

## ENTHALPIES OF ABSORPTION OF CARBON DIOXIDE IN AQUEOUS DIETHANOLAMINE SOLUTIONS

J.L. OSCARSON \*, R.H. VAN DAM, J.J. CHRISTENSEN \*\*, and R.M. IZATT

*Departments of Chemical Engineering and Chemistry, Brigham Young University, Provo,  
Utah 84602 (U.S.A.)*

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### ABSTRACT

An isothermal flow calorimeter was used to measure the enthalpies of absorption of carbon dioxide in aqueous 20, 35, and 50 wt.% diethanolamine (DEA) solutions. The experimental temperature and pressure ranges were 299.82–399.82 K and 0.087–1.121 MPa, 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<sub>2</sub> in the DEA solutions. Both enthalpy of absorption and equilibrium concentration data for CO<sub>2</sub>-aqueous DEA systems are reported and compared with existing values from other investigations. The enthalpy of absorption of CO<sub>2</sub> in aqueous DEA solutions was found to be independent of pressure and DEA concentration, and linearly dependent upon the temperature. 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,  $\Delta H_{\text{abs}}$ , of acid gases (H<sub>2</sub>S, CO<sub>2</sub>, SO<sub>2</sub>, 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  $\Delta H_{\text{abs}}$ , 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 the  $\Delta H_{\text{abs}}$  of the acid gas in the solvent and the solution heat capacity is essential for the calculation of the intermediate cooling or heating required 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 dissocia-

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\* Author to whom all correspondence should be addressed.

\*\* Deceased 5 September 1987.

tion of the acid gas-amine complexes and vaporization of a portion of the amine solvent. The required reboiler heat duty of a stripper can be calculated from  $\Delta H_{\text{abs}}$  data, together with heat capacity, enthalpy of vaporization, and vapor-liquid equilibrium data.

The  $\Delta H_{\text{abs}}$  for  $\text{CO}_2$  in aqueous solutions of diethanolamine (2,2'-imino-diethanol, abbreviated to DEA) reported in this paper will help to provide a data base of  $\Delta H_{\text{abs}}$  values useful to the gas processing industry.

## EXPERIMENTAL

The chemicals employed were carbon dioxide (Whitmore Oxygen Co., 99.98 mol% pure), diethanolamine (Aldrich Chemical Company, 98 wt.% pure), and distilled, deionized water. The  $\text{CO}_2$  was filtered through a Matheson gas purifier model 450 containing a molecular sieve desiccant. Prior to preparation of the aqueous DEA solutions, the deionized, distilled water was boiled for 20 minutes to drive out any dissolved  $\text{CO}_2$ . During cooling, a  $\text{CO}_2$ -absorbing tube was attached to the top of the boiling flask with a one-hole stopper to prevent contamination of the water by atmospheric  $\text{CO}_2$ . The various weight percent DEA solutions were kept from exposure to  $\text{CO}_2$  in the air by mixing only one liter at a time and by minimizing the time of exposure to the surroundings, and were then stored in sealed one liter bottles. All of the aqueous solutions were degassed in an ultrasonic bath for approximately 10 min prior to use.

The  $\Delta H_{\text{abs}}$  measurements were obtained using moderate temperature (244–550 K), high pressure (0.1–41 MPa), isothermal flow calorimeters. The measurements at the two lower temperatures (299.82 and 349.82 K) were made with a calorimeter submerged in a constant temperature water bath [1], while a calorimeter surrounded by a constant temperature air bath was used to collect data at the higher temperature (399.82 K) [2]. Two different pump systems (a Varian, Inc. 8700 series, and an ISCO Model-314 series) were used in the operation of the units, both of which are positive displacement syringe pumps.

The procedure used to measure the  $\Delta H_{\text{abs}}$  has been described [3]. The accuracy of the calorimeters has been shown to be better than  $\pm 1\%$  for heat of mixing runs made with certain liquid-liquid test systems [4]. However, in the determination of  $\Delta H_{\text{abs}}$  for gaseous ( $\text{CO}_2$ ) and liquid (aqueous amine solution) reactants, 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  $\pm 5\%$ . The precision of the  $\Delta H_{\text{abs}}$  measurements can be estimated by examining the earlier results of duplicate runs for selected systems. In these systems, duplicate runs were made for 5  $\text{CO}_2$  and aqueous methyldiethanolamine

(MDEA) [5] solutions and for 6 CO<sub>2</sub> and aqueous diglycolamine (DGA) [3] solutions. The results for these systems showed agreement to within 4%.

## RESULTS AND DISCUSSION

Values of  $\Delta H_{\text{abs}}$  for CO<sub>2</sub> in DEA-water solutions were measured under the conditions listed in Table 1. The experimental  $\Delta H_{\text{abs}}$  values in units of J g<sup>-1</sup> CO<sub>2</sub> were plotted versus CO<sub>2</sub> loading (mol CO<sub>2</sub>/mol DEA) for each of the 18 systems. The plots of  $\Delta H_{\text{abs}}$  against CO<sub>2</sub> loading for all 18 systems are available [6]. Results are given in Fig. 1 for a representative system, i.e., 20 wt.% DEA, 349.82 K, and 1.121 MPa. This figure reveals that the measured  $\Delta H_{\text{abs}}$  is independent of the amount of CO<sub>2</sub> absorbed below the saturated loading point. This behavior was observed in all 18 systems studied. The  $\Delta H_{\text{abs}}$  value approaches zero asymptotically past the saturated loading point. This trend is consistent with the results found in similar studies recently completed on the absorption of CO<sub>2</sub> into aqueous DGA [3] and MDEA [5] systems.

In Fig. 2,  $\Delta H_{\text{abs}}$  values are plotted in units of J g<sup>-1</sup> DEA for the same system as in Fig. 1. The slope of the initial straight line portion prior to the saturated loading point was found by a modified least-squares linear regression which forces the line describing the experimental data below the saturated loading point to pass through the origin. The numerical value in Fig. 1 (-1698 J g<sup>-1</sup> CO<sub>2</sub>) is identical to the slope of the initial linear portion of the plot in Fig. 2. The data were manipulated in this way because it was found that small deviations from linearity in the data plotted in units of J g<sup>-1</sup> DEA were greatly magnified when the data were plotted in units of J g<sup>-1</sup> CO<sub>2</sub>.

Pressure was found to have virtually no effect on the values of  $\Delta H_{\text{abs}}$  for a given DEA concentration. At the lowest temperature (299.82 K), experimental runs were made at 0.087, 0.156, and 1.121 MPa for each DEA concentration (a total of nine runs). In all of these runs, the calculated  $\Delta H_{\text{abs}}$  values below the saturated loading point differed by less than five

TABLE 1

Experimental conditions at which enthalpies of absorption ( $\Delta H_{\text{abs}}$ ) were measured

Temperature (K)	299.82, 349.82, 399.82
Concentration (wt.% DEA)	20, 35, 50
Pressure (MPa)	0.087 at 299.82 K 0.225 at 299.82 and 349.82 K 1.121 at 299.82, 349.82, and 399.82 K

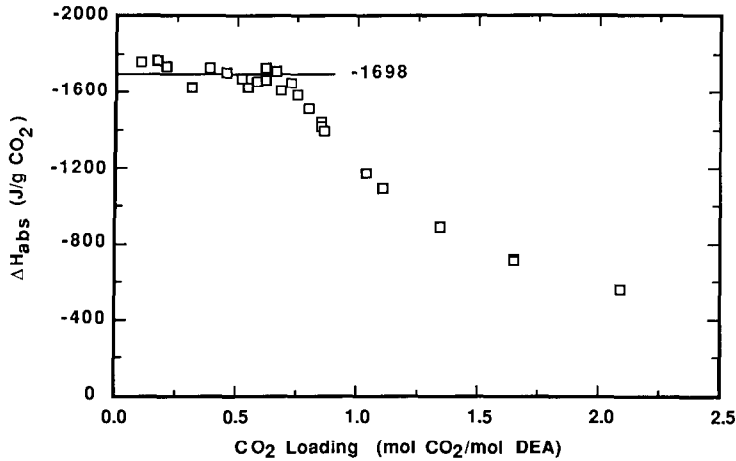


Fig. 1. Enthalpy of absorption versus  $\text{CO}_2$  loading for 20 wt.% DEA, 349.82 K, and 1.121 MPa.

percent between the high pressure runs and the low pressure runs. At 399.82 K, a system pressure of 1.121 MPa lead to greater ease of measurement of  $\Delta H_{\text{abs}}$ . Because the total pressure within the calorimeter is only slightly greater than the partial pressure of  $\text{CO}_2$  above the aqueous solution,  $\Delta H_{\text{abs}}$  at loadings below the saturated loading point is essentially independent of the partial pressure of  $\text{CO}_2$  for partial pressures between 0.087 and 1.121 MPa. This result is also consistent with the findings of the DGA [3] and MDEA studies [5]. Within the  $\text{CO}_2$  partial pressure ranges of this study, the experimentally determined  $\Delta H_{\text{abs}}$  values ranged from  $-69 \text{ kJ mol}^{-1} \text{ CO}_2$

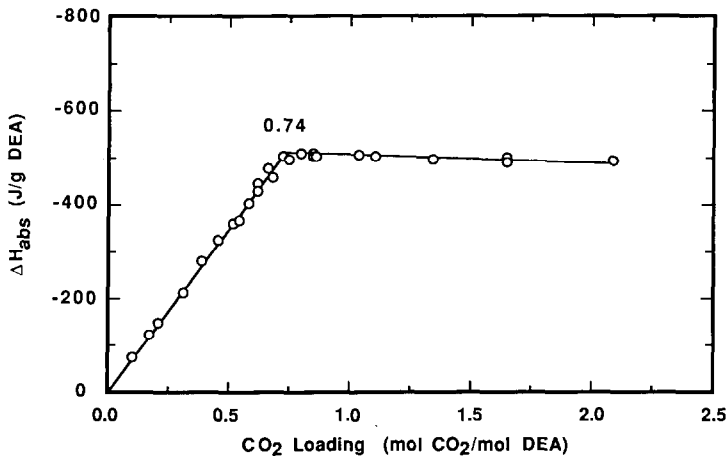


Fig. 2. Enthalpy of absorption versus  $\text{CO}_2$  loading for 20 wt.% DEA, 349.82 K, and 1.121 MPa. The saturated loading point is indicated at 0.74 mol  $\text{CO}_2$ /mol DEA.

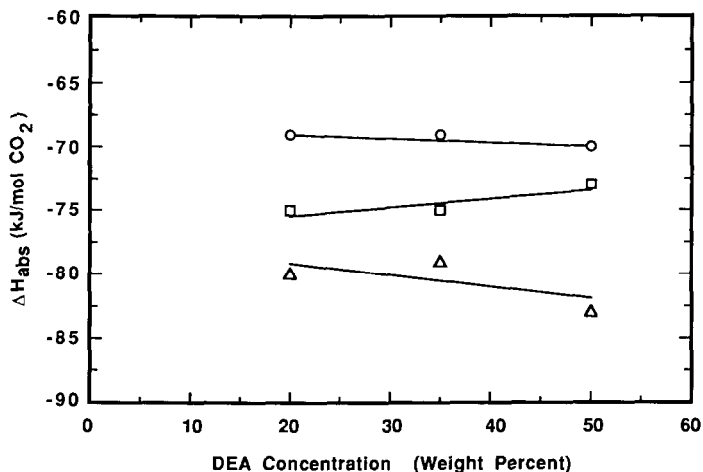


Fig. 3. Enthalpy of absorption versus DEA concentration for CO<sub>2</sub> loadings below the saturated loading point and at a total pressure of 1.121 MPa at temperatures of: ○, 299.82 K; □, 349.82 K; △, 399.82 K. Solid lines, —, are given by eqn. (1).

for 20 wt.% DEA solutions at 299.82 K to  $-83 \text{ kJ mol}^{-1} \text{ CO}_2$  for 50 wt.% DEA solutions at 399.82 K.

Figure 3 is a plot of the  $\Delta H_{\text{abs}}$  values for CO<sub>2</sub> loadings below the saturated loading point as a function of DEA concentration at each of the three temperatures investigated. It is apparent from this plot that  $\Delta H_{\text{abs}}$  is a stronger function of temperature than of concentration. These findings are in contrast to the results of the DGA study in which  $\Delta H_{\text{abs}}$  was found to be dependent upon the DGA concentration but independent of the temperature, and also to the results of the MDEA study in which  $\Delta H_{\text{abs}}$  was found to be dependent upon both the MDEA concentration and the temperature. The DGA and MDEA studies were conducted over the same ranges of concentration and temperature as the study presented here. A linear regression of the experimental data points shown in Fig. 3 gives the equation

$$\Delta H_{\text{abs}} (\text{kJ mol}^{-1} \text{ CO}_2) = -0.113 T - 35.2 \quad (1)$$

where  $T$  represents the temperature in K. The solid lines in Fig. 3 are calculated using eqn. (1). Equation (1) can be used to determine  $\Delta H_{\text{abs}}$  of CO<sub>2</sub> in aqueous DEA solutions within the temperature range 299.82–399.82 K, and the CO<sub>2</sub> partial pressure range of 0.087–1.121 MPa, for solutions between 20 and 50 wt.% DEA. It is important to recognize that the  $\Delta H_{\text{abs}}$  values reported in Fig. 3 and given by eqn. (1) are valid only for CO<sub>2</sub> loadings less than the saturated loading concentration of CO<sub>2</sub> in the solution.

In addition to providing  $\Delta H_{\text{abs}}$  values for CO<sub>2</sub> in aqueous DEA solutions, the calorimetric data provided a means of determining the saturated loading point of CO<sub>2</sub> in the solution. An examination of Fig. 2 reveals that

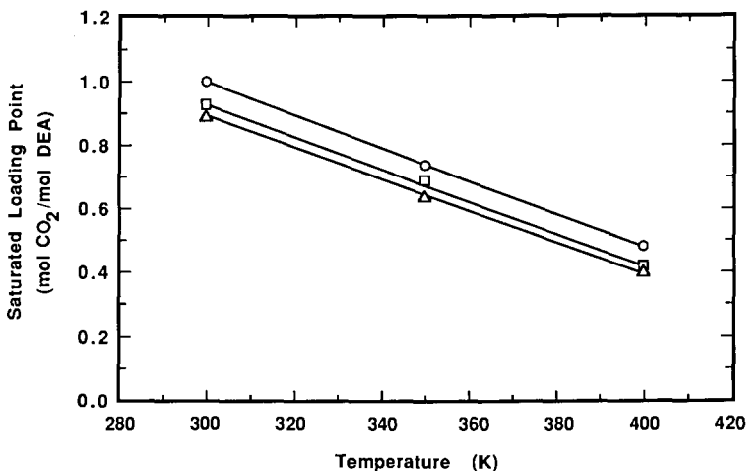


Fig. 4. Saturated loading points versus temperature at a constant pressure of 1.121 MPa for three DEA concentrations of:  $\circ$  20 wt.%;  $\square$ , 35 wt.%; and  $\triangle$ , 50 wt.%.

$\Delta H_{\text{abs}}$  is a linear function of the loading (mol CO<sub>2</sub>/ mol DEA) both above and below the saturated loading point. The saturated loading point was taken to be the abscissa value corresponding to the sharp discontinuity in the slope of the curve. As is seen in Fig. 4, there is a linear relationship between saturated loading point and temperature.

It is important to establish that chemical equilibrium is reached in the calorimeter under the flow conditions used. For the similar DGA study [3], the attainment of chemical equilibrium was established. In the DGA study, the  $\Delta H_{\text{abs}}$  values were found to be independent of flow rate for a wide range of calorimeter residence times. In addition, a visual flow apparatus (transparent tubing) was constructed that had approximately the same configuration as the flow calorimeter in order to observe the absorption of CO<sub>2</sub> into the amine solution. Under conditions of temperature, pressure, and molar flow rates similar to those used during operation of the calorimeter, complete absorption of the gas was observed in half or less time than the normal residence time in the calorimeter. In the present study with CO<sub>2</sub> and DEA, data points representing certain CO<sub>2</sub> loadings were taken at several different volumetric flow rates (giving residence times of 3–12 min) to see if the value of  $\Delta H_{\text{abs}}$  changed with flow rate. Had equilibrium conditions not existed, a dependence of  $\Delta H_{\text{abs}}$  on flow rate would have been observed. No flow rate dependency was observed, so conditions at or close to equilibrium were assumed to exist for all DEA runs.

In Table 2,  $\Delta H_{\text{abs}}$  values are given together with literature values. Good agreement is seen between the values reported in this study and those reported by others. The  $\Delta H_{\text{abs}}$  values reported by us and by Kahrim and Mather [7] were determined calorimetrically. All other values were obtained

TABLE 2

Comparison of enthalpies of absorption ( $\Delta H_{\text{abs}}$ ) of  $\text{CO}_2$  in diethanolamine solutions

Source	Ref.	$-\Delta H_{\text{abs}}$ ( $\text{kJ mol}^{-1} \text{CO}_2$ )									
		Conditions		$M^a = 2.0$		$M = 3.5$		$M = 5.0$		$M = 3.5$	
		$T = 298 \text{ K}$		$T = 298 \text{ K}$		$T = 298 \text{ K}$		$T = 298 \text{ K}$		$T = 348 \text{ K}$	
Loading =		0.2	0.4	0.2	0.4	0.2	0.4	0.2	0.4	0.2	0.4
		(mol $\text{CO}_2$ /mol DEA)									
This study <sup>b</sup>	[6]	69	69	69	69	70	70	75	75		
Kahrim and Mather	[7]	74.6	74.6	74.6	74.6	74.6	74.6	74.3	55.1		
Lee, Otto, Mather	[8]	67.2	59.5	76.3	65.4	84.3	70.5	76.3	65.4		
Murzin and Leites	[9]	65.5	–	71.6	–	74.6	–	71.6	–		
Bottoms	[10]	66.9	66.9	66.9	66.9	66.9	66.9	66.9	66.9		

<sup>a</sup>  $M$  = molarity of the DEA solution.

<sup>b</sup> Temperatures for this study (300 and 350 K) are slightly different than those given (298 and 348 K). Also, the  $\Delta H_{\text{abs}}$  values given for this work are for a total pressure of 1.121 MPa.

from the temperature variation of partial pressure versus concentration data. The  $\Delta H_{\text{abs}}$  values from the literature given in Table 2 were measured at temperatures of 298 and 348 K which are close to the temperatures of this work, namely 300 and 350 K. The results of Kahrim and Mather and of Bottoms [10] show no temperature dependence of  $\Delta H_{\text{abs}}$ . In contrast, the  $\Delta H_{\text{abs}}$  values in the present study do show a temperature dependence. The remaining studies [8,9] are inconclusive on this point. Lee et al. [8] found that the absolute magnitude of  $\Delta H_{\text{abs}}$  decreases as the moles  $\text{CO}_2$  to moles DEA ratio becomes greater than 0.2. This result was not found in the remaining studies, including our own. In our investigations of the MDEA and DGA systems, it was found that  $\Delta H_{\text{abs}}$  is independent of loading up to the saturated loading point.

## SUMMARY

Isothermal flow calorimetry provides an accurate ( $\pm 5\%$ ) means of measuring the  $\Delta H_{\text{abs}}$  of a gas in an aqueous solution containing a reactive solute. In addition, the data allow a determination of the saturated loading point of  $\text{CO}_2$  in the solution. The following conclusions can be drawn from the  $\Delta H_{\text{abs}}$  data. First,  $\Delta H_{\text{abs}}$  is constant over the  $\text{CO}_2$  loading range of 0 mol  $\text{CO}_2$ /mol DEA to near the saturated loading point of  $\text{CO}_2$ . Second,  $\Delta H_{\text{abs}}$  below the saturated loading point is essentially independent of the partial pressure of  $\text{CO}_2$  above the DEA solutions for total pressures between 0.087 and 1.121 MPa. Third,  $\Delta H_{\text{abs}}$  values below the saturated loading point can be represented, within experimental error, as a linear function of tempera-

ture (between 299.82 and 399.82 K), and are independent of the concentration (between 20 and 50 wt.% DEA).

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