

Available online at www.sciencedirect.com**ScienceDirect**

Energy Procedia 63 (2014) 1854 – 1862

Energy
Procedia

GHGT-12

Screening tests of new hybrid solvents for the post-combustion CO₂ capture process by chemical absorption

Julien Gervasi^a, Lionel Dubois^a and Diane Thomas^{a*}^a *Chemical and Biochemical Engineering Department, Faculty of Engineering, University of Mons, 20 Place du Parc, 7000 Mons, Belgium*

Abstract

This study focused on the screening of new hybrid solvents (mixture of a chemical (usually an amine) and a physical (ether, alcohol, etc.) solvent) for the post-combustion CO₂ capture process by chemical absorption. Such scrubbing solutions aim at combining the advantages of the two components, namely: a low regeneration energy and a high absorption capacity of the physical solvent at intermediate CO₂ partial pressures, a better absorption performances of the chemical solvent at low CO₂ partial pressures and also high absorption kinetics due to chemical reactions with CO₂. The innovative aspect of our approach was based on the use of acetals as physical components of the hybrid solvent. The purpose of our study was to characterize and compare these new hybrid solvents in terms of absorption and regeneration performances using two types of screening tests. Different blended solutions (composed of a conventional amine such as monoethanolamine (MEA), diethanolamine (DEA), 2-amino-2-methyl-1-propanol (AMP)) and an acetal compound such as 2,5,7,10-tetraoxaundecane (TOU) were tested.

Regarding the absorption performances, a double stirred cell reactor was used to compare the absorption efficiencies of the solvents at 298 K. It was observed that the addition of the acetal compound improves significantly the absorption efficiencies, especially at the beginning of the batch absorption test, namely at low CO₂ loadings of the solution. Meanwhile, regeneration tests were performed using a regeneration cell allowing to compare the regeneration efficiency of the solvents at fixed heating power (600 W). The higher cyclic capacities and better regeneration efficiencies with acetals base solvents were also highlighted.

Globally, this work confirms through this first step that new hybrid solvents, composed of amine(s) and acetal, could be a very promising alternative to classical solvents.

© 2014 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Peer-review under responsibility of the Organizing Committee of GHGT-12

* Corresponding author. Tel.: +32 65 37 44 04; fax: +32 65 37 44 07
E-mail address: Diane.Thomas@umons.ac.be

Keywords: postcombustion CO₂ capture ; chemical absorption ; hybrid solvents ; screening

Nomenclature

A	[%]	CO ₂ absorption ratio of the scrubbing solution
C _{CO₂}	[mol m ⁻³]	CO ₂ concentration of the scrubbing solution
G _{CO₂,in}	[m ³ s ⁻¹]	CO ₂ gas flow rate at the inlet of the gas-liquid contactor
G _{CO₂,out}	[m ³ s ⁻¹]	CO ₂ gas flow rate at the outlet of the gas-liquid contactor
IC	[kg m ⁻³]	inorganic carbon content of the scrubbing solution
t	[s]	time
Y _{CO₂,in}	[vol.%]	CO ₂ volume fraction of the gas phase at the inlet of the gas-liquid contactor
Y _{CO₂,out}	[vol.%]	CO ₂ volume fraction of the gas phase at the outlet of the gas-liquid contactor
η _{regen}	[%]	regeneration efficiency of the scrubbing solution

1. Introduction

The reduction of industrial CO₂ emissions is an important issue in order to reduce the greenhouse gas emissions. In this context, the post-combustion CO₂ capture process by chemical absorption appears to be one of the CO₂ capture technology that is close to an industrial deployment. Nevertheless, there is still a need for new solvents that can replace the conventional ones, such as for example the aqueous solution of monoethanolamine (MEA), especially to reduce the operating costs of the process, the main part of these costs being linked to the heating energy needed for the solvent regeneration at the stripper (around 3.5 GJ/t_{CO₂} [1-3] for the benchmark MEA 30%)

In this study, we focused on the second generation of solvents and especially on hybrid solvents. These ones result of a mixing between: a chemical solvent (which can be an amine) and a physical solvent (composed of an ether, an alcohol, etc.). The main interest of such absorption liquid is the fact that it aims at combining the advantages of the components of the solvents, namely: a low regeneration energy and a high absorption capacity of the physical solvent at intermediate CO₂ partial pressures, better absorption performances of the chemical solvent at low CO₂ partial pressures and also high absorption kinetics thanks to the chemical reactions with CO₂.

The innovative aspect of this study was based on the use of acetals as physical components of the hybrid solvent. Such chemical compounds are characterized by two ether groups attached to the same carbon atom. Furthermore, such organic compounds are already used in several applications (painting, pharmaceutical chemistry, cosmetics, textile industry, detergents, etc.) that make them very cheap. Among the acetals available, first screening tests reveal that the focus should be put on the 2,5,7,10 -Tetraoxaundecane (TOU) (see Fig. 1).

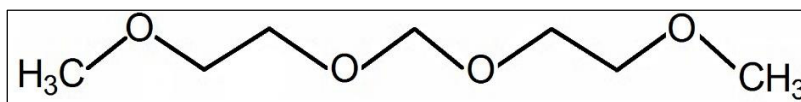


Fig. 1. Chemical structure of 2,5,7,10 -Tetraoxaundecane (TOU) (CAS number: 4431-83-8)

Regarding the chemical part of the solvents tested, different amine based compounds were considered, namely: monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP) and also piperazine (PZ) as absorption activator.

Among the different criteria that must be taken into account in the choice of a solvent (absorption performances and energy consumption for the solvent regeneration, solvent resistance against degradation [4] which can induce corrosion problems [5] and higher solvent consumption, solvent toxicity [6] and volatility [7], etc.), many technical

and economic studies (such as [8]) highlighted that the two most important criteria in a solvent screening are absorption and regeneration efficiencies. The purpose of our study was therefore to characterize and compare our new hybrid solvents in terms of absorption and regeneration performances using two types of batch screening tests.

2. Experimental devices and procedures

2.1. Absorption tests

The absorption performances of the different hybrid solvents were measured and compared using the experimental apparatus illustrated on Fig. 2, which includes a gas-liquid contactor, a gas supply, and a gas sampling part.

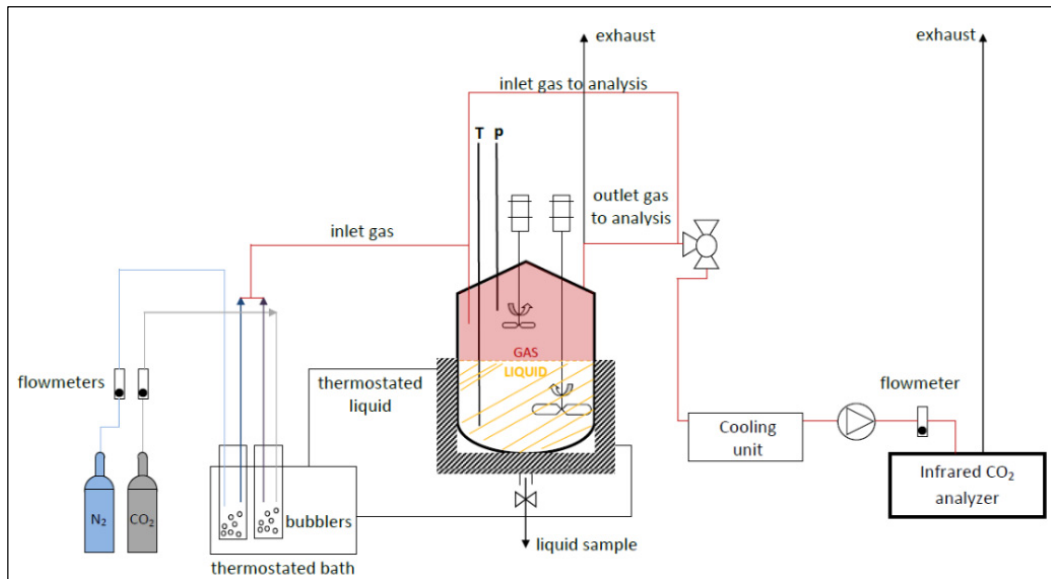


Fig. 2. Experimental apparatus used for the absorption tests including the double stirred cell contactor (DSCR)

The gas-liquid contactor, namely a glass double-stirred cell reactor (0.15 m in diameter and 0.245 m in tank height) has a constant gas-liquid interfacial area. It has six lid holes: two for the gas inlet and outlet, two for the liquid temperature probe (type Pt100) and for the electronic pressure probe in the gas phase, and the two last for the gas stirring bar (helical shape of 5 cm, located in the upper part of the reactor) and for the liquid stirring bar (PTFE anchor with a wingspan of 8 cm, located in the lower part) agitated separately by two stirring motors. The reactor is pre-filled with $1 \cdot 10^{-3} \text{ m}^3$ of the solution to be tested. The jacket of the cell is flowed by water coming from an external thermostating system whose heating power is automatically controlled providing the desired solution temperature within the cell. The absorption solution is stirred to ensure proper mixing of the liquid phase but also to maintain a perfectly flat gas-liquid interface (without wrinkles). The gas phase, previously humidified in a gas bubbler, is composed of N₂ and CO₂ at the desired concentration ($y_{\text{CO}_2, \text{in}} = 10 \text{ vol. } \%$) and is continuously fed into the reactor.

The total inlet gas flow rate is metered by a rotameter. Sampling of gas at the input and the output of the contactor is performed alternatively through a cooling unit followed by an IR analyzer (Fuji Electric, model: ZRJ-3) giving respectively the temporal evolution of $y_{\text{CO}_2, \text{in}}$ and $y_{\text{CO}_2, \text{out}}$ and allowing to calculate the temporal evolution of the CO₂ absorption ratio (A) [%] for different scrubbing solutions:

$$A(t) = \frac{G_{\text{CO}_2, \text{in}} - G_{\text{CO}_2, \text{out}}(t)}{G_{\text{CO}_2, \text{in}}} = \frac{y_{\text{CO}_2, \text{in}} - y_{\text{CO}_2, \text{out}}(t)}{y_{\text{CO}_2, \text{in}} (1 - y_{\text{CO}_2, \text{out}}(t))} \quad (1)$$

where $G_{\text{CO}_2,\text{in}}$ [$\text{m}^3 \text{s}^{-1}$] and $y_{\text{CO}_2,\text{in}}$ [vol.%] are respectively the CO_2 flow rate and volume fraction in the gas phase at the inlet of the contactor, $G_{\text{CO}_2,\text{out}}$ [$\text{m}^3 \text{s}^{-1}$] and $y_{\text{CO}_2,\text{out}}$ [vol.%] being the CO_2 flow rate and volume fraction in the gas phase at the outlet of the contactor. All semi-continuous tests reported here were carried out at atmospheric pressure and at a temperature equal to 298 K. Hydrodynamic conditions, namely the total gas flow rate ($8.33 \cdot 10^{-5} \text{ m}^3/\text{s}$) and stirring speeds (35 rpm for the liquid phase and 500 rpm for the gas phase), were kept constant in all the experiments, comparing only the use of different chemical and hybrid solvents. For the liquid phase, samples of the solvent were analyzed in terms of pH (pH meter Mettler Toledo, electrode LE438 in polypropylene) and by a Total Organic Carbon analyzer (Shimadzu, TOC-VCSH, NDIR detector) which gives information about the concentration of inorganic compounds, leading to the quantity of CO_2 absorbed per volume unit of solvent.

2.2. Regeneration tests

The regeneration performances of the different hybrid solvents were measured and compared using the device presented on Fig. 3. It is composed of a regeneration cell corresponding to a three-necked flask of $0.25 \cdot 10^{-3} \text{ m}^3$, and it includes a thermo-regulated heating system (Ika, RCT Basic, maximum heating power of 600 W) with a Pt100 temperature sensor immersed in the solution and a magnetic stirring system (operating stirring speed of 500 rpm) to ensure the homogeneity of the liquid phase. A condenser (length of 0.35 m) installed at the top of the flask and flowed by cooling water (278 K) provided by an external cooling system aims at condensing the vapor products issued from the evaporation of the aqueous CO_2 -solvent solution.

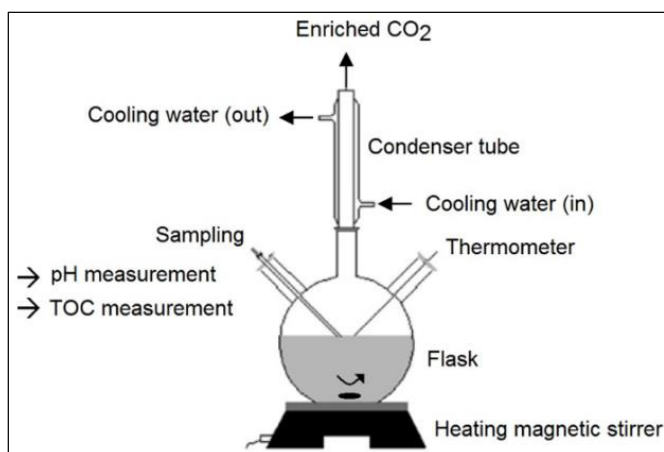


Fig. 3. Experimental apparatus used for the regeneration tests

Prior to the regeneration experiment, the hybrid solvent is gradually loaded with CO_2 up to its saturation thanks to a gas bubbler flowed by a pure CO_2 flow rate. At the end of this saturation step, the pH of the loaded solvent is measured and its CO_2 concentration (in terms of inorganic carbon concentration, $IC(0)$ [$10^{-6} \text{ kg C m}^{-3}$]) is determined with the TOC analyzer. The solution (volume of $0.25 \cdot 10^{-3} \text{ m}^3$) is then transferred in the regeneration cell in which it is stirred (stirring speed of 500 rpm) and heated (constant heating power of 600 W) up to its boiling point. The duration of the test was fixed at 120 min. During the test, samples of the solution are regularly withdrawn and analyzed to determine their pH and their CO_2 concentration (C_{CO_2} [mol m^{-3}]) deduced from the inorganic carbon content, $IC(t)$ [$10^{-6} \text{ kg C m}^{-3}$]) allowing to deduce the regeneration efficiency ($\eta_{\text{regen}}(t)$) of the solution, conventionally defined as:

$$\eta_{\text{regen}}(t) = \frac{IC(t) - IC(0)}{IC(0)} \quad (2)$$

Although such tests do not give direct access to the regeneration energy of the hybrid solvents, the measure of the temporal evolution of the regeneration efficiency at identical operating conditions advantageously allows comparing the regeneration potential of such solvents.

3. Results and discussion

The absorption and regeneration performances measured with various hybrid solvents are compared to the ones obtained for a reference solvent, namely MEA 30 wt.% (benchmark solvent for post-combustion CO₂ capture). Globally, the tested systems were generally made of 30 wt.% of amine, 35 wt.% of TOU and 35 wt.% of water. The proportion of TOU (physical part of the solvent) and the amine (chemical part of the solvent) were chosen considering another existing hybrid process as reference, namely the Sulfinol [9] one.

3.1. Absorption results

Fig. 4 (a) and 4 (b) compare the temporal evolution of the absorption ratio and of the CO₂ content in the liquid phase measured with the reference solvent (namely MEA 30%) and with the hybrid solvent (composed of MEA 30% and TOU 35%).

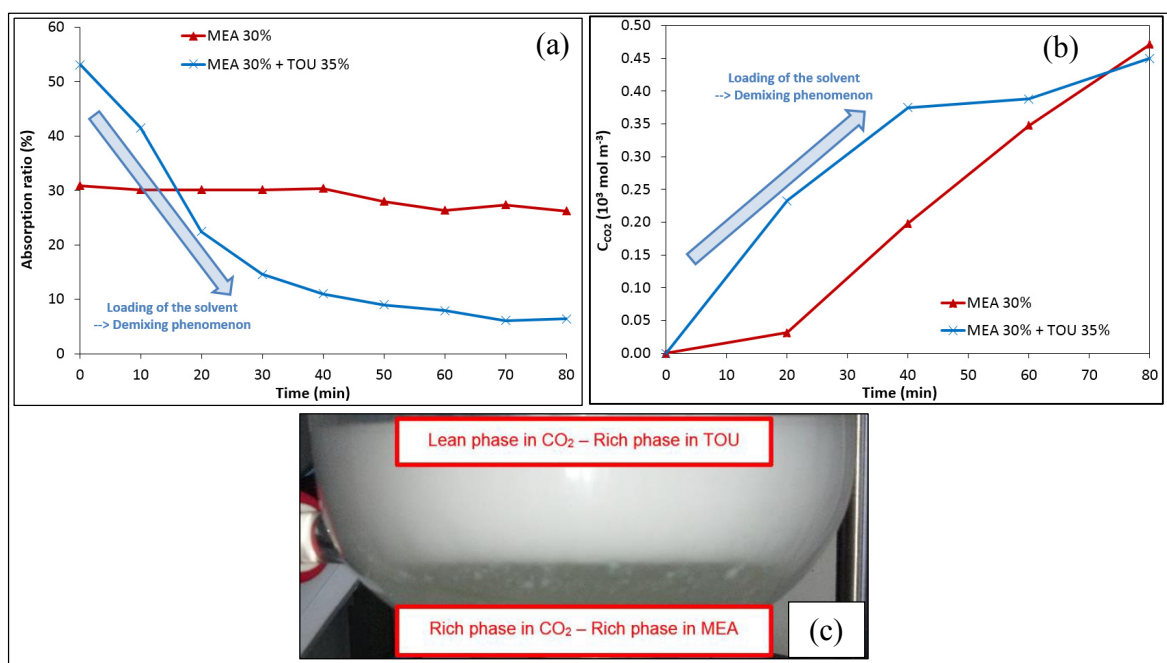


Fig. 4. Temporal evolution of the absorption ratio (a) and of the CO₂ concentration (b) measured with MEA 30% and MEA 30% + TOU 35% solvents (c) Demixing phenomenon enhanced with pure CO₂ bubbling

It can be observed on Fig. 4 (a) that the initial absorption performances of the hybrid solvent are clearly better than the MEA 30% ones (53% against 31%). Logically, as represented on Fig. 4 (b), the CO₂ concentration increases more quickly in the hybrid solvent (heavy phase) than in MEA 30%, the final CO₂ concentrations being almost identical for the two solvents (around 0.45 10³ mol CO₂ m⁻³). Unfortunately, the absorption performances of the hybrid solvent decrease dramatically during the absorption test. This phenomenon was linked to the progressive apparition of a layer in the solvent at the gas-liquid interface. As illustrated on Figure 4 (c), this layer is becoming bigger while the CO₂ is absorbed by the solvent. This demixing phenomenon prevents the CO₂ to be directly absorbed into the solvent which

leads to the decrease of the absorption performances. Note that this decrease is partially linked to the particular hydrodynamics of our contactor (horizontal and flat gas-liquid interface).

Thanks to additional tests like TOC/IC/pH measurements and FTIR (Fourier Transform Infrared Red spectroscopy) analyses it was possible to confirm that the light phase of the hybrid solvent was poor in CO₂ and mainly composed of water and TOU, while the heavy phase was rich in CO₂ and mainly composed of water and MEA. It should be noted that in an industrial process, it is possible to take advantage of this demixing phenomenon, as for example in the DMX™ process [10]. Indeed, in such process, by installing a decanter between the two columns, only the phase rich in CO₂ is sent to the stripper, which reduces the liquid flow rate in this column and thus the energy requirement for the regeneration of the solvent. Thanks to the use of such demixing process, [10] predict a reduction of around 40% of the regeneration energy in comparison with the classical process using MEA 30%.

Fig. 5 (a) and (b) allow the comparison of the absorption performances of different hybrid solvents in terms of initial (unloaded solution), mid-test (partially loaded solution after 40 min of the absorption experiment) and final (loaded solution at the end of the test corresponding to 80 min of the absorption experiment) absorption ratios, and in terms of mid-test and final CO₂ concentrations (always measured in the rich phase in CO₂).

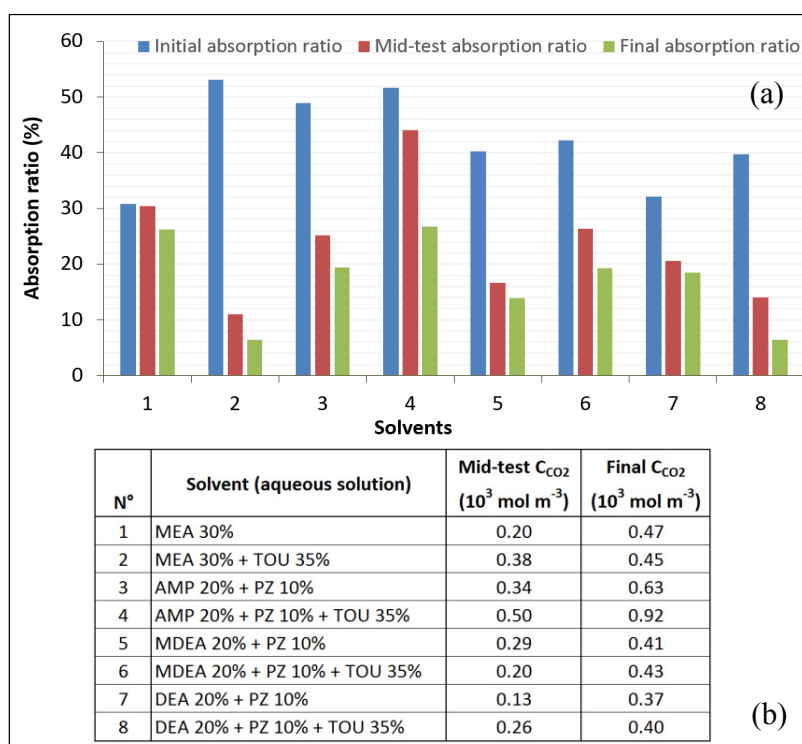


Fig. 5. (a) Initial, mid-test (after 40 min) and final absorption ratios of different amine(s) based and hybrid solvents
(b) Mid-test (after 40 min) and final CO₂ concentrations of the different solvents tested

It can be observed that for all the systems with TOU (N°2, 4, 6 and 8) where a similar demixing phenomenon was observed, the initial absorption performances of the hybrid solvents (with TOU 35%) are better than the amine(s) based solvents ones, especially for MEA 30% and DEA 20% + PZ 10%. The decrease of the absorption ratio due to the CO₂ loading of the solution is also clearly illustrated, especially in the presence of TOU. The best final absorption performances of hybrid solvents were measured with the blend composed of AMP 20% + PZ 10% + TOU 35%, this solution (N°4) leading to the highest final CO₂ concentration (respectively 0.63 and 0.92 10³ mol CO₂ m⁻³ for the

solvent without and with TOU, see Fig. 5 (b)), all the final C_{CO_2} measured with the other solvents being in the range 0.37 to $0.47 \cdot 10^3 \text{ mol CO}_2 \text{ m}^{-3}$.

Note that the mid-test C_{CO_2} values confirm the fact that the hybrid systems (containing TOU) involve a lower CO_2 transfer during the second part of the test (from 40 min to 80 min) due to the demixing phenomenon.

3.2. Regeneration results

The regeneration performances of different solvents are compared in terms of temporal evolution of the CO_2 concentration (C_{CO_2}), the regeneration efficiency (η_{regen}) and the pH on Fig. 6 (a), (b) and (c) respectively.

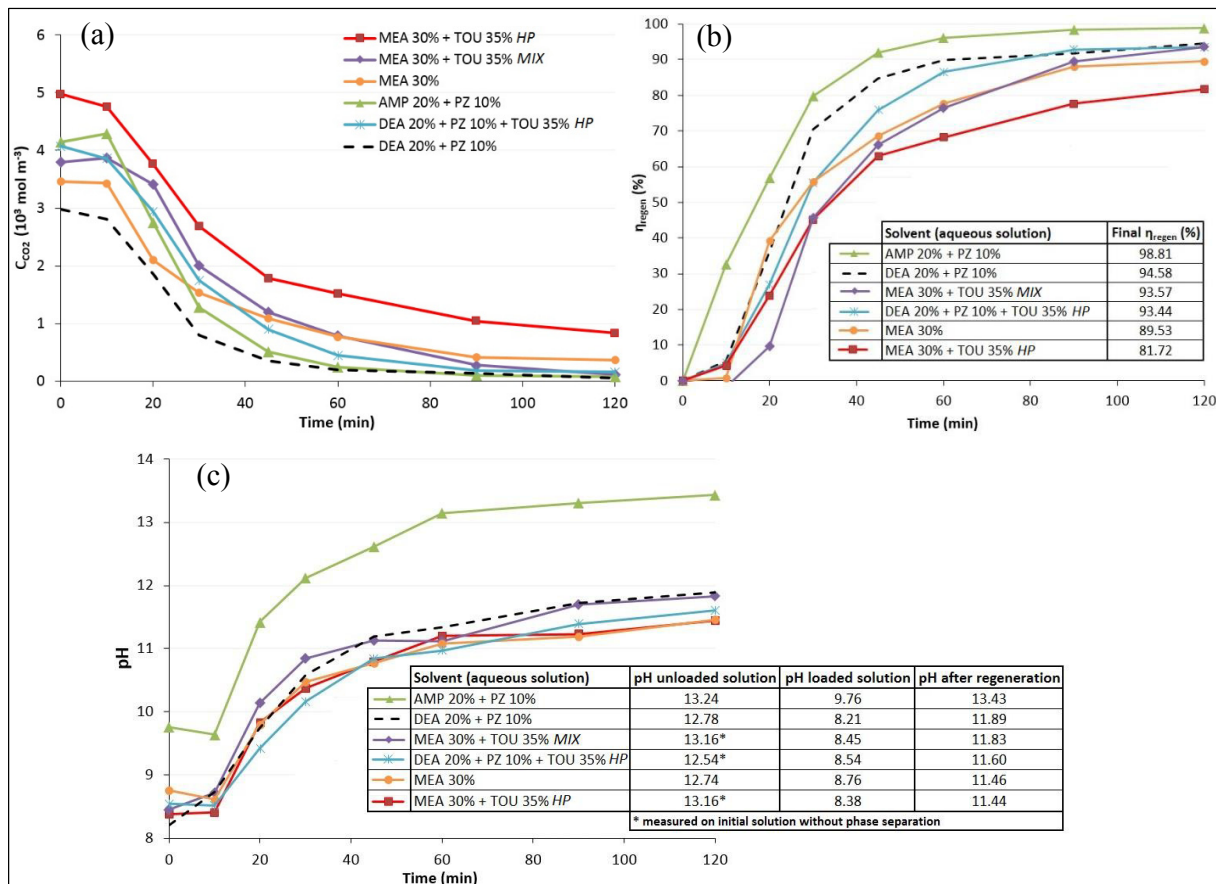


Fig. 6. Temporal evolution of the CO_2 concentration (a), the regeneration efficiency (b) and the pH (c) of the different solvents

It must be noted that the regeneration of the AMP 20% + PZ 10% + TOU 35% solution was not possible due to crystallization problems during the saturation step before the regeneration test. Furthermore, two types of regeneration tests were performed with MEA 30% + TOU 35%: with the emulsion obtained by mixing the two phases (noted “MIX” in the graphs legends) and by regenerating the heavy phase only (noted “HP” in the graphs), namely the CO_2 rich phase. Regarding the blend composed of DEA 20% + PZ 10% + TOU 35%, only the heavy phase was regenerated. It can be observed on Fig. 6 (a) and (b) that logically, C_{CO_2} is decreasing during the regeneration test which leads to an increase of the regeneration efficiency. The highest initial CO_2 concentration was measured with the MEA 30% + TOU 35% HP solution (namely $4.97 \cdot 10^3 \text{ mol CO}_2 \text{ m}^{-3}$) and the lowest with the DEA 20% + PZ 10% solution ($2.97 \cdot 10^3 \text{ mol CO}_2 \text{ m}^{-3}$). This parameter gives an idea of the absorption capacity of the solution.

Regarding more specifically the final regeneration efficiency (see legend of Fig. 6 (b)), the best performances were measured with the AMP 20% + PZ 10% solution (η_{regen} around 99%). Concerning the hybrid solvents, η_{regen} (around 93.5%) for DEA 20% + PZ 10% + TOU 35% HP and for MEA 30% + TOU 35% MIX are higher than for MEA 30% (around 90%). Note that even if the final value of η_{regen} for MEA 30% + TOU 35% HP (82%) is lower than the one of the mixed phase solution, the interest of regenerating only the rich phase is already confirmed in other studies [10] in terms of lower energy consumption linked to a lower liquid flow rate fed into the regeneration column.

Finally, the observations of the regeneration performances were confirmed with the comparison of the pH temporal profiles (see Fig. 6 (c)) to the pH values of the loaded and unloaded solutions (see the graph legend of Fig. 6 (c)). Indeed, the final pH of the AMP 20% + PZ 10% solution (13.43) is very close to the pH value of unloaded AMP 20% + PZ 10% solution (13.24) indicating an almost complete regeneration of the solution. On the contrary, the final pH of MEA 30% + TOU 35% HP solution (11.44) is still clearly different from the pH value of unloaded solution (13.16) due to substantial CO₂ quantities remaining in solution. Such observation was confirmed with the other solvents, namely better regeneration performances lead to a final pH value close to the value measured with the unloaded solution.

4. Conclusions

The purpose of this study was to highlight new solvents than could replace the conventional ones, such as MEA, for the post-combustion CO₂ capture process by chemical absorption. The innovative aspect of this research was the use of acetal, and especially the 2,5,7,10-tetraoxaundecane (TOU), as physical part of new hybrid solvents composed of amine(s) based compound(s).

In order to compare the absorption and regeneration performances of the solvents two types of experiments were performed. For the first aspect, namely the absorption performances, a double stirred cell reactor was used to compare the absorption efficiencies of the solvents with fixed operating conditions at 298 K. From all the screening tests performed with different blended solutions (composed of a conventional amine such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine, 2-amino-2-methyl-1-propanol (AMP) and piperazine (PZ) as absorption activator) and an acetal compound (namely (TOU)), it was observed that the addition of the acetal compound improves significantly the absorption efficiencies, especially at the beginning of the batch absorption test, namely at quite low CO₂ loadings of the solution. Indeed, all the results showed quite logically a decrease of the performances with an increase of the CO₂ loading of the solution. This decrease was also partially linked to a demixing phenomenon which is still under investigations.

In the second step of our experimental works, regeneration tests were performed with the same solvents by using a regeneration cell which allows to compare the regeneration efficiency of the solvents at fixed heating power (600 W). The promoting effects of the acetal were also highlighted for the MEA 30% + TOU 35% solution in terms of better regeneration efficiencies. Note that the pH of each solution tested during these screening tests was also measured and found to be related to the CO₂ concentration of the solvent.

Globally, this work confirms that new hybrid solvents, composed of amine(s) and acetal, could be a very promising alternative to classical solvents. Such chemical systems still need more investigations in order to optimize the solvent composition and to better understand the demixing phenomenon observed. In a next step, after the selection of the most promising hybrid solvents, the absorption-regeneration performances will be evaluated by carrying out tests with a CO₂ capture laboratory micro-pilot. This device will be also adapted to test biphasic solvents and we expect to be able to simulate the absorption tests carried out with such hybrid systems.

Acknowledgements

J. Gervasi is grateful to the Chemical Engineering Department of the University of Mons for this research achieved during his Master's thesis and Research Fellowship. UMONS acknowledges Lambiotte Company for providing the acetals in order to carry out the screening tests. UMONS would like also to acknowledge the European Cement Research Academy (ECRA) and HeidelbergCement Company that allowed the presentation of this research at the GHGT-12 conference thanks to the financial support according to the ECRA Academic Chair.

References

- [1] M. Karimi et al., *Chem. Eng. Res. Des.*, 2011, 89 (8), 1229.
- [2] J.N. Knudsen et al., *Energy Procedia*, 2009, 1, 783.
- [3] P. Moser et al., *Energy Procedia*, 2011, 4, 1310.
- [4] I. Eide-Haugmo et al., *Energy Procedia*, 2011, 4, 1631.
- [5] J. Kittel et al., *Energy Procedia* 2009, 1, 791.
- [6] I. Eide-Haugmo et al., *Energy Procedia* 2009, 1, 1297.
- [7] T. Nguyen et al., *Int. J. Greenhouse Gas Control* 2010, 4 (5), 707.
- [8] L. Raynal et al., *Distillation Absorption Proceedings*, Eindhoven University of Technology, Eindhoven 2010, 121.
- [9] M. T. Angaji et al., *J. Nat. G. Sci. Eng.*, 2013, 15, 22.
- [10] L. Raynal et al., *Energy Procedia*, 2011, 4, 779.