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Tuning critical solution temperature for CO₂ capture by aqueous solution of amine

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Abstract

Aqueous solution of amine is a mature technology to selectively absorb CO₂ from an industrial exhaust. Monoethanolamine (MEA) is still considered as the reference amine and unfortunately, the energy necessary to desorb CO₂ and recycle the solvent is limiting its use at industrial scale. The main cost of the process is the energy needed to heat the solvent over 100 °C to desorb the CO₂. Several options to decrease this expense have been considered including the use of phase separation to reduce the volumes to be treated. It was then proposed to use aqueous solution of an amine exhibiting a lower critical solution temperature (LCST) at an adequate temperature. However, it is challenging to found a solvent able to absorb large quantity of CO₂ and having an LCST at a suitable temperature. Deep eutectic solvent (DES) composed of oleic acid (hydrophobic) and lidocaine (amphiphilic) can be separated from water with either temperature or CO₂ as stimuli. This DES has been used to adjust the critical solution temperature after sorption of CO₂ in an aqueous solution of demixing amine. By only changing the ratio of the two components of the DES, the critical solution temperature can be tuned from around 30 to 70°C. The addition of this DES into an aqueous solution of demixing amine could then substantially help to adapt the critical solution temperature of a solvent to the require conditions of CO₂ capture process.

Keywords

Deep eutectic solvent, CO₂ capture, lower critical solution temperature

1 Introduction

2
3 Currently the industrial technologies for CO₂ capture processes are based on a CO₂ separation
4 from post-combustion effluent by gas dissolution in chemical absorbent solutions. The
5 technology is mature enough to be integrated into industrial sites without strong modification of
6 the plant.[1] The principle is based on CO₂ absorption-desorption cycles. Carbon dioxide
7 contained in gaseous effluents is selectively absorbed by solvents. Aqueous solutions of
8 alkanolamine are selective absorbents[2] used in the decarbonation of natural gases. The affinity
9 between the absorbent and the CO₂ has to be precisely adjusted: if the interaction is too weak, the
10 CO₂ is not enough absorbed, however, if the interaction is too strong, the amount of energy to
11 desorb will be extensive, the cycling process will be costly and not applicable at industrial scale.
12 Aqueous solution of monoethanolamine (MEA) is the benchmark for post-combustion capture
13 (PCC).[3] This amine has a strong affinity with CO₂ leading to favorable kinetic of absorption. In
14 the cycling process with this type of system, the CO₂ desorption from an alkanolamine solution is
15 highly energy consuming and not compatible with CO₂ remediation applications. It is thus
16 necessary to imagine new breakthrough processes allowing substantial energetic cost reduction.
17 Tertiary alkanolamines such as methyldiethanolamines (MDEA) have therefore been
18 proposed,[4] as the affinity between such amine and CO₂ is reduced, decreasing the energetic
19 cost of the regeneration. However, in that case, the kinetic of absorption is unfavorable, and if the
20 solvent is really efficient to treat gases containing high concentrations of CO₂, it necessitates very
21 large installations and solvent quantities to treat the fume from post-combustion processes.
22 Another option is to use an aqueous switchable solvent[5] possessing an LCST (lower critical
23 solution temperature): while increasing the temperature, the solvent present a liquid – liquid
24 phase separation at its critical temperature. The topic of phase change solvents for PCC have
25 been recently reviewed.[3] In 2011 IFPEN proposed the DMX[®] process based on the use of high
26 capacity and chemically stable demixing amines to replace classical alkanol amines for CO₂
27 capture in industrial effluents.[6, 7] Thermomorphic biphasic solvent (TBS) have been widely
28 studied by Zhang *et al.*[8-14] and Tan[15]. The solvent is an aqueous mixture of lipophilic
29 amines exhibiting a liquid – liquid phase transition upon heating leading to a high carbon dioxide
30 desorption at temperatures well below the boiling point of aqueous solutions. This technology
31 uses heterogeneous absorbent solutions which becomes homogeneous upon carbon dioxide

1 absorption and returns to two phases through heating. The organic phase acts as an extractive
2 agent, removing the amines from the aqueous phase and thus favorably displacing the
3 regeneration equilibrium. Zhang *et al.* have intensively worked on replacing steam stripping used
4 for carbon dioxide release with nucleation or agitation techniques.[9, 11] They pointed out that
5 the benefit of adding a hydrophobic organic solvent to reduce the operating temperature for
6 carbon dioxide desorption. Mixed phase-changed solvents have been investigated by Svendsen
7 and coworkers[16-20] as a part of the European Union project iCap. The process is very similar
8 to DMX® developed by IFPEN. Screening investigations to evaluate the CO₂ absorption and
9 desorption facilities of phase-change solvents have been completed.[21, 22]

10 Since the initial work from Abbott and collaborators, deep eutectic solvents (DES) have
11 gained a large interest from the scientific community.[23, 24] DES are mixtures with melting
12 temperatures far below the melting temperature of the initial components.[25] The existence of
13 DES is generally explained by favorable specific interactions between the different chemicals of
14 the mixture. Many DES are obtained by the mixing of a donor and an acceptor of hydrogen bond.
15 DES with specific properties can be designed to target particular physico-chemical properties: as
16 example, hydrophobic DES has been developed for extraction of a broad range of molecules[26]
17 and ions[27] from water. A first DES – water system with an LCST at 25°C has been recently
18 observed.[28] This DES is composed of oleic acid (OA) and lidocaine (LD) which was first
19 introduced by Bica *et al.*[29] The existence of the LCST has been explained by the variation of
20 pKa of the amine: the temperature increase is inducing a fast decrease of the solubility of the
21 amphiphilic lidocaine in water up to the phase separation. Although the system is fully miscible
22 below 25°C, at 50°C only 5 wt% of water is present in the organic phase and less than 0.5 wt% of
23 DES is detected in the aqueous phase.[28]

24 Herein, we focus on aqueous solutions of a DES composed of lidocaine (LD) and oleic acid
25 (OA). First, we found that the addition of carbon dioxide into an aqueous solution of DES
26 (OA:LD) is triggering a switch from monophasic to biphasic. However, the quantity of CO₂
27 absorbed in the aqueous solution of DES (OA:LD) is irrelevant for the topic of CO₂ capture. We
28 then decided to add another amine to increase the amount of absorbed CO₂. Several amines
29 including monoethanol amine (MEA), piperidine, 2-methylpiperidine, 4-methylpiperidine, N-
30 methylpiperidine, N-ethylpiperidine were evaluated. The existence of an LCST between 25 and

1 80°C after addition of CO₂ for several compositions were tested for each amine. LCST was only
2 observed for mixtures with N-methylpiperidine (NMPi) and N-ethylpiperidine. NMPi was
3 selected as the most promising amine for CO₂ capture application. This tertiary amine with a pKa
4 around 10, [30] is also increasing the CO₂ absorption compared to the LD with a pKa of around
5 8. [31] Therefore, NMPi was selected to evaluate the ability of {DES (OA:LD) + water + Amine}
6 mixtures to be efficient for CO₂ capture. Most studies using aqueous amine solutions for CO₂
7 capture are using concentrations of around 30 wt% of organic molecules.[20, 32] Therefore in the
8 present study, the experiments are realized with solvents composed of DES (OA:LD), NMPi and
9 water and with fixe amount of water at 70 wt%. In particular, we studied the impact of DES and
10 NMPi concentrations on the critical solution temperature. After this optimization step, we finally
11 evaluated the quality of the separation of this new solution for carbon capture.

12 **Results and discussion**

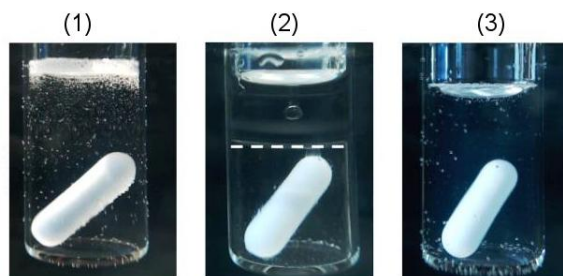
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14 **Inducing a reversible phase separation by addition of CO₂ in aqueous solution of DES** 15 **(OA:LD)**

16

17 While mixed with water at 20°C, only the DES (OA:LD) with initial concentrations of x_{OA}
18 between 0.45 and 0.60 are homogeneous. For lower concentrations of OA, the DES is partially
19 solid, and for higher concentration of OA, the aqueous mixtures are biphasic liquid – liquid at
20 20°C.[28] The addition of CO₂ into the aqueous DES were then realized for OA:LD molar ratios
21 of 45:55, 50:50, 55:45 and 60:40. At 20°C, when CO₂ is bubbled at atmospheric pressure in an
22 aqueous DES with 70 wt% of water, the mixture became white within few minutes under stirring.
23 The possibility to induce the phase separation by an increase of the temperature was avoided by
24 keeping the samples at 20°C in water bath and under a vigorous stirring. After 1 hour when the
25 flow of CO₂ and the stirring are stopped, a decantation in 2 liquid phases is observed. Then,
26 stirring is restarted and N₂ is bubbled into the biphasic mixtures, and the systems are coming back
27 to monophasic liquid in less than 1 hour. An example of these visual observations is given in
28 Figure 1. All tested ratio of DES (OA:LD molar ratios of 45:55, 50:50, 55:45 and 60:40) give the
29 same behavior : monophasic before addition of CO₂, biphasic liquid – liquid after absorption of
30 CO₂ at 20°C and monophasic again after flushing N₂. These observations are comparable to those
31 made on an ionic liquid based on tetrabutylphosphonium N-trifluoromethanesulfonyl leucine.

1 CO₂ bubbling at 20°C was inducing the phase separation while bubbling N₂ was switching back
2 the system to monophasic.[33]



3
4 Figure 1: Pictures of DES (OA:LD) – water mixture, before addition of CO₂ (1), after addition of CO₂
5 (2), and after addition of N₂ (3). The DES is composed of 60 mol% of OA and 40 mol% of LD and before
6 the addition of CO₂ the mixture is composed of 30 wt% of DES and 70 wt% of H₂O. The experiment was
7 performed in a water bath thermostated at 20 °C. The vial is containing 2.5 ml of solution, and the
8 aqueous phase is the bottom phase. White dashes have been added to help discerning the liquid – liquid
9 interface.

10
11 Switch hydrophobicity of this DES-water with temperature has already been investigated. [28]
12 The system is composed of OA (an oil), water and LD. At low temperature, the amphiphilic
13 lidocaine is making oil and water to remain together in a single phase. When the temperature is
14 increased, the quantity of ions is decreased[28] and the solubility of neutral LD is much smaller
15 than cationic LD.[31] Therefore, the affinity between water and organic compounds is disrupted
16 by the increase of temperature and the liquid – liquid phase separation is induced with DES on
17 one side and water on the other. The similar behavior is observed here with CO₂ absorption in
18 DES-water at ambient temperature. Indeed, pH of solution is acidified when CO₂ is absorbed,
19 thus solubility of LD in water is reduced initiating a phase separation.

20 For the considered concentrations of (OA:LD), the density of the DES is always between 0.94
21 and 0.96 g/cm³. [29] In the example shown in Figure 1, the volume ratio between the organic and
22 aqueous phase is close to the ratio of water and DES. Nevertheless, for mixture with higher
23 amount of OA, the volume of the aqueous phase tends to decrease. This could illustrate the non-
24 ideal separation between the DES and water. In particular, since the water volume is smaller than
25 expected, the quantity of water in the organic phase should be significant.

26 A small increase of temperature and the addition of CO₂ are two stimuli that are inducing a
27 phase separation between the DES (OA:LD) and water. In either case, the phase separation is

1 reversible by decreasing the temperature or by removing the CO₂. Depending on the application,
2 CO₂/N₂ stimulus could be more appropriate than changing the temperature.

3 pKa of LD is 8.0 at 25°C,[31] and because of its low pKa, this tertiary amine could not be
4 considered as a good amine for CO₂ capture.[34] Indeed, the mixture with 30 wt% of DES (2:1)
5 can only absorb around 0.3 wt% of CO₂ which is far from a benchmark system like MEA –
6 water which are absorbing more than 10 wt% (g of CO₂/g of solvent).[35] It was then decided to
7 add another tertiary amine with a higher pKa to improve the absorption of CO₂. DES (OA:LD) –
8 NMPi – water – CO₂ was selected after a screening over potential amines.

9

10 **Impact of the composition of the solvent on the LCST in DES – NMPi – water – CO₂** 11 **mixtures**

12

13 To evaluate CO₂ absorption in different conditions, the loading charge α is often used: α is the
14 molar ratio of carbon dioxide per amine. Since aqueous solution of LD has not shown high ability
15 to absorb the CO₂, LD has not been considered for the calculation of the loading charge of CO₂
16 and only the concentration of NMPi has been taken into account:

$$\alpha = \text{mole CO}_2 / \text{mole NMPi}$$

17 This parameter is employed to describe CO₂ absorption. However, α is only utilized when a
18 reactive amine is added to the solvent. To facilitate the comparison with other processes, CO₂
19 absorption can also be defined by the mass ratio (wt%): g of CO₂ / g of solvent.

20 CO₂ sorption experiments was first realized in a solution containing 70 wt% of water, 15 wt%
21 of DES (OA:LD) and 15 wt% of NMPi. Flowing gaseous CO₂ above the solution for 45 min.
22 induce a CO₂ sorption up to α around 0.6 which correspond to 4 wt% (g of CO₂ / g of solvent).
23 When bubbling directly CO₂ in the liquid phase, the sorption is faster and an $\alpha = 0.4$ is reach in
24 only 6 min. The addition of NMPi has been clearly improving the solubility of CO₂; it has
25 increased from 0.3 wt% with DES to 4 wt% when replacing half of the DES by NMPi. After the
26 CO₂ sorption, a vial containing 2 ml of sample is transfer into a water bath to measure the critical
27 solution temperature while increasing the temperature up to 80°C. In the case of $\alpha = 0.40$, a phase
28 separation is observed at 43°C (Table 1, entry 1) while without CO₂ this mixture does not show a
29 critical solution temperature up to 80°C.

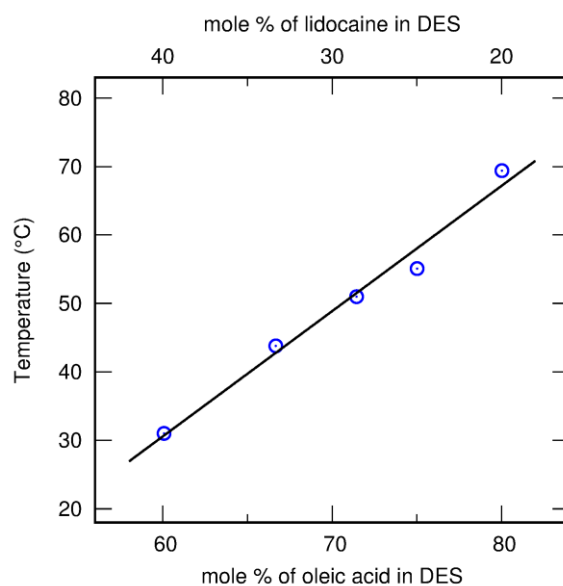
1 The impact of the concentrations of each component was evaluated by modifying their
2 concentrations. First, the ratio of DES and NMPi were changed while keeping the quantity of
3 water constant at 70 wt% and the quantity of CO₂ at $\alpha = 0.4$. Compared to the 70-15-15 (Table 1,
4 entry 1), the critical solution temperature is lowered with other DES / NMPi ratios tested. With
5 10 wt% of DES, the critical solution temperature is at 28°C, while with 20 wt%, it is 36°C
6 (Table 1, entries 2 and 3). Without NMPi (30 wt% DES 2:1 and 70 wt% H₂O) the system is
7 already biphasic at room temperature. In absence of DES (30 wt% of NMPi in 70 wt% of water)
8 the system is also already biphasic in presence of CO₂ ($\alpha = 0.4$) at room temperature. While
9 keeping 70 wt% of water, $\alpha = 0.40$ and OA/LD = 67/33, (Table 1, entries 1-5), the highest critical
10 solution temperature observed is when using the same quantity of NMPi and DES; 15 wt% of
11 each component. Therefore, the solvent composed of DES-NMPi-water 15-15-70 (wt%) is
12 selected as an optimal composition of the solvent for CO₂ capture. Indeed, its LCST is
13 appropriate for the application: above the typical temperature of CO₂ capture process (40°C) and
14 not too high to reduce required energy.

15 Table 1: Critical solution temperature of mixtures after absorption of CO₂. ¹: LCST: low critical solution
16 temperature corresponding to the cloud point while heating. ²:L-L correspond to a system which is always
17 biphasic liquid – liquid between 25 and 80°C. ³:L is a mixture which is always monophasic in this range
18 of temperature.

| Entry | Solvent composition | | | DES ratio OA/LD (mol%) | CO ₂ loading mol CO ₂ / mol NMPi | LCST ¹ (°C) |
|-------|---------------------|--------------|---------------------------|------------------------------|--|---------------------------|
| | NMPi (wt%) | DES (wt%) | H ₂ O (wt%) | | | |
| 1 | 15 | 15 | 70 | 67/33 | 0.40 | 43 |
| 2 | 30 | 0 | 70 | - | 0.40 | L-L ² |
| 3 | 20 | 10 | 70 | 67/33 | 0.40 | 28 |
| 4 | 10 | 20 | 70 | 67/33 | 0.40 | 36 |
| 5 | 0 | 30 | 70 | 67/33 | - | L-L ² |
| 6 | 15 | 15 | 70 | 50/ 50 | 0.40 | L-L ² |
| 7 | 15 | 15 | 70 | 60/40 | 0.40 | 31 |
| 8 | 15 | 15 | 70 | 71/29 | 0.40 | 51 |
| 9 | 15 | 15 | 70 | 75/25 | 0.40 | 55 |
| 10 | 15 | 15 | 70 | 80/20 | 0.40 | 69 |
| 11 | 15 | 15 | 70 | 67/33 | 0.00 | L ³ |
| 12 | 15 | 15 | 70 | 67/33 | 0.19 | 65 |
| 13 | 15 | 15 | 70 | 67/33 | 0.25 | 56 |
| 14 | 15 | 15 | 70 | 67/33 | 0.37 | 51 |
| 15 | 15 | 15 | 70 | 67/33 | 0.47 | 33 |

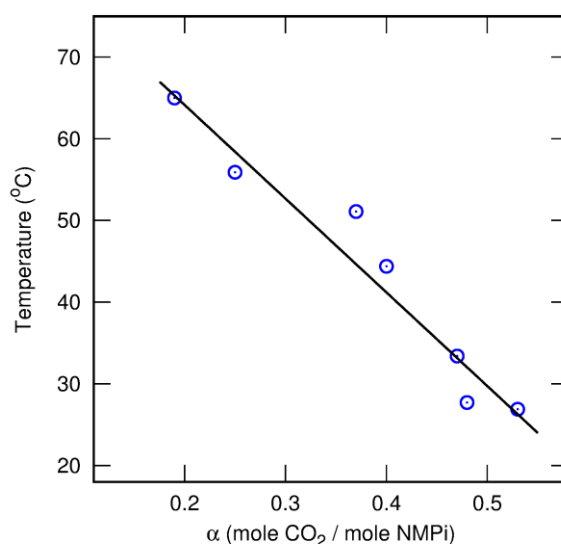
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|----|----|----|----|-------|------|----|
| 16 | 15 | 15 | 70 | 67/33 | 0.48 | 28 |
| 17 | 15 | 15 | 70 | 67/33 | 0.53 | 27 |

1
2 As the ratio of the two constituents of the DES can be modified, we decided to study the
3 impact of their molar concentrations on the critical solution temperature after absorption of CO₂
4 ($\alpha = 0.40$). While the phase separation was observed to be 43°C with the concentration of
5 67 mol% of OA (DES 2:1), changing the molar ratio of the two constituents has an obvious
6 impact on the critical temperature. The temperature of the phase separation increases
7 continuously from around 30 to 70°C when increasing the amount of OA from 60 to 80 mol% in
8 the DES (Figure 2). All concentrations and temperatures are given in Table 1, entries 1 and 7 to
9 10. With lower concentration of OA (DES 1:1) the mixture is already biphasic at room
10 temperature. It is worth to mention that for the range of concentrations considered in this work,
11 oleic acid is the main substance of the DES and it is a fatty acid obtained from vegetal oil. Oleic
12 acid is up to 80 wt% of the fatty acid composition of high oleic vegetable oils.[36] It is then
13 interesting to note that it is possible to tune the property of the solution to have the separation at a
14 specific temperature in order to adapt to the requirement of a chemical process. This adjustment
15 of the critical temperature can be achieved simply by changing the composition of the solvent
16 (ratio of DES/NMPi as well as ratio OA/LD) without changing any of the others parameters.



1 Figure 2: Evolution of critical solution temperature while changing the ratio of OA and LD in the DES.
2 Initial composition of all samples is 70 wt% of water, 15 wt% of DES and 15 wt% of NMPi and the
3 loading of CO₂ is $\alpha = 0.40$. Black line is only a guide for the eye.

4 We also studied the impact of the CO₂ concentration on the critical temperature. This
5 investigation was realized with solvent composed of 70, 15 and 15 wt% of water, DES and
6 NMPi, respectively, and with a 2:1 (OA:LD) molar ratio in the DES. Changing the CO₂ loading
7 is also impacting the critical solution temperature. When increasing the CO₂ loading from 0.19 to
8 0.54, the temperature constantly decreases from around 65 to 27°C (Figure 3). Without CO₂, the
9 phase separation could not be observed up to 80°C. The decrease of the critical solution
10 temperature with the addition of CO₂ is coherent with the observation of other tertiary amine –
11 water mixture, where the addition of CO₂ is also inducing a phase separation at constant
12 temperature in similar condition.[37] This is also in accordance with the behavior of aqueous
13 solutions of alkyl-piperidines in presence of CO₂ (with similar concentrations of amine and
14 CO₂).[38]



15
16 Figure 3: Impact of the amount of CO₂ on the critical solution temperature. Initial composition of all
17 samples is 70 wt% of water, 15 wt% of DES (2:1) and 15 wt% of NMPi. Black line is only a guide for the
18 eye.

19 **Evaluation of the separation in an optimized solution composed of DES (OA:LD) –**
20 **NMPi – water – CO₂**

1 For a carbon capture application the kinetic of separation of two phases is a critical factor.
2 While considering the DES (2:1) – NMPi – water system (15, 15 and 70 wt%, respectively) with
3 a sorption of CO₂ ($\alpha = 0.40$) at 70°C, the separation of the two phases is occurring within few
4 minutes. Above this temperature, separation of two phases is not improved (see supplementary
5 information, Figure S1) and would require more energy. Thus, 70°C has been selected as optimal
6 separation temperature. The kinetic of separation is naturally depending of several parameters
7 including residual movement of the fluids and shape of the container. In the illustration presented
8 in Figure 4, the apparition of the two phases occurs during the first minute, and the volume of the
9 two phases is constant after only three minutes. The bottom phase (aqueous) is clear during the
10 all experiment while it takes dozens of minutes for the top phase (organic) to become nearly
11 transparent. The cloudiness of the phase is most probably corresponding to remaining droplets of
12 water in the organic phases.

13

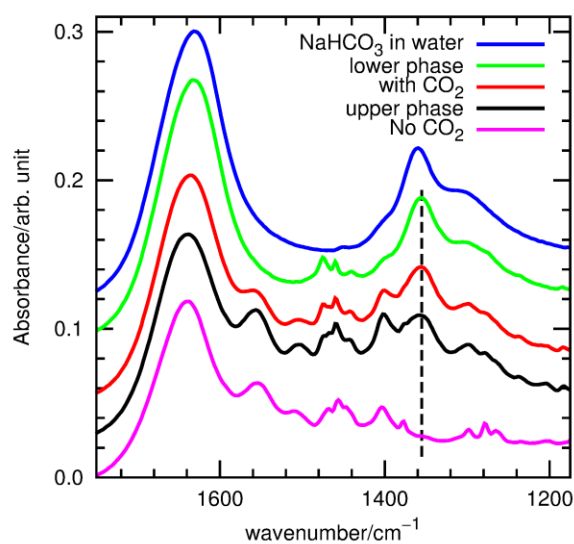


14

15 Figure 4: Pictures of the separation of the two phases without stirring at 70°C of a solvent with DES
16 2:1, NMPi and water (15, 15, and 70 wt%) after sorption of CO₂ ($\alpha = 0.40$). After an equilibration of 15
17 minutes at 40°C (homogeneous transparent liquid), the vial containing 0.67 g of solution was place in a
18 water bath at 70°C.

19 DES and water have similar densities and the initial amount of water in the solution being
20 70 wt%, we could then expect that, if water and DES are well separated, the aqueous phase
21 should be around 70% of the total volume. Nevertheless, as observed on Figure 4, the volume of
22 the aqueous phase is smaller than the organic phase. Then, an experiment was realized in a NMR
23 tube to assess the volume ratio of the two phases (see supplementary information Figure S1). In
24 coherence with the picture of Figure 4, the volume of the organic phase was estimated to be 70%
25 +/-3% of the total volume at 70°C. Water should then be poorly separated and present in large
26 quantity in both phases.

1 The system was then evaluated by estimating the amount of chemical after 15 minutes at 70°C
2 in both phases. Karl-Fischer titration was used to determine the quantity of water in aqueous and
3 organic phases. Water is present in both phases in large quantity: water is the main compound in
4 the two phases with 81 and 57 wt% in aqueous and organic phases, respectively. Quantifications
5 of OA, LD and NMPi were obtained by quantitative proton NMR (^1H NMR, spectra are given
6 in SI). In the aqueous phase, OA has not been detected and the quantity of LD is below 0.5 wt%.
7 In the organic phase, the ratio of OA and LD is 2:1, identical to the initial ratio, as expected
8 because of the low concentrations of DES constituents in the aqueous phase. Unlike OA and LD,
9 NMPi is poorly separated with 16 and 11 wt% in organic and aqueous phase, respectively.
10 Finally, the amounts of CO_2 present in both phases are obtained by IR spectroscopy. The CO_2
11 signal at around 2340 cm^{-1} has not been observed indicating the absence of physisorption, even at
12 40°C before heating, meanings that all absorbed CO_2 have reacted with the aqueous solution. One
13 band is clearly visible at 1357 cm^{-1} when comparing solution before and after sorption as shown
14 in Figure 5. This band is assigned to the carboxylate symmetric stretching vibration of HCO_3^-
15 .[39] Variation of the quantity of HCO_3^- in both phases is obtained using the intensity at this
16 wavenumber. The phase separation induces an increase by 20% in the aqueous phase (green
17 spectra in Figure 5), while the concentration decreases by 15% in the organic phase (black
18 spectra).



19
20 Figure 5: Infrared spectra of sample with DES 2:1, NMPi and water (15, 15, and 70 wt%) before
21 CO_2 sorption (purple spectra), after sorption of CO_2 ($\alpha = 0.40$) and before phase separation (red spectra),

1 and after phase separation at 70°C: top – organic phase (black spectra) and bottom – aqueous phase (green
2 spectra). IR spectra of aqueous solution of CO₂ (HCO₃⁻) is also given as comparison (blue spectra). Dotted
3 line at 1357 cm⁻¹ corresponds to the signal used to estimate the quantity of CO₂. IR spectra have been
4 shifted for clarity reason.

5 Considering the concentration of CO₂ estimated from IR spectroscopy, we can evaluate that
6 around 60% of the absorbed CO₂ remains in the organic phase and only 36% of the CO₂ is in the
7 aqueous phase. The residual 4% could be explained by a possible small desorption of CO₂ during
8 the heat from 40 to 70°C and also by the uncertainty of this rough methodology. For each
9 compound, the estimation of the distribution between the two liquid phases is given in table 2.

10
11 Table 2: Evaluation of the separation at 70 °C after 15 minutes calculated from the concentrations
12 obtained from Karl-Fischer titration (H₂O), q ¹H NMR spectroscopy (NMPi and DES) and IR
13 spectroscopy (chemisorbed CO₂). The percentages given correspond to the proportion of chemical present
14 in each phase considering a 70/30 volume ratio between organic and aqueous phases.

| | Organic phase | Aqueous phase |
|------------------|---------------|---------------|
| Volumes | 70% | 30% |
| CO ₂ | 60% | 36% |
| H ₂ O | 62% | 38% |
| NMPi | 77% | 23% |
| DES | 99% | 1% |

15
16 While the volume of the aqueous phase is 30%, the amount of CO₂ in this phase is 36% which
17 correspond to a moderate improvement of its concentration with the phase separation. This
18 modest separation is probably linked to the high concentration of water in the organic phase: H₂O
19 and HCO₃⁻ are similarly distributed between aqueous and organic phases. The majority of the
20 CO₂ has clearly not been concentrated in aqueous phase and the phase separation induced by
21 heating is inappropriate for a CO₂ capture process in the conditions tested in this work. These
22 results could be compare to a well characterized biphasic system composed of water, CO₂ and
23 three amines DMCA (N,N-dimethylcyclohexylamine), MCA (methylcyclohexylamine) and
24 MAPA (3-methylaminopropylamine) with around 30 wt% of amine at 60°C, above the liquid –

1 liquid separation.[40] In this case, concentrations of CO₂ in both phases are around 1 and 5 wt%
2 in the organic and aqueous phase, respectively.[40] With such a large difference of concentration
3 between both phases, the organic phase could be send back directly to the sorption unit without
4 further treatment and the phase separation could be beneficial. In the case of DES (2:1), NMPi
5 and water (15, 15, and 70 wt%), the difference of concentration of CO₂ between both phases is
6 too small to apply this system in the field of carbon capture; 2.2 and 3.2 wt% of CO₂ in organic
7 and aqueous phase, respectively. However, these primary results show the correct tendency. In
8 fact, it is remarkable to observe that both OA and LD are very well concentrated in the organic
9 phase while CO₂ and water are poorly accumulated in the aqueous phase.

1 Conclusions

2
3 A first example of an aqueous DES solution with a phase separation induced by the addition of
4 CO₂ at 20°C has been presented. In an aqueous solution of this DES based on OA and LD,
5 bubbling N₂ into the biphasic liquid – liquid system is switching back to a monophasic liquid.
6 The quantity of CO₂ absorbed into DES (OA:LD) – water mixture is moderate and this system
7 could not be employ for the issue of carbon capture. However, aqueous solution of DES (OA:LD)
8 could still be employed as a switchable hydrophobic solvent, where temperature or CO₂ can be
9 the stimulus inducing the switch.

10 Another amine (NMPi) was added into the solution to increase substantially the absorption of
11 CO₂. In the mixture with DES – NMPi – water – CO₂, it is possible to tune the critical
12 temperature with constant concentrations of water, DES, amine and CO₂, simply by changing the
13 (OA:LD) molar ratio of the DES. The temperature could be increase from around 30 to 70°C
14 with higher concentrations of oleic acid. This possibility to adapt the critical temperature simply
15 by changing the ratio of the two components of the DES is a practical way to adapt the property
16 of the solvent to a specific application.

17 Unfortunately, the current system evaluated in this work does not have a good CO₂ separation.
18 Even if the DES is very well separated, the CO₂ has been concentrated by only 20% in the
19 aqueous phase compared to the homogenous solution. This system is a pioneer for upcoming
20 research on CO₂ capture by demixing solvent; it is illustrating the possibility to concentrate the
21 CO₂ in the aqueous phase using a DES composed of an amphiphilic (LD) and a hydrophobic
22 (OA) molecules. Our forthcoming project will then focus on the screening of many parameters;
23 concentrations of OA, LD, amine, water and CO₂ as well as the possibility to test other DES and
24 amine in order to found composition where the CO₂ and water are less present in the organic
25 phase.

1 **Experimental details**

2 **Chemicals**

3 Lidocaine (LD, 99% purity) and oleic acid (OA, 99% purity) were obtained from TCI
4 chemical while N-methylpiperidine (NMPi, 99% purity) was purchased from Sigma-Aldrich.
5 CO₂ (99.995%) and N₂ (99,2%) were supplied by Air Products. The water used was mono-
6 distilled and the methanol-d₄ and D₂O used for q ¹H NMR (99%) was purchased from Eurisotop.

7 **DES preparation**

8 DES (OA:LD) were prepared by heating the mixture at 80°C (above the melting temperature
9 of the LD) for few minutes followed by a stirring to obtain a perfectly transparent liquid. DES
10 and other liquid mixtures of 10 g were prepared with microbalance (precision of +/- 0.05 mg).

11 **Phase separation induced by CO₂ sorption in aqueous solutions**

12 4 aqueous DES mixtures were prepared with 70 wt% of water. The compositions of DES were
13 45, 50, 55 or 60 mol% of OA. A magnetic stirrer and 2.5 g of the mixture were placed in a vial of
14 4 ml (with a septum) and was equilibrated at 20°C in a thermostated bath (Julabo, ME-18V) for
15 at least 15 minutes. A first picture of each vial was taken after stirring vigorously the monophasic
16 liquid phase. Images were obtained using a camera (Logitech, C920). Some small bubbles could
17 be observed at this stage because of the stirring. At this first stage, the gas phase in the vial was
18 air at atmospheric pressure. Then, two needles have been used to flush gases into the vials. The
19 first needle was used to add gas (either N₂ or CO₂) and was immersed into the liquid phase, while
20 the other was used to release any overpressure. The gas was added using a balloon. During the
21 second step, the CO₂ was bubbled into the liquid under continuous stirring using a magnetic
22 stirrer bar during 1 hour. Bubbles appearing out the first needle are used to confirm that the gas is
23 flushing slowly through the solution. The liquid was systematically becoming white during this
24 step. The stirrer was then stopped and a second picture was taken after equilibration. Then, N₂
25 has been flushed slowly during 1 hour under stirring of the solution and a third picture has been
26 taken for each sample to illustrate the switch back to monophasic liquid. Identical results were
27 obtained by two separated experiments.

28 **CO₂ loading**

1 CO₂ sorption was realized under continuous stirring at 40°C and under constant pressure of
2 0.2 MPa of CO₂ using a high pressure syringe pump (Teledyn Isco 260D). When the CO₂ is in
3 contact with the aqueous solution, the CO₂ is absorbed and increase the weight of the solution.
4 The CO₂ sorption was then calculated with the mass uptake of the sample after sorption. CO₂ was
5 not bubbling directly into the liquid to prevent the loss of the solvent in the needle. The sorption
6 was then slow as taking place only at the gas – liquid interface. A typical CO₂ sorption with 5 g
7 of solution (water, DES and NMPi with 70, 15 and 15 wt%, respectively) took about 40 minutes.
8 After the vial was opened shortly to replace the 0.2 MPa of CO₂ of the gas phase by air at
9 atmospheric pressure. The typical uptake is around 160 mg of CO₂ with $\alpha = 0.5$ for 5 g of
10 solution. This experimental protocol was validated was the sorption of CO₂ of well-known
11 MEA/H₂O systems. The uncertainty of loading charges is estimated at 2%.

12 **Visual determination of critical solution temperatures**

13 Critical solution temperatures were observed using a 2ml sample in a thermostated water bath
14 equipped with two insulated glass windows (Julabo ME-18V). The bath was heated at a constant
15 rate of 0.25°C per minute up to 80°C using the controller of the thermostated bath. Temperature
16 of the water bath was measured with a 100 Ω platinum resistance thermometer immersed in the
17 water bath. During the heating, images were taken every two minutes by a camera (webcam,
18 Logitech C920) and Yawcam software. The temperature was defined as the temperature of the first
19 picture where the solution became cloudy. Uncertainty of critical temperatures is estimated at +/-
20 1°C.

21 **Quantification of chemicals in both phases**

22 NMR spectra were recorded in Fourier transform mode with a Bruker AVANCE 400
23 spectrometer at 298 K. For the quantification, q ¹H NMR sequence (128 scans) according to
24 references [41, 42] was used. Internal standard for q ¹H NMR measurement of the organic phase
25 (with DES) was 1,4-dimethoxybenzene (1,4-DMB, Aldrich), recrystallized twice in cyclohexane.
26 Its purity (99.5%) was determined using q ¹H NMR sequence with malonic acid (gold reference
27 Aldrich). Methanol-d₄ as solvent was used. Methoxy of the standard (s, 3.75 ppm), methyl of the
28 NMPi (s, 2.50 ppm), aliphatic methyl of lidocaine and oleic acid, (t, 1.18 ppm and t, 0.92 ppm
29 respectively) were used for the calculations. For the aqueous phase, 3-(trimethylsilyl)-

1 propanesulfonic acid sodium salt (98%, Aldrich) was used as standard in an 80/20 methanol-
2 d₄/D₂O mixture as solvent. Trimethylsilyl (0.0 ppm, standard), methyl of NMPi (s, 2.63 ppm) and
3 methyl of lidocaine (1.15 ppm) were used.

4 The quantity of water in both phases was estimated with a Karl-Fischer Coulometer DL32 from
5 Mettler Toledo.

6 The relative concentration of CO₂ before separation and in both phase after separation at 70°C
7 was obtained by ATR-FTIR spectroscopy. IR spectra were measured with a Nicolet 380 FT-IR
8 spectrometer equipped with a single reflection diamond ATR cell from Specac (Golden Gate) and
9 a DTGS detector. IR spectra were recorded at room temperature with a co-addition of 32 scans
10 and a resolution of 4 cm⁻¹. Similar results (+/-2%) were obtained from two separates samples for
11 all analyses (NMR, IR, KF). More technical details can be found elsewhere.[43-45]

12

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