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KINETICS OF CARBON DIOXIDE ABSORPTION INTO AQUEOUS MDEA SOLUTIONS

KINETYKA ABSORPCJI CO₂ W WODNYCH ROZTWORACH MDEA

Abstract: The CO₂ absorption rate in aqueous methyldiethanolamine solutions was measured using a stirred cell with a flat gas-liquid interface. The measurements were performed in the temperature range of (293.15 to 333.15) K and amine concentration range of (10 to 20) mass %. Measurements were based on a batch isothermal absorption of the gas. The kinetic experiments were conducted under pseudo-first-order regime. The calculated initial absorption rates enabled to estimate the forward, second order reaction rate constant of CO₂ reaction with MDEA in aqueous solution.

Keywords: CO₂ removal, absorption, methyldiethanolamine, stirred cell

Absorption by aqueous alkanolamine solutions is the dominant industrial process for separation of acid gases such as CO₂ and H₂S, from gas mixtures in natural gas processing, petroleum refining, coal gasification and ammonia manufacturing industries. Another possible application of amine-based technologies is CO₂ separation from the large quantities of flue gases from industrial sources such as fossil-fuel power plants. Since CO₂ is regarded as a greenhouse gas, potentially contributing to global warming, there has been considerable interest in developing effective technologies for its capture, recently. The chemical absorption of CO₂ is generally recognized as the most efficient post-combustion CO₂ separation technology at present. The idea of carbon dioxide sequestration which includes its capture and storage in underground rock formations has progressed steadily over the past ten years. It is claimed that this solution could play an important role in solving the problem of increasing greenhouse gas emissions. As opposed to other capture options which include pre-combustion method and oxy-fuel processes, the post-combustion technology can be fairly installed in the existing power plants while other options involve innovative ways of power generation technology. The amines that have been proved to be of principal commercial interest are monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) [1]. In the last decade interest in using

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methyldiethanolamine, which is a tertiary amine, increased significantly. The main advantages of MDEA as opposed to more traditionally used primary and secondary amines are its relatively high capacity, small enthalpy of reaction with acid gases and a low vapour pressure. Since, the CO₂ reaction rate with MDEA is slow, the addition of small amounts of fast reacting amines is necessary to apply this process in flue gas treatment.

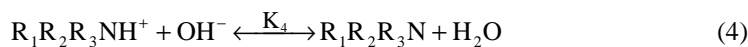
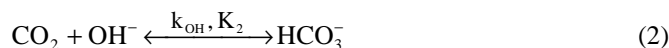
Many studies were performed on the kinetics of the reaction of CO₂ with aqueous MDEA [2-5]. A comprehensive overview on that subject is provided by Vaidya and Kenig [6]. There is an agreement on the reaction mechanism which implies that tertiary amines do not react directly with CO₂. In an aqueous solution, MDEA catalyzes the CO₂ hydration reaction according to the mechanism proposed by Donaldson and Nguyen [7]. However, there are still many discrepancies in the literature concerning the interpretation of the kinetic data.

This causes the relatively high difference in the forward rate coefficient of the MDEA-catalyzed reaction which is ranging from 1.44 m³ kmol s⁻¹ [2] to 5.15 m³ kmol s⁻¹ [3] at 293 K. These discrepancies may be attributed to the different experimental techniques used and the inconsistency of the physical data such as CO₂ solubility and diffusivity applied for interpretation of the absorption rate data. Moreover, there is a disagreement on the effect of the reaction of hydroxide with CO₂ on the measured rate of CO₂ absorption into aqueous MDEA solutions [6].

In the present paper, additional data on the kinetics of the reaction between CO₂ and aqueous MDEA solutions are reported. The CO₂ absorption rate in aqueous MDEA solutions was measured using a stirred cell with a flat gas-liquid interface. The measurements were performed in the temperature range of (293.15 to 333.15) K and amine concentration range of (10 to 20)% mass MDEA. The obtained results were applied to determine the initial CO₂ absorption rate. A simplified film model, which assumes that the reaction between CO₂ and MDEA is irreversible, has been applied for interpreting the experimental data and estimation of the reaction rate coefficient.

Theory

In accordance with the convention used in the amine literature, MDEA is represented as R₁R₂R₃N, where R₁ = R₂ = CH₂CH₂OH and R₃ = CH₃. When CO₂ is absorbed in aqueous MDEA solutions, the following reactions may occur in the liquid phase [3]:



where: k_2 , k_{OH} - forward second order rate constants, K_i - equilibrium constant of reaction „i”.

Reactions (1)-(2) are taking place with the finite rates which are described by the forward second order rate constants k_2 i k_{OH} and equilibrium constants K_1 and K_2 . Reactions

(3)-(5) are instantaneous with respect to mass transfer as they involve only a proton transfer. Kinetics of direct reaction of CO_2 with OH^- is firmly established [8], however its influence on the absorption rate should be considered vary carefully as the reaction of CO_2 with OH^- may have a significant contribution to the observed reaction rate, especially at very low partial pressure [3].

Versteeg et al [9] concluded that in a large number of studies of CO_2 -MDEA system with an absorption technique, the influence of the OH^- reaction with CO_2 is overestimated due to the presence of other negative charged ions like HCO_3^- and CO_3^{2-} . Littel et al [10] and Moniuk et al [11] claim that the effect of this reaction is negligible due to the low concentration of the hydroxide ions in the solution. According to the numerical simulation of Rinker et al [3] and Glasscock and Rochelle [12] only at low CO_2 concentrations, corresponding to low CO_2 partial pressure, the hydroxide reaction has the largest effect and must be taken into account in predicting the second order reaction rate constant k_2 . As the partial pressure is increasing, the hydroxide becomes depleted in the boundary layer and MDEA has a major contribution to the absorption rate. Shi and Zhong [13] demonstrated that in order to obtain the true kinetics of reaction (1), the rigorous mathematical model should be applied for interpreting the absorption rate data. They claim that a better prediction of the CO_2 absorption rate is achieved while applying a model according to a more realistic kinetic mechanism where all chemical reactions are taking into account and treated as reversible, especially at high temperatures.

In the present work, the simplified kinetic model was applied which assumes that the main reaction (1) of CO_2 with MDEA is irreversible and the contribution of reaction (2) on the mass transfer rate is negligible. The conditions for the absorption of CO_2 in MDEA solutions were selected in such a way as to ensure that the absorption occurs in the fast pseudo-first order reaction regime. After these assumptions, the total rate of CO_2 reaction in an aqueous solution of MDEA may be expressed as:

$$r_{\text{ov}} = k_2 [\text{MDEA}] [\text{CO}_2] = k_{\text{ov}} [\text{CO}_2] \quad (6)$$

The overall reaction kinetic constant k_{ov} is defined as:

$$k_{\text{ov}} = k_2 [\text{MDEA}]_0 \quad (7)$$

where $[\text{MDEA}]_0$ states for the initial MDEA concentration in the solution.

Experimental

Apparatus

The measurements were performed in the heat flow reaction calorimeter (Chemical Process Analyser, Chemsens AB, Sweden) which is a fully automated and computer-controlled stirred reactor vessel with possibility of an on-line measurement of thermal power developed by the process. The reactor is a cylindrical, double walled glass vessel with an effective volume of 250 cm^3 . It is capped, top and bottom, with stainless steel 316. The reactor lid holds the shaft seal and the necessary armature for charging and sampling both from gas and liquid phases. The schematic diagram of an experimental set-up is shown in Figure 1.

The reactor was equipped with four stainless steel baffles and an impeller stirrer. While in use it is submerged in the thermostating liquid bath. A Peltier element mounted inside the

bottom of the reactor serves as an efficient heating and cooling device and keeps temperature constant to ± 0.1 K. The absolute pressure was measured by a pressure transducer mounted on the reactor flange. A separate tube on the top flange allows either to evacuate the cell or to introduce a gas into the reactor. The measurement accuracy of the digital pressure transducer was 0.1% of the full range of (0–2000) kPa. The gas-liquid interface, A, was flat and could be geometrically estimated.

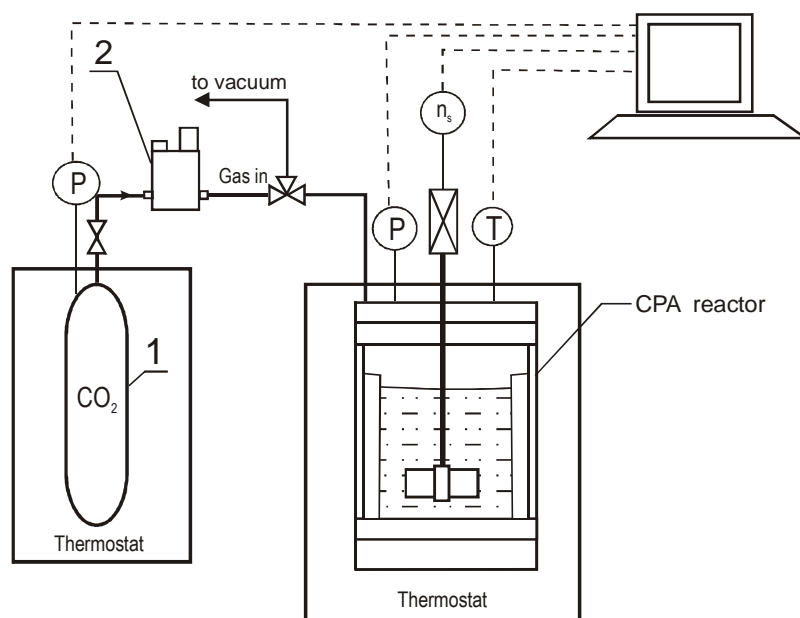


Fig. 1. Experimental set-up: 1 - storage tank; 2 - downstream pressure regulator; n_s - stirring speed transducer; T - temperature sensors; P - pressure transducers

Procedure

A series of experiments was conducted at temperature range of (293–333 K). The initial MDEA concentration in the aqueous solution was varied in the range of $0.83\text{--}1.7$ kmol/m³ which corresponds to amine weight fraction from 10 to 20 mass %. In each experiment, the reactor was charged with 100 cm³ of the alkanolamine solution. After the reactor was filled with the desired solution, the liquid was degassed and heated to the set temperature under stirring conditions. When the thermal equilibrium was established eg the temperature in the reactor became constant to ± 0.01 K, the stirring was stopped for a moment. Pure gas from the CO₂ reservoir was then introduced during a very short time in the upper part of the cell. The resulting initial pressure in the range of (25–110) kPa was set by the back pressure regulator (Brooks, 5866). Then the absorption process was initiated by switching on the stirrer at the desired stirring speed. The decrease in the system pressure due to absorption of the gas was monitored by the pressure transducer and the “ p_{CO_2} vs t ” data were recorded as a function of time until the gas-liquid equilibrium state was reached.

The initial “ p_{CO_2} vs t ” data from $t = 0$ to 60 s were plotted and the absorption rate was calculated from the value of the slope ($-dp_{\text{CO}_2}/dt$). This method based on the fall-in-pressure technique was used previously by other investigators [5, 10, 14] and enabled a simple and straightforward estimation of the absorption rates. The main advantage of the present experimental technique is that no analysis of the liquid phase is required and the recorded pressure decrease versus time was the only parameter necessary for the evaluation of absorption kinetics.

The CO_2 partial pressure in the reactor, p_A , was calculated according to the total pressure in the system P measured by the pressure transducer, corrected for solution vapour pressure by use of Raoult's law. In these calculations, the amine vapour pressure was neglected, as it was very small as compared with the solvent vapour pressure.

The experiments were carried out at three temperatures: 293.15, 313.15 and 333.15 K and with partial pressure of CO_2 in the range of (25÷110) kPa. The chemicals employed, CO_2 (L'Air Liquide, 99.995 vol % pure) and MDEA (Fluka, 99 mass % pure) were used without any further purification. Alkanolamine aqueous solutions were prepared from the distilled, deionized water. Experiments were performed with initial CO_2 loadings of the solutions equal to zero.

The solution volume was maintained at (100 ± 0.1) cm^3 in each experiment. The respective mass of the solutions was determined within ± 0.01 g. In the range of stirring speed of 100÷180 min^{-1} , the absorption rate was independent of the stirring speed indicating a pseudo-first-order regime. Thus, in the present work all experimental runs were performed at a constant stirring speed of 120 min^{-1} . Mixing of the liquid under such a stirring speed did not affect the smoothness of the gas liquid interface which could be easily estimated.

Results and discussion

In order to determine the kinetic parameters in the stirred cell using the pressure drop technique, it is essential that the absorption process takes place in the fast reaction regime, without depletion of the amine at the gas-liquid interface [15]. The necessary condition for the fast pseudo-first-order reaction regime is:

$$3 < \text{Ha} \ll E_i \quad (8)$$

where Hatta number is based on reaction (1) and is given by:

$$\text{Ha} = \frac{\sqrt{k_{ov} D_{\text{CO}_2}}}{k_L} \quad (9)$$

E_i is the enhancement factor for an irreversible instantaneous reaction and defined as follows:

$$E_i = 1 + \frac{D_{\text{MDEA}} [\text{MDEA}]}{v_{\text{MDEA}} D_{\text{CO}_2} [\text{CO}_2]_i} \quad (10)$$

where v_{MDEA} is the stoichiometric coefficient of amine in reaction (1).

In the case of the present experimental technique, for a given temperature and amine concentration, the Hatta numbers and enhancement factors may be varied by changing the liquid mass transfer coefficient, k_L and CO_2 partial pressure, respectively.

The general expression for CO₂ absorption rate has the following form:

$$N_{\text{CO}_2} = E_A k_L ([\text{CO}_2]_i - [\text{CO}_2]) \quad (11)$$

where N_{CO_2} is expressed in $[\text{kmol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}]$, k_L $[\text{m}/\text{s}]$ is the mass transfer coefficient of CO₂ in the liquid phase, $[\text{CO}_2]_i$ and $[\text{CO}_2]$ $[\text{kmol}/\text{m}^3]$ are the interfacial and bulk CO₂ concentrations, respectively. The enhancement factor E_A describes the influence of a chemical reaction on the mass transfer rate. The enhancement factor is defined as the ratio of the absorption rate of a gas in the liquid in the presence of a chemical reaction to the absorption rate in the absence of a reaction at identical concentration differences of the absorbing gas between the interface and the liquid bulk. When condition (8) is satisfied, the enhancement factor E_A is equal to the Ha number:

$$E_A = \text{Ha} \quad (12)$$

The bulk CO₂ concentration at the initial state of the batch absorption run is equal to zero as the aqueous MDEA solutions used in the absorption experiments were not initially loaded with CO₂. Thus, the specific rate of mass transfer of CO₂ becomes:

$$N_{\text{CO}_2} = \sqrt{k_{ov} D_{\text{CO}_2}} [\text{CO}_2]_i \quad (13)$$

As can be seen from eq. (13), in the pseudo-first-order chemical absorption regime, the absorption rate is independent of the liquid side mass transfer coefficient k_L and hence it should not depend on the stirring speed. Under the present experimental conditions, no change in the absorption rate was observed while varying the stirring speed in the range of 100–180 rpm. Hence, it was preliminary assumed that the CO₂ absorption takes place under fast pseudo-first-order regime.

The interfacial concentration of CO₂ can be obtained from Henry's law:

$$[\text{CO}_2]_i = \frac{p_{\text{CO}_2}}{\text{He}} \quad (14)$$

where p_{CO_2} $[\text{Pa}]$ is the CO₂ partial pressure and He $[\text{Pa}\cdot\text{m}^3/\text{mol}]$ is the Henry's law constant of CO₂ in aqueous MDEA.

After taking into account the eq. (14), eq. (13) is further transformed to:

$$N_{\text{CO}_2} = \frac{\sqrt{k_{ov} D_{\text{CO}_2}}}{\text{He}} p_{\text{CO}_2} \quad (15)$$

The eq. (15) is the basis for the interpretation of the measured absorption rate data. In the fast pseudo-first-order regime, it is possible to determine the overall reaction kinetic rate constant, k_{ov} knowing He and D_{CO_2} for CO₂ in the amine.

The CO₂ absorption rate can be calculated from the experimental data by the mass balance in the reactor gas phase according to:

$$-\frac{V_G}{R \cdot T \cdot A} \frac{dp_{\text{CO}_2}}{dt} = N_{\text{CO}_2} \quad (16)$$

where V_G $[\text{m}^3]$ is the gas phase volume in the reactor, T $[\text{K}]$ is the temperature, R $[\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}]$ is a gas constant and A $[\text{m}^2]$ is the gas-liquid interfacial area. In eq. (16), the ideal gas equation was applied.

For the calculation of the overall reaction kinetic rate constant and interpretation of the absorption rate data, many physicochemical properties of the system under consideration are required. The viscosities of MDEA aqueous solutions and Henry's constants for CO₂ were obtained with the correlation proposed by Glasscock [16]. The diffusion coefficient of MDEA was estimated according to the correlation proposed by Pani et al [17]. The diffusion coefficient of CO₂ in aqueous MDEA is calculated according to the modified Stokes-Einstein relation proposed by Versteeg and van Swaaij [18]. The densities of MDEA aqueous solutions were obtained from Rinker et al [19]. The computed physicochemical properties are summarized in Table 1.

Table 1

Physicochemical properties of CO₂-MDEA-H₂O system

T [K]	$\eta \times 10^3$ [Pa·s] [16]	
	10 mass %	20 mass %
293	1.459	2.19
313	0.931	1.37
333	0.608	0.824
	$D_{\text{MDEA}} \times 10^9$ [m ² /s] [17]	
293	0.564	0.443
313	0.896	0.7098
333	1.43	1.19
	$D_{\text{CO}_2} \times 10^9$ [m ² /s] [18]	
293	1.27	0.923
313	2.03	1.48
313	3.29	5.28
	He [MPa m ³ /kmol] [16]	
293	2.71	2.91
313	4.43	4.65
333	6.08	6.21
	ρ [kg/m ³] [19]	
293	1008.1	1017.3
313	1000.7	1009.3
333	993.3	1001.3

The value of physical mass transfer coefficient, k_L attainable in the experimental apparatus is an important parameter in identifying chemical absorption regime. The mass transfer characteristics were investigated by measuring physical absorption rates for CO₂ in water and N₂O in aqueous MDEA solutions under various operating conditions. The results obtained were correlated as:

$$\text{Sh} = 0.3929\text{Re}^{0.6632}\text{Sc}^{0.33} \quad (17)$$

where Sh, Re and Sc are, respectively the Sherwood, Reynolds and Schmidt dimensionless numbers defined as:

$$\text{Sh} = \frac{k_L d_s}{D_{\text{CO}_2}} \quad (18)$$

$$\text{Re} = \frac{n_s d_s^2 \rho}{\eta} \quad (19)$$

$$Sc = \frac{\eta}{\rho D_{CO_2}} \quad (20)$$

where d_s and n_s are the dimension and the speed of the stirrer, respectively.

From eq. (15) the overall pseudo-first-order constant k_{ov} can be estimated from measured CO_2 absorption rates, assuming that the condition (8) is met. It should be noted however, that one of the most important drawback of this method is that a priori information is required on the values of the liquid side mass transfer coefficient k_L and a rate constant k_{ov} . Otherwise, neither the lower limit of $Ha > 3$ cannot be estimated nor the fulfilling of condition (8).

The CO_2 absorption rates in MDEA aqueous solutions at various temperatures and initial amine concentrations are presented in Table 2.

Table 2

CO_2 absorption rates into aqueous solutions of MDEA ($n_s = 120 \text{ min}^{-1}$)

Temperature	[MDEA] ₀	$k_L \times 10^5$	p_{CO_2}	$N_{CO_2} \times 10^6$
[K]	[kmol/m ³]	[m/s]	[kPa]	[kmol/(m ² s)]
293	0.845	2.02	108.3	2.32
			97.0	2.22
			93.0	2.06
			86.0	1.87
			67.5	1.53
			42.5	0.99
			33.8	0.93
			34.9	1.05
293	1.706	1.43	67.4	1.62
			59.0	1.55
			52.3	1.38
313	0.840	3.19	46.8	1.23
			77.1	2.66
			58.2	2.21
			55.6	1.93
			43.9	1.68
313	1.694	2.28	36.4	1.39
			88.0	3.61
			57.8	2.19
			37.8	1.60
			35.9	1.66
333	0.834	5.07	34.7	1.40
			51.1	2.68
			46.2	2.24
			42.7	2.11
333	1.681	3.91	33.9	1.77
			52.3	3.11
			48.2	2.96
			43.7	2.49
			26.0	1.82

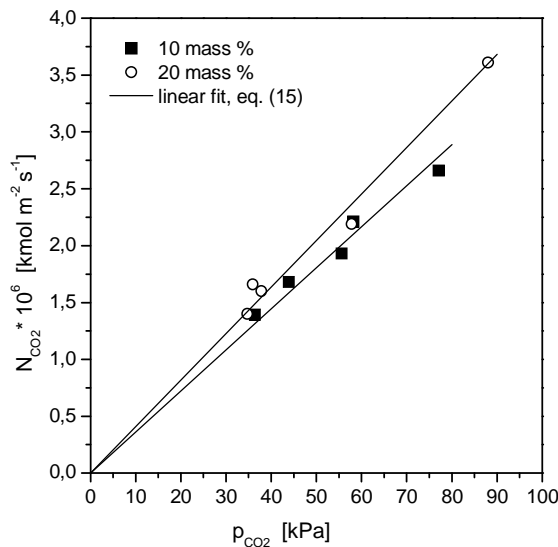
For measurements performed at a given temperature and MDEA concentration, the Hatta number is constant at the given stirring speed. Changing the CO_2 partial pressure in the reactor within the applied range of (25÷110) kPa, changes the infinite enhancement factor E_i which consequently can change the absorption regime. If the reaction takes place

under fast reaction regime under certain conditions, the CO_2 absorption rate N_{CO_2} vs p_{CO_2} should yield the straight line with the slope related to k_{ov} . Thus, plotting experimental N_{CO_2} as a function of p_{CO_2} in the fast reaction regime, should give a straight line passing through the origin at a given temperature and amine concentration and would enable calculation of the combined parameter $\sqrt{k_{\text{ov}}D_{\text{CO}_2}}/\text{He}$. Such plots at 313 K for two amine concentrations are shown in Figure 2. From the slope of the fitted line for 10 mass % MDEA, $\sqrt{k_{\text{ov}}D_{\text{CO}_2}}/\text{He}$ at 313 K was found to be equal to $3.61 \cdot 10^{-5} [\text{kmol m}^{-2} \text{s}^{-1} \text{MPa}^{-1}]$. Using the values of D_{CO_2} and He given in Table 1, the second order rate constant k_2 of $15.02 \text{ m}^3/(\text{kmol}\cdot\text{s})$ was subtracted from this combined parameter. The overall and second order kinetic rate constants were calculated using the described methodology for 10 and 20 mass % MDEA at each temperature. Table 3 shows the computed results of combined parameter and k_2 .

Table 3

Experimental results of k_2 determination

Temperature	[MDEA] ₀	$\sqrt{k_{\text{ov}}D_{\text{CO}_2}}/\text{He}$	k_{ov}	k_2	k_2 , average
[K]	[kmol/m ³]	[kmol m ⁻² s ⁻¹ MPa ⁻¹]	[1/s]	[m ³ /(kmol s)]	[m ³ /(kmol s)]
293	0.85	2.21×10^{-5}	2.83	3.35	3.43
293	1.71	2.55×10^{-5}	5.98	3.51	
313	0.84	3.61×10^{-5}	12.61	15.02	14.67
313	1.69	4.09×10^{-5}	24.27	14.33	
333	0.83	5.06×10^{-5}	31.84	38.20	38.11
333	1.68	6.03×10^{-5}	63.89	38.02	

Fig. 2. The absorption rate as a function of CO_2 partial pressure at 313 K - determination of k_{ov}

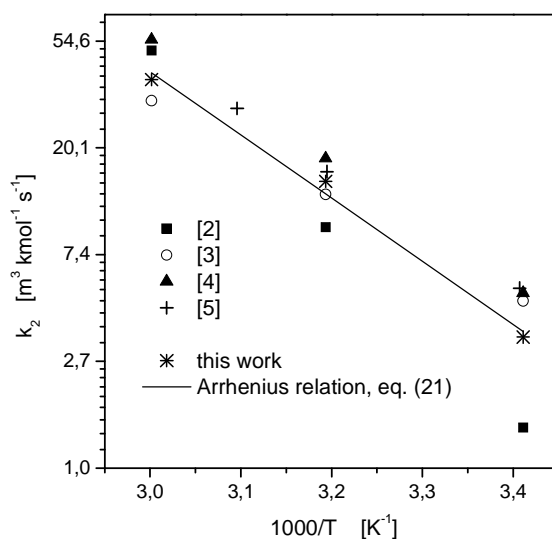


Fig. 3. Comparison of the second-order rate constant for CO₂-MDEA reaction determined in this work with those reported in the literature

Once the values of k_2 were obtained, the values of Ha and E_i were calculated for all the experiments. The Hatta numbers vary from the lowest value of 3.1 (for 10 mass % MDEA at 293 K) to the highest one of 10.4 (for 20 mass % MDEA at 333 K). The instantaneous enhancement factors E_i strongly depend on the applied pressure and vary from 11 to 110 corresponding to the lowest pressure. Enhancement factors for instantaneous reaction are a few times higher than the values of Hatta numbers. The condition given by eq. (8) was found to be satisfied for all the experiments. Thus, the preliminary assumption of fast pseudo-first-order regime was justified in the present study and eq. (15) is valid for interpretation of the measured absorption rate. However, it is noticeable that the Hatta number for 10 mass % MDEA at 293 K is very close to the lower limit of that number above which the reaction can be treated as a fast pseudo-first-order reaction.

The estimates of k_2 are plotted in Figure 3 for comparison with selected literature values. The values of k_2 obtained in this work are in good agreement with those derived by Rinker et al [3] over the whole temperature range. As shown in Figure 3, the k_2 of Jamal et al [4] and Benamour et al [5] are slightly higher than the present ones. The results of Haimour et al [2] are significantly smaller than other literature values and those determined in this work for $T < 313$ K. The observed discrepancies may come from the different absorption apparatus and the assumptions involved while interpreting the observed overall kinetic rate constant.

The estimates of k_2 are fitted by the following Arrhenius equation:

$$k_2 [\text{m}^3 \text{kmol}^{-1} \text{s}^{-1}] = 2.07 \times 10^9 \exp(-5912.7/T) \quad (21)$$

The activation energy, as determined from eq. (21) has been found to be 49.16 kJ/mol.

Conclusions

The CO₂ absorption rate in aqueous methyldiethanolamine solutions was measured using a stirred cell with a flat gas-liquid interface. The apparatus was operating batchwise with respect to both the gas and liquid phases. Data were obtained over the temperature range 293–333 K and for MDEA concentrations ranging from 10 to 20 mass %.

In the present work, the simplified kinetic model was applied which assumes that the main reaction (1) of CO₂ with MDEA is irreversible and the contribution of CO₂ reaction with OH⁻ ions is negligible on the rate of mass transfer. The conditions for the absorption of CO₂ in MDEA solutions were selected in such a way as to ensure that absorption occurs in the fast pseudo-first order reaction regime. The experimental absorption data obtained in this study were interpreted to give an overall rate constant. Based on the assumptions made, the second order rate constants of CO₂ reaction with MDEA were determined. New data for the k_2 were found to be in a good agreement with published values. The activation energy for the second order rate constant was determined to be 49.16 kJ/mol.

Notation

A	gas-liquid interfacial area [m ²]	
c	concentration [mol·m ⁻³]	
D _i	diffusion coefficient of species i in liquid phase [m ² ·s ⁻¹]	
d _s	turbine diameter [m]	
E _i	infinite enhancement factor	
E _A	enhancement factor	
Ha	Hatta number	
He	Henry's law constant for CO ₂ [Pa·m ³ ·mol ⁻¹]	
k _L	liquid side mass transfer coefficient of dissolved CO ₂ [m·s ⁻¹]	
k _{ov}	the overall rate constant [s ⁻¹]	
k ₂	second-order rate constant of reaction (1) [m ³ ·kmol ⁻¹ ·s ⁻¹]	
K	equilibrium constant	
n _s	stirring speed [s ⁻¹]	
p	partial pressure [Pa]	
N _{CO₂}	absorption rate of CO ₂ [kmol·m ⁻² ·s ⁻¹]	
Re	Reynolds number	
r	chemical reaction rate [kmol·m ⁻³ ·s ⁻¹]	
Sc	Schmidt number	
Sh	Sherwood number	
t	time [s]	
T	temperature [K]	
R	universal gas constant 8.314 J/(mol·K)	
V	volume [m ³]	
		Greek letters
ρ	solution density [kg·m ⁻³]	
η	solution viscosity [Pa·s]	
		Subscripts
i	gas-liquid interface	

0	initial state
CO ₂	carbon dioxide
G	gas phase
L	liquid phase
MDEA	methyldiethanolamine

References

- [1] Kohl A.L. and Nielsen R.: Gas Purification, 5th ed. Gulf Publishing, Houston 1997.
- [2] Haimour N., Bidarian A. and Sandall O.: *Kinetics of the reaction between carbon dioxide and methyldiethanolamine*. Chem. Eng. Sci., 1987, **42**, 1393-1398.
- [3] Rinker E.B., Ashour S.S. and Sandall O.C.: *Kinetics and modeling of carbon dioxide absorption into aqueous solutions of N- methyldiethanolamine*. Chem. Eng. Sci., 1995, **50**, 755-768.
- [4] Jamal A., Meisen A. and Jim Lim C.: *Kinetics of carbon dioxide absorption and desorption in aqueous alkanolamine solutions using a novel hemispherical contactor. I. Experimental apparatus and mathematical modeling*. Chem. Eng. Sci., 2006, **61**, 6571-6589.
- [5] Benamor A. and Aroua M.K.: *An experimental investigation on the rate of CO₂ absorption into aqueous methyldiethanolamine solutions*. Kore. J. Chem. Eng., 2007, **24**(1), 16-23.
- [6] Vaidya P.D. and Kenig E.Y.: *CO₂-alkanolamine reaction kinetics: A review of recent studies*. Chem. Eng. Tech., 2007, **30**(11), 1467-1474.
- [7] Donaldson T.L. and Nguyen Y.N.: *Carbon dioxide reaction and transport into aqueous amine membranes*. Ind. Eng. Chem. Fundam., 1980, **19**, 260-266.
- [8] Pinsent J.P. and Roughton J.: *The kinetics of combination of carbon dioxide with hydroxide ions*. Trans. Faraday Soc., 1956, **52**, 1512-1516.
- [9] Versteeg G.F., Van Dijk L.A.J. and Van Swaaij W.P.M.: *On the kinetics between CO₂ and alkanolamines both in aqueous and non-aqueous solutions. An overview*. Chem. Eng. Comm., 1996, **144**, 133-158.
- [10] Littell R.J., Versteeg G.F. and van Swaaij W.P.M.: *Kinetics of CO₂ with tertiary amines in aqueous solution*. A.I.Ch.E.J., 1992, **36**, 1633-1640.
- [11] Moniuk W. and Pohorecki R.: *Absorpcja CO₂ w wodnych roztworach N-metylodwuetanoloaminy*. Inż. Chem. Proces., 2000, **21**, 183-197.
- [12] Glasscock D.A. and Rochelle G.T.: *Numerical simulation of theories for gas absorption with chemical reaction*. AIChE J., 1989, **35**(8), 1271-1281.
- [13] Shi Y. and Zhong Z.: *A rigorous model for absorption of carbon dioxide into aqueous N-methyldiethanolamine solution*. Chem. Eng. Comm., 2005, **192**(7-9), 1180-1193.
- [14] Vaidya P.D. and Kenig E.Y.: *Absorption of CO₂ into aqueous blends of alkanolamines prepared from renewable resources*. Chem. Eng. Sci., 2008, **62**(24), 7344-7350.
- [15] Doraiswamy L.K. and Sharma M.M.: Heterogenous Reaction: Analysis, Examples, and Reactor Design. Vol. 2, 1st ed. Wiley, New York 1984.
- [16] Glasscock D.A.: Modeling and experimental study of carbon dioxide absorption into aqueous alkanolamines. PhD Dissertation. The University of Texas at Austin, 1990.
- [17] Pani F., Gaunand A., Cadours R., Bouallou C. and Richon D.: *Kinetics of absorption of CO₂ in concentrated aqueous methyldiethanolamine solutions in the range 296 K to 343 K*. J. Chem. Eng. Data, 1997, **42**, 353-359.
- [18] Versteeg G.F. and van Swaaij W.P.M.: *Solubility and diffusivity of acid gases (CO₂ and N₂O) in aqueous alkanolamine solutions*. J. Chem. Eng. Data, 1988, **33**, 29-34.
- [19] Rinker E.B., Oelschlager D.W., Colussi A.T., Henry K.R., and Sandale O.C.: *Viscosity, density, and surface tension of binary mixtures of water and N- methyldiethanolamine and water and diethanolamine and tertiary mixtures of these amines with water over the temperature range 20-100°C*. J. Chem. Eng. Data, 1994, **39**, 392-395.

KINETYKA ABSORPCJI CO₂ W WODNYCH ROZTWORACH MDEA

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Abstrakt: Metody absorpcyjne usuwania CO₂ z wielu mieszanin gazowych mają szerokie zastosowanie przemysłowe. W niniejszej pracy wykonano pomiary szybkości absorpcji CO₂ w wodnych roztworach metyldietanoloaminy w reaktorze zbiornikowym z mieszadłem z płaską powierzchnią kontaktu. Pomiary wykonano w zakresie temperatur (293,15÷333,15) K i stężeń (10÷20)% mas. MDEA. Absorpcję realizowano w warunkach okresowych w stosunku do fazy ciekłej i gazowej. Stwierdzono, że w warunkach doświadczenia absorpcja przebiegała w reżimie szybkiej reakcji chemicznej pseudopierwszego rzędu. Na podstawie zmierzonej szybkości procesu w chwili początkowej wyznaczono stałe szybkości drugorzędowej reakcji CO₂ w roztworze MDEA. Otrzymane wartości stałej szybkości reakcji skorelowano za pomocą równania Arrheniusa.

Słowa kluczowe: usuwanie CO₂, absorpcja, metyldietanoloamina, reaktor z mieszadłem