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ENTHALPIES OF ABSORPTION OF HYDROGEN SULFIDE IN AQUEOUS DIETHANOLAMINE SOLUTIONS *

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ABSTRACT

An isothermal flow calorimeter was used to measure the enthalpies of absorption of hydrogen sulfide in aqueous 2.0, 3.5 and 5.0 M diethanolamine (DEA) solutions. The experimental temperature and pressure ranges were 299.9–399.9 K and 0.087–1.121 MPa respectively. The calorimetric data were found to be useful in determining the equilibrium concentrations of H_2S in the DEA solutions. Enthalpy of absorption and equilibrium concentration data for H_2S–aqueous DEA systems are reported. The enthalpy of absorption of H_2S in aqueous DEA solutions was found to be independent of pressure, and linearly dependent on temperature and concentration. An equation is given for predicting the enthalpy of absorption over the ranges of temperature, pressure and concentration investigated.

INTRODUCTION

A knowledge of the enthalpies of absorption ΔH_{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 enthalpy of absorption ΔH_{abs}, the amounts of 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 enthalpy of absorption 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

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* Dedicated to Professor James J. Christensen (deceased 5 September 1987) in memory of his contribution to innovation in calorimetry.

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complexes and vaporization of a portion of the amine solvent. The required reboiler heat duty of a stripper can be calculated from ΔH_{abs} data, together with heat capacity, enthalpy of vaporization and vapor–liquid equilibrium data.

The ΔH_{abs} values for H_2S in aqueous solutions of diethanolamine (2,2′-iminodiethanol, abbreviated DEA) reported in this paper will help to provide a database of ΔH_{abs} values useful to the gas processing industry.

EXPERIMENTAL

The chemicals employed were hydrogen sulfide (Matheson gas products; purity 99.5%), diethanolamine (Aldrich Chemical Company; purity, 98 wt.%) and distilled, deionized water. Prior to preparation of the aqueous DEA solutions, the distilled, deionized water was boiled for 20 min to drive off 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 DEA 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 in sealed bottles (1 l). All of the aqueous solutions were degassed in an ultrasonic bath for approximately 10 min prior to use.

The ΔH_{abs} measurements were carried out using moderate temperature (244–550 K), high pressure 0.1–41 MPa), isothermal flow calorimeters. The measurements at the two lower temperatures (299.9 and 349.9 K) were made with a calorimeter submerged in a constant temperature water or ethylene glycol (commercial antifreeze) bath [1], while a calorimeter surrounded by a constant temperature oil bath was used to collect data at the highest temperature (399.9 K) [2]. Two ISCO model-314 series positive displacement syringe pumps were used in the operation of the units.

The procedure used to measure the enthalpy of absorption 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 the enthalpy of absorption 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 have 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 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 plus aqueous methyldiethanolamine (MDEA) solutions [5] and for six CO_2 plus aqueous diglycolamine (DGA) solutions [3]. The results for each of these systems showed agreement to within 4%.

RESULTS AND DISCUSSION

Values of ΔH_{abs} for H_2S in DEA–water solutions were measured under the conditions listed in Table 1. The experimental ΔH_{abs} values in units of joule per gram of H_2S were plotted vs. H_2S loading (mol H_2S (mol DEA)$^{-1}$) for each of the 17 systems. The plots of ΔH_{abs} vs. H_2S loading for all 17 systems are available [6]. Results are given in Fig. 1 for a representative system, i.e. 5.0 M DEA at 399.9 K and 1.121 MPa. Figure 1 reveals that the measured ΔH_{abs} value is roughly independent of the amount of H_2S absorbed below the saturated loading point. However, preliminary work on a fundamental computer model has indicated that the ΔH_{abs} value shows a small dependence on the loading, noticeably at low loading values. This behavior was observed in all 17 systems studied. The ΔH_{abs} value approaches zero asymptotically past the saturated loading point. This trend is consistent with the results of similar studies completed on the absorption of CO_2 in aqueous DGA [3], MDEA [5] and DEA [7].

In Fig. 2, ΔH_{abs} values are plotted in units of joule per gram of 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

TABLE 1

Experimental conditions of measurement of enthalpy of absorption H_{abs}

Temperature (K)	299.9, 349.9, 399.9
DEA concentration (M)	2.0, 3.5, 5.0
Pressure (MPa)	0.087 at 299.9 K
	0.225 at 299.9 and 349.9 K
	1.121 at 299.9, 349.9 and 399.9 K

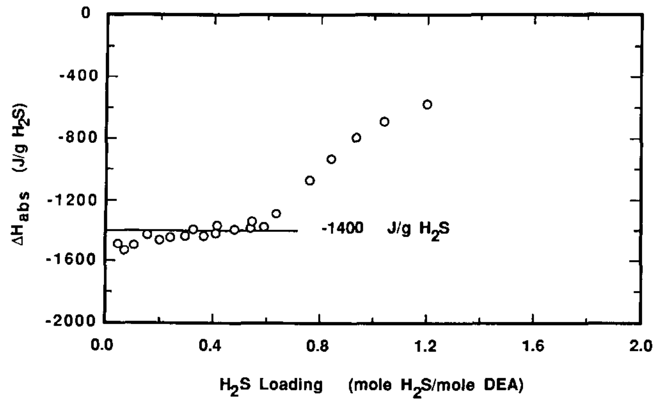

Fig. 1. Enthalpy of absorption vs. H_2S loading for 5.0 M DEA at 399.9 K and 1.121 MPa.

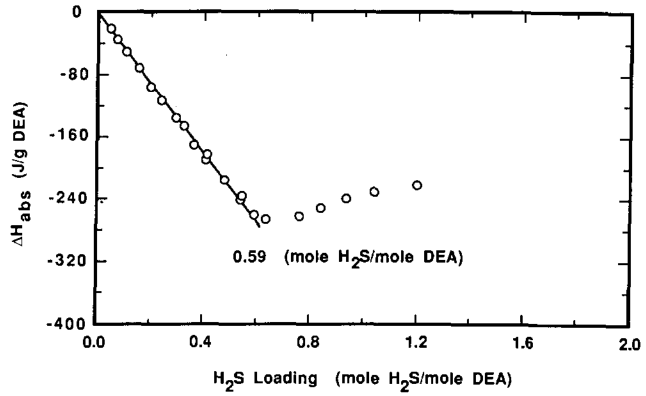

Fig. 2. Enthalpy of absorption vs. H_2S loading for 5.0 M DEA at 399.9 K and 1.121 MPa. The saturated loading point is indicated at 0.59 mol H_2S (mol DEA)$^{-1}$.

below the saturated loading point to pass through the origin. The numerical value in Fig. 1 (-1400 J (g H_2S)$^{-1}$) is identical with 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 joule per gram of DEA were greatly magnified when the data were plotted in units of joule per gram of H_2S.

Pressure was found to have virtually no effect on the values of ΔH_{abs} for a given DEA concentration. At the lowest temperature (299.9 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 ΔH_{abs} values below the saturated loading point differed by less than 10% between the high pressure runs and the low pressure runs. At 399.9 K, a system pressure of 1.121 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, the value of 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 1.121 MPa. This result is also consistent with the findings of the DGA [3], MDEA [5] and DEA [7] studies. Within the H_2S partial pressure ranges of this study, the experimentally determined ΔH_{abs} values range from -37 kJ (mol H_2S)$^{-1}$ at 299.9 K to -51 kJ (mol H_2S)$^{-1}$ at 399.9 K.

Figure 3 shows a plot of the ΔH_{abs} values for H_2S 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 ΔH_{abs} is a function of temperature and concentration. These findings are in contrast with the results of the DEA–CO_2 system in which ΔH_{abs} was found to be independent of DEA concentration but dependent on temperature and in contrast with the DGA–CO_2 system in which ΔH_{abs} was found to be dependent on DGA concentration but independent of temperature. How-

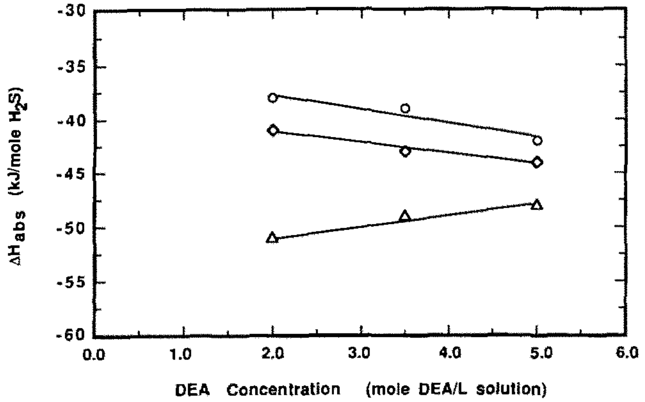

Fig. 3. Enthalpy of absorption vs. DEA concentration for H_2S loadings below the saturated loading point at a total pressure of 1.121 MPa and at temperatures of: ○, 2.99 K; ◇, 349.9 K; △, 399.9 K. Full lines are given by eqn. (1).

ever, the findings are consistent with the MDEA–CO_2 system in which ΔH_{abs} was found to be dependent on both the MDEA concentration and the temperature. The DGA, MDEA and DEA 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

$$\Delta H_{abs}\left(\mathrm{kJ(mol\ H_2S)}^{-1}\right) = 14.69x_M - 98.01T - 9467 \tag{1}$$

where x_M is the molarity of DEA in solution and T is the temperature in Kelvins. The full lines in Fig. 3 were calculated using eqn. (1). Equation (1) can be used to determine the enthalpy of absorption of H_2S in aqueous DEA solutions within the temperature range 299.9–399.9 K and the H_2S partial pressure range 0.087–1.121 MPa for solutions between 2.0 and 5.0 M DEA. 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 DEA solutions, the calorimetric data provide a means of determining the saturated loading point of H_2S in the solution. An examination of Fig. 2 reveals that ΔH_{abs} is a linear function of the loading (mol H_2S (mol DEA)$^{-1}$) below the saturated loading point. The saturated loading point is 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 data also 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 Henry's law constant for the gas increases dramatically with temperature.

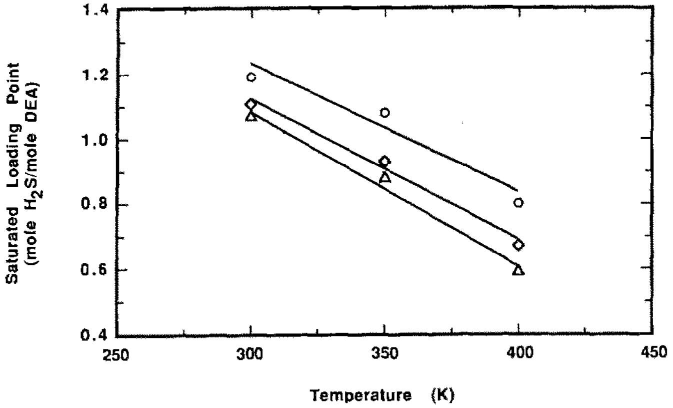

Fig. 4. Saturated loading points vs. temperature at a constant pressure of 1.121 MPa for three DEA concentrations of: ○, 2.0 M; ◇, 3.5 M; △, 5.0 M.

It is important to establish that chemical equilibrium is reached in the calorimeter under the flow conditions used. For the similar CO_2–DGA study [3], 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 time than the normal residence time in the calorimeter. In the study with CO_2 and DEA, data points representing certain CO_2 loadings were taken at several different volumetric flow rates (giving residence times of 3–12 min) to see if 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.

CONCLUSIONS

Isothermal flow calorimetry provides an accurate ($\pm 5\%$) means of measuring the enthalpy of absorption of a gas in an aqueous solution containing a reactive solute. In addition, the data allow a determination to be made of the saturated loading point of H_2S in the solution. The following conclusions can be drawn from the ΔH_{abs} data. Firstly, ΔH_{abs} is constant over an H_2S loading range of 0.0 mol H_2S (mol DEA)$^{-1}$ to near the saturated loading point of H_2S. Secondly, ΔH_{abs} below the saturated loading point is essentially independent of the partial pressure of H_2S above the DEA solutions for total pressures between 0.087 and 1.121 MPa. Thirdly, ΔH_{abs} values below the saturated loading point can be represented, within experimental error, as a linear function of temperature (between 299.9 and 399.9 K) and concentration (between 2.0 and 5.0 M DEA).

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