



# A performance comparison study of five single and sixteen blended amine absorbents for CO<sub>2</sub> capture using ceramic hollow fiber membrane contactors

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## ABSTRACT

The present study has endeavored to establish the relations between the CO<sub>2</sub> absorption properties of five single amine-based absorbents including monoethanolamine (MEA), diethylamine (DEA), *N*-methyl-diethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), and piperazine (PZ), and their sixteen binary mixtures in the blended amine-based absorbents for CO<sub>2</sub> chemical absorption using a hydrophobic modified ceramic hollow fiber membrane contactor (HFMC). Keeping all other variables constant, the CO<sub>2</sub> absorption properties of single and blended amine-based absorbents for CO<sub>2</sub> chemical absorption using hydrophobic modified ceramic HFMCs are highly dependent on their chemical nature and concentration. MEA and DEA have the highest CO<sub>2</sub> absorption flux among the single amine solutions. For the CO<sub>2</sub> absorption in the blended amine-based absorbents, the replacement of MDEA with 20 wt% DEA increased the CO<sub>2</sub> chemical absorption from  $1 \times 10^4$  mol/m<sup>2</sup> s to about  $7 \times 10^4$  mol/m<sup>2</sup> s. Aqueous MDEA blended DEA reaches a percentage of increase of CO<sub>2</sub> absorption flux over 500% in comparison with the corresponding aqueous solution of single MDEA.

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## Introduction

The conventional post-combustion CO<sub>2</sub> separation method includes the CO<sub>2</sub> chemical absorption process with different kinds of chemical solvents to absorb CO<sub>2</sub> [1–3]. In recent years, amine-based absorbents receiving considerable attention worldwide due to both the simplicity of the CO<sub>2</sub> capture process and the CO<sub>2</sub> performance achieved [4,5]. The amine-based absorbents form a bonded intermediate compound with CO<sub>2</sub> and release the trapped CO<sub>2</sub> when heated at the desorption heat. However, it is essential to reduce the absorbent regeneration cost by developing better performing absorbents (i.e., increase the chemical absorption capacity and CO<sub>2</sub> chemical absorption rate) and developing more effective processes (i.e., reduce the regeneration cost by decrease the desorption heat and then, in turn, solvent regeneration energy) avoiding, at the same time, the amine-based absorbent degradation [6].

Monoethanolamine (MEA), diethanolamine (DEA), *N*-methyl-diethanolamine (MDEA), piperazine (PZ), and 2-amino-1-methyl-

2-propanol (AMP), are the most widely used chemical absorbents for the CO<sub>2</sub> chemical absorption process [7,8]. MEA is a primary amine and it is considered to be the main solvent in aqueous alkanolamine based capture processes of CO<sub>2</sub> because of its low cost [9]. However, it has some disadvantages over other amine-based absorbents such as low CO<sub>2</sub> chemical absorption capacity, low resistance to oxidative and thermal degradation, relatively low heat of CO<sub>2</sub> chemical absorption (about –85 kJ/mol of CO<sub>2</sub>), and then high energy requirements for CO<sub>2</sub> regeneration [9,10]. So that, in the case of MEA-based absorbent, the temperature to release the CO<sub>2</sub> and regenerate it makes up 70–80% of operating cost [4]. DEA is a secondary amine where two ethanol substituents (CH<sub>3</sub>CH<sub>2</sub>OH) bound to the nitrogen together with one hydrogen, and it has some significant advantages over other amines, including high CO<sub>2</sub> loading capacity at low cost [11]. The secondary amines like DEA usually own better heat absorption in comparison with MEA [9]. MDEA is a tertiary amine, and its advantages include high equilibrium loading capacity and low heat of reaction with CO<sub>2</sub>, which in turn leads to lower energy requirement for regeneration and relatively low heat of CO<sub>2</sub> chemical absorption process [9]. The regeneration of tertiary amines requires less heat energy than for primary and secondary amines [12]. However, low rates of CO<sub>2</sub> chemical absorption make MDEA complicated to use for CO<sub>2</sub>

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removal [13]. PZ is an example of a cyclic diamine-based absorbent that has been investigated due to its high CO<sub>2</sub> chemical absorption rate and CO<sub>2</sub> capture capacity [10,14]. PZ has two secondary nitrogen atoms of each cycle and, in strict terms, it is not an alkanolamine but it reacts rapidly with CO<sub>2</sub> to form a carbamate [15]. Since PZ has two secondary amino groups (NH), and can theoretically absorb two mol of CO<sub>2</sub> per single mol of amine, the CO<sub>2</sub> chemical absorption rate of aqueous PZ is more than double that of 7 m MEA [14]. AMP is a sterically hindered primary amine where the amino group is attached to a tertiary carbon [16]. Hindered amines are characterized by forming carbonates with low stability [16,17]. Despite its potential capacity, the CO<sub>2</sub> chemical absorption rate of AMP is considerably slower than other primary amines (i.e., MEA) [18]. The mechanism of the reaction between CO<sub>2</sub> and amine-based absorbents have been discussed frequently in the literature [9,16,19–23].

The literature has demonstrated the success of an approach based on blended amine absorbents – usually composed of two single amines in varying compositions – to increase the reaction rate coefficient, the CO<sub>2</sub> absorption, and absorbent regeneration – and then reduce capital and operating costs – by altering the chemical characteristics of liquid phase [24–29]. In general, blended amines can enhance CO<sub>2</sub> chemical absorption performance, owing to synergistic effects of the primary, secondary, and tertiary amines; i.e., primary and secondary amines exhibit a fast reaction rate constant [26], whereas tertiary amines exhibit high CO<sub>2</sub> chemical absorption capacity and low regeneration energy [30]. For its properties, the PZ has been mostly used as a rate promoter agent [31]. Binary MDEA-PZ blend offers advantages over MEA and MDEA alone because of its resistance to thermal and oxidative degradation [32]. The economics of the CO<sub>2</sub> separation processes using PZ-blended amines was improved by an average of 10% compared to the corresponding base amine-only systems [29]. Such blended amine absorbents can simultaneously avoid the disadvantages of single alkanolamines (i.e., high regeneration energy, high corrosion rate, easily oxidized and degraded, etc.) and preserve their advantages where there are other benefits to the high CO<sub>2</sub> chemical absorption capacity, such as fast reaction kinetics.




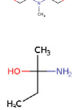

In terms of membrane material selection, the literature mostly deals with those investigations involving polymeric hollow fiber membrane contactors (HFMC) [1,24,28,33,34]. However, one well-known problem is that the singles and blended amine absorbents for CO<sub>2</sub> capture are extremely aggressive substances at high concentrations against polymeric HFMCs [35,36] and it

was found that in gas sweetening plants using aqueous amine solutions a quarter of the maintenance budget was committed to corrosion control [37–39]. Ceramic HFMCs show high chemical and thermal stabilities, which are suitable to use with single and blended amine absorbents at high-temperature applications [40]. Up to now, compared to the extensive studies on polymeric HFMCs for CO<sub>2</sub> chemical absorption, there is scarce literature information on the development of ceramic HFMCs with singles amines [40–42]. As ceramic hollow fiber membranes can be modified to be hydrophobic [43,44], the hydrophobic modified ceramic HFMCs for CO<sub>2</sub> chemical absorption can potentially be used not only with a single amine but also with blended amine absorbents.

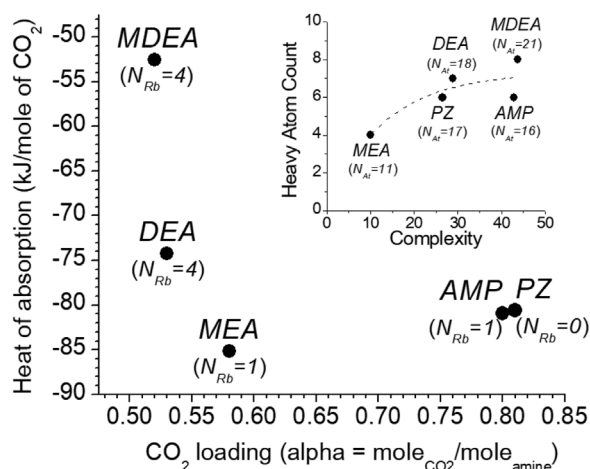
A novelty of the present work is that it systematically investigates the CO<sub>2</sub> chemical absorption performance of five single amines including MEA, DEA, MDEA, AMP, and PZ, and their combinations (MEA-MDEA, MEA-AMP, MEA-PZ, DEA-MDEA, DEA-AMP, DEA-PZ, MDEA-PZ, and AMP-PZ) using hydrophobic modified ceramic HFMCs. Table 1 shows the physical and chemical properties of the amines investigated in this work. The physical and chemical properties included the number of atoms ( $N_{At}$ ), heavy atom count ( $N_{h-At}$ ), molecular complexity ( $C_m$ ) [45], topological polar surface area (TPSA), and rotatable bond count ( $N_{Rb}$ ). In brief, the  $C_m$  is an intrinsic measure of molecular complexity and is not dependent on external conditions such as CO<sub>2</sub> absorption, hollow fiber membrane, etc. TPSA is a molecular descriptor defined as the sum of surfaces of polar atoms in a molecule, whereas the rotatable bond count is the number of the single bonds bound to a non-terminal heavy atom.

According to Ref. [9], Fig. 1 shows the relationship of the CO<sub>2</sub> loading and heat of CO<sub>2</sub> absorption associated with the five amines studied in this work. The number of rotatable bonds ( $N_{Rb}$ ) for each amine is surrounded by parentheses. The inset of Fig. 1 shows the molecular complexity ( $C_m$ ) versus the number of heavy atoms ( $N_{h-At}$ ) for every amine. These five amines were selected to determine the influence of different mixing conditions and other factors like the concentration on the CO<sub>2</sub> capture capacity by using porous alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) HFMC. The present work aims to offer a deep contribution to our knowledge of the sole amines as well as a new contribution to the role of blended amine absorbents for CO<sub>2</sub> capture in hydrophobic modified ceramic HFMC. To the best of our knowledge, this is the first report on the chemical absorption of CO<sub>2</sub> in a large sample of amine-based solutions consisting of both single amines and blended amine absorbents using porous ceramic HFMCs.

**Table 1**  
List of the amines investigated in this work and their chemical physic characteristics.

n.	Common name {IUPAC name} (acronym)	Formula	Structure	CAS	$M_W$ (g/mol)	$T_B$ (°C)	$N_{At}$	$N_{h-At}$	$C_m^a$	TPSA (Å <sup>2</sup> )	$N_{Rb}$
1	Monoethanolamine (MEA) {2-aminoethanol}	C <sub>2</sub> H <sub>7</sub> NO		141-43-5	61.08	170	11	4	10	46.2	1
2	Diethanolamine (DEA) {2-(2-hydroxyethylamino)ethanol}	C <sub>4</sub> H <sub>11</sub> NO <sub>2</sub>		111-42-2	105.14	269	18	7	28.9	52.5	4
3	N-Methyldiethanolamine (MDEA) {2-[2-hydroxyethyl(methyl)amino]ethanol}	C <sub>5</sub> H <sub>13</sub> NO <sub>2</sub>		105-59-9	119.16	247	21	8	43.7	43.7	4
4	2-Amino-2-methyl-1-propanol (AMP) {2-amino-2-methylpropan-1-ol}	C <sub>4</sub> H <sub>11</sub> NO		2854-16-2	89.14	165.5	17	6	42.8	46.2	1
5	Piperazine (PZ) {piperazine}	C <sub>4</sub> H <sub>10</sub> N <sub>2</sub>		110-85-0	86.14	146	16	6	26.5	24.1	0

$M_W$  = molecular weight;  $T_B$  = boiling point,  $N_{At}$  = number of atoms;  $N_{h-At}$  = heavy atom count;  $C_m$  = molecular complexity; TPSA = topological polar surface area;  $N_{Rb}$  = rotatable bond count.



**Fig. 1.**  $CO_2$  loading and heat of  $CO_2$  chemical absorption in aqueous amine solution at 30 wt%, 40 °C and 1 bar (15%  $CO_2$  and 85%  $N_2$ ) [7]. The corresponding number of rotatable bonds ( $N_{Rb}$ ) associated to the amines studied in this work are surrounded by parentheses. The inset shows the molecular complexity ( $Cm$ ) versus the number of heavy atoms ( $N_{H-At}$ ) for the five amines studied in this work. Number of atoms ( $N_{At}$ ) are placed in parentheses.

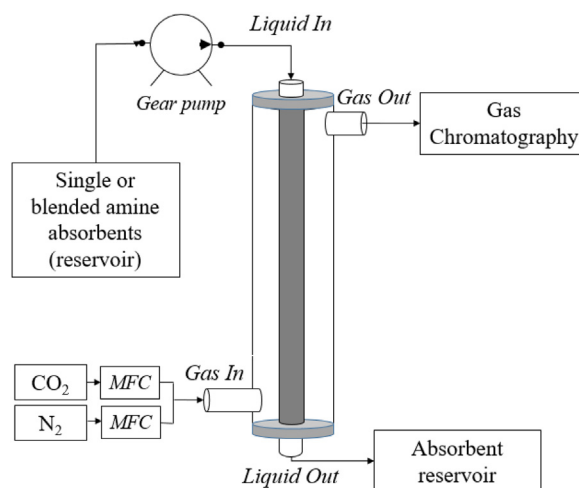
## Experimental

### Preparation of the hydrophobic modified ceramic hollow fiber membrane

Ceramic hollow fiber membranes were prepared by a phase inversion technique followed by a sintering process from commercial  $\alpha-Al_2O_3$  powder with an average particle size of 0.5  $\mu m$ . The procedure used has been described elsewhere [41–44]. In brief, spinning pressure was maintained constant at 1 bar in all preparations. The inner coagulant flow was fixed at 5 mL/min. Deionized water at room temperature was used as a coagulant for the phase inversion process with an air gap distance of 10 cm. The obtained green body was dried in an oven at 120 °C for 24 h and then placed into a high-temperature electric resistance furnace at a temperature of 1300 °C for 4 h. The sintered ceramic hollow fiber membranes were hydrophobic modified by heptadecafluoro-1,1,2,2-tetrahydrodecyltrimethoxysilane (FAS,  $\geq 98\%$ , Sooyang Chemtec Co., Ltd.). After the coating operation is completed, the hollow fiber membranes were washed with a solution of *n*-hexane and dried at 120 °C overnight. The hydrophobic modified hollow fiber membranes were then sealed with epoxy resin in a membrane contactor system with an effective length of 15 cm. Every single hydrophobic modified hollow fiber membrane was tested to ensure that it was free from leakage before use.

### Characterization of the ceramic hollow fiber membranes

The pore characteristics of the membrane were studied using a capillary flow porometry instrument (CFP-1100, PMI, USA). To measure the gas permeability, a 15 cm long ceramic hollow fiber membrane was sealed from one side and fixed to a gas permeation device from another one. Nitrogen gas with high purity (99.999%) was supplied inside the ceramic hollow fiber membrane. The permeated gas was measured using a bubble flow meter (Gilian® Gilibrator™ 2, Sensidyne Inc., Clearwater, FL, USA). The effective surface porosity of ceramic hollow fiber membrane was determined based on the theory of gas diffusion [9,27,46–48]. Further, the overall porosity of the membrane was calculated by the gravimetric method.



**Fig. 2.** Schematic diagram of the  $CO_2$  absorption experimental setup (MFC = mass flow controller).

### $CO_2$ chemical absorption tests with single and blended amine absorbents

The chemical absorption of  $CO_2$  with various amine solutions was investigated by conducting experiments in a lab-scale ceramic HFMC unit. Fig. 2 shows the experimental setup for the determination of  $CO_2$  absorption performance [39]. The absorbent was applied to the lumen side of the ceramic hollow fiber membrane using a gear pump (Reglo-Z Digital, Ismatec, U.S.A.). The operating liquid pressure was controlled using a needle valve, whereas the gas flow rate and  $CO_2$  concentration were controlled using a mass flow controller (MFC, 5850E, Brooks, Japan). In all experiments, the gas flow rate and liquid flow rate were maintained at 50 mL/min (15%,  $N_2$  balanced) and 5 mL/min, respectively. A gas chromatography (GC-TCD, Master GC, Dani, Italy) was used in the system to measure the  $CO_2$  concentration in the outlet of the gas stream. The  $CO_2$  removal efficiency refers to the percentage of  $CO_2$  removed into the amine absorbent is described in detail in previous works [41,43].

Monoethanolamine (MEA, 99%, Samchun Pure Chemical Co., Ltd., Korea), diethylamine (DEA, 40 wt% aqueous solution, Samchun Pure Chemical Co., Ltd., Korea), *N*-methyldiethanolamine (MDEA, 99+%, Acros Organics, U.S.A.), 2-amino-2-methyl-1-propanol (AMP, 95%, Sigma-Aldrich, U.S.A.), and piperazine (PZ, 99.0%, Samchun Pure Chemical Co., Ltd., Korea) were diluted to appropriate concentrations (10, 20, 30, and 40 wt%) and tested as  $CO_2$  absorbents. The aqueous solutions were prepared only from distilled water and amine or blended amine. The experiments for all the aqueous amine solutions were conducted at least 6 times to obtain consistent values. The sample standard deviation of six consecutive  $CO_2$  chemical absorption measures is  $s = 0.09$ . The values of all other variables like pore size, effective surface porosity, overall porosity, gas flow rate, liquid flow rate, and temperature were kept constant at 0.9002  $\mu m$ , 99.70  $m^{-1}$ , 49.79, 50 mL/min, 5 mL/min, and 25 °C respectively.

The single amines and blended amine absorbents used in this work are shown in Table 2 and Table 3, respectively. The idea is to study the effects of different binary combinations of the amines on the  $CO_2$  absorption flux. The experiment combined both the excellent  $CO_2$  loading and heat of  $CO_2$  absorption in aqueous amine solution reported in Fig. 1 to obtain a big-picture perspective of  $CO_2$  chemical absorption performance in ceramic HFMC. No systematic study of such combinations has been carried out by ceramic HFMCs.

**Table 2**

Single amine absorbents and their concentrations used in this study.

MEA	DEA	MDEA	AMP	PZ
10 wt% MEA	10 wt% DEA	10 wt% MDEA	10 wt% AMP	10 wt% PZ
20 wt% MEA	20 wt% DEA	20 wt% MDEA	20 wt% DEA	20 wt% PZ
30 wt% MEA	30 wt% DEA	30 wt% MDEA	30 wt% DEA	/
40 wt% MEA	40 wt% DEA	40 wt% MDEA	40 wt% DEA	/

**Table 3**

Blended amine absorbents and their binary ratios used in this study.

Blended amine absorbents	Binary ratios	Note
MEA MDEA	20 wt% MEA + 10 wt% MDEA	MEA > MDEA
	15 wt% MEA + 15 wt% MDEA	MEA = MDEA
MEA AMP	10 wt% MEA + 20 wt% MDEA	MEA < MDEA
	20 wt% MEA + 10 wt% AMP	MEA > AMP
	15 wt% MEA + 15 wt% AMP	MEA = AMP
	10 wt% MEA + 20 wt% AMP	MEA < AMP
MEA PZ	20 wt% MEA + 10 wt% PZ	MEA > PZ
	15 wt% MEA + 15 wt% PZ	MEA = PZ
	10 wt% MEA + 20 wt% PZ	MEA < PZ
DEA MDEA	20 wt% DEA + 10 wt% MDEA	DEA > MDEA
	15 wt% DEA + 15 wt% MDEA	DEA = MDEA
DEA AMP	10 wt% DEA + 20 wt% MDEA	DEA < MDEA
	20 wt% DEA + 10 wt% AMP	DEA > AMP
	15 wt% DEA + 15 wt% AMP	DEA = AMP
	10 wt% DEA + 20 wt% AMP	DEA < AMP
DEA PZ	20 wt% DEA + 10 wt% PZ	DEA > PZ
	15 wt% DEA + 15 wt% PZ	DEA = PZ
	10 wt% DEA + 20 wt% PZ	DEA < PZ
MDEA PZ	20 wt% MDEA + 10 wt% PZ	MDEA > PZ
	15 wt% MDEA + 15 wt% PZ	MDEA = PZ
AMP PZ	20 wt% AMP + 10 wt% PZ	AMP > PZ
	15 wt% AMP + 15 wt% PZ	AMP = PZ

## Results

### Characterization of the ceramic hollow fiber membrane

N<sub>2</sub> gas permeance was measured as a function of the mean pressure between the inside and outside of the modified hydrophobic aluminum oxide hollow fiber membrane in the range of 10–35 kPa (see Supplementary material, Fig. S1) to calculate the average pore size and effective surface porosity of the prepared ceramic hollow fiber membrane. The result of this measurement shows that the nitrogen permeability increases with the increase in the mean pressure. For example, the N<sub>2</sub> permeance increased from about  $1.36 \times 10^{-5}$  to  $1.90 \times 10^{-5}$  mol/m<sup>2</sup> Pa s (40% increase) when the mean pressure was increased from 10 to 35 kPa. The prepared Al<sub>2</sub>O<sub>3</sub> hollow fiber membrane had an open pore structure allowing the gas to penetrate the pores, which is in accordance with results previously published by Tang et al. [47].

The average pore size and effective surface porosity of the prepared ceramic hollow fiber membrane were determined by a

**Table 4**

Characteristics of the ceramic hollow fiber membrane.

Parameters	Value
Fiber outer diameter (mm)	1.65
Fiber inner diameter (mm)	0.95
Mean pore size (μm)	0.9002
Effective surface porosity, $\varepsilon/L_p$ (m <sup>-1</sup> )	99.70
Overall porosity	49.79 ± 2.09

mathematical analysis [48,49] of the linear fit parameters for the data shown in the Supplementary materials (Fig. S1). Table 4 shows the properties of the obtained ceramic hollow fiber membranes studied in this work.

### CO<sub>2</sub> chemical absorption by single amine-based absorbents using hydrophobic modified ceramic HFMC

Fig. 3(a–e) shows the relationship between the amine concentrations, CO<sub>2</sub> absorption flux (mol/m<sup>2</sup> s), and CO<sub>2</sub> removal efficiency (%) in five single aqueous amine solutions, namely MEA, DEA, MDEA, AMP, and PZ. While all other experimental conditions are constant in the ceramic HFMC (mean pore size: 0.9002 μm, effective surface porosity: 99.70 m<sup>-1</sup>, overall porosity: 49.79 ± 2.09, gas flow rate: 50 mL/min, liquid flow rate: 5 mL/min, temperature 25 °C), the single amine concentration was varied from 10 to 40 wt% to elucidate its influence on the CO<sub>2</sub> absorption performances. However, it is now well established that PZ has limited solubility in water, where solid PZ occurs at relatively high concentrations [50]. Fig. 3(f) shows the photograph of the aqueous solutions of the PZ amine with various concentrations (10, 20, 30, and 40 wt%). As shown in Fig. 3(f), two aqueous piperazine solutions were precipitated in a concentration range from 30 to 40 wt%. For this reason, the PZ concentration was ranged between 10 and 20 wt%.

In general, the CO<sub>2</sub> absorption fluxes (mol/m<sup>2</sup> s), and then in turn the CO<sub>2</sub> removal efficiencies (%), increased with increasing amine concentration to a maximum of 6.92 and  $6.98 \times 10^4$  mol/m<sup>2</sup> s for MEA and DEA, respectively. These are a factor of ~6 greater than for MDEA-based absorbent and ~2 greater than for AMP-based absorbent in the concentration range studied in this work. CO<sub>2</sub> removal efficiencies hardly increased from 60% to about 80% when the MEA concentration was increased from 10 to 40 wt%. The obtained CO<sub>2</sub> chemical absorptions are in the range of those reported for typical polymeric HFMC [34].

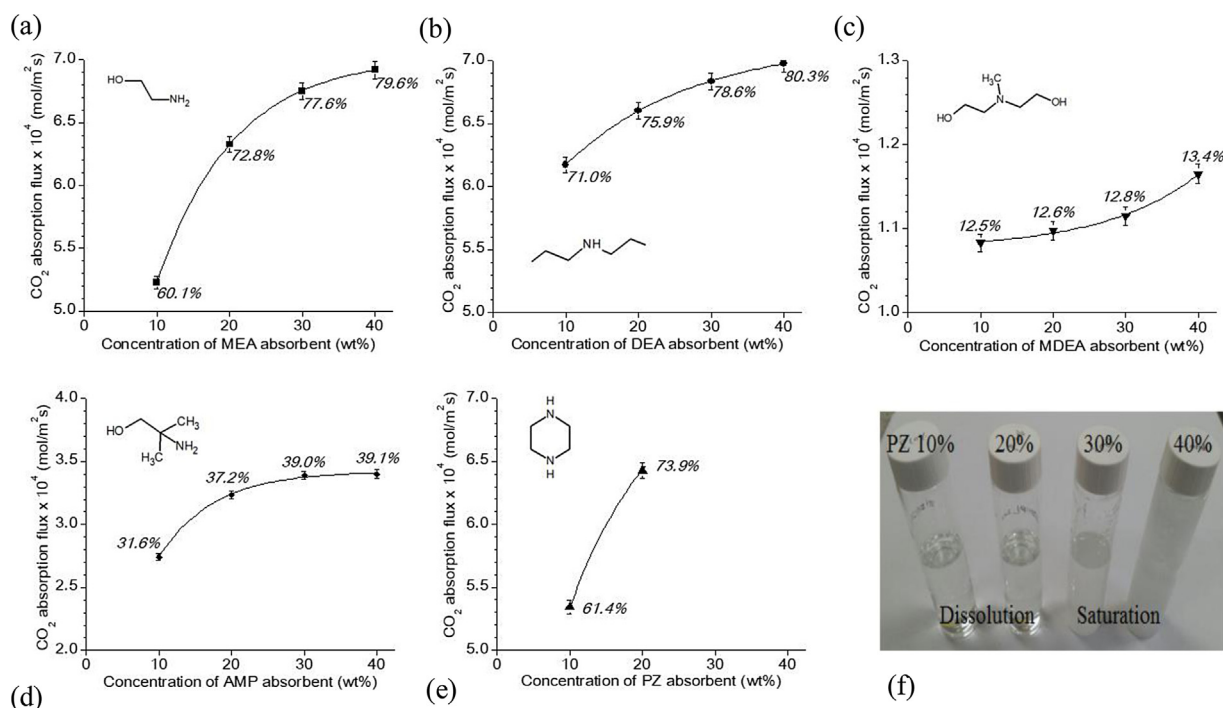
The behavior and values of the CO<sub>2</sub> chemical absorptions of PZ-based absorbents are similar to those observed for primary and secondary amines. For instance, at a gas flow rate of 50 mL/min, DEA was found to exhibit the highest CO<sub>2</sub> removal efficiency (80.3%), whereas MDEA offered the lowest CO<sub>2</sub> removal efficiency of 13.4%. These results are in good agreement with data reported in the literature [51,52]. It may be attributed to the fact that the reaction rate constant for the chemical reaction between MDEA and CO<sub>2</sub> is about 8–10 m<sup>3</sup>/kmol s (25 °C) [53], whereas the reaction rate constant is about 1400 and 7300 m<sup>3</sup>/kmol s for single DEA and MEA amines, respectively [8]. When the HFMC system was operated under identical conditions, the CO<sub>2</sub> chemical absorption performance using hydrophobic modified ceramic HFMC can be ranked in the following amine order: MEA ≥ DEA ≥ PZ > AMP > MDEA in good agreement with data reported for a bench-scale absorber packed with high-efficiency packings [8].

In addition, based on the results in Fig. 3, the CO<sub>2</sub> chemical absorption generally increased following an exponential decay function of amine concentrations for MEA, DEA, and AMP. Instead, the experimental data regarding MDEA can be well described by an exponential model, while in the case of PZ there were too few points to fit the data. In detail, the relationship between the CO<sub>2</sub> chemical absorption and the amine concentration reported in Fig. 3(a–e) was examined using the following exponential model:

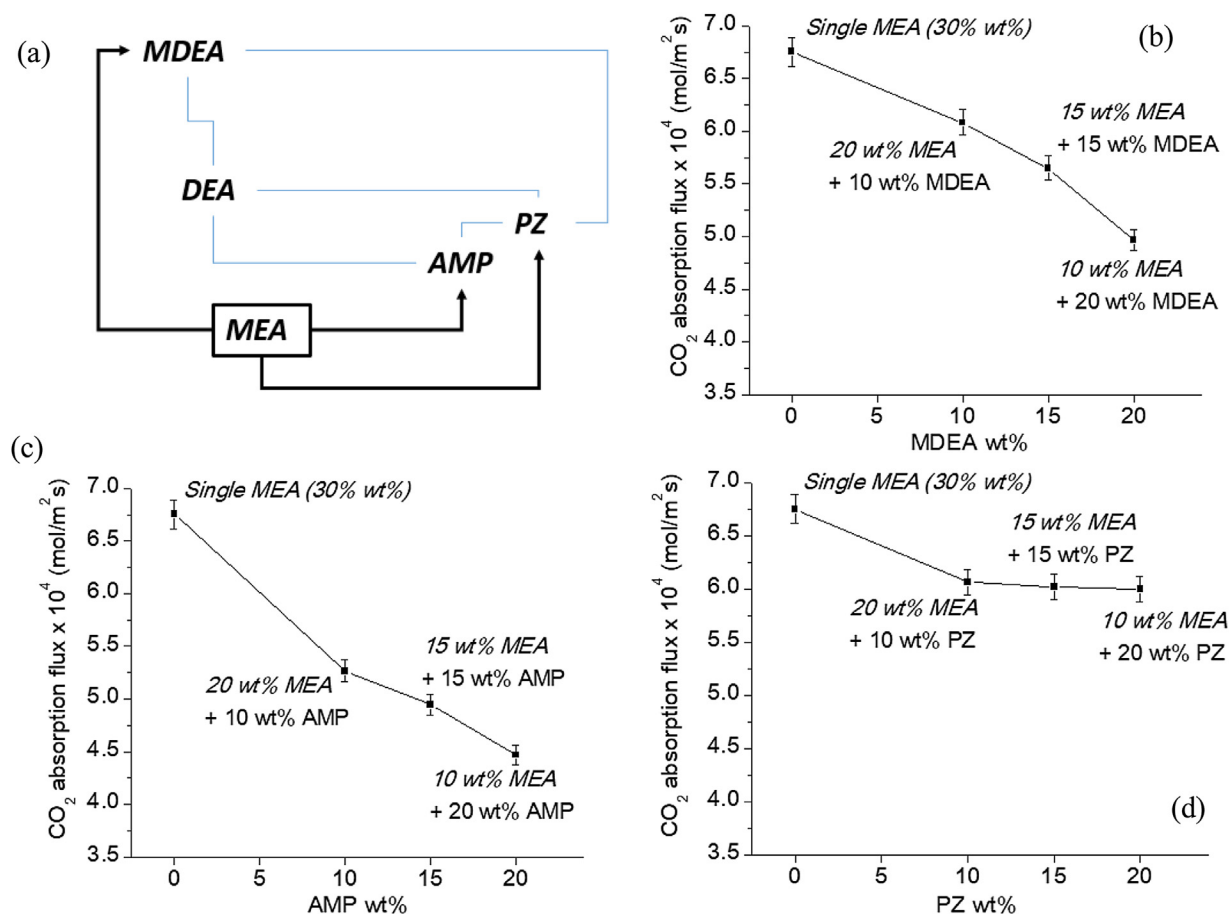
$$y = y_0 + A_1 e^{(-x/t_1)} \quad (6)$$

where  $t_1$  is the growth constant. The selected fit was studied in terms of two statistical parameters such as chi-square (Chi<sup>2</sup>) and R-square (R<sup>2</sup>). As is well known, the lower the chi-square value, and





**Fig. 3.** Effects of amine solution concentration of single (a) MEA, (b) DEA, (c) MDEA, (d) AMP, and (f) PZ on  $\text{CO}_2$  absorption flux using a ceramic HFMC. Photograph of the aqueous solutions of the PZ amine with various concentrations (10, 20, 30, and 40 wt%). One-percent error bars are added.



**Fig. 4.** (a) Flowchart of the performed experimental test of MEA based binary solutions regarding  $\text{CO}_2$  chemical absorption process using a ceramic HFMC in blends containing MEA and (b) MDEA, (c) AMP, and (d) PZ as blend components.

**Table 5**

Results of regressions and statistical analysis performed with exponential model (see Eq. (6)).

Amine absorbents	y0	A	t1	Chi <sup>2</sup>	R <sup>2</sup>
MEA	7.02	−4.64	10.52	2.73495E-6	1
DEA	7.15	−1.73	17.43	5.11586E-5	0.99986
MDEA	1.08	0.004	12.91	1.42601E-5	0.99626
AMP	3.42	−2.57	7.53	3.67521E-4	0.99872

the larger the R-square value, the better the equation fits experimental data. The results of regressions and statistical analysis of exponential models are also presented in Table 5. Notably, the first-order exponential model has  $R^2$  values near unity in almost all single amines but a slightly smaller for the MDEA case, and this implies that Eq. (6) does not fit very well to the ternary amine.

As evident in Table 5, the growth constant  $t_1$  obtained for AMP was lower than those of all other samples. From DEA to AMP,  $t_1$  ranges from  $\sim 17.4$  to a low value of  $\sim 7.5$ , respectively. Regarding the  $R^2$  indicator, the best result obtained with a first-order exponential decay function was the unity for the MEA solution. In summary, the first-order exponential model showed good approximation properties for the chemical absorption of  $\text{CO}_2$  in the selected amine solution by a ceramic HFMC. As shown in Fig. 3(a–e), simulation results obtained using the first-order exponential model showed good agreement with the experimental data obtained in this work. A possible explanation for this different

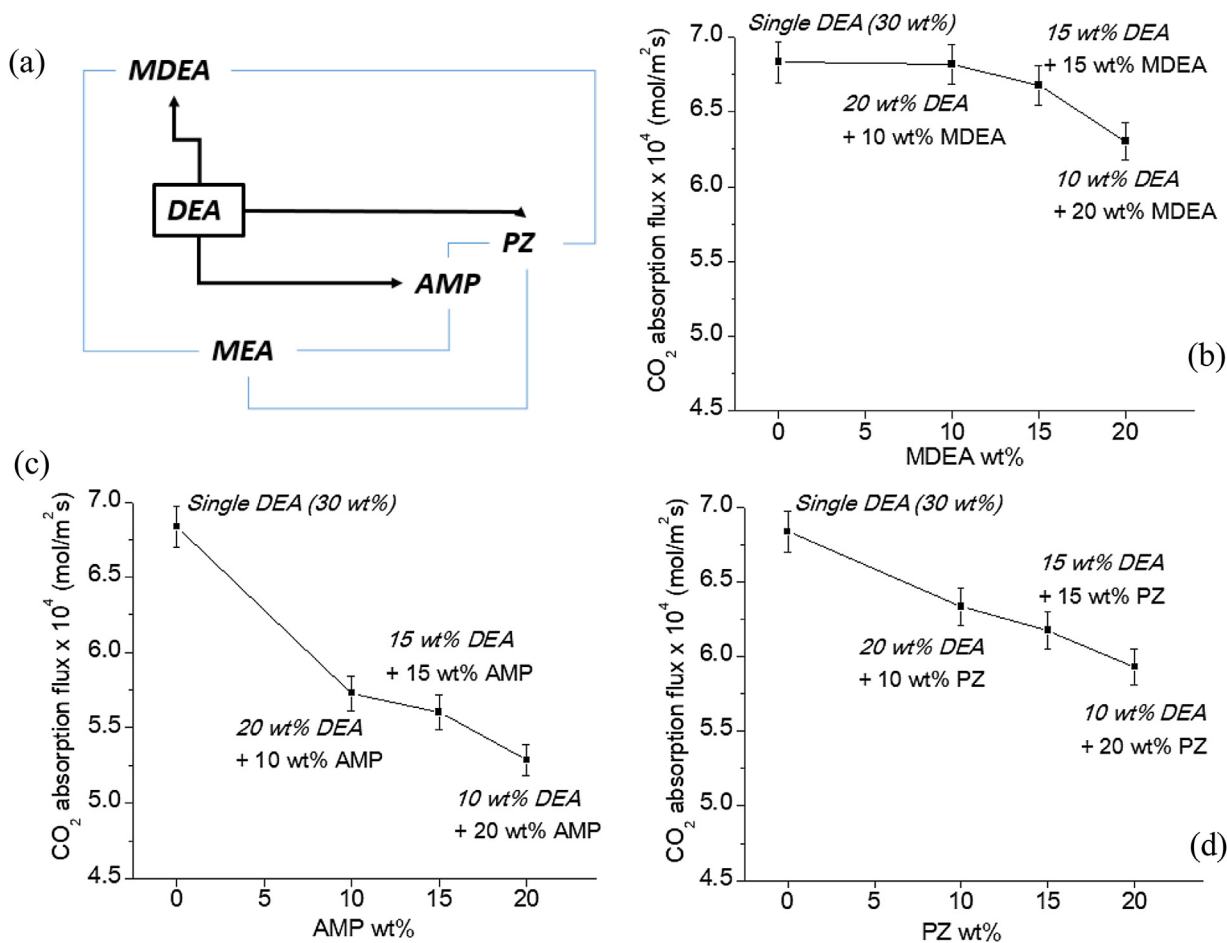
behavior could be that MDEA has high molecular complexity ( $C_m$ ) between the studied amines, and this can be influenced and altered the mass transfer phenomenon and then, in turn, the absorption of  $\text{CO}_2$  in the small pore size of HFMC. Rongwong et al. reported the same trend of the results for the case of polyvinylidene fluoride (PVDF) HFMC [27].

*$\text{CO}_2$  chemical absorption by blended amine-base absorbents using ceramic HFMC: influence of amine-to-amine ratio and comparison with single amine-based absorbents*

*Aqueous MEA blended MDEA, AMP, and PZ*

Fig. 4(a) shows the flowchart of the performed experimental test in this part of the work representing different binary combinations between a primary amine (MEA) and the other three amines (MDEA, AMP, and PZ). Fig. 4(b–d) shows the relationship between different blended conditions and  $\text{CO}_2$  chemical absorption in three aqueous amine solutions, namely MEA-MDEA, MEA-AMP, and MEA-PZ. The total amine concentration was always maintained at 30 wt%.

Compared with the single MEA, blended solvents with MDEA, AMP, and PZ show worse absorption performance. The  $\text{CO}_2$  chemical absorption of the single MEA solution decreased significantly with the introduction of an additional amine. For example, the behavior of MEA-MDEA blends reported in Fig. 4(b) may be attributed that the amount of MDEA limits the reaction with  $\text{CO}_2$  through the ceramic HFMC, which is in agreement with



**Fig. 5.** (a) Flowchart of the performed experimental test of DEA based binary solutions regarding  $\text{CO}_2$  chemical absorption process using a ceramic HFMC in blends containing DEA and (b) MDEA, (c) AMP, and (d) PZ as blend components.

the results reported in Fig. 3(a–e). A high amount of MEA in the solution with another amine gives a higher CO<sub>2</sub> absorption flux because of its higher reaction rate constant [27]. Thus, when the MDEA, AMP, and PZ amine content increases in the aqueous MEA blended MDEA, AMP, and PZ, there is a proportional decrease in the CO<sub>2</sub> chemical absorption. However, for MEA-MDEA blends, the rate of decrease is much higher than that for MEA-PZ blends [51]. An explanation of the fact that the CO<sub>2</sub> chemical absorption in aqueous blends MEA-PZ is not decreased significantly by the increase of the relative amount of PZ can be given based on the fact that the reaction rate of CO<sub>2</sub> for PZ is about 2–3 times faster than with MEA at comparable CO<sub>2</sub> partial pressures [54]. This is mostly since the amine concentration does not significantly affect the value of the CO<sub>2</sub> flux normalized by the liquid side partial pressure driving force for MEA or PZ solutions [54].

#### Aqueous DEA blended MDEA, AMP, and PZ

The blends of secondary amine DEA with MDEA, AMP, and PZ as absorption solvents for CO<sub>2</sub> capture were investigated in terms of the CO<sub>2</sub> chemical absorption process using hydrophobic modified ceramic HFMC. The experiment scheme of the aqueous DEA blended MDEA, AMP, and PZ is shown in Fig. 5(a), while total amine blends concentration was kept at 30 wt% for all different binary systems.

Fig. 5(b–d) shows the CO<sub>2</sub> absorption performance of single DEA and DEA blended MDEA, AMP, and PZ. The CO<sub>2</sub> absorption flux decreases with the decreasing of relative content of DEA in the aqueous blended amine solutions. In the case of the DEA blended MDEA system, the CO<sub>2</sub> absorption flux decreases more slowly than that of blended DEA-AMP and DEA-PZ solutions. For the DEA blended MDEA system, the flux of CO<sub>2</sub> is observed to be almost

constant at low MDEA contents (10–15 wt%). The CO<sub>2</sub> chemical absorptions in the DEA blended PZ solutions at 10 wt% DEA is higher, compared to those in DEA-MDEA and DEA-AMP blends.

#### Aqueous MDEA blended MEA, DEA, or PZ

Three binary systems – which MDEA mixed with various MEA, DEA, and PZ concentrations – were studied, and the results are shown in Fig. 6(b)–(d).

As shown in Fig. 6(b) and (c), the addition of small amounts of MEA and DEA to MDEA solution results in a significant enhancement in the rates of CO<sub>2</sub> chemical absorption for both blended solutions. By adding ten wt% of MEA to the MDEA-based absorbent, the capture of CO<sub>2</sub> increases significantly. However, the increase in the rate of chemical absorption for MDEA-MEA and MDEA-DEA mixtures is relatively higher than that for MDEA-PZ (see Fig. 6(d)). Gong et al. [26] have reported the experiments and simulation of CO<sub>2</sub> removal in a PP HFMC consisting of 210 fibers using aqueous blends of MDEA and MEA aqueous solutions. In their work, the authors reported that the CO<sub>2</sub> chemical absorption increase as the MEA content in the MDEA-MEA mixture increases because the reaction rate constant of MEA with CO<sub>2</sub> is much higher than that of MDEA with CO<sub>2</sub> [26]. In conclusion, the addition of primary amine MEA or secondary amine DEA or cyclic diamine-based amine PZ into the MDEA-based absorbent helps chemical absorption of CO<sub>2</sub> while maintaining the advantages of MDEA [32,55,56], in good agreement with previous studies on polymeric HFMCs [24,25].

#### Aqueous AMP blended MEA, DEA, and PZ

Different mechanisms have been proposed for the AMP-CO<sub>2</sub> reaction like the zwitterion mechanism through direct reaction between the sterically hindered primary amine AMP and CO<sub>2</sub> to

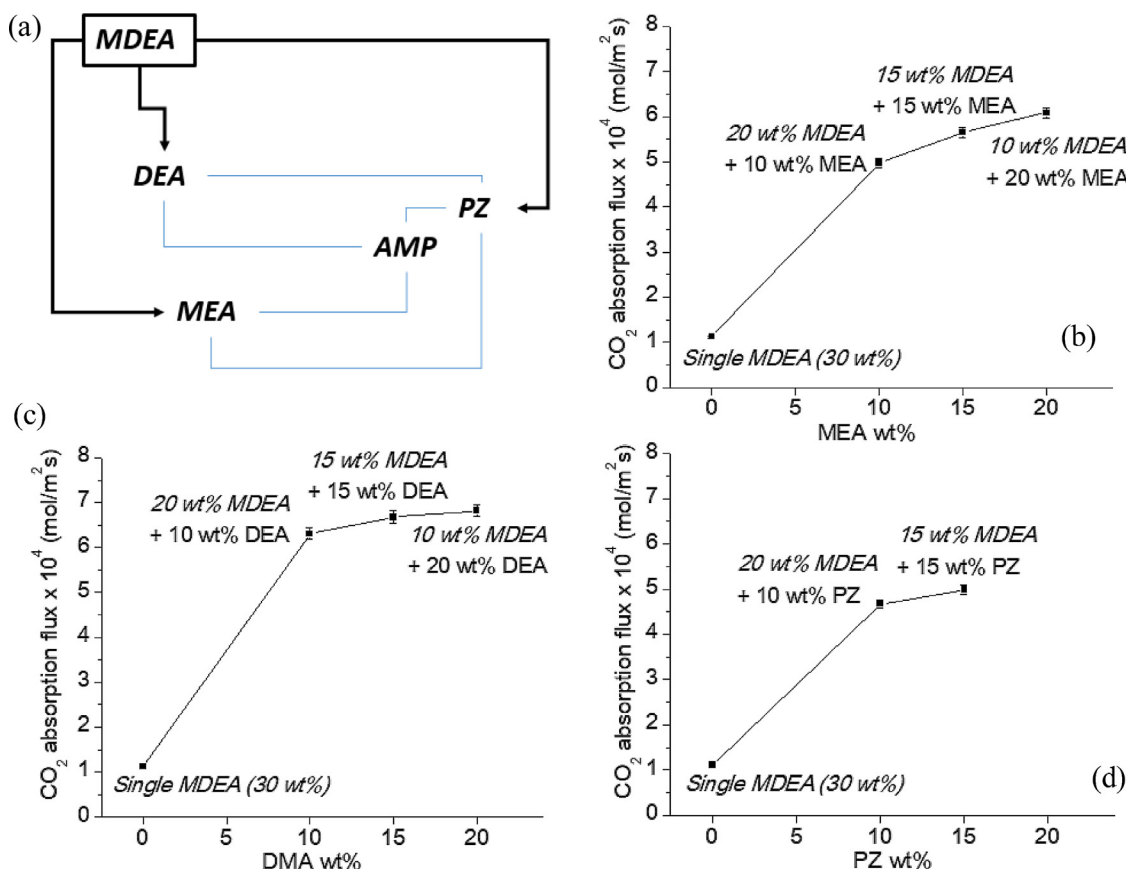
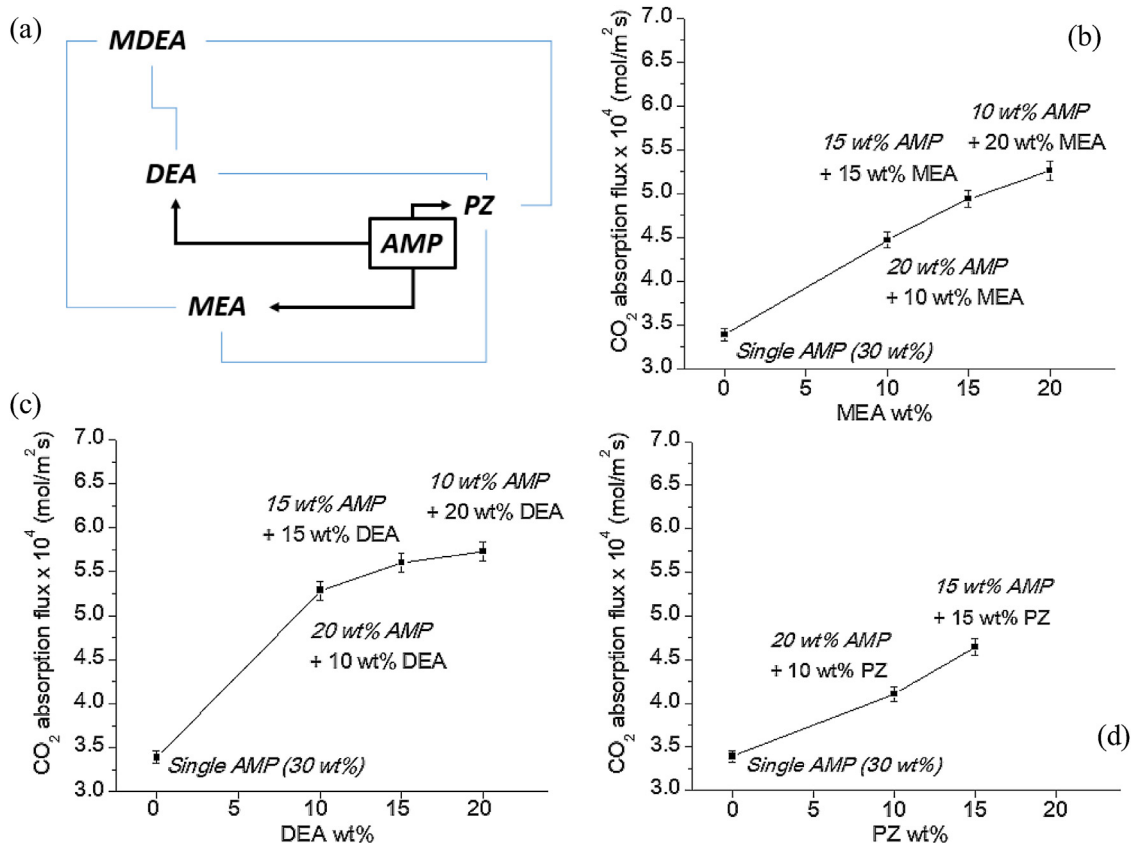


Fig. 6. (a) Flowchart of the performed experimental test of MDEA based binary solutions regarding CO<sub>2</sub> chemical absorption process using a ceramic HFMC in blends containing MDEA and (b) MAE, (c) DEA, and (d) PZ as blend components.



**Fig. 7.** (a) Flowchart of the performed experimental test of AMP based binary solutions regarding CO<sub>2</sub> chemical absorption process using a ceramic HFMC in blends containing AMP and (b) MAE, (c) DEA, and (d) PZ as blend components.

form carbamate [14,21,22], or bypassing the formation of carbamate through a direct hydrolysis of the zwitterion form [16,23]. The experimental data for the aqueous solution of AMP-based absorbent blended MEA, DEA, and PZ are plotted in Fig. 7.

Fig. 7 shows the absorption rates of CO<sub>2</sub> by AMP-MEA, AMP-DEA, and AMP-PZ blended amines as a function of MEA, DEA, and PZ concentrations. In all cases studied, Fig. 7(b)–(d) reveals that the CO<sub>2</sub> absorption flux of the AMP blended MEA, DEA, and PZ solutions using a ceramic HFMC increased with the MEA, DEA, or PZ concentration. In detail, the replacement of AMP with 20 wt% DEA increased the CO<sub>2</sub> chemical absorption from  $3.4\text{--}5.7 \times 10^4 \text{ mol/m}^2 \text{ s}$ . These results agree with those obtained by Iliuta et al. [57]. Their simulations indicated that DEA and AMP through a PTFE HFMC gave much higher CO<sub>2</sub> chemical absorptions compared to the single MDEA-based absorbent.

The CO<sub>2</sub> absorption flux of AMP blended PZ increases with the increase of the PZ content. This result is in apparent contradiction with the previous finding on AMP-PZ blended amines [16]. While maintaining the total amine mass fraction constant, the replacement of AMP with PZ reduced the CO<sub>2</sub> mole-ratio loading capacity by 8% and 12.5% for “25 wt% AMP + 5 wt% PZ” and “20 wt% AMP + 10 wt% PZ” respectively, compared with 30 wt% AMP [18]. However, the addition of PZ to an aqueous solution of AMP results in a significant enhancement in the rates of absorption [58]. Samanta and Bandyopadhyay [58] experimentally studied the effect of PZ on the absorption of CO<sub>2</sub> in aqueous solutions of AMP using a wetted wall contactor. As a result, the absorption rate of CO<sub>2</sub> in 20 mass% AMP + 10 mass% PZ reported by them from their absorption experiments appear to be more than 5.6 times that in 30 mass% AMP. These data are in good accord with the results of this study however additional studies on the physicochemical

properties (densities, viscosities, etc.) of the aqueous AMP-PZ blended amines are needed for better understanding the relationships between different results.

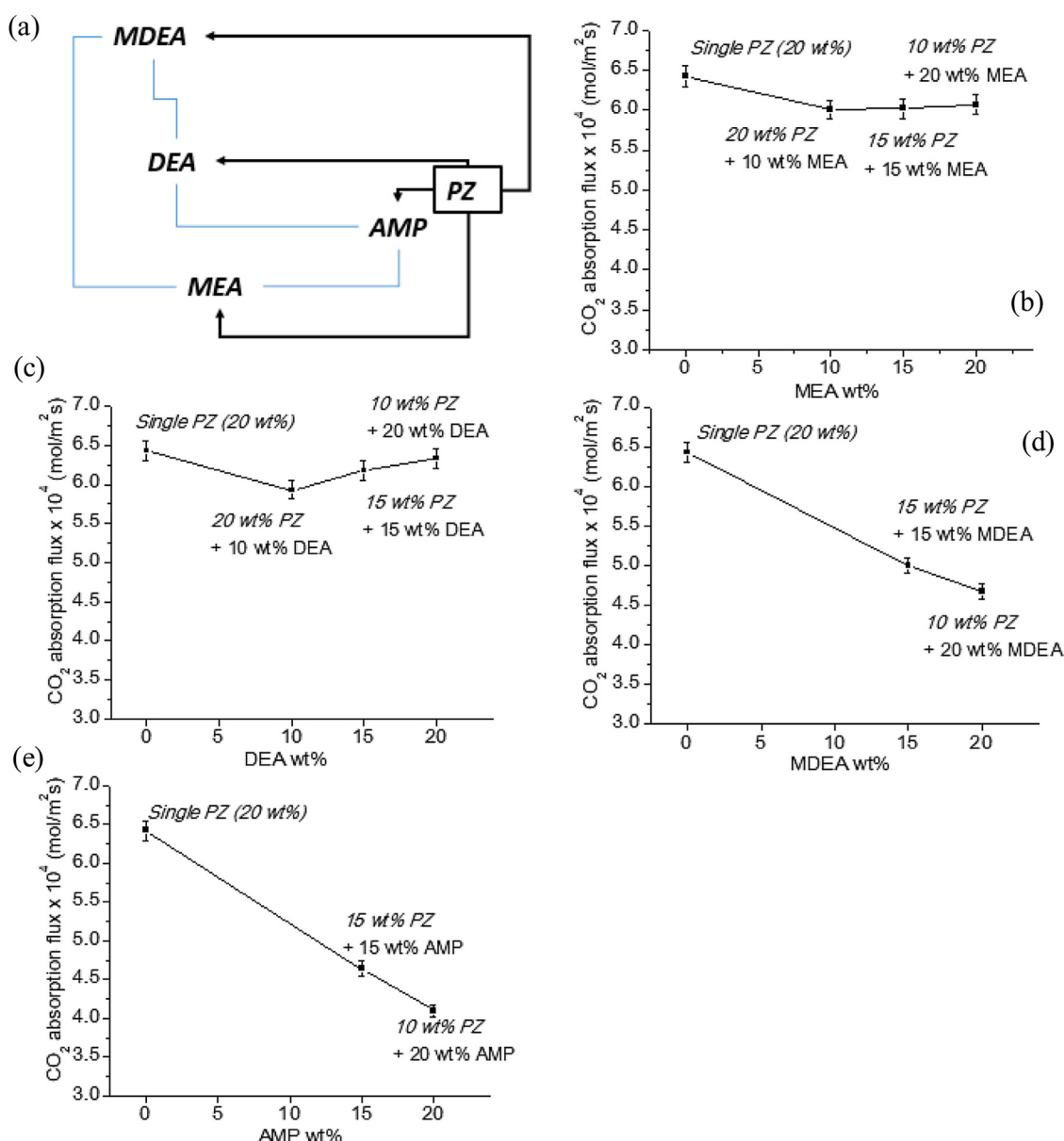
#### Aqueous PZ blended MEA, DEA, MDEA, and AMP

The CO<sub>2</sub> absorbing tests were performed with relatively low PZ concentrations from 10 to 20 wt% due to examine the effect of PZ-based absorbent on different binary blended amines (MEA, DEA, MDEA, or AMP). The results of these CO<sub>2</sub> absorption flux measurements are reported in Fig. 8. For the CO<sub>2</sub> chemical absorption process in the blends of PZ-MDEA and PZ-AMP, the CO<sub>2</sub> absorption flux decreases as the concentration of MDEA and AMP increases [50]. For the PZ-MEA and PZ-DEA systems, the flux of CO<sub>2</sub> is observed to be almost constant with different blend compositions. This fact means that there was no improvement concerning the CO<sub>2</sub> absorption flux with PZ-MEA and PZ-DEA blended amines using a ceramic HFMC.

#### Discussion

Little work has been carried out to determine the CO<sub>2</sub> chemical absorption using hydrophobic modified ceramic HFMC with single amine-based absorbents [38–40]. Most of the available data on blended amine-based absorbents have been obtained using a polymeric HFMC [24–28,34] or deduced from mathematical models [52,59–62]. The experimental results reported in the previous section provide clear evidence that the CO<sub>2</sub> chemical absorption process by ceramic HFMC using a blended amine absorbent is mainly dependent on their concentration and chemical nature. The different types of behavior are due to their intrinsic properties and chemical affinity between the amine





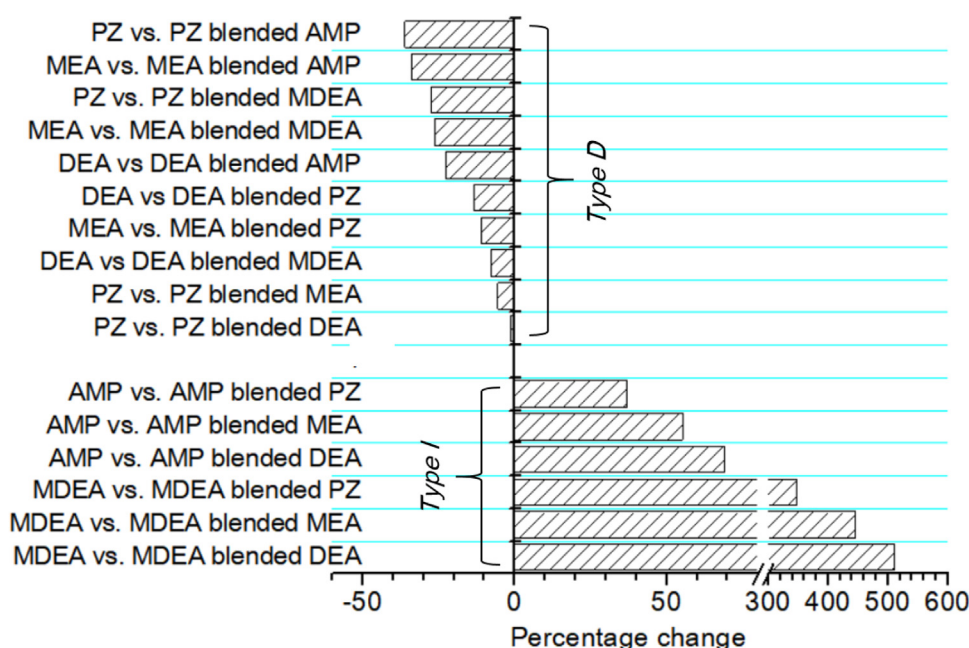
**Fig. 8.** (a) Flowchart of the performed experimental test of PZ based binary solutions regarding CO<sub>2</sub> chemical absorption process using a ceramic HFMC in blends containing PZ and (b) MEA, (c) DEA, (d) MDEA, and (e) PZ as blend components.

absorbers and CO<sub>2</sub> through a hydrophobic modified ceramic HFMC. The objective here is to determine the different types of behavior of CO<sub>2</sub> absorption flux and aqueous binary solutions of blended amines in terms of performance and implementation efficiency and to establish a ranking system based on a systematic analysis of the experimental results.

Considering only the trends behavior reported from Figs. 4 to 8, it can be seen that all patterns behaviors regarding sixteen correlations between single and blended amine-based absorbents can be classified into two main categories from its dependence on aqueous binary solutions of blended amines. One is Type D, in which the function values decrease as the blend component increases from zero to 10 wt%. The other is Type I, in which the functions increase as the blend component increases from zero to 10 wt%. The results of this qualitative analysis are shown in Fig. 9, with the respective percentages of increase and decrease including one displaying a positive percentage change value (increasing performance, Type I) and the other a negative value

(decreasing performance, Type D) of CO<sub>2</sub> absorption flux performance in comparison with the single amine absorbents. In particular, Fig. 9 shows the percentages of increase and decrease by using the single amine scenario (MEA, DEA, MDEA, AMP, and PZ) of each experiment measure as a reference so that the CO<sub>2</sub> absorption flux of the single amine is compared directly with the CO<sub>2</sub> absorption flux obtained by the blended amine-based absorbents.

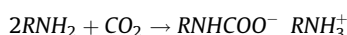
Keeping all other variables constant, this analysis shows that, for the CO<sub>2</sub> absorption in the PZ blended AMP, MEA blended AMP, PZ blended MDEA, MEA blended MDEA, DEA blended AMP, DEA blended PZ, MEA blended PZ, DEA blended MDEA, PZ blended MEA, and PZ blended DEA, the flux always decreases (Type D) with the different trend as the concentration of the second blend component increases in the binary blends. On the contrary, the behavior of AMP blended PZ, AMP blended DEA, AMP blended MEA, MDEA blended PZ, MDEA blended DEA, and MDEA blended MEA were significantly different. The performance of these



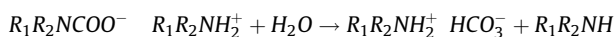
**Fig. 9.** Schematic representation of the trends behavior between CO<sub>2</sub> absorption flux and single versus blended amine-based absorbents for CO<sub>2</sub> chemical absorption in a hydrophobic modified ceramic HFMCs.

blended amine-based absorbents exhibited a strong increasing trend (Type I) in comparison with single amine as a reference. A strong increasing trend was observed in the AMP blended PZ, MEA, and DEA, as well as MDEA blended PZ, MEA, and DEA. In both blended cases, the increase in performances is as follows: DEA > MEA > PZ. Among the increasing trends, MDEA based binary absorbents (+500%) are always greater than the respective percentages of increase of AMP blended amine-based absorbents (+350%).

The reaction of primary amine for CO<sub>2</sub> chemical absorption is presented as follows:

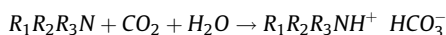


The reaction between a secondary amine like DEA and CO<sub>2</sub> is presented as follows



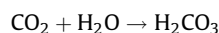
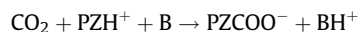
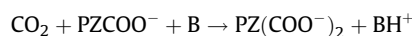
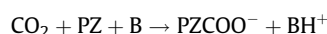
In both cases, it can be seen that 1 mol of primary or secondary amine reacts with 0.5 mol of CO<sub>2</sub>, thought a carbamate group.

The chemical absorption reaction between a tertiary amine (i.e., MDEA) and CO<sub>2</sub> can be represented as follows:



where 1 mol of tertiary amine reacts with 1 mol of CO<sub>2</sub>. Therefore, the CO<sub>2</sub> absorption capacity of tertiary amines is higher than those of the primary and secondary amines since tertiary amines do not form carbamates [63]. The adsorption of CO<sub>2</sub> on primary and secondary amine solutions could be explained by two mechanisms, namely nucleophilic reaction, and acid-base neutralization. It is known that carbamate derivatives are formed by nucleophilic reaction, following which bicarbonate compounds are generated by acid-base neutralization [64]. Further, carbamate derivatives are converted to carbonate and bicarbonate by hydrolysis. However, since tertiary amines have no N—H bonds, carbamates are not formed in the reaction with CO<sub>2</sub> [63].

The reaction between PZ and CO<sub>2</sub> in aqueous solutions seems to be as follows:



where B is any base present in solution [20] so that theoretically this cyclic diamine-based absorbent absorbs 2 mol CO<sub>2</sub> per 1 mol PZ through carbamates.

Different mechanisms have been proposed for the AMP–CO<sub>2</sub> reaction like the zwitterion mechanism through a direct reaction between the sterically hindered primary amine AMP and CO<sub>2</sub> to form carbamate [16,21,22] with low stability [16,17], or bypassing the formation of carbamate through direct hydrolysis of the zwitterion form [16,23] so that the sterically hindered amines like AMP also exhibit almost the same characteristics as the MDEA tertiary amine. This is confirmed by the similitude between the behavior of the variables between MDEA (Fig. 6) and AMP (Fig. 7).

To summarize, from a CO<sub>2</sub> absorption performance point of view, blended AMP/PZ, AMP/MEA, AMP/DEA, MDEA/PZ, MDEA/MEA, and MDEA/DEA offer the most useful blended amine absorbents for CO<sub>2</sub> chemical absorption by hydrophobic modified ceramic HFMCs in comparison with the single amine absorbents.

## Conclusions

A novelty of the present work is that it investigates systematically five single amine-based absorbents and sixteen correlations

between single and blended amine-based absorbents for CO<sub>2</sub> chemical absorption using the hydrophobic modified ceramic HFMCs, in which all other variables (preparation and nature of hollow fiber membrane, pore size, effective surface porosity, overall porosity, gas flow rate, liquid flow rate, and temperature) than the ones directly studied were held constant. To the best of our knowledge, no blended amine-based absorbents in ceramic HFMC for CO<sub>2</sub> capture have ever been reported.

In conclusion, keeping all other variables constant, the major points covered in this paper may be summarized as follows.

- (1) The CO<sub>2</sub> absorption properties of single and blended amine-based absorbents for CO<sub>2</sub> chemical absorption using a hydrophobic modified ceramic HFMC are highly dependent on their chemical nature and concentration.
- (2) The CO<sub>2</sub> absorption flux always increased with increasing single amine concentration in the range studied in this work (10–40 wt%).
- (3) The aqueous solution of MEA and DEA-based absorbents have the highest CO<sub>2</sub> absorption flux among the single amine solutions, where they reached values of 6.92 and  $6.98 \times 10^4$  mol/m<sup>2</sup>s at 40 wt% and then these are a factor of ~6 greater than for MDEA (1.16 mol/m<sup>2</sup>s) in the same concentration conditions.
- (4) The CO<sub>2</sub> chemical absorption performance using hydrophobic modified ceramic HFMC can be ranked in the following decreasing order: MEA ≥ DEA ≥ PZ > AMP > MDEA.
- (5) The CO<sub>2</sub> chemical absorption generally increased following an exponential decay function of amine concentrations for single MEA, DEA, and AMP.
- (6) For the CO<sub>2</sub> absorption in the aqueous PZ blended AMP, MEA blended AMP, PZ blended MDEA, MEA blended MDEA, DEA blended AMP, DEA blended PZ, MEA blended PZ, DEA blended MDEA, PZ blended MEA, and PZ blended DEA, the flux decreases (Type D) as the concentration of the second blend component increases in the binary blends.
- (7) For the CO<sub>2</sub> absorption in the aqueous AMP blended PZ, AMP blended DEA, AMP blended MEA, MDEA blended PZ, MDEA blended DEA, and MDEA blended MEA, the flux increases (Type I) as the concentration of the second blend component increases in the binary blends.
- (8) A strong increase of CO<sub>2</sub> absorption flux versus second blend component concentration was observed in the MDEA blended MEA, DEA, and PZ.
- (9) In the end, aqueous MDEA blended DEA reaches a percentage of increase of CO<sub>2</sub> absorption flux over 500% in comparison with the corresponding aqueous solution of single MDEA.

## Declaration of interests

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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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jiec.2021.05.025>.

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