Calorimetric Measurements of CO_2 Absorption into Aqueous *N*-Methyldiethanolamine Solutions

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A reaction calorimeter was used to study the rate and heat effects during CO_2 absorption into aqueous solutions of *N*-methyldiethanolamine (MDEA). The experiments were carried out at constant pressure of 0.1 MPa and 0.3 MPa over a range of temperature from 293 K to 333 K. The amine content changed from 10 to 30 mass %. The experimental equipment and procedure were described with the emphasis on complexity originating from the difficulty of interpreting the chemical absorption data and measuring the enthalpy of absorption. The employed technique was also found to be useful in determining the CO_2 solubility in aqueous MDEA. The enthalpy of absorption was found to be independent of pressure and amine concentration and it increased with temperature. A new method to estimate the chemical reaction rate from heat flow data has been developed and proved to be valid for the CO_2—H_2O—MDEA system. The present results show that the employed technique offers a big advantage of simultaneous monitoring of many data which are involved in the absorption process.

Absorption by aqueous alkanolamine solutions is the dominant industrial process for removing acid gases such as CO_2 and H_2S, from natural gas. Commercial implementation of *N*-methyldiethanolamine (($CH_2CH_2OH)_2CH_3N$) as a treating solution did not follow immediately because of the high cost of MDEA relative to the cost of either MEA or DEA. However, it is now used in a number of treating plants and it is apparent that MDEA processing technology will find an interesting application in natural gas treatment, and also in petroleum refining, coal gasification, and hydrogen production. Because of its wide industrial importance absorption in amines solutions has been extensively studied during the last 15 years. Many studies have been performed on the kinetics of the reaction of aqueous MDEA with CO_2 but there have been remarkably few attempts to investigate the heat effects of this process.

The subject of industrial interest in CO_2 removal by alkanolamine solutions is the influence of operating conditions on the rate of mass and heat transfer. Design and scale up of the new absorber for this process requires a knowledge of the hydrodynamics and mass as well as heat transfer characteristics under various specific process conditions. The measurements in the typical laboratory absorption equipment are performed under conditions far from industrial ones and in most of the cases cannot be applied in simulating the plant conditions. A reaction calorimetry seems to be the best laboratory technique for measuring the heat and mass transfer characteristics with fulfilling the mentioned requirements. It is surprising that despite of the great number of researches dealing with the CO_2—H_2O—MDEA system, no reaction calorimetric measurements have been undertaken until now on CO_2 absorption rate in aqueous solutions of MDEA. Moreover, there are only two papers in the open literature [1, 2] on direct calorimetric measurements of heat effects of this process and the presented data do not cover the range of temperatures, concentration, and pressures studied in this work.

Because of the lack of reports on calorimetric absorption measurements in the literature, this paper is primarily concerned with the application of the laboratory reaction calorimeter in determining the mass and heat transfer characteristics during the CO_2 absorption into MDEA aqueous solutions under different operating conditions. The proposed experimental technique was used for studying gas solubility, and also the rate and mechanism of absorption. Contrary to previous investigations, the present experimental technique additionally enabled the measurement of the thermal power developed by the process and thus determination of the enthalpy of absorption. Information on solubilities and enthalpies of absorption of CO_2 in aqueous solutions of MDEA is of primary importance for designing unit operations of acid gas removal.

For the reaction of CO_2 with tertiary alkanolamines (R_3N), *Donaldson* and *Nguyen* [3] proposed the reaction mechanism according to the eqn (*C*). The

reaction mechanism is essentially a base-catalyzed hydrogenation of CO_2, and implies that tertiary amines cannot react directly with CO_2. Rate equations generally accepted for the forward chemical reaction between CO_2 and MDEA are first-order with respect to the concentrations of each of these species. However, there are still many discrepancies in the literature concerning the interpretation of the kinetic data. In particular, there is not any consensus on the effect of the CO_2/OH^- reaction on the measured rate of CO_2 absorption and which is more important, on the estimation of the kinetic rate coefficient of the reaction between CO_2 and MDEA. This causes the relatively high difference in the overall reaction rate constant which is ranging from 1.44 m^3 kmol s^{-1} [4] to 4.75 m^3 kmol s^{-1} [5] at 293 K.

Some of the discrepancies in estimating the kinetic parameters may also come from the inconsistency of the physical data such as solubility and diffusivity of CO_2 in MDEA aqueous solutions and from the different experimental techniques. Studies on CO_2 absorption kinetics in MDEA solutions were carried out in typical laboratory apparatus containing the wetted-sphere absorber [5—7], the wetted-wall column [8], the laminar jet [4, 9], and the stirred cell [10—13]. The major drawback of the models used for kinetic studies in the above equipment is that in most cases their validity is limited due to the assumptions involved. It concerns especially the assumption of pseudo-first-order conditions and also the values of diffusivities, physical solubilities, and mass transfer coefficients, which cannot be measured directly by experimental methods because the gas chemically reacts with the absorbing liquid. So the latter properties must be estimated from the corresponding data of similar nonreacting systems. All authors use the "N_2O analogy" in order to obtain information on the solubility and diffusivity of CO_2. However, as was shown by *Kreulen et al.* [14] the analogy cannot be applicable over the complete concentration range, so its use is rather limited. Moreover, significant discrepancies appear between published physicochemical data on the N_2O—H_2O—MDEA system. The above facts indicate that purely theoretical approaches to mass transfer rate in MDEA solutions based on the doubtful kinetic and physicochemical data make them questionable and may be erroneous. In the case of the system under consideration the experimental information on the absorption rate under specific process conditions seems to be much more reliable than theoretical calculations.

EXPERIMENTAL

The chemicals employed, CO_2 (99.995 vol. % pure) and MDEA (Riedel—de Haën, 98.5 mass % pure) were used without any further purification. Alkanolamine aqueous solutions were prepared from distilled water. In order to provide additional data on the gas solubility and the enthalpy of absorption, the measurements were carried out in the industrially important operating conditions: temperature range 293—313 K and pressure range 0.1—0.3 MPa. The applied contents of MDEA solution from 10 to 30 mass % correspond to 0.845—2.586 kmol m^{-3} at 293 K. The liquid volume was maintained at 150 cm^3. The stirring speed was changed from 1000 to 1800 min^{-1}. Each absorption experiment for given conditions was repeated at least twice. The reproducibility of the solubility measurements was better than 3 %.

The reaction calorimeters are fully automated and computer-controlled stirred reactor vessels suited for simulating the plant conditions, with possibility of an on-line measurement of thermal power developed by the process. The commercially available reaction calorimeter CPA (Chemical Process Analyser, ChemiSens AB, Sweden) used in this work is a mechanically agitated stainless steel/glass reactor with an effective volume of 250 cm^3. The reaction vessel is suitable for work under pressure ($<$ 2 MPa). A Peltier element mounted inside the bottom of the reactor serves as an efficient heating and cooling device and keeps temperature at nearly constant level. Ports in the lid enable charging and sampling from both the gas and liquid phase. The system continuously measures heat production rate, the reactor temperature, pH, the stirring speed, power, and the system pressure. All operating conditions as a function of time are recorded using the special data acquisition system based on the Wonderware InTouch environment [15].

Procedure

Calorimetric studies on mass transfer in the CO_2—H_2O—MDEA system involved measurements of the gas phase pressure in the storage tank and heat generation rate with respect to time during semibatch isothermal absorption of the gas. The scheme of experimental set-up modified with the aim of absorption studies is shown in Fig. 1. The gas was charged to the reactor by a special feed line through the downstream pressure controller (Brooks, 5866), which allowed the constant total pressure (P) of 0.1 MPa or 0.3 MPa to be kept in the reactor. The pressure decrease in the storage tank was measured by means of an IDA transducer (Nobel Electronic), working in the range from 0 to 2 MPa.

Before starting the experiment, the amine solution was first vacuumed and heated to a given temperature. After equilibrium was established, under solution vapour pressure, the pure carbon dioxide was introduced during a short time to the upper part of the cell. After a few seconds when the pressure in the reactor reached the set value, the process was initiated by switching on the stirrer at the desired mixing speed. The subsequent decline of the gas pressure in the storage tank $p'_A(t)$ and additionally the rate of heat pro-
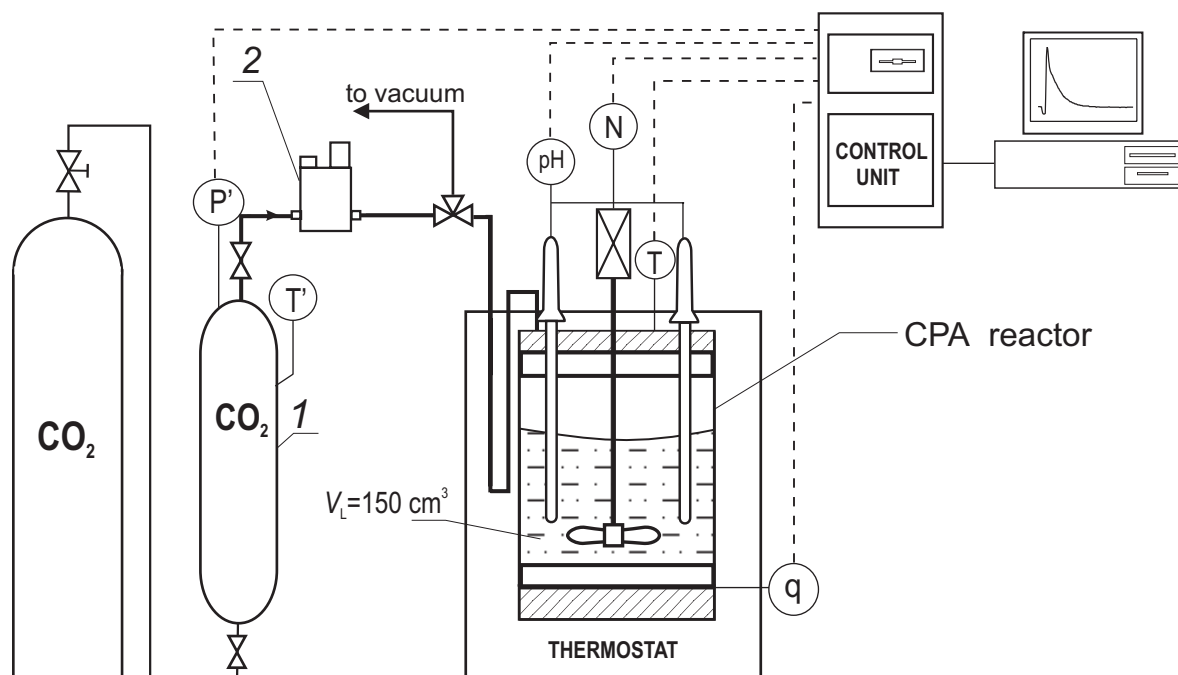
Fig. 1. Experimental set-up. *1* – Storage tank, $V_G = 504$ cm³, *2* – downstream pressure regulator, N – stirring speed transducer, T – temperature sensor in the reactor, T' – temperature sensor in the storage tank, P' – pressure transducer, q – heat flow transducer, pH – pH electrodes.

duction $q(t)$ were recorded as a function of time until the equilibrium state was reached. The pressure in the storage tank varied from the initial value of p'_{A1} to the final value of p'_{A2}. The total pressure drop in the storage tank was necessary for calculating the gas solubility, while the function $p'_A(t)$ enabled the absorption rate $R_A(t)$ to be determined. Additionally, the pH value of the reaction mixture was measured but these values were not used for the calculations in the present study. The set of pH electrodes simultaneously worked as the baffles and offered the possibility to increase the stirrer speed without disturbing the gas-liquid interface by which larger mass transfer coefficients (k_L) could be obtained.

The run of any selected experiment is presented graphically in Fig. 2. The curves illustrate that switching of the stirrer initiated the absorption process, which was manifested by the pressure decline in the storage tank and the heat generation. The power dissipated by the stirrer was constant during the experiment and thus could be automatically subtracted from the measured heat generation rate as a baseline. Hence the monitored value of q stands for the absolute heat generation rate, which corresponds only to the absorption heat effects.

In calculation of the amount of CO_2 the Beatty—Bridgeman state equation was used. The amount of substance of absorbed gas necessary for calculating the gas solubility corresponds to the total pressure change in the storage tank from p'_{A1} to p'_{A2}. The actual amount of carbon dioxide in the storage tank of a known volume, n_{AG}, was calculated from the instanta-
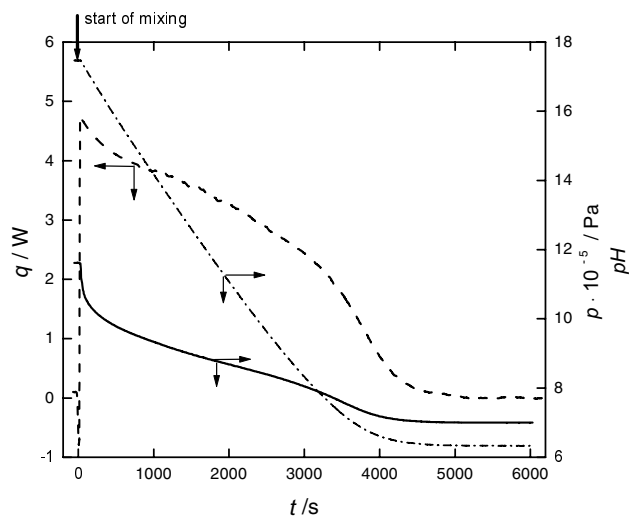

Fig. 2. Illustration of the absorption experiment (293 K, 0.3 MPa, 20 mass % MDEA, 1500 min⁻¹). Solid line – pH of the solution, dashed line – heat generation rate q, dashed dotted line – pressure decrease in the storage tank p'_A.

neous pressure which is continuously monitored. The absorption rate, R_A, could be thus obtained from the present experimental data by differentiating the time curve of n_{AG} based on the pressure decrease in the storage tank recorded as a function of time, according to the following equation

$$R_A = -\frac{dn_{AG}}{dt} \qquad (1)$$

Table 1. Conditions of CO_2 Absorption into Aqueous MDEA at 293 K

w_{MDEA}	p_A	E_∞	N	$k_L \cdot 10^5$	Ha^*	Ha^{**}
mass %	MPa		min^{-1}	$m\ s^{-1}$		
			1000	2.43	1.7	3.1
	0.098	10.5	1300	3.15	1.3	2.4
10			1500	3.62	1.1	2.0
	0.298	4.2	1800	4.34	0.9	1.7
			1000	1.98	2.6	4.7
	0.098	21.3	1300	2.56	2.0	3.6
20			1500	2.95	1.7	3.1
	0.298	7.8	1800	3.53	1.4	2.6
			1000	1.11	4.5	8.1
	0.098	42.9	1300	1.44	3.4	6.3
30			1500	1.66	3.0	5.4
	0.298	15	1800	1.99	2.5	4.5

*Estimated using $k_2 = 1.44\ m^3\ kmol^{-1}\ s^{-1}$ [4]; **estimated using $k_2 = 4.75\ m^3\ kmol^{-1}\ s^{-1}$ [5].

The CO_2 partial pressure in the reactor (p_A) was calculated according to the measured total pressure in the system (0.1 MPa, 0.3 MPa) corrected for solution vapour pressure by use of Raoult's law

$$p_A = P - x_{H_2O} p^v_{H_2O} - x_{MDEA} p^v_{MDEA} \qquad (2)$$

where x is the mole fraction, and p^v is the vapour pressure. The last term in eqn (2) was very small for the temperature range covered in this study and was neglected.

RESULTS AND DISCUSSION

For the interpreting the chemical absorption data, the values of physical mass transfer coefficient of CO_2 in MDEA aqueous solutions are required. In order to determine these quantities, a mass transfer correlation between dimensionless numbers (Sh, Re, Sc) has been established for our apparatus from CO_2 absorption experiments into the pure water at 293 K. The 0.5 power dependence of the Sh number on Sc number was assumed as suggested by *Versteeg* and *Swaaij* [16] for a similar reactor. The exponent of the Re number was easily determined experimentally by the variation of the stirrer speed. Hence the power dependence of k_L on the stirring speed was found to be about 0.99. To adapt this mass transfer correlation for aqueous MDEA system, all needed physical properties were estimated using correlations summarized by *Rinker et al.* [5]. The calculations of the Ha number and enhancement factor for the instantaneous reaction E_∞ at 293 K are given in Table 1. Henry's constants necessary for estimating the CO_2 interfacial concentration were obtained with the correlation proposed by *Rinker et al.* [5]. Due to the large difference in kinetic parameters published in the literature, Ha numbers were calculated for two extreme values of second-rate constants determined by *Haimour et al.* [4] and *Rinker et al.* [5].
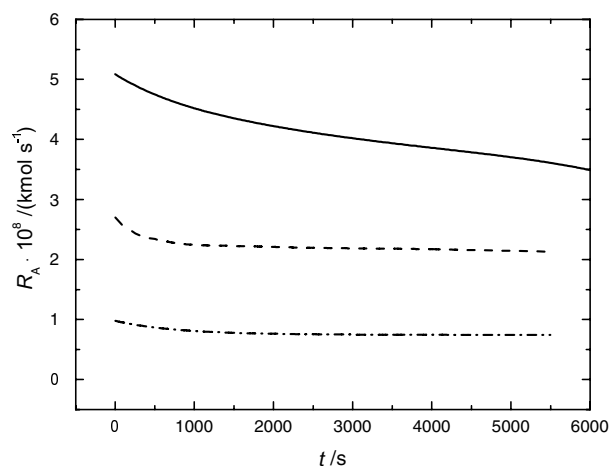

Fig. 3. Time dependence of absorption rate into a 30 mass % MDEA (0.1 MPa, 293 K) for different stirring speeds/min^{-1}: solid line – 1800, dashed line – 1500, dashed dotted line – 1000.

As can be seen from the data in Table 1, when higher values of k_2 were used in calculations, the Ha numbers are greater than 2 for almost all conditions, indicating the fast reaction regime. Also, for the experiments of 30 mass % MDEA, the requirement $Ha < E_\infty$ is satisfied irrespective of adopted kinetic parameters. The fulfilling of both requirements for a 30 mass % MDEA means that absorption occurs in the fast pseudo-first-order reaction regime.

However, this theoretical prediction was not proved by experimental findings. Fig. 3 shows the time dependence of absorption rate into a 30 mass % MDEA at 0.3 MPa for stirring speed ranging from 1000 to 1800 min^{-1}. As can be seen from this plot, the absorption rate strongly depends on stirring speed suggesting the diffusion limitation regime. The similar dependence was observed for a 10 mass % and 20 mass % MDEA. From the above facts it can be concluded that
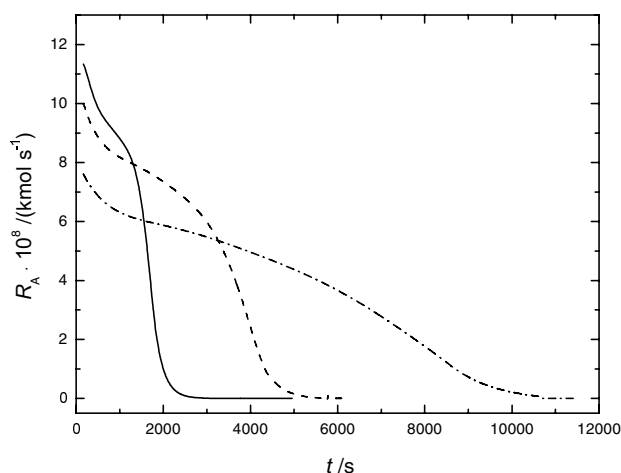
Fig. 4. Time dependence of absorption rate at 293 K (1500 min^{-1}, 0.3 MPa) for different MDEA content/mass % MDEA: solid line – 10, dashed line – 20, dashed dotted line – 30.
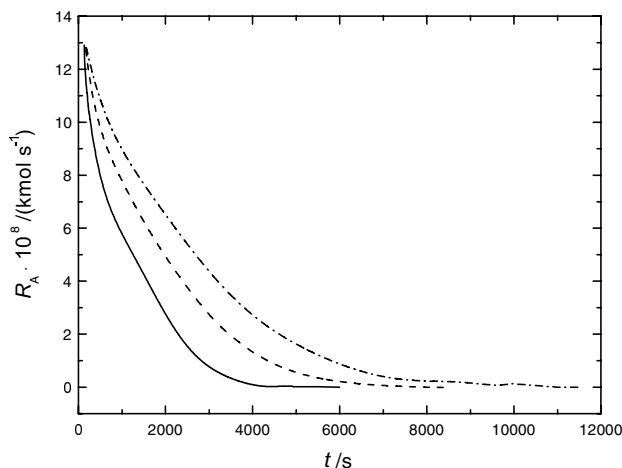

Fig. 5. Time dependence of absorption rate at 333 K (1500 min^{-1}, 0.3 MPa) for different MDEA content/mass % MDEA: solid line – 10, dashed line – 20, dashed dotted line – 30.

in the case of the system studied, purely theoretical approaches are erroneous in predicting the chemical reaction regime. The main disadvantage of the theoretical calculations in this case comes not only from the inconsistency of the physicochemical data but additionally, from impossibility of direct k_L determination for CO_2 in aqueous MDEA. Namely, as was shown by *Versteeg* and *Swaaij* [16], a *Sh, Sc, Re* relationship does not describe all phenomena which affect the liquid phase mass transfer coefficient in aqueous MDEA. According to them, an important parameter, which is not included in such a relationship, seems to be the surface tension. Due to this fact, the k_L determined from the power-law correlation of dimensionless numbers can be treated only as the rough estimation of its real value.

An interesting phenomenon can be observed while studying the dependence of amine concentration on the absorption rate as is shown in Figs. 4 and 5. At a temperature of 293 K, the presented data show that absorption kinetics becomes faster when the MDEA concentration increases while at 333 K the opposite trend is observed. Additionally, for a 20 mass % and 30 mass % MDEA content, the absorption rate always increases with temperature in the range from 293 K to 333 K, while for a 10 mass % MDEA the absorption rate seems to decrease with temperature. This behaviour comes from an opposite influence of MDEA concentration upon chemical kinetics, CO_2 diffusivity, and CO_2 solubility. The results indicate that at lower temperature the mass transfer phenomena play a more important role, while at higher temperatures the CO_2 absorption rate becomes more determined by chemical reaction than by the resistance in the liquid phase. However, the strict analysis is complicated due to the fact that the process is carried out at unsteady state conditions.

The gas solubility was expressed by a mole ratio α $(n(CO_2)/n(MDEA))$. The amount of substance of absorbed gas was calculated from the total pressure change in the storage tank. It should be stressed that contrary to all previous investigations the gas phase was assumed nonideal. The chemical reaction that is described by eqn (C) is stoichiometrically limited to 1 mol of CO_2 per mol of amine. Absorption of CO_2 to a loading exceeding unity is possible if physical absorption is considered.

The results of solubility measurements are listed in Table 2 along with those determined by *Jou et al.* [17] for a 30 mass % MDEA. In general, the CO_2 solubility per mole of MDEA increases with decreasing temperature and solution content. Obviously, the increase in pressure resulted in an increase of CO_2 solubility. The observed trends agree with literature reports. The comparison of the solubilities obtained in this work with those of *Jou et al.* [17] shows a relatively good agreement within the accuracy of the determination.

Carbon dioxide undergoes the following steps in aqueous MDEA solutions

$$CO_2(g) \leftrightarrow CO_2(l) + \Delta H_{phys} \qquad (A)$$

$$CO_2(l) + R_3N + H_2O \leftrightarrow R_3NH^+ + HCO_3^- + \Delta H_r \quad (B)$$
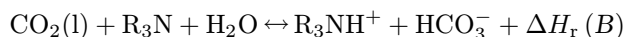
where the first equation describes the physical process characterized by the enthalpy ΔH_{phys}, and the second equation describes the overall chemical reaction according to the mechanism proposed by *Donaldson* and *Nguyen* [3].

For practical reasons, the knowledge of the overall enthalpy of chemical absorption ΔH_{abs} is more important, *i.e.* the enthalpy of the following process
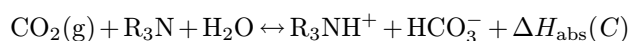
$$CO_2(g) + R_3N + H_2O \leftrightarrow R_3NH^+ + HCO_3^- + \Delta H_{abs}(C)$$

Table 2. Experimental Results of CO_2 Solubility in Aqueous Solutions of MDEA Compared with the Values from the Literature

T	p_A	w_{MDEA}	α, this paper	α^*, [17]
K	MPa	mass %	$n(CO_2)/n(MDEA)$	$n(CO_2)/n(MDEA)$
293	0.098	10	1.025	–
		20	0.98	–
		30	0.92	–
293	0.298	10	1.13	–
		20	1.06	–
		30	0.995	–
313	0.093	10	0.94	–
		20	0.88	–
		30	0.79	0.75
313	0.293	10	1.07	–
		20	0.98	–
		30	0.93	0.95
333	0.081	10	0.73	–
		20	0.61	–
		30	0.49	0.55
333	0.281	10	0.95	–
		20	0.84	–
		30	0.78	0.80

*Literature values obtained by interpolation of the experimental data.

where $\Delta H_{abs} = \Delta H_{phys} + \Delta H_r$.

The enthalpy of chemical absorption ΔH_{abs} cannot be calculated directly by integrating of the heat production rate curve and from the total amount of substance of absorbed gas as it is typically done in the case of physical absorption [18]. Here, at the final process conditions, which correspond to the equilibrium state, part of the absorbed CO_2 is physically dissolved. The enthalpy of absorption must be thus determined from the heat flow data when the process takes place in the fast reaction regime where no accumulation of absorbed CO_2 occurs.

In the light of difficulties in estimating the absorption regime by the classical method based on Hatta number and the enhancement factor for instantaneous reaction, the following procedure was proposed. The overall heat production rate measured by the calorimeter reflects the heat flow due to both the physical dissolution of gas in the solvent (q_{phys}) and the chemical reaction between CO_2 and aqueous MDEA (q_r). It leads to the equation

$$q = q_{phys} + q_r = -(R_A \Delta H_{phys} + r_A V_L \Delta H_r) \quad (3)$$

where R_A is the absorption rate calculated from the time dependence of pressure in the storage tank and $r_A V_L$ is the chemical reaction rate related to the whole amount of liquid phase.

When the absorption rate is controlled entirely by mass transfer, i.e. the chemical reaction is very fast with respect to the mass transfer, the chemical reaction rate becomes equal to the absorption rate. In this case eqn (3) can be rearranged to the form

$$q = -R_A (\Delta H_{phys} + \Delta H_r) = -R_A \Delta H_{abs} \quad (4)$$

Taking into acount the following relationships

$$Q_t = \int_0^t q \, dt \quad (5)$$

$$n_{A,t} = \int_0^t R_A \, dt \quad (6)$$

eqn (4) can be written as

$$Q_t = -n_{A,t} (\Delta H_{phys} + \Delta H_r) = -n_{A,t} \Delta H_{abs} \quad (7)$$

where Q_t is the amount of heat evolved from $t = 0$ until t and $n_{A,t}$ is the amount of carbon dioxide absorbed in the period under consideration.

Eqn (7) corresponds to the straight line with the slope representing the enthalpy of absorption. From the data of experiments where the dependence of the heat evolved vs. the amount of substance of absorbed gas could be described by the straight line in the initial stage, the enthalpy of absorption ΔH_{abs} was determined. Fig. 6 shows the example of ΔH_{abs} determination for the absorption experiment into a 30 mass % MDEA at 293 K. As can be seen from this figure, in the initial stage the dependence of Q_t vs. $n_{A,t}$ is actually linear and later it deviates from the straight line. This phenomenon indicates that the chemical reaction rate is becoming smaller than the absorption rate. As a result, part of the absorbed carbon dioxide is being accumulated in the solution in the unreacted form.

As CO_2 reacts with the amine in aqueous solutions, it is not possible to determine the enthalpy of physical absorption denoted as ΔH_{phys}. The only way to
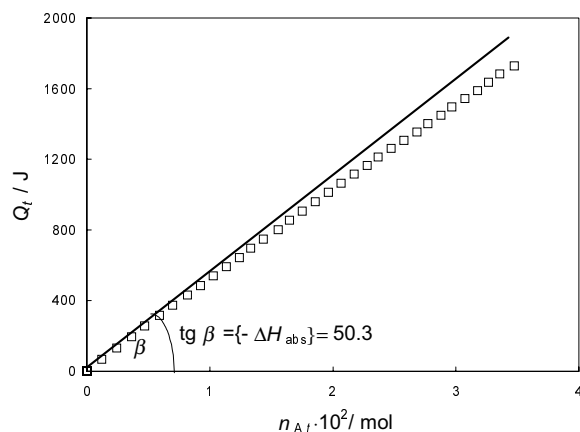
Fig. 6. Determination of ΔH_{abs} from the initial data of the experiment carried out in the fast reaction regime (293 K, 0.1 MPa, 30 mass % MDEA, 1000 min^{-1}). $\square$ Experimental data, solid line – linearization of eqn (7), $r = 0.9998$.
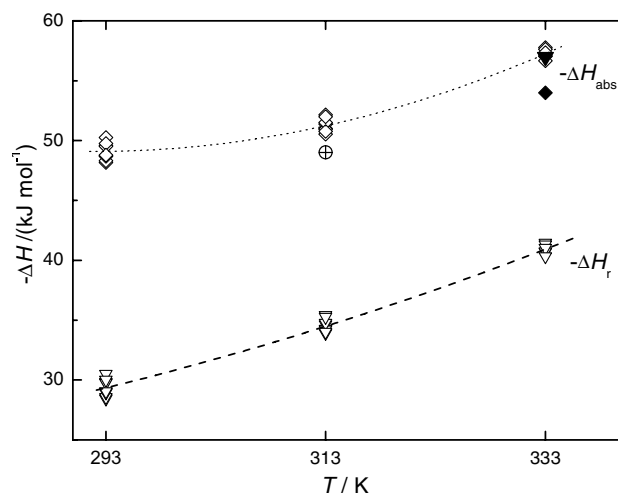

Fig. 7. Measured enthalpies of absorption *vs.* temperature compared with literature data. ΔH_{abs}: $\diamondsuit$ this work for 10—30 mass % MDEA, $\oplus$ [2] for 30 mass % MDEA, $\blacklozenge$ [1] for 20 mass % MDEA, $\blacktriangledown$ [1] for 30 mass % MDEA; ΔH_{r}: $\triangledown$ this work for 10—30 mass % MDEA. Dashed, dotted lines – regression of experimental points.

proceed with further calculations is to incorporate the assumption that the values of ΔH_{phys} are the same as those for the CO$_2$—H$_2$O system at a given temperature. The necessary data were determined in separate experiments, which were also carried out in the reaction calorimeter at a constant pressure. The obtained values were -19.9 kJ mol^{-1}, -16.9 kJ mol^{-1}, and -16.3 kJ mol^{-1} for temperatures 293 K, 313 K, and 333 K, respectively.

All the presented results of ΔH_{abs} and ΔH_{r} determination are plotted in Fig. 7 along with those obtained by microcalorimetric techniques [1, 2]. The data of *Merkley et al.* [1] were obtained by means of an isothermal heat leak flow calorimeter. The measure-

ments of *Mathonat et al.* [2] were performed in a flow-mixing unit connected with a differential SETARAM C-80 heat conduction calorimeter. In the present work, the measured enthalpies of absorption were found to be independent of pressure. Contrary to previous studies of this system, no influence of MDEA concentration on the values of ΔH_{abs} was reported. The difference between values obtained for various amine concentrations was within experimental accuracy of ± 4 %. Therefore a mean value for a given temperature was calculated, taking into account all data points irrespective of pressure and amine concentration. The obtained values of ΔH_{abs} are -49.1 kJ mol^{-1}, -51.3 kJ mol^{-1}, -57.2 kJ mol^{-1} for 293 K, 313 K, 333 K, respectively.

It can be seen from Fig. 7 that the values of $-\Delta H_{\text{abs}}$ at 313 K obtained in this work are slightly higher than those of *Mathonat et al.* [2] determined for a 30 mass % MDEA solution. At the temperature of 333 K, the obtained mean value of -57 kJ mol^{-1} falls in the upper limit of the range quoted by *Merkley et al.* [1] for 20—30 mass % MDEA content. Although both values are in reasonable agreement, it seems more reliable that our experimental results, arising from macroscopic measurements, are less prone to errors derived from low signal comparable to noise ratios as it often occurs in microcalorimetric techniques. Moreover, the analysis of the experimental procedure of previous authors reveals that the measured heat effect reflected both the exothermic heat effect corresponding to absorption of the gas and endothermic effect corresponding to vaporization of water into the gas stream. This is an explanation for higher enthalpies of absorption (lower absolute values) measured in [1, 2] than our results. Obviously, at higher temperatures the vaporization of water was much more important and significantly influenced the enthalpy of absorption determined in their work. In the present experimental technique this phenomenon does not take place because before starting the experiment the amine solution was in equilibrium with its vapour. At such conditions, the dosing of pure carbon dioxide was not followed by the further evaporation of water.

Since the heat flow rate is proportional to the absorption rate, monitoring of this value over the course of the experiment gives an indirect, continuous measure of the chemical reaction rate. The subtraction of enthalpy of chemical reaction from the overall enthalpy of absorption enables to estimate the chemical reaction rate from eqn (3). The result of the chemical reaction rate ($r_{\text{A}}V_{\text{L}}$) determination from the measured heat production and absorption rate data is shown in Fig. 8. As can be seen from this figure, at the initial stage of the process, the rate of chemical reaction is equal to the absorption rate and then it becomes smaller. From a comparison of the areas under these curves the amount of free CO$_2$ (unreacted) in the solution can be estimated. For all the experiments, at
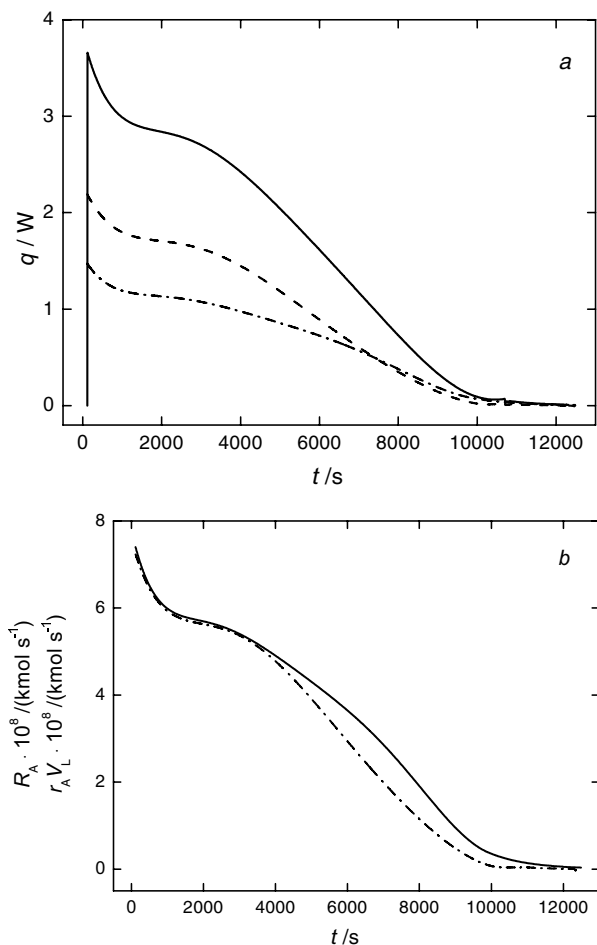
Fig. 8. Determination of the chemical reaction rate from calorimetric data (293 K, 0.3 MPa, 30 mass % MDEA, 1500 min^{-1}). a) Subtraction of heat generation rate evolved due to the chemical reaction. Solid line – q, overall heat generation rate, dashed line – q_r, heat generation rate evolved due to the chemical reaction (C), dashed dotted line – q_{phys}, heat generation rate evolved due to the physical dissolution of gas in the solvent. b) Comparison of the absorption rate and chemical reaction rate. Solid line – R_A, absorption rate, dashed dotted line – $r_A V_L$, chemical reaction rate related to the whole amount of the liquid phase.

the initial amine content, the initial absorption rate was very close to the absorption rate, confirming the diffusion limitation conditions.

CONCLUSION

The reaction calorimeter was successfully used in studying the rate and heat effects during carbon dioxide absorption into aqueous solutions of MDEA. The results on chemical reaction regime at 293 K were compared with theoretical predictions based on the estimation of Hatta number and enhancement factor for the instantaneous reaction. The comparison revealed that in the case of the system studied, this classical method requiring many assumptions appeared far

from reliable and was certainly the point for which supplementary experiments were necessary for confirmation. Generally, in all experiments the increase in stirring speed and pressure resulted in the increasing mass transfer rate.

Contrary to previous studies [1, 2], in this work the heat effects of CO_2 absorption into aqueous solutions of MDEA were investigated in a macro-scale. A new method of measuring the enthalpy of absorption was proposed. The enthalpy of absorption was found to be independent of pressure and MDEA concentration and increased with temperature. Where the comparison was possible, the obtained values of $-\Delta H_{abs}$ were slightly higher than those reported in the literature. This difference is attributed to the fact that the previously measured enthalpies additionally included the heat effect corresponding to the vaporization of water into the CO_2 stream.

The measured heat evolution rate coupled with mass transfer rate was proposed to be used in estimating the chemical reaction rate. The obtained results showed that heat flow data could serve as an effective measure of absorption progress and reaction rate without any analytical sampling. It is worth noticing that the experimental technique applied demonstrates an advantage of continuous monitoring of several quantities, which are involved in the absorption process. A single calorimetric run gives several pieces of information on gas solubility, enthalpy of absorption, and also the process rate.

SYMBOLS

c	liquid phase concentration	kmol m^{-3}
c^*	interfacial concentration	kmol m^{-3}
D_i	diffusion coefficient of species i in the liquid phase	m^2 s^{-1}
d_s	turbine diameter	m
E_∞	enhancement factor for the instantaneous reaction, $E_\infty = 1 + \dfrac{D_{MDEA} c_{MDEA}}{D_A c_A^*}$	
Ha	Hatta number, $Ha = \dfrac{\sqrt{k_2 c_{MDEA} D_A}}{k_L}$	
k_L	liquid side mass transfer coefficient of dissolved CO_2	m s^{-1}
k_2	second-order rate constant	m^3 kmol^{-1} s^{-1}
n	amount of substance	kmol
N	stirring speed	min^{-1}
p	partial pressure	MPa
P	total pressure	MPa
q	heat flow rate	W
Q	amount of heat	J
R_A	absorption rate of CO_2	kmol s^{-1}
Re	Reynolds number, $Re = \dfrac{n d_s^2 \rho_L}{\eta_L}$	
r	correlation coefficient	

r_A	chemical reaction rate of CO$_2$	kmol m^{-3} s^{-1}
Sc	Schmidt number, $Sc = \dfrac{\eta_L}{\rho_L D_A}$	
Sh	Sherwood number, $Sh = \dfrac{k_L d_s}{D_A}$	
t	time	s
x	mole fraction	
w_{MDEA}	amine mass fraction	mass %
V	volume	m^3
ΔH_{abs}	enthalpy of chemical absorption	kJ mol^{-1}
ΔH_{phys}	enthalpy of physical absorption	kJ mol^{-1}
ΔH_r	enthalpy of chemical reaction	kJ mol^{-1}

Greek Letters

α	mole ratio in the liquid phase (n(CO$_2$)/n(MDEA))	
ρ	density	kg m^{-3}
η	viscosity	Pa s

Subscripts

A	carbon dioxide
G	gas phase
L	liquid phase

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