

ENTHALPIES OF ABSORPTION OF HYDROGEN SULFIDE IN AQUEOUS METHYLDIETHANOLAMINE SOLUTIONS

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ABSTRACT

An isothermal flow calorimeter was used to measure the enthalpies of absorption of hydrogen sulfide in aqueous 1.7, 3.0 and 4.3 M methyldiethanolamine (MDEA) solutions. The experimental temperature and pressure ranges were 299.8–399.8 K and 0.087–1.12 MPa respectively. The calorimetric data were found to be useful in determining the equilibrium concentrations of H₂S in the MDEA solutions. Both enthalpy of absorption and equilibrium concentration data for H₂S–aqueous MDEA systems are reported. The enthalpy of absorption of H₂S in aqueous MDEA solutions was found to be independent of pressure, and linearly dependent upon the temperature and concentration. An equation is given for predicting the enthalpy of absorption over the temperature, pressure, and concentration ranges investigated.

INTRODUCTION

A knowledge of the enthalpies of absorption, ΔH_{abs} , of acid gases (H₂S, CO₂, SO₂, etc.) in aqueous amine solutions is useful in the design of equipment used to separate the acid gas impurities from raw natural gas streams. This paper is the fifth in a series [1–4] reporting enthalpies of absorption of CO₂ and H₂S in alkanol amine solutions. In an absorber, the ΔH_{abs} values, 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 ΔH_{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 dissociation of the acid gas–amine complexes and vaporization of a portion of the solution. The required reboiler heat duty of a stripper can

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be calculated from ΔH_{abs} data, together with heat capacity, enthalpy of vaporization, and vapor–liquid equilibrium data.

The ΔH_{abs} for H_2S in aqueous solutions of methyldiethanolamine (2,2'-methyliminodiethanol; MDEA) reported in this paper will help to provide a data base of ΔH_{abs} values useful to the gas processing industry.

EXPERIMENTAL

The chemicals employed were hydrogen sulfide (Matheson gas products, 99.5% purity), MDEA (Aldrich Chemical Company, 99 wt.% pure), and distilled, deionized water. Prior to preparation of the aqueous MDEA solutions, the deionized, distilled water was boiled for 20 min to drive out any dissolved CO_2 . 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 . Exposure of the MDEA solutions to CO_2 in the air was minimized by mixing only 1 l at a time, limiting the time of exposure to the surroundings, and storing the solutions in sealed 1 l bottles. All of the aqueous solutions were degassed in an ultrasonic bath for approximately 10 min prior to use.

The ΔH_{abs} measurements were obtained using a moderate temperature (244–550 K), high pressure (0.1–41 MPa), isothermal flow calorimeter with the calorimeter submerged in a constant temperature oil bath [5]. Two ISCO model 314 series positive displacement syringe pumps were used in the operation of the units.

The procedure used to measure the ΔH_{abs} values has been described [1]. 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 [6]. However, in the determination of ΔH_{abs} for gaseous (H_2S) 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 [1]. As a result of these complexities, the accuracy of the calorimetric measurements reported here is estimated to be $\pm 5\%$. The precision of the ΔH_{abs} measurements can be estimated from earlier results of duplicate runs for selected systems. In these systems, duplicate runs were made for five CO_2 and aqueous MDEA [2] solutions and for six CO_2 and aqueous diglycolamine (DGA) [1] solutions. The results for each of these systems agreed to within 4%.

RESULTS AND DISCUSSION

Values of ΔH_{abs} for H_2S in MDEA–water solutions were measured at the conditions listed in Table 1. The experimental ΔH_{abs} values in units of J (g

TABLE 1

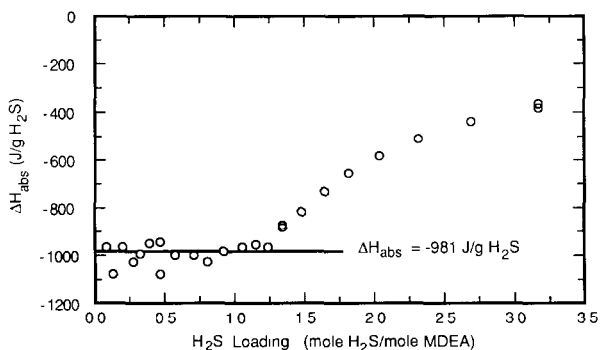
Experimental conditions at which enthalpies of absorption (ΔH_{abs}) were measured

Temperature	299.8, 349.8, 399.8
MDEA concentration (M)	1.7, 3.0, 4.3
Pressure (MPa)	0.087 at 299.8 K ^a
	0.156 at 299.8 and 349.8 K
	1.12 at 299.8, 349.8 and 399.8 K

^a Determined only at 3.0 M.

$\text{H}_2\text{S})^{-1}$ were plotted vs. H_2S loading (moles of H_2S per mole of MDEA) for each of the 15 systems. The plots of ΔH_{abs} vs. H_2S loading for all 15 systems are available [7]. Results are given in Fig. 1 for a representative system, i.e. 3.0 M MDEA, 299.8 K, and 1.12 MPa. Figure 1 reveals that the measured ΔH_{abs} values are roughly independent of the amount of H_2S absorbed below the saturated loading point. However, a computer model indicates that ΔH_{abs} shows a small but significant dependence on the loading [8]. This behavior was observed in all 15 systems studied. The ΔH_{abs} value approaches zero asymptotically past the saturated loading point. This trend is consistent with the results of similar studies of the absorption of CO_2 into aqueous DGA [1], MDEA [2], and DEA [3] and on the absorption of H_2S into aqueous DEA [4].

In Fig. 2, ΔH_{abs} values are plotted in units of $\text{J} (\text{g MDEA})^{-1}$ 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 ($-981 \text{ J} (\text{g H}_2\text{S})^{-1}$) 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 $\text{J} (\text{g MDEA})^{-1}$ were greatly magnified when the data were plotted in units of $\text{J} (\text{g H}_2\text{S})^{-1}$.

Fig. 1. Enthalpy of absorption vs. H_2S loading for 3.0 M MDEA, 299.8 K, and 1.12 MPa.

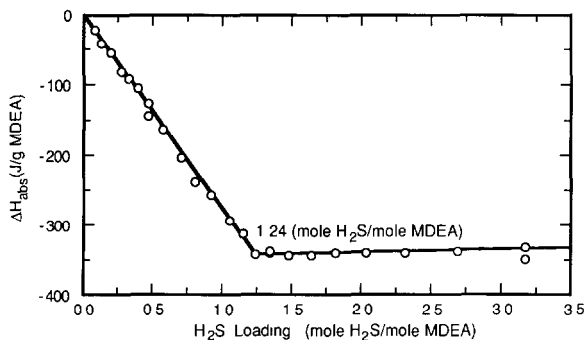


Fig. 2. Enthalpy of absorption vs. H_2S loading for 3.0 M MDEA, 299.8 K, and 1.12 MPa. The saturated loading point is indicated at $1.24 \text{ mol H}_2\text{S (mol MDEA)}^{-1}$.

Pressure was found to have virtually no effect on the values of ΔH_{abs} for a given MDEA concentration. At the lowest temperature (299.8 K), experimental runs were made at 0.087 (3.0 M), 0.156 (1.7 and 3.0 M), and 1.12 (1.7, 3.0, and 4.3 M) MPa for a total of six runs. At this temperature, the calculated ΔH_{abs} values below the saturated loading point differed by less than 10% between the high pressure runs and the low pressure runs at the same concentration. At 399.8 K, a system pressure of 1.12 MPa led to greater ease of measurement of ΔH_{abs} . Since the total pressure within the calorimeter is only slightly greater than the partial pressure of H_2S above the aqueous solution, ΔH_{abs} at loadings below the saturated loading point is essentially independent of the partial pressure of H_2S for partial pressures between 0.087 and 1.12 MPa. This result is also consistent with the findings of the $\text{CO}_2 + \text{DGA}$ [1], $\text{CO}_2 + \text{MDEA}$ [2], $\text{CO}_2 + \text{DEA}$ [3], and $\text{H}_2\text{S} + \text{DEA}$ [4] studies. Within the H_2S partial pressure ranges of this study, the experimentally determined ΔH_{abs} values ranged from $-28 \text{ kJ (mol H}_2\text{S)}^{-1}$ at 299.8 K to $-45 \text{ kJ (mol H}_2\text{S)}^{-1}$ at 399.8 K.

A linear regression of 14 of the 15 data points (the point collected at 299.8 K, 1.12 MPa and 4.3 M MDEA was omitted because of excessive scatter of the data) gives the equation

$$\Delta H_{\text{abs}} \left[\text{kJ (mol H}_2\text{S)}^{-1} \right] = -1.072x_{\text{M}} - 0.1094T + 2.389 \quad (1)$$

where x_{M} is the molarity of MDEA in solution, and T represents the temperature in K. Figure 3 is a plot of the ΔH_{abs} values calculated from eqn. (1) (solid lines) and the ΔH_{abs} values measured experimentally for H_2S loadings below the saturated loading point as a function of MDEA concentration at 1.12 MPa and at each of the three temperatures investigated. This curve fit indicates that ΔH_{abs} becomes more negative with increasing temperature and concentration. These findings are in contrast to the results of the $\text{DEA}-\text{CO}_2$ system in which ΔH_{abs} was found to be independent of DEA concentration but dependent on temperature and in contrast to the

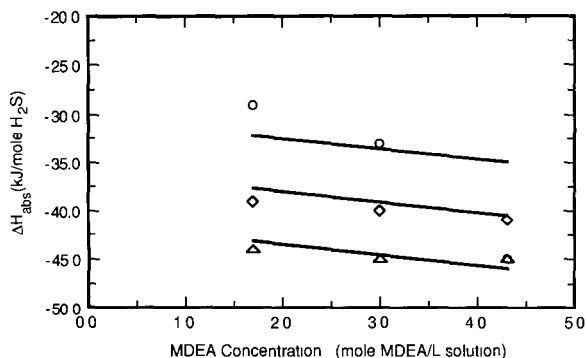


Fig. 3. Enthalpy of absorption vs. MDEA concentration for H_2S loadings below the saturated loading point at a total pressure of 1.12 MPa and at temperatures of: ○, 299.8 K; ◇, 349.8 K; △, 399.8 K. —, Given by eqn. (1).

DGA- CO_2 system in which ΔH_{abs} was found to be dependent upon DGA concentration but independent of the temperature. However, these findings are consistent with the MDEA- CO_2 and DEA- H_2S systems in which ΔH_{abs} was found to be dependent upon both the amine concentration and the temperature. The DGA- CO_2 , MDEA- CO_2 , DEA- CO_2 , and DEA- H_2S studies were conducted over the same ranges of concentration and temperature as the study presented here. Equation (1) can be used to determine ΔH_{abs} of H_2S in aqueous MDEA solutions within the temperature range 299.8–399.8 K, and the H_2S partial pressure range from 0.087 to 1.12 MPa, for solutions between 1.7 and 4.3 M MDEA. It is important to recognize that the ΔH_{abs} values reported in Fig. 3 and given by eqn. (1) are valid only for H_2S loadings less than the saturated loading concentration of H_2S in the solution.

In addition to providing ΔH_{abs} values for H_2S in aqueous MDEA solutions, the calorimetric data can be used to determine the saturated loading point of H_2S in the solution. Figure 2 shows ΔH_{abs} to be a linear function of the loading (moles of H_2S per mole of MDEA) 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, the saturated loading points determined from the enthalpy data are approximately linear functions of temperature (the point at 299.8 K and 4.3 M was ignored in calculating the lines since the data from which the loading point was determined exhibited excessive scatter). The data in Table 2 show that the saturated loading point is a function of pressure. This pressure dependence is more pronounced at the higher temperatures as is expected since the Henry's law constant for the gas increases dramatically with temperature. A summary of the ΔH_{abs} values and of the saturated loading points of all of the runs is given in Table 2.

It is important to establish that chemical equilibrium is reached in the calorimeter under the flow conditions used. For the similar CO_2 -DGA

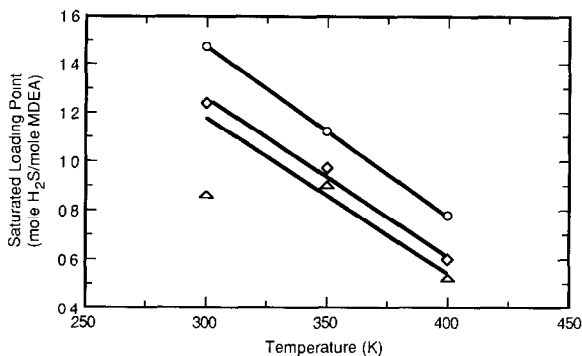


Fig. 4. Plot of saturated loading point vs. temperature at a constant pressure of 1.12 MPa for three MDEA concentrations of: \circ , 1.7 M; \diamond , 3.0 M; and \triangle , 4.3 M. The point at 299.8 K and 4.3 M was ignored because of excessive scatter in the data used to calculate the value.

study [1], the attainment of chemical equilibrium was established. In the DGA study, the ΔH_{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_2 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 of the normal residence time in the calorimeter. In the study with CO_2 and

TABLE 2

Enthalpies of solution ΔH_{abs} for H_2S in aqueous MDEA solutions below the saturated loading point together with saturated loading point values

System			ΔH_{abs} (kJ (g mol $\text{H}_2\text{S})^{-1})$	Saturated loading point (mol H_2S (mol MDEA) $^{-1}$)
1.7 M MDEA,	299.8 K,	0.156 MPa	-28	1.02
1.7 M MDEA,	299.8 K,	1.12 MPa	-29	1.47
3.0 M MDEA,	299.8 K,	0.087 MPa	-36	0.74
3.0 M MDEA,	299.8 K,	0.156 MPa	-36	0.93
3.0 M MDEA,	299.8 K,	1.12 MPa	-33	1.24
4.3 M MDEA,	299.8 K,	1.12 MPa	-45	0.86
1.7 M MDEA,	349.8 K,	0.156 MPa	-38	0.67
1.7 M MDEA,	349.8 K,	1.12 MPa	-39	1.12
3.0 M MDEA,	349.8 K,	0.156 MPa	-38	0.55
3.0 M MDEA,	349.8 K,	1.12 MPa	-40	0.97
4.3 M MDEA,	349.8 K,	0.156 MPa	-38	0.48
4.3 M MDEA,	349.8 K,	1.12 MPa	-41	0.90
1.7 M MDEA,	399.8 K,	1.12 MPa	-44	0.78
3.0 M MDEA,	399.8 K,	1.12 MPa	-45	0.60
4.3 M MDEA,	399.8 K,	1.12 MPa	-45	0.52

DEA [3], data points representing certain CO₂ loadings were taken at several different volumetric flow rates (giving residence times of 3–12 min) to see whether the value of ΔH_{abs} changed with flow rate. Had equilibrium conditions not existed, a dependence of ΔH_{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.

SUMMARY

Isothermal flow calorimetry provides an accurate ($\pm 5\%$) means of measuring the ΔH_{abs} value of a gas in an aqueous solution containing a reactive solute. In addition, the data allow a determination of the saturated loading point of H₂S in the solution. The following conclusions can be drawn from the ΔH_{abs} data. First, ΔH_{abs} is nearly constant over the H₂S loading range of 0.0 mol H₂S (mol MDEA)⁻¹ to near the saturated loading point of H₂S. Second, ΔH_{abs} below the saturated loading point is essentially independent of the partial pressure of H₂S above the MDEA solutions for total pressures between 0.087 and 1.12 MPa. Third, ΔH_{abs} values below the saturated loading point can be represented, within experimental error, as a linear function of temperature (between 299.8 and 399.8 K) and concentration (between 1.7 and 4.3 M MDEA).

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