# REACTION KINETICS OF $CO_2$ IN AQUEOUS METHYLDIETHANOLAMINE SOLUTIONS USING THE STOPPED-FLOW TECHNIQUE

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The kinetics of the reaction between $CO_2$ and methyldiethanolamine in aqueous solutions have been studied using the stopped-flow technique at 288, 293, 298 and 303 K. The amine concentration ranged from 250 to 875 mol·m$^{-3}$. The overall reaction rate constant was found to increase with amine concentration and temperature. The acid base catalysis mechanism was applied to correlate the experimentally determined kinetic data. A good agreement between the second order rate constants for the $CO_2$ reaction with MDEA computed from the stopped-flow data and the values reported in the literature was obtained.

Keywords: $CO_2$ capture, reaction kinetics, methyldiethanolamine, stopped-flow technique

## 1. INTRODUCTION

Absorption by aqueous alkanolamine solutions is the dominant industrial process for separation of acid gases such as $CO_2$ and $H_2S$ from gas mixtures in natural gas processing, petroleum refining, coal gasification and ammonia manufacturing industries. Another possible application of amine-based technologies is $CO_2$ capture from large quantities of flue gases from fossil-fuel power plants classified as the post-combustion method. As opposed to other capture options which include pre-combustion methods and oxy-fuel processes, the post-combustion technology can be freely installed in the existing power plants while other options involve innovative ways of power generation technology. However, the application of amine based technologies for separation of $CO_2$ from flue gases is faced with a number of technical challenges. The major disadvantage of this method is its high energy requirements associated with the regeneration of the solvent, thereby affecting the reduction of the energy efficiency by about 9-11 absolute percentage points, depending on the solvent used (Figueroa et al., 2008; Notz et al., 2011; Steeneveldt et al., 2006).

The solvents that have been proven to be of principal commercial interest are primary amines: monoethanolamine (MEA) and giglycolamine (DGA), the secondary amines: diethanolamine (DEA) and diisopropanolamine (DIPA) and the tertiary amines: methyldiethanolamine (MDEA) and triethanolamine (TEA) (Kohl and Riesenfeld, 1997; Vaidya and Kenig, 2007). In the last decade, interest in using methyldiethanolamine increased significantly. The main advantages of MDEA over the extensively used MEA are its relatively high capacity, small enthalpy of reaction with $CO_2$ and a low vapour pressure. Other worthy properties of MDEA include higher resistance to degradation and fewer corrosion problems compared to MEA. MDEA has, however, low reactivity with respect to $CO_2$ due to its tertiary amine characteristics.

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The primary and secondary alkanolamines react directly and reversibly with $CO_2$ through the formation of a zwitterion intermediate which is deprotonated by the bases present in the solution to form a stable carbamate. The formation of carbamate increases the reaction rate but limits the loading to 0.5 mol $CO_2$/mol amine. In contrast, tertiary alkanolamines do not react directly with $CO_2$ to form carbamates. In aqueous solutions, tertiary amines catalyse $CO_2$ hydrolysis to form bicarbonate ions and the protonated amine as was firstly proposed by Donaldson and Nguyen (Donaldson and Nguyen, 1980). Tertiary amines have a high $CO_2$ loading capacity of 1 mol $CO_2$/mol amine. The reaction heat released in bicarbonate formation is lower than that of carbamate formation, thus resulting in lower solvent regeneration costs. On the other hand, the formation of bicarbonate ions is relatively slow compared to the carbamate ion formation, so the kinetics of $CO_2$ removal by tertiary amines is generally slower than that for primary and secondary amines (Vaidya and Kenig, 2007). Several works revealed that an addition of a small amount of fast reacting amines to conventional tertiary amines presents the advantage of combining high $CO_2$ absorption capacity of tertiary amines and an elevated absorption rate of additives (Ramachandran et al., 2006; van Loo et al., 2007; Zhang et al., 2002).

The kinetics of the reaction of $CO_2$ with aqueous MDEA was widely investigated (Haimour et al., 1987; Jamal et al., 2006; Kierzkowska-Pawlak and Chacuk, 2010; Ko and Li, 2000; Littel et al., 1990; Moniuk and Pohorecki, 2000; Pani et al., 1997; Rinker et al., 1995) using several experimental techniques. Kinetic data of the reaction between $CO_2$ and aqueous MDEA available in the literature are summarised in Table 1. There is a general agreement that tertiary amines act as catalysts for $CO_2$ hydrolysis reaction. However, there are still many discrepancies in the literature concerning the interpretation of kinetic data. This causes a relatively high difference in the forward rate constant of the MDEA-catalyzed reaction which is ranging from 1.44 $m^3$ kmol $s^{-1}$ (Haimour et al., 1987) to 5.15 $m^3$ kmol $s^{-1}$ (Jamal et al., 2006) at 293 K. Some of these discrepancies in the reported rate constants may be attributed to various experimental techniques and the assumptions made as well as the inconsistency of the physical data such as $CO_2$ solubility and diffusivity applied to interpret absorption rate data.

Table 1. Selected literature data on the reaction between $CO_2$ and aqueous MDEA

| Reference | $T$, K | [MDEA], kmol/$m^3$ | $k_2$, $m^3$ kmol$^{-1}$s$^{-1}$ | Experimental technique |
|---|---|---|---|---|
| Haimour et al., 1987 | 288-308 | 0-1.7 | $8.741 \times 10^{12} \exp(-8625/T)$ | laminar liquid jet |
| Rinker et al., 1995 | 293-423 | 0.83-2.5 | $2.91 \times 10^{7} \exp(-4579/T)$ | wetted-sphere absorber |
| Pani et al., 1997 | 296-343 | 0.83−4.38 | $2.07 \times 10^{9} \exp(-5912.7/T)$ | stirred cell |
| Littel et al., 1990 | 293-333 | 0.2-3 | $1.2919 \times 10^{9} \exp(-5760.56/T)$ | stirred cell |
| Ko and Li, 2000 | 303-313 | 1-2.5 | $4.01 \times 10^{8} \exp(-5400/T)$ | wetted wall column |
| Jamal et al., 2006 | 293-383 | 0.4-3.2 | $2.0 \times 10^{9} \exp(-5797.8/T)$ | hemispherical contactor |
| Moniuk and Pohorecki, 2000 | 293 | 0.83-2.5 | 5.7 | stirred cell |
| Kierzkowska-Pawlak and Chacuk, 2010 | 293-333 | 0.84-1.706 | $2.07 \times 10^{9} \exp(-5912.7/T)$ | stirred cell |

Generally, the most widely used apparatus for studying reaction kinetics in $CO_2$–amine systems is a laminar jet absorber, a stirred cell with a flat gas-liquid interface, and a wetted-wall column, which involves a gas-liquid operation. These techniques are classified as indirect methods because several

physicochemical properties are needed in the analysis of kinetic data. In this paper, additional data on the kinetics of the reaction between $CO_2$ and aqueous MDEA are reported at the temperature range of 288.15–303.15 K. Present experiments were performed using the stopped-flow technique, where both reagents (MDEA and $CO_2$) were dissolved in water before mixing. Therefore, the results of the direct method used here correspond to the intrinsic homogeneous reaction rate in an aqueous solution and are more accurate than those received using indirect techniques. It is worth adding that this is the first research on reaction kinetics between $CO_2$ and MDEA using a stopped-flow apparatus where a Fast-Fourier-Transform (FFT) method with an alternating current is applied for signal detection.
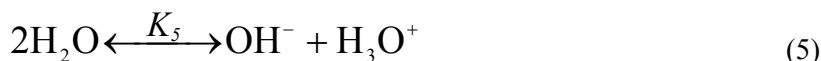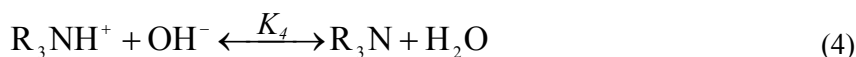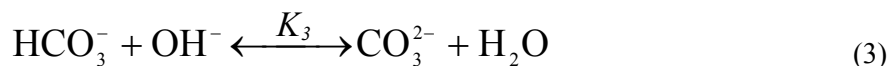
## 2. REACTION MECHANISM

In the reaction of tertiary amines with $CO_2$, a protonated amine and bicarbonate ions are produced. The reaction is consistent with a single step mechanism and water must be present for this reaction to proceed. According to Donaldson and Nguyen (Donaldson and Nguyen, 1980), the reaction can be described as a base catalyzed hydration of $CO_2$:

$$CO_2 + R_3N + H_2O \xleftrightarrow{k_2, K_1} R_3NH^+ + HCO_3^- \tag{1}$$

This most accepted mechanism goes through the formation of a hydrogen bond between the tertiary amine and water, thus weakening the O-H bond in water and increasing the reactivity towards $CO_2$. This reaction involves two bases: water, which catalyses $CO_2$ hydrolysis and the amine.

The following reactions also occur in aqueous solutions:

$$CO_2 + OH^- \xleftrightarrow{k_{OH}, K_2} HCO_3^- \tag{2}$$

$$HCO_3^- + OH^- \xleftrightarrow{K_3} CO_3^{2-} + H_2O \tag{3}$$

$$R_3NH^+ + OH^- \xleftrightarrow{K_4} R_3N + H_2O \tag{4}$$

$$2H_2O \xleftrightarrow{K_5} OH^- + H_3O^+ \tag{5}$$

Reactions (1)-(2) take place in parallel 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 as they involve only a proton transfer. Kinetics of the direct reaction of $CO_2$ with $OH^-$ is very fast and is firmly established (Pinsent and Roughton, 1956; Pohorecki and Moniuk, 1988). However, its influence on the reaction rate should be considered very carefully as the reaction of $CO_2$ with $OH^-$ is fast and may have a significant contribution to the observed rate, especially at very low $CO_2$ partial pressure or short contact times (Kierzkowska-Pawlak and Chacuk, 2010).

Both parallel chemical reactions (1)-(2) are second-order reactions and are treated as irreversible in the present work. The initial $CO_2$ loading in the solution was very small and therefore, ignoring the effect of the reverse reaction (1) and (2) to the overall reaction rate is justified. The respective kinetic rate expressions have the form:

$$r_1 = k_2 [CO_2][MDEA] \tag{6}$$

$$r_2 = k_{OH} [CO_2][OH^-] \tag{7}$$

The general expression for the overall chemical reaction rate is as follows:

$$r_{ov} = r_1 + r_2 \tag{8}$$

The concentration of OH⁻ ions is negligible at the experimental conditions applied in this work and is much smaller than the concentration of $CO_2$ in an aqueous solution. As Reaction (2) is much faster than Reaction (1), hydroxide ions are consumed in the initial stage of the two parallel reactions. Thus the contribution of Reaction (2) to the observed reaction rate was assumed to be negligible. Moreover, the conditions for the chemical reaction of dissolved $CO_2$ with MDEA in an aqueous solution were selected in such a way as to ensure that the chemical reaction takes place in pseudo-first order reaction conditions with respect to $CO_2$. This means that the amine concentration was constant throughout the course of the experiment as it was used in a large excess. After these assumptions, the total rate of $CO_2$ reaction in an aqueous solution of MDEA may be interpreted according to:

$$r_{ov} = k_{ov}[CO_2] \tag{9}$$

where $k_{OV}$ denotes the observed reaction rate constant which can be measured and is given by:

$$k_{ov} = k_2[MDEA] \tag{10}$$

MDEA concentration in Eq. (10) states for the initial amine concentration in the mixer, where the reaction starts.


## 3. EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental technique considered in this study for determination of homogenous kinetics between $CO_2$ and MDEA is a direct method using the SFM-20 stopped-flow system, designed for single mixing rapid-kinetics applications. The SFM-20 module is connected with MCS-200 module allowing conductivity measurements. The whole experimental equipment is manufactured by Bio-Logic SAS (France).

The mechanical subsystem of the stopped-flow module SFM-20 consists of two syringes installed vertically, drive screws, an observation cuvette and a valve system allowing its isolation. The syringes are driven by two independent stepping motors. All these parts are enclosed in a water jacket to allow temperature regulation of the reactants. Figure 1 shows a schematic drawing of the stopped-flow equipment used in the present study.

The experimental method used in this research involves measurements of the solution's electrical resistance or conductance. The main part of the MCS-200 (Modular Conductivity System) is an impedance spectrometer unit. The working electrodes were glassy carbon electrodes. The system allows to measure steady-state spectra of the impedance of a solution and to follow rapid changes in the solution's impedance in the course of chemical reactions. The principle of the detection method is to impose a high-frequency electrical voltage in the solution between two electrodes and to monitor the time course of the resulting current. By means of a Fast-Fourier-Transform (FFT) technique, the two components of the complex impedance – the real part called resistance and the imaginary part called reactance – can be recorded at frequencies up to 200 kHz.

In a typical experiment, aqueous solutions of $CO_2$ and MDEA are pushed through a mixer, where the reaction is initiated, to an observation cell. The time required for the reactants to flow from the final point of mixing to the observation cell is referred to as a dead time. The SFM-20 stopped-flow system can routinely reach the dead time of 5-6 milliseconds.

During the process, the conductance of reaction mixture increases as ionic products are formed. In the observation cell, the kinetics is monitored by recording resistance (in Ohm) or specific conductance (in Siemens/cm) as a function of time. The present experimental technique was previously used for studying a fast kinetics of chemical reaction of $CO_2$ with diethanolamine in aqueous solutions

(Siemieniec et al. 2012). The obtained results of kinetic constants were in agreement with the literature values thereby validating the experimental setup used in this study.
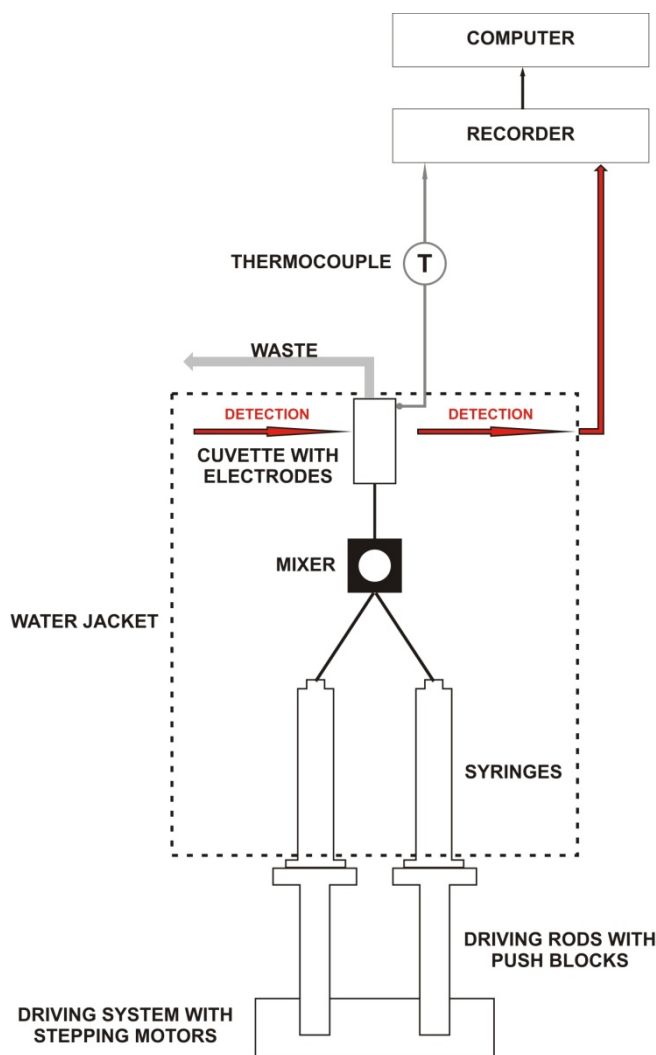


Fig. 1. SFM-20 schematic drawing of the experimental set-up

Before proceeding with kinetic measurements, the apparatus was calibrated by measuring the conductance of aqueous solutions of KCl at 298 K in the concentration range of 0-0.08 M. A linear relationship between the measured conductance and the concentration of the solution was observed. Based on the data collected in this calibration procedure and the theoretical specific conductance of the solutions, the cell constant of 8 cm$^{-1}$ was determined, which was in agreement with the value supported by the manufacturer.

Reagent-grade MDEA with a purity of 99% was obtained from Sigma-Aldrich and used without further purification. Ultra pure water was used to prepare both amine and $CO_2$ solutions. For each experiment, a freshly saturated $CO_2$ solution is prepared by mixing the gas through the water in a stirred cell reactor. Owing to the independent control of each syringe it is possible to make variable reagents mixing ratios to ensure an appropriate ratio of amine molar concentration to that of $CO_2$ after pushing it into a mixer. An amine is always used in excess and the concentration ratio of MDEA to $CO_2$ should be greater than 15 for any run. This ensures pseudo-first-order conditions with respect to $CO_2$.

Measurements were performed in the temperature range of 288÷303 K. The amine concentration varied from 250 mol/m$^3$ to 875 mol/m$^3$. Each run for certain experimental conditions was repeated 10 times and the averaged trace from these replicates was processed on-line and further analysed.

The averaged conductivity traces which were measured as a function of time were fitted according to an exponential equation corresponding to a first-order kinetic equation (Knipe et al. 1974):

$$\kappa = A \cdot \exp(-k_{ov}t) + \kappa_\infty \qquad (11)$$

where κ is the specific conductance of the reaction mixture at time *t*, $\kappa_\infty$ is the constant value of the signal at the end of the reaction which is referred to as a baseline, and *A* denotes an amplitude of the signal. The Bio-Kine software that controls stopped-flow experiments provided such a fitting option to extract rate constants directly from the measured data. The kinetic equation (11) expressed in terms of conductance that is proportional to the concentration is commonly used in analysing the first-order kinetic traces in a stopped-flow apparatus with a conductivity detection (Li et al. 2007, Khorassani et al. 2011).

It should be noticed however that this equation is valid for diluted electrolyte solutions. Only in this case, the conductance of the specific ion is a linear function of its concentration. In the present case, the conductance of the reaction mixture is the sum of conductances of two ions: $R_3NH^+$ and $HCO_3^-$. For the present experimental conditions, the individual concentrations of both ions are small and do not exceed the initial concentration of $CO_2$ which is in the range of 15-60 mol/m$^3$. Thus, the assumption regarding the linear dependence of the concentration of the ion and its conductance is justified and Equation (11) can be used for interpreting the measured reaction traces.

## 4. RESULTS AND DISCUSSION

All kinetic measurements were carried out under pseudo-first order conditions as explained earlier, which means that the amine concentration was in large excess. 10 kinetic runs were recorded under the same conditions and the averaged traces were analysed.

The validity of fitting the kinetic traces to the first order exponential function is evaluated by inspection of residuals and the sum of squared residuals. If the assumption regarding the mechanism of the reaction and the derived kinetic rate expression is correct, a single exponential function could adequately describe the recorded traces. Figure 2 shows a typical result of the stopped-flow experiment at 293 K and MDEA concentration of 0.8 kmol/m$^3$.

As can be seen, fitting the data to the exponential function described by Eq. (11) over the whole time range results in a poor fit as indicated by visual inspection of the residual plot. The observed kinetics cannot be adequately described by the exponential function of the first order over the whole time range. It seems that the second reaction path for the formation of bicarbonate ion through the reaction of OH$^-$ ions cannot be excluded from the observed kinetics.

However, by narrowing the time range starting from about 0.2 s to the end of the run results in a much better fit. As can be seen, the recorded trace could be fitted with excellent statistical confidence to a single exponential function in the selected time range which indicates that a single, direct reaction between $CO_2$ and MDEA dominates in the time range under consideration.

In the first stage of the process which is very short, two parallel chemical reactions described by Eqs. (1) and (2) take place and their influence is evidenced in the recorded kinetic trace. The reaction of dissolved $CO_2$ with amine is slower than the formation of bicarbonate ions in the reaction with hydroxide ions. The concentration of hydroxide ions is very low but their reactivity is significant with respect to that of amine. After a fast depletion of OH$^-$ ions due to Reaction (2) within a short period

(<0.2 seconds), the direct reaction between $CO_2$ and MDEA described by Eq. (1) is exclusively monitored. In other words, after Reaction (2) is completed at the initial stage, the measured trace corresponds exclusively to the first reaction (1). Only at this stage, an interpretation of the experimental data by a single, pseudo-first order kinetics is justified.
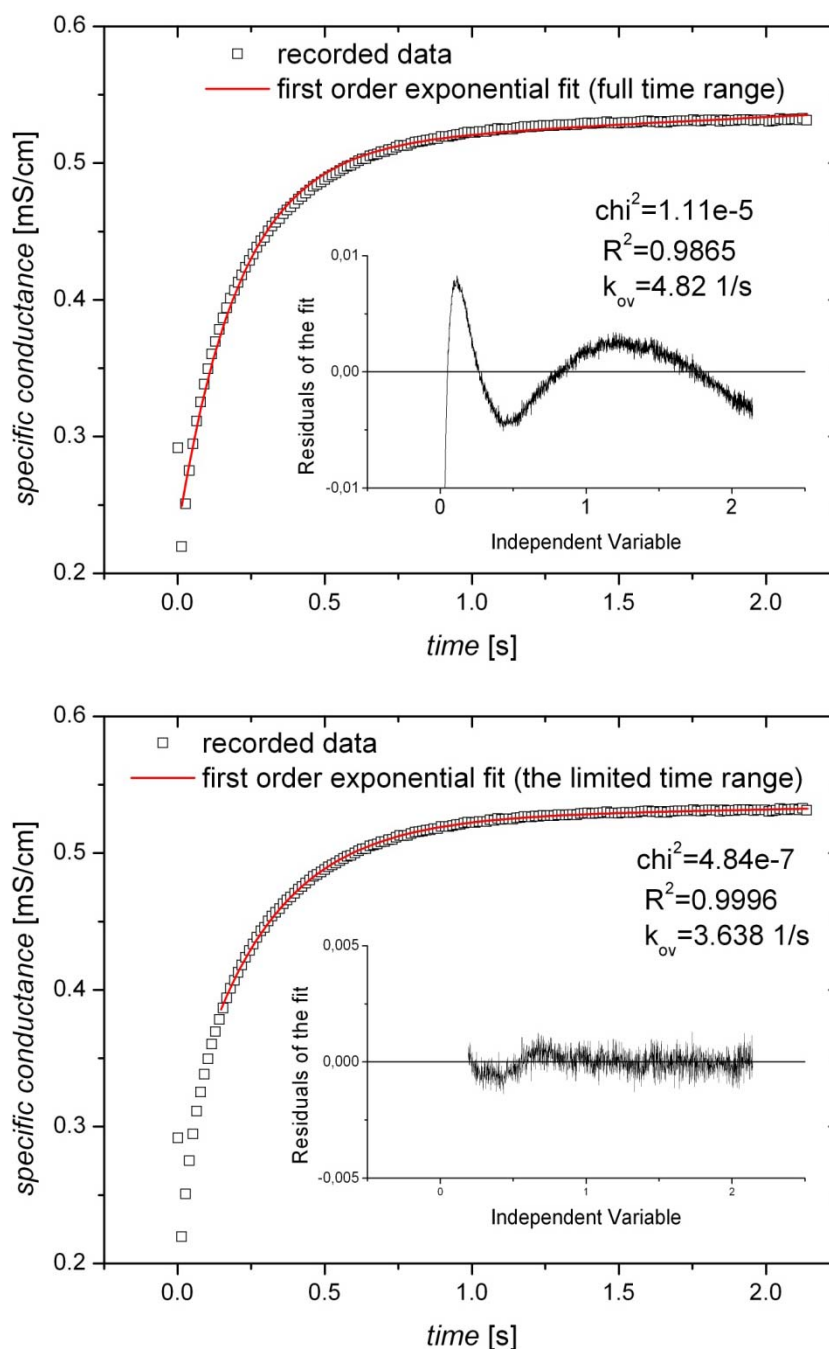


Fig. 2. A typical result of the stopped-flow experiment at 293 K and MDEA concentration of 0.8 kmol/m³ – an example of data treatment

All the stopped-flow data gave very satisfactory pseudo-first order plots according to Eq. (11) and allowed to extract the overall rate constants which are summarised in Tab. 2. Since the reaction between $CO_2$ and $OH^-$ was detected only at the initial stage of the process which was subsequently excluded from further analyses, the fitted rate constants correspond directly to $k_{OV}$ in Eq.(9). As expected, the $k_{OV}$ values increase with temperature and amine concentration. Moreover, the rate constant $k_{OV}$ is a linear function of amine concentration as predicted from Eq. (10). In Figure 3, the

observed rate constants $k_{OV}$ at four temperatures are shown as a function of MDEA concentration with the corresponding linear fit.

Table 2. Experimental data of the stopped-flow experiments

| [MDEA], kmol/m³ | $k_{OV}$, s⁻¹ | [MDEA], kmol/m³ | $k_{OV}$, s⁻¹ |
|---|---|---|---|
| 288.15 K | | 293.15 K | |
| 0.250 | 1.141 | 0.300 | 1.240 |
| 0.273 | 1.184 | 0.333 | 1.359 |
| 0.300 | 1.259 | 0.364 | 1.736 |
| 0.333 | 1.317 | 0.400 | 2.008 |
| 0.333 | 1.384 | 0.438 | 2.286 |
| 0.364 | 1.468 | 0.467 | 2.475 |
| 0.364 | 1.397 | 0.533 | 2.674 |
| 0.400 | 1.473 | 0.500 | 2.332 |
| 0.438 | 1.751 | 0.545 | 2.431 |
| 0.467 | 1.662 | 0.600 | 2.691 |
| 0.500 | 1.887 | 0.667 | 3.071 |
| 0.533 | 1.851 | 0.727 | 3.254 |
| 0.533 | 1.977 | 0.800 | 3.638 |
| 0.563 | 1.993 | | |
| 0.600 | 1.991 | | |
| 0.667 | 2.208 | | |
| 0.727 | 2.462 | | |
| 0.800 | 2.941 | | |
| 0.875 | 3.220 | | |
| 298.15 K | | 303.15 K | |
| 0.300 | 2.051 | 0.250 | 2.723 |
| 0.333 | 2.240 | 0.273 | 3.182 |
| 0.364 | 2.756 | 0.333 | 3.713 |
| 0.400 | 2.981 | 0.364 | 3.720 |
| 0.438 | 3.159 | 0.400 | 4.187 |
| 0.467 | 3.464 | 0.438 | 4.508 |
| 0.500 | 3.751 | 0.467 | 4.694 |
| 0.533 | 3.980 | 0.500 | 5.404 |
| 0.563 | 4.293 | 0.533 | 5.604 |
| 0.600 | 4.862 | 0.563 | 6.283 |
| | | 0.600 | 6.452 |

Table 3. Second order rate constants for $CO_2$ reaction with MDEA by fitting to Eq. (10)

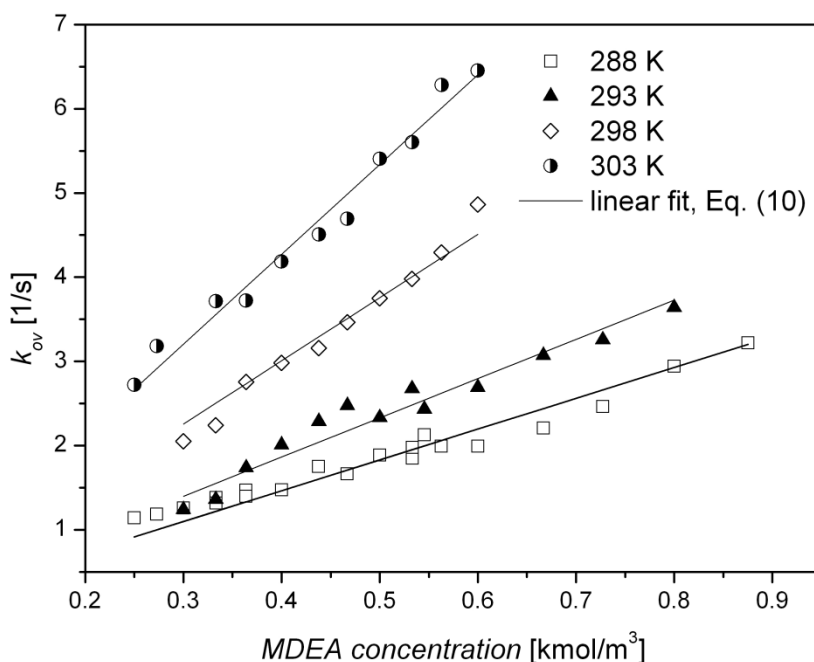| T, K | $k_2$, m³ kmol s⁻¹ | $R^2$ |
|---|---|---|
| 288.15 | 3.658 | 0.939 |
| 293.15 | 4.658 | 0.9458 |
| 298.15 | 7.515 | 0.9638 |
| 303.15 | 10.677 | 0.978 |

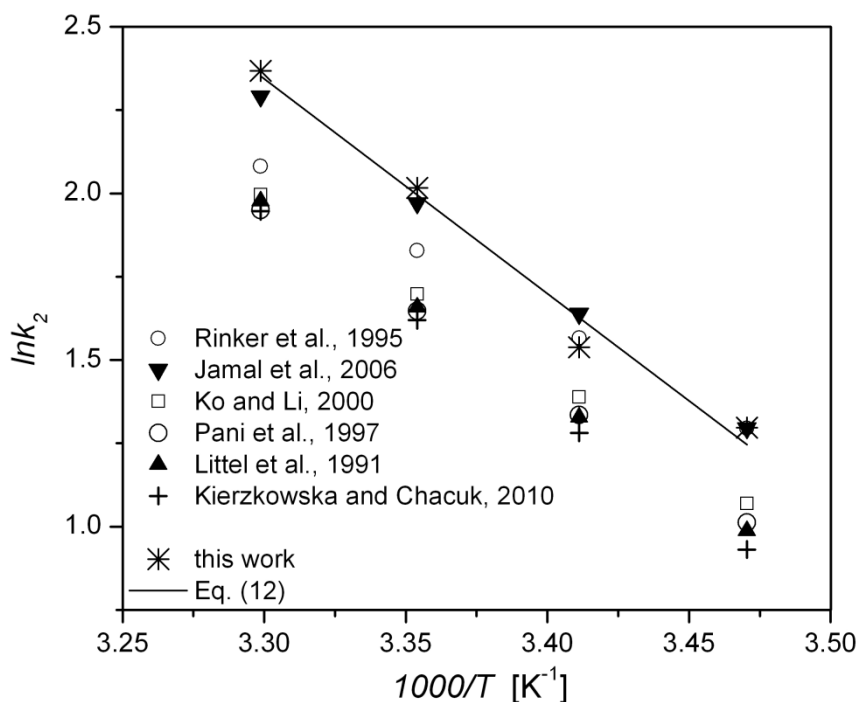Fig. 3. Determination of second-order rate constants $k_2$



Fig. 4. Comparison of the second-order rate constant for $CO_2$-MDEA reaction determined in this work
with those reported in the literature

The estimates of $k_2$ are plotted in Figure 4 for comparison with selected literature values determined by the use of different research methods. The values of $k_2$ obtained in this work are in good agreement with those derived by Jamal et al. (2006) over the whole temperature range. As shown in Figure 4, the $k_2$ of Rinker et al. (1995) and Pani et al. (1997) are slightly smaller than the present ones. The results of Haimour et al. (1987) are significantly smaller than other literature values, and consequently they were not plotted in Fig. 4. The observed discrepancies in the reported data and our previous results

(Kierzkowska-Pawlak, et al. 2010) can be attributed to a different, heterogeneous experimental technique and the assumptions involved in the processing and subsequent interpretation of the kinetic rate data. These discrepancies may mainly result from the inability to determine the exact contact area between gas and liquid in the absorption process and uncertainty about the physical properties such as solubility and diffusivity of $CO_2$ in MDEA aqueous solutions which have an influence on the estimation of the reaction rate constant of the reaction between $CO_2$ and MDEA. It is worth emphasising that it is not possible to compare our results obtained by using the stopped-flow technique with other analogous studies because no such measurements have so far been made.

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

$$k_2[\text{m}^3\text{kmol}^{-1}\text{s}^{-1}] = 1.78 \times 10^{10} \exp(-6441.9/T) \tag{12}$$

The activation energy, as determined from Eq. (12) has been found to be 53.56 kJ/mol.

## 5. CONCLUSIONS

For the first time, the kinetics of the reaction of $CO_2$ with MDEA in aqueous solutions has been studied using the stopped-flow apparatus and the impedance spectroscopy in which an alternating current coupled with Fast-Fourier-Transform (FFT) technique is applied for signal detection. The measurements were performed in a concentration range of (250 to 875) $\text{mol·m}^{-3}$ and a temperature range of 288 to 303 K. The overall reaction rate constant was found to increase with amine concentration and temperature. A simplified kinetic model was applied which assumes that the main reaction of $CO_2$ with MDEA is irreversible and the contribution of $CO_2$ reaction with $OH^-$ ions is significant only at the initial stage of the process. The conditions for the reaction of $CO_2$ in MDEA solutions were selected in such a way as to ensure pseudo-first order conditions with respect to $CO_2$. Based on the assumptions made, the second order rate constants of $CO_2$ reaction with MDEA were determined. New data for the $k_2$ constants were found to be in a good agreement with published values. The activation energy for the second order rate constant was determined to be 53.56 kJ/mol.

The experimental technique employed in this work is therefore verified and will be used to determine kinetics of $CO_2$ reactions in novel amines.

## SYMBOLS

| | |
|---|---|
| $A$ | amplitude of the specific conductance, $\text{mS·cm}^{-1}$ |
| $chi^2$ | the sum of the squared residuals |
| $c$ | concentration, $\text{mol·m}^{-3}$ |
| $K_i$ | equilibrium constant of reaction "$i$" |
| $k_2$ | second-order reaction rate constant of reaction (1), $\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ |
| $k_{OH}$ | second-order reaction rate constant of reaction (2), $\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ |
| $k_{OV}$ | overall rate constant, $\text{s}^{-1}$ |
| MDEA | methyldiethanolamine |
| $R^2$ | correlation coefficient |
| $r_{OV}$ | overall chemical reaction rate, $\text{mol·m}^{-3}\text{·s}^{-1}$ |
| $T$ | temperature, K |

| | |
|---|---|
| *t* | time, s |

*Greek symbols*

| | |
|---|---|
| $\kappa_\infty$ | specific conductance at the end of the reaction, mS·cm$^{-1}$ |
| $\kappa$ | specific conductance, mS·cm$^{-1}$ |

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