Absorption of carbon dioxide into aqueous blends of glycerol and monoethanolamine in a microchannel reactor

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Abstract
This paper provides the experimental results of mass transfer performance of the aqueous mixture of MEA+Glycerol, as an industrially eco-friendly hybrid solvent, instead of a typical commercial alkanolamine solvent for CO_2 capture in a microchannel. The CO_2 absorption was performed at constant temperature of 40 °C and atmospheric pressure. The importance of the operational variables, including the input solvent flow rate (4-11 ml/min), MEA (10-30 %wt), and glycerol concentration (6-12 %wt) in the solvent were assessed on the mass transfer performance in terms of CO_2 removal efficiency (e_f) and volumetric overall gas-phase mass transfer coefficient ($K_G a_V$). The values of $K_G a_V$ are ranging from 70.68 to 96.95 kmol/m^3.h.kPa. It is confirmed that comparing aqueous solution of 20 %wt MEA, adding dilute concentrations of glycerol to 20 %wt MEA, can give rise to the enhancement of $K_G a_V$ and e_f in the hybrid mixture of MEA-Gly.

Keywords: Absorption, CO_2, efficiency, Glycerol, Monoethanolamine, Microchannel

Introduction
Global warming is a serious concern which is mainly caused by emission of greenhouse gases produced by combustion of fossil fuels. The recent focus has been on finding technologies to decrease and capture these gases [1]. Chemical adsorption is a well-known process to capture CO_2 in industry, involving an aqueous amine solution such as monoethanolamine (MEA) [2]. There are advantages such as stability in process performance, high capacity, and high reactivity. The main drawback is the high energy consumption of the process-around 30% of the total energy of the power plant. Other obstacles include poor thermal stability, solvent losses due to the evaporation, and equipment corrosion [3]. To overcome the drawbacks of an amine solvent, researchers have devised mixtures of amines and other carbon capture solvents with acceptable energy efficiency and being budget-friendly.
Recently, a novel carbon capture solvent, glycerol, has been introduced. It is available in large quantities as a by-product from bio-diesel production. Glycerol is nontoxic, green, highly soluble for CO_2, a stable solvent with low vapour pressure [4]. This new discovery is influential and beneficial because glycerol is abundant and relatively inexpensive.On the other hand, the CO_2 absorption process strongly depends on the size of the surface area in the two phases[5]. The

microchannel, as a microscale phase contactor devices, is a new technology, with significant potential for increasing the surface area between phases, which can provide optimal mixing performance and low transfer resistance in the process of CO_2 capture [6].
A review of existing studies shows that no study has been conducted on the unit operation of hybrid MEA-Glycerol aqueous solution in a microchannel. This study incorporates the benefits of amine-based solvent MEA and glycerol mixtures in a CO_2 removal efficiency in a microchannel. The effect of operational variables, including solvent flow rate, MEA, and glycerol concentration in the solvent were investigated on the CO_2 removal efficiency (e_f) and volumetric overall gas-phase mass transfer coefficient ($K_G a_V$).

Experimental

Commercially available industrial MEA with the purity of 99.3 % was supplied from Kermanshah petrochemical Companies (KPIC), Kermanshah, Iran. Carbon dioxide purity (> 99.9%) was purchased from Alborz Persian Gas, Karaj, Iran. Glycerol (> 98%) was supplied by Kian Kaveh Azma, Iran. Fig. 1 illustrates a detailed schematic of the laboratory-scale set-up, used for experimental measurements of CO_2 absorption.

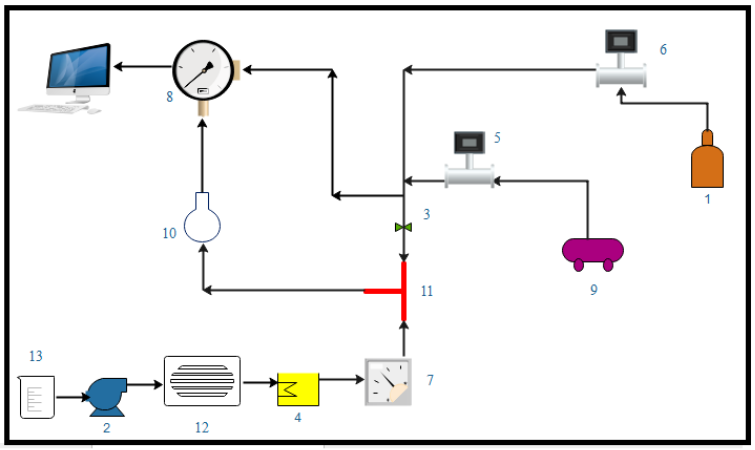


Fig. 1. Schematic diagram of the laboratory setup: 1) CO_2 cylinder 2) pump 3) Valve 4) Heater (5) Air Mass flow meter 6) CO_2 Mass flow meter 7) Thermometer 8) CO_2 sensor 9) Compressor 10) Ellen Flash 11) microchannel 12) Coil 13) Solvent.

The absorption experiments were performed in a T-shaped microchannel, made of transparent plastic, with a diameter of 1.13 mm. The hybrid absorbent with the desired concentration, and the feed gas, composed of a saturated 15% CO_2 gas stream,were fed into the microchannel. Considering the previous studies, it was determined that the absorption temperature is not a significant parameter for affecting CO_2 absorption by MEA aqueous solution. As such, regarding industrial requirements, the absorption temperature were kept constant at 40 °C. For all the CO_2 absorption experiments, the inlet gas flow rate was kept constant at 300 ml/min. Table 1 presents the variables and related operating ranges. The Box-Behnken design (BBD) was created to minimize the required numbers of experiments to achieve the absorption response in the microchannel.

Table 1. Levels of the operational variables

Factors	Unit	Level of factors		
MEA concentration	%wt	10	20	30
Glycerol concentration	%wt	6	9	12
solvent flow rate	ml/min	4	7.5	11

The values of CO_2 concentration in the gas-phase before and after passing through the packed column have been measured to calculate the CO_2 removal efficiency (e_f), using the following relation:

$$e_f = 1 - \frac{C_{out}}{C_{in}} \quad (1)$$

To determine the overall gas-phase mass transfer coefficient, $K_G a_v$ (kmol/m^3.h.kPa) in the absorption packed column, the following relatively simplified correlation, suggested by Zeng et al., was directly applied [7]:

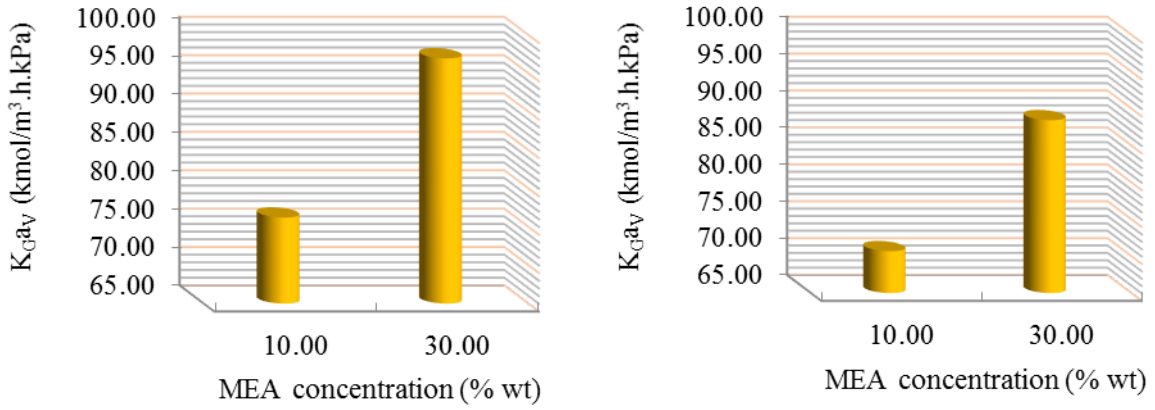
$$K_G a_V = \frac{G}{ZP}\left[\ln\left(\frac{Y_{in}}{Y_{out}}\right) + (Y_{in} - Y_{out})\right] \quad (2)$$

Where Y_{in} and Y_{out} denote the mole ratio of CO_2 in feed and leaving gas. Besides, G, Z, and P represent the molar flow rate of the inert gas (kmol/h.m^2), the height of absorption bed (m), and the system pressure (kPa), respectively.

Results and discussion

Input MEA concentration

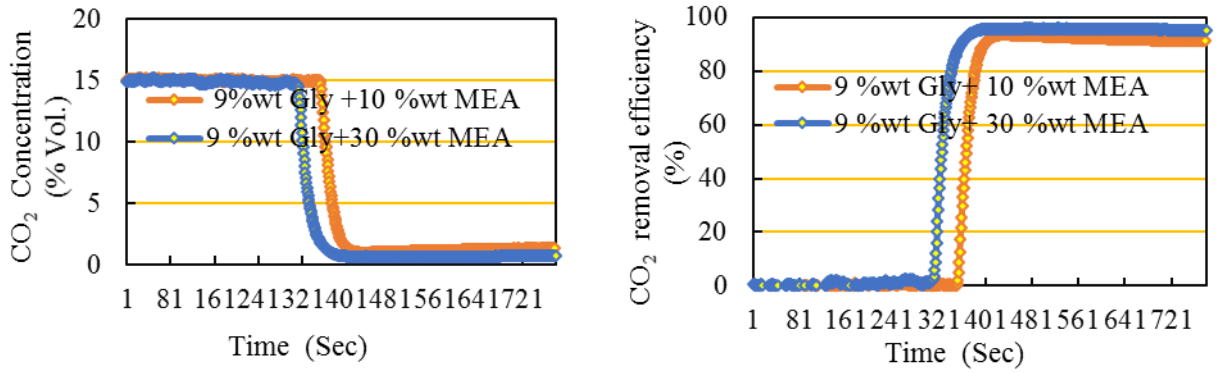
Fig. 2 displays the effect of initial amine concentration, ranging from 10 to 30 wt %, on the experimental values of the $K_G a_V$. As seen, for all mixture of MEA+Gly, the $K_G a_V$ has experienced an increase with increasing amine concentration in the aqueous solution of MEA. This is because the driving force during the mass transfer is supplied by the available reactive alkanolamine concentration. As such, the number of active sites for chemical absorption of CO_2 significantly increases with the amount of MEA in the solvent. However, the mixture of 12 %wt Gly offers lower values of the $K_G a_V$ than 6 %wt Gly



(a) **(b)**

Fig. 2. The effect of MEA concentration on the gas phase volumetric mass transfer coefficient at Ql=7.5 ml/min for: (a) 6 %wt glycerol , (b) 12 %wt glycerol

Fig. 3a illustrates the initial variation trend of CO_2 concentration during the total time of the CO_2 absorption experiments. It is observed that at the beginning of each experiment, the CO_2 concentration in the gaseous phase is 15%. After a short time of 32 Sec, saturating the solvent makes the gas absorption process to be stopped. Based on the Fig. 3b, a significant increase of the CO_2 removal efficiency was observed from 92 % to 95 % with increasing the MEA concentration for constant concentration of 9 %wt Gly.



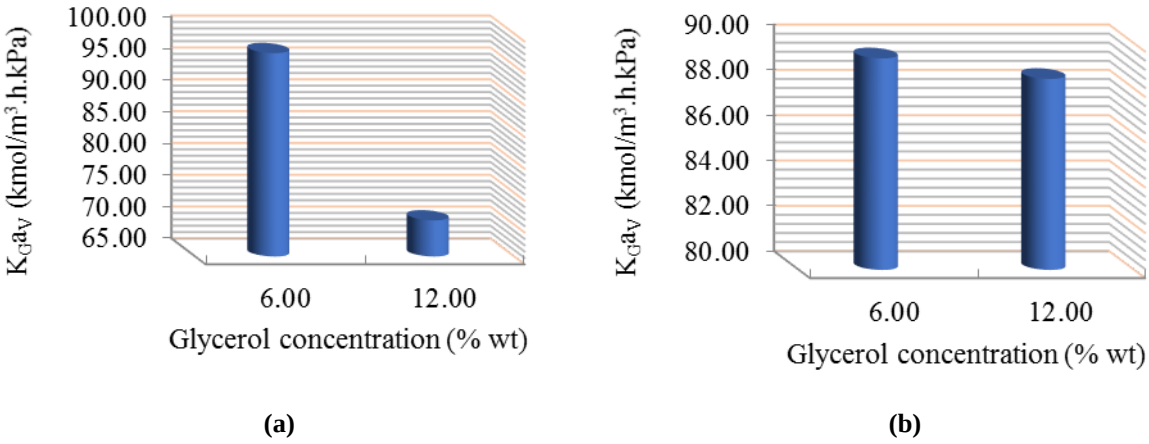
(a) **(b)**

Fig. 3. The effect of MEA concentration on the (a) CO_2 concentration and (b) CO_2 removal efficiency at 9 %wt glycerol and Ql= 4 ml/min

Input Glycerol concentration

Fig. 4a,b demonstrates the impact of glycerol concentration on the gas phase volumetric mass transfer coefficient at constant solvent flow rate of 7.5 ml/min. As seen, for all MEA concentrations, the values of K_Ga_V are ranging from 70.68 to 96.95 kmol/m^3.h.kPa. Besides, rising the glycerol concentration from 6% up to a level of 12% decreases the values of K_Ga_V. However, at high MEA concentrations, 30 %wt, the decrease is not significant, as the value of the K_Ga_V only decreased by 1%. This can be explained by the fact that the increase in the glycerol concentration results in a rise in the viscosity, leading to inhibit the CO_2 diffusion into

MEA+glycerol mixture. As such, the resistance of absorption will be increased, which is making it harder to increase the e_f, and $K_G a_V$ in the absorption process [8].

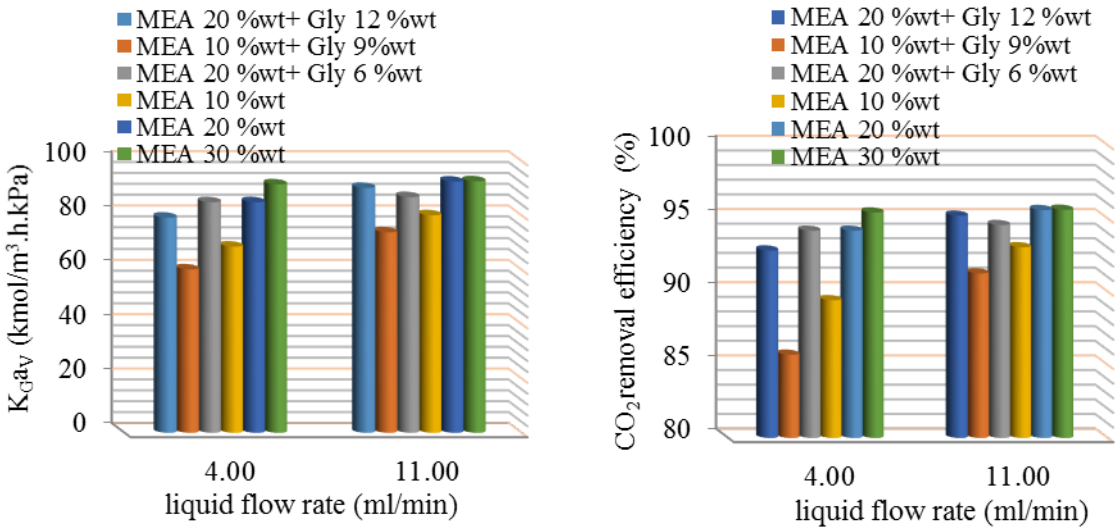


(a) **(b)**

Fig. 4. The effect of the glycerol concentration on the gas phase volumetric mass transfer coefficient at Ql=7.5 ml/min: (a) 10 % wt MEA , (b) 30 %wt MEA.

Input solvent flows

Fig. 5 a, b reveal the impact of the solvent flow rate on the experimental values of the e_f and $K_G a_V$. It is seen that for MEA+glycerol system, increasing the solvent flow from 4 to 11 ml/min, has a direct influence on and $K_G a_V$.



(a) **(b)**

Fig. 5. Effect of the solvent flow rate on the experimental values of the a) e_f , and b) $K_G a_V$.

This can be explained according to the two-film theory [9]; increasing the solvent flow rate will not only provide more actively available sites for CO_2 absorption but will also be beneficial to the effective interfacial area of gas-liquid (a_V) in the microchnnel. Besides, comparing the

values of $K_G a_V$ and e_f for the blend of 20 %wt MEA+ 6 %wt and the pure 20 %wt MEA indicate that the presence of dilute glycerol in hybrid mixture of MEA-Gly gives rise to the enhancement of $K_G a_V$ and e_f.

Conclusions

The new contribution of MEA-glycerol blended mixture, as an industrially green CO_2 capture solvent was introduced for the CO_2 absorption process. A set of experiments were designed in terms of inlet gas flow rate, glycerol concentration, and MEA concentration in a microchannel o inspect the desirable potential of the alternative hybrid solvent for CO_2 capture. It was found that raising the gas flow rate gives rise to the value of the gas phase mass transfer coefficient, $K_G a_V$. Besides, the amine concentration in the hybrid solvent of MEA+ Gly has a crucial role in the e_f and $K_G a_V$. Moreover, rising the glycerol concentration from 6% up to a level of 12 %, does not intensify the values of *ef* and $K_G a_V$. However, at high concentrations of 30 %wt MEA, the decrease is not significant, as the value of the $K_G a_V$ only decreased by 1%. Finally, the presence of the dilute concentration of glycerol in hybrid mixture of MEA-Gly can be employed as a promoter with MEA to improve CO_2 uptake and avoid the equipment corrosion.

References

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