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# ENTHALPIES OF ABSORPTION OF CARBON DIOXIDE IN AQUEOUS METHYLDIETHANOLAMINE SOLUTIONS *

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## ABSTRACT

An isothermal flow calorimeter was used to measure the enthalpies of absorption of carbon dioxide in aqueous 20, 40, and 60 wt.% methyldiethanolamine (MDEA) solutions. The experimental temperature and pressure ranges were 288.71 to 422.04 K and 156 to 1466 kPa, respectively. The experimental equipment and procedure are described, with emphasis on the complexities originating from the difficulty of measuring the enthalpy of absorption of a gas in an aqueous solution. The calorimetric data were also found to be useful in determining the equilibrium concentrations of $CO_2$ in the MDEA solutions. Both enthalpy of absorption and equilibrium concentration data for $CO_2$–aqueous MDEA systems are reported and compared with existing values from other investigations. The enthalpy of absorption of $CO_2$ in aqueous MDEA solutions was found to be independent of pressure and linearly dependent upon both the temperature and the MDEA concentration. An equation is given for predicting the enthalpy of absorption over the ranges of temperatures, pressures, and concentrations investigated.

## INTRODUCTION

A knowledge of the enthalpies of absorption, $\Delta H_{abs}$, of acid gases ($H_2S$, $CO_2$, $SO_2$, etc.) in aqueous solutions of amine solvents is useful in the design of equipment used to separate the acid gas impurities from raw natural gas streams. In an absorber, the $\Delta H_{abs}$, the amounts of the acid gases absorbed, the heat capacities of the solutions, and the heat losses from the column determine the temperatures of the exiting solutions. A knowledge of both

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* We, the authors, dedicate this paper to Professor W.W. Wendlandt in honor of his 60th birthday and in recognition of his long and dedicated service to the journal "Thermochimica Acta". We have been associated with Professor Wendlandt since the inception of the journal and have always found him to be an outstanding editor and a pleasant person with whom to work. He has achieved through much hard work and effort a major journal representing and servicing the many areas of thermodynamics and analytical chemistry.

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the enthalpies of absorption of the acid gas in the solvent and the solution heat capacity is essential for the calculation of the required intermediate cooling or heating to achieve a desired exit temperature and a desired concentration of the acid gas in the solution exiting an absorber. In a stripping column, heat supplied to the reboiler raises the temperature of the solution, causing both dissociation of the acid gas–amine compounds and vaporization of a portion of the amine solvent. The required reboiler heat duty of a stripper can be calculated from $\Delta H_{abs}$ data, together with heat capacity, enthalpy of vaporization, and vapor–liquid equilibrium data.

The enthalpies of absorption of $CO_2$ in aqueous solutions of methyldiethanolamine (2,2′-(methylimino)bis-ethanol, abbreviated MDEA) reported in this paper will help provide a data base of $\Delta H_{abs}$ values useful to the gas processing industry.

## EXPERIMENTAL

The chemicals employed were carbon dioxide (Whitmore Oxygen Co., 99.98 mol% pure), methyldiethanolamine (Aldrich Chemical Company, 99 wt.% pure), and distilled, deionized water. The $CO_2$ was filtered through a Matheson model 450 gas purifier containing a molecular sieve desiccant. Prior to preparation of the aqueous MDEA solutions, the deionized, distilled water was boiled for 20 min to drive out any dissolved carbon dioxide. During cooling, a $CO_2$ absorbing tube was attached to the top of the boiling flask with a one-hole stopper to prevent contamination of the water by atmospheric $CO_2$. The various weight percent MDEA solutions were kept from exposure to $CO_2$ in the air by mixing only one liter at a time, and by minimizing the time of exposure to the surroundings. To reduce exposure of the solution to the atmosphere, the solutions were not filtered. All of the aqueous solutions were degassed in an ultrasonic bath for approximately 10 min prior to use.

The $\Delta H_{abs}$ measurements were obtained with two isothermal flow calorimeters that were developed at Brigham Young University. The calorimeters used were moderate temperature (244 to 550 K), high pressure (0 to 41 MPa) isothermal, flow calorimeters. They have been described previously in the literature [1,2]. The measurements at the two lower temperatures (288.71 and 333.15 K) were made with a calorimeter submerged in a constant temperature water bath, while a calorimeter surrounded by a constant temperature air bath was used to collect data at the two higher temperatures (388.71 and 422.04 K). Two different pump systems (a Varian, Inc. 8700 series, and an ISCO Model 314 series) were used in the operation of the units.

The procedure used to measure $\Delta H_{abs}$ has been described [3]. The accuracy of the calorimeters has been shown to be better than ± 1% for heat of mixing runs made with certain liquid–liquid test systems. However, in the determination of $\Delta H_{abs}$ of a gaseous reactant ($CO_2$) in an aqueous amine solution, the complexity of the experimental measurements is increased. The major difficulties encountered and how they were handled has been discussed [3]. As a result of these complexities, the accuracy of the calorimetric measurements reported here is estimated to be ± 5%. The precision of the $\Delta H_{abs}$ measurements can be estimated by examining the results of repeat runs which were made for 5 of the 18 experimental systems. Comparing the two results for each of the 5 systems showed that in each case, the two results agreed within 4%.

## RESULTS

Enthalpies of absorption for $CO_2$ in MDEA–water solutions were measured at the conditions listed in Table 1. The experimental $\Delta H_{abs}$ were plotted versus $CO_2$ loading (mol $CO_2$/mol MDEA) for each of the 18 systems. The plots of $\Delta H_{abs}$ vs. $CO_2$ loading for all 18 systems can be found in ref. 4. Figure 1 is a plot for the 40 wt.% MDEA, 388.71 K, 1121 kPa system. This figure reveals that the measured $\Delta H_{abs}$ is independent of the amount of $CO_2$ absorbed below the saturation concentration (loading point). This behavior was observed in all 18 systems. Past the loading or saturation point, $\Delta H_{abs}$ fell toward zero. This trend is consistent with the results found in a similar study completed recently on the absorption of $CO_2$ into aqueous diglycolamine (DGA) systems [3].

The numerical value of the straight line portion in Fig. 1 was obtained from the slope of the line describing the data below the loading point plotted in units of kJ/mol MDEA. Figure 2 is a plot of the $\Delta H_{abs}$ data in units of kJ/mol MDEA for the 40wt.% MDEA, 388.71 K, 1121 kPa system. The slope of the straight line portion below the saturation point was found by a modified least-squares linear regression which forces the line describing the experimental data below the loading point to pass through the origin. The data were manipulated in this way because it was found that small deviations from linearity in the data plotted in units of kJ/mol MDEA were

TABLE 1

Experimental conditions at which enthalpies of absorption were measured

| | |
|---|---|
| Temperature, K: | 288.71, 333.15, 388.71, 422.04 |
| Concentration, wt.% MDEA: | 20, 40, 60 |
| Pressure, kPa: | 156 at 288.71 and 333.15 K<br>1121 at 288.71, 333.15 and 388.71 K<br>1466 at 422.04 K |

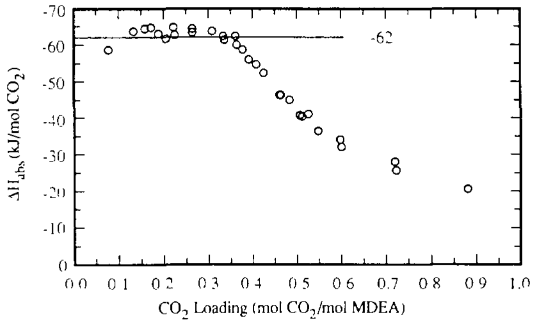

Fig. 1. Enthalpy of absorption vs. $CO_2$ loading for 40 wt.% MDEA, 388.71 K, 1121 kPa.

greatly magnified when the data were plotted in units of kJ/mol $CO_2$.

Pressure was found to have virtually no effect on the values of $\Delta H_{abs}$ for a given MDEA concentration. At the two lower temperatures (288.71 and 333.15 K) experimental runs were made at both 156 kPa and 1121 kPa for each MDEA concentration (a total of 12 runs, 6 at the lower pressure). In the case of 4 of the 6 lower pressure runs, the values of $\Delta H_{abs}$ below the loading point differed by less than 2% from the results of the higher pressure runs. For the other 2 lower pressure systems, the higher pressure and lower pressure determinations agreed to within 9%. Based upon these observations, it was decided to forego measurements at the lower pressure for all MDEA solutions at 388.71 and 422.04 K. In addition, it was observed that at 422.04 K higher system pressures lead to greater ease of measurement of $\Delta H_{abs}$. Thus, the assumed pressure independence was extended to 1466 kPa. Since the total presssure within the calorimeter is equivalent to the partial pressure of $CO_2$ above the aqueous solution, $\Delta H_{abs}$ at loadings below the saturation point is essentially independent of the partial pressure of $CO_2$ for partial pressures between 156 and 1466 kPa. This result is also consistent with the findings of the DGA study [3] referred to previously.

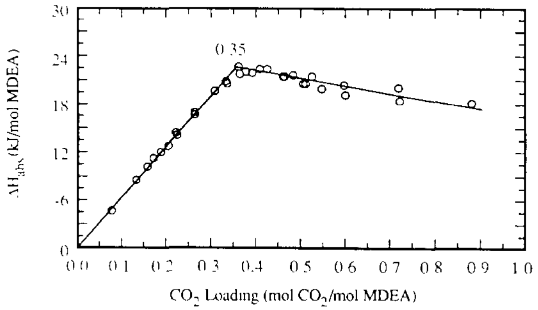

Fig. 2. Enthalpy of absorption vs. $CO_2$ loading for 40 wt.% MDEA, 388.71 K, 1121 kPa.

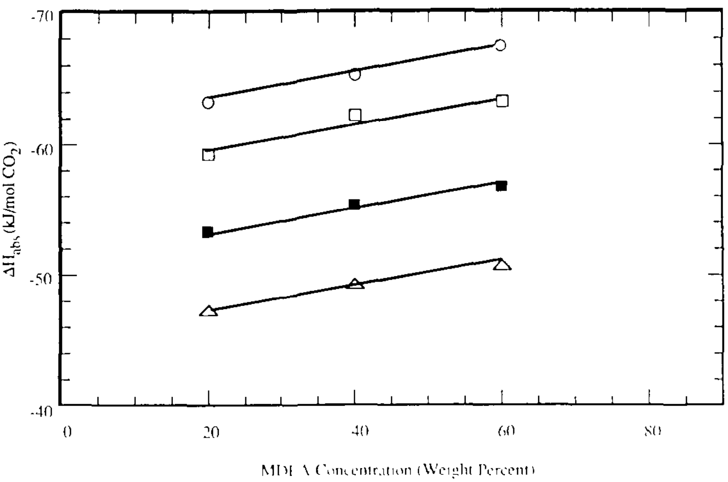

Fig. 3. Enthalpy of absorption vs. MDEA concentration at several temperatures. Values applicable for $CO_2$ loadings below the saturation point, $CO_2$ partial pressures between 156 and 1466 kPa and temperatures of: Δ, 288.7 K; ■, 333.2 K; □, 388.7; and ○, 422.07 K. Solid lines, ———, are given by eqn. (1).

Within the carbon dioxide partial pressure ranges of this study, the experimentally determined $\Delta H_{abs}$ ranged from − 47 kJ/mol $CO_2$ for 20 wt.% MDEA solutions at 288.71 K to − 66 kJ/mol $CO_2$ for 40 wt.% MDEA solutions at 422.04 K (the negative enthalpy values indicate exothermic absorption reactions).

Figure 3 is a plot of the $\Delta H_{abs}$ values for $CO_2$ loadings below the saturation point as a function of MDEA concentration at each of the four temperatures investigated. It is apparent from this plot that $\Delta H_{abs}$ below the loading point is a function of both MDEA concentration and temperature. This finding is in contrast to the results of the DGA study [3] in which $\Delta H_{abs}$ was found to be dependent upon DGA concentration but independent of temperature over the same ranges of concentration and temperature as this study. A multiple linear regression of the experimental data points shown in Fig. 3 gives the equation:

$$\Delta H_{abs}[\mathrm{kJ/mol\ CO_2}] = -0.101x_w - 0.126T - 8.60 \qquad (1)$$

where $x_w$ represents the weight percent of the MDEA in solution, and $T$ is the temperature in K. Equation (1) (plotted on Fig. 3) represents a good fit of the experimental data. Equation (1) can be used to determine $\Delta H_{abs}$ of carbon dioxide in aqueous MDEA solutions within the temperature range 288.71 to 422.04 K and the $CO_2$ partial pressure range 156 to 1466 kPa for solutions between 20 and 60 wt.% MDEA. It is important to recognize that the $\Delta H_{abs}$ values reported in Fig. 3 and given by eqn. (1) are valid only for $CO_2$ loadings less than the saturation concentration of carbon dioxide in the solution.

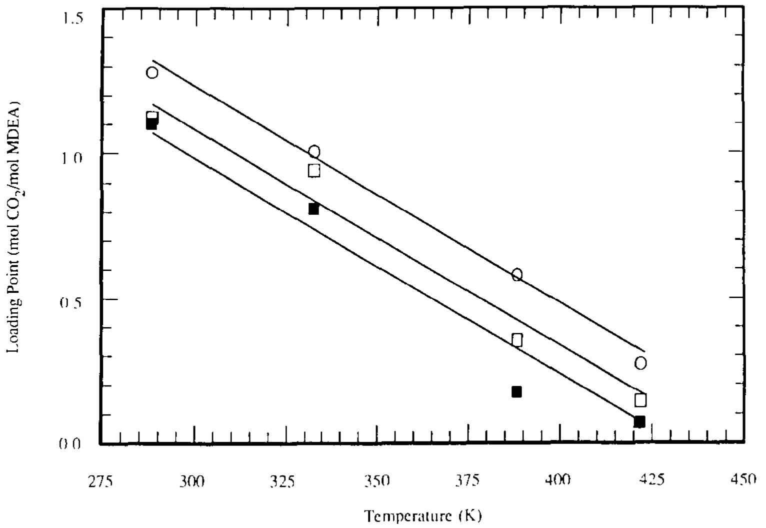

Fig. 4. Calorimetrically determined loading points vs. temperature for three MDEA concentration at a constant pressure of 1121 kPa (1466 kPa at 422.04 K) and three MDEA concentrations of: ○, 20 wt.%; □, 40 wt.%; and ■, 60 wt.%.

In addition to providing the $\Delta H_{abs}$ of $CO_2$ in aqueous MDEA solutions, the calorimetric data provided a means of determining the saturation concentration (loading point) of $CO_2$ in the solution. An examination of Fig. 2 reveals $\Delta H_{abs}$ [kJ/mol MDEA] to be a linear function of the loading (mol $CO_2$/mol MDEA) both above and below the saturation point. The loading point was taken to be the loading at which the data points started to deviate from the line representing the data beyond saturation (0.35 mol $CO_2$/mol MDEA for the data plotted in Fig. 2). The experimentally determined loading points are approximately linear functions of temperature, as can be seen in Fig. 4 which is a plot of these loading points as a function of temperature and MDEA concentration at a constant pressure of 1121 kPa (except at 422.04 K where the system pressure was 1466 kPa).

## DISCUSSION

The question of whether equilibrium is obtained in the calorimeter under flow conditions needs to be discussed. For the very similar DGA study [3], the equilibrium question was investigated several times, and all indications were that conditions either at or close to equilibrium were present for all of the DGA experimental runs. For this DGA study, identical experimental points (i.e., measurement of $\Delta H_{abs}$ at a specified loading value) were taken over a wide range of flow rates (calorimeter residence times) and all $\Delta H_{abs}$ results were found to agree, within the experimental error. Preliminary runs were made at very low flow rates giving residence times of 19, 38, 187, and 281 minutes (3–12 minutes is normal residence time for most of the experimental data reported here). $\Delta H_{abs}$ values for the runs with long residence times matched a previously determined set of data (taken at residence times from 3–12 minutes) for the 20 wt.% DGA solution at 288.71 K and 156 kPa. This indicates that conditions at or very near equilibrium were present for the DGA system. In addition, a visual flow apparatus (transport tubing) was constructed that had approximately the same configuration as the flow calorimeter in order to observe the absorption of carbon dioxide into the amine solution. Under conditions of temperature, pressure, and molar flow rates similar to calorimeter operating conditions, complete absorption of the gas was observed in less time (half or less) than the normal residence time in the calorimeter. In the case of this MDEA study, on several occasions a data point representing a certain $CO_2$ loading was taken repeatedly at differing volumetric flow rates (giving residence times of 3–12 minutes) to see if the value of $\Delta H_{abs}$ changed with flow rate. Had equilibrium conditions not existed, a flow rate dependent $\Delta H_{abs}$ value would have been observed. This flow rate dependency would have indicated that conditions closer to equilibrium were present at the higher residence times than at the lower residence times. No flow rate dependency was observed, so conditions at or close to equilibrium were assumed present for all MDEA runs.

Few literature values of $\Delta H_{abs}$ for aqueous MDEA solutions are available for comparison. Dibble [5] reports a value of $-49$ kJ/mol $CO_2$. His method of obtaining this value is unknown, as are the temperature, pressure, MDEA concentration, and loading at which the $\Delta H_{abs}$ value is valid. The values reported here range from $-47$ to $-66$ kJ/mol $CO_2$ and enclose the single value of Dibble. Pearce [6] reports a value of $-59$ kJ/mol $CO_2$ for unknown conditions of temperature, pressure, concentration, and loading. Again, the results of this study enclose this single value. Polasek and Bullin [7] report a value of $-61$ kJ/mol $CO_2$ for an unknown temperature, a solution between 30 and 50 wt.% MDEA and unlimited gas loadings. From eqn. (1) and the range of temperatures encountered in this study, the values reported here range from $-48$ to $-68$ kJ/mol $CO_2$. Thus, the data of this study enclose the single value reported above, although this study shows a concentration dependency in contrast to Polasek's results.

Of the results that have been published, only Jou et al. [8] report data over a wide range of conditions of temperature, pressure, and concentration. Jou et al. [8] measured the solubility of carbon dioxide in two different MDEA solutions (23.5 wt.% MDEA and 52 wt.% MDEA) at temperatures from 298 to 393 K and pressures up to 6600 kPa. They found approximate values of $\Delta H_{abs}$ of $CO_2$ in MDEA solutions from solubility data using an equation equivalent to the Clausius–Clapeyron equation, as proposed by Crynes and Maddox [9]. They report that $\Delta H_{abs}$ values calculated in this manner are

TABLE 2

Comparison of calorimetrically determinated enthalpies of absorption with values from literature sources

| $\Delta H_{abs}$ [kJ/mol $CO_2$] This study | | $\Delta H_{abs}$ [kJ/mol $CO_2$] From literature | | |
|---|---|---|---|---|
| $\Delta H_{abs}$ | Method/Conditions | $\Delta H_{abs}$ | Method/Conditions | Ref. |
| −47 to −66 | Experimental data; 20 wt.%, 288.7 K to 40 wt.%, 422.0 K | −49 | Unknown method; $T$, $P$, % MDEA, and loading ranges unknown | 5 |
| −47 to −66 | Experimental data; 20 wt.%, 288.7 K to 40 wt.%, 422.0 K | −59 | Unknown method; $T$, $P$, % MDEA, and loadings ranges unknown | 6 |
| −50 to −67 | From eqn. (1); 30 wt.%, 288.7 K to 50 wt.%, 422.0 K | −61 | Unknown method; Unknown $T$, 30–50 wt.% MDEA, all loadings | 7 |
| −47 to −64 | From eqn. (1); 23.5% MDEA from 288.7 to 422.0 K, independent of loading | −42 to −65 | Solubility measurement; 23.5% MDEA, dependent on loading, independent of $T$ | 8 |
| −50 to −67 | From eqn. (1); 52% MDEA from 288.7 to 422.0 K, independent of loading | −53 to −65 | Solubility measurement; 52% MDEA, dependent on loading, independent of $T$ | 8 |

independent of temperature, but dependent upon the weight percent MDEA and upon the loading of the solution at loadings greater than 0.3 mol $CO_2$/mol MDEA. The results reported here show that the $\Delta H_{abs}$ are functions of concentration and temperature but independent of loading. Jou et al. report $\Delta H_{abs}$ values below the loading point ranging from − 42 to − 65 kJ/mol $CO_2$ for the 23.5 wt.% MDEA solution (independent of temperature). The values of this study (from eqn. 1), which ranged from − 47 kJ/mol $CO_2$ at 288.71 K to − 64 kJ/mol $CO_2$ at 422.04 K, compare favorably with Jou's results. Likewise, Jou et al. report $\Delta H_{abs}$ values below the loading point ranging from − 53 to − 65 kJ/mol $CO_2$ for the 52 wt.% MDEA solution. From eqn. (1), the values of this study (−50 kJ/mol $CO_2$ at 288.71 K and −67 kJ/mol $CO_2$ at 422.04 K) match well with the range of values reported by Jou et al.

These comparisons (summarized in Table 2) show a good agreement between the experimentally measured $\Delta H_{abs}$ and those found in the literature. However, the experimental data of this study contradict some of the trends of $\Delta H_{abs}$ with temperature and concentration as reported in the literature.

A comparison of the experimental loading points and the loading points

TABLE 3

Comparison of calorimetrically determined loading points with those measured with a static equilibrium cell

| System | | | Loading point | | |
|---|---|---|---|---|---|
| Wt.% MDEA | Temperature (K) | Pressure (kPa) | Calorimeter [a] | Static cell | Lit. ref. for static cell data |
| 20 | 310.93 | 1121 | 1.14 | 1.11 | 10 |
| 20 | 338.71 | 1121 | 0.93 | 1.01 | 10 |
| 20 | 388.71 | 1121 | 0.58 | 0.54 | 11 |
| 23.5 | 298.15 | 1121 | 1.21 | 1.20 | 8 |
| 23.5 | 373.15 | 1121 | 1.10 | 1.12 | 8 |
| 23.5 | 373.15 | 1121 | 0.64 | 0.68 | 8 |
| 23.5 | 393.15 | 1121 | 0.49 | 0.49 | 8 |

[a] Those values not specifically measured in this study were obtained by interpolation of the experimental data.

determined by the static cell method of measuring vapor–liquid equilibrium is included in Table 3. The values of this study show good agreement (within 9%) to the direct measurement of the loading. The values of the experimental loading points listed in Table 3 for conditions not specifically investigated in this research were found by linear interpolation of the experimental loading points.

## SUMMARY

Isothermal flow calorimetry provided an accurate means of measuring $\Delta H_{abs}$ of a gas in a liquid. The $\Delta H_{abs}$ measurements reported in this paper for the absorption of carbon dioxide in aqueous MDEA solutions have an estimated accuracy of ± 5% and a demonstrated precision of ± 4%. In addition, the calorimetrically obtained data allow a determination of the equilibrium concentration of $CO_2$ in the solution.

An analysis of the experimental $\Delta H_{abs}$ data for the 18 test systems revealed the following:

(1) $\Delta H_{abs}$ are constant over the $CO_2$ loading range of 0 mol $CO_2$/mol MDEA to near the saturation point of $CO_2$ in the aqueous solutions.

(2) $\Delta H_{abs}$ below the loading point is essentially independent of the partial pressure of $CO_2$ above the MDEA solutions for partial pressures between 156 and 1466 kPa.

(3) $\Delta H_{abs}$ below the loading point is a linear function of temperature (between 288.71 and 422.04 K), and concentration (between 20 and 60 wt.% MDEA). This functionality is given by eqn. (1).

## ACKNOWLEDGEMENTS

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