Experimental and modeling study of CO$_2$ capture by phase change blend of triethylenetetramine-ethanol solvent

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ABSTRACT

Post combustion Carbon capture based on chemical absorption is the best-known technology to reduce CO$_2$. Recently, attention has been paid to biphasic solvents due to their excellent potential in reducing energy consumption. This study investigated carbon dioxide absorption by biphasic non-aqueous triethylenetetramine (TETA)-ethanol solvent in a T-shaped microchannel. Effect of four parameters including: concentration of TETA (4–8 wt%), liquid flow (2–5 ml/min), inlet CO$_2$ concentration (5–20 vol%) and gas flow (100–175 ml/min) have been examined. Mass transfer characteristics has been assessed by investigation of absorption percentage, molar flux and overall mass transfer coefficient. The results show that increasing the concentration of amine diminishes all three responses by increasing the solution viscosity. As a result, it decreases the penetration of CO$_2$ in the solution and the rate of absorption.

Furthermore, the TETA-ethanol phase change solvent has been compared with aqueous monoethanolamine (MEA). The results of this comparison indicated that the efficiency of CO$_2$ absorption and mass transfer coefficient, for TETA-ethanol biphasic solvent are higher than MEA solvent, respectively. Finally, the dimensionless Damköhler number (Da) was utilized in the new correlation to predict $K_L a$ for CO$_2$ absorption into TETA-Ethanol solution with acceptable accuracy.

1. Introduction

One of the main drivers of global warming and its associated environmental issues, such as climate change and rising sea levels, is the excessive emission of CO$_2$. Hence, finding new ways to capture and remove CO$_2$ using advanced materials, techniques, and devices has been a significant research focus in recent decades [1–3]. Carbon capture and storage (CCS) technology includes capture, transfer and storage of the carbon. Meanwhile, the capture process constitutes 80 % of the total costs. Post-combustion capture (PCC) technology is considered as a cost-effective method to diminish greenhouse gases emissions by elimination of CO$_2$ from flue gas. Compared to other PCC strategies including adsorption, membrane and cryogenic separation, chemical absorption has been developed for industrial applications, extensively. Solvent-based absorption using amines is one of the most promising methods. This process is an economically possible option and is easily implemented in various industries [1,4,5]. The chemical absorption process based on monoethanolamine (MEA) was developed as the conventional technology for PCC, with advantages such as a significant rate

of absorption and high capacity. On the other hand, CO$_2$ capture using MEA increases the cost of the fossil fuel based electricity production [6], and is accompanied by high energy consumption. In the regeneration stage, most energy is consumed to regenerate loaded amine. The high heat requirement has been an obstacle to using MEA on an industrial scale. For this reason, the developing of novel solvents with low energy demand in the regeneration stage has attracted particular attention [7–10]. Recently, a new generation of solvents called biphasic solvents has been developed. This category of solvents are homogeneous absorbents before Carbon dioxide absorption. But, after Carbon dioxide absorption and temperature change, they create a two-phase system consisting of a CO$_2$-rich phase and a CO$_2$-lean phase to undergo liquid-liquid or liquid-solid phase change. In this method, only the rich phase is fed to the desorption tower for regeneration. Consequently, the solvent flow that needs to be regenerated is reduced. This causes a significant reduction in energy consumption during the regeneration process [11–13]. Moreover, these solvents have a good potential in reducing equipment costs [11,12]. The energy consumption in these processes is in the range of 2-2.5 MJ/kg CO$_2$, which reduces about

Table 1

Uncertainty values of main variables in experimental measurements.

Parameter	Uncertainty (RSD%)
Absorption percentage	3.6
Volumetric molar flux	3.3
The overall mass transfer coefficient	5.3

Table 2

Physical properties of non-aqueous solution of the TETA-ethanol at constant temperature of 25 °C.

TETA concentration (wt.%)	Kinematic viscosity (mm²/s)	Density (gr/ml)	Surface tension (mN/mm)
4	1.63	0.801	22.383
5	1.67	0.802	22.470
6	1.71	0.804	22.547
7	1.77	0.805	22.560
8	1.87	0.808	22.690

30–40 % of the energy requirement in comparison to the benchmark MEA process [14,15]. The liquid-liquid phase change is observed in systems consisting of several amines and the DMX process, which can be separated from each other based on the difference in the density of the phases. Liquid-solid phase change is observed in systems including ionic liquids/alkanolamine, chilled ammonia and polyamine/ethanol solutions [16]. In phase change solvents, an amine is always used to absorb CO_2 and a physical solvent including alcohols, sulfolane, tertiary amines, hydrophobic ionic liquids and ethers to promote phase separation. Therefore, the selection of the physical solvents for phase change absorbents is essential. Ionic liquids have few industrial applications due to their high viscosity and cost, despite their many advantages and creating a liquid-solid phase change [17,18]. To overcome these weaknesses and achieve CO_2 absorption with phase change, organic solvents such as alcohols are suggested. In addition to the lower cost and viscosity compared to ionic liquids, these solvents have favorable characteristics, including high solubility for amines and Carbon dioxide, lower corrosion rates, low evaporation heat compared to water, reduction in the temperature of the desorption tower due to the low boiling point and they offer a reduction in energy consumption during the regeneration process [19–22]. In this research, ethanol was chosen as a solvent for polyamine triethylenetetramine (TETA). Ethanol is a

relatively inexpensive and widely used solvent. Due to its low boiling point and low viscosity compared to other organic solvents used for Carbon dioxide absorption, it provides an effective mass transfer medium for absorption. The absorption of the Carbon dioxide with alcoholic solutions including TETA causes precipitation [23]. Besides the advantages of using organic solvents, the liquid-solid phase change will also result in higher energy efficiency in the CO_2 absorption process. Hence, the sediment resulting from CO_2 absorption is easily separated from the liquid. Based on Le Chatelier's principle, by removing the reaction product from the solution, the absorption capacity will be improved, whereby only the product needs to be heated for regeneration. As a result, energy efficiency increases. This can be developed for more efficient carbon sequestration technology [11,13,24].

Zheng et al. [23] investigated the Carbon dioxide uptake by the non-aqueous solution consisting of 0.2 M TETA and ethanol in a bubble

Table 3

Components and characteristics of experimental equipment.

Components	Model	Company	Manufacturing Country
Microchannel	Length = 29 cm Width = 8 cm Diameter = 900 μm	–	–
Peristaltic Pump	BT-100	Omega tools	China
Air and CO_2 MFC	BREEZENS	Apasco	Iran
Carbon dioxide Sensor	CM-0123	COZIR-WR	Germany

Table 4

Experimental conditions in the experiment.

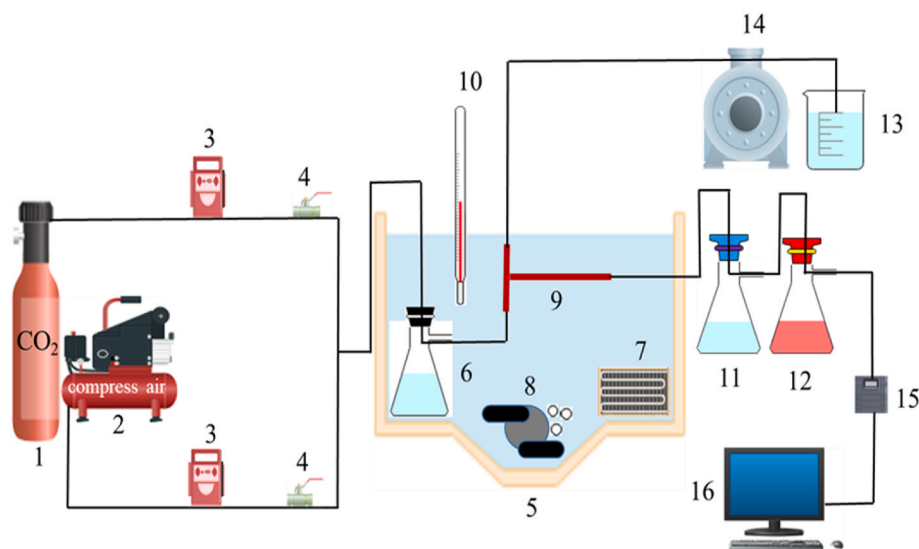| The investigated parameters	Range
Absorbent	The non-aqueous solution of the TETA-ethanol
Temperature (°C)	25
Liquid flow (ml/min)	2–5
Gas flow (ml/min)	100–175
TETA concentration (wt.%)	4–8
Carbon dioxide concentration (vol %)	5–20

Fig. 1. Schematic of the device used in CO_2 absorption: 1) CO_2 storage tank, 2) Compressed air tank, 3) Air and CO_2 MFC, 4) Valve, 5) Water bath, 6) Gas humidifier, 7) Heater, 8) Circulation pump, 9) Microchannel, 10) Thermometer, 11) Separator, 12) Gas washing bottle, 13) Feed tank, 14) Peristaltic pump, 15) CO_2 concentration measuring sensor, 16) Data recording system.
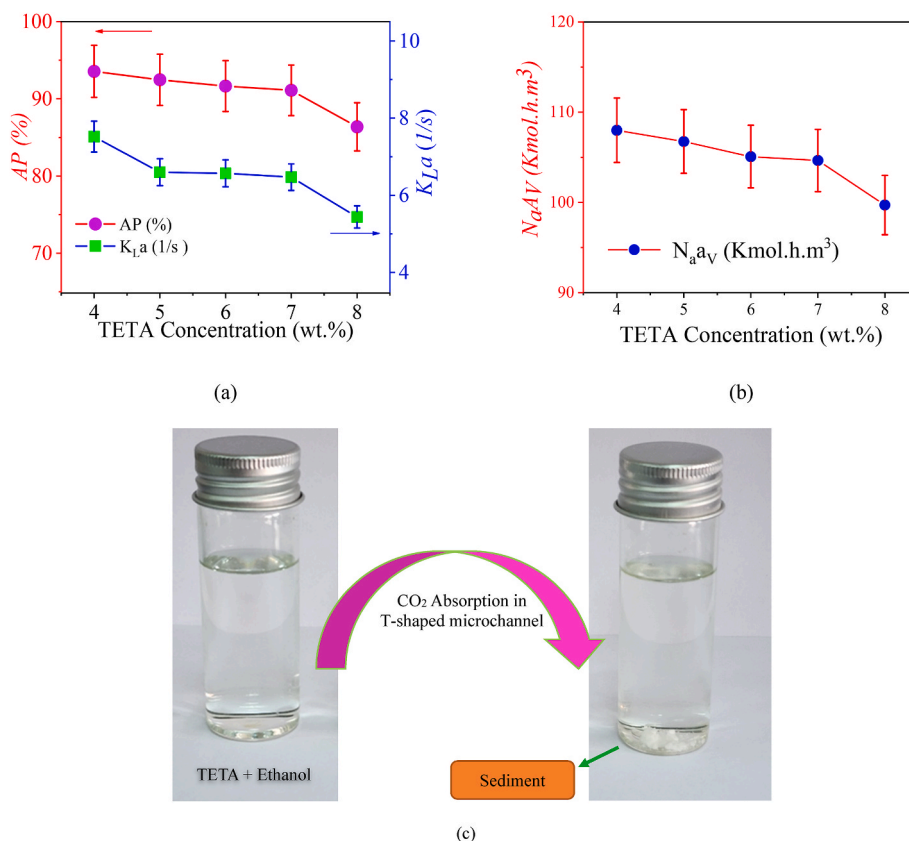
Fig. 2. Effect of TETA concentration on (a) *AP* and K_La, (b) K_La and $N_{co_2}a_V$ in constant gas flow of 125 ml/min, liquid flow of 4 ml/min and carbon dioxide concentration of 10 vol%, and (c) formation of sediment after CO_2 absorption at the outlet.

column reactor. These phase change solutions were compared in terms of the CO_2 uptake rate and capacity with 0.2 M TETA aqueous solution. The results of their work showed that the Carbon dioxide absorption rate and solvent capacity in TETA-ethanol phase change solution is considerably higher than that of TETA aqueous solution. Physical solvents such as ethanol, increases the solubility of the Carbon dioxide and the formation of the TETA-carbamate precipitate changes the reaction balance and this causes more Carbon dioxide absorption in the TETA-ethanol solution. While, no sediment is formed in the aqueous solution of the TETA. Also, based on Barzali et al. [25] study, ethanol facilitates the reaction between amine and CO_2.

Tao et al. [26] investigated Carbon dioxide absorption in ethylenediamine (EDA)-ethanol and PZ-ethanol non-aqueous solutions in a container equipped with a flat blade mixer to keep the gas-liquid interface horizontal. They observed that both solutions can produce solid precipitates of carbamate for EDA and PZ after absorbing CO_2. The regeneration heat for EDA and PZ carbamate is 25 % lower than that of benchmark MEA solutions. The comparative findings demonstrated that the diamine-alcohol has a higher capacity than the diamine-water. The Carbon dioxide absorption rate in the non-aqueous EDA solution is nearly twice as high as that of the aqueous EDA solution. At the same time, this amount for the non-aqueous PZ-ethanol solution has only slightly increased compared to the aqueous PZ solution.

One of the novelties of this study is the investigation of the mass transfer performance of biphasic solutions. To date, only a limited number of studies have been undertaken with regards to the examination of mass transfer efficacy of these specific solutions. Since, the majority of prior investigations concerning biphasic solutions have primarily examined the energy associated with their regenerative. Moreover, TETA is often used as a promoter in conjunction with other amines due to its high reactivity with CO_2 and the sediment formation. Therefore, it can be of particular importance to investigate mass transfer

performance by this amine. There are few studies in this field. Yihan Yin et al. [27] studied the mass transfer behavior in the phase change solvent for CO_2 absorption in a packed column. They used an aqueous solution of the MEA/sulfolane, which is an inexpensive phase change absorbent with a fast absorption rate. They also compared this phase change absorbent with MEA at the same concentration in terms of the mass transfer effectiveness. The results of their comparison indicated that the use of the phase change solvent has demonstrated a substantial enhancement in the mass transfer efficiency compared to conventional solvent. Moreover, the contact surface area between the two phases is one of the essential factors in the absorption process. When the contact area between phases increases, absorption takes place in a shorter period of time. The phenomenon mentioned above results in a notable decrease in equipment costs. Today, microchannels have been noticed more than other contactors due to optimal mixing and a substantial increase in the contact surface between phases [28,29]. This type of contactors make process control easier and by reducing the mass transfer resistance, they create a massive revolution in the field of carbon dioxide absorption [30].

The purpose of this research is to examine CO_2 absorption process through TETA-ethanol biphasic solvent. The examination of this non-aqueous solution was carried out by a T-shaped microchannel and the effect of the operational parameters of this solution such as: TETA concentration, liquid and gas flow, and carbon dioxide concentration on CO_2 removal efficiency, mass transfer coefficient, and mass transfer flux has been studied.

2. Theory

In general, the reaction of the carbon dioxide with a primary or secondary amine is described by the zwitterion mechanism. The mechanism was first proposed via Capello and then reintroduced via
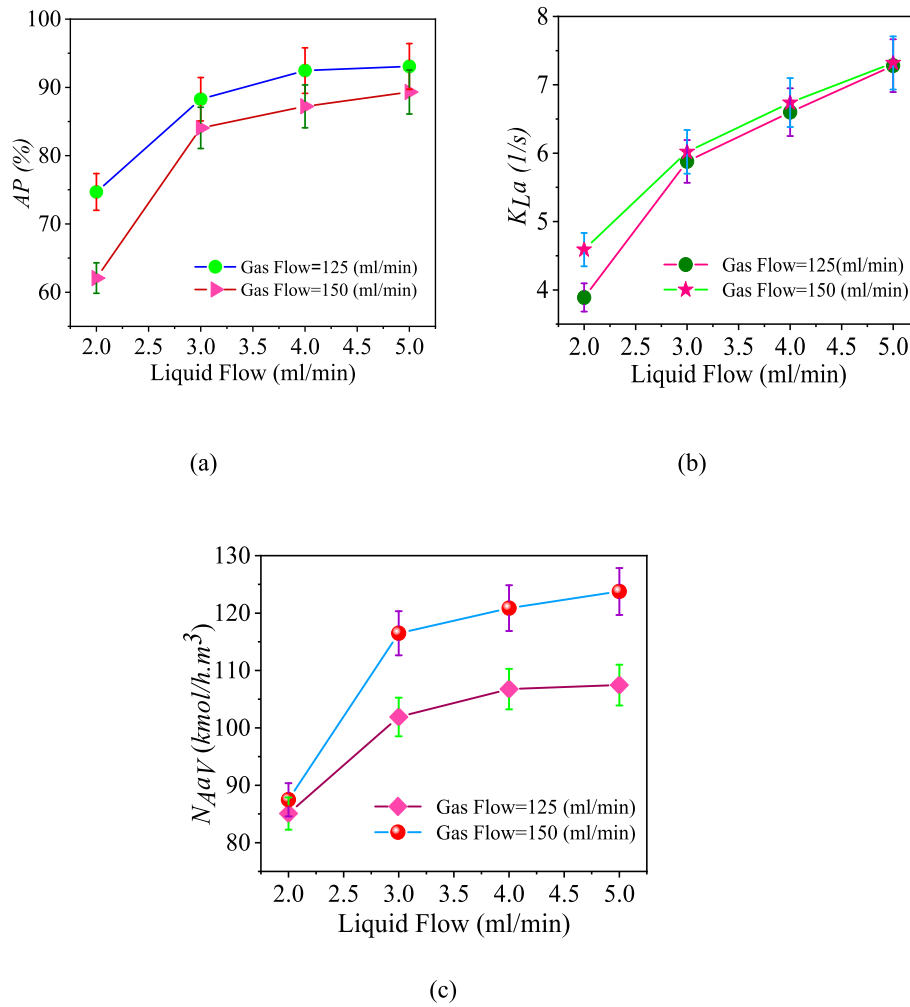
(a)

(b)

(c)

Fig. 3. Effect of liquid flow on (a) AP, (b) $K_L a$, and (c) $N_{co_2} a_V$ with amine concentration of 5 wt% and carbon dioxide concentration of 10 vol%.
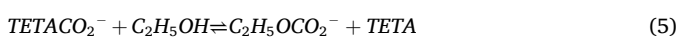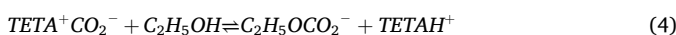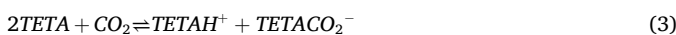
Dankurts. This mechanism can be divided into two stages [31,32].

1) zwitterion formation
2) conversion to carbamate

The reaction of the non-aqueous absorbents with carbon dioxide has a different mechanism compared to aqueous absorbents. In the case of the non-aqueous mixture of TETA-ethanol, this mechanism is more complicated due to the number of amine groups in TETA. TETA has four amino groups: two primary and two secondary [31]. The reaction kinetics of the primary amino group is 100 times higher than that of the secondary amino group. Therefore, the two primary amino groups of the TETA first react with carbon dioxide, and then the two secondary amino groups react with CO_2 [33]. Accordingly, primary and secondary amine groups perform reactions (1) and (2) to form polycarbamate [21].

$$TETA + CO_2 \rightleftharpoons TETA^+CO_2^- \tag{1}$$

$$TETA + TETA^+CO_2^- \rightleftharpoons TETAH^+ + TETACO_2^- \tag{2}$$

Then, the formed zwitterion can further react with ethanol to produce alkyl carbonate as follows [21]:

$$2TETA + CO_2 \rightleftharpoons TETAH^+ + TETACO_2^- \tag{3}$$

$$TETA^+CO_2^- + C_2H_5OH \rightleftharpoons C_2H_5OCO_2^- + TETAH^+ \tag{4}$$

$$TETACO_2^- + C_2H_5OH \rightleftharpoons C_2H_5OCO_2^- + TETA \tag{5}$$

The study conducted by Fan Liu et al. [21] shows that, unlike the aqueous solution, TETA carbamates exist in the non-aqueous solution after CO_2 absorption.

2.1. Calculation of uncertainty of experimental data

The values obtained in experimental measurements may not have sufficient accuracy. Therefore, repeating the experiment and calculating the uncertainty is one of the ways to achieve the accuracy of the results. As a result, according to the following relations, the uncertainty values can be evaluated:

$$\bar{x} = \frac{1}{N} \sum_{i=1}^{N} x_i \tag{6}$$

$$SD = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (x_i - \bar{x})^2} \tag{7}$$

$$RSD(\%) = \frac{SD}{\bar{x}} * 100 \tag{8}$$

In these relations, $\bar{x}$, SD and RSD represent the average of experimental data, the standard deviation of the population and the relative value of the standard deviation, respectively. These values are calculated for a quantity such as x_i from N sets of measured values. Table 1, shows the uncertainty values of the parameters measured in this research.
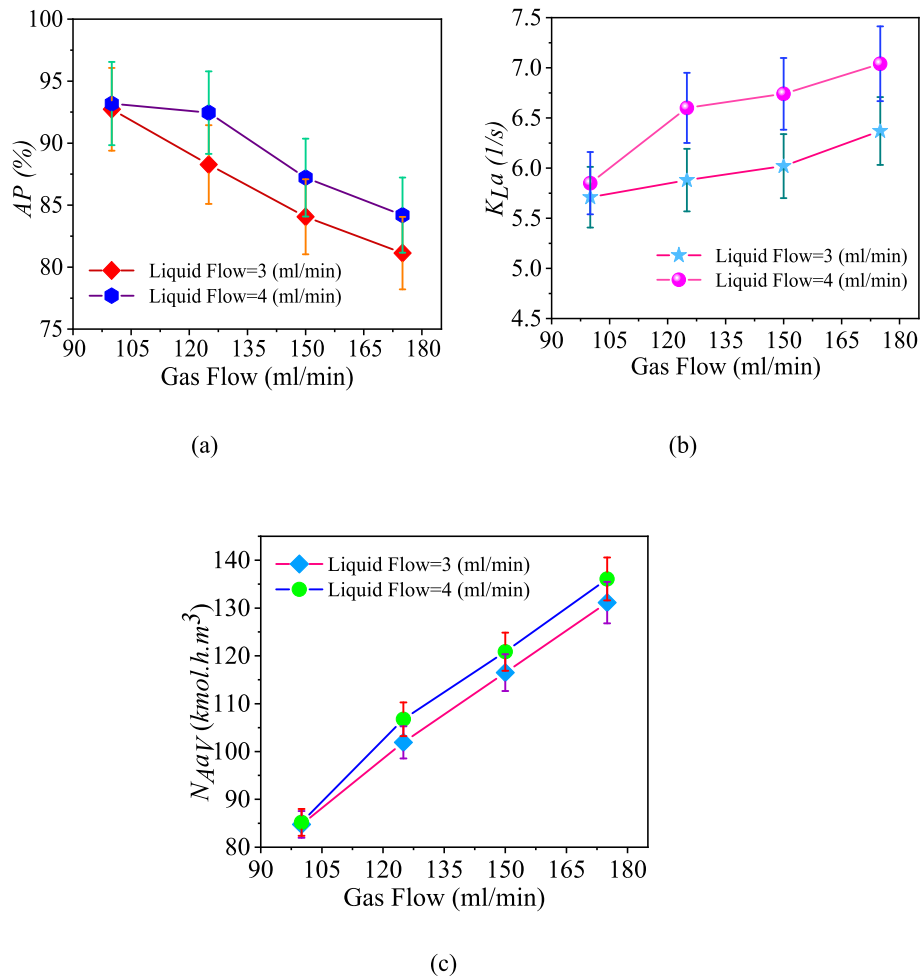
(a)

(b)

(c)

Fig. 4. Effect of gas flow on (a) *AP*, (b) K_La, and (c) $N_{co_2}a_V$ in different liquid flow rates, amine concentration of 5 wt% and carbon dioxide concentration of 10 vol%.

2.2. Responses

2.2.1. CO_2 absorption percentage

To calculate the percentage of absorption, the following relationship is used [30]:

$$AP(\%) = 1 - \left[\frac{y_{out}(1 - y_{in})}{y_{in}(1 - y_{out})} \right] \tag{9}$$

In this relation, *AP* (%), represent the percentage of CO_2 absorption and *y* indicates the mole fraction of the carbon dioxide.

2.2.2. Volumetric molar flux

The volumetric molar flux of CO_2 ($N_{co_2}a_V$) is also defined as another response by the following relationship [30]:

$$N_{co_2}a_V = \frac{G}{Z}(Y_{in} - Y_{out}) \tag{10}$$

In this relation, $N_{co_2}a_V$ was calculated in terms of kmol/h.m³, G represents the flow of the inert gas (kmol/h.m²), Z represents the microchannel length (m), and *Y* is the molar ratio of the CO_2.

2.2.3. Overall mass transfer coefficient

For gas-liquid interphase mass transfer, based on two-film theory, the following relation was applied to determine the volumetric mass transfer coefficient based on the liquid phase:

$$N_{co_2}a_V = K_La(C^* - C) \tag{11}$$

K_La is the volumetric overall mass transfer coefficient based on the liquid (1/s), $N_{co_2}a_V$ is the volumetric molar flux of the mass transfer (kmol/h.m³), C^* is the CO_2 concentration in the interface and *C* is the liquid concentration of CO_2 in bulk, which is close to zero [34]. Therefore, the relationship K_La can be simplified as below:

$$N_{co_2}a_V = K_LaC^* \tag{12}$$

The concentration of the C^* can be calculated from Henry's law [35]:

$$C^* = H_{Co_2-ethanol} \bullet P_{co_2} \tag{13}$$

In the above relation, P_{CO_2} is the average partial pressure of CO_2 (kPa), and $H_{Co_2-ethanol}$ is the Henry's constant of ethanol (1/kPa) [36]. Therefore:

$$N_{co_2}a_V = K_La \bullet H_{co_2} \bullet P_{co_2} \tag{14}$$

On the other hand, the average pressure is also needed to calculate K_La:

$$P_{co_2} = \frac{P_{co_2in} - P_{co_2out}}{\ln \frac{P_{co_2in}}{P_{co_2out}}} = \frac{P_T(y_{in} - y_{out})}{\ln \frac{y_{in}}{y_{out}}} \tag{15}$$

Finally, the overall mass transfer coefficient was calculated from the subsequent equation:

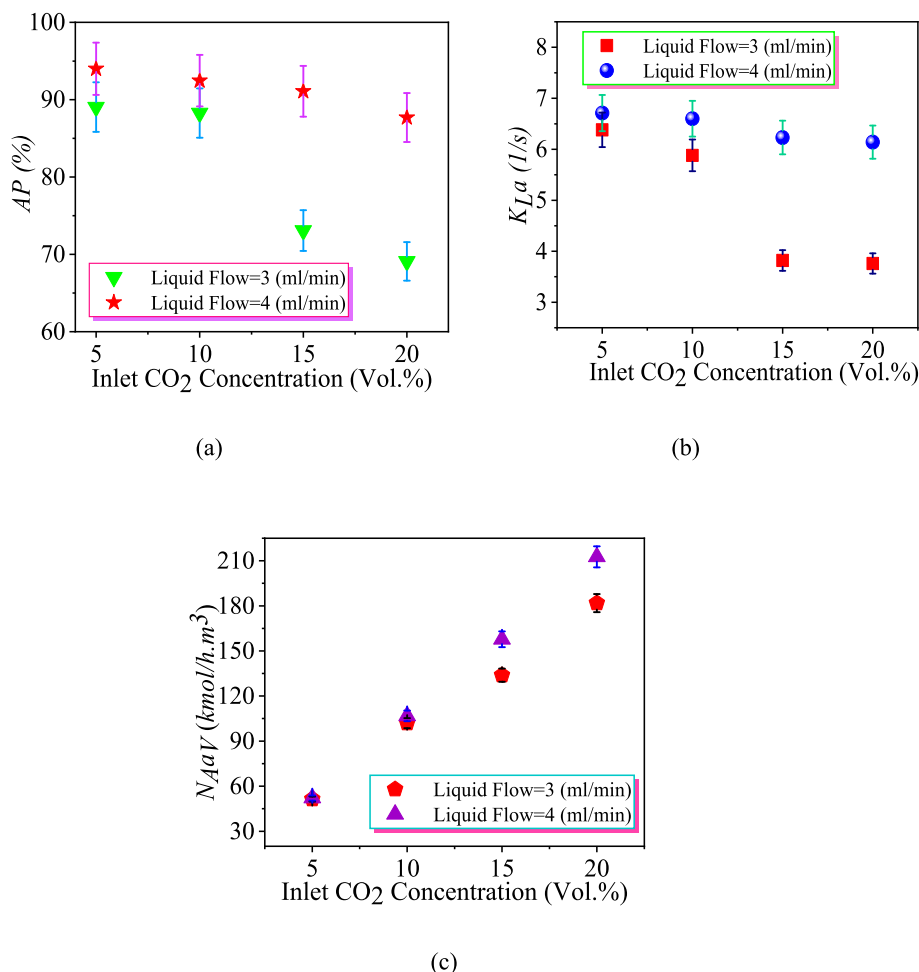$$K_La = \frac{N_{co_2}a_V}{H_{Co_2-ethanol}P_{CO_2}} \tag{16}$$

(a)

(b)

(c)

Fig. 5. Effect of carbon dioxide concentration on (a) AP, (b) $K_L a$, and (c) $N_{co_2} a_V$ at constant gas flow of 125 ml/min and the amine concentration of 5 wt%.

3. Experiments

3.1. Materials

In this research, TETA (96 wt%), ethanol (99.8 wt%) and MEA (99.5 wt%) were obtained from Behzist Tab Tehran Company and Shiraz Petrochemical Company, respectively. CO_2 was also purchased with a purity of 99.99 % from Caspian company.

3.2. Physical properties

Studying the physicochemical properties of an absorber plays an essential role in determining the optimal operating conditions and choosing the right equipment for CO_2 absorption. In this part, the properties such as viscosity, density, and surface tension for TETA-ethanol non-aqueous solution were determined. The viscosity of the non-aqueous TETA-ethanol solution has been measured by a Cannon-Fenske viscometer. The results of this measurement show that viscosity has a direct relationship with the concentration of TETA. A Gay-Lussac pycnometer was utilized for density measurement. According to the obtained outcomes, increasing TETA concentration leads to an increase in density. Finally, to extent the surface tension of this non-aqueous solution, a force tensiometer has been used. The results of these measurements also indicate that surface tension has a direct relationship with TETA concentration. The investigation of these physical properties has been done in different TETA concentration ranges and at a constant temperature of 25 $°C$. In these measurements, each reported number results from the average of three experiments. The

results are displayed in Table 2.

3.3. Working method and experimental device

Initially, the simulated gas inlet flow, which includes carbon dioxide and air, is regulated separately by two mass flow controllers (MFCs) before mixing. The incoming carbon dioxide flow is supplied from a carbon dioxide storage tank and air from a compressed air tank. After the carbon dioxide in the inlet gas reaches the desired percentage, the concentration of the carbon dioxide in the inlet gas is measured using a carbon dioxide sensor. To moisten the incoming gas, the gas flow is passed through a humidifier containing alcohol. On the other hand, the flow of the non-aqueous solution of the TETA and ethanol is continuously controlled and sent toward the microchannel by a peristaltic pump. The T-shaped microchannel is immersed inside the bain-marie with temperature control and a circulation pump to maintain the uniformity of the water bath. Finally, the gas and liquid are directed simultaneously towards the microchannel where CO_2 absorption process is occurred. The resulting liquid-gas mixture exits the microchannel and enters a separator then effluent gas is dehumidified by concentrated sulfuric acid. Lastly, the concentration of CO_2 in the outlet gas stream is analyzed by the sensor and recorded every second by a computer. All the experiments were carried out under atmospheric pressure and 25 $°C$. To ensure the accuracy of the obtained results, the experiments were repeated three times. In Fig. 1 and Table 3, a schematic and characteristics of the experimental setup were presented.
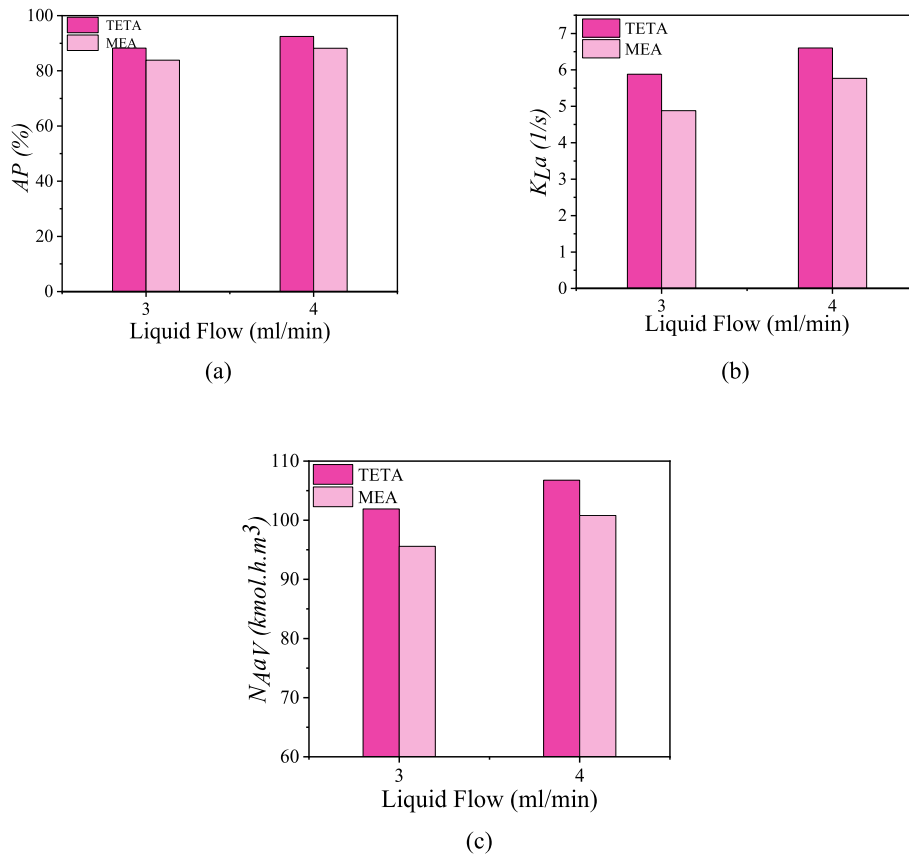
Fig. 6. Comparison of TETA and MEA concentration on (a) AP, (b) K_La and (c) $N_{co_2}a_V$ at gas flow of 125 ml/min and liquid flow range of the 3–4 ml/min.

Table 5
Comparison of overall volumetric mass transfer coefficient based on liquid phase in different contactors and solvents used in CO_2 absorption process.

Contactor type	K_La (1/s)	Solvent	Reference
Microchannel	2.50–8.66	TETA-Ethanol	This study
Microchannel	0.5–6	MDEA-DEA-Water	[52]
Microchannel	0.02–0.26	CO_2-water	[53]
Bubble column	0.003–0.018	CO_2-water	[54]
Stirred reactor	0.0056–0.0333	CO_2-water	[55]
Spray tower	0.015–0.022	Na_2SO_3	[56]

4. Results and discussion

In this study, effect of the solvent flow, TETA concentration, carbon dioxide concentration and gas flow on three responses have been investigated. These three primary responses include removal efficiency, mass transfer coefficient, and molar flux. Table 4 lists these variables and their operating range.

4.1. TETA concentration

Fig. 2 shows effect of the TETA concentration in the range of the 4–8 wt% on AP, K_La, and $N_{co_2}a_V$. This investigation has been done in a liquid flow of 4 ml/min. Furthermore, other parameters have been kept constant, including: the carbon dioxide concentration and the gas flow at 10 vol% and 125 ml/min, respectively. Usually, it is expected that when the concentration of the amine increases, the number of active sites for more absorption of CO_2 in the solution will increase. However, in this study, the obtained results indicate that the increase in amine concentration causes a decrease in the efficiency of CO_2 absorption, mass transfer coefficient and mass transfer flux. In fact, it can be said that increasing
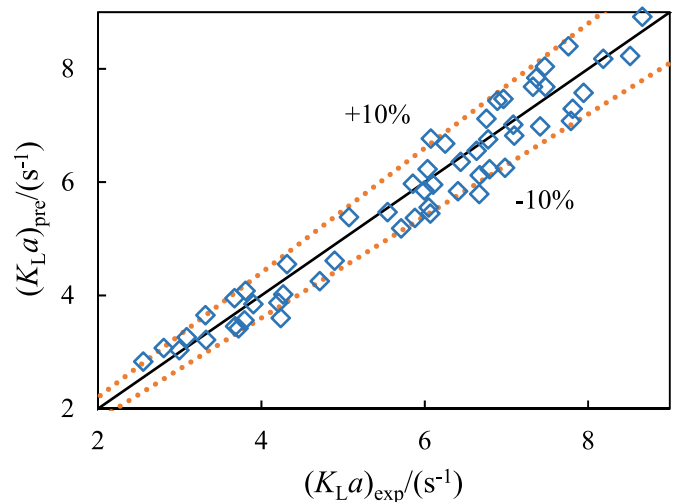

Fig. 7. Parity chart compares predicted and experimental values of K_La for CO_2 absorption by TETA-ethanol biphasic solvent.

the concentration of the amine has a negative effect on these three studied responses. Based on Table 2, increasing the concentration of the TETA in the solution, increases the solution viscosity. As a result, it decreases the penetration of CO_2 in the solution and the rate of CO_2 absorption [26]. Therefore, an increase in TETA concentration due to an increase in viscosity, has a negative effect on the CO_2 absorption process [37]. On the other hand, the increase in viscosity increases the mass transfer resistance in the liquid phase. Consequently, the rate of mass transfer and CO_2 absorption decreases. Also, based on equation (16),

there is a direct relationship between the overall mass transfer coefficient of the liquid phase and volumetric molar flux. Therefore, as the amine concentration increases and the mass transfer coefficient decreases, the molar flux also decreases. It can be stated that the physical properties of the TETA are dominant in CO_2 absorption and mass transfer performance. Therefore, the outlet CO_2 concentration increases and the absorption of the CO_2 decreases. Also, the increase in viscosity of the solution due to the increase in amine concentration compensates for the advantage of the increase in free amine molecules. It leads to a decrease in $K_L a$ [38]. As mentioned, with a further increase in amine concentration, there is a decrease in performance. Similar observations have been reported in other works. Kadiwala et al. [39] stated that with increasing concentration of amine, the reaction of the amine with CO_2 decreases. In addition, Liang et al. [40] also reported this phenomenon for amines with multiple amino positions. They stated that if the concentration was high, the viscosity of the solution increases, and the agility of the solute decreases. As a result, CO_2 absorption efficiency decreases [32]. Another remarkable phenomenon that was observed during the experiments was that in concentrations less than 5 wt% of TETA, the absorption efficiency of CO_2, $K_L a$, and $N_A a_V$ increases. But at the same time, it is impossible to continue the reaction and carry out the absorption process at lower TETA concentration due to the formation of the excessive sediment and the blockage in the microchannel as presented in Fig. 2(c). On the other hand, in concentrations of more than 5 wt% of TETA, due to the increase in viscosity the absorption efficiency of CO_2, $K_L a$, and $N_A a_V$ decreases. Accordingly, based on this information and the available evidence during the experiments, the concentration of the 5 wt% of TETA was chosen as the standard concentration for further analysis.

4.2. Liquid and gas flow

In Fig. 3 effect of the liquid flow in the range of the 2–5 (ml/min) on AP, $K_L a$ and $N_{co_2} a_V$ has been displayed. This investigation has been done in different gas flow ranges of 125–150 (ml/min). The other parameters, such as: concentration of the TETA and concentration of the carbon dioxide, were constant at 5 wt% and 10 vol%, respectively. Investigating the liquid flow, plays a vital role in estimating and determining the cost and volume of the absorbent. As presented in the figure, with an increase of the liquid flow from 2 to 5 (ml/min), AP, $K_L a$, and $N_{co_2} a_V$ increases. According to this diagram, at a constant gas flow rate of 125 (ml/min), with an increase of the liquid flow from 2 to 5 (ml/min), the absorption efficiency increases from 74.69 % to 93.07 %. Also, the values of $K_L a$ and molar flux increase by 87.14 % and 26.3 %, respectively. The reasons for these phenomena can be stated as follows: By increasing the solvent flow rate, the replacement rate of active sites for carbon dioxide absorption increases. As a result, the rate of absorption increases. Also, increasing the solvent flow rate increases the efficiency of the CO_2 absorption due to the increase in the driving force of the mass transfer. On the other hand, the obtained results indicate that the liquid flow rate has a significant effect on the mass transfer performance and molar flux. An increase in the liquid flow rate also leads to an increase in the values of the $K_L a$ and $N_A a_V$ in the relevant operating conditions. According to the study conducted by Ganapati et al. [41] with the increase in the liquid flow in the microchannel, $K_L a$ increases. Also, in the study conducted by Tan et al. [42] it has been observed that $K_L a$ increases with the increase in gas and liquid flow velocity in the microchannel. Increasing the liquid flow rate increases turbulence in the liquid film, which reduces the thickness of the liquid film and decreases the mass transfer resistance in the liquid phase. Furthermore, with the increase in the liquid flow, the volume of the gas phase decreases. Consequently, the mass transfer coefficient of the liquid phase as well as molar flux increases [32,38,43,44].

Fig. 4 shows effect of the gas flow in the range of the 100–175 (ml/min) on the responses. According to the results, with increasing the gas flow, the percentage of Carbon dioxide uptake decreases. Consequently,

the velocity of the gas molecules elevates, resulting in a reduction in their residence time within the microchannel. Thus, there is insufficient time for contact between the liquid and gas phases. As a result, there is no practical collision between amine molecules and Carbon dioxide. On the other hand, increasing the gas flow increases the amount of the incoming CO_2 per time. This increase in the entry of the Carbon dioxide gas also increases the concentration of the Carbon dioxide through the microchannel. All these factors, leads to a decrease in CO_2 absorption efficiency [44]. Besides, increasing the gas flow causing gas phase turbulence and as a result increases the velocity of the gas and the formation of more bubbles along the length of the microreactor. This increase in turbulence improves mass transfer. Hence, the mass transfer coefficient increases and, consequently, the mass transfer flux. According to the research done by Chunying Zhu et al. [35], the mass transfer coefficient increases with the increase of the gas flow. Similarly, the presence of the non-aqueous environment in the experiment increases the absorption of Carbon dioxide and causes more mass transfer between phases [32,45].

4.3. CO₂ concentration

CO_2 concentration in the flue gas strongly depend on carbon content of the fossil fuel. Fig. 5 displays effect of carbon dioxide concentration on removal efficiency, mass transfer coefficient and molar flux. This investigation has been done in two different ranges of the liquid flow (3,4 ml/min). The other parameters, such as: concentration of the TETA and gas flow, have been kept constant at the values of the 5 wt% and 125 ml/min, respectively. As can be seen, changes in carbon dioxide concentration from 5 to 20 percent by volume have adverse effects on the mass transfer coefficient and carbon dioxide absorption efficiency. However, increasing the inlet CO_2 concentration increases volumetric molar flux. According to in equation (11), mass transfer flux is directly linked to the CO_2 concentration. Usually, with the increase of CO_2 concentration, more carbon dioxide molecules move from the bulk gas towards the liquid-gas interface moreover, the partial pressure and the loading of carbon dioxide in the solution. As a result, more active free amine molecules are consumed in the solution. In addition, the higher the carbon dioxide loading in the solution, the lower the carbon dioxide absorption capacity. Also, the increase in the driving force of the mass transfer due to the rise in carbon dioxide partial pressure leads to a decrease in the overall mass transfer coefficient. Consequently, increasing the inlet carbon dioxide concentration leads to a reduction in carbon dioxide absorption efficiency and a reduction in $K_L a$ [38,44,46].

4.4. Comparison of the biphasic TETA/ethanol solvent with other solvent systems

In this section, the performance of biphasic TETA-Ethanol solution for CO_2 capture was compared with benchmark aqueous MEA solution and other solvent systems. Fig. 6 shows the performance of TETA and MEA with the same concentration of 5 wt% amine on AP, $K_L a$, and $N_{co_2} a_V$. This investigation has been done in two different ranges of the liquid flow (3–4 ml/min). Other parameters, such as: carbon dioxide concentration and gas flow rate, have been kept constant at 10 vol% and 125 ml/min, respectively. The results of this comparison indicate that at the same concentration of both amines, the non-aqueous biphasic solvent of TETA-ethanol has better performance on these three responses. This can be justified with the following reasons; TETA is an alkylamine with several amino groups in its structure. This polyamine has four functional groups, including two primary amine groups and two secondary amine groups. This means that TETA has four active reaction sites for Carbon dioxide capture. Meanwhile, MEA is a primary amine with a functional amino group. Therefore, it has only one site to react with CO_2. In other words, more reaction takes place between CO_2 and polyamine and more absorption takes place. Therefore, polyamines show a greater capacity and absorption rate compared to alkanolamines

[33,47]. Furthermore, the Solubility of the Carbon dioxide in ethanol is significantly higher than in water. The presence of the non-aqueous environment can increase the mass transfer of the gas molecules and thus increases the absorption of Carbon dioxide. Also, the diffusion coefficient of CO_2 in alcoholic solvents is higher than that of the water, which facilitates the capture of the Carbon dioxide. A high diffusion coefficient can increase mass transfer, which increases the rate of Carbon dioxide absorption. In addition, the heat capacity, boiling temperature, and lower viscosity of the alcoholic solvents compared to water improve CO_2 absorption performance [23,32,48,49]. The obtained results are compatible with researcher conducted by Singh et al. [50] that investigated the absorption of Carbon dioxide in different alkylamines. The findings indicate that alkylamines, particularly those featuring numerous amino groups, possess favorable qualities for replacing alkanolamines such as MEA. Mochan et al. [51]. studied the effect of the number of the amine groups in the structure of the polyamines such as (TETA, DETA, TEPA and EDA) on the amount of Carbon dioxide absorption. Their results indicate that the amount and capacity of Carbon dioxide absorption increases with the increase in the number of the amine groups.

In Table 5, the overall volumetric mass transfer coefficient based on liquid phase in different contactors and solvents that was used in CO_2 absorption process has been compared. As can be seen in the table, the mass transfer coefficient in microchannel significantly is higher than other contactors. Furthermore, the order of magnitude of K_La that was obtained in this study was the same for amines in microchannel.

4.5. Estimation of mass transfer coefficient

The overall volumetric mass transfer coefficient can be influenced by various parameters including physical properties of the fluid, gas and liquid phase flow, etc. Based on multiple investigations, different correlations have been suggested for absorption processes to estimate mass transfer coefficients in microchannels. Yang et al. proposed the following empirical relationship to forecast dimensionless Sherwood number and mass transfer coefficient for CO_2 absorption in a T-junction microfluidic device [57]:

$$Sh = 9 \cdot 6 \, Re_G{}^{0 \cdot 33} Re_L{}^{0 \cdot 5} Sc^{0 \cdot 33} \tag{17}$$

In this relationships, *Sh* indicates the ratio of convective mass transfer to mass transfer by molecular diffusion diffusion, *Sc* indicates the proportion of the kinematic viscosity to the diffusion coefficient, and Re reflecting stream condition. Moreover, some researchers have been considered dimensionless Capillary numbers to evaluate the effect of viscous drag forces versus surface tension forces between liquid and gas in the proposed correlations [58]:

$$Sh_L a \, d_h = 0 \cdot 094 Re_G{}^{0 \cdot 0656} Re_L{}^{0 \cdot 654} Sc_L{}^{1 \cdot 449} Ca^{0 \cdot 839} \tag{18}$$

Where, *Ca* is the ratio of fluid viscosity to surface tension. Lin et al. [52] investigated the Carbon dioxide capture process in a T-shaped microreactor by MDEA and DEA aqueous solution. The impact of chemical reactions on the mass transfer phenomenon was included in the proposed correlation by application of the Hatta number:

$$Sh_L a \, d_H = 0 \bullet 6481 Re_G{}^{0 \bullet 7171} Re_L{}^{0 \bullet 1703} Sc_L{}^{0 \bullet 5} Ha^{0 \bullet 8366} \tag{19}$$

In the present investigation, the dimensionless parameter Da, commonly known as the Damköhler number, is utilized as a productive tool for characterizing the effect of chemical reactions on the mass transfer phenomenon [34]. Damköhler number (Da) represents the quotient of the chemical reaction rate and the rate of mass transfer. The novel correlation was obtained by fitting experimental data:

$$Sh_L a \, d_H = 10 \bullet 194 Re_G{}^{0 \bullet 093} Re_L{}^{0 \bullet 231} Sc_L{}^{1 \bullet 472} Ca^{0 \bullet 231} Da^{-0 \bullet 583} \tag{20}$$

The predicted value and experimental data was compared in Fig. 7.

As presented in the figure, the estimated values of K_La for CO_2 absorption by TETA/Ethanol biphasic solvent calculated from Eq. (20) agrees well with the experimental data, where the mean deviation is 4.32 %, representing a respectable precision of the proposed correlation [59].

5. Conclusion

This research examines, the performance of CO_2 absorption using a non-aqueous biphasic TETA-ethanol solvent in T-shaped microchannel under different operating conditions. The operating variables that investigated in this study are: concentration of TETA, liquid flow, carbon dioxide concentration and gas flow at a constant temperature of 25 °C. The overall mass transfer coefficient, the volumetric molar flux, and the CO_2 absorption percentage were assessed as three primary responses. According to the obtained results, with the increase of liquid flow rate AP%, K_La and $N_{co_2}a_V$ increase by 43.88 %, 87.14 % and 41.48 %, respectively. Increasing the gas flow decreases the absorption efficiency and increases the mass transfer coefficient and mass transfer flux by 20.34 % and 59.75 %, respectively. Interestingly, amine concentration had adverse effect on all three responses. Furthermore, increasing the inlet carbon dioxide concentration rises molar flux by 307.94 % and decreases the other two responses. In comparison with aqueous MEA solvent by the same amine concentration (5 wt%), the results indicate that the efficiency of CO_2 absorption, mass transfer coefficient and molar flux, for TETA-ethanol biphasic solvent are 4.85 %, 14.38 %, and 5.91 % higher than aqueous MEA, respectively. Finally, a new correlation was also suggested to predict K_La of CO_2 absorption into TETA-Ethanol non-aqueous solution. The dimensionless Damköhler number was utilized in the new correlation. A respectable precision with a mean deviation of 4.32 % was calculated for the proposed correlation.

CRediT authorship contribution statement

Farnoush Shaterabadi: Writing – original draft, Visualization, Validation, Methodology, Investigation. **Hamed Rashidi:** Writing – review & editing, Resources, Project administration, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Data availability

No data was used for the research described in the article.

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