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Lipophilic Amine Aqueous Solutions for CO_2 Capture: Comparison of Absorption Rates For Hexylamine (Hxa), Dimethylcyclohexylamine (DMCA) And Hxa-DMCA Mixtures

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The low attractiveness and competitiveness of carbon dioxide capture processes play against their deployment. Besides considerable investment costs for capture units and potential leakage of amines into the environment, conventional amine-aqueous solvents commonly used consume steam at temperatures ranging from 120 °C till 140 °C for the regeneration of solvent. A series of novel lipophilic amine solvents with low regeneration temperature are here studied with the aim to improve CO_2 capture processes. This paper presents a comparison of the performance of single HexylAmine 3 M solvent and the mixture of DiMethylCyclohexylAmine/HexylAmine, at different compositions and temperatures. The absorption of CO_2 was performed at 20 °C, 30 °C and 40 °C, in order to define the respective kinetic law. Experimental results obtained in a Lewis cell apparatus show the impact of amines composition on the kinetics of absorption. Besides, both absorption and regeneration rates are studied. Results show outstanding outcomes compared to the conventional aqueous solvent containing MonoEthanolAmine (MEA) and enable novel lipophilic solvents to be suggested for low energy carbon capture processes.

1. Introduction

Bottoms et al. (1931) was the first, as early as 1931, to study amines in the absorption of CO_2. Indeed, it has shown that monoethanolamine (MEA) has a high capacity of absorption of acid gases. Work on amines, both experimentally (Rivera-Tinoco and Bouallou, 2010) and modelling (Cadours and Bouallou, 1998) has made it possible to confirm such results. Alkanolamines and their aqueous solutions became the most widely used solvents in gas treatment processes; these amines (referred to as conventional amines) require a regeneration temperature of about 120 °C. Amines are subdivided into primary, secondary and tertiary depending on the position of the nitrogen atom in the molecule. In fact, the primary and secondary amines exhibit faster reaction kinetics than the tertiary amines which, on the other hand, exhibit better absorption capacity and a lower stripping energy than the primary and secondary amines. The choice of an amine during the treatment of acid gases depends, essentially, on the content and kind of acid gases to be removed, as well as on the equipment (investment and operating) costs. The step of solvent regeneration 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 Amman and Bouallou (2009).
According to Zhang et al. (2011) all scientific progress aiming at reducing regeneration energy with conventional solvent mixtures have yielded only very modest reduction results with an unsatisfactory CO_2 absorption capacity. Only biphasic solvents, known as thermomorphic solvents, allegedly offer a potential energy reduction of 35 % compared to the MEA solvents (Goto et al., 2009). These solvents are characterized by a limited solubility in water. Stirring the mixture at temperatures of 30 °C to 40 °C allows the formation of hydrogen bonds between the hydrogen in the amine molecule and the oxygen in the water molecule; thus forming a homogeneous medium and allowing the absorption of CO_2 in the absorber. Phase equilibrium of these solvents when heat is supplied (increase of temperature) leads to a separation into two liquid phases, a lower aqueous phase rich in CO_2 and an organic upper phase rich in amines (Tan, 2010). A miscibility gap is induced starting from

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temperatures of about 70 °C. While regenerating, the heat supply increases the kinetic energy of the molecules and thus weakens the intermolecular bonds. The auto-associative nature of water causes the creation of intramolecular bonds (between molecules of the same nature) between the water molecules (Hydrogen-Oxygen), driving therefore the water outside the organic phase, and generating in the process a two liquid phase separation. This mechanism has been explained by Tan (2010).

The lower critical solution temperature (LCST) of the CO_2 loaded solvent, above which there is liquid-liquid separation, is around 70 °C to 90 °C depending on the amine. The solubility of lipophilic amines in water decreases proportionally with temperature. The organic nature of the amine causes CO_2 to be extracted in the organic phase, thus disturbing the chemical equilibrium of the aqueous phase which reverses the absorption reaction according to the principle of LE CHATELIER. This causes the regeneration of the solvent and the release of CO_2 in a gaseous phase. The regeneration temperature of 70 °C to 90 °C makes it possible to use the residual heat to regenerate the solvent (Zhang et al., 2013). Moreover, the absorption of CO_2 by these novel solvents has high driving force during regeneration via liquid-liquid separation and an absence of precipitation phenomena related to amine degradation by-products as low regeneration temperature inhibits amine decomposition.

2. Thermomorphic amines screening

Various studies have been carried out to determine the best performing thermomorphic solvent. Zhang et al. (2012) have carried out a selective study, involving more than 32 thermomorphic amines. Tan (2010) also carried out a similar study. The main criteria on which the amine selection work is based are the following:

1- Volatility: low vapour pressure reduces loss of solvent during regeneration.

2- Phase change temperatures: the chosen solvent must have a high enough LCST, so the absorption would occur in a homogenous liquid. After solvent gets loaded of CO_2, the solvent must have phase separation at temperatures within the range of 60 °C to 90 °C.

3- Absorption capacity: The solvent absorption capacity must be high or at least comparable to the conventional aqueous MEA solvent (30 % mass).

4- Regeneration capacity: The solvent retained must have a regeneration rate higher than 90 %.

5- Precipitation phenomenon: Precipitates of stable elements (stable salts) are undesired as they reduce heat transfer in the regeneration column.

6- Kinetics: The solvent retained must show fast absorption kinetics in order to reduce the size of absorption columns.

All studies comparing lipophilic amines have concluded that no amine can perfectly match the six criteria. Thus, the research is oriented towards mixtures of amines which will make it possible to satisfy the criteria stated above. Given their fast kinetics, primary and secondary amines are considered as activators of the absorption, while tertiary amines are considered regeneration promoters since they require little energy for regeneration (Zhang et al., 2011).

For the sake of this study, about 30 thermomorphic amines are thoroughly studied in order to select the better fits to serve as a base for the study of amine mixtures. The benchmarking is based on the above mentioned criteria. The thermomorphic amines selected are listed in Table 1.

Table 1: Selected thermomorphic amines for blend solvents

Category	Amine	Acronym	Type
Activator	Hexylamine	HA	Primary
Regeneration promoter	N,N-dimethylcyclohexylamine	DMCA	Tertiary

It should be noted that Ye et al. (2015) have already studied the mixture hexylamine and dimethylcyclohexylamine, but as a demixing solvent which was expected to present a phase separation at between 30 °C to 40 °C. However, this mixture has never been examined as a thermomorphic solvent which would exhibit a phase change at temperatures within the range of 70 °C to 90 °C.

3. Experimental

3.1 Aqueous amine solvents preparation

All the solvents examined were prepared at 3 M concentration (3 mol/L), with a volume of water corresponding to 100 ml, the volume of the amine varies from one sample to another. Four samples were tested: 3 M hexylamine, 3 M dimethylcyclohexylamine, and 2 amine blends of hexylamine-dimethylcyclohexylamine mixture at different proportions (1:2, 2:1) adding up to 3 M of total amine concentration.

3.2 Lewis cell apparatus

The proposed absorption and regeneration experiments are conducted in a Lewis cell apparatus (Amararene and Bouallou, 2004). The Lewis cell is equipment that allows monitoring the variation of the pressure inside the isothermal cell (considered closed system). Thus, the contact of the solvent with the gaseous volume of the CO_2 makes the absorption to occur. Collected data consist of values of the decrease of the pressure inside the cell. The equipment enables to carry out the absorption tests at different temperatures in order to evaluate the kinetics over a wide temperature range. Besides, at temperature range close to 80 °C to 90 °C, the cell enables to monitor the operation of the regeneration of loaded solvents by measuring the increase of pressure (kinetics of desorption). The cell is initially in equilibrium, the pressure value indicated by the acquisition system corresponds to the value of the saturating pressure of the solvent. The peak occurs when the CO_2 is injected. The absorption then begins, until it reaches a new point of thermodynamic equilibrium. Throughout the absorption process, the pressure decreases, and its variation is plotted against time. This apparatus has been used for many kinetic studies for gas absorption (Pani et al., 1997).

3.3 Operation procedure

Prior to the absorption tests, the saturating pressure of the mixture at different temperatures should be determined, to avoid biased pressure values. The measurements of the saturating vapour pressure of each solvent as a function of the temperature were carried out. The partial pressure of CO_2 during the regeneration tests would therefore take into account the partial pressure of the evaporated solvent at regeneration temperatures. The absorption tests were carried out at three temperatures (20 °C, 30 °C, 40 °C) in order to determine the absorption rate and the mathematical expression of the kinetic constant according to the Arrhenius law. The cell is set at the desired temperature and experiments begin only once thermal equilibrium is reached inside the cell (constant temperature). The solvent is then introduced into through the cell's syringe and stirred till it reaches the test temperature. CO_2 is then introduced to the system. This operating procedure was followed by many authors to evaluate the kinetics of absorption (Zhang et al., 2011, Rivera-Tinoco and Bouallou, 2010).

4. Results and discussion

4.1 Absorption experiments

All samples presented immiscibility of amine-water at room temperature. Once injected into the Lewis cell and after stirring, an emulsion is formed. After CO_2 absorption (temperatures: 20 °C, 30 °C, 40 °C) the amine-water mixture becomes miscible (Figure 1). A two-liquid phase separation begins to be visible at temperatures around 70 °C and the desorbed gas bubbles, representing a third phase, patently leave the aqueous phase to the outside passing through the organic phase. This phenomenon is in agreement with the literature, and the results confirm the hypothesis previously stated (Zhang et al., 2011) and more recently Zhang et al. (2013).

Pressure data collected are processed in order to obtain the maximum load capacity of the mixture, the kinetics characterizing the absorption mechanism, and the regeneration rate. The solvent composed of hexylamine (HxA) and water presented very rapid absorption rate (143 seconds), the CO_2 is almost immediately fully absorbed. The DMCA and water solvent takes about 5000 seconds to fully absorb the CO_2. The mixture of DMCA and HxA at 3 M concentration and 1:2 ratio almost resumed the same kinetics of CO_2 absorption by hexylamine with a more improved absorption capacity and a return to equilibrium at 181 seconds. The mixture of DMCA and HxA at 3 M concentration and proportions 2:1 also showed an absorption rate close to that of hexylamine alone (234 s), with a rapid return to thermodynamic equilibrium. The inert pressures (cell pressure before CO_2 injection) and the quantities of CO_2 injected at each test are different, so in order to be able to make a fair comparison taking into account the differences in the operating conditions we suggest comparing the normalized pressures.

(a) (b)

Figure 1: Amine blends before (a) and after (b) agitation

4.2 Regeneration experiment

In order for the preliminary examination to be exhaustive, the regeneration of the solvents studied should also be assessed. The fact that the Lewis cell stands no more than 3 bar made the regeneration in the cell complicated. Hence, we used low-solvent solutions so that the regeneration would take place without damaging the cell. Although this study is not intended to determine the maximum regeneration rate of the solvents studied, it can nevertheless serve as a basis for comparison of primary desorption between the examined mixtures.

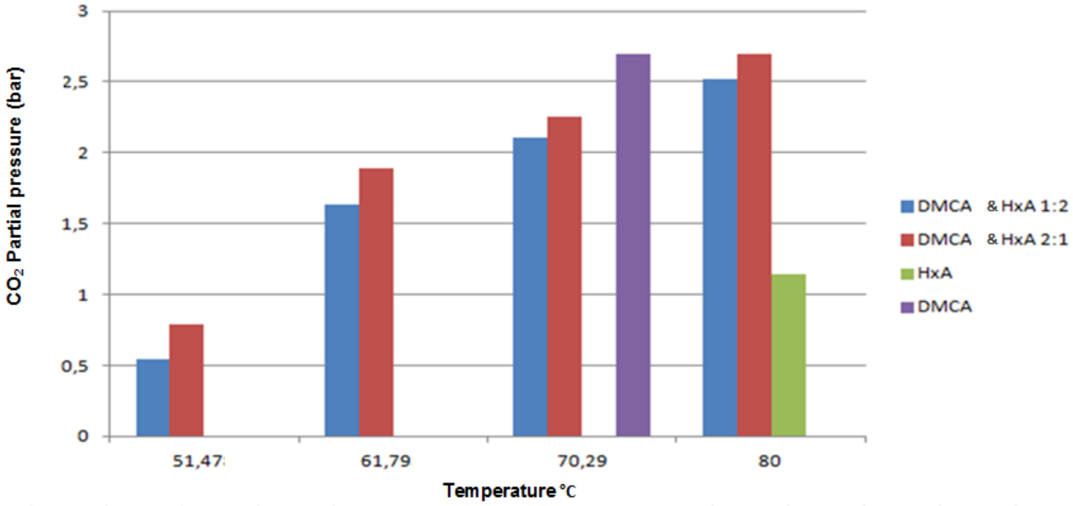

Figure 2: Regeneration temperatures for the tested thermomorphic solvents

Figure 2 allows evaluating the partial pressure of the CO_2 released. Total pressure in the cell results from this partial pressure of CO_2 and the vapour pressure of the solvent initially measured. The regeneration of hexylamine was carried out at 80 °C; however for DMCA it was sufficient to bring it to a temperature of 70 °C to observe both the phase change and the desorption of the previously absorbed CO_2. The mixture of DMCA and HxA at 3 M concentration and 1:2 ratios also showed better regeneration than hexylamine, and a phase change was observed at a temperature of 80 °C. As for the mixture of DMCA and HxA at 3 M concentration and proportions of 2:1, 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.

4.3 Absorption kinetics

Versteeg and Swaaij (1988) work has been one of the first to address the kinetics of CO_2 absorption by amines. While modelling CO_2 absorption, the CO_2 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 CO_2. These assumptions have been verified for other work under the same conditions (Gonzalez-Garza et al., 2009).

In the case of mass transfer with chemical reaction, an enhancement factor E is introduced. This factor E makes it possible to compare the impact of the chemical reaction on the mass transfer (Pani et al., 1997). E is expressed by Eq (1).

$$E = \frac{\Phi}{k_L\ A\ (C_{CO2,int} - C_{CO2,mix})} \quad (1)$$

The concentration in the liquid bulk ($C_{CO2,\ mix}$) is constant during the experiment and can be neglected. Similarly, the CO_2 flux absorbed by the mixture is expressed as follows (Derks & Versteeg, 2009, Pani et al., 1997):

$$\Phi \times A = -\frac{dn(CO_2)}{dt} = \frac{-V_g}{RT}\left(\frac{dP_{CO2}}{dt}\right) \quad (2)$$

Eq(1) and Eq(2) yield the following equation:

$$k_L E\left(C_{CO2,int}\right) A = \frac{-V_g}{RT}\left(\frac{dP_{CO2}}{dt}\right) \tag{3}$$

The concentration at the interface is determined by Henry's law as follows:

$$C_{CO2,int} = \frac{P_{CO2}}{H_{CO2}} = \frac{P_T - P_I}{H_{CO2}} \tag{4}$$

Consequently:

$$Ln\left(\frac{P_T - P_I}{P_{T,0} - P_I}\right) = \frac{-k_L \times E \times A \times RT}{V_g H_{CO2}}\,(t - t_0) \tag{5}$$

$$Ln\left(\frac{P_T - P_I}{P_{T,0} - P_I}\right) = -\beta\,(t - t_0) \tag{6}$$

The slope β enables the enhancement of absorption phenomena to be quantified, and is directly linked to the kinetics. In Figure 3 are compared the performances of each mixture through the slope value resulting from time and normalized pressure values.

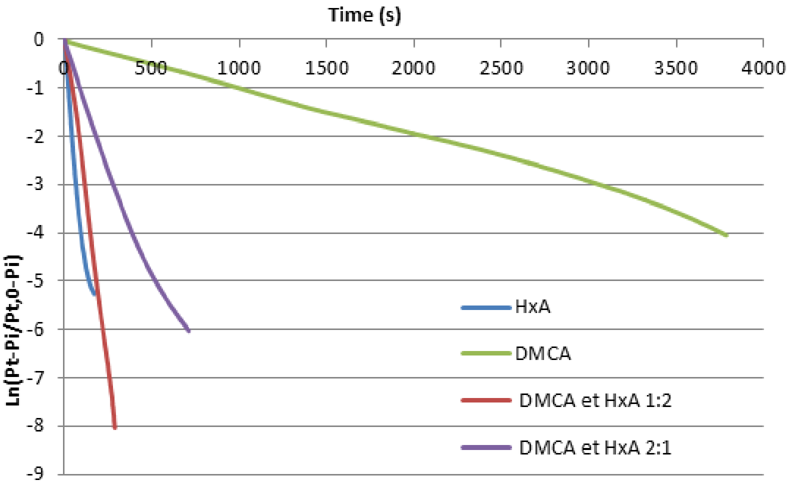

Figure 3: Determination of the slopes for the studied thermomorphic

The most pronounced enhancement (corresponding to the fastest kinetics) is noticed in the case of hexylamine, while the less one is observed in the case of dimethylcyclohexylamine. The mixtures of different proportions also show rapid kinetics translated by high enhancement of the absorption phenomena. In fact, results are sufficient to confirm the potential of the solvent resulting from the mixture of DMCA and HxA due to its rapid kinetics, absorption capacity and regenerative potential. The data processing made it possible 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 makes it possible to activate the solvent. The DMCA-HxA blend at 1:2 proportion appears to be the most promising solvent, since its kinetics is approximately as rapid as the HxA while its regenerative capacities at 80 °C were as good as those of DMCA.

5. 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. 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 showed a very rapid kinetics very similar to the HxA’s kinetics and a good regenerability. Follow up studies should be performed to evaluate the solvents degradation and loss, so it would be suitable for CO_2 removal from streams of industrial processes.

Nomenclature

A: Interface area (m^2)
$C_{CO2,int:}$ CO_2 concentration in the gas-liquid interfacial area ($mol.m^{-3}$)
$C_{CO2,mix}$: CO_2 concentration in the liquid bulk ($mol.m^{-3}$)
E: Enhancement factor
H_{CO2}: CO_2 Henry’s constant ($Pa.\ m^3.mol^{-1}$)
k_L: Liquid phase mass transfer coefficient ($m.s^{-1}$)
P_{CO2}: CO_2 pressure (Pa)
P_I: Inert pressure (Pa)
P_T: Total pressure at t (Pa)
$P_{T,\,0}$: Initial total Pressure at t = 0 (Pa)
R: Ideal gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$)
T: Temperature (K)
t: time (s)
V_g: Gas volume (m^3)
Φ: CO_2 flow rate ($mol.m^{-2}.s^{-1}$)

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