

## ENTHALPIES OF SOLUTION OF CARBON DIOXIDE IN AQUEOUS DIGLYCOLAMINE SOLUTIONS

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### ABSTRACT

An isothermal flow calorimeter was used to measure the enthalpies of solution of carbon dioxide in aqueous 10, 20, 40, and 60 wt.% diglycolamine (DGA) solutions. The experimental temperature and pressure ranges were 288.71–422.04 K and 156–1121 kPa, respectively. The experimental equipment and procedure are described, with emphasis on peculiarities originating from the difficulty of measuring the enthalpy of solution of a gas in a liquid. The calorimetric data were also found to be useful in determining the equilibrium concentrations of CO<sub>2</sub> in the DGA solutions. Both enthalpy of solution and equilibrium concentration data for CO<sub>2</sub>-aqueous DGA systems are reported and compared with existing values from other investigations. The enthalpy of solution of CO<sub>2</sub> in aqueous DGA solutions was found to be independent of temperature and pressure and linearly dependent on the concentration of DGA in solution. An equation is given for predicting the enthalpy of solution over the ranges of temperatures, pressures, and concentrations investigated.

### INTRODUCTION

A knowledge of the enthalpies of solution of acid gases (H<sub>2</sub>S, CO<sub>2</sub>, SO<sub>2</sub>, etc.) in liquid amine solvents is useful in the design of equipment used to separate the acid gas impurities from gas streams. In absorbers, the enthalpies of solution, the amounts of the acid gases absorbed, the heat capacities of the solutions, and the heat losses from the columns determine the temperatures of the solutions. The saturation concentration of a given acid gas in solution is a function of the solution temperature. Thus, a knowledge of the enthalpies of solution of the acid gases in the solvent is essential for the calculation of the required intermediate cooling or heating to achieve the desired solution temperature and the desired concentrations of acid gases in the liquid leaving absorbers. In stripping columns, heat supplied to the

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reboilers raises the temperatures of the solutions, dissociates the acid gas-amine compounds, and vaporizes some of the solvent. Enthalpy of solution measurements, together with heat capacity, enthalpy of vaporization, and vapor-liquid equilibria data, allow for the determination of the necessary reboiler heat duties in strippers.

The enthalpies of solution of  $\text{CO}_2$  in aqueous solutions of diglycolamine (2-(2-aminoethoxy)ethanol, abbreviated DGA) reported in this paper will help provide a database of enthalpy of solution values useful to the gas processing industry.

## EXPERIMENTAL

The chemicals employed were carbon dioxide (Whitmore Oxygen, Co., 99.98 mol% pure), DGA (Texaco Chemical Company, 98 wt.% pure), and distilled water. Before use, the  $\text{CO}_2$  was filtered through a Matheson gas purifier model 450 which also contains a molecular sieve dessicant. The DGA-water solutions were prepared gravimetrically, stored in sealed 4-l bottles, and, just prior to use, filtered through a Sargent No. 501 filter and degassed for 10 min in an ultrasonic bath.

The calorimeter used is a moderate temperature (244–450 K), high pressure (0.10–41 MPa), isothermal flow calorimeter that has been described previously [1,2]. Only a brief description is given here.

Isothermal calorimetry is based on maintaining, during the course of the reaction, the reaction vessel at a temperature which is constant and equal to that of the surrounding container. This condition is achieved by adjusting the energy output of a variable heater to balance the total heat generated from the chemical and physical processes plus the energy removed at a constant rate by a Peltier cooler. The method is applicable to both endothermic and exothermic reactions. No heat capacity measurements are required and no corrections are necessary for the heat exchange between the reaction chamber and its surroundings. The data can be printed out in digital form and/or obtained as a strip chart recording. Two calorimeters of the same design were used in order to cover the temperature range desired. The measurements at the two lower temperatures of the study (288.71 and 333.15 K) were made with a calorimeter submerged in a constant temperature water bath while a calorimeter contained in a constant temperature air bath was used at the two higher temperatures (388.71 and 422.04 K). Two different, positive displacement syringe pump systems (a Varian, Inc. 8700 series, and an ISCO model 314 series) were used in the operation of the units.

A block diagram of the calorimeter and constant temperature bath, the fluid circuit, and the data control and output components is shown in Fig. 1. Several components of the fluid circuit are instrumental in allowing measurements of enthalpies of solution of gaseous  $\text{CO}_2$  in aqueous DGA

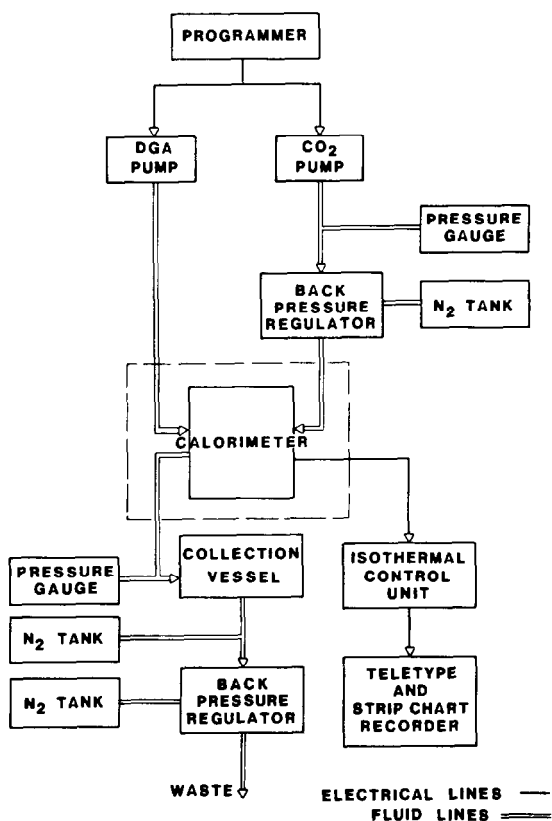


Fig. 1. Block diagram of the main components of the flow calorimeter.

solutions. The back pressure regulator on the  $\text{CO}_2$  line entering the calorimeter provides a consistent flow of gas at a constant pressure. The pressure of the  $\text{CO}_2$  is read off the gauge located between the  $\text{CO}_2$  pump and the  $\text{CO}_2$  back pressure regulator. The collection vessel traps the viscous DGA solution and prevents it from entering the outlet back pressure regulator. The DGA solution adheres to the diaphragm and the walls of the regulator and limits the ability of the regulator to maintain a constant total pressure in the system. The nitrogen tank connected to the system immediately before the outlet back pressure regulator provides a slow flow of nitrogen through the regulator at the total pressure required, thereby maintaining a constant total pressure.

The reaction vessel (Fig. 2) contains the isothermal plate and equilibration coil. Under the plate are a control heater and a high-temperature model Peltier thermoelectric cooler. The cooler is in contact with the bottom of the reaction vessel to facilitate transfer of heat from the vessel. The isothermal plate consists of an equilibration coil soldered between two round brass

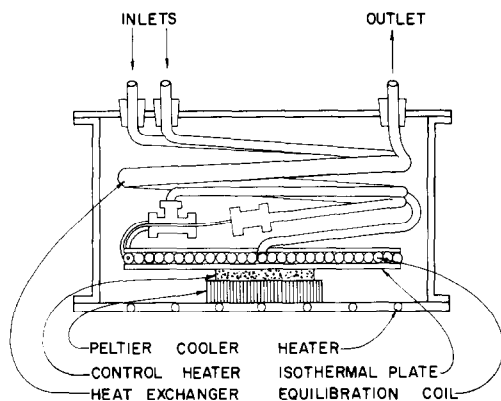


Fig. 2. Calorimeter reaction vessel and components.

plates. The equilibration coil is constructed of stainless steel tubing coiled in a flat helical shape and filled with segments of crimped stainless steel wire. The wire promotes thorough mixing of the reactants as they flow through the coil. The reactants and products are at all times contained in the stainless steel tubing comprising the inlet and outlet lines and the equilibration coil.

The procedure used to measure the enthalpies of solution is as follows. First, both components (the liquid DGA solution and the gaseous  $\text{CO}_2$ ) are run individually at the total flow rate chosen for the reaction to determine baseline heater pulse rates. Then, both components are run together (at flow rates required to obtain the desired ratio of reactants) and the reaction steady state heater pulse rate determined. The difference in the amount of energy supplied by the heater during the reaction and the amount of energy supplied by the heater during the baseline runs determines the enthalpy of reaction. The calorimeter can be calibrated either chemically, by carrying out a standard reaction, or electrically, by adding a known amount of energy via the calibration heater. For most runs, only an electrical calibration is made with a chemical calibration being made periodically to confirm the results of the electrical calibrations.

The accuracy of the two calorimeters has been shown to be better than  $\pm 1\%$  for heat of mixing runs made with two liquid reactants. Because of the difficulties of mixing and gas metering introduced when attempting to measure the enthalpy of solution of a gas in a liquid, the accuracy of the calorimetric measurements reported here is estimated to be  $\pm 3\%$ .

The precision of the enthalpy measurements can be accurately estimated because repeat runs were made for 6 of the 26 experimental systems. Comparisons between the two results obtained for each of the 6 systems show that in each case the values agree within 3%.

## RESULTS

Enthalpies of solution of carbon dioxide ( $\text{CO}_2$ ) in DGA–water solutions were measured at the conditions listed in Table 1. The experimental enthalpies of solution,  $H^s$  ( $\text{J g}^{-1} \text{CO}_2$ ), were plotted versus  $\text{CO}_2$  loading (moles  $\text{CO}_2$ /mole DGA) for each of the 26 systems. The plots of  $H^s$  vs.  $\text{CO}_2$  loading for all 26 systems can be found in ref. 3. Figure 3 is such a plot for the 40 wt.% DGA, 333.15 K, 1121 kPa system. An examination of Fig. 3 reveals that the measured enthalpy of solution is independent of the amount of  $\text{CO}_2$  absorbed below the saturation concentration (loading point). This behavior was observed in all 26 systems. The straight line portion in Fig. 3 was obtained by a modified least squares fit of the data plotted in units of  $\text{J g}^{-1}$  DGA. Figure 4 is a plot of the  $H^s$  data in units of  $\text{J g}^{-1}$  DGA for the 40 wt.% DGA, 333.15 K, 1121 kPa system. The modified least squares fit forces the line which fits the 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  $\text{J g}^{-1}$  DGA are greatly magnified when the data are plotted in units of  $\text{J g}^{-1} \text{CO}_2$ .

A plot of  $H^s$  (in units of  $\text{J g}^{-1} \text{CO}_2$ ) versus temperature at a constant pressure of 1121 kPa for  $\text{CO}_2$  loadings below the saturation point is given in Fig. 5 for the four DGA solutions investigated. An analysis of the results reported in Fig. 5 indicates that between 288.71 and 422.02 K,  $H^s$  is independent of temperature (within the estimated experimental accuracy of  $\pm 3\%$ ) for a given DGA concentration.

Pressure was also found to have virtually no effect on the values of  $H^s$  for a given DGA concentration. No systems measured showed a change in  $H^s$  ( $\text{J g}^{-1} \text{CO}_2$ ) below the loading point of greater than 3.5% between the low and high pressure ranges investigated (156–1121 kPa). Based upon this observation, it was decided to forego measurements at the lower pressure for 10 wt.% DGA solutions at all four temperatures and for 20 wt.% DGA solutions at 388.71 and 422.04 K. Since the total pressure within the calorimeter is the partial pressure of  $\text{CO}_2$  above the solvent,  $H^s$  ( $\text{J g}^{-1} \text{CO}_2$ ) at  $\text{CO}_2$  concentrations below the loading point is essentially independent of

TABLE 1

Experimental conditions at which enthalpies of solution were measured

Temperature (K)	288.17, 333.15, 388.71, 422.04
Concentration (wt.% DGA)	10, 20, 40, 60
Pressure (kPa)	1121 at all temperatures 570 at 422.04 K (except for 10 and 20 wt.% DGA) 225 at 388.71 K (except for 10 and 20 wt.% DGA) 156 at 288.71 and 333.15 K (except for 10 wt.% DGA)

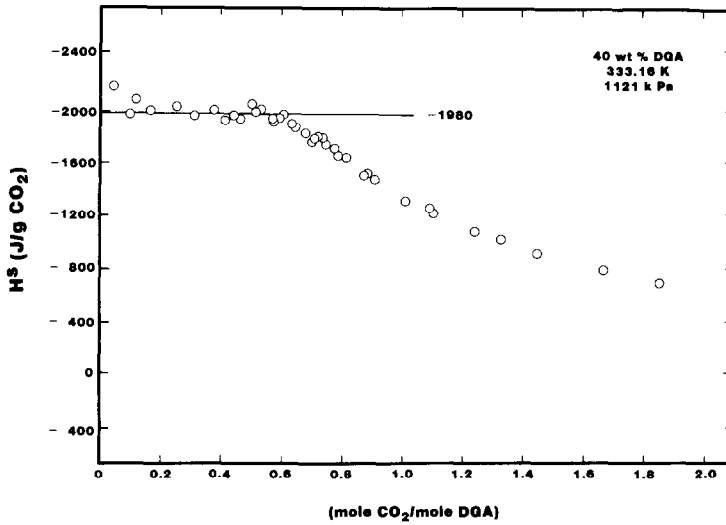


Fig. 3.  $H^s$  ( $\text{J g}^{-1} \text{CO}_2$ ) vs.  $\text{CO}_2$  loading for 40 wt.% DGA, 333.15 K, 1121 kPa.

the partial pressure of  $\text{CO}_2$  above the solution for partial pressures between 156 and 1121 kPa.

The above results indicate that the enthalpy of solution of  $\text{CO}_2$  in aqueous DGA solutions at the experimentally encountered conditions is dependent only upon the concentration of DGA in the solvent. Within the temperature and  $\text{CO}_2$  partial pressure ranges of the experimental study, the enthalpy of solution is  $-1880 \text{ J g}^{-1} \text{CO}_2$  for 10 wt.% DGA solutions,

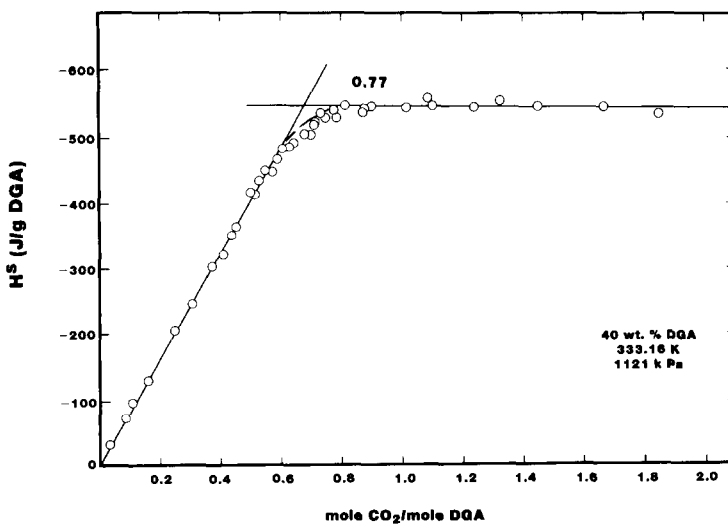


Fig. 4.  $H^s$  ( $\text{J g}^{-1} \text{DGA}$ ) vs.  $\text{CO}_2$  loading for 40 wt.% DGA, 333.15 K, 1121 kPa.

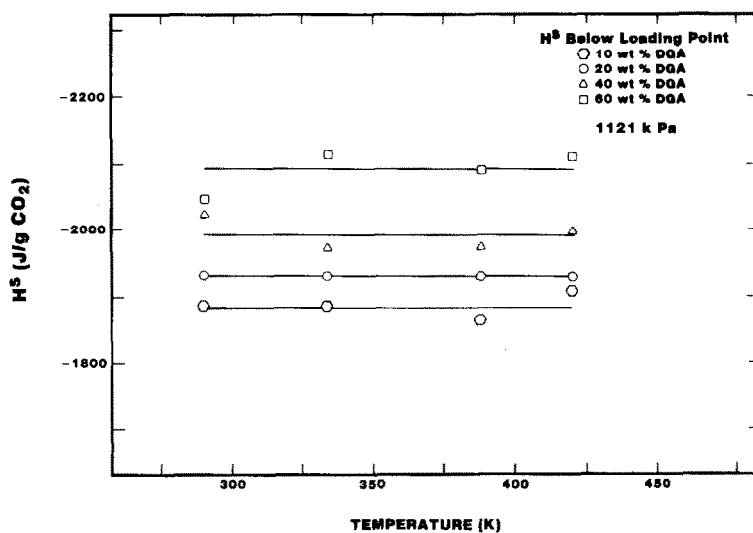


Fig. 5.  $H^s$  ( $\text{J g}^{-1} \text{CO}_2$ ) below the loading point vs. temperature at a constant pressure of 1121 kPa.

$-1930 \text{ J g}^{-1} \text{O}_2$  for 20 wt.% DGA solutions,  $-2000 \text{ J g}^{-1} \text{CO}_2$  for 40 wt.% DGA solutions, and  $-2090 \text{ J g}^{-1} \text{CO}_2$  for 60 wt.% DGA solutions (the negative enthalpy values indicate exothermic absorption reactions). Figure 6 is a plot of  $H^s$  ( $\text{J g}^{-1} \text{CO}_2$ ) versus DGA concentration. A least squares fit of

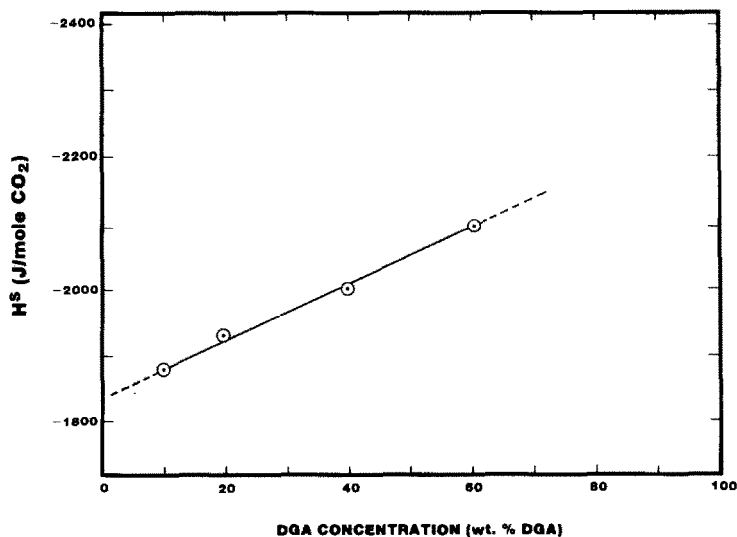


Fig. 6.  $H^s$  ( $\text{J g}^{-1} \text{CO}_2$ ) vs. DGA concentration (wt.% DGA). Values applicable for  $\text{CO}_2$  loadings below the loading point, temperatures between 288.71 and 422.04 K, and  $\text{CO}_2$  partial pressures between 156 and 1121 kPa.

the data plotted in Fig. 6 gives the equation

$$H^s(\text{J g}^{-1} \text{CO}_2) = -4.1x_w - 1840 \quad (1)$$

where  $x_w$  is the wt.% of DGA in solution. Equation (1) can be used to determine the enthalpy of solution of  $\text{CO}_2$  in aqueous DGA solutions within the temperature range 288.71–422.04 K and the  $\text{CO}_2$  partial pressure range 156–1121 kPa for solutions between 10 and 60 wt.% DGA. It is important to recognize that the  $H^s$  values reported in Figs. 5 and 6 and given by eqn. (1) are valid only for  $\text{CO}_2$  loadings less than the saturation concentration of  $\text{CO}_2$  in the solvent.

In addition to providing the enthalpy of solution of  $\text{CO}_2$  in the DGA–water solvent, the calorimetrically determined data provided a means of measuring the saturation concentration of  $\text{CO}_2$  in the solvent at 22 of the 26 test conditions. Measurements made with 10 wt.% DGA solutions were done to determine enthalpies of solution only, and therefore extensive data at  $\text{CO}_2$  loadings above the loading point (necessary for the determination of the loading point) were not taken. An examination of Fig. 4 reveals the enthalpy of solution ( $\text{J g}^{-1}$  DGA) to be a linear function of the loading (moles  $\text{CO}_2$ /mole DGA) for loadings both below and above the saturation point. The saturation concentration was taken to be the point where the data points begin to deviate from the line representing the data after the loading point (0.77 moles  $\text{CO}_2$ /mole DGA for the data in Fig. 4). The plots from which the loading points for the other 21 test conditions were determined can be found in ref. 3. The loading points determined from the enthalpy

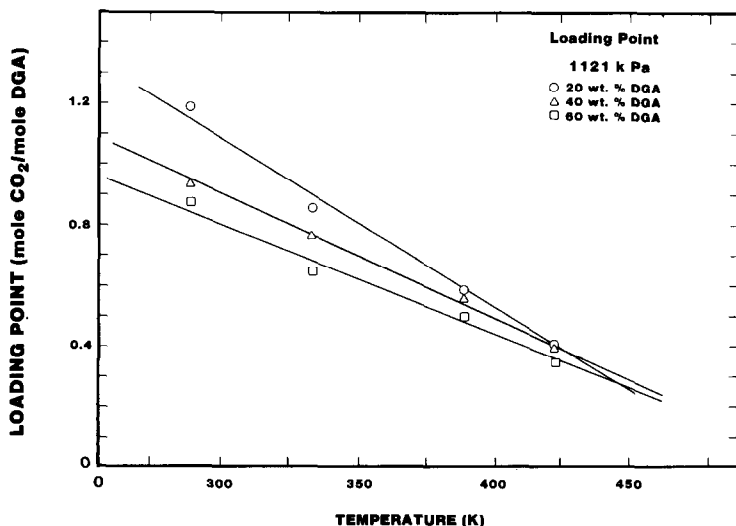


Fig. 7. Calorimetrically determined loading points vs. temperature at a constant pressure of 1121 kPa.



data are linear functions of temperature as can be seen in Fig. 7 which is a plot of the calorimetrically determined loading points versus temperature at a constant pressure of 1121 kPa.

## DISCUSSION

The question of whether equilibrium is obtained in the flow calorimeter has been investigated several times and all indications are that conditions either at or close to equilibrium are present during all runs in the calorimeter. Runs have been made over a wide range of flow rates (residence times) with all results agreeing to within the experimental error. The runs were made at very low flow rates giving residence times of 19, 38, 187, and 281 min (7–12 min is the normal residence time for most of the runs). The experimentally measured enthalpies all fell on a previously determined set of data (residence time 7–12 min) for the 20 wt.% DGA, 288.71 K, 156 kPa system. These runs quite definitely indicate that conditions either at or close to equilibrium are present in the calorimeter. Also, a visual flow apparatus was constructed that has approximately the same configuration as the flow calorimeter in order to observe the absorption of CO<sub>2</sub> in the DGA–water solution. During a run made at atmospheric pressure and ambient temperature with CO<sub>2</sub> and solvent molar flow rates similar to those encountered during the calorimetric measurements, complete absorption of the CO<sub>2</sub> was observed in less time (half or less) than the normal residence time in the calorimeter.

Few values of  $H^s$  are available for comparison. A value of  $-1980 \text{ J g}^{-1} \text{ CO}_2$  is reported [4] for the enthalpy of solution of CO<sub>2</sub> in a 95 wt.% DGA solution at a loading of 0.2 moles CO<sub>2</sub>/mole DGA. This is lower than the  $-2230 \text{ J g}^{-1} \text{ CO}_2$  value obtained by an extrapolation to 95 wt.% DGA using eqn. (1). An evaluation of the accuracy of the value reported [4] is not possible since no description of the experimental technique is given. However, the value  $-1980 \text{ J g}^{-1} \text{ CO}_2$  is reported [5] to be an approximate value for all amine concentrations.

A method has been proposed [6] that can be used to estimate  $H^s$  from equilibrium partial pressure data with an equation equivalent to the Clausius–Clapeyron equation. This method has been used recently to estimate enthalpies of solution of H<sub>2</sub>S in monoethanolamine (MEA) [6], enthalpies of solution of CO<sub>2</sub> in diethanolamine (DEA) [7,8], and enthalpies of solution of CO<sub>2</sub> and H<sub>2</sub>S in methyldiethanolamine (MDEA) [9]. Three studies determining solubility data for CO<sub>2</sub> in aqueous DGA solutions have been conducted [10–12]. Only the data presented in ref. 12 are extensive enough to allow estimation of the enthalpy of solution at a CO<sub>2</sub> loading (moles CO<sub>2</sub>/mole DGA) low enough to assure that the  $H^s$  value obtained is

TABLE 2

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

System	Loading point determined with	
	Calorimeter	Static cell <sup>a</sup>
40 wt.% DGA, 333.15 K, 1121 kPa	0.77	0.73
40 wt.% DGA, 333.15 K, 156 kPa	0.56	0.59

<sup>a</sup> Taken from ref. 10.

the enthalpy of solution below the loading point. The value of  $H^s$  in a 65 wt.% DGA solution estimated from the data in ref. 12 is  $-2070 \text{ J g}^{-1} \text{ CO}_2$  which is within 2.5% of the value obtained with the use of eqn. (1) ( $-2110 \text{ J g}^{-1} \text{ CO}_2$ ).

Loading point data measured with a static equilibrium cell at the same conditions as one of the present test systems have been reported [10]. Comparison of the loading points for the 40 wt.% DGA solution at 333.15 K determined by the authors and by the static cell method [10] shows good agreement as indicated in Table 2.

## SUMMARY

Isothermal flow calorimetry provided an accurate means of measuring enthalpies of solution of a gas in a liquid. The enthalpy of solution measurements reported in this paper for  $\text{CO}_2$ -aqueous DGA systems have an estimated accuracy of  $\pm 3\%$  and a demonstrated precision of  $\pm 3\%$ . In addition, the calorimetrically obtained data allow a determination of the equilibrium concentration of  $\text{CO}_2$  in the solution.

An analysis of the experimental enthalpy of solution data for the 26 test systems revealed the following:

(1) The enthalpy of solution ( $\text{J g}^{-1} \text{ CO}_2$  absorbed) is constant over the  $\text{CO}_2$  loading range of 0 moles  $\text{CO}_2$ /mole DGA to near the saturation point of  $\text{CO}_2$  in the DGA-water solution.

(2)  $H^s$  ( $\text{J g}^{-2} \text{ CO}_2$ ) below the loading point is independent of temperature for a given DGA concentration between 288.71 and 422.04 K.

(3)  $H^s$  ( $\text{J g}^{-1} \text{ CO}_2$ ) below the loading point is essentially independent of the partial pressure of  $\text{CO}_2$  above the DGA-water absorbent for  $\text{CO}_2$  partial pressures between 156 and 1121 kPa.

(4)  $H^s$  ( $\text{J g}^{-1} \text{ CO}_2$ ) below the loading point is a linear function of DGA concentration and is conveniently given by eqn. (1).

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