

Experimental investigation of phase change amine solutions used in CO₂ capture applications: Systems with dimethylcyclohexylamine (DMCA) and N-cyclohexyl-1,3-propanediamine (CHAP) or 3-methylaminopropylamine (MAPA)

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ABSTRACT

Solvent-based absorption/desorption is a promising CO₂ capture technology, but its wide industrial implementation is prohibited by the high energetic requirements incurred by conventional amine solvents. Such challenges can be addressed by phase-change solvents that have been shown to enable both lower energy consumption and capture costs. Despite their clear advantages, the limited availability of detailed phase equilibrium data hinders their consideration in scaling-up studies of phase-change CO₂ capture processes. In this study, CO₂ loading and phase compositions of novel phase change aqueous amine solutions are experimentally investigated. Phase equilibrium experiments are carried out to measure the CO₂ loading of aqueous mixtures containing *N,N*-dimethylcyclohexylamine (DMCA) with 3-methylaminopropylamine (MAPA) and *N,N*-dimethylcyclohexylamine (DMCA) with *N*-Cyclohexyl-1,3-propanediamine (CHAP) at 40, 60 and 90 °C. It is observed that both systems exhibit phase change behavior, while DMCA-CHAP presents higher cyclic capacity and rather low volatility losses.

1. Introduction

Chemical absorption using amine solutions is used for decades in gas purification. It is considered as a mature technology and, consequently, it was suggested for CO₂ capture processes (Aaron and Tsouris, 2005; Rochelle, 2009; Keith, 2009; Bui et al., 2018). The major drawback, however, that hinders wider commercialization of such processes in existing industrial plants is of economic nature. It is estimated that electricity cost increases more than 80%, if a traditional fossil fuel power plant is coupled with a carbon capture unit that uses ethanolamine (MEA) as solvent (Li et al., 2016). This is due to the fact that flue gas, e.g. from fossil fuel combustion, contains only 10–15% CO₂, requiring high capital and operational expenditures to develop efficient separation systems (Zhang et al., 2019). Moreover, the energy demands for solvent

regeneration via heating, are significant, since the amount of water is high in traditional solvents (e.g., 30% wt. MEA solutions) mainly due to the corrosive nature of more concentrate amine solutions.

The energy requirements of solvent-based CO₂ capture systems should be minimized to less than 2.0 GJ per metric ton of captured CO₂ (Rochelle, 2009; Bui et al., 2018), in order to facilitate wide industrial proliferation. The majority of carbon capture technologies, however, are still far from commercialization (Bhown, 2014), with notable exceptions being the Petra Nova and the Boundary Dam plants in US and Canada, respectively (Singh and Stéphenne, 2014; Jenkins, 2015). Vigorous research efforts in the last 25 years embarked on an intense race to develop new solvent systems that could substitute conventional solvents such as MEA (Papadopoulos et al., 2019; Zhang et al., 2019).

Towards that goal, the so called phase change solvents represent a

Abbreviations: AMP, 2-Amino-2-methyl-1-propanol; BDA, 1,4-Butanediamine; CHAP, *N*-cyclohexyl-1,3-propanediamine (also known as S1N); DEAPD, 3-(diethylamino)-1,2-propanediol; DEEA, Diethylethanolamine; DETA, Diethylenetriamine; DMBA, *N,N*-dimethylbutylamine; DMCA, *N,N*-dimethylcyclohexylamine; MAPA, 3-Methylaminopropylamine; MCA, *N*-Methylcyclohexylamine; MEA, Monoethanolamine; PMDETA, *N,N,N',N'*-Pentamethyldiethylenetriamine; TETA, Triethylenetriamine; VLE, Vapor - Liquid Equilibrium; VLLE, Vapor - Liquid - Liquid Equilibrium.

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promising class of chemicals (Jessop et al., 2005; Chen et al., 2011; Zhang et al., 2011a,b,c; Zhang et al., 2012a,b; Zhang et al., 2013). Such solvents are usually aqueous amine systems that may present one liquid phase at ambient conditions and two liquid phases at different process conditions, upon reaction with CO₂ (Xu et al., 2019). Among the two emerging liquid phases in equilibrium, only the CO₂-rich phase needs thermal regeneration, hence decreasing the energy requirements (Ye et al., 2015; Zhuang et al., 2016; Liu et al., 2019). By exploiting such phase behavior, it is estimated that the reboiler duty could be reduced to approximately ~2.1–2.4 GJ per ton of CO₂ without process modifications other than the addition of a decanter (Raynal et al., 2011a; Liebenthal et al., 2013). In this direction, several amine mixtures that exhibit phase change behavior have been suggested and were recently thoroughly reviewed by Papadopoulos et al. (2019) and Zhang et al. (2019).

The most studied processes using amine phase change solvents are constituted of the iCap process (Pinto et al., 2014a,b), the DMXTM process (Raynal et al., 2011a,b; Raynal et al. 2014; Gomez et al., 2014; Dreillard et al., 2017) and the TBS system (Zhang et al., 2011c, 2012a). While these studies pertain to aqueous amine mixtures, some authors also suggested nonaqueous (or partly non aqueous) solutions, often replacing water with alcohols (Barzagli et al., 2013, 2017; Barbarossa et al., 2013; Kim et al., 2014; Zheng et al., 2014; Zhang et al., 2017b; Tao et al., 2018; Guo et al., 2019).

In literature, the available experimental data include mostly CO₂ solubility in amine solutions that exhibit a single liquid phase (systems that present Vapor-Liquid equilibrium, VLE). On the other hand, the experimental data for phase change aqueous amine solutions that exhibit Vapor-Liquid-Liquid equilibrium (VLLE) are scarce (Zhang et al., 2011b, 2012a; Zhang, 2013; Pinto et al., 2014a). Table 1 summarizes literature studies regarding the CO₂ loading of aqueous amine mixtures that contain promising solvents, including DMCA, MAPA and CHAP.

More specifically, Vapor - Liquid - Liquid Equilibrium (VLLE) experimental data have been reported for the amine mixture of DEEA-MAPA, which is one of the most studied systems (Kim and Svendsen, 2011; Hartono et al., 2013; Ciftja et al., 2013; Pinto et al., 2014a; Arshad et al., 2016). MAPA is used as absorption activator, as it exhibits fast kinetics and high CO₂ solubility, while DMCA is used as regeneration promoter, which facilitates the CO₂ desorption and induces the phase separation, being less hydrophilic than MAPA. Furthermore, various phase change solvents were tested and critically compared by

Table 1

Literature studies regarding the CO₂ loading of aqueous amine mixtures that contain DMCA, MAPA, CHAP and systems from literature.

Amine	References
CHAP (also known as SIN)	Papadopoulos et al. (2020)
DMCA	Tan (2010); Zhang (2013)
MAPA	Chen et al. (2011); Arshad et al. (2013a,b); Pinto et al. (2014a,b); Knuutila and Nannestad (2017)
Amine Blends	References
Amine-ether-amide-H ₂ O	Zheng et al. (2014); Barzagli et al. (2017); Machida et al. (2017, 2019); Zhang et al. (2017a,b); Tao et al. (2018); Li et al. (2018a); Yang et al. (2018)
BDA-DEEA	Xu et al. (2013d)
DEEA-MAPA	Kim et al. (2011); Ciftja et al. (2013); Pinto et al. (2014a,b); Arshad et al. (2014)
DEEA-TETA	Lee et al. (2017); Li et al. (2018b); Zhang et al. (2018)
DEEA-DMBA	Wang et al. (2017)
DETA-PMDETA	Ye et al. (2017)
DETA-Sulfolane	Luo et al. (2016); Wang et al. (2018)
DMCA-CHAP	Papadopoulos et al. (2020)
DMCA-MCA	Zhang (2013)
DMCA-MCA-AMP	Zhang (2013); Tzirakis et al. (2019)
DMCA-TETA	Zhang et al. (2018)
Screening experiments	Chen et al. (2011); Xu et al. (2013a); Ye et al. (2015); Zhuang et al. (2016); Liu et al. (2019); Xu et al. (2019)

Zhang (2013), who, subsequently, suggested a promising solvent, such as the DMCA-MCA-AMP aqueous system. The phase behavior of such solvent was further experimentally investigated by Tzirakis et al. (2019), who presented experimental data for 3 M and 5 M DMCA-MCA-AMP aqueous solutions upon loading with CO₂.

Very recently, Papadopoulos et al. (2020), using computer aided molecular design (CAMD) and Pareto optimization, suggested *N*-Cyclohexyl-1,3-propane diamine (CHAP) (mentioned as SIN in that study) as a promising novel solvent. CHAP is a diamine and is used as absorption activator (Fig. 1). This is because it contains a primary and a secondary amine group, which are associated with fast kinetics, similarly to MAPA. As shown in Fig. 1, CHAP presents high molecular weight, presents low vapor pressure, while its aqueous solutions present relatively low vaporization losses (Papadopoulos et al., 2020).

This study is prompted by our previous works (Tzirakis et al., 2019; Papadopoulos et al., 2020), in which it was found that the addition of DMCA in aqueous MAPA or CHAP solutions can induce phase change behavior, in a similar fashion that the introduction of DEEA induces phase separation of aqueous MAPA mixtures (Arshad et al., 2014). As described by Tzirakis et al. (2019) and Papadopoulos et al. (2020), such phase change behavior can be achieved in relatively low amine concentrations compared to the ones (7 M) used in the relevant DEEA-MAPA (Pinto et al., 2014a,b; Arshad et al., 2014) or in BDA-DEEA (Xu et al., 2013a,b,c,d) aqueous systems.

The promising results of Tzirakis et al. (2019) and Papadopoulos et al. (2020) reveal the need for extensive phase equilibrium measurements in a wide range of conditions. In this direction, the aqueous DMCA-MAPA system is experimentally investigated for the first time at three temperatures and various CO₂ partial pressures. Solutions of DMCA-MAPA with total molarity of 3 M (DMCA:MAPA mole ratio 2:1) are studied at 40 °C, 60 °C, and 90 °C and various CO₂ partial pressures. Furthermore, the DMCA-CHAP aqueous system is experimentally investigated at the same temperature and pressure range, as well as for the same amine concentrations (3 M with DMCA:CHAP mole ratio equal to 2:1), in order to study the effect of absorption activators, i.e. MAPA and CHAP, on the behavior of such multicomponent solvent systems.

The presented experimental data are important for simulation purposes in dynamic transitions, where conditions may vary. Moreover, the obtained data can enable the development of predictive thermodynamic models that will successfully describe the phase behavior of such highly non ideal mixtures. Such models and simulations are important in chemical process design. They could help in reaching solid conclusions regarding the potential of scaling up the processes for phase separation solvents through the identification of process characteristics that allow further reduction of energy requirements and the overall process optimization.

2. Experimental

The purity of the materials used in this study is presented in Table 2. Chemicals are used as received without further purification.

The experimental apparatus, which is presented in Fig. 2, and the experimental procedure are described in detail by Tzirakis et al. (2019) and are briefly presented here. In more detail, mixtures of CO₂ and N₂ are prepared using mass flow controllers and pass through a series of four gas-wash bottles, which are placed inside a water/oil bath of constant temperature (temperature stability ±0.1 °C at 40 °C and ±0.8 °C at 90 °C). The first bottle (H1) contains pure double distilled water, the second one (H2) contains the investigated amine solution (approximately 25 mL), the third one is used as a trap for potential drifted liquid drops (not observed in this study), while the fourth one is kept at lower than the experimental temperature and is used as a trap for volatile components. Consequently, such experimental apparatus allows the compensation of water vaporization losses. However, although high boiling point amines are used, some amine losses are observed, similarly to all pilot scale absorbers. Nevertheless, the final composition of the

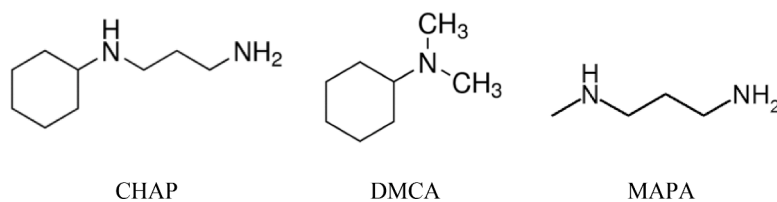


Fig. 1. Chemical structure of CHAP, DMCA and MAPA.

Table 2
Chemicals used in this work.

Product Name	Abbreviation	CAS-number	Purity	Supplier
Carbon dioxide	CO ₂	124-38-9	99.9 (vol%)	Air Liquide
Nitrogen	N ₂	7727-37-9	99.9 (vol%)	Air Liquide
Helium	He	7440-59-7	99.99 (vol%)	Air Liquide
N,N-dimethylcyclohexylamine	DMCA	98-94-2	99%	Sigma Aldrich
3-methylaminopropylamine	MAPA	6291-84-5	99%	Sigma Aldrich
N-Cyclohexyl-1,3-propanediamine	CHAP	3312-60-5	98%	TCI

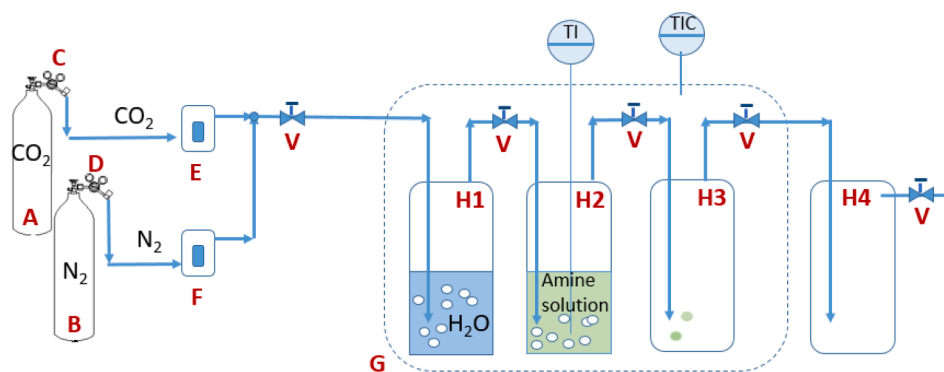


Fig. 2. Scheme of the experimental apparatus: A: CO₂ tank, B: N₂ tank, C and D: Pressure Regulators, E and F: Mass flow controllers, H: Gas wash bottles (250 mL), G: Thermostatic bath, V: valves (reproduced from Tzirakis et al. (2019) with permission from Elsevier).

loaded solution (final amine content and CO₂ loading) are presented in the Results and Discussion section.

The systems remain at stable conditions for at least four hours, a period of time that was found to be sufficient for the loading of such amine solutions. The end time of each experiment is ascertained by two subsequent chromatographic analyses.

In this study, the final amine content of the solution was measured using an appropriate acid titration method (Jeffery et al., 1989), while the CO₂ content was measured using the BaCl₂ titration method as described in detail by Tzirakis et al. (2019). The amine mole ratio at each coexisting liquid phase was determined using a Gas - Chromatograph (GC) equipped with a Thermal Conductivity Detector (TCD) and a J&W CP-Volamine capillary column (60.0 m x 320 μm). Helium was used as a carrier gas, while the GC temperature program was as follows: heating from 60 °C to 121 °C with 5 °C min⁻¹, 5 min hold time at 121 °C, heating from 121 °C to 260 °C with 10 °C min⁻¹, 5 min hold time at 260 °C. The injector temperature was equal to 210 °C. Split flow was set to 30 mL min⁻¹, with a split ratio equal to 30:1. At least four chromatograms were obtained for each sample.

Uncertainties in the CO₂ loading and amine content experimental values were obtained by estimating the most probable error, through propagation of errors, considering the uncertainties of all measurements (i.e. volumes and weights of materials used in the titration). In cases of chromatographic measurements (i.e. considering the estimation of the amine mole ratio in each liquid phase) the reported uncertainties denote the standard deviation of values obtained from at least four chromatograms.

Using the aforementioned procedure, the chemical absorption of CO₂

in aqueous solutions containing mixtures of CHAP and DMCA is experimentally investigated at 40, 60 and 90 °C and CO₂ partial pressures 10 - 80 kPa. Experiments are performed starting from an aqueous amine solution with total amine content equal to 44.3 wt% (app. 3 M) and DMCA-CHAP at a mole ratio of 2:1 (DMCA 27.4 wt%, app. 2.0 M, plus CHAP 16.9 wt%, app. 1.0 M).

The CO₂ - water - DMCA - MAPA system is experimentally investigated at 40, 60 and 90 °C and CO₂ partial pressures 10 - 80 kPa. Experiments are performed using aqueous amine solutions with total amine content equal to 36.9 wt% (app. 3 M), and DMCA-MAPA at a mole ratio of 2:1 (DMCA 27.4 wt%, app. 2.0 M, plus MAPA 9.5 wt%, app. 1.0 M).

3. Results and discussion

3.1. Loading of aqueous DMCA-CHAP solutions

Snapshots for all investigated solutions are presented in Figure S2 and S4 of the ESI. Results, in terms of CO₂ loading, are presented in Table 3 and the obtained data are illustrated in Figs. 3-5 (approximate volume ratios of phases in equilibrium and densities are shown in Table S1 of the ESI). Interestingly, at 40 °C the system presents VLE at relatively high CO₂ partial pressures (higher than 33 kPa), while it presents VLLE at lower CO₂ partial pressures. At 60 °C, the system presents VLE at CO₂ partial pressures higher than 80 kPa, while it presents VLLE at low CO₂ partial pressures. At 90 °C, the system presents VLLE at all investigated conditions (CO₂ partial pressures up to 73.4 kPa). Consequently, at typical operating conditions of the absorption

Table 3Solubility of CO₂ in aqueous DMCA-CHAP system (total amine content equal to 44.3 wt%, app. 3 M, DMCA-CHAP mole ratio 2:1).

Temp. (°C)	CO ₂ Partial Pressure (kPa)	Phase equilibrium		CO ₂ loading, α (mole CO ₂ per mole of amine)	Final amine content (on water basis), %wt.	Amine mole ratio in the loaded phase (CHAP/DMCA)
40	10.1	VLLE	Organic Phase	0.026±0.003	87.9 ± 1.5	0.009±0.001
			Aqueous Phase	0.826±0.069	33.2 ± 0.6	0.752±0.220
	33.8	VLE	Liquid Phase	0.894±0.060	41.4 ± 0.7	0.498±0.202
			Liquid Phase	1.000±0.068	40.2 ± 0.7	0.459±0.037
60	10.1	VLLE	Organic Phase	0.024±0.002	88.0 ± 1.5	0.010±0.001
			Aqueous Phase	0.768±0.069	26.3 ± 0.4	1.064±0.326
	17.3	VLLE	Organic Phase	0.027±0.003	91.1 ± 1.5	0.007±0.001
			Aqueous Phase	0.803±0.055	32.6 ± 0.6	0.991±0.266
	50.6	VLLE	Organic Phase	0.029±0.003	82.0 ± 1.4	0.002±0.001
			Aqueous Phase	0.903±0.058	38.7 ± 0.7	0.716±0.088
	81.0	VLE	Liquid Phase	0.928±0.061	38.6 ± 0.7	0.573±0.131
			Liquid Phase	1.012±0.068	42.0 ± 0.7	0.461±0.068
90	30.4	VLLE	Organic Phase	0.040±0.012	76.4 ± 1.3	0.081±0.034
			Aqueous Phase	0.606±0.050	27.9 ± 0.5	1.615±0.221
	50.6	VLLE	Organic Phase	0.028±0.003	87.3 ± 1.5	0.029±0.002
			Aqueous Phase	0.617±0.038	26.4 ± 2.8	0.002±0.001
	73.4	VLLE	Organic Phase	0.025±0.003	87.1 ± 1.4	0.027±0.003
			Aqueous Phase	0.756±0.053	28.6 ± 0.5	1.188±0.369

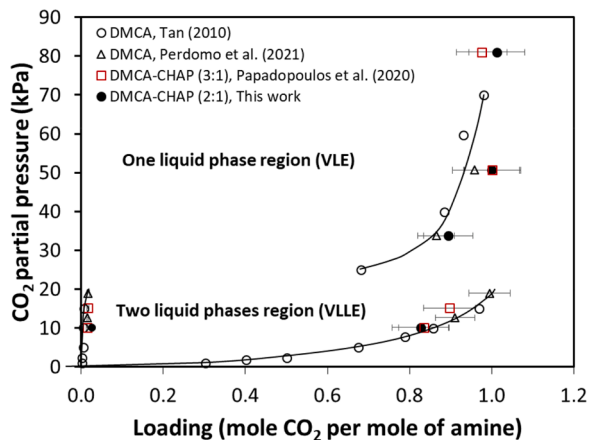


Fig. 3. The phase behavior of CO₂-water-CHAP-DMCA and CO₂-water-DMCA mixtures at 40 °C. Lines show qualitatively the phase behavior and were added only as a visual aid (open triangles show DMCA (3 M) from [Perdomo et al. \(2021\)](#) and open circles DMCA (3 M) data from [Tan \(2010\)](#), while open squares show DMCA-CHAP (3:1) from [Papadopoulos et al. \(2020\)](#) and dense circles show DMCA-CHAP (2:1) from this work.

column, i.e., 40 °C and 10 kPa of CO₂ partial pressure, the system presents two liquid phases.

The results of [Table 3](#) reveal that the organic phase mainly consists of DMCA, which is a lipophilic amine, whereas CHAP, which is more hydrophilic than DMCA, is mainly found in the CO₂-rich aqueous phase. Furthermore, as shown in [Fig. 3](#), the phase behavior of 3 M aqueous DMCA ([Perdomo et al., 2021](#); [Tan, 2010](#)), DMCA-CHAP (app. 3 M, 2:1 mole ratio, data from this work) and DMCA-CHAP (app. 3 M, 3:1 mole ratio, data from [Papadopoulos et al., 2020](#)) is rather similar, while small differences are observed for the loading of the aqueous CO₂-rich phase.

However, differences become more pronounced as the temperature increases to 60 °C ([Fig. 4](#)) and 90 °C ([Fig. 5](#)). For example, at 90 °C, the loading of the aqueous CO₂ rich phase, expressed as mole of CO₂ per mole of amine, is higher in the DMCA-water system and becomes lower upon the addition of CHAP ([Fig. 5](#)).

3.2. Loading of aqueous DMCA-MAPA solutions

The results for aqueous DMCA-MAPA solutions, in terms of CO₂ loading, are presented in [Table 4](#) (app. volume ratios of phases in equilibrium and densities are presented in Table S2 of the ESI). Snapshots for all investigated solutions are presented in [Figure S3](#) and [S5](#) of

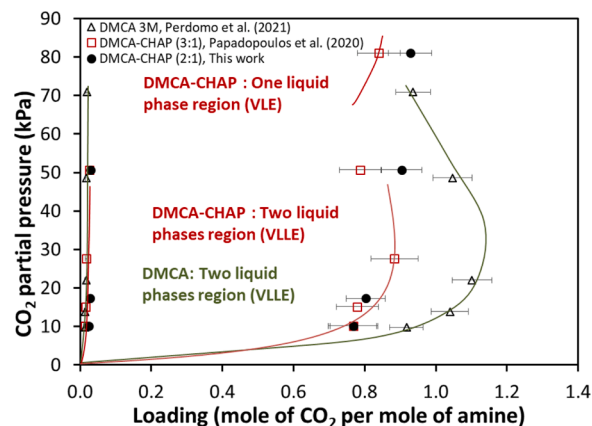


Fig. 4. The phase behavior of CO₂-water-CHAP-DMCA and CO₂-water-DMCA mixtures at 60 °C. Lines show qualitatively the phase behavior and were added only as a visual aid (open triangles show DMCA (3 M) from [Perdomo et al. \(2021\)](#), while open squares show DMCA-CHAP (3:1) from [Papadopoulos et al. \(2020\)](#) and dense circles show DMCA-CHAP (2:1) from this work.

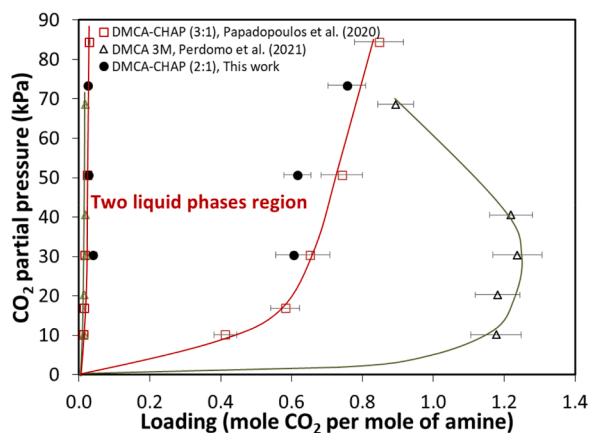


Fig. 5. The phase behavior of CO₂-water-CHAP-DMCA and CO₂-water-DMCA mixtures at 90 °C. Lines show qualitatively the phase behavior and were added only as a visual aid (open triangles show DMCA (3 M) from Perdomo et al. (2021), while open squares show DMCA-CHAP (3:1) from Papadopoulos et al. (2020) and dense circles show DMCA-CHAP (2:1) from this work.

the ESI. The obtained data are illustrated in Figs. 6–8, which reveal that such loaded DMCA-MAPA aqueous system present VLLE at 40 °C and below app. 20 kPa CO₂ partial pressure, while it presents VLE at higher CO₂ partial pressures. VLLE appears below app. 52 kPa at 60 °C and at all investigated CO₂ partial pressures at 90 °C.

The results of Table 4 reveal that, similarly to the DMCA-CHAP system presented in the previous section, the organic phase mainly consists of DMCA, which is a lipophilic amine. On the other hand, MAPA, which is more hydrophilic than DMCA, is mainly found in the aqueous phase. Such behavior was also observed by Pinto et al. (2014a), who studied the loading of aqueous MAPA-DEEA systems and report that MAPA is mainly accumulated in the aqueous phase. Furthermore, the upper phase (organic phase) achieves low CO₂ solubility, while the aqueous phase is rich in CO₂.

Finally, the phase behavior of loaded DMCA-MAPA-H₂O, DMCA-CHAP-H₂O and DMCA-H₂O mixtures (with app. 3 M amine content) is similar. For example, at 40 °C and CO₂ partial pressures lower than app. 20 kPa, all systems present VLLE (see Table 4 and Fig. 3), while they present VLE at relatively higher CO₂ partial pressures, meaning that the addition of CO₂ and the subsequent reaction with amines renders the two liquid phases more compatible enhancing miscibility. This is also shown by the volume ratios of the two liquid phases presented in Tables S1 and S2 of the ESI for 60 °C. As the CO₂ partial pressure increases, the volume of the organic phase decreases as amine molecules, and mainly the lipophilic DMCA, are transformed in hydrophilic ionic species that end up in the aqueous phase.

The same behavior was experimentally observed by Zhang et al. (2018), who studied the speciation of both liquid phases in the DMCA-TETA aqueous system. They report that the CO₂ absorption is initiated by the reaction of CO₂ with the primary amine groups of TETA and, upon consumption of such groups, the reaction continues through the secondary amine groups. With depletion of TETA, the reaction with DMCA molecules becomes significant, which results in the regeneration of TETA and the gradual transformation of the lipophilic DMCA to ionic species that are accumulated in the lower (aqueous phase), resulting in the volume expansion of such phase. It is reasonable to assume that TETA and MAPA present a similar behavior, since they exhibit similar amine groups in their molecules. Consequently, having in mind the observations of this study and the experimental results of Zhang et al. (2018), a reasonable mechanism for DMCA-MAPA aqueous system is as shown in Fig. 9. Initially CO₂ reacts with MAPA and, upon depletion of MAPA, the reaction with DMCA becomes significant, while the produced ionic species are accumulated in the aqueous phase, rendering the organic phase poor in CO₂.

In Figs. 6 and 7, the experimental data of Pinto et al. (2014a) for the DEEA-MAPA aqueous systems are also presented for comparison. Aqueous DEEA-MAPA (7 M) and DMCA-MAPA (app. 3 M) systems present similar CO₂ loadings, expressed as mole of CO₂ per mole of amine.

3.3. Comparison of potential phase change solvent systems

The screening of solvents for CO₂ capture applications is usually performed in terms of absorption capacity and cyclic capacity, expressed as mole of CO₂ per mass of solvent. Results are usually compared with MEA, which is a benchmark solvent. However such comparison is not trivial, some solvents exist in a single phase at both the absorption and the regeneration temperatures (i.e. MEA), some exist in a single phase at the absorption temperature and in two liquid phases at the regeneration temperature (i.e. DMCA-MCA-AMP) and some of them exist in two liquid phases at both the absorption and the regeneration temperatures (i.e. DMCA, DMCA-CHAP, DMCA-MAPA, MAPA-DEEA). Hence, in this section results are presented as mole of CO₂ per unit mass of solvent (in case of non-phase change solvents, i.e. MEA or CHAP) or per unit mass of the aqueous phase solvent in case of phase change systems (i.e. DMCA, DMCA-MCA-AMP, DMCA-MAPA and DMCA-CHAP).

The absorption capacity for various phase change solvents and MEA, calculated at typical conditions of the absorption column, i.e., 40 °C and 10 kPa of CO₂ partial pressure, is presented at Fig. 10. It is revealed that only MAPA-DEEA 7 M aqueous solution presents similar absorption capacity with MEA, around 2.5 mole of CO₂ per kg, while most others present an absorption capacity around 2 mole of CO₂ per kg.

The amount of CO₂ that the solvent can absorb is a crucial screening property, but not the only one. The amount of CO₂ that is released through the series of the absorption and desorption processes is equally important. Thus, the cyclic capacity is also a good indicator for the evaluation of solvents. The CO₂ cyclic capacity of various solvent systems, calculated at similar experimental conditions, is compared in Fig. 11. In all cases, it was calculated assuming 10 kPa of CO₂ partial pressure and absorption temperature equal to 40 °C. The regeneration temperature was considered equal to 90 °C for most systems shown in Fig. 11 (i.e., for CHAP, DMCA, DMCA-MAPA, DMCA-CHAP, DMCA-MCA-AMP), which is a typical temperature for processes with phase change solvents. However, due to lack of data for 90 °C, the regeneration temperature of MAPA-DEEA was assumed equal to 80 °C (the closest temperature to 90 °C for which data are available), while calculations for MEA were performed assuming regeneration temperature equal to 80 °C (the closest temperature to 90 °C for which data are available) and 120 °C (the typical regeneration temperature of the conventional process).

Despite the lack of data at the desirable 90 °C, it is still possible to draw reasonable insights regarding the performance of MEA and MAPA-DEEA compared to solvents of interest in this work. The data presented in Fig. 11 show that the cyclic capacity of MEA (regenerated at 120 °C) is 1.45 mol CO₂/kg, whereas the cyclic capacity of DMCA-MCA-AMP (3.6 M-regenerated at 90 °C) is 1.39 mol CO₂/kg. This large regeneration temperature difference of 30 °C between the two solvents results in the very small cyclic capacity difference of 0.06 mol CO₂/kg. In other words, the 3% lower cyclic capacity of DMCA-MCA-AMP compared to MEA corresponds to a 25% lower regeneration temperature of the former. The latter is a very desirable feature, as the 2.5 GJ/ton CO₂ of regeneration energy of DMCA-MCA-AMP compared to the 4.0 GJ/ton CO₂ of MEA are partly due to this large temperature difference (Papadopoulos et al., 2019). On the other hand, the cyclic capacity of MEA regenerated at 80 °C is 0.58 mol CO₂/kg. This indicates a cyclic capacity difference of 58% from DMCA-MCA-AMP at 90 °C, which clearly cannot be compensated by MEA within a 10 °C difference, since the two solvents exhibit almost the same cyclic capacity at a 30 °C difference. A similar conclusion can be drawn for DMCA-CHAP (44.3 wt%) which is investigated in this work; results indicate a 52% higher cyclic capacity compared to MEA at

Table 4
Solubility of CO₂ in DMCA-MAPA-H₂O at 40, 60, 90 °C.

Temp. (°C)	CO ₂ Partial Pressure (kPa)	Phase equilibrium		CO ₂ loading, α (mole CO ₂ per mole of amine)	Final amine content (on water basis), %wt.	Amine mole ratio in the loaded phase (MAPA/DMCA)	
40	10.1	VLE	Organic Phase	0.011±0.006	90.8 ± 4.6	0.007	
			Aqueous Phase	0.946±0.054	21.6 ± 1.6	1.13	
	16.9	VLE	Organic Phase	0.012±0.001	94.0 ± 1.6	0.007	
			Aqueous Phase	0.943±0.062	26.7 ± 0.5	0.73	
	36.7	VLE	Liquid Phase	0.803±0.058	34.5 ± 0.6	0.38	
	51.5	VLE	Liquid Phase	0.863±0.058	34.9 ± 0.6	0.29	
	81.0	VLE	Liquid Phase	0.922±0.062	37.9 ± 0.6	0.33	
	60	10.1	VLE	Organic Phase	0.011±0.002	86.3 ± 1.5	0.005
				Aqueous Phase	0.854±0.072	19.9 ± 0.3	1.68
		16.2	VLE	Organic Phase	0.011±0.002	90.7 ± 1.5	0.006
			Aqueous Phase	0.871±0.059	22.5 ± 0.4	1.02	
31.9		VLE	Organic Phase	0.013±0.001	92.3 ± 1.6	0.007	
			Aqueous Phase	0.950±0.063	24.9 ± 0.4	0.87	
51.7		VLE	Organic Phase	0.020±0.005	89.2 ± 1.5	0.008	
			Aqueous Phase	0.956±0.065	29.2 ± 0.5	0.51	
81.0		VLE	Liquid Phase	0.875±0.059	33.6 ± 0.6	0.43	
90		10.1	VLE	Organic Phase	0.010±0.002	93.0 ± 1.6	0.004
			Aqueous Phase	0.614±0.040	14.8 ± 0.3	6.43	
	16.9	VLE	Organic Phase	0.010±0.002	89.0 ± 1.5	0.005	
			Aqueous Phase	0.784±0.056	15.5 ± 0.3	3.56	
	31.4	VLE	Organic Phase	0.011±0.001	96.4 ± 1.6	0.005	
			Aqueous Phase	0.844±0.052	17.2 ± 0.3	2.54	
	52.5	VLE	Organic Phase	0.013±0.002	96.0 ± 1.6	0.005	
			Aqueous Phase	0.940±0.066	17.9 ± 0.3	1.67	
	84.4	VLE	Organic Phase	0.015±0.002	94.0 ± 1.6	0.005	
			Aqueous Phase	0.896±0.062	18.0 ± 0.3	1.89	

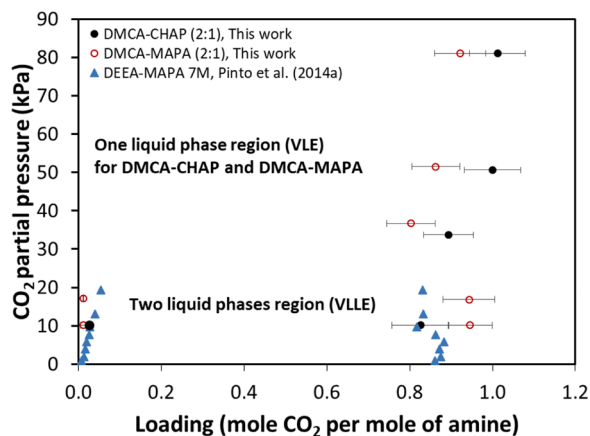


Fig. 6. Loading of CO₂ in DMCA-MAPA (3 M, 2:1 mole ratio, open circles), DMCA-CHAP (3 M, 2:1 mole ratio, dense circles) and DEEA-MAPA (7 M, dense triangles), Pinto et al. (2014a) aqueous systems at 40 °C.

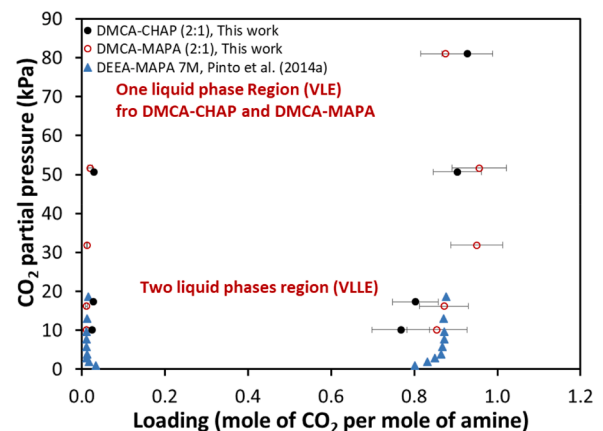


Fig. 7. Loading of CO₂ in DMCA-MAPA (3 M, 2:1 mole ratio, open circles), DMCA-CHAP (3 M, 2:1 mole ratio, dense circles) and DEEA-MAPA (7 M, dense triangles), Pinto et al. (2014a) aqueous systems at 60 °C.

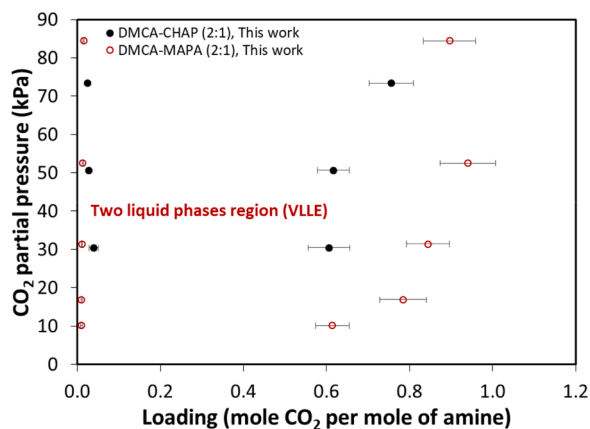


Fig. 8. Loading of CO₂ in DMCA-MAPA (3 M, 2:1 mole ratio, open circles) and DMCA-CHAP (3 M, 2:1 mole ratio, dense circles) aqueous systems at 90 °C.

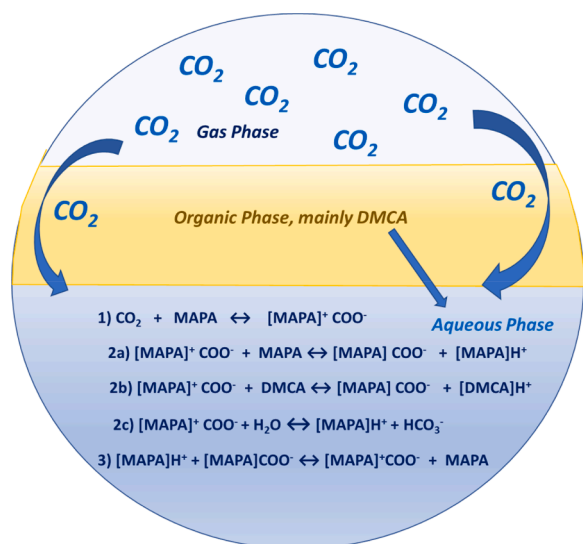


Fig. 9. Reaction mechanism of DMCA-MAPA aqueous system.

a regeneration temperature of only 10 °C higher than MEA. MAPA-DEEA is the other solvent for which data are only available at 80 °C. This solvent exhibits considerably lower cyclic capacity than MEA at this

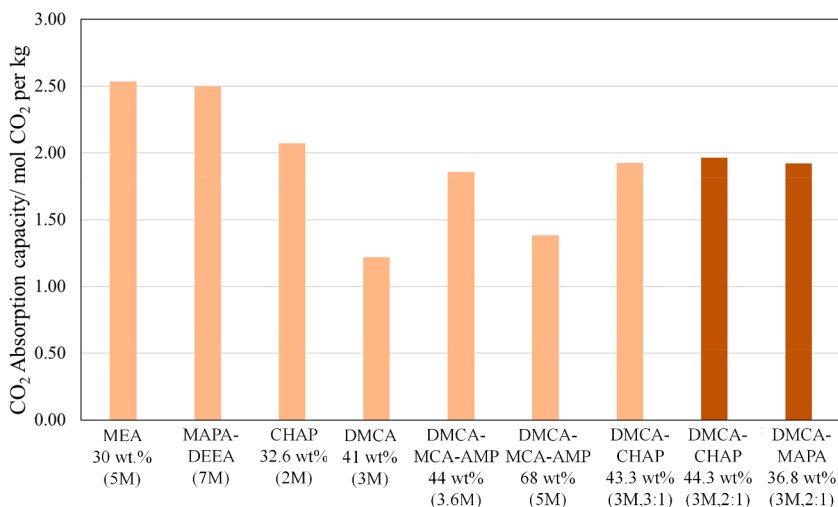


Fig. 10. CO₂ absorption capacity expressed as mole of CO₂ per unit mass of solvent (or aqueous phase solvent in phase change systems) calculated at 40 °C and app. 10 kPa of CO₂ partial pressure, which are typical absorption conditions. Experimental data for DMCA-MAPA and DMCA-CHAP (2:1) were taken from this work, for DEEA-MAPA from Pinto et al. (2014a), for MEA and DMCA-MCA-AMP from Tzirakis et al. (2019), for CHAP and DMCA-CHAP (3:1) from Papadopoulos et al. (2020) and, finally, for DMCA from Perdomo et al. (2021).

temperature. It is therefore more unlikely (compared to MEA) that at 90 °C it could reach the cyclic capacity of DMCA-MCA-AMP (3.6 M) or of DMCA-CHAP (44.3 wt%). Among the rest of solvents, the aqueous DMCA and DMCA-MAPA systems present cyclic capacity around 0.95 mole of CO₂ per kg, which is one of the lowest among the phase change systems. Nevertheless, aqueous solutions of DMCA are recommended only in mixtures with other amines, since, as a tertiary amine, it presents high loading values, but rather slow absorption kinetics and high volatility losses from aqueous solutions (Zhang, 2013).

Consequently, besides the cyclic absorption capacity, several other properties should be accounted for, in order to select the optimum solvent system. In this direction, one very important issue is the volatility losses of amines during the absorption process. An approximate comparison of the volatility losses for various aqueous amine solutions is presented in Figure S6 of the ESI. Since DMCA is a tertiary amine and, consequently, presents weak hydrogen bonds with water, it exhibits relatively high volatility losses, while diamines, such as CHAP and MAPA, that contain one primary and one secondary amine group present lower losses than DMCA. However, all systems containing DMCA with CHAP or MAPA present higher volatility losses than MEA, which is an alkanolamine, and as expected exhibits the strongest hydrogen bonds with water molecules. Among the phase change solvents, thus excluding MEA that does not show such behavior, DMCA-MAPA (2:1) and DMCA-CHAP (2:1) present the lowest volatility losses. Furthermore, as shown by Papadopoulos et al. (2020), the loaded DMCA and DMCA-CHAP systems present dynamic viscosity similar to that of MEA, while other phase change solvents, such as MCA or DMCA-MCA-AMP present relatively higher values.

4. Conclusions

The CO₂-DMCA-CHAP-H₂O and CO₂-DMCA-MAPA-H₂O systems were experimentally investigated at 40, 60 and 90 °C, using an aqueous amine solution with total amine content of 44.3 wt% and 36.9 wt%, respectively, (app. 3 M) and at a 2:1 DMCA to CHAP or MAPA mole ratio. Both mixtures present VLLE at 40 °C, below approximately 20 kPa of CO₂ partial pressure, and VLE at relatively high CO₂ partial pressures. VLLE appears below approximately 52 kPa at 60 °C and at all investigated CO₂ partial pressures at 90 °C. It is found that in all cases that exhibit liquid-liquid phase separation, the hydrophilic CHAP or MAPA is accumulated in the aqueous CO₂ rich phase, while the more hydrophobic DMCA in the CO₂ lean organic phase. Moreover, it was observed that the volume of the upper phase decreases as the CO₂ partial pressure increases, which reveals the mechanism of CO₂ absorption in biphasic systems, i.e. as the CO₂ partial pressure increases, more amine

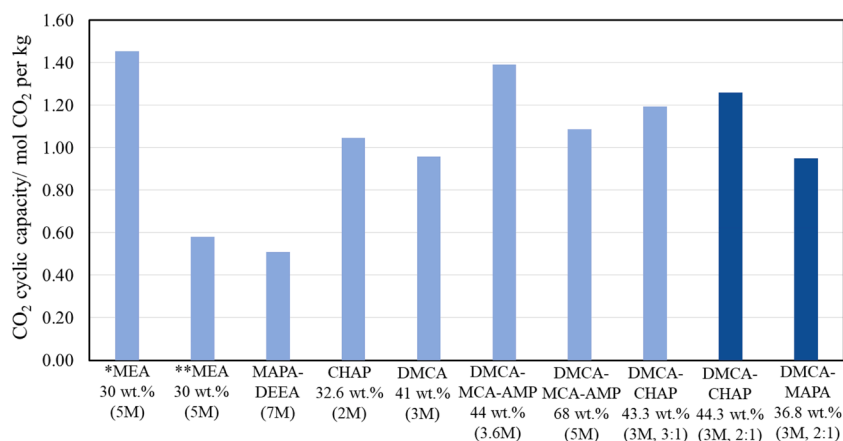


Fig. 11. CO₂ cyclic capacity expressed as mole of CO₂ per unit mass of solvent (or aqueous phase solvent in phase change systems) calculated assuming app. 10 kPa of CO₂ partial pressure, 40 °C as the absorption temperature and regeneration temperature equal to 120 °C for *MEA (or 80 °C for **MEA), 80 °C for MAPA-DEEA and 90 °C (for all other solvents). Experimental data for DMCA-MAPA and DMCA-CHAP (2:1) were taken from this work, for DEEA-MAPA from Pinto et al. (2014a), for MEA and DMCA-MCA-AMP from Tzirakis et al. (2019), for CHAP and DMCA-CHAP (3:1) from Papadopoulos et al. (2020) and, finally, for DMCA from Perdomo et al. (2021).

molecules, and mainly the lipophilic DMCA, are transformed in hydrophilic ionic species that end up in the aqueous phase. Finally, DMCA-CHAP achieves higher cyclic absorption capacity than DMCA-MAPA, whereas the volatility losses DMCA-CHAP and DMCA-MAPA systems are found to be much lower than that of DMCA.

CRediT authorship contribution statement

Fragkiskos Tzirakis: Investigation, Methodology, Validation, Formal analysis, Writing - original draft, Writing - review & editing, Funding acquisition. **Ioannis Tsivintzelis:** Methodology, Validation, Formal analysis, Resources, Supervision, Writing - original draft, Writing - review & editing, Funding acquisition. **Athanasios I. Papadopoulos:** Conceptualization, Resources, Supervision, Writing - original draft, Writing - review & editing, Funding acquisition. **Panos Seferlis:** Conceptualization, Resources, Supervision, Writing - review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.ijggc.2021.103353](https://doi.org/10.1016/j.ijggc.2021.103353).

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