

Volatility of monoethanolamine and tetramethylethylene diamine in aqueous solution for CO₂ capture at different loading

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ABSTRACT

Amine volatility is an important parameter to be considered when used as a solvent for CO₂ capture. If the volatility is high, there is a need to inject the solvent so as to compensate the loss consequently the cost of the process increases. In this work CO₂ solubility and amine volatility in loaded and non-loaded aqueous 30 wt% MEA (monoethanolamine), 10, 30 and 50 wt% TMEDA (N,N',N'-tetramethylethylene diamine) were studied in the range of temperature (293 to 353 K) and pressure (2 Pa–400 kPa). Volatility measurements, in terms of partial pressures, were performed using a static apparatus with on-line analysis of the gas phase by GC to determine CO₂, water and amine partial pressures above the solution. The dissolved CO₂ in the liquid was determined by titration. The experimental data of the system (water + MEA), (water + TMEDA), and (water + MEA + CO₂) are in a good agreement with literature data. No data for comparison were found for the system (water + TMEDA + CO₂). Experimental partial pressures of the amines (P_{MEA} and P_{TMEDA}) were correlated using the empirical models developed by (Xu, 2011). Both models represent well the experimental data.

1. Introduction

Post-combustion absorption-stripping using aqueous amine is the leading process for CO₂ capture. Aqueous monoethanolamine (MEA) is considered to be the reference solvent for this application. This is the case of the pilot plant inaugurated in 2006 in Elsam (Denmark).

However several alternative solvents among which tertiary class of amine, compound with several function of amine, ionic liquids ... are studied to assess their CO₂ absorption load, degradation and evaporation ratio.

The use of a solvent with high volatility, in addition to the environmental impact of the solvent vapors, will increase the cost of the CO₂ capture process because of the need to reload the solvent to optimize the reaction (Nguyen, 2013). For these reasons, it is important to determine the volatility (vapor pressures) of solvents with the aim of developing thermodynamic model to optimize the process performance.

Several authors studied vapor-liquid equilibrium of aqueous amine but very few determined the mole fraction of the amine in the vapor

phase (volatility). (McLees, 2006) measured the volatility of MEA between 308 and 343 K in the binary system (water + MEA) as well as in blends with piperazine (PZ) as a promoter. The data was obtained using infrared spectroscopy (FTIR). (Nguyen, 2013) studied 20 aqueous alkanolamines, in the temperature range between 313 and 343 K using FTIR analytical method. Recently, (Du et al., 2017) measured the volatility (expressed in Henry's law constant) of 24 novel amines with different molecular structure (tertiary amines, hindered amines, ether amines and pyridine derivative) at 313 K using FTIR technique.

This work investigates the volatilities of two aqueous amine solvents: monoethanolamine (MEA) and N,N',N'-tetramethylethylene diamine (TMEDA) at different temperatures (293, 313, 333 and 353 K). The compositions of the systems are 30 wt% of MEA in water and 10, 30 and 50 wt% of TMEDA in water. These solutions were also studied at different CO₂ loading. The partial pressure of amine, water and CO₂ were obtained using a static apparatus with on-line GC analysis of the vapor phase. The loading of CO₂ was determined by volumetric titration (Mahi et al., 2019).

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Table 1

Cas number and purity of the used compounds.

Chemical	Acronym	CAS Number	Purity (mass fraction)	Purity GC	Source
Carbon dioxide	CO ₂	124-38-9	0.999	0.998	Air Liquide
Ethanolamine	MEA	141-43-5	≥0.990	0.990	Sigma Aldrich
N, N, N', N'-Tetramethylethylenediamine	TMEDA	110-18-9	0.990	0.993	Sigma Aldrich

Table 2

Analytical conditions used to study the vapor phase using GC Agilent 7890B

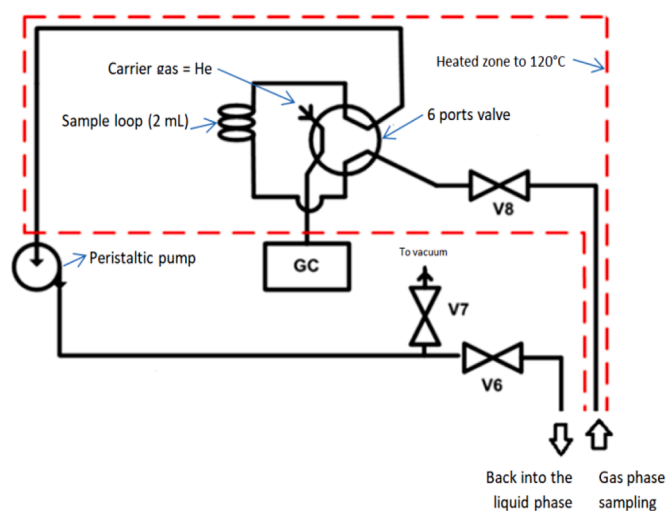
Analytical column	Nature	"PoraPlot Q" for water and CO ₂ analysis	"RTX-35 Amine" for amines analysis
	Geometry (m/ μm/ μm)	25/ 320/ 10	30/ 320 /1
	Température max (°C)	250	220
Carrier gas	Nature	H ₂	
	flow (ml. min ⁻¹)	4	
Oven	Initial temperature-time (min)	120 - 8	
	Temperature rate (°C. min ⁻¹)	40	
	Final temperature (°C) - time (min)	200 - 5	
Injector	Temperature (°C)	250	
	Mode	Split	
	Pressure (psi)	6.5	
	Total flow (ml/min)	23.6	
	Ratio Split	10 : 1	
Detector	Type	TCD	FID
	Temperature (°C)	250	250
	Make-up (ml/min)	3	2

Table 3Vapor-liquid equilibria of (water + MEA) mixtures: partial pressures, mole fraction of the liquid phase (x_{MEA}) and the vapor phase (y_{MEA} , y_{water}).

T (K)	P MEA (Pa)	P water (Pa)	P Total (Pa)	y_{MEA}	y_{water}
$x_{\text{MEA}} = 0.1121$					
294.1	0.97	1951	1952	0.00049	0.999
313.6	10.3	6369	6379	0.0016	0.998
333.3	42.4	17,162	17,204	0.0025	0.997
353.1	210	42,245	42,455	0.0049	0.995
$x_{\text{MEA}} = 0.1642$					
293.6	1.62	1980	1982	0.00082	0.999
313.6	11.4	6252	6263	0.0018	0.998
333.7	66.2	16,884	16,950	0.0039	0.996
353.4	268	40,670	40,938	0.0065	0.994

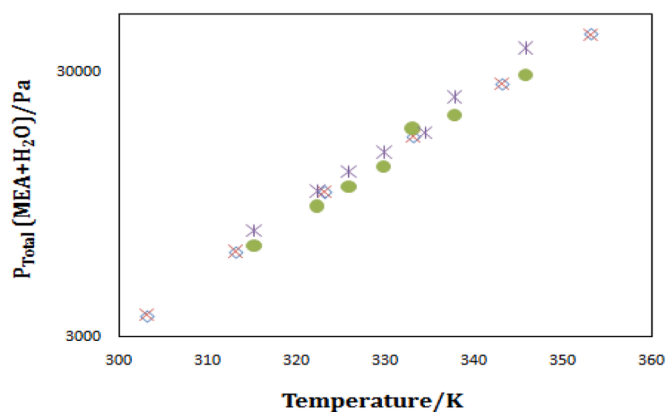
 $u(x_i) = \pm 0.0001$; $u(T) = \pm 0.1$ K; $u_r(P_i) = 4\%$; $u_r(y_i) = 8\%$.
Table 4Vapor-liquid equilibria of (water + TMEDA) mixtures: partial pressures, mole fraction of the liquid phase (x_{TMEDA}) and the vapor phase (y_{TMEDA} , y_{water}).

T (K)	P TMEDA (Pa)	P water (Pa)	P Total (Pa)	y_{TMEDA}	y_{water}
$x_{\text{TMEDA}} = 0.0169$ (10 wt% TMEDA)					
294.2	11.4	2430	2442	0.0047	0.995
294.2	12.0	2425	2437	0.0049	0.995
313.7	102	7409	7511	0.014	0.986
333.4	606	19,839	20,444	0.030	0.970
353.2	2500	47,073	49,574	0.050	0.950
$x_{\text{TMEDA}} = 0.0623$ (30 wt% TMEDA)					
294.1	75.8	2099	2175	0.035	0.965
313.7	439	6679	7118	0.062	0.938
333.4	1860	18,413	20,273	0.092	0.908
353.1	6653	47,067	53,720	0.124	0.876
$x_{\text{TMEDA}} = 0.1341$ (50 wt% TMEDA)					
294.2	308.4	2124	2432	0.127	0.873
313.7	1154	6382	7536	0.153	0.847
333.3	3754	17,797	21,551	0.174	0.826
353.1	11,273	44,805	56,078	0.201	0.800

 $u(x_i) = \pm 0.0001$; $u(T) = \pm 0.1$ K; $u_r(P_i) = 4\%$; $u_r(y_i) = 8\%$.
**Fig. 1.** Gas phase sampling-analysis system with the 6 ports valve in the loading position of the loop.

In a second step, the volatilities of these amines, in terms of partial pressures, were correlated using two empirical models developed by Xu (2011). The models represent well our experimental data.

As mentioned previously, the system (MEA+H₂O+CO₂) has already been studied in the literature using different analytical methods. Its study was undertaken in the present work in order to validate our analytical GC method.

**Fig. 2.** Total pressure of the binary system : water + MEA 30 wt%. Comparison with literature data: \diamond , the present study; \times , (Belabbaci et al., 2009); \bullet , (Hilliard, 2008); $*$, (McLees, 2006).

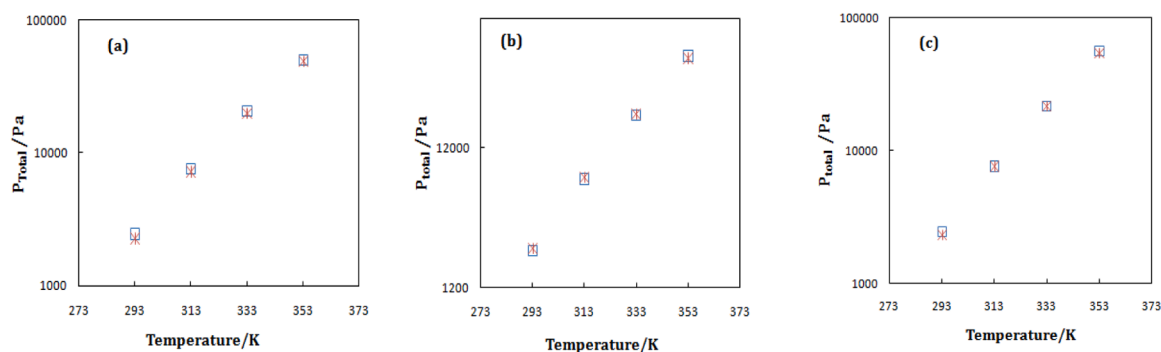


Fig. 3. Total pressure of the binary system : water + TMEDA; (a): 10 wt% TMEDA; (b): 30 wt% TMEDA ; (c): 50 wt% TMEDA. Comparison with literature data: □, the present study; *, (Bouzina et al., 2015).

Table 5

Vapor-liquid equilibria of (water + 30 wt% MEA+CO₂): partial pressures (P_{MEA}, P_{water}, P_{CO₂}), loading CO₂, α.

T/K	α	P _{MEA} /kPa	P _{water} /kPa	P _{CO₂} /kPa
313.6	0	0.0103	6.37	0
313.7	0.128	0.0068	6.30	0.0028
314.4	0.140	0.0077	6.13	-
314.6	0.237	0.0073	6.36	-
313.8	0.259	0.0049	6.26	0.0145
313.1	0.322	-	6.11	-
314.1	0.399	0.0034	6.33	0.071
314.1	0.404	-	6.14	0.558
314.2	0.512	0.0018	6.33	3.005
314.1	0.549	-	6.08	-
333.3	0	0.0424	17.2	0
333.4	0.128	0.0307	17.1	0.0195
334.4	0.140	0.0343	17.2	0.0355
334.3	0.237	0.0283	17.6	0.126
333.6	0.259	0.0216	17.2	-
333.3	0.322	-	16.6	0.581
333.6	0.399	0.0112	17.2	-
333.6	0.404	-	16.4	2.41
333.7	0.512	0.0063	17.2	13.48
333.6	0.549	-	16.6	-
353.1	0	0.210	42.2	0
353.1	0.128	0.144	42.9	-
354.3	0.140	0.179	43.4	0.229
354.3	0.237	0.128	41.5	0.791
353.2	0.259	0.113	43.2	-
353.3	0.399	0.0439	42.3	-
353.2	0.322	0.0801	41.6	3.317
353.3	0.404	0.0415	42.4	15.21
353.4	0.512	0.0240	40.1	-
353.3	0.549	-	-	110.4

$u(x_i) = \pm 0.0001$; $u(T) = \pm 0.1$ K ; $u_r(P_i) = 4\%$; $u_r(\alpha) = 2\%$.

2. Experimental section

2.1. Materials

The chemicals, monoethanolamine (MEA), N,N,N',N'-Tetramethylethylene diamine (TMEDA) and hydrochloric acid (HCl, 5 N used for volumetric titration of CO₂) were purchased from Sigma-Aldrich and were used without further purification. CO₂ was supplied by Air Liquide with mole fraction purity > 0.999, Table 1. High purity deionized water (conductivity = 18 MΩ.cm) was used. A digital balance (Mettler-Toledo AG204) having an accuracy of 0.0001 g was used.

2.2. Experimental procedures

The description of the apparatus and the experimental procedure can be found in our earlier work (Mahi et al., 2019). The prominent information is given here. The apparatus is composed of a glass equilibrium

cell with a double envelope for thermoregulated water circulation. The sample is stirred (2000 rpm) by a self-aspirating hollow stirrer. The injected CO₂ and the total pressure of the solution are controlled by an absolute pressure gage (relative uncertainty of 0.5%). The temperature of the solution is monitored by a thermocouple (absolute uncertainty of ± 0.1 K).

The gaseous phase is analyzed by a gas chromatograph GC Agilent 7890B equipped with two detectors: TCD (for water and CO₂ analysis) and FID (for MEA and TMEDA analysis). For a good separation, two capillary columns were mounted in parallel at the outlet of the injector. In Table 2 are reported the analytical conditions.

At the beginning of the experimental procedure, the degassed solution is introduced into the autoclave previously maintained at high vacuum and heated (for cleaning) along with the gas transfer line, Fig. 1. A first injection of CO₂ is then carried out.

Once the equilibrium of the solution amine + water/CO₂ is obtained and as long as the total pressure is under the atmospheric pressure, helium gas (slightly above 1 bar) is introduced into the cell. This operation allows the transport of the vapor phase for analysis towards the gas chromatograph using the peristaltic pump and via the sampling loop, Fig. 1. The next increment of CO₂ is injected after purging the vapor phase of the cell.

The calibration of the GC is carried out in the same way as the partial pressure determinations described above. The pure degassed amine or water is introduced into the cell and stirred. A chromatogram with a peak corresponding to the amine/water is obtained. The area of the peak is function of the vapor pressure of the pure compound at the studied temperature. The vapor pressures of pure MEA is from (Belabbaci et al., 2009), whereas for pure TMEDA and water, we used (Bouzina et al., 2015) data. Several temperatures are studied to obtain enough points to plot the calibration curve which is a straight line: $P/Pa = f(\text{peak area})$. As for CO₂ calibration, various CO₂-helium standard mixtures were prepared, introduced in the cell, sampled and analyzed using the system in Fig. 1. The total pressure of the mixture (fixed in the vicinity of the atmospheric pressure) is taken into account to deduce the partial pressure of CO₂.

The determinations of the partial pressures, P_i , of the amines, water and CO₂ were repeated several times until the relative standard deviation, RSD, is less than 2%, Eqs. (1) and (2):

$$P_i = a_i * A_i \quad (1)$$

Where

a_i is the slope of the calibration curve

A_i is the peak area

$$RSD = 100 * \frac{\sigma}{P_{i,mean}} \quad (2)$$

σ , is the standard deviation of P_i . The relative uncertainty, u_r , of the P_i is estimated to be 2 times the RSD, 4%.

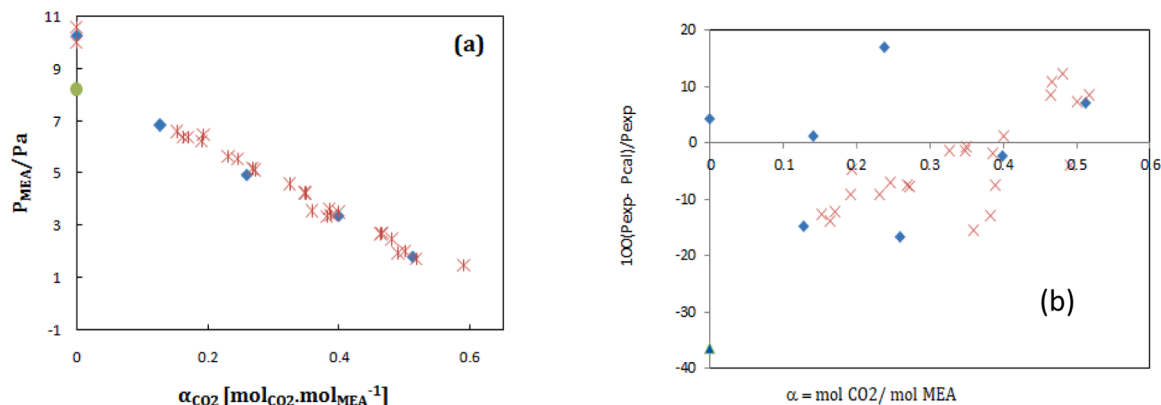


Fig. 4. Partial pressure of MEA in (H₂O-30 wt% MEA-CO₂) mixture at 313 K (a). Comparison between experimental and calculated partial pressures: ◆, this work; *, (Hilliard, 2008); •, (Belabbaci et al., 2009).

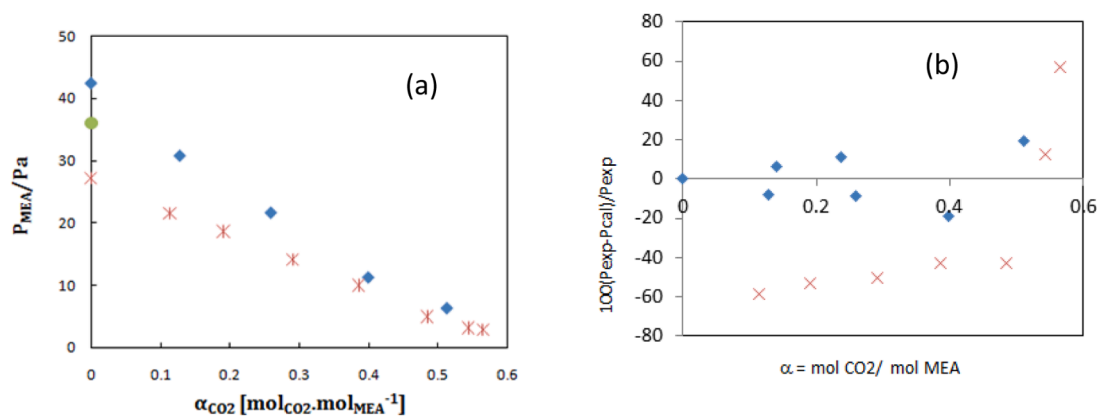


Fig. 5. Partial pressure of MEA in (H₂O-30 wt% MEA-CO₂) mixture at 333 K (a). Comparison between experimental and calculated partial pressures: ◆, this work; *, (Hilliard, 2008); •, (Belabbaci et al., 2009).

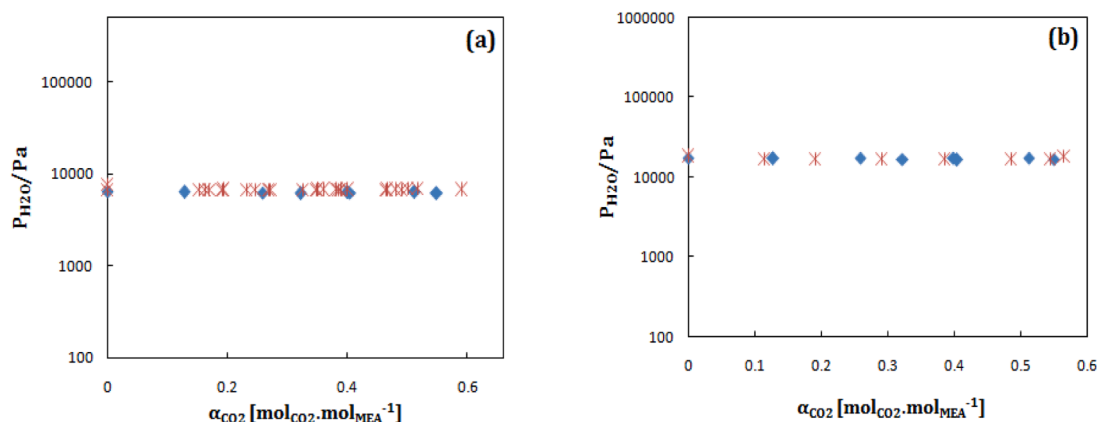


Fig. 6. Partial pressure of water in (H₂O-30 wt% MEA-CO₂) mixture at 313 K (a) and 333 K (b) -Comparison with literature data: ◆, this work; *, (Hilliard, 2008).

3. Results and discussion

3.1. Vapor-liquid equilibria of water + MEA or TMEDA

The VLE of the binary systems were studied at different temperatures and for different compositions (30, 40 wt% MEA and 10, 30, 50 wt% TMEDA), Tables 3 and 4.

The partial pressures of MEA and TMEDA are not determined in the literature but only the total pressures of the aqueous solutions. For the sake of comparison, we calculated the total pressure of the binary system

which is the sum of the 2 experimental partial pressures ($P_{amine} + P_{water}$). We assumed that the non-ideality of the vapor phase ($y_i = P_i/P_b$) could be neglected. In Fig. 2 we plotted the total vapor pressures of water + 30 wt% MEA from this work and those reported by Belabbaci et al. (2009) obtained by a direct method, (Hilliard, 2008) and (McLees, 2006). A very good agreement is observed with our experimental data.

In the same way, experimental vapor pressures of the system water + TMEDA (10, 30 and 50 wt%) from chromatographic analysis show good agreement with (Bouzina et al., 2015) data, Fig. 3. The authors determined the vapor pressures of the solution by a direct method using

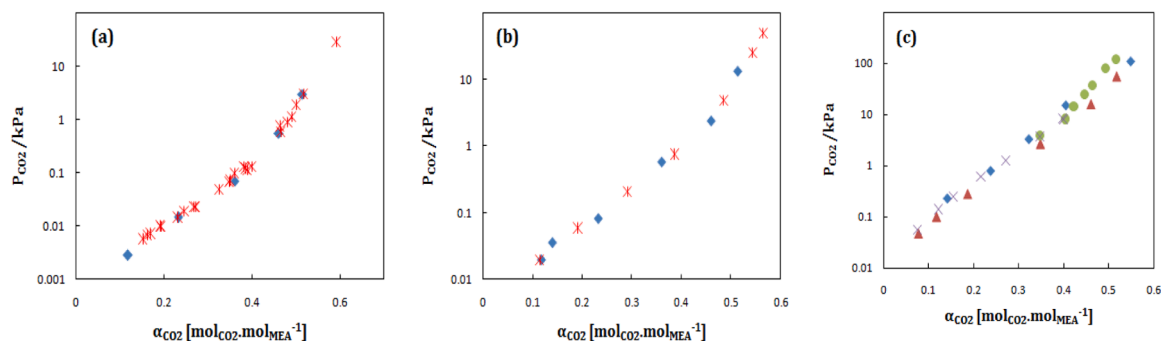


Fig. 7. Partial pressures of CO₂ in (H₂O-30 wt% MEA-CO₂) mixtures at 313 (a), 333 K (b) and 353 K (c). Comparison with literature data: this work, (Hilliard, 2008), (Jou et al., 1995); •, (Shen and Li, 1992); ×, (Aronu et al., 2011).

Table 6

Vapor-liquid equilibria of (water+10 wt%TMEDA+CO₂): partial pressures (P_{TMEDA}, P_{water}, P_{CO2}), loading CO₂, α .

T /K	α	P _{TMEDA} /kPa	P _{water} /kPa	P _{CO2} /kPa
294.25	0	0.012	2.43	0
294.45	0.123	0.010	2.39	0.093
294.45	0.204	0.008	2.47	0.219
294.65	0.433	0.005	2.40	0.955
295.15	0.534	0.004	2.46	1.63
295.25	0.726	0.002	2.46	9.13
313.75	0	0.102	7.41	0
313.75	0.123	0.088	7.421	0.281
313.85	0.204	0.078	7.490	0.683
314.35	0.433	0.051	7.36	2.79
314.55	0.534	0.040	7.32	4.46
314.85	0.726	0.019	7.43	19.01
333.45	0	0.606	19.8	0
333.55	0.123	0.523	19.7	0.939
333.55	0.204	0.475	19.6	2.16
333.85	0.433	0.341	19.6	8.42
333.95	0.534	0.286	19.5	12.68
334.15	0.726	0.181	19.7	32.57
353.15	0	2.50	47.1	0
353.15	0.123	2.30	48.2	3.13
353.35	0.204	2.08	47.7	6.96
353.35	0.433	1.60	47.2	24.17
353.55	0.534	1.36	45.5	29.21
353.65	0.726	0.979	42.4	51.92

$u(x_i) = \pm 0.0001$; $u(T) = \pm 0.1$ K; $u_r(P_i) = 4\%$; $u_r(\alpha) = 2\%$.

Table 7

Vapor-liquid equilibria of (water+30 wt%TMEDA+CO₂): partial pressures (P_{TMEDA}, P_{water}, P_{CO2}), loading CO₂, α .

T (K)	α	P _{TMEDA} /kPa	P _{water} /kPa	P _{CO2} /kPa
294.15	0	0.076	2.10	0
294.35	0.254	0.077	2.02	0.833
295.35	0.585	0.059	2.06	4.303
294.95	0.772	0.021	1.91	16.560
313.75	0	0.439	6.68	0.000
313.85	0.254	0.466	6.33	3.148
314.55	0.585	0.392	6.42	15.47
314.25	0.772	0.183	6.22	48.17
333.35	0	1.860	18.4	0
333.35	0.254	2.022	17.5	11.515
333.65	0.238	2.041	17.5	10.87
333.95	0.585	1.874	17.6	48.88
333.75	0.772	1.006	14.6	98.13
353.05	0	6.653	47.1	0
353.25	0.238	7.488	45.4	39.21
353.55	0.585	5.696	37.6	97.56
353.45	0.772	2.797	45.4	150.09

$u(x_i) = \pm 0.0001$; $u(T) = \pm 0.1$ K; $u_r(P_i) = 4\%$; $u_r(\alpha) = 2\%$.

Table 8

Vapor-liquid equilibria of (water+50 wt%TMEDA+CO₂) mixtures: partial pressures (P_{TMEDA}, P_{water}, P_{CO2}), loading CO₂, α .

T /K	α	P _{TMEDA} /kPa	P _{water} /kPa	P _{CO2} /kPa
294.25	0	0.308	2.12	0
294.45	0.157	0.397	1.873	2.191
294.75	0.257	0.400	1.747	3.395
295.35	0.354	0.375	1.772	4.757
295.75	0.482	0.303	1.826	7.530
295.85	0.689	0.211	1.823	14.132
295.25	0.816	0.139	1.963	16.856
313.65	0	1.154	6.382	0
313.85	0.157	1.496	5.923	9.266
314.15	0.257	1.561	5.804	14.476
314.45	0.354	1.500	5.630	20.203
314.75	0.482	1.342	5.804	30.884
314.95	0.689	1.074	5.711	51.253
313.15	0.816	0.811	6.031	50.246
333.35	0	3.754	17.80	0
333.45	0.157	4.819	16.63	33.62
333.65	0.257	4.963	15.62	52.279
333.85	0.354	4.559	14.62	60.87
333.95	0.482	3.928	14.05	77.62
334.45	0.689	3.477	13.90	106.5
334.95	0.816	2.935	13.85	101.4
353.05	0	11.27	44.81	0
353.15	0.157	12.63	30.46	81.728
353.45	0.257	12.71	38.10	132.55
353.55	0.354	10.73	35.49	257.88
353.65	0.482	9.109	30.12	323.17
354.15	0.689	7.952	28.22	369.72
355.15	0.816	7.364	28.24	370.49

$u(x_i) = \pm 0.0001$; $u(T) = \pm 0.1$ K; $u_r(P_i) = 4\%$; $u_r(\alpha) = 2\%$.

a pressure sensor.

3.2. Vapor-liquid equilibria of (water+MEA+CO₂) and (water+TMEDA+CO₂)

Partial pressures of water, MEA, TMEDA and CO₂ were determined at 293, 313, 333 and 353 K. The CO₂ loading, α , determined by titration is as follows, Eq. (3):

$$\alpha = \frac{\text{mol of CO}_2 \text{ in the liquid phase}}{\text{mol of amine}} \quad (3)$$

3.3. Vapor-liquid equilibria of (water + 30 wt% MEA + CO₂)

The experimental results, (T, partial pressures P_i of water, or MEA, or CO₂ along with α) are reported in Table 5. The gradual decrease of the partial pressure of amine, P_{MEA}, when the CO₂ loading α increases, is shown in Figs. 4 and 5 (a). This behavior is expected because the amine reacts with CO₂ and there is less free amine in the solution as the loading

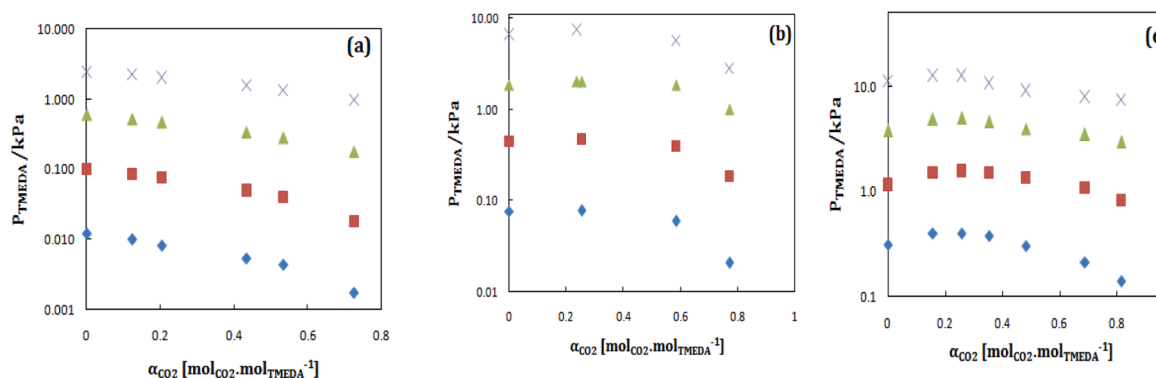


Fig. 8. Partial pressure of TMEDA in (H₂O-TMEDA-CO₂) mixtures. (a): 10 wt%TMEDA; (b), 30 wt% TMEDA; (c), 50 wt% TMEDA at 293; □, 313; 333 and ×, 353 K.

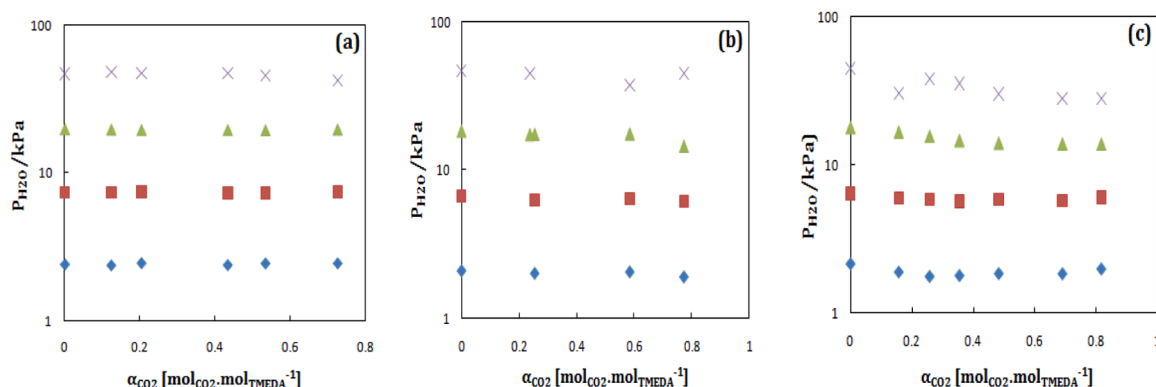


Fig. 9. Partial pressure of H₂O in (H₂O-TMEDA-CO₂) mixtures. (a): 10 wt%TMEDA; (b), 30 wt% TMEDA; (c), 50 wt% TMEDA at , 293; 313, 333 and ×, 353 K.

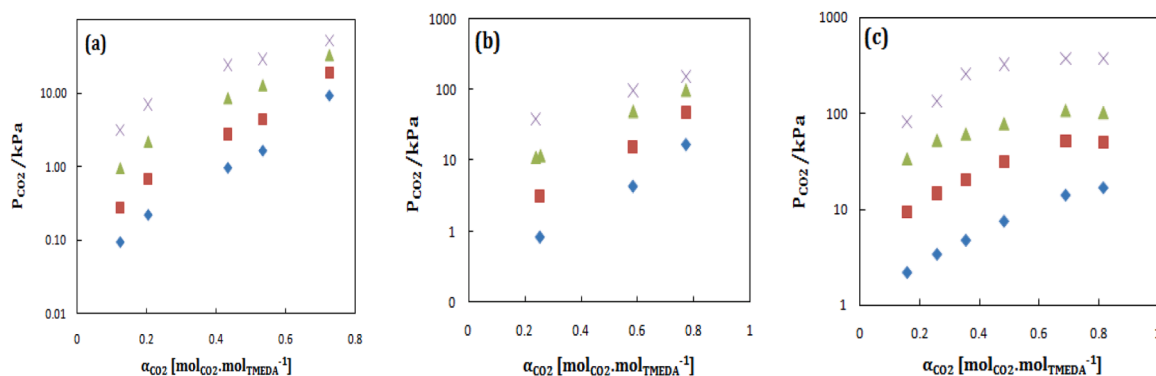


Fig. 10. Partial pressure of CO₂ in (H₂O-TMEDA-CO₂) mixtures. (a): 10 wt%TMEDA; (b), 30 wt% TMEDA; (c), 50 wt% TMEDA at 293, 313; 333 and ×, 353 K.

of CO₂ increases. For a loading equal to $\alpha = 0.5$, the chemical absorption of CO₂ by the MEA is at the maximum: all MEA molecules have been consumed to form the carbamate salts, RNHCOO⁻, practically non-volatile. Consequently P_{MEA} tends to zero.

Having observed a regular decrease in the partial pressure of MEA when α increases, we fitted by a straight line our experimental partial pressures, P_{exp} versus α . From the obtained parameters (slope and intercept of the line), we determined P_{cal} . In Figs. 4 and 5 (b) we represented the relative deviation between experimental data (from this work and from literature) and P_{cal} at 313 and 333 K. At 313 K, our data are in a good agreement with (Hilliard, 2008) but at 333 K, there is an offset between the two sets of measurements when the loading (α) is less than 0.4. These deviations must be put into perspective because the partial pressures of MEA are very low (between 1 and 8 Pa at 313 K and between 6 and 42 Pa at 333 K).

Belabbaci et al. (2009) determined experimentally the total vapor pressures of the binary mixture (MEA+eau), P_t , and calculated the vapor composition, $y_{\text{MEA}}^{\text{cal}}$, using Barker method (Barker, 1953). From Eq. (4), we deduced the partial pressure of MEA, $P_{\text{MEA}}^{\text{cal}}$, assuming an ideal behavior of the vapor phase:

$$P_{\text{MEA}}^{\text{cal}} = y_{\text{MEA}}^{\text{cal}} * P_t \quad (4)$$

In a second step, we compared $P_{\text{MEA}}^{\text{cal}}$ with the experimental P_{MEA} , Figs. (4) and (5) (a). At 313 K, the calculated value is higher by 2 Pa comparing with our value whereas at 333 K, the difference is 10 Pa. Our data are systematically higher. Here again, the difference is acceptable with regard of the low explored pressures. On the other hand (Hilliard, 2008) data at 333 K ($\alpha = 0$) is lower comparing to (Belabbaci et al., 2009) value.

As for the partial pressures of water, no variation is observed in

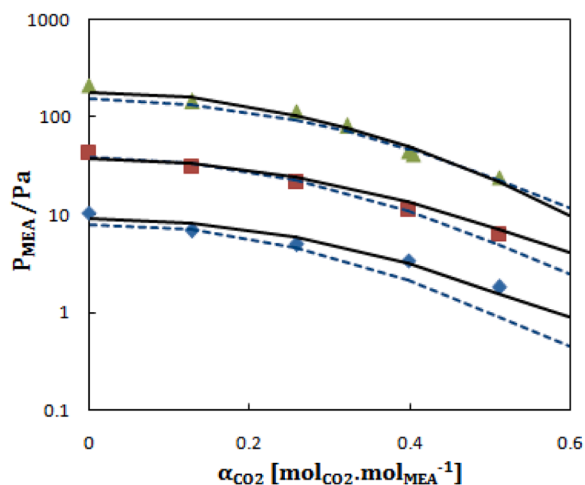


Fig. 11. Partial pressure of MEA in (H₂O-MEA-CO₂) mixtures, 30 wt% MEA. Experimental points: 313 K; 333 K; 353 K. Solid lines: (Xu, 2011) empirical model, Eq. (5), fitted on our experimental points; dashed lines: calculated data using the parameters obtained by Xu (2011).

function of α : water concentration in the liquid is stable with the addition of CO₂ because there is no reaction with water in the studied range ($\alpha \leq 0.5$), Fig. 6. Water only plays a role during the hydrolysis of carbamates which takes place when $\alpha > 0.5$. The data are in very good agreement with those of (Hilliard, 2008) at both temperatures (313 and 333 K), Fig. 6.

Fig. 7 (a–c) shows the comparison of P_{CO_2} data with those of literature (Aronu et al., 2011; Hilliard, 2008; Jou et al., 1995; Shen and Li, 1992) at 313, 333 and 353 K. A very good agreement is observed with the different authors.

3.4. Vapor-liquid equilibria of water + TMEDA + CO₂

TMEDA is a compound with two tertiary amine functions. The system (water+TMEDA+CO₂) was studied at 10, 30 and 50 wt%, Tables 6–8. In Fig. 8 (a–c) are plotted the partial pressures of the amine function of the loading of CO₂. We observe a decrease of P_{TMEDA} when α increases. In addition a maximum seems to be emerging for 30 wt% TMEDA and clearly observed at 50 wt% TMEDA.

The gradual appearance of the maximum could be explained by the existence of two "antagonistic" contributions when α increases. First, the decrease of P_{TMEDA} is due to the chemical reaction between the amine and CO₂ which decreases the concentration of the amine remaining in solution. Secondly, an increase of P_{TMEDA} is due to a "salt effect" phenomenon because of the increasing quantity of ammonium salt formed. It should be noted that TMEDA is an "aprotic" amine, with a

hydrophobicity characterized by the appearance of a demixing of TMEDA-water mixtures when heating at temperature over 363 K which is the Lower Critical Solution Temperature (LCST), (De Oliveira, 2010). Above this temperature, the thermal energy is sufficient to disrupt the chemical interactions between TMEDA and water and cause demixing.

The partial pressure of water function of α is almost constant, Fig. 9, whereas the partial pressures of CO₂ increase with CO₂ loading. Comparing to the MEA solutions, the curves have not the same shape: no inflection at $\alpha = 0.5$ is observed. In the case of MEA, this inflection indicates that the absorption of CO₂ is changing from a chemical mode (chemical reaction between amine and CO₂) to a physical absorption for $\alpha > 0.5$ (steeper slope).

TMEDA is a diamine, the inflection point must be around $\alpha = 1$. We have not explored the ($\alpha > 1$) range and therefore the physical absorption does not appear in Fig. 10 (a–c).

No literature data for comparison was found for these mixtures.

3.5. Correlation of amines partial pressure

For the correlation of MEA volatility, (Xu, 2011) developed an empirical expression which is function of the partial pressure of the primary amine, the initial mole fraction of the amine in the liquid phase (x_{MEA}), the equilibrium temperature and the CO₂ loading (α), Eq. (5):

Table 9
pKa of the two amine functions of TMEDA and PZ (El-Hadri, 2012).

	pKa ₁	pKa ₂
TMEDA	8.9	5.6
PZ	9.73	5.35

Table 10
Regressed parameters of Eq. (5)*.

	A	B	C
Xu (2011)	30.0	-8153	-2594
This work	27.8	-7317	-2100

$$*\ln\left(\frac{P_{MEA}}{x_{MEA}}\right) = A + \frac{B}{T} + C * \frac{\alpha^2}{T}$$

Table 11
Regressed parameters of Eq. (6)*.

	A	B	C	D
10 wt%TMEDA + H ₂ O	-177.30	32.35	-2.39	-0.88
30 wt%TMEDA + H ₂ O	-106.70	20.17	-0.90	-0.88
50 wt%TMEDA + H ₂ O	-143.60	26.54	-1.33	-0.88

$$*\ln\left(\frac{P_{TMEDA}}{x_{TMEDA}}\right) = A + B * \ln T + C * \alpha + D * \frac{\alpha^2}{T}$$

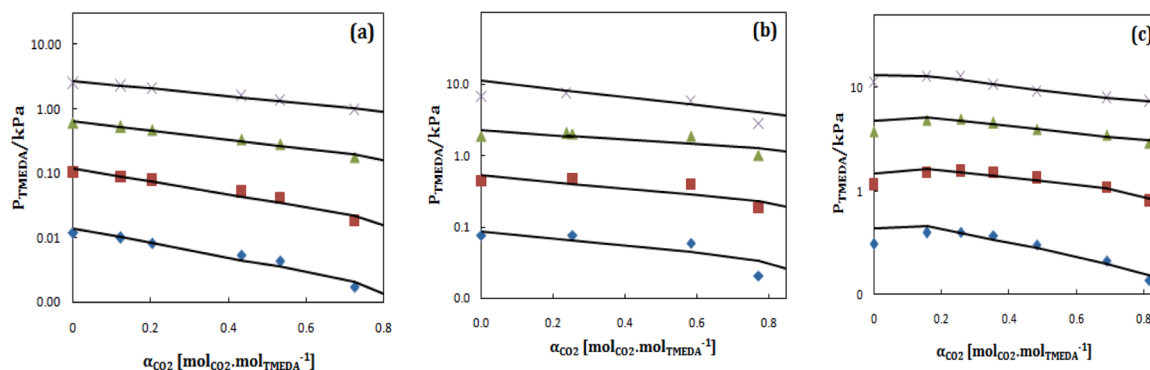


Fig. 12. Partial pressure of TMEDA in (H₂O-MEA-CO₂) mixtures:(a), 10 wt% TMEDA; (b), 30 wt% TMEDA;(c), 50 wt% TMEDA. Experimental points: 293 K; 313 K, 333 K; ×, 353 K. Solid lines: empirical model, Eq. (6), fitted on our experimental points.

$$\ln\left(\frac{P_{MEA}}{x_{MEA}}\right) = A + \frac{B}{T} + C * \frac{\alpha^2}{T} \quad (5)$$

In the same way (Xu, 2011) developed a second empirical equation for diamine (with 2 amine functions) namely for Piperazine (PZ) which is a secondary diamine, Eq. (6):

$$\ln\left(\frac{P_{PZ}}{x_{PZ}}\right) = A + B * \ln T + C * \alpha + D * \frac{\alpha^2}{T} \quad (6)$$

In a first step we fitted the experimental data of P_{MEA} function α , using Eq. (5) and then compared with the values calculated from (Xu, 2011) parameters, Fig. 11. For the isotherms at 333 and 353 K, a good agreement is obtained, however at 313 K differences appear at higher CO_2 loading (α above 0.2). This result is expected as (Xu, 2011) signaled in his paper that the regression model has a lack of consistency and for that reason excluded (Hilliard, 2008) data at 313 K from the empirical regression model.

Partial pressures of TMEDA were fitted using Eq. (6). The empirical model developed for piperazine, PZ, represents well the partial of TMEDA function α due certainly of the similarity of the chemical properties of these two amines, Fig. 12. PZ and TMEDA are two diamines with very similar acid-base characteristics, Table 9. The parameters of Eqs. (5) and (6) are reported in Tables 10 and 11.

4. Conclusion

Vapor-liquid equilibria of binary systems were studied using an apparatus with on-line analysis by GC of the vapor phase: (water + MEA) and (water + TMEDA) at different temperatures (from 293 to 353 K) and different weight percent of amine (10%, 30%, 40% and 50%) depending of the amine. The partial pressures, P_{MEA} or P_{TMEDA} , P_{H_2O} were determined using gas chromatography. A good agreement of the total pressure of the solution, P_t , with literature data is obtained. As for the partial pressures, P_{MEA} or P_{TMEDA} , P_{H_2O} , no data was found for comparison.

In a second step, the systems (water+MEA+ CO_2) and (water+TMEDA+ CO_2) were studied at several temperatures, different weight percent of amine and various loading of CO_2 . In the same way the partial pressures, P_{MEA} or P_{TMEDA} , P_{H_2O} along with P_{CO_2} were determined.

The explored partial pressures range from 2 Pa to approximately 400 kPa, which is broad. Partial pressures of the system (water+MEA+ CO_2) are in a good agreement with literature data. As for the mixtures (water+TMEDA+ CO_2), no literature data was found for comparison. The empirical expressions developed by (Xu, 2011) satisfactorily correlate the partial pressure

CRediT authorship contribution statement

M-Ridha Mahi: Conceptualization. **Ilham Mokbel:** Supervision, Writing – review & editing. **Latifa Negadi:** Supervision. **Joseph Saab:** Formal analysis, Validation. **Jacques Jose:** Visualization.

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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