

APPLICATION OF A HYDROPHOBIC POLYMERIC MEMBRANE FOR CARBON DIOXIDE DESORPTION FROM AN MEA-WATER SOLUTION

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Carbon dioxide desorption from a monoethanolamine (MEA) solution using a hydrophobic polydimethylsiloxane (PDMS) tubular membrane on a ceramic support is presented. The effects of operating parameters such as feed temperature, liquid flow rate and MEA concentration on mass transfer were examined. The mass transfer of CO₂ from the liquid to gaseous phase was predicted by a multilayer film model with an accuracy of ±25%. Research into new selective materials is needed to develop more efficient and environmentally friendly CO₂ capture technology

Keywords: MEA, desorption, carbon dioxide, hydrophobic membrane, PDMS

1. Introduction

Fossil fuel combustion from power plants is one of the most significant sources of CO₂ emissions [1]. The separation of carbon dioxide from gases can be realized by processes such as adsorption, absorption, low temperature distillation and membrane separation. The absorption of carbon dioxide in amine based solutions is currently the most widespread method in industry for the post-combustion capture of CO₂ [2].

The advantage of chemical absorption in amine solutions is the fact that at higher temperatures the chemical reaction can be reversed and the amine recycled. On the other hand, obstacles include a relatively low CO₂ capture capacity, solvent losses caused by evaporation, thermal stability, highly corrosive characteristics, ecotoxicity and biodegradability in the natural environment [2-4]. It was shown that MEA and diethanolamine (DEA) might promote potential long-term toxicity effects towards living organisms [5,6]. In addition the regeneration step may increase the total operating costs of the capture plant by up to 70%, especially for primary and tertiary amines where the heat of reaction is quite high [7].

The amine scrubbing processes carried out in packed columns are currently most widely used in industry for the post-combustion capture of CO₂. Limiting factors for the application of this technology are its size and large capital costs. The mass transfer performance of this solution can be reduced by flooding, foaming and entrainment conditions.

In comparison to the studies on CO₂ absorption in MEA solutions there are only a few concerning CO₂ desorption, despite the fact that the stripping unit is responsible for most of the separation cost of the process [8].

It is important that materials used in the processes concerning post-combustion capture of CO₂ exhibit low or no environmental effects. Various tubular membranes were operated as catalyst supports [9]. Recently a new type of ceramic hollow fiber membrane contactor has been studied [10]. This kind of membrane can be modified to be hydrophobic which enables it to be applied for CO₂ absorption-desorption in amine solutions. In this study the process of CO₂ removal from an MEA solution using a hydrophobic polydimethylsiloxane (PDMS) tubular membrane on a ceramic support was investigated.

2. Experimental

2.1. Experimental setup

The experimental setup shown in *Fig.1* consisted of a membrane module, reactor vessel, cooling system, as well as circulation and vacuum pumps. The hydrophobic PDMS membranes on ceramic support (ceramic tubes with an outer diameter of 0.01 m and length of 0.25 m using a PVM 250 membrane module made by Pervatech BV) was studied.

The feed was circulated by a pump and the flow rate was controlled by a flowmeter. In all experiments the feed temperature was stabilized by a thermostat (±1°C). The permeate was condensed and collected in cold traps immersed in liquid nitrogen. The vacuum pump was used to maintain the pressure between 7 and 10 mmHg on the permeate side. The concentration of

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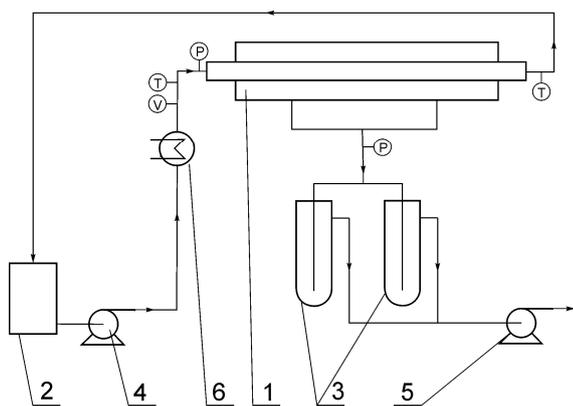


Figure 1. The experimental setup: 1 – membrane contactor, 2 – feed tank, 3 – cold traps, 4 – circulation pump, 5 – vacuum pump, 6 – heater

carbon dioxide in the permeate was calculated by measuring the mass of carbon dioxide and water in the analyzed permeate sample. The pressures on the feed and permeate sides were measured by pressure gauges. The temperatures of the feed in the reactor vessel, before and after the membrane module were measured by thermocouples.

Pure monoethanolamine (MEA) and deionised water were used to prepare the liquid-feed solution. Afterwards the obtained solution was loaded with CO₂ by bubbling pure CO₂ in a magnetically stirred vessel until the required carbonation ratio, α , was achieved. In our experiments the carbonation ratio was determined by measuring the mass of absorbed CO₂ in the amine solution at a given temperature.

Additionally, independent pervaporation experiments with the same PDMS membrane under similar thermal and hydrodynamic conditions for a 2-propanol – water mixture were performed to estimate the membrane resistance ($1/k_M$).

2.2. Experimental results

The performance of the PDMS membrane was examined experimentally. The operating temperature was between 323 and 348K (50 and 75°C), liquid flow rate between 20 and 600 l/h and the MEA concentrations were 5, 10 and 15 wt%.

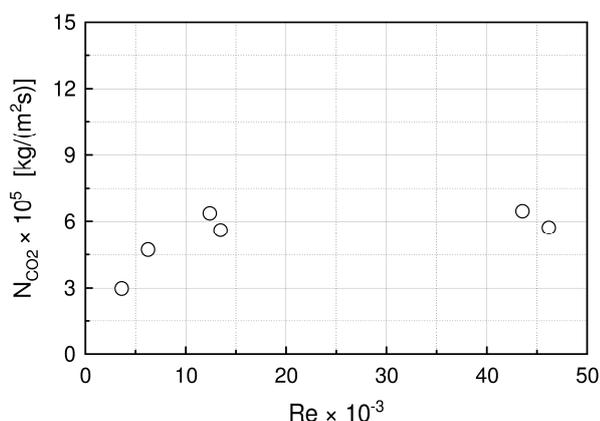


Figure 2. The effect of Re number on CO₂ mass flux (T = 50°C, w_{MEA} = 10 wt%)

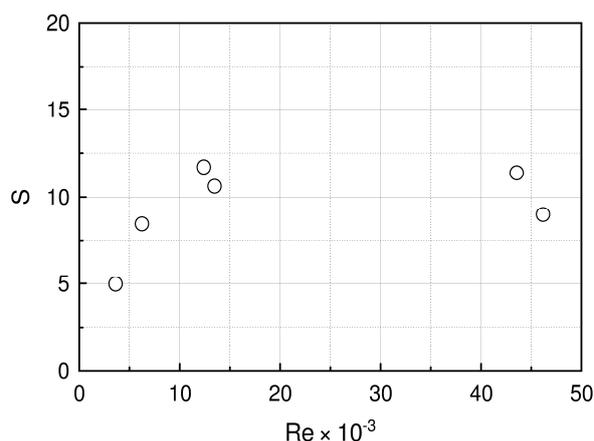


Figure 3. The effect of Re number on selectivity (T = 50°C and w_{MEA} = 10 wt%)

The effect of liquid flow rate on the CO₂ mass flux and selectivity is presented in Figs.2 and 3 for the temperature of 323K (50°C) and 10% MEA concentration. The selectivity of the process is defined as follows:

$$S = \frac{(w_{\text{CO}_2}(1-w_{\text{CO}_2}))_p}{(w_{\text{CO}_2}(1-w_{\text{CO}_2}))_f} \quad (1)$$

The measured fluxes increase with the Reynolds number. The highest values were obtained for Re>10,000 (turbulent flow). This can be explained by the CO₂ mass transfer increase in the liquid phase for turbulent regime. The measured selectivities rise with the Reynolds number and for turbulent flows reach the value of 10.

The operating temperature is an important parameter as far as the efficiency of the membrane is concerned as shown in Fig.4. For a given turbulent liquid flow rate the measured CO₂ mass fluxes rise with the feed temperatures due to the increased driving force in favour of CO₂ mass transfer. The selectivity does not change significantly with the operating temperature, Fig.5.

The effect of the MEA concentration on mass flux and selectivity is presented in Figs.6-7 at an operating temperature of 323K (50°C) and turbulent flow (Re of about 40,000).

The measured mass fluxes do not change significantly with MEA concentration (Fig.6), because of the

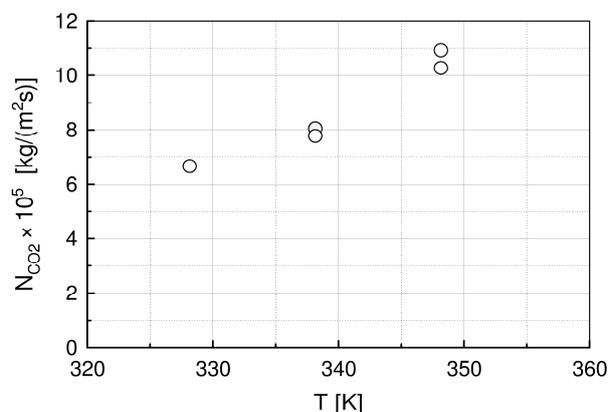


Figure 4. The effect of feed temperature on CO₂ mass flux (w_{MEA} = 10 wt%)

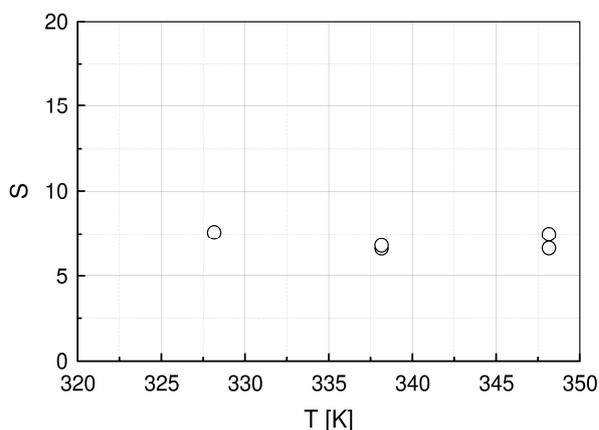
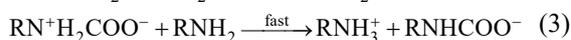


Figure 5. The effect of feed temperature on selectivity ($w_{\text{MEA}} = 10 \text{ wt}\%$)

relationship between equilibrium constants of the CO₂ - MEA reaction and the CO₂ solubility in water at a given temperature. The selectivity decreases with MEA concentration as a result of the rising amount of CO₂ absorbed in the MEA solution and the constant CO₂ flux in the permeate, see Fig. 7.

3. Mathematical model and calculation results

When CO₂ is absorbed in aqueous monoethanolamine (MEA) solution, the following reactions can be written as [11]:



The formation of carbamate is well understood and the rate of the forward reaction has been determined as first order with respect to both CO₂ and RNH₂:

$$r = k_{\text{CF}}[\text{CO}_2][\text{RNH}_2] \quad (4)$$

During the desorption process the differences in the concentration of the component and the temperature

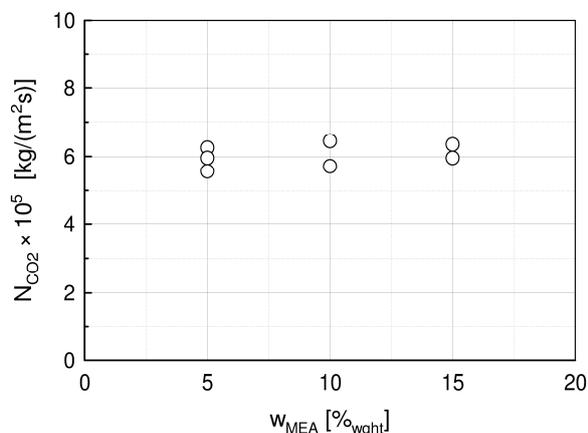


Figure 6. The effect of MEA concentration on CO₂ mass flux

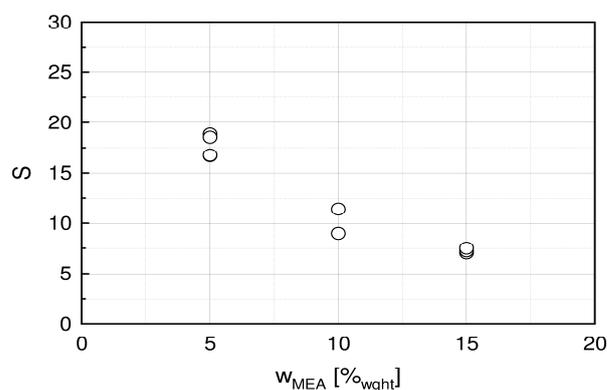


Figure 7. The effect of MEA concentration on selectivity

between the inlet and outlet in the liquid phase are very small. Therefore, the desorption rate may be simply calculated using the arithmetic mean value of CO₂ in the liquid phase.

With this assumption we can calculate the mass fluxes of CO₂ can be calculated as follows:

$$N_{\text{CO}_2} = K_L(x_{\text{CO}_2} - x_{\text{CO}_2}^*) \quad (5)$$

where N_{CO_2} [kmol/s] is the flux of CO₂ and K_L [kmol/m²s] is the overall mass-transfer coefficient of the liquid phase.

The overall mass-transfer coefficient for CO₂ can be evaluated by a resistance-in-series model [12].

The numerical calculations based on model equations were performed and estimated values of membrane resistance ($1/k_M$) used. In the calculations the experimental values of the Henry's constant for CO₂ in water and MEA under standard conditions are 1.2456 and 1.5732, respectively [13]. The enhancement factor of the chemical reaction of CO₂ in the liquid phase, as defined by DeCoursey [14], was between 20 and 60. The viscosity of the water-MEA mixture was calculated according to a Grunberg and Nissan equation [15]. Calculated and experimental values of CO₂ mass fluxes are

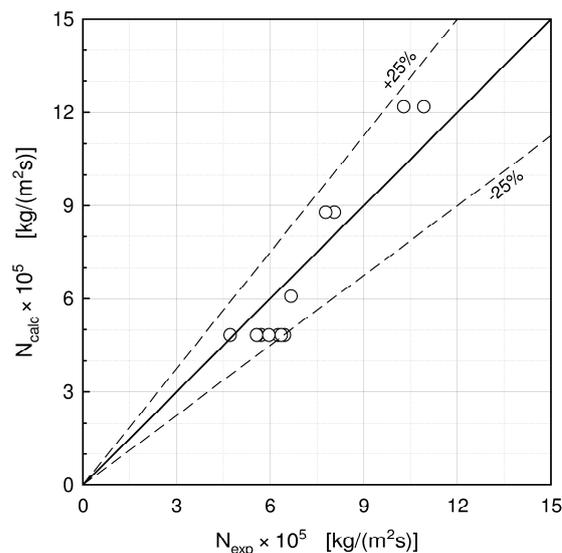


Figure 8. Comparison of calculated values of CO₂ fluxes with experimental ones

shown in Fig.8. The scattering of calculated and experimental values of CO₂ mass fluxes was within the range of $\pm 25\%$.

The experimental values of CO₂ mass fluxes were compared with those obtained from the literature for CO₂ stripping in a ceramic hollow fiber membrane contactor [10]. In spite of the different types of membrane type and hydrodynamic conditions the measured values of CO₂ mass fluxes were comparable in both cases.

Conclusions

The application of a membrane in the process of CO₂ stripping from MEA solutions avoids some technical problems that are encountered in industrial practices.

The PDMS hydrophobic tubular membrane on a ceramic support can be applied for the removal of CO₂ from MEA solutions. In developed turbulent flows the measured CO₂ mass fluxes and selectivities do not change significantly with Re number (Figs.2-3). The measured CO₂ mass fluxes increase as the feed temperature rises (Fig.4) and slightly depend on the MEA concentration (Fig.6). The measured and calculated CO₂ mass fluxes are in good agreement with each other (Fig.8). The $\pm 25\%$ variation in scattering can be explained by the accuracy of the correlations, experimental precision and simplification of the model.

4. SYMBOLS

C – concentration, kmol m⁻³
 D – diffusion coefficient, m² s⁻¹
 K_L – overall mass transfer coefficient, kmol m⁻² s⁻¹
 k_M – mass transfer coefficient of the membrane, kmol m⁻² s⁻¹
 N – mass flux kmol m⁻² s⁻¹
 r – reaction rate, kmol s⁻¹
 Re – Reynolds number
 S – selectivity
 T – temperature, K
 w – mass fraction
 x – mole fraction of CO₂ in the liquid phase

superscripts

* - refers to equilibrium

subscripts

calc – calculation
 CO₂ – carbon dioxide
 exp - experimental
 f – feed
 G – gaseous phase
 L – liquid phase
 p - permeate

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