

KINETICS OF CARBON DIOXIDE ABSORPTION INTO N-METHYLDIETHANOLAMINE SOLUTIONS

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ABSTRACT

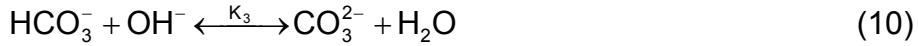
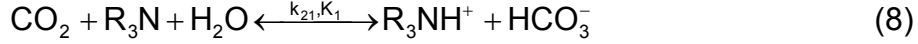
The kinetics of carbon dioxide absorption in aqueous solutions of N-methyldiethanolamine (MDEA) as well as in aqueous solutions mixtures of MDEA and 2-ethylaminoethanol (EAE) has been investigated. Measurements of the absorption rate were carried out in a stirred vessel of known interfacial area under atmospheric pressure at the temperature of 20°C. The ranges of parameters used were as follows: stirrer speed: 40 – 80 rpm; concentration of MDEA: 10, 20 and 30 mass %; concentration of EAE: 5, 10 and 15 mass %. The values of the reaction rate constant between CO₂ and MDEA were determined and compared with the literature data. It was found that the addition of EAE significantly increases the absorption rate.

INTRODUCTION

Absorption methods are the most wide-spread in commercial practice of industrial gas purification. CO₂ and H₂S removal methods are of special importance because these compounds are present as impurities in many gaseous mixtures. A number of gas purification processes using absorption methods exists. These processes are based on either physical dissolution of gases in liquids or on dissolution combined with chemical reaction in the liquid phase. The cost of purifying a gaseous mixture is generally very high. In the ammonia production the synthesis gas contains considerable amounts of CO₂ (10 – 20%). For the removal of CO₂ from those gas BENFIELD process is most wide-used. In this process CO₂ is absorbed into aqueous NaHCO₃/Na₂CO₃ solutions, containing diethanolamine (DEA) at temperature 70 - 115°C and under elevated pressure (2.0 – 2.5 MPa). Our earlier works [1-4] were aimed at improving this process and making it more effective economically and technically. BASF developed a method of the removal of CO₂ from the synthesis gas using aqueous N-methyldiethanolamine (MDEA) solutions, containing suitable activator (also amine) [5]. Many studies on the kinetics of the reaction of CO₂ in aqueous MDEA solutions have been reported, but there are still some discrepancies as to the values of the reaction rate constant and as to the influence of the amine concentration on these values. The aim of the present work was to determine the values of the reaction rate constant in the system: CO₂ – aqueous MDEA solutions. As the first step, measurements of the kinetics of CO₂ absorption into aqueous MDEA solutions were carried out in a stirred vessel. The measurements of the

solutions. Versteeg and van Swaaij [11] showed that the absorption rate of CO₂ into an MDEA-ethanol solution could be described as completely physical absorption with the rate almost identical to the absorption rate of N₂O corrected for the differences in the physical constants. Pohorecki and Možeński [12] showed, that the absorption of CO₂ into TEA-propylene carbonate solution can be treated as a physical absorption.

The reactions occurring during absorption of CO₂ into aqueous tertiary alkanolamine (e.g. MDEA) solutions can be expressed by the following equations [13]:



The first two reactions (8-9) have finite reaction rates given by the following reaction rate expressions:

$$r_1 = k_{21}[\text{CO}_2][\text{R}_3\text{N}] - \frac{k_{21}}{K_1}[\text{R}_3\text{NH}^+][\text{HCO}_3^-] \quad (13)$$

$$r_2 = k_{22}[\text{CO}_2][\text{OH}^-] - \frac{k_{22}}{K_2}[\text{HCO}_3^-] \quad (14)$$

where

$$K_2 = \frac{[\text{HCO}_3^-]}{[\text{CO}_2][\text{OH}^-]} \quad (15)$$

$$K_1 = \frac{[\text{R}_3\text{NH}^+][\text{HCO}_3^-]}{[\text{CO}_2][\text{R}_3\text{N}]} \quad (16)$$

Instantaneous reactions (10-12) (the removal of the proton) is assumed to be at equilibrium:

$$K_3 = \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-][\text{OH}^-]} \quad (17)$$

$$K_4 = \frac{[\text{R}_3\text{N}]}{[\text{R}_3\text{NH}^+][\text{OH}^-]} \quad (18)$$

$$K_5 = [\text{OH}^-][\text{H}_3\text{O}^+] \quad (19)$$

Rinker et al. [13] investigated the kinetics of the CO₂ absorption into aqueous MDEA solution in a wetted-sphere absorber. For the interpretation of the results obtained they used three different mathematical models which are based on Higbie's penetration theory.

- Model 1.
In this model, reactions (8-12) are included and are considered to be reversible.
- Model 2.
Model 2 is the same as model 1 except that reaction (9) is neglected.
- Model 3.
In this model reaction (8) can be treated as a pseudo-first-order irreversible reaction, and the effect of reactions (9-12) on the absorption rate of CO₂ into aqueous MDEA solutions can be neglected.

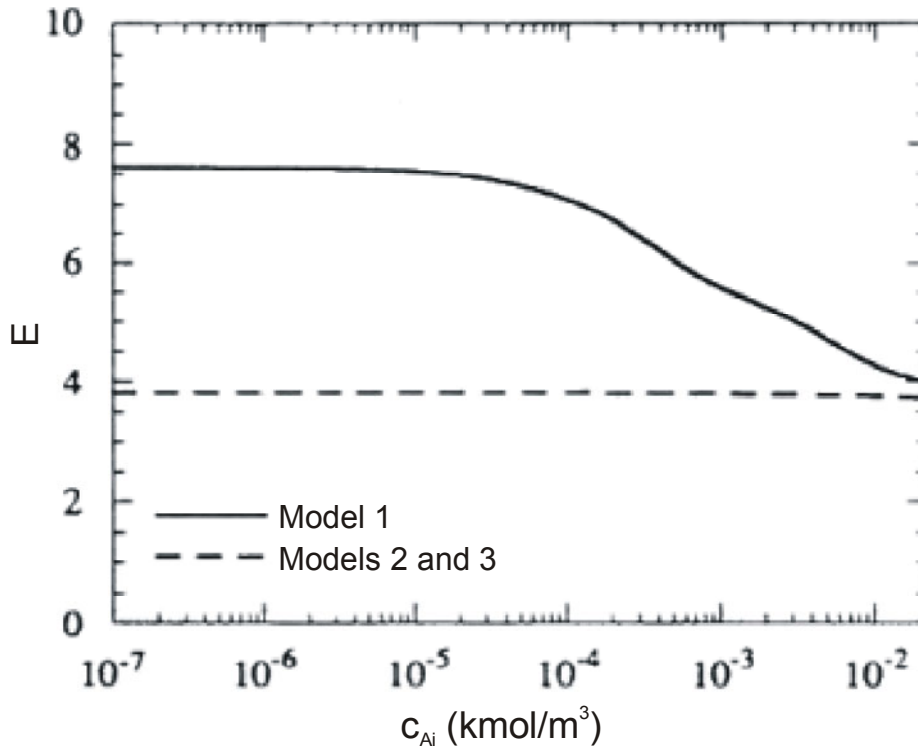


Fig. 1. Dependence of the enhancement factor E on the interfacial concentration of CO_2 [13].

Fig. 1 represents the enhancement factors predicted by models 1-3 for the absorption of CO_2 into aqueous MDEA solution (20 mass %) as a function of the CO_2 interfacial concentration. As is seen, the value predicted by models 2 and 3 is the same and does not depend on the interfacial concentration of CO_2 . For small CO_2 interfacial concentrations ($c_{Ai} < 10^{-4}$ kmol/m³) the enhancement factor predicted by model 1 is twice larger than that from models 2 and 3. When the interfacial concentration of CO_2 decreases, the contribution of reaction (9) to the enhancement factor and to the rate of absorption of CO_2 increases. This is because the reaction (9) rate constant, k_{22} , is much larger than that of reaction (8), k_{21} . When CO_2 is present in small quantities, such that its interfacial concentration is comparable to the hydroxide concentration, reaction (9) becomes a major contributor to the overall absorption of CO_2 .

EXPERIMENTAL APPARATUS AND PROCEDURE

Measurements of the rate of CO_2 absorption into aqueous solutions of MDEA were carried out in a stirred vessel, designed according to Danckwerts and Gilham [14]. In this apparatus the stirrer only cuts through the flat surface of liquid, thus renewing it. The schema of the experimental apparatus is shown in Fig. 2. The gas absorber 1, immersed in a thermostatic tank 3, was 0.1 m in diameter and was equipped with a glass stirrer 0.094 in diameter. The total reactor volume was 1 dm³, and 0.5 dm³ of liquid was used in each experiment. The rate of CO_2 absorption was measured by soap-film meter 10. The measurements were carried out under atmospheric pressure at 20°C. The interfacial area was $a = 0.0073$ m² (flat surface minus the surface of stirrer blades).

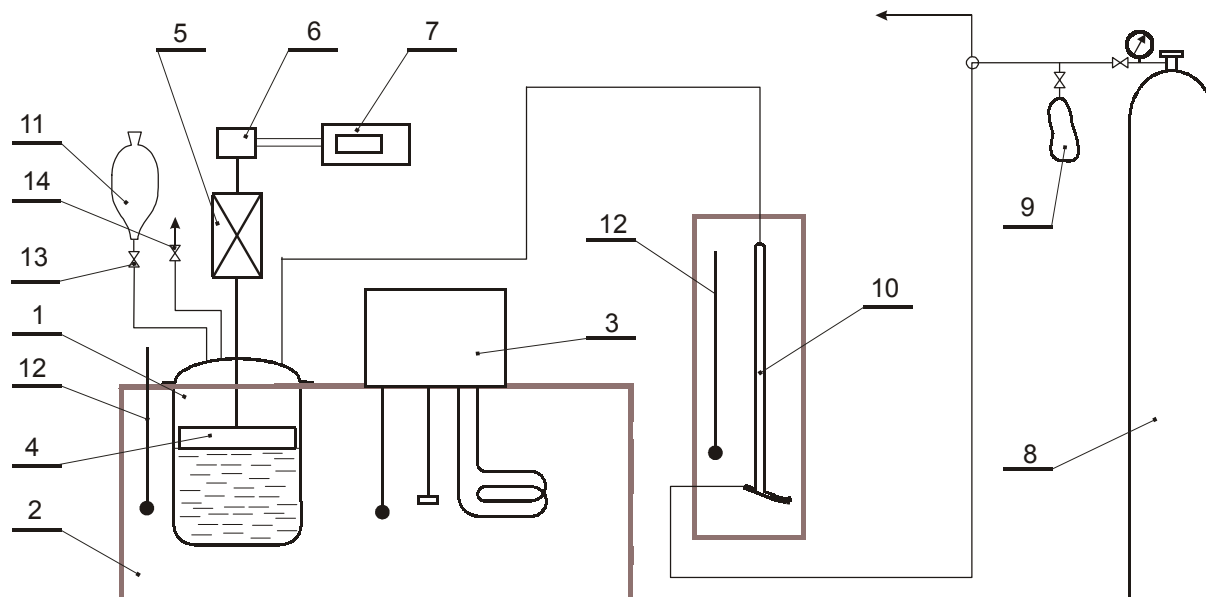


Fig. 2. The experimental apparatus: 1 – absorber, 2 – thermostatic tank, 3 – thermostat, 4 – stirrer, 5 – motor, 6 – rate generator, 7 – speed indicator, 8 – gas cylinder, 9 – CO₂ balloon, 10 – soap-film meter, 11 – dropping funnel, 12 – thermometers, 13, 14 – valves.

The ranges of parameters were as follows:

- stirrer speed: 40 – 80 rpm
- stirrer immersion depth: 0.5 mm
- concentration of MDEA: 10, 20 and 30 mass %
- concentration of EAE: 5, 10 and 15 mass %

The aqueous solutions were prepared from distilled water and amines. The MDEA was supplied by Aldrich Chemical Co. and the EAE was supplied by Merck Schuchardt Co.

The rate of CO₂ absorption is equal

$$R = N \cdot a = \frac{V_g \cdot p_{\text{CO}_2}}{R_g \cdot T} \quad (20)$$

The partial pressure of CO₂ was equal to the total pressure of the gas in CO₂ balloon 9 minus partial pressure of the solvent (water) at the temperature T.

The concentration of CO₂ at the interface was calculated from Henry's law:

$$p_{\text{Ai}} = H \cdot c_{\text{Ai}} \quad (21)$$

In the calculation of the partial pressure at the interface the mass transfer resistance in the gas phase was neglected (pure CO₂). Since CO₂ reacts in aqueous MDEA solutions, the solubility and diffusivity of CO₂ in the solutions could not be measured directly. Instead, Henry's constant was estimated by using "N₂O analogy" technique. According to "N₂O analogy", Henry's constant of CO₂ (H) and N₂O (H_{N₂O}) in the aqueous MDEA solutions and pure water (respectively H⁰ and H⁰_{N₂O}) are related by the following equation [13]

$$\frac{H}{H^0} = \frac{H_{\text{N}_2\text{O}}}{H_{\text{N}_2\text{O}}^0} \quad (22)$$

The values of Henry's constant for the CO₂ – water system were calculated from the equation [13]:

$$H^{\circ} = 23314 \cdot \exp\left(-\frac{1984.8}{T}\right) \quad (23)$$

The values of Henry's constant for the N₂O – water and N₂O – aqueous MDEA solutions were calculated from the expressions given in Table 1.

Table 1. Henry's law constant and diffusion coefficients of N₂O in pure water and in aqueous MDEA solutions [13].

% mass MDEA kg MDEA/kg solution	H _{N₂O} atm m ³ /kmol	D _{N₂O} m ² /s
0	60456·exp(-2178.1/T)	4.009E-6·exp(-2288.4/T)
10	38759·exp(-2036.2/T)	1.0297E-6·exp(-1954.4/T)
20	31231·exp(-1957.2/T)	1.8451E-6·exp(-2197.8/T)
30	19049·exp(-1787.5/T)	5.4724E-6·exp(-2656.5/T)

In our experiments, concentrations of CO₂ at the interface, calculated from the Eqs (21-23) changed in the range: (3.0 – 3.4)·10⁻² kmol/m³. Thus, in our experimental conditions, model 3 [13] was used for the interpretation of experimental results. For an irreversible pseudo-first order chemical reaction the molar flux of the absorbed component is equal:

$$N = k_L^* \cdot c_{Ai} \quad (24)$$

The diffusion coefficient of CO₂ in aqueous MDEA solutions, D_A was also estimated using "N₂O analogy" technique from the following expressions [13]:

$$\frac{D_A}{D_A^0} = \frac{D_{N_2O}}{D_{N_2O}^0} \quad (25)$$

$$D_A^0 = 3.0651 \cdot 10^{-6} \exp\left(-\frac{2196.1}{T}\right) \quad (26)$$

The values of the diffusion coefficient N₂O in water (D⁰_{N₂O}) and diffusion coefficient N₂O in MDEA solutions (D_{N₂O}) were calculated from expressions given in Table 1. The diffusion coefficients of MDEA were correlated with the temperature and viscosity of MDEA solution by the equation:

$$D_B = 4.682 \cdot 10^{-14} \cdot T \cdot \mu^{-0.569842} \quad (27)$$

The viscosities of aqueous MDEA solutions were calculated from expressions given in Table 2.

Table 2. Viscosity of aqueous MDEA solutions [13].

% mass MDEA kg MDEA/kg solution	μ·10 ⁻³ kg/(m·s)
10	2,18907-0,041617 t+0,00025444 t ²
20	3,25676-0,060144 t+0,00032664 t ²
30	5,44936-0,10896 t+0,000608464 t ²

RESULTS AND DISCUSSION

In Fig. 3 the dependence of the mass transfer coefficient for absorption with chemical reaction, k_L^* on the stirrer speed is presented.

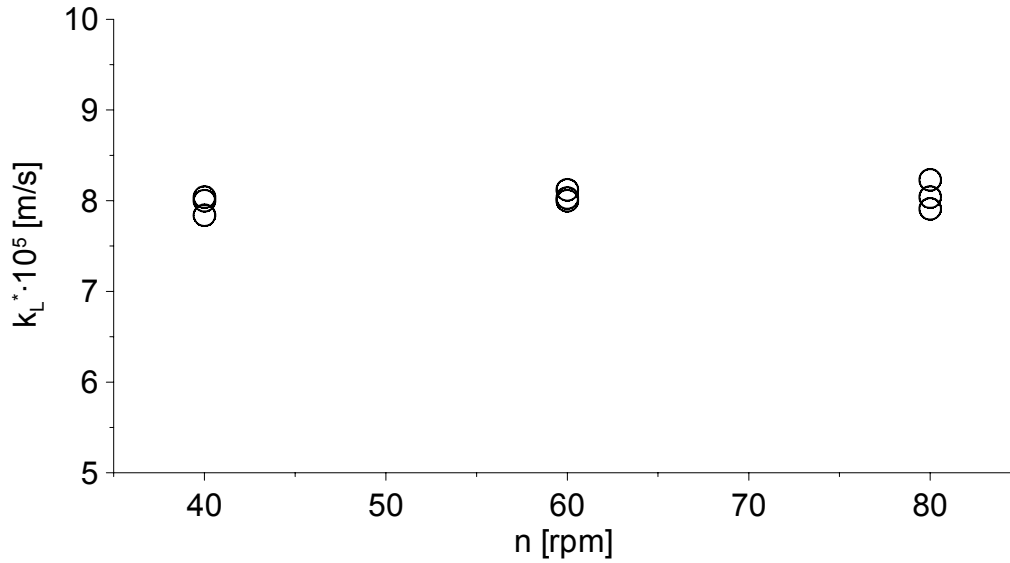


Fig. 3. Dependence of the mass transfer coefficient for absorption with chemical reaction on the stirrer speed (20 mass % MDEA).

As it is seen, the mass transfer coefficient k_L^* practically does not depend on the stirrer speed. In our earlier work [19], it was found, that the physical mass transfer coefficient in the used absorber, k_L , distinctly depends on the stirrer speed. This means that the mass transfer coefficient with chemical reaction, k_L^* does not depend on the physical mass transfer coefficient. The experimental values of the enhancement factor, E , change from 3.6 to 7.8 (Table 3).

For the fast pseudo-first order chemical reaction the following criterion must be satisfied

$$Ha = \frac{\sqrt{D_A k_{21} c_{B0}}}{k_L} = \frac{\sqrt{D_A k}}{k_L} \gg 1 \quad (28)$$

(practically $Ha > 2$)

In order to determine the reaction regime one can use the van Krevelen and Hoftijzer diagram [20]:

$$E = \frac{k_L^*}{k_L} = f(Ha, E_m - 1) \quad (29)$$

where

$$E_m - 1 = \frac{c_{B0}}{b \cdot c_{Ai}} \frac{D_B}{D_A} \quad (30)$$

or the approximate analytical solution (accuracy 10%) [20]

$$E = \frac{Ha \cdot \sqrt{\frac{E_m - E}{E_m - 1}}}{\operatorname{tgh} Ha \cdot \sqrt{\frac{E_m - E}{E_m - 1}}} \quad (31)$$

Making use of the experimental values of the enhancement factor, E , and the calculated values of the enhancement factor for instantaneous reaction, E_m , (Eq. 30) the values of Hatta number were calculated from Eq. (31). The results of calculations are presented in Table 3. As it is seen, the criterion (28) is satisfied (in all experiments $Ha > 2$) and the values of the enhancement factor, E , are practically equal to the values of the Hatta number. It follows that reaction (8) can be treated as a fast pseudo-first order irreversible reaction. The pseudo-first order reaction rate constant is equal to:

$$k = k_{21} \cdot c_{B0} \quad (32)$$

where c_{B0} is a total concentration of MDEA.

The values of the reaction rate constant, k_{21} , were calculated from the relation:

$$k_L^* = \sqrt{D_A \cdot k_{21} \cdot c_{B0}} \quad (33)$$

The results of the calculations are presented in Table 3.

Table 3. Results of experiments and calculations.

No.	c_{B0} kmol/m ³	$k_L^* \cdot 10^5$ m/s	E	$E_m - 1$	Ha	k s ⁻¹	k_{21} m ³ /kmol·s
1	0.846	7.08	3.56	10.21	4.11	4.87	5.76
2	0.846	7.25	3.64	10.21	4.22	5.10	6.03
3	0.846	7.02	3.53	10.02	4.08	4.78	5.65
4	1.707	8.00	4.94	35.33	5.24	9.63	5.64
5	1.707	8.03	4.93	34.95	5.23	9.70	5.68
6	1.707	8.12	4.98	35.72	5.28	9.92	5.81
7	1.707	8.00	5.82	35.57	6.26	9.62	5.64
8	1.707	8.04	5.85	35.57	6.29	9.71	5.96
9	1.707	7.84	5.70	35.77	6.12	9.25	5.42
10	1.707	8.04	3.74	36.07	3.89	9.72	5.69
11	1.707	8.23	3.76	36.07	3.91	10.17	5.96
12	1.707	7.91	3.67	35.14	3.82	9.40	5.51
13	2.560	9.48	7.40	43.96	8.00	13.51	5.28
14	2.560	10.02	7.83	44.39	8.50	15.62	6.11
15	2.560	9.95	7.77	44.08	8.44	14.89	5.82

In Fig. 4 the dependence of the reaction rate constant, k_{21} , on the total amine concentration is shown. These are the values directly determined by the relevant authors at temperature 20°C, or recalculated using the values of energy activation of reaction (8) proposed by these authors. As it is seen, the value of reaction (9) rate constant, k_{21} , is practically constant ($k_{21} \cong 5.7 \text{ m}^3/\text{kmol}\cdot\text{s}$) and does not depend on the total amine concentration. It qualitatively agrees with the data of Tomcej and Otto [15], Rangwale et al. [16] and Versteeg and van Swaaij [11]. According to the Haimour et al. [17] data, reaction rate constant k_{21} slightly decreases when the total amine concentration increases. On the other hand, from the Rinker et al. [13] data, it follows that the reaction rate constant, k_{21} increases when the total amine

concentration increases. The values of the reaction rate constant, k_{21} determined in the present work agree with Benitez-Garcia data [18] for 10% mass MDEA solution as well as with the Rinker et al. [13] data for the 20% mass MDEA solution.

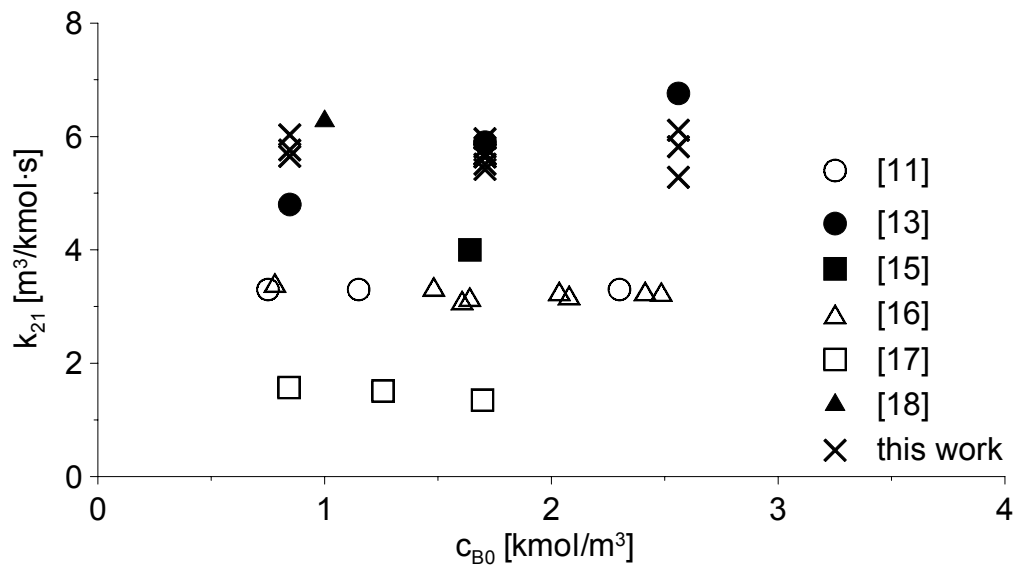


Fig. 4. Dependence of the reaction rate constant on the amine concentration ($t = 20^\circ\text{C}$).

For the measurements of the absorption rate of CO_2 into aqueous MDEA solution (10 mass %). containing respectively 5, 10 and 15 mass % of EAE, the values of the enhancement factor E were calculated. In Fig. 5 the dependence of the enhancement factor on the amine concentration is presented for two runs:

- absorption of CO_2 into aqueous MDEA solutions (10, 20 and 30% mass)
- absorption of CO_2 into aqueous MDEA solution (10% mass) containing EAE (5, 10 and 15% mass).

As it is seen, addition of EAE into the aqueous MDEA solution significantly increases the enhancement factor E , and therefore increases the absorption rate of CO_2 .

CONCLUSIONS

Measurements of the rate of CO_2 absorption into aqueous solutions of MDEA as well as into aqueous solutions of MDEA containing EAE were carried out in a stirred vessel of known interfacial area. The values of the reaction rate constant between CO_2 and MDEA were determined and compared with literature data. It was found that the addition of EAE significantly increases the absorption rate.

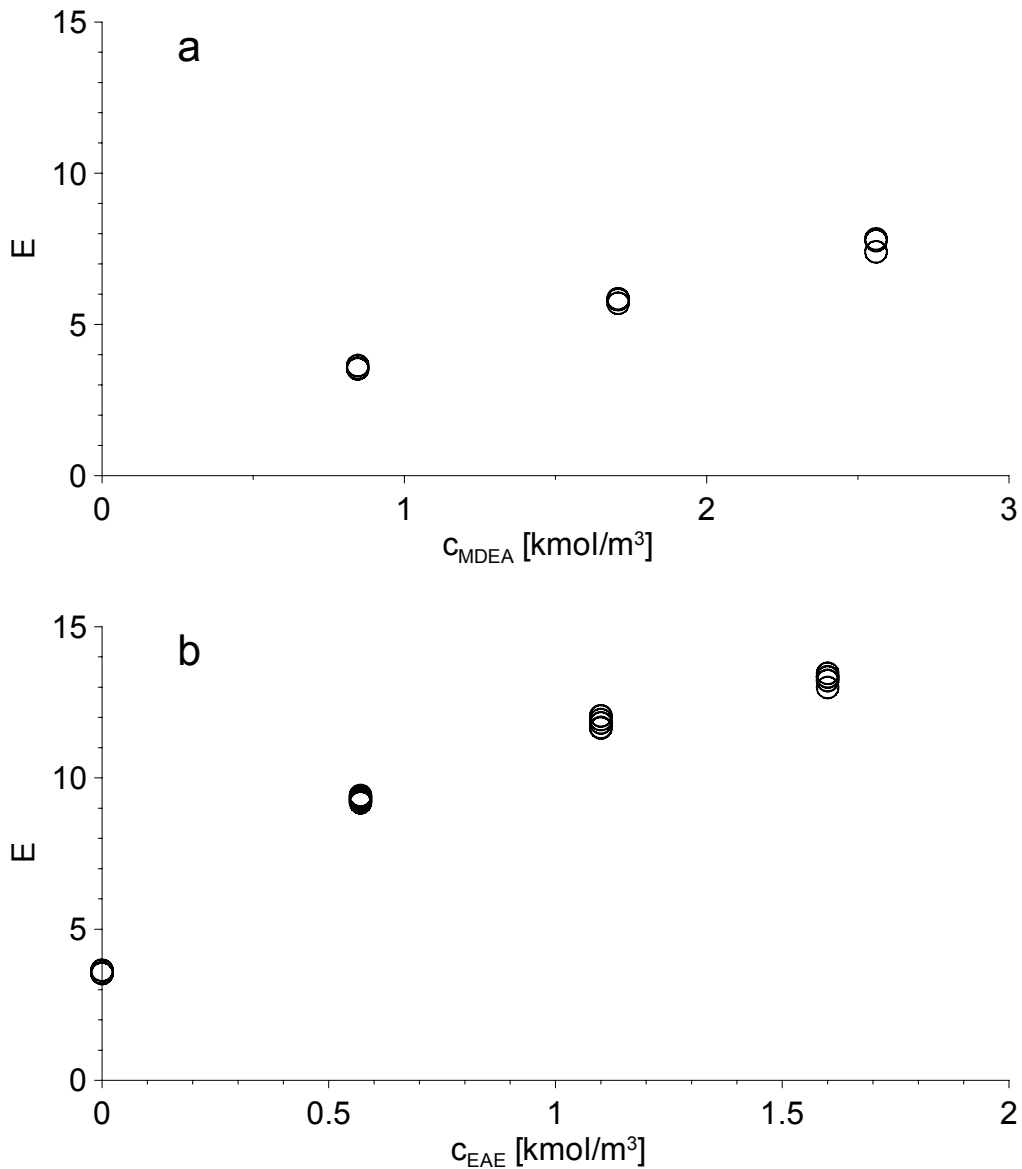


Fig. 5. Dependence of the enhancement factor on the amine concentration ($n = 60$ rpm).

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NOMENCLATURE

- a - interfacial area, m²
- Am - amine
- b - stoichiometric coefficient
- [B] - base concentration, kmol·m⁻³
- c_{Ai} - concentration of the absorbed component at the interface, kmol·m⁻³
- c_{B0} - total concentration of amine, kmol·m⁻³

D_A - diffusion coefficient of the absorbed component in the liquid, $m^2 \cdot s^{-1}$
 D_B - diffusion coefficient of amine in the liquid, $m^2 \cdot s^{-1}$
 DEA - diethanoloamine
 E - enhancement factor
 E_m - enhancement factor for instantaneous reaction
 H - Henry's constant, $atm \cdot m^3 \cdot kmol^{-1}$
 Ha - Hatta number
 k - pseudo-first order reaction rate constant, s^{-1}
 k_1 - reaction (1) rate constant (from the left to the right), $m^3 \cdot kmol^{-1} \cdot s^{-1}$
 k_{-1} - reaction (1) rate constant (from the right to the left), $m^3 \cdot kmol^{-1} \cdot s^{-1}$
 k_{21} - reaction (8) rate constant, $m^3 \cdot kmol^{-1} \cdot s^{-1}$
 k_{22} - reaction (9) rate constant, $m^3 \cdot kmol^{-1} \cdot s^{-1}$
 k_B - reaction (2) rate constant, $m^3 \cdot kmol^{-1} \cdot s^{-1}$
 k_L - physical mass transfer coefficient, $m \cdot s^{-1}$
 k_L^* - mass transfer coefficient for absorption with chemical reaction, $m \cdot s^{-1}$
 K_1 - equilibrium constant of reaction (8)
 K_2 - equilibrium constant of reaction (9), $m^3 \cdot kmol^{-1}$
 K_3 - equilibrium constant of reaction (10), $m^3 \cdot kmol^{-1}$
 K_4 - equilibrium constant of reaction (11), $m^3 \cdot kmol^{-1}$
 K_5 - ionic product of water $kmol^2 \cdot m^{-6}$
 MEA - monoethanoloamine
 MDEA - methyldiethanoloamine
 n - stirrer speed, rpm
 N - molar flux, $kmol \cdot m^{-2} \cdot s^{-1}$
 p_{Ai} - partial pressure at the interface, bar, atm.
 p_{CO_2} - partial pressure of CO_2 , bar, atm.
 r - reaction rate, $kmol \cdot m^{-3} \cdot s^{-1}$
 r_1 - reaction (8) rate $kmol \cdot m^{-3} \cdot s^{-1}$
 r_2 - reaction (9) rate, $kmol \cdot m^{-3} \cdot s^{-1}$
 R - absorption rate, $kmol \cdot s^{-1}$
 R_g - gas constant, $J \cdot mol^{-1} \cdot K^{-1}$
 t - temperature, $^{\circ}C$
 T - absolute temperature, K
 TEA - triethanoloamine
 V_g - volumetric gas flow rate, m^3/s
 [z] - concentrate of zwitterion, $kmol \cdot m^{-3}$

Subscript

m - instantaneous reaction

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KEYWORDS

Carbon dioxide, amines, mass transfer, reaction kinetics, enhancement factor.