparent kinetic constant

The general Arrhenius law equation for kinetics is expressed as shown in the (Equation 20), where Ea and a are constants to be determined. In fact, by obtaining at least three values of k_{app} at different temperatures, it would be possible to determine the constants Ea and a , and further determining the expression of k_{app} as a function of temperature. The linearization that facilitates Ea and a of the Arrhenius law is carried out by calculating $\ln(k_{app})$ as a function of $1/T$.

$$k_{app} = a e^{\left(\frac{-Ea}{RT}\right)} \quad (20)$$

Except for DMCA and DPA [11], apparent kinetic constants for lipophilic solvents seem barely studied. Thus, we will first treat the CO₂ absorption data with a DMCA solution in order to confirm the chosen method of calculation, as well as the precision, due to the different approximations. The results of the calculations for the DMCA are summarized in Table 3.

Table 3. Apparent kinetic constants of CO₂ in the case of absorption by the DMCA

Temperature	293 K	303 K	313 K	313 K (by Tan 2010)
$k_{app} [m^3 \cdot mol^{-1} \cdot s^{-1}]$	2.13×10^{-7}	7.77×10^{-7}	2.59×10^{-6}	2.84×10^{-6}

The results obtained by our calculations are consistent with the values given by Tan [11]. Thus, the method used is validated, and the approximations made during the calculation do not affect the accuracy of values obtained. Table 4 presents the constants of kinetic law for solvents of 3M DMCA and 3M HxA for the absorption of CO₂.

Table 4. Constants of kinetic law for DMCA and HxA

Temperature	293 K	303 K	313 K	Activation energy [kJ·mol ⁻¹]	Pre-exponential factor [mol·m ² ·s ⁻¹]
DMCA	2.13×10^{-7}	7.77×10^{-7}	2.59×10^{-6}	95.19	2.004×10^{10}
HxA	0.0012	0.0017	0.0021	18.76	2.89

The calculation of the apparent kinetic constants in the case of HxA and DMCA blends is obtained according to the correlation (21) developed by Littel *et al.* [24] for mixtures of primary or secondary amines with tertiary amines. The correlation can only be used in cases of excessive amine concentrations.

$$k_{obs} = k_{app1} + k_{app,R3N}[R_3N] \quad (21)$$

The (Equation 21) makes it possible to obtain three values of apparent kinetic constant for blends throughout the apparent kinetic constant for DMCA 3M and HxA 3M solvents, with attention to the concentration of each amine in the blend. Table 5 presents the kinetic calculations of the pre-exponential factor A and activation energy for the studied blends.

Table 5. Constants of kinetic law for DMCA and HxA blends at different compositions

Temperature	293 K	303 K	313 K	Activation energy [kJ·mol ⁻¹]	Pre-exponential factor [mol·m ² ·s ⁻¹]
DMCA & HxA (1 : 2)	0.0012894	0.001749	0.002150	19.35	3.97
DMCA & HxA (1 : 1)	0.0012919	0.001757	0.002178	19.95	4.72
DMCA & HxA (2 : 1)	0.0012942	0.001766	0.002210	20.44	5.77

Results presented in Table 5 confirm the qualitative comparison of different blends kinetics related to the CO₂ absorption. In fact the quantitative method based on apparent kinetics constants calculations confirms results obtained on the qualitative behavior of HxA-DMCA blends through the k_{app} values. The calculations presented by both Tables 4 and 5 are new to literature since, as far as we know, haven't been published before. This would enable any modelling and simulation work, and would encourage the use of lipophilic solvents and their blends. Further work shall focus in the mechanisms of reaction and the kinetics of each step of chemical reaction, as presented by Charry Prada *et al.* [36] and previously by Rivera-Tinoco and Bouallou [37].

CONCLUSIONS

This study presents a comparative analysis between the aqueous solvent of HxA, the aqueous solvent of DMCA and their blends at two different proportions through two approaches. Encouraging results were yielded from the absorption/regeneration experiments. Processed data from the Lewis cell demonstrated that the blends were able to retrace almost the same rapid kinetics of the HxA and the outstanding regenerability of DMCA at 80 °C. In particular the DMCA-HxA at 1 : 2 proportions respectively

showed a very rapid kinetics very similar to the HxA's kinetics and a good regenerability. While the calculations of the apparent kinetics constant confirmed the initial results, follow up studies should be performed to evaluate the solvents degradation and loss, so it would be suitable for CO₂ removal from streams of industrial processes.

LIST OF NOTATIONS

[amine]	Amine concentration ($\text{mol}\cdot\text{m}^{-3}$)
[R3N]	Tertiary amine concentration ($\text{mol}\cdot\text{m}^{-3}$)
A	Interface area (m^2)
a	Pre-exponential factor
$C_{\text{CO}_2, \text{int}}$	CO ₂ concentration in the gas-liquid interfacial area ($\text{mol}\cdot\text{m}^{-3}$)
$C_{\text{CO}_2, \text{mix}}$	CO ₂ concentration in the liquid bulk ($\text{mol}\cdot\text{m}^{-3}$)
D_{CO_2}	Diffusivity of CO ₂ in solvents
d_{cellule}	Lewis cell diameter (m)
D_{ag}	Agitator diameter (m)
E	Enhancement factor
E_a	Activation energy ($\text{kJ}\cdot\text{mol}^{-1}$)
H_{CO_2}	CO ₂ Henry's constant ($\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$)
Ha	Hatta coefficient
k_L	Liquid phase mass transfer coefficient ($\text{m}\cdot\text{s}^{-1}$)
k_{app}	Apparent kinetics constant
k_{app1}	Primary amine apparent kinetic constant
$k_{\text{app,R3N}}$	Tertiary amine apparent kinetic constant
k_{obs}	Overall kinetic constant
n	Partial amine order in the reaction
N	Turn speed rps (90 rps in this case)
P_{CO_2}	CO ₂ pressure (Pa)
P_1	Inert pressure (Pa)
P_T	Total pressure at t (Pa)
$P_{T,0}$	Total Pressure at 0 (Pa)
R	Ideal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
Re	Reynolds dimensionless number
R_i	Carbon group bonded to the nitrogen atom
Sc	Schmidt dimensionless number
Sh	Sherwood dimensionless number
T	Temperature (K)
t	Time (s)
V_g	Gas volume (m^3)
Φ	CO ₂ flow rate ($\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)
ρ	Density ($\text{kg}\cdot\text{m}^{-3}$)
μ	Dynamic viscosity ($\text{N}\cdot\text{s}\cdot\text{m}^{-2}$)

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