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# Enthalpies of Absorption and Solubility of $CO_2$ in Aqueous Solutions of Methyldiethanolamine

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# Enthalpies of Absorption and Solubility of $CO_2$ in Aqueous Solutions of Methyldiethanolamine

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**Abstract:** Absorption in aqueous alkanolamine solutions is frequently used for $CO_2$ separation from various gas streams. In the present study, a reaction calorimeter was used to measure solubilities and enthalpies of absorption of $CO_2$ in aqueous solutions of N-methyldiethanolamine in the temperature range of (293.15 to 333.15) K and amine concentration range of (10 to 40) mass%. Experiments were performed at $CO_2$ partial pressures of (0.1 and 0.3) MPa. 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 enthalpy of absorption was found to be independent of pressure and linearly dependent upon the temperature and amine concentration.

**Keywords:** $CO_2$ separation, alkanolamines, enthalpy of absorption, reaction calorimetry

## INTRODUCTION

Absorption by aqueous alkanolamine solutions is the dominant industrial process for separation of acid gases such as $CO_2$ and $H_2S$, from industrial and natural gas streams. The latter case is often referred as a gas sweetening process. Carbon dioxide present in the natural gas needs to be removed in order to increase the heating value of the gas, prevent corrosion of the pipeline, and the gas process equipment. The amines that have been proven to

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be of principal commercial interest for gas purification are monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) (1). In the last decade interest in using methyldiethanolamine, which is a tertiary amine, increased significantly. The main advantage of MDEA as opposed to more traditionally used primary and secondary amines is its relatively high capacity, small enthalpy of reaction with acid gases, and a low vapor pressure.

Another important application of amine-based technologies is $CO_2$ separation from flue gases at power plants. The idea of carbon dioxide sequestration which includes the capture and storage of it 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. The chemical absorption of $CO_2$ is generally recognized as the most efficient post-combustion $CO_2$ separation technology at present. As opposed to other capture options which includes pre-combustion technology and oxy-fuel processes, this technology can be fairly easily installed in the existing power plants while other technologies involve new ways of power plant technology.

Tertiary amines are particularly suited for this purpose, as their efficiency in removing $CO_2$ and their regenerability have been demonstrated in a host of applications in the petroleum and the chemical industries. Energy costs play a significant role in the feasibility of any commercial $CO_2$ removal technology. For amine-scrubbing systems, the most significant energy demand is for the solvent regeneration step. A precise knowledge of $\Delta H_{abs}$ of acid gases in the solution is therefore essential for the calculation of heat supplied to the stripper column.

$CO_2$ absorption in amine solutions has been extensively studied during the last 20 years. Several authors investigated the mechanism and kinetics between $CO_2$ and MDEA. It is concluded that because of the N-atom in the amine, which does not have a free hydrogen atom, no carbamate ions can be formed contrary to the reaction with the primary and the secondary amines. The $CO_2$ must first react with water to form bicarbonate (2). Then the proton combines with the amine via an acid-base neutralisation reaction. The overall reaction is given by

$$\begin{aligned} &CO_2 + CH_3(CH_2CH_2OH)_2N + H_2O \\ &\leftrightarrow CH_3(CH_2CH_2OH)_2NH^+ + HCO_3^- \end{aligned} \tag{1}$$

Most prior research on $CO_2$ removal by amines has concentrated on measuring and predicting gas-liquid equilibrium data. As opposed to the large amount of the kinetics and solubility investigations, the direct measurements of enthalpy of $CO_2$ absorption in aqueous MDEA solutions are limited. Although the differential enthalpy of solution may be estimated from solubility data using the Gibbs-Helmholtz equation, the operation of differention magnifies any errors in the solubility data and the resulting values are often less accurate than ±10%. Therefore, direct calorimetric measurements of the enthalpy of absorption are preferred. The enthalpy of absorption of $CO_2$ has been measured in aqueous MDEA at the temperature range of (288.15 to 433.15) K and amine concentration range of (20 to 60) % mass MDEA by Merkley et al. (3) using an isothermal heat leak flow calorimeter. Mathonat et al. (4) performed measurements in a flow-mixing unit connected with a differential SETARAM C-80 heat conduction calorimeter for a 30% mass MDEA and the temperature range of (313.15 to 393.15) K. Carson et al. (5) provides data at 298.15 K for an amine concentration range from (10 to 30) mass% by the use of isothermal displacement calorimetry. Besides few low quality values of $\Delta H_{abs}$ are available in the literature. Dibbie (6) reports a value of $-49$ kJ/mol. The method of obtaining this value is unknown, as are the temperature, pressure, and MDEA concentration at which it is valid. Polasek and Bullin (7) report a value of $-61$ kJ/mol for MDEA concentration range of (30 to 50) mass% and an unknown temperature.

In this work, a new experimental methods based on the reaction calorimetry for determining the enthalpy of chemical absorption, was proposed. Contrary to previous studies, the present technique enables the continuous monitoring of heat flow rate under different gas loadings and provides the direct measurement of $CO_2$ solubility in MDEA aqueous solutions in the one experiment. The new experimental data are presented for the temperature range of (293.15 to 313.15) K and solution concentration range of (10 to 40) mass% MDEA. Some of my previously published data on heat effects in $CO_2$-$H_2O$-MDEA system are revised and reinterpreted (8). Information on solubilities and enthalpies of absorption in $CO_2$-$H_2O$-MDEA system is of primary importance for designing unit operations of acid gas removal.

## EXPERIMENTAL

The measurements were performed in a commercially available reaction calorimeter (Chemical Process Analyser CPA202, ChemiSens AB, Sweden)-which is a fully automated and computer-controlled stirred reactor vessel with the possibility of an on-line measurement of the thermal power developed by the process. A schematic diagram of the calorimeter and the entire setup modified with the aim of absorption studies is shown in Fig. 1. Its heart is a mechanically agitated reactor with a total volume of 250 $cm^3$ where the useful volume ranges from 40 to around 180 $cm^3$. This is different from traditional reaction calorimeters which usually are based on 2 liters laboratory reactors. The reactor is a cylindrical, double-walled glass vessel. 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.

While in use, it is located in a fixed position in the thermostating liquid bath. A Peltier element mounted inside the bottom of the reactor serves as

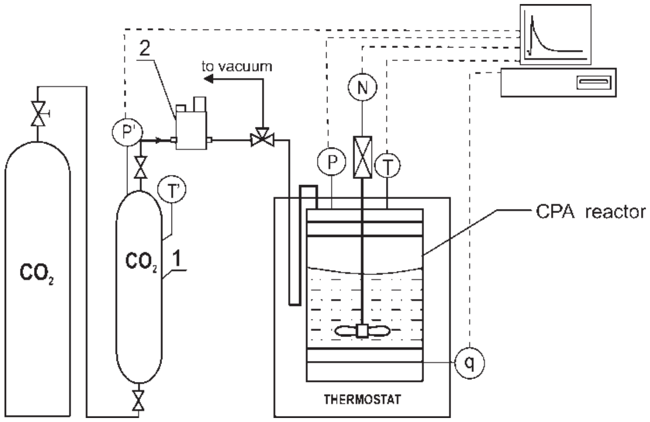

***Figure 1.*** Experimental set-up: 1, storage tank; 2, downstream pressure regulator, N, stirring speed transducer; T, temperature sensor in the reactor; T', temperature sensor in the storage tank; P', pressure transducer; q, heat flow transducer.

an efficient heating and cooling device and keeps the temperature constant to ±0.01 K. All operating conditions, including the reactor temperature, the stirring speed, the system pressure, and the heat flow rate as a function of time are recorded using the special data acquisition system.

One significant difference between the CPA202 and ordinary heat flow calorimeters is the method of heat flow measurement based on the heat conduction equation. The Peltier element creates the temperature difference that forces the heat flow which is exchanged between the reactor content and the thermostating liquid only through the reactor base. The value of the heat flow signal is based on temperature measurements at several locations between the reactor bottom and the Peltier element. Thus changes in the heat transfer coefficient do not affect the heat flow measurement and the baseline is therefore known throughout the whole experiment. The CPA calorimeter is pre-calibrated, which means that the instrument presents the value of heat production rate directly on-line.

The resolution of the heat flow measurement is about 0.01 W. The smallest detectable amount of heat is 2 J. The accuracy of the calorimetric measurements has been shown to be better than ±1% for enthalpy of chemical reaction in different liquid-liquid systems. However, in the determination of $\Delta H_{abs}$ for gas-liquid systems, the complexity of the experimental procedure and calculations is increased. As a result, the accuracy of the calorimetric measurements in the case of physical absorption of a gas in several solutions was found to be ±2%.

The experimental procedure involved measurements of the gas phase pressure in the storage tank and the heat flow rate with respect to time during isothermal absorption of the gas under isobaric conditions. The process was operated batchwise with respect to the liquid phase while the gas was continuously fed to the reactor. The schematic diagram of an experimental setup is shown in Fig. 1. The gas was charged from the storage tank of a known volume (504 ± 0.5) $cm^3$ to the reactor through the downstream pressure controller (Brooks, 5866), which allowed the constant total pressure (P) of (0.1 or 0.3) MPa to be maintained in the reactor during the whole absorption experiment. After the reactor was filled with the desired solution, the liquid was degassed and heated to a given temperature. When the thermal equilibrium was established for example. the temperature in the reactor became constant to ±0.01 K, the stirring was stopped for a moment. Then, under the solution vapor pressure, pure carbon dioxide was started to feed to the upper part of the cell up to a fixed pressure of 0.1 or 0.3 MPa. After a few seconds, when the pressure in the reactor reached the set value, the absorption process was initiated by switching on the stirrer. The pressure in the storage tank began to decrease as the gas was being absorbed in the solution while the pressure in the reactor remained constant. The subsequent decline of the gas pressure in the storage tank $p_A'(t)$ and additionally the heat flow rate q(t) were recorded as a function of time until the gas-liquid equilibrium state was reached. 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 heat generation and the pressure decline in the storage tank. The power dissipated by the stirrer was continuously measured during the experiment and thus could be automatically subtracted from the measured heat flow rate as a baseline. Hence, the monitored value stands for the absolute heat flow rate, which corresponds only to the absorption heat effects.

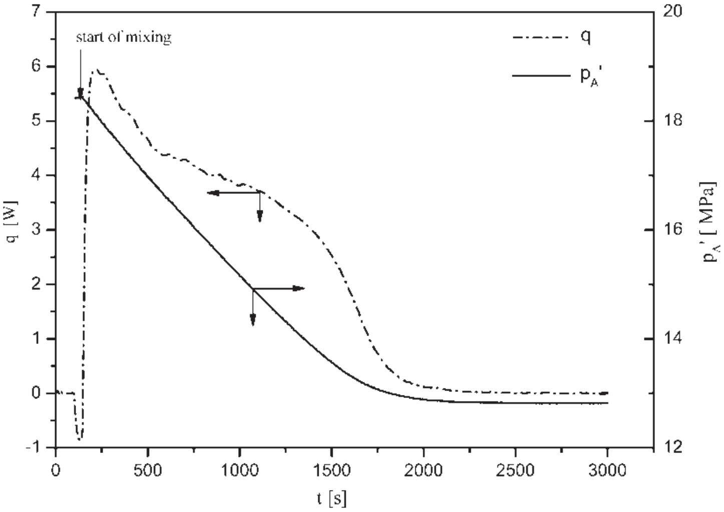

***Figure 2.*** Illustration of the absorption experiment (293.15 K, 0.3 MPa, 10 mass% MDEA, stirring speed 1500 $min^{-1}$).

The pressure drop in the storage tank from the moment of switching on the stirrer until the final equilibrium state was necessary for calculating the amount of gas absorbed in the liquid. This pressure change in my experiments was in the range of (0.4 to 1.7) MPa. In an analysis, a small amount of gas which was absorbed during the initial dosing of $CO_2$ up to a set pressure (a period of 0–8 s) could be ignored as it was negligible as compared to the amount of the absorbed gas under stirring conditions. The single absorption run lasted from 1 to 3 hours depending on the operating conditions. The time dependence of pressure, $p_A$’(t), was used for determining the actual amount of gas absorbed in the liquid, denoted as $n_{A,t}$. The $CO_2$ partial pressure in the reactor, $p_A$, was calculated according to the total pressure in the system (which was controlled and measured by Brooks downstream pressure regulator) corrected for solution vapor pressure by use of Raoults’s law. In these calculations the MDEA vapor pressure was neglected, as it was very small as compared to the solvent vapor pressure. In calculations of the amount of substance of $CO_2$, a nonideal behavior of the gas phase was assumed. The Beatty–Bridgeman state equation coupled with mass balances were used to calculate the amount of substance of absorbed gas.

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 the distilled, deionized water. The solution volume was maintained at $(150 \pm 0.1)\ cm^3$ in each experiment. The respective mass of the solutions was determined within $\pm 0.01$ g. The pressure in the storage tank, $p_A$’, was measured by means of an IDA transducer (Nobel Electronik)with the accuracy of $\pm 0.005$ MPa. The stirring speed was in the range of (1000 to 1500) $min^{-1}$. Each absorption experiment for a given temperature, MDEA concentration, and pressure was repeated at least 3 times. The repeatabilty of the solubility measurements was always below 2%. The estimated experimental uncertainty in the measured solubility is about ±2%.

Validity of the experimental procedure and approximations made in the calorimetric calculations was tested by performing several experiments on a well-known gas-liquid system. As a reference example, the absorption of $CO_2$ in pure water was investigated at 293,15 K. The percent of difference between the measured value of $\Delta H_{abs} = (-20.2 \pm 0.3)\ kJ \cdot mol^{-1}$ and a literature reference of $\Delta H_{abs} = -19.9\ kJ \cdot mol^{-1}$ (9) is shown to be 1.5%. The maximum uncertainty for the measured enthalpies was ±2%.

## RESULTS AND DISCUSSION

### The Gas Solubility Measurements

The gas solubility was expressed by a loading $\alpha$ which is defined as the ratio of moles of absorbed carbon dioxide per moles of alkanolamine in the solution. It is apparent from the Eq. (1) that the reaction between $CO_2$ and tertiary amines is limited to a loading of 1 mol of $CO_2$ per mol of amine. However, absorption of $CO_2$ exceeding this limit is possible considering physical absorption.

The results of solubility measurements are listed in Table 1 along with the selected literature data. In general, $CO_2$ solubility per mole of MDEA increases with decreasing temperature and amine concentration. Obviously, an increase in pressure resulted in an increase of $CO_2$ solubility. The observed trends agree with literature reports (10–12).

To date there have been many sets of experimental solubility data of $CO_2$ in aqueous MDEA solutions at various temperatures, pressures, and solvent concentrations from different investigators, which have been summarized by Kamps et al. (10). However, the qualitative comparison of the solubilities obtained in this work with the data from other sources is difficult as most of these data do not cover a range of the present operating parameters. The

***Table 1.*** Experimental results of $CO_2$ solubility in aqueous solutions of MDEA compared with the literature values

| | | | $CO_2$ loading [mol $CO_2$/mol MDEA] | |
|---|---|---|---|---|
| 100 $w_B$ | T [K] | $p_A$[MPa] | this work | literature data[a] |
| 10 | 293.15 | 0.098 | 1.025 | |
| | | 0.298 | 1.13 | |
| | 313.15 | 0.093 | 0.94 | |
| | | 0.293 | 1.07 | |
| | 333.15 | 0.080 | 0.73 | |
| | | 0.280 | 0.95 | |
| 20 | 293.15 | 0.098 | 0.98 | |
| | | 0.298 | 1.06 | |
| | 313.15 | 0.093 | 0.88 | 0.85 (12) |
| | | 0.293 | 0.98 | 0.99 (12) |
| | 333.15 | 0.081 | 0.61 | 0.63 (12) |
| | | 0.281 | 0.84 | 0.81 (12) |
| 30 | 293.15 | 0.098 | 0.92 | |
| | | 0.298 | 0.995 | |
| | 313.15 | 0.093 | 0.79 | 0.83 (11) |
| | | 0.293 | 0.93 | 0.95 (11) |
| | 333.15 | 0.081 | 0.51 | 0.53 (11) |
| | | 0.281 | 0.73 | 0.72 (11) |
| 40 | 293.15 | 0.098 | 0.85 | |
| | | 0.298 | 0.93 | |
| | 313.15 | 0.093 | 0.73 | 0.77 (11) |
| | | 0.293 | 0.87 | 0.89 (11) |
| | 333.15 | 0.082 | 0.44 | 0.47 (11) |
| | | 0.282 | 0.63 | 0.62 (11) |

[a] Literature values obtained by interpolation of the experimental data.

comparison with results of Jou et al. (11) is limited for MDEA concentrations and temperatures above 25 mass% and 298.15 K, respectively. The comparison with the data from Maddox et al. (12) is possible for a 20 mass% MDEA solution. In both cases the literature data needs to be interpolated for the aim of comparison. As shown in Table 1, the presented data are in good agreement within the uncertainty of the determination.

## The Enthalpy of Absorption Measurements

Carbon dioxide undergoes the following steps in aqueous MDEA solutions

$$CO_{2_{(g)}} \leftrightarrow CO_{2_{(aq)}} + \Delta H_{phys} \tag{2}$$

$$\begin{aligned} &CO_{2_{(aq)}} + CH_3(CH_2CH_2OH)_2N + H_2O \\ &\quad \leftrightarrow CH_3(CH_2CH_2OH)_2NH^+HCO_3^- + \Delta H_r \end{aligned} \tag{3}$$

where the first equation describes the physical process characterized by the enthalpy $\Delta H_{phys}$, and the second equation describes the overall chemical reaction taking place in the liquid phase.

For any practical calculations, the value of overall enthalpy of chemical absorption $\Delta H_{abs}$ is adopted, i.e. the enthalpy of the following process:

$$\begin{aligned} &CO_{2_{(g)}} + CH_3(CH_2CH_2OH)_2\,N + H_2O \\ &\quad \leftrightarrow CH_3(CH_2CH_2OH)_2NH^+ + HCO_3^- + \Delta H_{abs} \end{aligned} \tag{1}$$

where

$$\Delta H_{abs} = \Delta H_{phys} + \Delta H_r \tag{4}$$

The enthalpy of chemical absorption $\Delta H_{abs}$ cannot be calculated directly by integrating of the heat production rate curve as plotted in Fig. 2 and divided by the amount of substance of absorbed gas as it is typically done in the case of physical absorption measurements. Here, at the final process conditions, which correspond to equilibrium state, a small part of the total amount of absorbed $CO_2$ is physically dissolved. The enthalpy of absorption must be thus determined from the limited region of heat flow data when the carbon dioxide is completely absorbed (e.g. the solution is not saturated with the free $CO_2$).

Taking into account the above difficulties, some preliminary tests of chemical absorption regime were performed by analyzing the effect of the variation of stirrer speed on the absorption rate. The tests showed that in the range of experimental conditions, the chemical reaction is controlled entirely by mass transfer, i.e. the chemical reaction is very fast with respect to mass transfer. Consequently, the overall heat flow rate measured by the calorimeter reflects the heat flow due to both the physical dissolution of gas in the solvent and to its chemical reaction in aqueous MDEA as follows:

$$q = -R_A \Delta H_{abs} \tag{5}$$

where $R_A$ is the $CO_2$ absorption rate expressed in moles per second. By integrating both the heat flow and the absorption rate in certain limits the Eq. (5) can be written in analogues form

$$Q_t = -n_{A,t} \Delta H_{abs} \tag{6}$$

where $Q_t$ is the amount of heat evolved from $t = 0$ until t and $n_{A,t}$ states for the amount of carbon dioxide absorbed in the period under consideration. Eq. (6) corresponds to the straight line with the slope representing the enthalpy of absorption. Figure 3 shows the example of $\Delta H_{abs}$ determination for the case of $CO_2$ absorption into a 30 mass% MDEA at 293.15 K. The slope of the relation was found by a modified least-squares linear regression which forces the line describing the experimental data to pass through the origin. As can be seen from this figure, in the low gas loading region the dependence of $Q_t$ versus $n_{A,t}$ is actually linear which supports the developed method and allows the value of $\Delta H_{abs}$ to be determined from the slope. While approaching the equilibrium state, an apparent downwards deviation from linearity in the data plotted in Fig. 3 can be observed. This phenomenon indicates that in the final stage of the process only the physical absorption occurs. As a

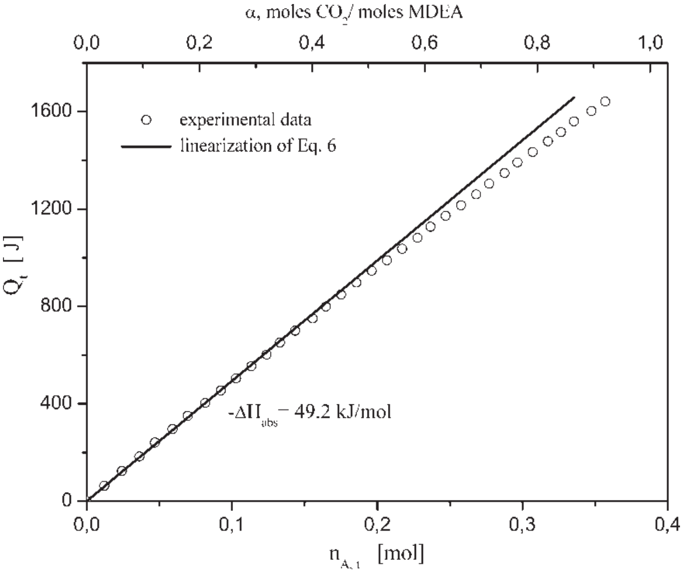

***Figure 3.*** The method of $\Delta H_{abs}$ determination (293.15 K, 0.1 MPa, 30 mass% MDEA).

result, the amount of substance of carbon dioxide absorbed is being accumulated in the solution in the molecular form.

However, a detailed analysis of the received data indicates that the slope of $\Delta H_{abs}$ shows a small dependence on the loading. This behavior was observed by other investigators (3, 4). Consequently, the results of linear regression can differ a little depending on the extent of experimental data sets considered in a correlation. Thus in determining the slope of relation (6) I always took into account the initial region of the absorption run which corresponded to about one third of the total amount of $CO_2$ absorbed in the solution. The correlation coefficient of such a fitting was very close to unity.

Analysis of the determined enthalpies of absorption indicates that pressure has no effect on the values of $\Delta H_{abs}$ in the range of our experimental pressures. The similar behavior was observed by others (3, 4). The difference between enthalpy values obtained for different pressures was within experimental accuracy of $\pm 3\%$. Therefore, a mean was calculated from at least six measurements for a given temperature and MDEA concentration with the standard deviation below $1.6\,\mathrm{kJ}\cdot\mathrm{mol}^{-1}$ in the worst case. The present $\Delta H_{abs}$ values and its standard deviation are tabulated in Table 2 together with literature data. The results obtained from present experiments are considerably more precise than those of previous workers. Figure 3 is a plot of $\Delta H_{abs}$ values as a function of MDEA concentration at each of the three temperatures investigated together with the data of Merkley et al. (3). The present results show that the absolute values of enthalpy of absorption increase with temperature and amine concentration. The observed trend is in contradiction with the findings of Carlson et al. (5) who observed enthalpy independence of amine concentration at 298.15 K. It should be noted however that in my previously published paper (8) this trend was also not depicted mainly due to the limited amount of data considered in the analysis compared with the present amount of data. The present trend is in agreement with that predicted in (3) where the enthalpy results were described as a linear function of temperature and amine concentration in the following form:

$$-\Delta H_{abs}/(\mathrm{kJ}\cdot\mathrm{mol}^{-1}) = 0.101w_B + 0.126T/K + 8.6 \qquad (7)$$

where $w_B$ represents the amine mass percent in the solution and $T$ is the temperature. The Eq. (7) is plotted in Fig. 4 by a dashed line and is valid in the range of (288.71 to 422.04) K and (20 to 60) mass% MDEA.

A multiple linear regression of the present experimental data gives the equation:

$$-\Delta H_{abs}/(\mathrm{kJ}\cdot\mathrm{mol}^{-1}) = 0.155w_B + 0.214T/K - 21.07 \qquad (8)$$

which perform a good fit of the measured values of $\Delta H_{abs}$ with the correlation coefficient of $r = 0.989$. However, the absolute values of $\Delta H_{abs}$ obtained in this work are higher than those of Merkley et al. (3) and the difference clearly increases with temperature. At 313.15 K, the obtained absolute value

***Table 2.*** Comparison of the molar enthalpies of $CO_2$ absorption in aqueous MDEA with the literature values

| $100\ w_B$ | T[K] | $p_A$ [MPa] | $-\Delta H_{abs}$ [$kJ \cdot mol^{-1}$] | $\sigma$ [$kJ \cdot mol^{-1}$] | Reference |
|---|---|---|---|---|---|
| 10 | | | 46.4 | 1.4 | |
| 20 | 293.15 | 0.1, 0.3 | 48.1 | 1.2 | |
| 30 | | | 49.8 | 1.3 | |
| 40 | | | 51.2 | 1.1 | |
| 10 | | | 50.3 | 1.3 | This work |
| 20 | 313.15 | 0.1, 0.3 | 52.1 | 1.5 | |
| 30 | | | 53.4 | 1.2 | |
| 40 | | | 54.8 | 1.4 | |
| 10 | | | 55.7 | 1.6 | |
| 20 | 333.15 | 0.1, 0.3 | 57.1 | 1.6 | |
| 30 | | | 58.4 | 1.5 | |
| 40 | | | 60.3 | 1.5 | |
| 10 | 298.15 | | 50.3 | 0.3 | Carson et al. (5) |
| 20 | 298.15 | | 48.8 | 0.2 | Carson et al. (5) |
| 30 | 298.15 | | 48.7 | 1 | Carson et al. (5) |
| 30 | 313.15 | 2, 5, 10 | 49 | 4 | Mathonat et al. (4) |
| 30 | 333.15 | 2, 5, 10 | 52 | 4 | Mathonat et al. (4)[a] |
| 20 | 293.15 | 0.156–1.456 | 47.5 | | Merkley et al. (3)[b] |
| 30 | 293.15 | 0.156–1.456 | 48.5 | | Merkley et al. (3)[b] |
| 20 | 313.15 | 0.156–1.456 | 50.5 | | Merkley et al. (3)[b] |
| 30 | 313.15 | 0.156–1.456 | 51.5 | | Merkley et al. (3)[b] |
| 20 | 333.15 | 0.156–1.456 | 52.6 | 2.6 | Merkley et al. (3) |
| 30 | 333.15 | 0.156–1.456 | 53.6 | 2.6 | Merkley et al. (3) |

[a] values obtained by interpolation of the experimental data.

[b] values calculated from Eq. (7).

of 53.4 $mol^{-1}$ for a 30 mass% MDEA solution is also higher than the value of 49 $kJ \cdot mol^{-1}$ determined by Mathonat et al. (4). The comparison with the data of Carson et al. (5) is difficult since their experiments applies to a single temperature of 298.15 K and a very low gas loading.

In the following, a few remarks on the literature enthalpy data are given. The calorimetric data of Merkley et al. (3) and Mathonat et al. (4) were calculated as the total heat evolved up to a certain loading, $\alpha$, divided by that loading, and is therefore an integral heat of absorption up to that point. However, the loading was not measured directly. As the process was operated continuously, the loading was estimated from a known flow rates of gas and liquid phases assuming that equilibrium is reached under the various flow rate conditions. That assumption appears to be questionable especially at loadings close to unity or higher. As the loading was not measured, one cannot be sure if the amount of $CO_2$ absorbed estimated

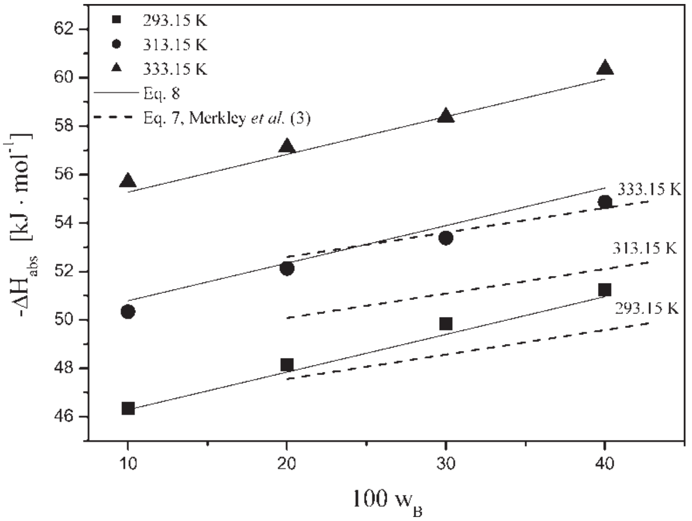

***Figure 4.*** Enthalpies of absorption of $CO_2$ in aqueous MDEA solutions compared with the literature data.

from that loading is not overestimated. Since the kinetics of the reaction of $CO_2$ with MDEA is not rapid, it is possible that the reaction (1) may not be completed by the time the mixed sample leaves the calorimeter. In consequence, it would result in underestimated absolute values of enthalpy of absorption. Finally, in the region close to saturation point, $CO_2$ is not completely absorbed e.g. it is present in the solution also in molecular form and the determined enthalpy actually does not state for the reaction described by Eq. (1). In both papers $\Delta H_{abs}$ values for a certain amine concentration and temperature were measured for different loadings which were achieved by adjusting the relevant flow rates. The authors claim that the values of $\Delta H_{abs}$ change insignificantly with loading but on the other hand, they are relatively scattered which makes it difficult to determine $\Delta H_{abs}$ precisely. Thus Merkley et al. (3) expressed the $\Delta H_{abs}$ data into (kJ per mole of MDEA). The enthalpy of absorption per mole of $CO_2$ was then determined as the slope of the linear ascending relationship of $\Delta H_{abs}$ per mole of MDEA versus loading. The method is somewhat analogous to the present method. Mathonat et al. (4) decided to associate $\Delta H_{abs}$ with the average of different enthalpy values (kJ per mole of $CO_2$) obtained for the range of loading from $\alpha$ close to zero ($\alpha \to 0$) until the saturation loading.

From the comparison of the present and literature enthalpy data, it is apparent that the difference between two sets of data is increasing with temperature. The analysis of the experimental procedure of previous authors (3, 4) reveals that the measured heat effect reflected both the exothermic heat effect corresponding to absorption of the gas in the solution and the endothermic effect corresponding to vaporization of water into the gas stream. It seems reasonable that occurrence of this phenomenon can result in higher enthalpies of absorption (lower absolute values) measured in previous papers 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 a start of the experiment the amine solution was in equilibrium with its vapor. At such conditions, the dosing of pure carbon dioxide was not followed by the further evaporation of solvent.

## CONCLUSIONS

The reaction calorimeter was successfully used in the measurement of gas solubility and heat effects during carbon dioxide absorption into aqueous solutions of MDEA. The experimental technique involved measurements of the gas phase pressure in the storage tank and heat flow rate with respect to time during semibatch isothermal absorption of the gas. Contrary to previous studies, in this work the heat effects of $CO_2$ absorption into aqueous solutions of MDEA were effectively investigated together with solubility measurements. A new method of measuring the enthalpy of absorption was proposed. The reaction calorimetry technique was found to be more accurate than microcalorimetric techniques used previously by other investigators (3, 4). The enthalpy of absorption was found to be independent of pressure and its absolute value increased linearly with temperature and MDEA concentration. The obtained values of $-\Delta H_{abs}$ were higher than those reported in the literature by Merkley et al. (3) and Mathonat et al. (4). This difference is attributed to the fact that the previously measured enthalpies additionally stood for the heat effect corresponded to the vaporization of water into the $CO_2$ stream. Moreover, the previous absolute values of $\Delta H_{abs}$ seem to be underestimated due to the assumptions involved in the calculation of the amount of substance of absorbed gas.

Where the comparison was possible, the solubility results were in reasonable agreement with those published in the literature. The obtained data of enthalpies of absorption and gas solubilities are essential for the design of absorption/desorption columns using MDEA to separate $CO_2$ from various gas streams. Since the enthalpy of absorption is directly related to the energy requirements for the solvent regeneration, it is desirable that the value should be determined accurately to avoid uneconomic overdesign.

## NOMENCLATURE

| | |
|---|---|
| $n_A$ | amount of substance of $CO_2$, kmol |
| N | stirring speed, $min^{-1}$ |

| | |
|---|---|
| $p_A$ | partial pressure, MPa |
| P | total pressure, MPa |
| r | correlation coefficient |
| $R_A$ | absorption rate of $CO_2$, kmol $\cdot$ $s^{-1}$ |
| t | time, s |
| T | temperature, K |
| q | heat flow rate, W |
| Q | amount of heat, J |
| $w_B$ | amine mass fraction |
| V | volume, $m^3$ |
| $\alpha$ | loading of $CO_2$ in amine, mol $CO_2$/mol MDEA |
| $\sigma$ | standard deviation of enthalpy data determination, kJ $\cdot$ $mol^{-1}$ |
| $\Delta H_{abs}$ | enthalpy of chemical absorption, kJ $\cdot$ $mol^{-1}$ |
| $\Delta H_{phys}$ | enthalpy of physical absorption, kJ $\cdot$ $mol^{-1}$ |
| $\Delta H_r$ | enthalpy of chemical reaction, kJ $\cdot$ $mol^{-1}$ |

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