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# Heats of mixing of gaseous $CO_2/CH_4$ mixtures with aqueous solutions of methyldiethanolamine and diethanolamine

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## Abstract

The heats of mixing of gaseous $CO_2/CH_4$ mixtures with aqueous solutions of methyldiethanolamine and diethanolamine have been determined using an isothermal flow calorimeter. Data were collected at 26.7, 76.7 and 126.7°C, at total pressures of 1.38, 3.45 and 6.90 MPa, with aqueous amine concentrations of 20, 35 and 50 wt%. The nominal partial pressure of $CO_2$ in the gaseous feed stream was 0.069 MPa at a total pressure of 1.38 and 0.69 MPa at 3.45 and 6.90 MPa total pressure. A model developed to predict thermodynamic properties of these systems includes reaction equilibria, dissolution of methane, vapor-phase non-idealities, vaporization of water and amines in addition to the acid gas absorption.

*Keywords:* Heats of mixing; Methyldiethanolamine; Diethanolamine; Acid gas absorption; Flow calorimetry

## 1. Introduction

Aqueous alkanolamine solutions are widely used in the gas processing industry for the removal of acid gases ($CO_2$, $H_2S$, $SO_2$, etc.) from industrial and natural gas streams. A knowledge of the solubilities and the enthalpies of solution of these acid gases in aqueous alkanolamine solutions is necessary for the design and operation of separation equipment. Accurate data on heats of mixing of acid gases with aqueous amine solutions are needed to assist in the design of economical new amine-treating systems and to improve the efficiency of existing plants.

In order to make the acid gas removal processes more efficient, interest in using the tertiary amine methyldiethanolamine (MDEA), rather than the more traditionally used primary amines, such as monoethanolamine (MEA), and secondary amines, such as diethanolamine (DEA), has increased significantly. One advantage of MDEA is its ability to selectively absorb $H_2S$ from gas streams containing $CO_2$ and $H_2S$. The selective removal of $H_2S$ by MDEA is a result of differing reaction mechanisms for the absorption of $CO_2$ and $H_2S$ into the amine. When $H_2S$ comes in contact with an aqueous amine, it dissociates into a bisulfide ion by an instantaneous proton-transfer reaction. The absorption of $CO_2$ into a tertiary amine such as MDEA involves a multi-step reaction. The $CO_2$ must first react with water to form bicarbonate. Then the proton combines with the amine via an acid–base neutralization reaction. The rate-controlling step is the formation of the bicarbonate ion. This step ensures that the rate of absorption of $CO_2$ into MDEA solutions is several orders of magnitude slower than the

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absorption of $H_2S$. Other advantages of MDEA as a solvent are a small enthalpy of reaction with acid gases and a low vapor pressure of MDEA above the solution.

DEA is currently used widely in the gas-processing industry. It does not selectively remove $H_2S$, because $CO_2$ reacts directly with the amine. The rate of this reaction is on the same order of magnitude as the reaction of $H_2S$ with the amine, so both $H_2S$ and $CO_2$ are absorbed into aqueous DEA solutions at about equal rates.

Previously, the heats of the mixing of pure $CO_2$ into alkanolamines have been measured [1–3]. In this study, $CO_2$ was mixed with $CH_4$ in proportions representative of those found in the gas-processing industry prior to mixing with the amine solutions. A predictive model for the heats of mixing based on these systems is expected to be more realistic than models based on the absorption of $CO_2$ from the pure $CO_2$ vapor phase into amine solutions. Though methane interacts with the amines to an insignificant extent, its presence in the gas feed has a marked effect upon the measured heats. Methane provides a vapor phase that affects fugacities and allows water to evaporate.

## 2. Experimental

Heats of mixing of gaseous $CO_2/CH_4$ mixtures with MDEA and DEA solutions were measured at conditions listed in Table 1. The nominal partial pressure of $CO_2$ in the gaseous feed stream was 0.069 MPa at a total pressure of 1.38 and 0.69 MPa at 3.45 and 6.90 MPa total pressure.

Materials used in the measurements were: $CO_2$ (Air Liquide, 99.89% pure), $CH_4$ (Scott, 99.99% pure), Methyldiethanolamine (Aldrich, 99% pure), Diethanolamine (Aldrich, 99% pure), and distilled, deionized, degassed water. Matheson model 450 gas purifiers were present on both gas feed lines to remove any water present in the gases as well as any oil that may have bled into the gas from the pressure reducers or valves. In the preparation of the alkanolamine solutions, the distilled, deionized water was boiled for 20 min to expel any dissolved $CO_2$. During cooling, a $CO_2$-absorbing tube was attached to the water-containing flask through a one-hole rubber stopper to avoid recontamination of the water with $CO_2$ present in the atmosphere. To minimize exposure of the alkanolamine solutions to the atmosphere, a maximum of 1 l of solution was prepared at a time. The solutions were submerged in an ultrasonic bath for approximately 10 min immediately prior to use to drive out any remaining supersaturated gases.

The calorimetric determinations were made using two high pressure isothermal flow calorimeters similar to that described elsewhere [4]. One was used to collect data at 26.7°C and the other to collect data at 76.7 and 126.7°C. The calorimeters used in this study differed from that described earlier in the design of the mixing device. The mixing device described by Gillespie et al. [4] is limited to use with liquids of similar density. This study involved the mixing of a

Table 1
Experimental conditions at which enthalpies of mixing were measured for ($CO_2$+$CH_4$) with alkanolamine solutions

| Temperature (°C) | System pressure (MPa) | $P_{CO_2}$ (Mpa) | Concentration |
|---|---|---|---|
| 26.7 | 1.38 | 0.069 | 20, 35 wt% MDEA |
| 26.7 | 3.45 | 0.69 | 20, 35 wt% MDEA |
| 76.7 | 1.38 | 0.069 | 20, 50 wt% MDEA |
| 76.7 | 3.45 | 0.69 | 20, 35, 50 wt% MDEA |
| 76.7 | 6.90 | 0.69 | 20, 35, 50 wt% MDEA |
| 126.7 | 1.38 | 0.069 | 20, 35, 50 wt% MDEA |
| 126.7 | 3.45 | 0.69 | 20, 35, 50 wt% MDEA |
| 126.7 | 6.90 | 0.69 | 20, 35, 50 wt% MDEA |
| 26.7 | 1.38 | 0.069 | 20 wt% DEA |
| 26.7 | 3.45 | 0.69 | 20 wt% DEA |
| 76.7 | 1.38 | 0.069 | 20, 50 wt% DEA |
| 76.7 | 3.45 | 0.69 | 20, 35, 50 wt% DEA |
| 126.7 | 1.38 | 0.069 | 20, 35, 50 wt% DEA |
| 126.7 | 3.45 | 0.69 | 20, 35, 50 wt% DEA |

gas with a liquid, and therefore an annulus-type mixing device was used. Amine solution flowed through the annulus. The gas mixture flowed through the inner tube. Mixing occurred on the isothermal cylinder, where the inner tube ends. The small diameter of the inner tube aided mixing, by increasing the velocity of the gas flow. At 26.7°C, the amine solutions are very viscous. To facilitate complete mixing, the last centimeter of the inner tube of the low-temperature calorimeter was tightly wrapped with platinum wire. This caused swirling in the amine solution near the wall and increased mixing.

Carbon dioxide and methane were mixed in proportions resulting in the desired partial pressure of carbon dioxide in the gaseous feed. Flow rates of the gas and the alkanolamine solution were both varied to provide a large range of feed ratios (moles $CO_2$ in feed/mole amine in feed). Heats were determined as a function of feed ratio. The procedure used to collect the heat data has been described [4]. Interpretation of the flow calorimetric data requires that the densities of the fluids at room temperature be known at the operating pressures. The density of $CH_4$ and $CO_2$ were calculated using the Peng–Robinson equation of state. The density of different amine solutions was measured at 25°C and 1 atm. The densities of the amine solutions were corrected for increased pressure assuming the compressibility of water for the amine solutions. Data at feed ratios below 0.2 could not be collected due to the limitations of the equipment. The measured heats for the systems studied are given in Table 2. The accuracy of the mixing calorimeter has been shown to be 1.5% for the ethanol–water reference system [5]. The maximum uncertainty for the mixing of gas and liquid systems in the measured heats is ±6.1%.

## 2.1. Development of a predictive model

Chen [6] developed a model using the approach presented by Kent and Eisenberg [7] to predict thermodynamic properties of the MDEA+$CO_2$ and DEA+$CO_2$ systems under the same temperatures, pressures, and alkanolamine concentrations as this study. In the present work, Chen's model was modified to allow for a non-reacting gas, methane, in the gas stream. Including methane in the gas stream necessitated several changes. First, methane was included in the material balances and in the equation of state. Second, the absorption of methane into the solution was included. Third, the aqueous-phase concentrations were adjusted to account for the evaporation of water into the vapor phase. Fourth, the heat due to the vaporization of water was also included [8].

The following set of reactions was assumed to occur when the vapor stream of carbon dioxide plus methane was mixed with an aqueous solution of MDEA.

$$H_2O = H^+ + OH^- \tag{1}$$

$$H^+ + CH_3(CH_2CH_2OH)_2N_{(aq)} = CH_3(CH_2CH_2OH)_2NH^+ \tag{2}$$

$$CO_{2(aq)} = CO_{2(g)} \tag{3}$$

$$CO_{2(aq)} + H_2O = H^+ + HCO_3^- \tag{4}$$

$$HCO_3^- = H^+ + CO_3^{2-} \tag{5}$$

$$H_2O_{(aq)} = H_2O_{(g)} \tag{6}$$

$$CH_{4(aq)} = CH_{4(g)} \tag{7}$$

$$CH_3(CH_2CH_2OH)_2N_{(aq)} = CH_3(CH_2CH_2OH)_2N_{(g)} \tag{8}$$

$$CH_3(CH_2CH_2OH)_2NH^+ + HCO_3^- = CH_3(CH_2CH_2OH)_2NH_2CO_3 \tag{9}$$

When the vapor stream of methane plus carbon dioxide was mixed with an aqueous solution of DEA, Reactions (1), (3), (4), (5), (6), and (7) above were assumed to occur as well as Reactions (10), (11), and (12) below.

$$H^+ + H(C_2H_4OH)_2N_{(aq)} = H(C_2H_4OH)_2NH^+ \tag{10}$$

$$(CH_2CH_2OH)_2NH_{(aq)} = (CH_2CH_2OH)_2NH_{(ag)} \tag{11}$$

$$(CH_2CH_2OH)_2NH_{(aq)} + HCO_3^- = (CH_2CH_2OH)_2NCO_2^- + H_2O_{(aq)} \tag{12}$$

In order to model thermodynamically the mixing of the streams, the equilibrium constants $K$ and the enthalpy changes $\Delta H$ as a function of temperature for each of the above reactions were needed. Modeling of the above systems also required the calculation of the fugacity coefficients of all the gaseous species and the activity coefficients of all the aqueous species. The thermodynamic model developed used literature

Table 2
Measured and calculated enthalpies of mixing of $CO_2/CH_4$ with alkanolamine solutions

| Feed ratio | $Q_m$ (kJ mol$^{-1}$) | $Q_c$ (kJ mol$^{-1}$) | Feed ratio | $Q_m$ (kJ mol$^{-1}$) | $Q_c$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| $CO_2/CH_4$+20 wt% MDEA at 126.7°C; 6.90 Mpa | | | $CO_2/CH_4$+20 wt% MDEA at 126.7°C; 3.45 Mpa | | |
| $P_{CO_2}$=0.86 MPa in feed gas | | | $P_{CO_2}$=0.70 MPa in feed gas | | |
| 0.01 | −33.8 | −47.9 | 0.02 | −42.1 | −54.4 |
| 0.03 | −53.3 | −49.0 | 0.03 | −41.1 | −51.9 |
| 0.08 | −44.0 | −47.0 | 0.09 | −34.8 | −46.3 |
| 0.20 | −36.3 | −37.1 | 0.24 | −31.7 | −32.6 |
| 0.41 | −23.2 | −23.6 | 0.49 | −17.4 | −17.5 |
| 0.62 | −15.7 | −15.1 | 0.74 | −9.4 | −9.0 |
| 0.92 | −8.6 | −7.8 | 1.10 | −2.7 | −2.1 |
| 1.23 | −3.0 | −3.3 | 1.47 | 0.5 | 1.8 |
| 1.64 | 0.1 | 0.4 | 1.96 | 3.6 | 5.0 |
| 2.48 | 3.2 | 4.4 | 2.94 | 6.9 | 8.3 |
| $CO_2/CH_4$+20 wt% MDEA at 126.7°C; 1.38 Mpa | | | $CO_2/CH_4$+35 wt% MDEA at 126.7°C; 6.90 Mpa | | |
| $P_{CO_2}$= 0.062 MPa in feed gas | | | $P_{CO_2}$=0.86 MPa in feed gas | | |
| 0.08 | 131.8 | 113.7 | 0.01 | −106.2 | −51.7 |
| 0.11 | 133.9 | 121.8 | 0.04 | −60.3 | −49.2 |
| 0.16 | 134.7 | 132.4 | 0.12 | −40.0 | −40.0 |
| 0.18 | 138.5 | 134.9 | 0.24 | −29.1 | −27.5 |
| 0.27 | 146.2 | 143.1 | 0.36 | −16.9 | −19.0 |
| 0.41 | 147.3 | 149.5 | 0.53 | −12.7 | −11.0 |
| 0.61 | 150.4 | 154.1 | 0.71 | −3.6 | −6.2 |
| 0.81 | 149.4 | 156.4 | 0.94 | −1.0 | −2.1 |
| | | | 1.41 | −1.3 | 2.4 |
| $CO_2/CH_4$+35 wt% MDEA at 126.7°C; 3.45 MPa | | | $CO_2/CH_4$+35 wt% MDEA at 126.7°C; 1.38 Mpa | | |
| $P_{CO_2}$=0.70 MPa in feed gas | | | $P_{CO_2}$=0.069 MPa in feed gas | | |
| 0.01 | −60.7 | −57.4 | 0.05 | 129.0 | 110.5 |
| 0.02 | −36.1 | −54.3 | 0.06 | 129.9 | 118.4 |
| 0.05 | −40.5 | −48.6 | 0.09 | 135.2 | 129.2 |
| 0.14 | −31.6 | −35.9 | 0.10 | 136.0 | 131.7 |
| 0.28 | −18.4 | −21.1 | 0.15 | 143.1 | 140.2 |
| 0.42 | −12.0 | −12.4 | 0.23 | 148.7 | 146.8 |
| 0.64 | −5.7 | −5.0 | 0.34 | 150.0 | 151.4 |
| 0.85 | 0.2 | −0.7 | 0.46 | 150.0 | 153.7 |
| 1.13 | 1.7 | 2.9 | | | |
| 1.70 | 4.9 | 6.6 | | | |
| $CO_2/CH_4$+50 wt% MDEA at 126.7°C; 6.90 MPa | | | $CO_2/CH_4$+50 wt% MDEA at 126.7°C; 3.45 Mpa | | |
| $P_{CO_2}$=0.86 MPa in feed gas | | | $P_{CO_2}$=0.70 MPa in feed gas | | |
| 0.01 | −28.1 | −53.7 | 0.01 | −35.6 | −58.2 |
| 0.01 | −27.9 | −52.9 | 0.01 | −47.0 | −54.8 |
| 0.03 | −37.9 | −49.1 | 0.04 | −51.8 | −47.6 |
| 0.16 | −22.3 | −24.2 | 0.10 | −27.9 | −32.6 |
| 0.24 | −16.5 | −15.9 | 0.20 | −15.8 | −17.6 |
| 0.36 | −9.6 | −8.6 | 0.30 | −9.6 | −9.3 |
| 0.49 | −4.6 | −4.2 | 0.44 | −4.0 | −2.7 |
| 0.97 | 2.5 | 3.4 | 0.59 | −0.2 | 1.1 |
| | | | 0.79 | 1.9 | 4.2 |
| | | | 1.18 | 5.6 | 7.4 |
| $CO_2/CH_4$+50 wt% MDEA at 126.7°C; 1.38 MPa | | | $CO_2/CH_4$+20 wt% MDEA at 76.7°C; 6.90 Mpa | | |
| $P_{CO_2}$=0.069 MPa in feed gas | | | $P_{CO_2}$=0.86 MPa in feed gas | | |
| 0.03 | 123.4 | 108.0 | 0.03 | −63.6 | −69.7 |
| 0.04 | 116.5 | 116.3 | 0.05 | −76.0 | −57.1 |

Table 2 (*Continued*)

| Feed ratio | $Q_m$ (kJ mol$^{-1}$) | $Q_c$ (kJ mol$^{-1}$) | Feed ratio | $Q_m$ (kJ mol$^{-1}$) | $Q_c$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| 0.07 | 121.6 | 126.5 | 0.08 | −61.3 | −52.4 |
| 0.07 | 124.0 | 128.8 | 0.41 | −56.7 | −39.2 |
| 0.11 | 130.7 | 136.3 | 0.58 | −47.2 | −35.0 |
| 0.16 | 133.0 | 141.7 | 0.62 | −49.8 | −34.0 |
| 0.24 | 134.9 | 145.2 | 0.93 | −38.0 | −26.6 |
| 0.32 | 133.8 | 146.8 | 1.24 | −29.8 | −21.1 |
| | | | 1.66 | −23.7 | −15.9 |
| | | | 2.31 | −16.8 | −11.2 |
| | | | 3.12 | −12.5 | −7.8 |
| | | | 4.99 | −8.5 | −4.1 |
| $CO_2/CH_4$+20 wt% MDEA at 76.7°C; 3.45 MPa | | | $CO_2/CH_4$+20 wt% MDEA at 76.7°C; 1.38 Mpa | | |
| $P_{CO_2}$=0.70 MPa in feed gas | | | $P_{CO_2}$=0.070 MPa in feed gas | | |
| 0.02 | −114.2 | −76.1 | 0.11 | −37.6 | −34.9 |
| 0.03 | −35.6 | −61.3 | 0.19 | −30.5 | −24.5 |
| 0.09 | −38.1 | −49.7 | 0.28 | −17.9 | −16.2 |
| 0.25 | −54.6 | −43.5 | 0.43 | −7.8 | −7.7 |
| 0.50 | −50.0 | −37.2 | 0.64 | 1.8 | 0.3 |
| 0.75 | −47.2 | −30.9 | 0.85 | 9.7 | 5.3 |
| 1.12 | −36.8 | −22.9 | | | |
| 1.49 | −29.4 | −17.6 | | | |
| 1.99 | −23.8 | −13.0 | | | |
| 2.98 | −15.6 | −8.1 | | | |
| $CO_2/CH_4$+35 wt% MDEA at 76.7°C; 6.90 MPa | | | $CO_2/CH_4$+35 wt% MDEA at 76.7°C; 3.45 Mpa | | |
| $P_{CO_2}$=0.93 MPa in feed gas | | | $P_{CO_2}$=0.70 MPa in feed gas | | |
| 0.01 | −78.3 | −80.9 | 0.01 | −60.4 | −85.6 |
| 0.04 | −83.7 | −61.7 | 0.02 | −45.3 | −70.7 |
| 0.21 | −65.2 | −48.9 | 0.05 | −55.1 | −58.1 |
| 0.32 | −63.8 | −45.5 | 0.14 | −54.1 | −51.7 |
| 0.47 | −52.3 | −40.4 | 0.28 | −54.0 | −46.7 |
| 1.26 | −28.2 | −20.8 | 0.42 | −50.0 | −41.8 |
| 1.57 | −22.1 | −16.8 | 0.64 | −41.8 | −34.5 |
| 2.52 | −16.6 | −10.2 | 1.13 | −30.6 | −22.3 |
| | | | 1.69 | −22.6 | −15.0 |
| $CO_2/CH_4$+50 wt% MDEA at 76.7°C; 6.90 MPa | | | $CO_2/CH_4$+50 wt% MDEA at 76.7°C; 3.45 Mpa | | |
| $P_{CO_2}$=0.86 MPa in feed gas | | | $P_{CO_2}$=0.70 MPa in feed gas | | |
| 0.01 | −61.1 | −85.6 | 0.01 | −113.1 | −92.6 |
| 0.03 | −58.0 | −66.7 | 0.01 | −63.8 | −77.6 |
| 0.17 | −51.3 | −54.4 | 0.04 | −69.5 | −64.4 |
| 0.25 | −49.8 | −51.2 | 0.10 | −59.6 | −58.2 |
| 0.38 | −42.9 | −45.3 | 0.20 | −53.4 | −53.7 |
| 0.51 | −34.3 | −39.9 | 0.30 | −48.3 | −49.5 |
| 0.65 | −34.4 | −34.3 | 0.44 | −43.3 | −42.8 |
| 1.01 | −24.8 | −24.4 | 0.79 | −30.2 | −29.7 |
| 1.96 | −16.9 | −12.9 | 1.18 | −27.9 | −20.9 |
| $CO_2/CH_4$+50 wt% MDEA at 76.7°C; 1.38 MPa | | | $CO_2/CH_4$+20 wt% MDEA at 26.7°C; 3.45 Mpa | | |
| $P_{CO_2}$=0.070 MPa in feed gas | | | $P_{CO_2}$=0.70 MPa in feed gas | | |
| 0.04 | −42.1 | −51.9 | 0.50 | −43.7 | −59.2 |
| 0.07 | −37.7 | −41.7 | 0.73 | −43.0 | −47.0 |
| 0.11 | −22.3 | −33.6 | 1.10 | −37.5 | −34.2 |
| 0.17 | −16.2 | −24.8 | 1.46 | −30.9 | −26.1 |
| 0.25 | −3.2 | −15.5 | 1.98 | −23.3 | −19.3 |
| 0.33 | 0.6 | −8.9 | 2.91 | −16.5 | −13.1 |

Table 2 (*Continued*)

| Feed ratio | $Q_m$ (kJ mol$^{-1}$) | $Q_c$ (kJ mol$^{-1}$) | Feed ratio | $Q_m$ (kJ mol$^{-1}$) | $Q_c$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| $CO_2/CH_4$+20 wt% MDEA at 26.7°C; 1.38 MPa | | | $CO_2/CH_4$+35 wt% MDEA at 26.7°C; 3.45 Mpa | | |
| $P_{CO_2}$=0.079 MPa in feed gas | | | $P_{CO_2}$=0.67 MPa in feed gas | | |
| 0.13 | −20.7 | −71.4 | 0.28 | −59.6 | −75.1 |
| 0.25 | −96.2 | −55.3 | 0.40 | −58.4 | −63.5 |
| 0.38 | −45.1 | −47.3 | 0.62 | −52.4 | −50.1 |
| 0.57 | −27.7 | −38.9 | 0.81 | −40.3 | −41.7 |
| 0.77 | −18.4 | −31.9 | 1.11 | −36.5 | −31.6 |
| 1.02 | −17.0 | −25.5 | 1.65 | −29.4 | −21.5 |
| 1.49 | −13.6 | −17.6 | | | |
| $CO_2/CH_4$+35 wt% MDEA at 26.7°C; 1.38 MPa | | | $CO_2/CH_4$+20 wt% DEA at 126.7°C; 3.45 Mpa | | |
| $P_{CO_2}$=0.076 MPa in feed gas | | | $P_{CO_2}$=0.74 MPa in feed gas | | |
| 0.07 | −40.4 | −86.5 | 0.09 | −34.5 | −60.2 |
| 0.13 | −89.9 | −71.4 | 0.24 | −43.4 | −49.7 |
| 0.19 | −67.3 | −64.3 | 0.47 | −30.5 | −35.1 |
| 0.29 | −54.4 | −56.9 | 0.71 | −19.3 | −24.1 |
| 0.39 | −47.2 | −51.0 | 1.06 | −9.9 | −13.7 |
| 0.52 | −42.8 | −44.0 | 1.42 | −4.0 | −7.7 |
| 0.76 | −31.9 | −33.8 | 1.89 | 0.0 | −2.7 |
| $CO_2/CH_4$+20 wt% DEA at 126.7°C; 1.38 MPa | | | $CO_2/CH_4$+35 wt% DEA at 126.7°C; 3.45 Mpa | | |
| $P_{CO_2}$=0.075 MPa in feed gas | | | $P_{CO_2}$=0.75 MPa in feed gas | | |
| 0.07 | 128.1 | 87.9 | 0.05 | −31.6 | −63.7 |
| 0.10 | 137.6 | 95.5 | 0.14 | −48.6 | −55.5 |
| 0.15 | 143.6 | 106.4 | 0.28 | −43.8 | −45.4 |
| 0.16 | 138.7 | 109.1 | 0.42 | −33.7 | −36.5 |
| 0.24 | 139.7 | 119.0 | 0.63 | −22.0 | −26.0 |
| 0.37 | 148.4 | 127.6 | 0.84 | −14.6 | −18.6 |
| 0.55 | 150.2 | 134.2 | 1.12 | −8.3 | −12.1 |
| 0.73 | 150.7 | 137.8 | 1.68 | −1.3 | −4.7 |
| $CO_2/CH_4$+35 wt% DEA at 126.7°C; 1.38 MPa | | | $CO_2/CH_4$+50 wt% DEA at 126.7°C; 3.45 Mpa | | |
| $P_{CO_2}$=0.072 MPa in feed gas | | | $P_{CO_2}$=0.74 MPa in feed gas | | |
| 0.04 | 119.9 | 81.5 | 0.04 | −36.0 | −65.5 |
| 0.05 | 121.9 | 88.5 | 0.10 | −47.3 | −57.5 |
| 0.08 | 129.8 | 98.6 | 0.28 | −45.7 | −41.7 |
| 0.09 | 126.2 | 101.1 | 0.43 | −32.3 | −32.8 |
| 0.14 | 140.1 | 111.5 | 0.57 | −22.3 | −25.9 |
| 0.20 | 130.1 | 120.6 | 0.76 | −16.6 | −19.2 |
| 0.30 | 133.8 | 128.0 | 1.14 | −7.9 | −10.8 |
| 0.40 | 132.4 | 132.1 | | | |
| $CO_2/CH_4$+50 wt% DEA at 126.7°C; 1.38 MPa | | | $CO_2/CH_4$+20 wt% DEA at 76.7°C; 3.45 Mpa | | |
| $P_{CO_2}$=0.072 MPa in feed gas | | | $P_{CO_2}$=0.75 MPa in feed gas | | |
| 0.03 | 108.8 | 73.8 | 0.09 | −35.8 | −73.7 |
| 0.04 | 97.2 | 80.5 | 0.23 | −72.0 | −59.7 |
| 0.06 | 107.1 | 91.0 | 0.46 | −58.7 | −51.4 |
| 0.06 | 108.6 | 93.6 | 0.69 | −49.3 | −43.1 |
| 0.09 | 112.2 | 103.7 | 1.03 | −36.3 | −31.2 |
| 0.14 | 113.5 | 112.7 | 1.38 | −27.5 | −23.5 |
| 0.21 | 115.0 | 120.1 | 1.84 | −20.6 | −17.3 |
| 0.28 | 120.2 | 124.2 | 2.76 | −13.2 | −10.9 |
| $CO_2/CH_4$+20 wt% DEA at 76.7°C; 1.38 MPa | | | $CO_2/CH_4$+35 wt% DEA at 76.7°C; 3.45 Mpa | | |
| $P_{CO_2}$=0.072 MPa in feed gas | | | $P_{CO_2}$=0.76 MPa in feed gas | | |
| 0.15 | −50.8 | −46.2 | 0.05 | −57.7 | −86.2 |
| 0.17 | −42.9 | −43.9 | 0.14 | −60.7 | −71.1 |

Table 2 (*Continued*)

| Feed ratio | $Q_m$ (kJ mol$^{-1}$) | $Q_c$ (kJ mol$^{-1}$) | Feed ratio | $Q_m$ (kJ mol$^{-1}$) | $Q_c$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| 0.25 | −43.3 | −34.7 | 0.27 | −64.5 | −62.8 |
| 0.37 | −30.8 | −24.8 | 0.41 | −61.1 | −56.6 |
| 0.56 | −15.4 | −14.2 | 0.61 | −52.0 | −47.1 |
| 0.75 | −3.9 | −7.1 | 0.81 | −43.3 | −37.9 |
| | | | 1.08 | −33.2 | −29.1 |
| | | | 1.63 | −21.9 | −19.3 |
| $CO_2/CH_4$+50 wt% DEA at 76.7°C; 1.38 MPa | | | $CO_2/CH_4$+50 wt% DEA at 76.7°C; 3.45 Mpa | | |
| $P_{CO_2}$=0.072 MPa in feed gas | | | $P_{CO_2}$=0.75 MPa in feed gas | | |
| 0.06 | −61.8 | −72.6 | 0.03 | −63.4 | −97.6 |
| 0.07 | −61.2 | −70.0 | 0.09 | −68.0 | −81.6 |
| 0.10 | −60.5 | −61.4 | 0.17 | −66.4 | −73.0 |
| 0.15 | −57.1 | −52.5 | 0.26 | −67.9 | −67.5 |
| 0.22 | −44.4 | −42.5 | 0.39 | −65.6 | −60.1 |
| 0.29 | −32.4 | −35.1 | 0.52 | −59.4 | −52.7 |
| | | | 0.69 | −47.7 | −43.2 |
| | | | 1.03 | −33.0 | −30.1 |
| $CO_2/CH_4$+20 wt% DEA at 26.7°C; 3.45 MPa | | | $CO_2/CH_4$+20 wt% DEA at 26.7°C; 1.38 Mpa | | |
| $P_{CO_2}$=0.69 MPa in feed gas | | | $P_{CO_2}$=0.079 MPa in feed gas | | |
| 0.43 | −60.2 | −59.2 | 0.10 | −22.4 | −96.6 |
| 0.63 | −58.8 | −60.0 | 0.20 | −97.1 | −79.0 |
| 0.96 | −45.6 | −41.2 | 0.30 | −81.7 | −69.7 |
| 1.27 | −35.1 | −31.1 | 0.45 | −65.2 | −58.8 |
| 1.72 | −27.8 | −22.8 | 0.60 | −45.5 | −49.3 |
| 2.53 | −18.8 | −15.4 | 0.80 | −40.7 | −38.7 |
| | | | 1.18 | −31.9 | −26.3 |

values for the $K$ and $\Delta H$ values where available and the unknown $K$ and $\Delta H$ values were regressed using the heat data measured in this study and partial pressures of $CO_2$ in equilibrium with the alkanolamine solutions reported in the literature.

The equations for the $K$ values, $\Delta H$ values, fugacity coefficients, activity coefficients, and the equation of state were combined with material balances in order to predict the species distribution of the incoming aqueous stream and exiting aqueous and vapor streams and the molar volumes of the incoming and exiting vapor streams. This species distribution was used together with the $\Delta H$ values for the reactions and the enthalpy departures found using the equation of state to calculate the enthalpies of the entering and exiting streams. Since all heats were measured isothermally, no heat capacity data were needed.

The $\Delta C_p$ values for Henry's coefficients and the aqueous equilibrium constants were assumed to be constant except in Reactions (1) and (7). The errors in the $K$ and $\Delta H$ values introduced by making this assumption are no larger than the uncertainty of these values. This leads to the following equations correlating equations for the $K$ and $\Delta H$ values

$$\ln K = \frac{C_1}{T} + C_2 \ln T + C_3 \tag{13}$$

$$\Delta H = -RC_1 + RTC_2 \tag{14}$$

where $R$ is the gas constant and $C_1$, $C_2$, and $C_3$ are fitting parameters and $T$ is the temperature in kelvins. The literature values used for Henry's coefficients and parameters for equations describing the ionization constants are listed in Table 3 along with references [6,9–12]. Reactions (6), (8), and (11) were treated as conventional vapor–liquid equilibria.

### 2.1.1. Equilibrium constants

Equilibrium constants for Reaction (12) (carbamate formation from bicarbonate and DEA) at temperatures ranging from 25 to 140°C were found by minimizing the differences between loading vs. $P_{CO_2}$ values predicted from the model reported here and those mea-

Table 3
Literature parameters for the equilibrium constants for indicated reactions

| Reaction | $C_1$ | $C_2$ | $C_3$ | Ref. |
|---|---|---|---|---|
| $H^+ + MDEA_{(aq)} \leftrightarrow MDEAH^+$ | 1974.40 | −7.5329 | 56.008 | [9] |
| $H^+ + DEA_{(aq)} \leftrightarrow DEAH^+$ | 3741.82 | −4.2726 | 32.241 | [9] |
| $MDEAH^+ + HCO_3^- \leftrightarrow MDEAH_2CO_{3(aq)}$ | −1404.6 | −14.3427 | 85.455 | [6] |
| $RRNH + HCO_3^- \leftrightarrow RRNCO_2^- + H_2O_{(aq)}$ | 7494.232 | 16.834 | −102.490 | n/a |
| $CO_{2(aq)} \leftrightarrow CO_{2(g)}$ | −7849.446 | −18.11777 | 132.9207 | [10] |
| $CH_{4(aq)} \leftrightarrow CH_{4(g)}$ | 7.403 | −1.344 | −8.308 | [11] |
| $CO_{2(aq)} + H_2O \leftrightarrow H^+ + HCO_3^-$ | −12092.1 | −36.7816 | 235.482 | [12] |
| $HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$ | −12431.7 | −35.4819 | 220.067 | [12] |

sured [13]. The $C_1$, $C_2$, $C_3$ values in Eq. (13) were varied until the predicted $P_{CO_2}$ vs. loading fit the literature data at 25, 75, and 140°C and the heat data measured in this study. In this way, all effects not taken into account by the other reactions with previously determined log $K$ and $\Delta H$ values have been incorporated into three adjustable parameters. The $\Delta H$ values calculated for all reactions are thermodynamically consistent with the log K values.

The resulting equilibrium constants for carbamate formation are of the same order of magnitude as the equilibrium constants for the formation of the MDEA complex, Reaction (9). This indicates that the formation of the analogous complex may be significant in the DEA system as well as in the MDEA system. The model developed in this study does not, however, account for the formation of a DEA complex. It should therefore be noted that the values for the carbamate formation equilibrium constants given in Table 3 may likely incorporate both the formation of carbamate as well as the formation of a DEA complex.

Equilibrium constants for the hydration of $CO_{2(aq)}$ and the subsequent ionization of the carbonate species (Eqs. (4) and (5)) were calculated using equations proposed by Renon [12], which have the same form as Eq. (13).

Oscarson et al. [9] derived equilibrium constants for the protonation of MDEA and DEA (Reactions (2) and (10)) using experimental heat of protonation data from 26.7 to 149°C and equilibrium constants at 25°C. Over the range of the experiments, $\Delta H$ was linear with temperature.

Thermodynamic values for the ionization of water (Reaction (1)) were calculated from the relationship determined by Marshall and Franck [14].

### 2.1.2. Henrys law constants for $CO_2$ and $CH_4$

The Henry's coefficient values for $CO_2$ (Reaction (3)) were calculated from equations proposed by Murray and Cobble [10]. These equations describe the $CO_2$ phase equilibria with pure water rather than with alkanolamine solutions. The differences in this system from those in pure water are accounted for by the use of activity coefficients. Haimour and Sandall [15] give values for Henry's coefficients for the $CO_2$ phase equilibria with MDEA solutions by assuming that these coefficients are the same as those measured by them for the solubility of $N_2O$ in MDEA solutions. However, these data are available over such a limited range of conditions that they could not be used in this study. The Henry's law constants (Reaction 7) for $CH_4$ were calculated from the relationships proposed by Crovetto et al. [11] which has the form of Eq. (15):

$$\ln K_{H(CO_2)} = \frac{C_1}{(T \times 10^{-3})} + \frac{C_2}{(T \times 10^{-3})^2} + C_3 \qquad (15)$$

### 2.1.3. Vapor–liquid equilibria

The following expression was used in determining the vapor–liquid equilibrium of $CO_2$.

$$\phi_{CO_2} y_{CO_2} P = m_{CO_2} K_{H(CO_2)} \gamma_{CO_2} \times \exp\left(\frac{\bar{V}_{CO_2}(P - P_W^S)}{RT}\right) \qquad (16)$$

where $y$ is the mole fraction in the vapor phase, $\bar{V}$ is the partial molal volume, $P$ is the system total pressure, $P_W^S$ is the saturation vapor pressure of water, and $K_H$ is the Henry's constant valid at the saturation pressure of water [6]. The partial molal volumes of $CO_{2(aq)}$ were calculated using the correlation given by Brelvi and O'Connel [16]. A similar expression, without the Poynting correction factor, was used in determining the vapor–liquid equilibrium of methane. Since the Poynting correction factor is only significant at higher pressures, the absence of the Poynting term in the methane vapor–liquid equilibrium expression is not considered to cause any significant errors.

The vapor–liquid equilibria for both water and the alkanolamines are given by

$$\phi_j P_j = a_j P_j^{\mathrm{S}} \phi_j^{\mathrm{S}} \quad \exp\left(\frac{\bar{V}_j(P - P_j^{\mathrm{S}})}{RT}\right), \tag{17}$$

where the subscript $j$ designates either DEA, MDEA, or water, $a$ is the activity expressed as a mole fraction, and $\phi_j^{\mathrm{S}}$ is the fugacity coefficient of substance $j$ at its saturation vapor pressure $P_j^{\mathrm{S}}$ [6].

The saturation vapor pressures of water and the alkanolamines were calculated using a three-parameter Antoine equation [6]:

$$\ln P_j^{\mathrm{S}} = A_1 - \frac{A_2}{T - A_3} \tag{18}$$

The values of parameters $A_1$, $A_2$, and $A_3$ for water, MDEA, and DEA were obtained by fitting experimental saturation vapor pressure data [6] and are given in Table 4. The partial molal volume of water was calculated using the following equation [6]:

$$\bar{V}_w(\mathrm{ml/mol}) = 23.3875 - 0.039135T + 7.16362 \times 10^{-5}T^2. \tag{19}$$

### 2.1.4. Activity coefficients

The Pitzer equation as modified by Edwards et al. [17] was used to calculate the activity coefficients of ionic and molecular species in solution as well as the activity of water. This equation requires the calculation of the Debye–Hückel limiting slope of the osmotic coefficient, $A_\phi$. Chen et al.'s [18] expression for the Debye–Hückel limiting slope was used for this purpose. An expression for the activity of water was derived by Edwards et al. [17] using an equation for the activity coefficients and the Gibbs–Duhem equation.

Table 4
Antoine parameters for water and alkanolamines

| Compound | $A_1$ | $A_2$ | $A_3$ |
|---|---|---|---|
| $H_2O$ | 11.6703 | 3816.42 | 46.13 |
| MDEA | 29.9726 | 22625.16 | −260.30 |
| DEA | 11.9371 | 5231.15 | 103.46 |

Interaction parameters required in the equation of state for species in the ternary systems $CO_2$/$CH_4$+alkanolamines/$H_2O$ are not available in the literature and were assumed to be zero. This leads to negligible errors in the gas phase at experimental conditions. Chen [6] determined the interaction parameters for use in the activity coefficient model by dividing the binary interactions into four groups: (a) the interaction between like-charged ions, (b) the interaction between positive and negative ions, (c) the interaction between ionic and molecular species, and (d) the interaction between molecules. Like-charged ionic interactions were ignored. The parameters were assumed to be the same for interactions within the same group. Chen fitted these parameters to his experimental data. The resulting interaction parameters are given in Table 5.

### 2.1.5. Equation of state

Fugacity coefficients and heat effects due to vapor-phase interactions were determined from the equation proposed by Nakamura et al. [19]. For a complete discussion of equations see Ref. [6]. The pure component parameters $\alpha_i^{(0)}$, $\alpha_i^{(1)}$ $\beta_i^{(0)}$ $\beta_i^{(1)}$, $\gamma_i$ $\delta_I$, and $c_i$ are listed in Table 6. The interaction parameter $\alpha_{ij}^{(0)}$ is given in Table 7. Interaction parameters for DEA and MDEA were not available, so the parameters were assumed to be equal to those of $NH_3$. Since the mole fractions of DEA and MDEA in the vapor phase are small (from $10^{-10}$ to $10^{-4}$), this assumption should not lead to any significant errors in the calculations of ln $\phi_I$s or $\Delta H_{\mathrm{gas}}$.

Table 5
Interaction parameters for activity coefficients

| Interaction-type | $\beta_{ij}^{(0)}$ | $\beta_{ij}^{(1)}$ |
|---|---|---|
| Between like-charged ions | 0.0 | 0.0 |
| Cation–anion | 0.0067 | 0.0223 |
| Ion–molecule | 0.0017 | 0.0052 |
| Molecule–molecule | $-0.1333+40.85/T$ | 0.0 |

Table 6
Pure component parameters for equation of state[a]

| Gas (l/mol) | $\alpha^{(0)}$ (atm. $l^2$/mole$^2$) | $\alpha^{(1)}$ (atm. $l^2$/mole$^2$) | $\beta^{(0)}$ (atm. $l^2$/mole$^2$) | $\beta^{(1)}$ (atm. $l^2$/mole$^2$) | $\lambda$ | $\delta$ | c |
|---|---|---|---|---|---|---|---|
| $CO_2$ | 3.1693 | 0.0 | 253.17 | 0.0 | 1.2340 | $0.467\times10^{-4}$ | 0.0 |
| $H_2S$ | 2.5194 | 1.10 | 16.62 | 437.7 | 1.1823 | $1.699\times10^{-4}$ | 0.0 |
| $H_2O$ | 1.0607 | 2.07 | 8.40 | 1153.3 | 1.5589 | $0.593\times10^{-4}$ | 0.01 |
| $NH_3$[a] | 1.8335 | 0.81 | 13.33 | 548.3 | 1.3884 | $1.470\times10^{-4}$ | 0.01 |

[a] The parameters for the alkanolamines are assumed to be the same as those of $NH_3$.

### 2.1.6. Comparison of literature and predicted loading vs. $P_{CO_2}$ data

The model was used to calculate loading vs. $P_{CO_2}$ data in order to provide a comparison with literature values to confirm the accuracy of the model. Loading is defined as the ratio of the number of moles of $CO_2$ absorbed into the solution to the number of moles of alkanolamine in the solution. Experimental data from Lee et al. [13] were compared to data predicted from the model at 25, 75, and 140°C and at DEA concentrations of 20, 35, and 50 wt%. Predicted data for MDEA were compared to Jou et al.'s [20] data at 40 and 100°C for a 35 wt% MDEA solution.

It is clear from Table 8 that the agreement between predicted and experimental (literature) loadings improves as $CO_2$ partial pressures increase. As previously discussed, values of $K$ for reaction $RRNH+HCO_3^-\leftrightarrow RRNCO_2^-+H_2O_{(aq)}$ were found by fitting predicted loadings to experimental loadings. No $K$ values were found that would provide excellent agreement over the entire $P_{CO_2}$ range. $K$ values were determined by emphasizing the agreement between predicted and experimental loadings in the high $P_{CO_2}$ region. This was reasoned to provide $K$ values with the smallest error possible, since the slope of the loading vs. $P_{CO_2}$ curve is less steep for high $P_{CO_2}$ values. In the low $P_{CO_2}$ region, where the slope is steep, minor errors in either calculations or experimental measurements would cause a much larger possible percentage error in the data than in the high $P_{CO_2}$ region.

Table 7
Interaction parameters for equation of state

| Gas mixture | $\alpha_{ij}^{(0)}$ (atm. $l^2$/mole$^2$) |
|---|---|
| $CO_2$–$H_2S$ | 2.8 |
| $CO_2$–$H_2O$ | 4.36 |
| $CO_2$–$NH_3$ | 3.1 |
| $H_2S$–$H_2O$ | 2.2 |
| $H_2S$–$NH_3$ | 2.1 |
| $H_2O$–$NH_3$ | 1.4 |

Table 8 shows good agreement between experimental (literature) [17] and predicted loadings for 35 wt% MDEA at 40°C. The agreement seems poorer at 100°C. However, since the experimental data are not smoothed, they may reflect a significant amount of experimental error, and it is difficult to determine the significance of the disagreement between predicted and experimental loadings. Since loadings at both high and low $P_{CO_2}$ values are in good agreement, the fit between experimental and predicted loadings is assumed to be acceptable.

## 3. Results

The most significant difference between the acid gas/$CH_4$+alkanolamine systems and the pure acid gas+alkanolamine systems [1–3] is the continual presence of a vapor space in the former systems. In the latter case, a definite discontinuity in the slope of the heat versus the mole acid gas per mole amine curve. This break point represents the loading point. After the loading point, no more $CO_2$ is absorbed into the solution, and the $CO_2$ creates a vapor phase, allowing water to evaporate, resulting in more positive heats. In the $CO_2$/$CH_4$+MDEA and the $CO_2$/$CH_4$+DEA systems, a vapor phase is always present due to the insolubility of $CH_4$. Water and amine are able to distribute to the vapor phase for all feed ratio values.

The $CO_2$/$CH_4$+MDEA system displays endothermic behavior at 126.7°C and 1.38 MPA ($P_{CO_2}=$ 0.069 MPa) due to the large amount of water that evaporates at such a high temperature and low pres-

Table 8
Comparison of $CO_2$ loadings from literature and those predicted by the model

| $P_{CO_2}$ | Loading | | $P_{CO_2}$ | Loading | |
|---|---|---|---|---|---|
| | Literature | Model | | Literature | Model |
| 35 wt% MDEA at 40°C[a] | | | 35 wt% MDEA at 100°C[a] | | |
| 0.00058 | 0.002 | 0.0035 | 0.14 | 0.0077 | 0.013 |
| 0.0013 | 0.0051 | 0.005 | 0.249 | 0.013 | 0.018 |
| 0.0058 | 0.013 | 0.0098 | 0.728 | 0.027 | 0.033 |
| 0.06 | 0.059 | 0.096 | 2.26 | 0.048 | 0.063 |
| 0.16 | 0.106 | 0.154 | 5.29 | 0.087 | 0.102 |
| 0.313 | 0.166 | 0.209 | 14.94 | 0.134 | 0.184 |
| 0.854 | 0.296 | 0.319 | 31.47 | 0.219 | 0.277 |
| 1.74 | 0.394 | 0.414 | 34.23 | 0.271 | 0.289 |
| 3.64 | 0.57 | 0.524 | | | |
| 14.5 | 0.795 | 0.734 | | | |
| 20 wt% DEA at 25°C[b] | | | 35 wt% DEA at 25°C[b] | | |
| 0.1 | 0.402 | 0.32 | 0.1 | 0.387 | 0.3 |
| 0.316 | 0.48 | 0.456 | 0.316 | 0.453 | 0.408 |
| 1.0 | 0.568 | 0.599 | 1.0 | 0.525 | 0.526 |
| 3.16 | 0.663 | 0.726 | 3.16 | 0.60 | 0.635 |
| 10 | 0.765 | 0.817 | 10 | 0.69 | 0.722 |
| 31.6 | 0.875 | 0.875 | 31.6 | 0.788 | 0.779 |
| 50 wt% DEA at 25°C[b] | | | 20 wt% DEA at 75°C[b] | | |
| 0.1 | 0.378 | 0.295 | 0.1 | 0.086 | 0.053 |
| 0.316 | 0.43 | 0.381 | 0.316 | 0.163 | 0.098 |
| 1.0 | 0.49 | 0.477 | 1.0 | 0.248 | 0.184 |
| 3.16 | 0.554 | 0.567 | 3.16 | 0.365 | 0.315 |
| 10 | 0.629 | 0.645 | 10 | 0.486 | 0.489 |
| 31.6 | 0.708 | 0.699 | 31.6 | 0.62 | 0.63 |
| 35 wt% DEA at 75°C[b] | | | 50 wt% DEA at 75°C[b] | | |
| 0.1 | 0.085 | 0.042 | 0.1 | 0.084 | 0.035 |
| 0.316 | 0.16 | 0.078 | 0.316 | 0.158 | 0.065 |
| 1.0 | 0.238 | 0.149 | 1.0 | 0.23 | 0.124 |
| 3.16 | 0.334 | 0.265 | 3.16 | 0.315 | 0.226 |
| 10 | 0.433 | 0.418 | 10 | 0.398 | 0.369 |
| 31.6 | 0.54 | 0.553 | 31.6 | 0.485 | 0.499 |
| 20 wt% DEA at 140°C[b] | | | 35 wt% DEA at 140°C[b] | | |
| 10 | 0.093 | 0.097 | 10 | 0.06 | 0.069 |
| 31.6 | 0.23 | 0.209 | 31.6 | 0.16 | 0.163 |
| 50 wt% DEA at 140°C[b] | | | | | |
| 10 | 0.035 | 0.045 | | | |
| 31.6 | 0.122 | 0.114 | | | |

[a] Literature values from Ref. [20].

[b] Literature values from Ref. [13].

sure. The differences between the results of the 3.45 ($P_{CO_2}$=0.69 MPa) and 6.90 MPa ($P_{CO_2}$=0.69 MPa) systems are slight.

At 76.7°C, very little water evaporates, and the major heat effects are from the absorption of $CO_2$ and the resulting liquid-phase reactions, regardless of system pressure. There is no significant difference between the data measured at 3.45 MPa and those measured at 6.90 MPa (both at $P_{CO_2}$=0.69 MPa). The data at 1.39 MPa ($P_{CO_2}$=0.069 MPa), however, differ greatly from the data at higher pressures.

As with the 76.7°C system, the major heat effects at 26.7°C are due to the absorption of $CO_2$ and the resulting chemical reactions. Much more $CO_2$ is available to be absorbed at 3.45 MPa than at 1.38 MPa (higher partial pressure of $CO_2$ in feed gas at 3.45 MPa total pressure), and the increased pressure, according to Henry's law will force more $CO_2$ into solution.

The lower the temperature, the more negative the measured heats become. At higher temperatures, more water evaporates than at lower temperatures, shifting the curve upwards (more positive). In addition, $CO_2$ is less readily absorbed at higher temperatures. The Henry's law constant for the $CO_{2(aq)}=CO_{2(g)}$ phase equilibrium increases with increasing temperature, thus decreasing the $CO_2$ solubility at the same partial pressure. As the absorption process is exothermic, less heat is measured at higher temperatures.

There is no clear trend in the concentration dependence of the $CO_2/CH_4$+MDEA and DEA systems. The absorption of $CO_2$ into the solution involves a series of reactions. At different concentrations, various reactions contribute more or less to the overall heat measured. At 26.7°C, the amine solutions are much more viscous than they are at the two higher temperatures. Though the calorimeter insert was rebuilt to provide better mixing, it was still impossible to record any repeatable data for DEA concentrations of 35 and 50 wt% and for a MDEA concentration of 50 wt% at 26.7°C.

The most important factors influencing the measured heats were found to be temperature and the partial pressure of carbon dioxide in the gas feed stream. The measured heats displayed negligible dependency upon the total pressure of the system and little dependency upon the amine solution concentration within the ranges of this study.

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