

CARBON DIOXIDE REMOVAL FROM MEA - WATER SOLUTION ON PDMS TUBULAR MEMBRANE

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The process of carbon dioxide removal from monoethanolamine (MEA) – water solution was investigated on Poly Di Methyl Siloxane (PDMS) hydrophobic tubular membrane with a ceramic support. The effects of feed temperature, liquid flow rate and MEA concentration on CO₂ mass transfer and selectivity were examined and found to be with a reasonable deviation ($\pm 25\%$) with predictions based on the multilayer film model. The membrane resistance was evaluated in separate experiments. The measured CO₂ mass fluxes (0.17-0.45 kg/(m²h)) were found to be independent of the MEA concentration in the feed.

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

1. INTRODUCTION

Fossil fuel combustion from power plants is one of the most important sources of CO₂ emissions. The influence of carbon dioxide on the greenhouse effect is an important worldwide issue with an increasing research range. The separation of CO₂ from gases can be achieved by different techniques such as adsorption and absorption, low temperature distillation and membrane separation. The absorption of CO₂ in amine solutions is presently the mostly favoured method for the removal of carbon dioxide from fuel combustion.

An advantage of chemical absorption into amine solution lies in the fact that at higher temperatures the chemical reaction can be reversed and the MEA recycled. In comparison to the numerous studies (Astarita and Sawage, 1980a; Astarita and Sawage, 1980b; Koonaphapdeelert et al., 2005; Kosarjan et al., 2005) concerning CO₂ absorption in MEA solution there are only few on CO₂ stripping (desorption) (Kierzkowska-Pawlak and Chacuk, 2011), despite the fact that the stripping unit is responsible for most separation cost of the process (Dugas and Rochelle, 2009).

The packed columns currently dominate as the contactor of choice for solvent stripping. However, limiting factors for the application of this technology are its size and large capital cost. Besides, additional conditions such as flooding, foaming and entrainment can reduce mass transfer performance of this solution.

Recently a novel type of a ceramic hollow fibre membrane contactor has been studied (Kosarjan et al., 2005). The membrane contactor consisted of 18-35 ceramic hollow fibre membranes with the outer diameter of 0.11-0.20 cm. 2.5 molar monoethanolamine and deionised water were used as the feed solution. Pure nitrogen was used as the stripping gas. This membrane could be modified to be

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hydrophobic which facilitates its application for the absorption-desorption system of CO₂ in amine solution.

In our study the process of CO₂ stripping from MEA solution using Poly Di Methyl Siloxane (PDMS) hydrophobic tubular membrane on a ceramic support was investigated. This solution enables to apply turbulent flow on the liquid side and consequently higher mass transfer coefficient. Additionally, some technical problems (flooding, maldistribution of liquid, amine loss due to evaporation) can be avoided. The mass transfer of the solute is proportional to the concentration gradient as illustrated in Fig.1 where PDMS dense membrane is in the middle of vapour and liquid phases.

The main goal of this study was to investigate a possibility of applying PDMS membrane in the process of CO₂ removal from aqueous MEA solution. Furthermore, the performance of this membrane including its selectivity and CO₂ mass fluxes and the effects of operating parameters were determined.

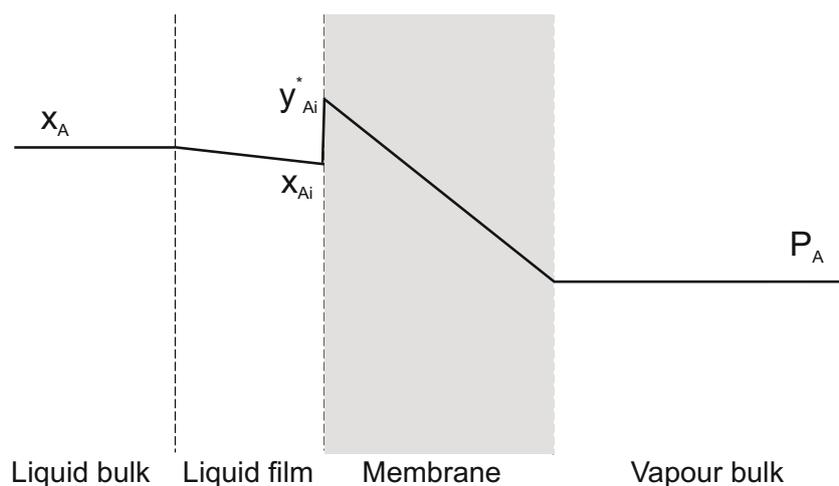


Fig. 1. The idea of the process

2. EXPERIMENTAL

The experiments were carried out in the setup shown in Fig.2 consisting of a membrane module, reactor vessel, cooling system, circulation and vacuum pumps. The hydrophobic PDMS membranes on ceramic support (ceramic tubes of 0.07 m in diameter and 0.25 m in length) made by Pervatech BV were studied. In all the experiments the feed temperature was stabilised by a thermostat ($\pm 1^\circ\text{C}$) in the range of 50-75 °C. The feed was circulated by a pump and the flow rate was controlled by a flowmeter.

In laboratory conditions the vacuum pump was used to maintain the pressure of 7-10 mm Hg on the permeate side. The permeate was condensed and collected in cold traps immersed in liquid nitrogen. The sample was heated and the mass of sublimed CO₂ and residual water were measured. No MEA was found in the permeate sample. The concentration of carbon dioxide in the permeate was calculated from the mass of carbon dioxide and water in the analysed permeate sample. The pressure at the feed and permeate sides was measured by pressure gauges. The temperatures of the feed in the reactor vessel, before and after the membrane module were determined by thermocouples.

Liquid feed solution was prepared from monoethanolamine (MEA) and deionised water. Thus obtained solution was loaded with CO₂ by bubbling pure CO₂ in a magnetically stirred vessel until reaching the demanded carbonation ratio, α . In our experiments the carbonation ratio was determined by measuring the mass of absorbed CO₂ in amine solution at a given temperature.

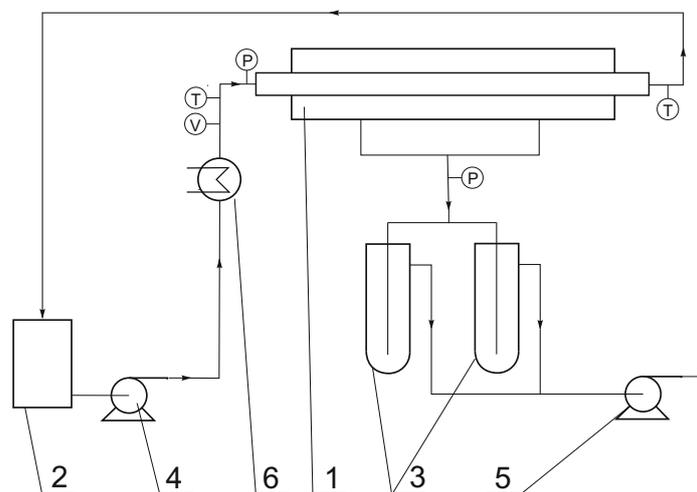


Fig. 2. The experimental setup: 1 – membrane contactor, 2 – feed tank, 3 – cold traps, 4 – circulation pump, 5 – vacuum pump, 6 – heater

During the experiments the concentration of CO₂ in the feed remained practically constant. The mass of the removed permeate sample (1-2 g) does not change significantly the feed composition (mass of the feed 2 000-2 500 g).

Additionally, independent pervaporation experiments with the same PDMS membrane and 2-propanol – water mixture were performed in order to determine mass transfer coefficient. The pervaporation experiments were done in the temperature range of 50-75 °C, for concentrations of 2-propanol of 1, 3, 5% wt. and *Re* about 40 000.

3. EFFECTS OF OPERATING PARAMETERS

The effects of the operating parameters such as: liquid flow rate, operating temperature and MEA concentration, on the performance of PDMS membrane were examined. The operating temperature was in the range of 50 °C to 75 °C, liquid flow rate 20 -600 l/h and MEA concentration 3, 5, 10, 15% wt.

Figs. 3, 4 present the effect of liquid flow rate on the CO₂ mass flux and selectivity of the process. The selectivity *S* was defined as that in the pervaporation process:

$$S = \frac{(w_{CO_2} / (1 - w_{CO_2}))_p}{(w_{CO_2} / (1 - w_{CO_2}))_f} \quad (1)$$

where *S* is the total selectivity of the process and *w*_{CO₂} is a weight concentration of CO₂.

As can be seen in the above figures the measured fluxes increase with the Reynolds number and reach the highest values in a turbulent flow region (for *Re*>10 000). This can be explained by the increase of mass transfer coefficient which lowers resistance in the liquid phase for turbulent regime. In the *Re* numbers range 10 000-45 000 the measured CO₂ fluxes do not change significantly. The obtained selectivity values rise with the Reynolds number and reach the value of 10 for turbulent flow.

The operating temperature plays an important role for the membrane efficiency as shown in Fig. 5. Higher fluxes were obtained at higher feed temperatures at a given liquid flow rate (the experimental data for a fully developed turbulent flow, *Re*>20 000, were taken into account).

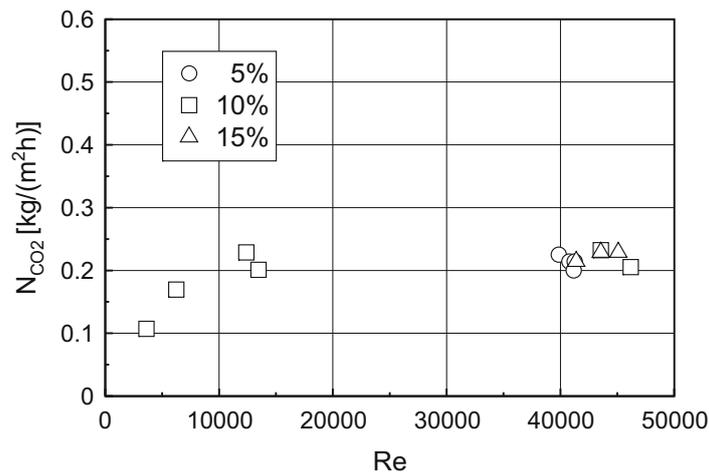


Fig. 3. The effect of Re number on CO_2 mass flux ($T = 50\text{ }^\circ\text{C}$, $w_{MEA} = 5, 10, 15\%$ wt.)

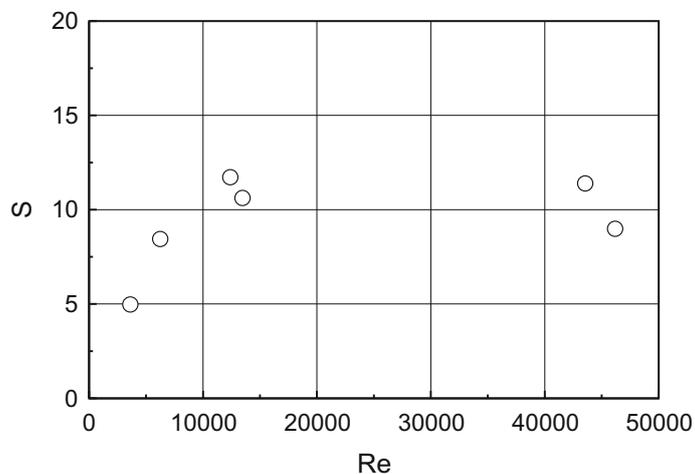


Fig. 4. The effect of Re number on selectivity ($T = 50\text{ }^\circ\text{C}$ and $w_{MEA} = 10\%$ wt.)

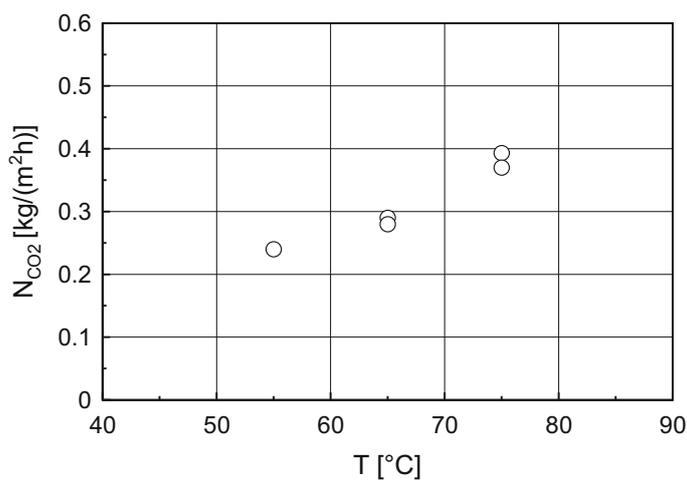


Fig. 5. The effect of feed temperature on CO_2 mass flux ($w_{MEA} = 10\%$ wt., $Re > 20\ 000$)

With a rising feed temperature the equilibrium of the dissolved CO_2 concentration is shifted to a lower value due to the increased driving force for CO_2 mass transfer. Selectivity does not change significantly with the operating temperature (Fig. 6).

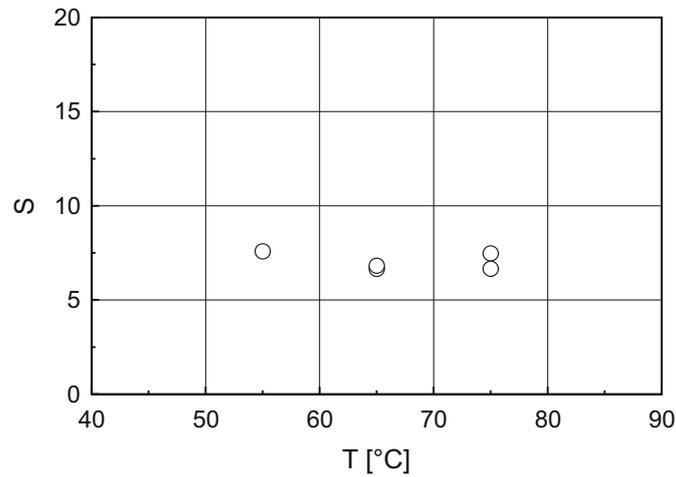


Fig. 6. The effect of feed temperature on selectivity ($w_{MEA} = 10\%$ wt., $Re > 20\ 000$)

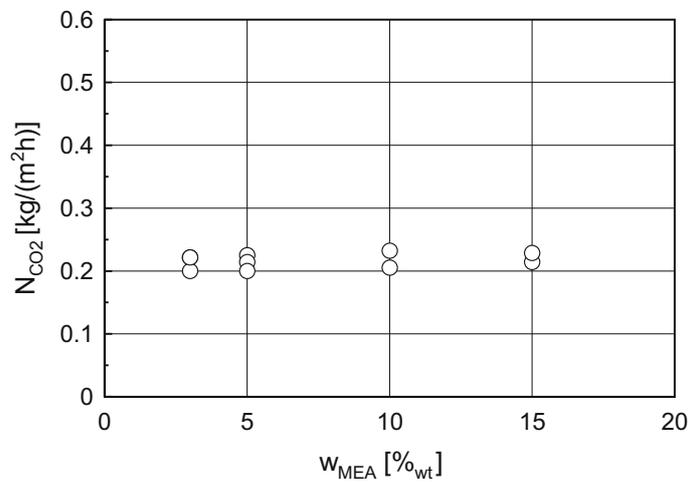


Fig. 7. The effect of MEA concentration on CO_2 mass flux ($T = 50^\circ C$, $Re > 20\ 000$)

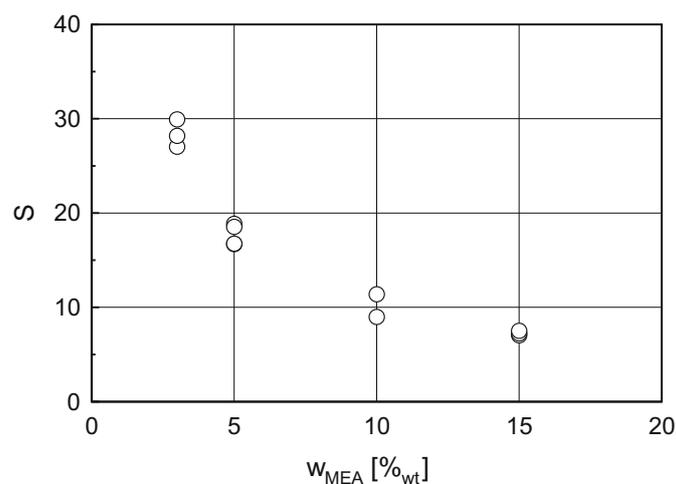


Fig. 8. The effect of MEA concentration on selectivity ($T = 50^\circ C$, $Re > 20\ 000$)

The effect of MEA concentration on mass flux and selectivity is presented in Figs. 7-8 for the operating temperature of $50^\circ C$ and turbulent flow (the experimental data for a fully developed turbulent flow, $Re > 20\ 000$, were taken into account). The measured mass fluxes, Fig. 7, do not change significantly

with MEA concentration. This may be caused by the relation between equilibrium constants of the chemical reaction of CO₂ desorption from MEA solution and thermodynamic solubility of CO₂ in water. Small amounts of CO₂ dissolved in water and transferred through the membrane are quickly supplemented from the absorbed CO₂ in MEA solution. With a high capacity of CO₂ absorbed in MEA and constant CO₂ solubility in water at a given temperature the measured mass fluxes in the process of CO₂ stripping using PDMS do not change significantly with MEA concentration. Selectivity decreases with MEA concentration because at a constant flux of CO₂ in the permeate, the amount of CO₂ absorbed in MEA solution rises, Fig.8.

4. MODEL

When CO₂ is absorbed in an aqueous monoethanolamine (MEA) solution, the overall reaction can be written as (Astarita et al., 1983):



Carbamate formation (2) is well understood and in the case of MEA has been extensively studied. Forward reaction rate has been established to be of first-order with respect to both CO₂ and RNH:

$$r = k_{CF}[\text{CO}_2][\text{RNH}] \quad (3)$$

During the operation of desorption the differences of component concentration and temperature between the inlet and outlet in the liquid phase are very small. Therefore, we may simply calculate the desorption rate using the arithmetic mean value of CO₂ in the liquid phase.

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

$$N_{\text{CO}_2} = k_L(x_{\text{CO}_2} - x_{\text{CO}_2}^*) \quad (4)$$

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

The vapour–liquid equilibrium data of CO₂ in MEA–water system are reported in the literature (Burkett, 1977; Disli, 1996; Weiland et al., 1982), in a form of correlation between CO₂ equilibrium partial pressure ($P_{\text{CO}_2}^*$) and carbonation ratio (α), which is the ratio between CO₂ mole and MEA mole in the solution. In our study the correlation proposed by Burkett was used (Eq. 5)

$$\begin{aligned} P_{\text{CO}_2}^* &= \exp(A + BT + CT^2) * 133.29 \\ A &= -47.91 + 112.8\alpha \\ B &= 0.7615 - 1.668\alpha \\ C &= -0.0029 + 0.007\alpha \end{aligned} \quad (5)$$

where $P_{\text{CO}_2}^*$ is the partial pressure [Pa], T is the liquid temperature [°C] and α is the carbonation ratio.

The overall mass transfer coefficient for CO₂ can be evaluated by the resistance series model (Kreulen et al., 1993).

Due to a very low pressure (vacuum) in the gas phase, mass transfer resistance in this phase can be neglected. Thus, the overall mass transfer coefficient K_L can be calculated as follows (Koonaphapdeelert et al., 2009):

$$\frac{1}{K_L} = \frac{1}{Hk_M} + \frac{1}{Ek_L} \quad (6)$$

where k_M and k_L are the individual mass transfer coefficients in the membrane and liquid film, respectively. E is the enhancement factor of the chemical reaction of CO_2 in the liquid phase while H is the Henry's law constant of CO_2 in water.

Mass transfer in liquid phase k_L was calculated based on heat and mass transfer analogy using Gnielinski equation (VDI Heat Atlas, 1993) for turbulent and transition range:

$$k_L = \frac{D_{\text{CO}_2}}{d_i} \frac{\xi/8(\text{Re}-1000)\text{Sc}}{1 + 12.7\sqrt{\xi/8}(\text{Sc}^{2/3}-1)} \left[1 + \left(\frac{d_i}{l} \right)^{2/3} \right] \quad (7)$$

where $\xi = (1.82 \log_{10} \text{Re} - 1.64)^{-2}$

The membrane resistance ($1/k_M$) was estimated on the basis of pervaporation experiments for 2-propanol - water mixture on the same membrane and similar thermal and hydrodynamic conditions. Thus obtained values of k_M for 2-propanol - water system were corrected by factor $D_{\text{CO}_2}/D_{2\text{-propanol}}$ (in the liquid phase).

Henry's constant was calculated as:

$$H = \frac{C_G}{C_L^*} \quad (8)$$

where C_G is CO_2 concentration in the gas phase. C_L^* is the concentration of CO_2 in the liquid phase which is in equilibrium with the gas phase. The experimental values of Henry's constant for CO_2 in water and MEA at standard conditions (STD) are 1.2456 and 1.5732, respectively, (Browning and Weiland, 1994).

A reversible reaction (2) occurs when CO_2 is absorbed/desorbed in an aqueous MEA solution. Enhancement factor E is defined as (DeCoursey, 1982):

$$E = \sqrt{1 + Ha^2} \quad (9)$$

where Hatta number Ha is calculated as:

$$Ha = \frac{\sqrt{k_{CF} C_{\text{CO}_2} D_{\text{CO}_2}}}{k_L} \quad (10)$$

where the reaction rate constant k_{CF} was found in the literature (Donaldson and Nguyen, 1980) $k_{CF} = 6\,000 \text{ [m}^3\text{kmol}^{-1}\text{s}^{-1}\text{]}$ at 298K.

5. CALCULATION RESULTS

Based on the model equations (2-10) and the estimated values of membrane resistance ($1/k_M$) numerical calculations were performed. In the calculations Ha and E were in the range of 20-60, and Sc number in the range of 170-55. The calculated values of CO_2 mass fluxes were compared with the experimental ones and shown in Fig. 9 (for Re numbers 6 000-45 000, temperatures of 50-75 °C and, $w_{\text{MEA}} = 5, 10, 15 \text{ \% wt.}$). As can be seen the scattering of the calculated and experimental values of CO_2 mass fluxes is in the range of $\pm 25\%$.

In Fig. 10 the effect of the feed temperature on the calculated and experimental values of overall mass transfer coefficient K_L is compared. The calculated results for different temperatures show good agreement with the experimental data ($Re > 20\,000$, $w_{\text{MEA}} = 10 \text{ \% wt.}$).

The experimental values of CO₂ mass fluxes are in a similar range as those found in the literature for CO₂ stripping in a ceramic hollow fiber membrane contactor (Koonaphapdeelert, 2009). A thorough comparison with the literature data could not be made on account of different membrane types and operating conditions.

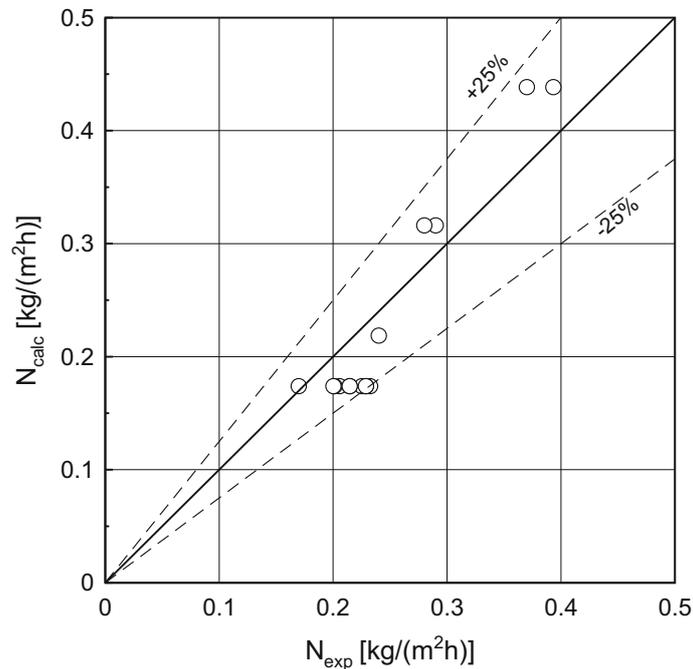


Fig. 9. Comparison of calculated values of CO₂ fluxes with experimental ones

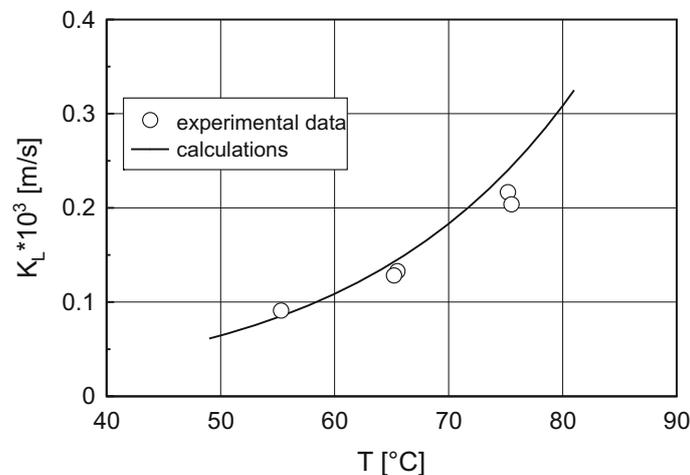


Fig. 10. Comparison of calculated and experimental values of overall mass transfer coefficient K_L

6. CONCLUSIONS

- The examined hydrophobic PDMS tubular membrane on a ceramic support can be applied for CO₂ removal from MEA solution.
- The measured CO₂ mass fluxes and selectivity values slightly depend on MEA concentration (Figs.7-8).
- In a fully developed turbulent flow the measured CO₂ mass fluxes and selectivity values do not change significantly with Re number (Figs.3-4).

- The measured CO₂ mass fluxes increase with a rising feed temperature (Fig.5).
- The applied PDMS membrane does not show any permeability of MEA across the membrane. This helps to avoid any MEA losses in a membrane contactor.
- The calculated and measured CO₂ mass fluxes show good agreement (Fig.9).
- The membrane application in the process of CO₂ stripping from MEA solution can help to avoid some technical problems encountered in industrial practice (flooding, maldistribution of liquid, amine loss due to evaporation).

SYMBOLS

C	concentration, kmol m ⁻³
d_i	inner diameter of membrane tube, m
D	diffusion coefficient, m ² s ⁻¹
E	enhancement factor, -
F	membrane area, m ²
H	Henry's constant, -
Ha	Hatta number, -
k_{CF}	reaction rate constant, m ³ kmol ⁻¹ s ⁻¹
k_L	mass transfer coefficient in liquid phase, kmol m ⁻² s ⁻¹
K_L	overall mass transfer coefficient, kmol m ⁻² s ⁻¹
k_M	mass transfer coefficient in membrane, kmol m ⁻² s ⁻¹
N	mass flux, kmol m ⁻² s ⁻¹
P	pressure, Pa
Re	Reynolds number, -
S	selectivity, -
Sc	Schmidt number, -
T	temperature, K
w	mass fraction, -
x	mole fraction of CO ₂ in liquid phase, -

Greek symbols

α	carbonation ratio
ζ	friction factor

Superscripts

*	refers to equilibrium
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Subscripts

CO_2	carbon dioxide
f	feed
G	gaseous phase
L	liquid phase
p	permeate

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