

# Enthalpy of Solution of Carbon Dioxide in Aqueous Solutions of Monoethanolamine at Temperatures of 322.5 K and 372.9 K and Pressures up to 5 MPa

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**ABSTRACT:** The enthalpies of solution ( $\Delta_{\text{sol}}H$ ) of carbon dioxide ( $\text{CO}_2$ ) in two aqueous solutions ( $w = 0.1500$  and  $w = 0.3000$ ) of monoethanolamine (MEA) have been measured at two temperatures (322.5 K and 372.9 K) and pressures up to 5 MPa. Measurements were carried out by a flow calorimetric technique using a custom-made flow-mixing unit combined with a SETARAM C-80 isothermal differential heat-flux calorimeter. Enthalpies of solution of  $\text{CO}_2$  ( $\Delta_{\text{sol}}H$ ) have been obtained as function of loading  $\alpha$  (moles  $\text{CO}_2$ /mol amine). Solubility data of the gas into the different absorbent ( $s$ ) were derived from the enthalpic data.

## 1. INTRODUCTION

The capture of carbon dioxide from postcombustion emission is one of the challenges for reducing the release of greenhouse gases into the atmosphere. Aqueous amine solutions are well-known to be efficient chemical solvents for the industrial capture of  $\text{CO}_2$ . Gas capture combines physical dissolution and subsequent reaction of  $\text{CO}_2$  into the absorbent solution. The acid–base reaction between the carbon dioxide and the amine is reversible, making it possible to separate the gas from the absorbent solution in a cyclic process. The purpose of actual research carried out on  $\text{CO}_2$  capture is the reduction of the energy cost of  $\text{CO}_2$  removal in the amine washing process. To design a new industrial process for gas treating operations, the development of better theoretical models describing the  $\{\text{CO}_2 + \text{amine} + \text{H}_2\text{O}\}$  systems is required. The existing models<sup>1–9</sup> are based on temperature-dependent liquid–vapor equilibria data from which the enthalpy of solution of  $\text{CO}_2$  was derived.<sup>4,7–9</sup> Although gas solubility data as a function of temperature, amine composition, and partial pressure of  $\text{CO}_2$  are available in the literature,<sup>10–26</sup> only a few experimental enthalpy studies have been published<sup>22,27,28</sup> for the system  $\{\text{CO}_2 + \text{monoethanolamine (MEA)} + \text{H}_2\text{O}\}$ . A literature review for both solubility data and enthalpy of solution of  $\text{CO}_2$  is reported in Tables 1 and 2. To develop thermodynamic models able to describe the  $\{\text{CO}_2 + \text{MEA} + \text{H}_2\text{O}\}$  system we decided to extend the existing enthalpy data.<sup>22,27,28</sup> In addition, the new proposed set of data makes it possible to investigate the amine composition effect on the enthalpy of solution.

In this paper, we report a new set of experimental data on the enthalpy of solution for the system  $\{\text{CO}_2 + \text{MEA} + \text{H}_2\text{O}\}$ . Measurements were performed for two aqueous amine solutions ( $w = 0.1500 \pm 0.0001$  and  $w = 0.3000 \pm 0.0001$ ) at temperatures of 322.5 K and 372.9 K and pressures from 0.5 MPa to 5 MPa for  $\text{CO}_2$  loadings up to the saturation of the absorbent solution. The measurements were carried out using a custom-made mixing cell developed for an isothermal differential heat flux calorimeter, the

Setaram C-80.<sup>29</sup> Solubilities of the gas into the different absorbents ( $s$ ) at the same temperature, pressure, and amine weight fraction were deduced from the experimental enthalpic data.

## 2. EXPERIMENTAL SECTION

**2.1. Experimental Arrangement.** The calorimetric technique was similar to the one used previously to study the dissolution of  $\text{CO}_2$  in aqueous solutions of 2-amino-2-methyl-1-propanol (AMP)<sup>30</sup> and *N*-methyl-diethanolamine (MDEA).<sup>31,32</sup> The heat of absorption of  $\text{CO}_2$  in aqueous solution of amine was measured using a custom-made flow-mixing cell adapted to a Setaram C-80 heat conduction differential calorimeter. This unit was housed in the calorimetric block, where the heat effect during the absorption of the gas into the aqueous solution of amine was detected by thermopiles. The overall experimental arrangement is depicted in Figure 1. The two fluids,  $\text{CO}_2$  and aqueous amine solution, were injected into the mixing unit supplied by two ISCO model 100 DM high-pressure syringe pumps. The syringe pumps were regulated at a constant temperature of 298.15 K, using water bath, to maintain a constant mass flow rate. The flow line was made out of stainless steel tubing of 1.6 mm outer diameter (o.d.) and 1.0 mm inner diameter (i.d.). The system pressure was maintained constant to 0.02 MPa using a Circle Seal backpressure regulator placed at the end of the flow line. The pressure was measured by three electronic Keller pressure transducers connected to pressure indicators WEST 8010 with an accuracy of 0.25 % of the full scale. The pressure gauges were located at the outlets of the acid gas and aqueous phase pumps and between the mixing cell and the backpressure regulator. The temperature of the injected fluids was adjusted to the working temperature of the calorimeter before entering the mixing cell using four preheaters:

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Table 1. Literature Review of Gas Solubility Data for the {CO<sub>2</sub> + MEA+ H<sub>2</sub>O} System

authors	composition	<i>T</i>	<i>p</i> <sub>CO<sub>2</sub></sub>	<i>p</i>	$\delta_{\max}$
		K	kPa	kPa	%
Mason and Dodge <sup>10</sup>	0.5–12.5 <sup>c</sup>	273–348	1.32–100		2
Jones et al. <sup>11</sup>	0.153 <sup>b</sup>	313–413	0.0027–930.1		0.5
Lee et al. <sup>12</sup>	2.5–5.0 <sup>c</sup>	313–373	1.1523–6621.24		3
Lee et al. <sup>13</sup>	1.0–5.0 <sup>c</sup>	298–393	0.1–10000		4
Lawson and Garst <sup>14</sup>	0.152 <sup>b</sup>	313–413	1.32–2750		9
Isaacs et al. <sup>15</sup>	2.5 <sup>a</sup>	353–373	0.0066–1.75		15
Austgen and Rochelle <sup>16</sup>	2.5 <sup>a</sup>	313–353	0.0934–228.7		-
Shen and Li <sup>17</sup>	0.153–0.300 <sup>b</sup>	313–373	1.1–2550		12
Dawodu and Meisen <sup>18</sup>	4.2 <sup>a</sup>	373	455–3863		13.5
Jou et al. <sup>19</sup>	0.300 <sup>b</sup>	273–423	0.0012–19954	200–20000	3
Song and Lee <sup>20</sup>	0.153 <sup>b</sup>	313	3.1–2359		12
Jane and Li <sup>21</sup>	2.5 <sup>a</sup>	353		3.57–121.8	5
Mathonat et al. <sup>22</sup>	0.300 <sup>b</sup>	313–393	5000–20000		7
Ma'mun et al. <sup>23</sup>	0.300 <sup>b</sup>	393	7.354–191.9		2

<sup>a</sup> Molarity in mol·L<sup>-1</sup>. <sup>b</sup> Mass fraction. <sup>c</sup> Normality in mol·L<sup>-1</sup>.

Table 2. Literature Review of Enthalpy Data for the System {CO<sub>2</sub> + MEA + H<sub>2</sub>O}

source	wt %	<i>T</i>	<i>p</i> <sub>CO<sub>2</sub></sub>	$\delta_{\max}$
		K	kPa	%
Mathonat et al. <sup>22</sup>	0.300	313–393	2000–10000	7
Kim and Svendsen <sup>27</sup>	0.300	313–393	100–300	3
Carson et al. <sup>28</sup>	0.100–0.300	298	265	2

two external to the calorimeter and two inside it. The two external heaters were located just above the calorimetric block. The temperature of the calorimeter was set up and controlled within 0.01 K using a Setaram G11 electronic control device.

**2.2. The Mixing Cell.** The design of the mixing cell (Figure 2) is the same as that described by Koschel et al.<sup>33</sup> However, when the cell, with its stainless steel tubing, was used for the study of acid gases, it was found to corrode.<sup>34</sup> The cell was thus rebuilt in Hastelloy C22. The “T” connection in the upper part of the mixing unit, used by Koschel et al.,<sup>33</sup> was also removed. Instead, the CO<sub>2</sub> and the aqueous solution were injected through by two Hastelloy 1/16” tubing (1.6 mm o.d.), and contacted one another in a small chamber at the bottom of the cell, shown as “M” in Figure 2, where the two input tubes and a 2.8 m mixing chamber were silver-soldered together. The quantitative mixing occurs in this 2.8 m long mixing chamber, which consisted of Hastelloy C22 1/16” tubing, coiled in good thermal contact with the inner wall of the confinement cylinder (18.7 mm i.d., 80 mm height).

**2.3. The Preheaters.** The preheaters are counter-current heat exchangers, shown in Figure 3. The two external heat exchangers (Figure 3a) consisted of a copper cylinder with the tubing coiled on its outer surface. The two internal heat exchangers (made also of copper, Figure 3b) were located inside the calorimeter block hole housing the mixing cell. They used the same Hastelloy tubing, tightly fitted in grooves inside the cylindrical

preheater cylinder. Both internal and external preheaters were thermoregulated by heating cartridges and a platinum resistance thermometer connected to a PID controller. The temperatures of the two external and the first internal preheaters were maintained constant to  $\pm 0.1$  K by means of RKC CB 100 regulators. The second internal preheater was connected to a PID controller from Fluke Hart Scientific model 2200 that controls the temperature with stability to  $\pm 0.01$  K.

**2.4. Operating Procedure.** The experiments were designed to measure the enthalpy of mixing between the two fluids (gas and aqueous solution) at constant temperature and pressure as a function of the CO<sub>2</sub> loadings,  $\alpha$  (moles CO<sub>2</sub>/mol amine). In our case, this enthalpy of mixing characterized the dissolution of the carbon dioxide into the amine solution and was defined as the enthalpy of solution of CO<sub>2</sub> in the aqueous solution of amine. This enthalpy of solution has also been called the enthalpy of absorption or heat of absorption by other authors.<sup>7,27,35</sup> The loading was determined by the total molar flow-rate of CO<sub>2</sub>  $\dot{n}_{\text{CO}_2}$  divided by the total molar flow-rate of amine  $\dot{n}_{\text{amine}}$  (eq 1).

$$\alpha = \frac{\dot{n}_{\text{CO}_2}}{\dot{n}_{\text{amine}}} \quad (1)$$

Typically the flow rates varied from 0.1 mL·min<sup>-1</sup> to 2 mL·min<sup>-1</sup> and 0.04 mL·min<sup>-1</sup> to 0.4 mL·min<sup>-1</sup> for CO<sub>2</sub> and the aqueous phase, respectively, with a relative uncertainty of 0.3 %. The molar flow rates were calculated from the pump flow rates using the densities, mass composition (for the aqueous amine solution), and molar mass of the fluids. The densities of aqueous MEA solutions were measured at 298.5 K (the regulation temperature of the syringe pump) as a function of the pressure using an Anton Paar densimeter DMA 512 (P model) following the Jacquemin procedure;<sup>36</sup> values are reported in Table 3. The densities of CO<sub>2</sub> were calculated from ALLPROPS software.<sup>37</sup>

The enthalpy was directly obtained from the thermopile signal  $S$  ( $\mu\text{V}$ ) of the calorimeter and the molar flow-rate  $\dot{n}$  (mol·s<sup>-1</sup>) of the solution. Before measuring the thermopile signal  $S_M$  ( $\mu\text{V}$ )

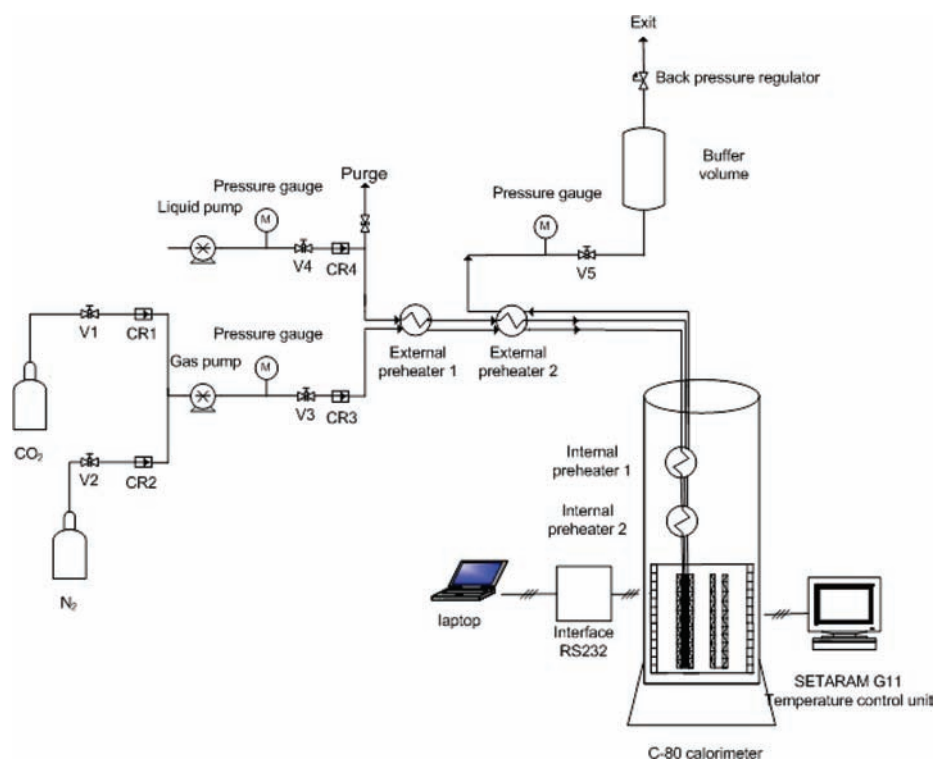


Figure 1. Schematic diagram of the flow-mixing calorimeter.

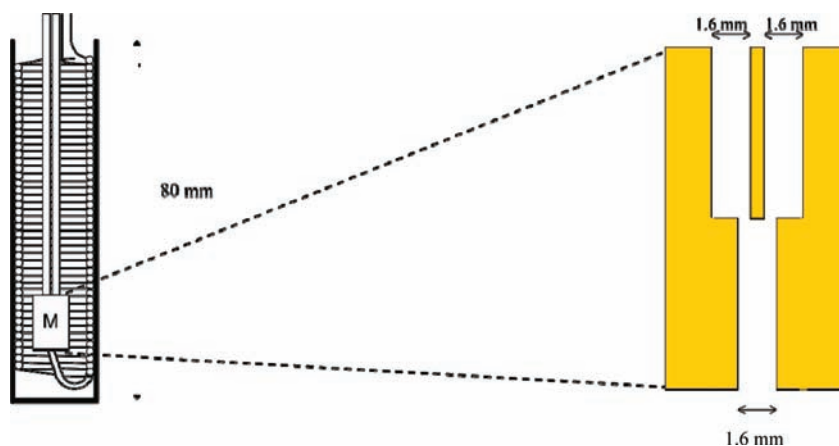


Figure 2. Schematic diagram of the mixing cell.

during the mixing process, a baseline signal  $S_{BL}$  ( $\mu V$ ) was recorded with only the aqueous phase flowing through the calorimeter. The baseline signal was kept close to zero by adjusting the thermoregulation of the entering fluids. The signal was recorded for 20 min before the gas injection. The heat effect due to the gas dissolution corresponded to a thermopile signal ( $S_M - S_{BL}$ ) ranging from 4 mV to 16 mV and typically had stability better than  $\pm 0.1$  mV. This signal was recorded for at least 30 min, and then the baseline signal was again recorded for 20 min.

Enthalpies of solution ( $\Delta_{sol}H$ ) expressed as  $\text{kJ}\cdot\text{mol}^{-1}$  of  $\text{CO}_2$  or  $\text{kJ}\cdot\text{mol}^{-1}$  of amine, were derived from the calorimetric signal using the molar flow rate of  $\text{CO}_2$  or the molar flow rate of amine, respectively. The enthalpy of solution ( $\Delta_{sol}H$ ) was calculated from eq 2 using the thermopile signals  $S_M$  and  $S_{BL}$  ( $\mu V$ ) and the

molar flow rate  $\dot{n}$  ( $\text{mol}\cdot\text{s}^{-1}$ ) of the gas ( $\Delta_{sol}H/\text{kJ}\cdot\text{mol}^{-1}$  of  $\text{CO}_2$ ) or the molar flow rate of amine ( $\Delta_{sol}H/\text{kJ}\cdot\text{mol}^{-1}$  of amine)

$$\Delta_{sol}H = \frac{\Delta \text{signal}}{E \cdot \dot{n}} \quad (2)$$

where  $\Delta \text{signal}$  represented the difference in the thermopile signal during the mixing process and the baseline (only when the aqueous amine solution was running through the mixing flow calorimeter). The molar flow rate  $\dot{n}$  was derived from the volumetric pump flow rates, the densities, and the amine concentration. The thermopile sensitivity  $E$  ( $\mu V\cdot\text{mW}^{-1}$ ) used to convert the thermopile signal to heat power was given by the constructor as a function of the temperature. However, it could

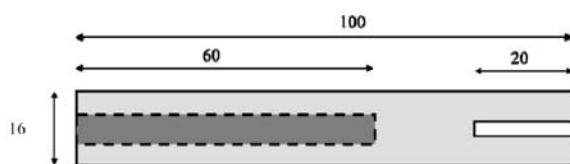


Figure 3-a.

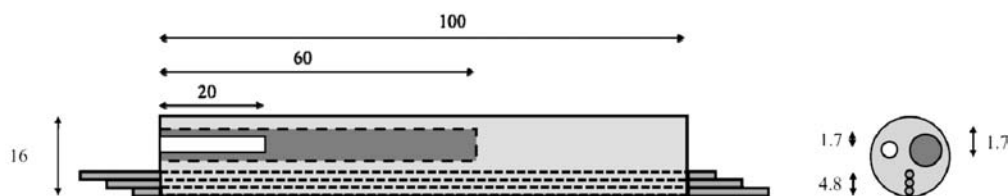


Figure 3-b.

Figure 3. Schematic diagram of preheaters: (a) external preheater, (b) internal preheater (dimensions are given in mm).

Table 3. Experimental Density of Aqueous MEA Solutions ( $w = 0.1500$  and  $0.3000$ )

$T$	$p$	$\rho$	$T$	$p$	$\rho$
K	MPa	$\text{kg}\cdot\text{m}^{-3}$	K	MPa	$\text{kg}\cdot\text{m}^{-3}$
{MEA + Water}					
$w = 0.1500$			$w = 0.3000$		
298.34	0.209	1002.9	298.31	0.207	1010.2
298.34	0.505	1003.0	298.31	0.507	1010.3
298.34	1.014	1003.2	298.31	1.011	1010.5
298.34	2.000	1003.6	298.31	2.006	1010.9
298.34	5.004	1004.9	298.32	5.002	1012.0

have slightly changed with time; it was thus recalibrated measuring the heat of mixing of a binary system whose enthalpy of mixing is well-known. For the purpose we chose the reference  $\{\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}\}$  system, using the enthalpy data provided by Ott et al.<sup>38,39</sup> The difference between the thermopile sensitivity obtained by chemical calibration and that reported by SETARAM was typically less than 5 %.

The experimental uncertainty on the enthalpy of solution,  $\delta(\Delta_{\text{sol}}H)$ , was determined as a statistical estimate from the expected error in  $E$ , uncertainties on the molar flow rate, and the heat power based on eq 2. The uncertainty on the molar flow rates depends on the uncertainty on the volumetric flow rates of the pumps and the accuracy of the fluid densities. For the gas it was estimated to be smaller than 0.3 % at 5 MPa and 3 % at 0.2 MPa, and for the aqueous amine solution it was estimated to be smaller than 1 %. The error on the heat power is related to the accuracy of the thermopile sensitivity  $E$  of the calorimeter, estimated to 2 %, and to the fluctuations of the calorimetric signal. The uncertainty in the difference in the thermopile signal during the mixing process and the baseline was between 1 % and 3 % and can reach 5 % for the smallest measured heat effects. Calculations for the determination of the experimental uncertainties are described in detail elsewhere.<sup>40</sup>

**2.5. Chemicals and Materials.** MEA was obtained from Fluka Organics with a purity > 99 % and was used without further purification. Carbon dioxide (purity of 99.998 %) was obtained from Saga. Water was distilled and degassed before used (resistivity  $18.2 \text{ M}\Omega\cdot\text{cm}$ ). Aqueous solutions were prepared and kept under nitrogen atmosphere by mass with an uncertainty in the mass fraction estimated as less than  $\pm 10^{-4}$ . Aqueous solutions were stored in glass bottle in an opaque cabinet to prevent any photodegradation.

### 3. RESULTS AND DISCUSSION

**3.1. Enthalpy Data.** The enthalpy of solution of  $\text{CO}_2$  in the aqueous amine (MEA) solutions ( $w = 0.1500$  and  $0.3000$ ) was measured at 322.5 K and 372.9 K at pressures from 0.5 MPa to 5 MPa. The experimental data were obtained for different gas–solvent flow rate ratios; they are presented in Tables 4 to 7. The uncertainties in the enthalpy were determined as indicated above. Experimental enthalpies are plotted versus loading  $\alpha$  (moles of  $\text{CO}_2$ /mol of amine) in Figures 4 and 5; large exothermic effects were observed at both temperatures. The graphs where the enthalpy ( $/\text{kJ}\cdot\text{mol}^{-1}$  of amine) is plotted versus the loading show up typically two domains that correspond:

- (i) to a total dissolution of  $\text{CO}_2$  injected (unsaturated solution);
- (ii) to a partial dissolution of  $\text{CO}_2$  injected (saturated solution).

When the enthalpy of solution  $\Delta_{\text{sol}}H$  is expressed in  $\text{kJ}\cdot\text{mol}^{-1}$  of  $\text{CO}_2$  (Figure 4) the graphs exhibit plateaus for the lowest loadings up to 0.5, and then the exothermic effect decreases as the loading increases. At the lowest loadings (Figure 4), the energetic effect per mole of gas seemed to be constant, within the experimental uncertainty, and independent of  $\text{CO}_2$  loading. This behavior was also observed and reported by other authors.<sup>4,35</sup>

The border between unsaturated and saturated absorbent is not obvious when the enthalpy is expressed per mole of gas. The absorption of  $\text{CO}_2$  in aqueous solutions of the primary (MEA) amine is a combination of chemical reactions and physical dissolution. Chemical absorption of  $\text{CO}_2$  in aqueous solutions

Table 4. Experimental Enthalpies of Solution of CO<sub>2</sub> in Aqueous Solutions of MEA ( $w = 0.1500$ ) at 322.5 K

$\alpha$	$\delta\alpha$	$-\Delta_{\text{sol}}H$	$\delta \Delta_{\text{sol}}H$	$-\Delta_{\text{sol}}H$	$\delta \Delta_{\text{sol}}H$
$\text{mol}_{\text{CO}_2}/\text{mol}_{\text{MEA}}$		$\text{kJ}\cdot\text{mol}^{-1}$ of MEA		$\text{kJ}\cdot\text{mol}^{-1}$ of CO <sub>2</sub>	
$p = 0.53 \text{ MPa}$					
0.136	0.003	12.3	0.6	89.9	3.0
0.182	0.003	17.0	0.6	93.4	3.0
0.215	0.004	20.8	0.3	96.7	1.3
0.263	0.005	24.3	0.3	92.6	1.0
0.324	0.006	28.8	0.6	88.9	2.0
0.350	0.007	30.7	0.2	87.5	0.7
0.396	0.007	33.7	0.4	85.0	1.0
0.417	0.008	35.7	0.3	85.5	0.7
0.438	0.009	36.3	0.4	82.8	0.9
0.487	0.009	38.5	0.4	79.2	0.7
0.525	0.010	40.0	0.5	76.1	1.0
0.556	0.010	40.3	1.1	72.4	1.9
0.613	0.011	42.0	0.4	68.5	0.7
0.673	0.012	43.5	0.4	64.7	0.6
0.769	0.014	43.7	0.5	56.9	0.7
0.927	0.017	43.7	0.6	47.1	0.6
1.510	0.028	42.3	0.6	28.0	0.4
$p = 1.04 \text{ MPa}$					
0.138	0.002	12.1	0.3	87.7	1.8
0.183	0.002	15.7	0.4	85.6	2.1
0.226	0.003	20.5	0.5	90.3	2.0
0.274	0.003	24.9	0.3	91.2	1.3
0.317	0.004	28.3	0.6	89.3	1.9
0.365	0.004	33.0	0.4	90.5	1.0
0.404	0.005	35.0	0.3	86.6	0.9
0.452	0.006	38.7	0.5	85.6	1.0
0.512	0.006	42.8	0.4	83.7	0.7
0.553	0.007	46.1	0.4	83.4	0.6
0.583	0.007	48.8	0.4	83.8	0.7
0.652	0.008	51.6	0.4	79.3	0.7
0.745	0.009	55.0	0.4	73.9	0.5
0.838	0.010	58.0	0.5	69.2	0.6
0.913	0.011	59.4	0.5	65.0	0.5
0.922	0.011	60.2	0.5	65.2	0.6
0.931	0.011	60.5	0.8	64.9	0.8
0.994	0.012	60.5	0.6	60.8	0.6
1.014	0.012	61.4	0.9	60.5	0.9
1.097	0.013	61.5	0.8	56.1	0.7
1.178	0.014	61.3	0.8	52.0	0.7
1.269	0.016	61.7	0.8	48.6	0.6
1.361	0.017	61.4	0.7	45.1	0.5
1.452	0.018	61.1	0.8	42.1	0.5
$p = 5.15 \text{ MPa}$					
0.411	0.002	35.9	0.6	87.2	1.4
0.424	0.002	37.2	0.3	87.6	0.6
0.453	0.002	39.7	0.2	87.6	0.5
0.483	0.003	40.3	0.5	83.5	1.0
0.487	0.003	42.2	0.3	86.7	0.7
0.524	0.003	45.1	0.4	86.1	0.7

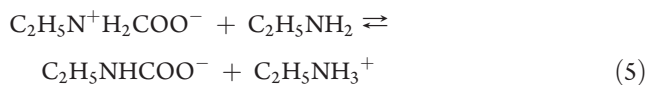
Table 4. Continued

$\alpha$	$\delta\alpha$	$-\Delta_{\text{sol}}H$	$\delta \Delta_{\text{sol}}H$	$-\Delta_{\text{sol}}H$	$\delta \Delta_{\text{sol}}H$
$\text{mol}_{\text{CO}_2}/\text{mol}_{\text{MEA}}$		$\text{kJ}\cdot\text{mol}^{-1}$ of MEA		$\text{kJ}\cdot\text{mol}^{-1}$ of CO <sub>2</sub>	
0.572	0.003	47.5	0.5	83.2	0.9
0.594	0.003	45.5	0.3	76.7	0.5
0.622	0.003	50.0	0.3	80.4	0.5
0.670	0.004	52.0	0.7	77.6	1.1
0.687	0.004	53.1	0.5	77.3	0.7
0.729	0.004	52.7	0.3	72.3	0.5
0.753	0.004	54.2	0.3	72.0	0.5
0.763	0.004	56.0	1.0	73.5	1.3
0.801	0.004	56.7	0.4	70.8	0.5
0.854	0.005	59.7	0.3	69.9	0.4
0.857	0.005	59.9	0.6	69.9	0.7
0.867	0.005	60.0	0.5	69.3	0.6
0.950	0.005	61.1	0.3	64.3	0.3
0.950	0.005	61.7	1.0	65.0	1.1
0.991	0.005	63.7	0.4	64.3	0.4
1.016	0.006	61.1	0.5	60.2	0.5
1.085	0.006	62.6	0.8	57.7	0.7
1.123	0.006	63.0	1.0	56.1	0.9
1.128	0.006	63.7	1.2	56.5	1.1
1.171	0.006	63.0	1.4	53.8	1.2
1.208	0.007	63.2	0.7	52.3	0.6
1.302	0.007	60.5	2.1	46.4	1.6
1.317	0.007	62.3	1.3	47.3	1.0
1.401	0.008	63.8	1.0	45.5	0.7
1.420	0.008	62.6	0.8	44.1	0.6
1.423	0.008	61.5	0.4	43.2	0.3
1.587	0.01	61.7	1.3	38.9	0.8
2.010	0.011	60.8	1.7	30.2	0.9

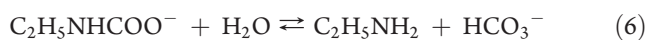
of primary amines has been described in the literature.<sup>41,42</sup> The primary amine (MEA) can react with carbon dioxide to form a carbamate (eq 3).



A two-step chemical mechanism (eqs 4 and 5) with a zwitterion formation was proposed by Caplow<sup>41</sup> to explain eq 3.



The solubility of the gas into the solution is thus limited by stoichiometry to a maximum loading  $\alpha = 0.5$  mol CO<sub>2</sub>/mol amine. However, due to possible carbamate hydrolysis, the loading may exceed 0.5 when increasing CO<sub>2</sub> pressure.<sup>42</sup>



In that case the dissolution process is not controlled anymore by the carbamate formation but by the carbon dioxide, which reacts with the amine to form a carbonate. The solubility can thus be extended up to  $\alpha = 1.0$  mol CO<sub>2</sub>/mol amine. The change of energetic behavior observed around  $\alpha = 0.5$  seems to be



Table 5. Experimental Enthalpies of Solution of CO<sub>2</sub> in Aqueous Solutions of MEA ( $w = 0.3000$ ) at 322.5 K

$\alpha$	$\delta\alpha$	$-\Delta_{\text{sol}}H$	$\delta \Delta_{\text{sol}}H$	$-\Delta_{\text{sol}}H$	$\delta \Delta_{\text{sol}}H$
$\text{mol}_{\text{CO}_2}/\text{mol}_{\text{MEA}}$		$\text{kJ}\cdot\text{mol}^{-1}$ of MEA		$\text{kJ}\cdot\text{mol}^{-1}$ of CO <sub>2</sub>	
$p = 0.51 \text{ MPa}$					
0.087	0.002	8.2	0.1	94.4	0.6
0.130	0.003	12.6	0.2	96.9	1.6
0.181	0.003	16.7	0.1	92.6	0.5
0.230	0.004	21.3	0.1	92.5	0.6
0.281	0.005	26.6	0.3	94.4	0.9
0.310	0.006	29.2	0.5	94.2	1.7
0.391	0.008	37.0	0.6	94.4	1.6
0.448	0.009	41.2	0.4	92.0	0.8
0.515	0.009	45.4	0.5	88.1	1.0
0.542	0.010	46.5	0.4	85.7	0.8
0.576	0.011	48.5	0.6	84.1	1.0
0.632	0.012	50.8	0.5	80.4	0.7
0.652	0.013	52.4	0.5	80.4	0.8
0.736	0.014	52.2	0.5	70.9	0.7
0.739	0.015	52.3	0.5	70.8	0.7
0.828	0.015	52.6	0.7	63.5	0.8
0.828	0.015	52.6	0.6	63.5	0.7
0.954	0.017	52.1	0.6	54.6	0.6
$p = 1.03 \text{ MPa}$					
0.183	0.002	15.7	0.2	85.9	0.9
0.227	0.003	19.4	0.2	85.6	1.0
0.267	0.003	23.2	0.1	86.8	0.5
0.317	0.004	28.1	0.7	88.6	2.1
0.356	0.004	31.4	0.4	88.4	1.0
0.405	0.005	34.6	0.5	85.5	1.1
0.455	0.006	37.8	0.4	83.0	0.9
0.495	0.006	42.3	0.3	85.3	0.7
0.544	0.007	46.8	0.3	86.1	0.6
0.580	0.007	48.2	0.4	83.2	0.6
0.635	0.008	50.9	0.4	80.1	0.6
0.662	0.008	52.2	0.5	78.9	0.7
0.695	0.009	54.4	0.4	78.2	0.6
0.782	0.010	56.7	0.6	72.5	0.7
0.854	0.011	56.6	0.5	66.3	0.6
0.863	0.011	57.3	1.8	66.4	2.0
0.908	0.011	56.9	0.6	62.7	0.6
0.990	0.012	56.7	0.5	57.3	0.5
1.071	0.013	56.4	0.5	52.6	0.5
1.284	0.016	57.4	0.6	44.7	0.5
1.454	0.018	57.5	0.5	39.5	0.4
$p = 5.16 \text{ MPa}$					
0.283	0.002	23.9	0.7	84.4	2.6
0.310	0.002	26.2	0.8	84.7	2.6
0.341	0.002	29.1	0.5	85.3	1.4
0.385	0.002	32.5	0.4	84.6	1.1
0.394	0.002	33.6	0.6	85.3	1.4
0.434	0.002	37.2	0.7	85.7	1.6
0.443	0.002	36.9	0.3	83.3	0.7
0.507	0.003	42.6	0.4	84.0	0.7

Table 5. Continued

$\alpha$	$\delta\alpha$	$-\Delta_{\text{sol}}H$	$\delta \Delta_{\text{sol}}H$	$-\Delta_{\text{sol}}H$	$\delta \Delta_{\text{sol}}H$
$\text{mol}_{\text{CO}_2}/\text{mol}_{\text{MEA}}$		$\text{kJ}\cdot\text{mol}^{-1}$ of MEA		$\text{kJ}\cdot\text{mol}^{-1}$ of CO <sub>2</sub>	
0.507	0.003	42.1	0.3	83.1	0.7
0.507	0.003	42.4	0.3	83.7	0.6
0.518	0.003	43.6	0.5	84.1	0.9
0.593	0.003	48.6	0.3	82.0	0.5
0.600	0.003	47.0	0.2	78.3	0.4
0.601	0.003	48.3	0.3	80.3	0.5
0.627	0.003	50.3	0.7	80.1	1.1
0.644	0.004	51.0	0.4	79.2	0.7
0.655	0.004	50.0	1.7	76.4	2.6
0.704	0.004	53.9	3.1	76.5	4.4
0.714	0.004	52.2	0.4	73.1	0.5
0.729	0.004	53.4	0.5	73.3	0.6
0.773	0.004	56.0	0.9	72.4	1.1
0.830	0.004	56.9	0.4	68.5	0.5
0.837	0.005	58.1	0.8	69.4	0.9
0.837	0.005	58.7	0.8	70.1	0.9
0.906	0.005	58.8	0.3	65.4	0.3
0.937	0.005	57.9	0.2	61.8	0.3
0.975	0.005	58.6	0.4	60.1	0.4
1.031	0.006	59.1	0.5	57.3	0.5
1.079	0.006	59.1	0.4	54.7	0.4
1.111	0.006	58.5	0.3	52.7	0.2
1.171	0.007	58.8	0.5	50.2	0.4
1.238	0.007	58.3	0.3	47.1	0.2
1.282	0.007	59.0	0.5	46.0	0.4
1.292	0.007	58.7	0.3	45.5	0.2
1.476	0.008	58.3	0.4	39.5	0.3
1.532	0.009	58.7	0.3	38.3	0.2
1.684	0.009	59.1	0.3	35.1	0.2
1.832	0.010	59.3	0.3	32.4	0.2

associated to the change of the governance for the chemical mechanisms involved in the CO<sub>2</sub> dissolution.

A discussion of the effects of temperature, pressure, and absorbent composition on the dissolution of carbon dioxide will be carried out by a comparison of enthalpies of solution when they were found to remain constant (i.e., average enthalpy values  $\Delta_{\text{sol}}H^{\text{av}}$  expressed in  $\text{kJ}\cdot\text{mol}^{-1}$  of CO<sub>2</sub>, estimated on the plateaus). Numerical values are reported in Table 8.

The enthalpy of solution  $\Delta_{\text{sol}}H^{\text{av}}$  was estimated to be  $88 \pm 2 \text{ kJ}\cdot\text{mol}^{-1}$  of CO<sub>2</sub> and  $89 \pm 4 \text{ kJ}\cdot\text{mol}^{-1}$  of CO<sub>2</sub> for  $w = 0.1500$  and  $w = 0.3000$ , respectively. The pressure and temperature effects on the enthalpy of solution of CO<sub>2</sub> in MEA solutions were not found to be significant regarding experimental uncertainty. However the enthalpy decreased drastically at  $p = 3.08 \text{ MPa}$  and at  $p = 5.13 \text{ MPa}$  for dissolution in a solution of mass composition  $w = 0.1500$  and  $w = 0.3000$ , respectively. The behavior was attributed to technical difficulties when experiments were carried out for low gas loading. In these conditions of elevated pressures the difference in volume flow rates of carbon dioxide and absorbent solution is important, leading to problems of mixing. This difference increases with the volumetric mass of CO<sub>2</sub>, that is, with pressure or when decreasing amine composition.

Table 6. Experimental Enthalpies of Solutions of CO<sub>2</sub> in Aqueous Solutions of MEA ( $w = 0.1500$ ) at 372.9 K

$\alpha$	$\delta\alpha$	$-\Delta_{\text{sol}}H$	$\delta \Delta_{\text{sol}}H$	$-\Delta_{\text{sol}}H$	$\delta \Delta_{\text{sol}}H$
$\text{mol}_{\text{CO}_2}/\text{mol}_{\text{MEA}}$		$\text{kJ}\cdot\text{mol}^{-1}$ of MEA		$\text{kJ}\cdot\text{mol}^{-1}$ of CO <sub>2</sub>	
$p = 0.55 \text{ MPa}$					
0.058	0.001	5.1	0.2	88.1	3.9
0.090	0.002	7.7	0.3	86.3	3.6
0.137	0.003	11.7	0.5	85.1	3.5
0.183	0.003	16.1	0.7	87.9	4.0
0.229	0.004	20.8	1.3	90.8	5.6
0.263	0.005	23.9	0.6	90.9	2.2
0.309	0.006	27.8	2.5	90.2	8.1
0.309	0.006	26.8	0.5	86.7	1.5
0.365	0.007	33.1	0.4	90.8	1.0
0.366	0.007	34.9	0.4	95.4	1.1
0.419	0.008	38.0	0.6	90.8	1.3
0.458	0.009	43.4	0.5	94.8	1.0
0.464	0.009	40.8	1.1	88.0	2.3
0.513	0.009	43.5	0.5	84.9	0.9
0.527	0.010	41.8	0.5	79.2	1.0
0.559	0.010	46.9	0.5	83.8	0.8
0.560	0.010	47.6	0.6	85.1	1.0
0.595	0.011	48.6	0.6	81.6	1.0
0.615	0.012	49.0	0.6	79.8	1.0
0.653	0.012	48.5	0.9	74.3	1.4
0.702	0.014	48.2	0.6	68.7	0.9
0.790	0.015	48.1	0.9	60.8	1.2
0.790	0.015	48.0	0.6	60.8	0.7
0.916	0.017	46.4	0.8	50.6	0.9
1.098	0.021	44.7	0.7	40.7	0.6
1.329	0.024	43.5	0.6	32.7	0.5
$p = 1.05 \text{ MPa}$					
0.133	0.002	12.1	0.4	91.0	2.9
0.179	0.002	15.2	1.2	85.3	6.7
0.221	0.003	19.9	0.2	89.9	0.7
0.223	0.003	20.3	0.9	91.1	4.0
0.223	0.003	19.9	0.2	89.4	1.0
0.267	0.003	23.9	0.5	89.5	1.7
0.316	0.004	27.8	0.3	87.7	1.0
0.354	0.004	30.6	0.7	86.6	1.9
0.358	0.004	30.4	0.6	85.0	1.6
0.407	0.005	34.7	0.4	85.2	1.0
0.441	0.006	37.6	0.8	85.3	1.7
0.441	0.006	37.1	0.3	84.2	0.7
0.528	0.007	41.6	1.3	78.7	2.5
0.537	0.007	42.0	0.6	78.2	1.0
0.537	0.007	43.4	5.4	80.9	10.0
0.539	0.007	43.4	0.5	80.6	1.0
0.592	0.007	45.9	0.4	77.6	0.7
0.621	0.008	47.5	0.4	76.5	0.7
0.668	0.008	47.9	1.4	71.6	2.1
0.708	0.009	48.9	0.4	69.1	0.5
0.805	0.010	48.5	0.4	60.3	0.5
0.887	0.011	46.9	1.3	52.9	1.5

Table 6. Continued

$\alpha$	$\delta\alpha$	$-\Delta_{\text{sol}}H$	$\delta \Delta_{\text{sol}}H$	$-\Delta_{\text{sol}}H$	$\delta \Delta_{\text{sol}}H$
$\text{mol}_{\text{CO}_2}/\text{mol}_{\text{MEA}}$		$\text{kJ}\cdot\text{mol}^{-1}$ of MEA		$\text{kJ}\cdot\text{mol}^{-1}$ of CO <sub>2</sub>	
1.060	0.013	47.0	1.0	44.4	1.0
1.238	0.016	46.6	0.8	37.6	0.6
1.443	0.018	45.9	0.6	31.8	0.4
$p = 3.08 \text{ MPa}$					
0.158	0.001	12.7	0.2	80.8	1.2
0.194	0.002	15.4	0.2	79.5	0.9
0.194	0.002	15.7	0.3	81.2	1.7
0.291	0.002	23.5	0.2	80.8	0.6
0.312	0.003	25.0	0.3	80.2	0.8
0.321	0.003	24.9	0.3	77.5	0.9
0.364	0.003	28.9	0.3	79.4	0.7
0.368	0.003	29.6	0.2	80.4	0.6
0.437	0.004	35.4	0.2	81.0	0.5
0.455	0.004	35.9	0.5	79.0	1.0
0.528	0.004	42.0	0.2	79.6	0.5
0.580	0.005	46.9	0.4	80.9	0.7
0.591	0.005	48.1	0.9	81.4	1.5
0.600	0.005	47.8	0.8	79.6	1.4
0.665	0.006	52.6	0.9	79.1	1.4
0.742	0.006	56.0	0.4	75.4	0.5
0.748	0.006	57.1	0.3	76.3	0.4
0.791	0.007	58.0	0.4	73.3	0.5
0.849	0.007	60.1	0.4	70.8	0.4
0.875	0.007	60.0	0.4	68.5	0.5
0.945	0.008	59.9	0.4	63.4	0.4
1.079	0.009	60.4	0.3	56.0	0.3
1.216	0.010	60.1	0.3	49.4	0.3
1.347	0.011	59.8	0.4	44.4	0.3
1.476	0.012	59.7	0.4	40.4	0.2
1.597	0.014	59.3	0.5	37.1	0.3
$p = 5.19 \text{ MPa}$					
0.372	0.002	22.6	2.3	60.8	6.2
0.438	0.002	25.6	2.2	58.5	4.9
0.506	0.003	30.4	1.0	60.1	2.0
0.612	0.003	38.0	0.8	62.2	1.4
0.614	0.003	38.6	0.3	62.8	0.4
0.688	0.004	42.1	0.6	61.2	0.9
0.791	0.004	48.0	1.1	60.7	1.4
0.844	0.005	50.4	0.8	59.7	0.9
0.877	0.005	51.0	3.5	58.2	4.0
0.888	0.005	53.3	0.3	60.1	0.3
0.942	0.005	52.2	0.4	55.4	0.4
0.984	0.006	54.8	0.3	55.7	0.3
0.992	0.005	55.9	0.8	56.3	0.9
1.036	0.006	56.2	0.6	54.2	0.6
1.052	0.006	57.8	3.1	54.9	2.9
1.060	0.006	57.9	0.3	54.6	0.3
1.154	0.007	56.1	0.9	48.6	0.8
1.256	0.007	58.3	0.7	46.5	0.5
1.326	0.007	58.1	0.5	43.8	0.3
1.470	0.008	58.2	0.4	39.6	0.3

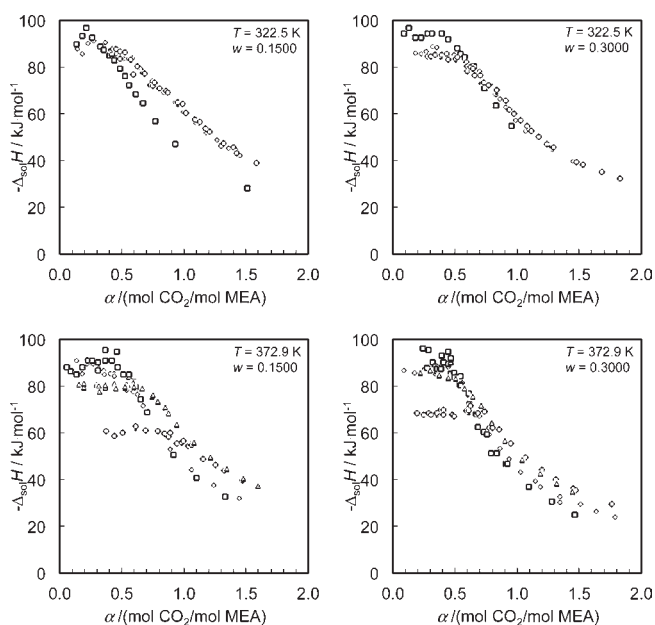
Table 7. Experimental Enthalpies of Solutions of CO<sub>2</sub> in Aqueous Solutions of MEA ( $w = 0.3000$ ) at 372.9 K

$\alpha$	$\delta\alpha$	$-\Delta_{\text{sol}}H$	$\delta \Delta_{\text{sol}}H$	$-\Delta_{\text{sol}}H$	$\delta \Delta_{\text{sol}}H$
$\text{mol}_{\text{CO}_2}/\text{mol}_{\text{MEA}}$		$\text{kJ}\cdot\text{mol}^{-1}$ of MEA		$\text{kJ}\cdot\text{mol}^{-1}$ of CO <sub>2</sub>	
$p = 0.54 \text{ MPa}$					
0.243	0.005	23.4	0.3	96.3	1.2
0.271	0.005	23.8	0.4	87.8	1.3
0.289	0.006	27.6	0.4	95.6	1.3
0.323	0.006	29.1	0.4	90.3	1.2
0.337	0.007	29.8	0.4	88.4	1.2
0.356	0.007	30.7	1.2	86.2	3.4
0.356	0.007	31.2	0.7	87.5	1.9
0.378	0.007	33.1	3.2	87.6	8.4
0.386	0.008	33.7	0.8	87.3	2.2
0.395	0.008	36.7	0.4	92.8	1.1
0.409	0.008	36.9	0.7	90.3	1.7
0.445	0.009	39.9	2.0	89.5	4.5
0.446	0.009	42.2	1.2	94.6	2.8
0.463	0.009	39.5	0.9	85.3	1.9
0.464	0.009	41.8	0.3	90.1	0.7
0.464	0.009	42.3	0.6	91.3	1.4
0.464	0.009	42.6	0.4	91.9	0.8
0.490	0.009	41.0	3.2	83.7	6.5
0.490	0.009	42.0	2.0	85.7	4.1
0.514	0.010	43.0	0.9	83.8	1.7
0.536	0.010	43.2	1.4	80.7	2.7
0.547	0.010	46.1	0.4	84.3	0.7
0.547	0.011	44.0	1.8	80.5	3.3
0.613	0.012	47.2	1.5	77.0	2.4
0.617	0.012	44.7	2.0	72.4	3.3
0.668	0.013	45.4	1.6	68.0	2.5
0.681	0.013	42.6	2.4	62.6	3.5
0.729	0.014	43.9	0.5	60.2	0.7
0.758	0.015	45.0	2.4	59.4	3.2
0.788	0.015	40.2	2.4	51.1	3.1
0.834	0.015	42.8	0.5	51.3	0.6
0.912	0.017	42.4	0.5	46.5	0.5
0.925	0.017	43.2	0.5	46.7	0.5
1.095	0.021	40.5	0.5	37.0	0.5
1.278	0.024	38.9	0.5	30.5	0.4
1.466	0.027	36.4	0.5	24.8	0.3
$p = 1.03 \text{ MPa}$					
0.089	0.001	7.7	0.2	86.5	2.3
0.178	0.002	15.2	0.2	85.6	1.0
0.256	0.003	22.3	2.2	87.2	8.7
0.341	0.004	29.1	0.3	85.3	0.9
0.444	0.006	39.1	0.3	88.1	0.7
0.475	0.006	40.9	0.4	86.1	0.9
0.533	0.007	44.8	0.6	84.1	1.0
0.561	0.007	45.6	1.1	81.3	2.0
0.607	0.008	46.2	2.5	76.1	4.1
0.694	0.009	46.5	0.9	67.0	1.3
0.774	0.010	46.0	0.4	59.5	0.5
0.861	0.011	45.8	0.4	53.2	0.5
0.934	0.012	45.4	0.4	48.6	0.4
1.027	0.013	44.3	1.1	43.2	1.1

Table 7. Continued

$\alpha$	$\delta\alpha$	$-\Delta_{\text{sol}}H$	$\delta \Delta_{\text{sol}}H$	$-\Delta_{\text{sol}}H$	$\delta \Delta_{\text{sol}}H$
$\text{mol}_{\text{CO}_2}/\text{mol}_{\text{MEA}}$		$\text{kJ}\cdot\text{mol}^{-1}$ of MEA		$\text{kJ}\cdot\text{mol}^{-1}$ of CO <sub>2</sub>	
1.144	0.014	44.9	0.4	39.2	0.4
1.186	0.015	43.7	1.7	36.9	1.4
1.344	0.018	40.6	2.5	30.2	1.8
1.346	0.017	43.9	0.5	32.6	0.3
1.509	0.018	44.2	0.5	29.3	0.3
1.636	0.020	43.3	0.5	26.5	0.3
1.786	0.022	42.7	1.1	23.9	0.6
$p = 3.07 \text{ MPa}$					
0.224	0.002	19.2	0.3	85.7	1.5
0.299	0.002	25.9	0.2	86.7	0.6
0.372	0.003	31.4	0.3	84.5	0.7
0.444	0.004	37.1	0.4	83.7	0.9
0.507	0.004	42.2	0.3	83.1	0.7
0.579	0.005	45.8	0.4	79.1	0.6
0.642	0.006	48.5	0.3	75.5	0.5
0.708	0.006	50.6	0.7	71.4	1.0
0.798	0.007	51.1	0.3	64.1	0.4
0.903	0.007	50.9	0.3	56.3	0.3
1.042	0.009	50.6	0.3	48.6	0.3
1.187	0.010	50.5	0.3	42.5	0.3
1.317	0.011	50.4	0.3	38.2	0.2
1.446	0.012	50.2	0.3	34.8	0.2
$p = 5.13 \text{ MPa}$					
0.194	0.001	13.3	0.3	68.3	1.5
0.248	0.001	16.8	0.9	67.6	3.6
0.287	0.002	19.6	0.4	68.4	1.5
0.307	0.002	20.7	2.0	67.6	6.5
0.356	0.002	24.1	0.1	67.6	0.3
0.356	0.002	24.4	0.4	68.5	1.0
0.387	0.002	27.0	0.4	69.7	1.1
0.405	0.002	28.3	1.7	69.9	4.3
0.409	0.002	27.8	0.3	67.8	0.6
0.479	0.003	32.4	0.4	67.6	0.8
0.490	0.003	32.9	0.7	67.1	1.4
0.593	0.003	41.3	3.2	69.6	5.4
0.612	0.003	42.1	1.2	68.7	2.0
0.612	0.003	42.6	0.5	69.6	0.8
0.612	0.003	43.1	0.2	70.4	0.3
0.614	0.003	42.7	0.7	69.6	1.1
0.625	0.004	44.8	2.8	71.7	4.5
0.685	0.004	46.8	0.4	68.3	0.5
0.735	0.004	50.9	0.4	69.3	0.5
0.777	0.004	48.2	0.7	62.1	0.8
0.805	0.005	50.0	2.0	62.1	2.5
0.857	0.005	52.7	0.3	61.5	0.3
0.950	0.005	52.8	0.4	55.6	0.4
1.071	0.006	52.9	0.2	49.4	0.2
1.197	0.007	52.7	0.2	44.0	0.2
1.315	0.007	52.6	0.4	40.0	0.3
1.452	0.008	52.5	0.3	36.2	0.2
1.471	0.008	52.2	0.2	35.5	0.2
1.761	0.010	52.1	0.2	29.6	0.1
2.086	0.012	52.0	0.2	24.9	0.1





**Figure 4.** Enthalpy of solution ( $-\Delta_{\text{sol}}H/(\text{kJ}\cdot\text{mol}^{-1}$  of  $\text{CO}_2$ )) versus  $\text{CO}_2$  loading for the aqueous solution of MEA:  $\square$ , 0.5 MPa;  $\diamond$ , 1.0 MPa;  $\circ$ , 5.0 MPa.

Considering the small temperature, pressure, and absorbent composition dependency on the dissolution of carbon dioxide into aqueous MEA solution (under  $\alpha = 0.5$  mol  $\text{CO}_2$ /mol amine), we decided to test a simplified thermodynamic model<sup>43</sup> that does not take into account the effects mentioned above for estimating the enthalpy of solution. In this model,<sup>43</sup> the reaction of  $\text{CO}_2$  with the amine is represented by a single equilibrium equation (eq 7):



The single equilibrium constant  $K_{\text{CO}_2}$  associated to eq 7 is defined by eq 8:

$$K_{\text{CO}_2} = p_{\text{CO}_2} \left( \frac{1 - \alpha}{\alpha \cdot x_{\text{CO}_2}} \right) \quad (8)$$

where  $p_{\text{CO}_2}$  is the partial pressure of  $\text{CO}_2$  and  $x_{\text{CO}_2}$  its molar fraction.

The equilibrium constant is then fitted to eq 9:

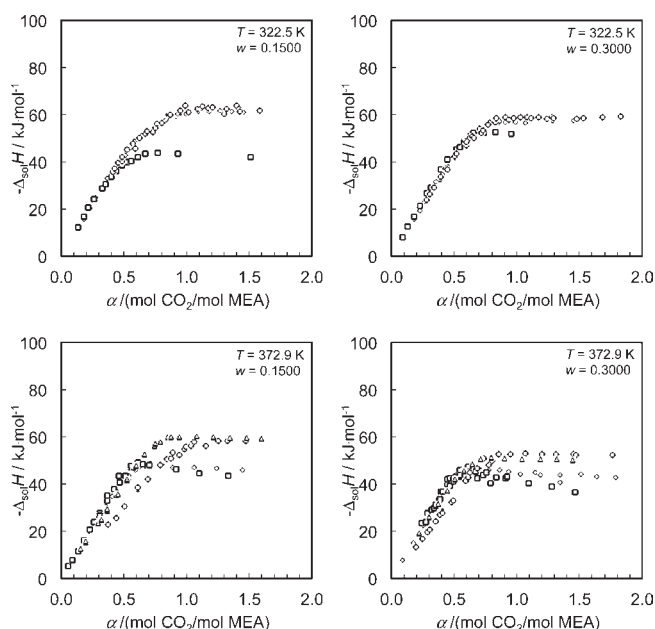
$$\ln(K_{\text{CO}_2}/\text{kPa}) = A + \frac{B}{T} + C(\alpha \cdot x_{\text{MEA}}^\circ) + D\sqrt{\alpha \cdot x_{\text{MEA}}^\circ} \quad (9)$$

where  $x_{\text{MEA}}^\circ$  is the gas free amine mole fraction and  $A$ ,  $B$ ,  $C$ , and  $D$  are fitting parameters.

The enthalpy of reaction (eq 7) is derived using the van't Hoff equation that leads also to the opposite of the enthalpy of solution (eq 10):

$$\Delta_r H = \left( \frac{\partial \ln K_{\text{CO}_2}}{\partial T} \right) = -BR = -\Delta_{\text{sol}}H \quad (10)$$

Parameters  $A$ ,  $B$ ,  $C$ , and  $D$  (Table 9) were obtained using solubility data selected from Table 1, gathering 99 equilibrium points. The experimental equilibrium constant  $K_{\text{CO}_2}^{\text{exp}}$  was



**Figure 5.** Enthalpy of solution ( $-\Delta_{\text{sol}}H/(\text{kJ}\cdot\text{mol}^{-1}$  of MEA)) versus  $\text{CO}_2$  loading for the aqueous solution of MEA:  $\square$ , 0.5 MPa;  $\diamond$ , 1.0 MPa;  $\triangle$ , 3.0 MPa;  $\circ$ , 5.0 MPa.

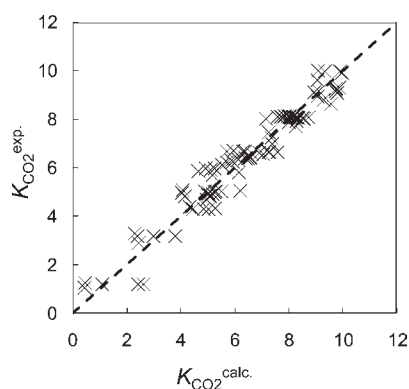
**Table 8.** Average Values for the Enthalpies of Solution at Low Loadings in Aqueous MEA Solutions ( $w = 0.1500$  and  $0.3000$ ) at 322.5 K and 372.9 K

$p$	$-\Delta_{\text{sol}}H^{\text{av}}$	$\delta\Delta_{\text{sol}}H^{\text{av}}$	$p$	$-\Delta_{\text{sol}}H^{\text{av}}$	$\delta\Delta_{\text{sol}}H^{\text{av}}$
MPa	kJ·mol <sup>-1</sup> of $\text{CO}_2$		MPa	kJ·mol <sup>-1</sup> of $\text{CO}_2$	
$T = 322.5 \text{ K}$					
$w = 0.1500$			$w = 0.3000$		
0.53	90	4	0.51	94	4
1.04	89	4	1.03	86	4
5.15	87	4	5.16	85	4
$T = 372.9 \text{ K}$					
$w = 0.1500$			$w = 0.3000$		
0.55	90	4	0.54	90	4
1.05	89	4	1.03	87	4
3.08	80	4	3.07	85	4
5.19	60	3	5.13	69	3

**Table 9.** Fitting Parameters and Correlation Coefficient Referring to the Simplified Thermodynamic Model<sup>43</sup>

$A$	$B$	$C$	$D$	$R^2$
$30.54 \pm 0.75$	$-10574 \pm 282$	$-55.7 \pm 19.5$	$18.2 \pm 4.8$	0.939

plotted against equilibrium constant  $K_{\text{CO}_2}^{\text{calc}}$  obtained with the simplified thermodynamic model<sup>43</sup> in Figure 6. Data from studies where the amine composition was expressed in molarity scale (for which the solution densities were not reported) or where pressure was given as the  $\text{CO}_2$  partial pressure were omitted. Only solubility data for  $\alpha$  below 0.5 were considered



**Figure 6.** Experimental equilibrium constant  $K_{\text{CO}_2}^{\text{exp}}$  against equilibrium constant  $K_{\text{CO}_2}^{\text{calc}}$  obtained with the simplified thermodynamic model.<sup>43</sup>

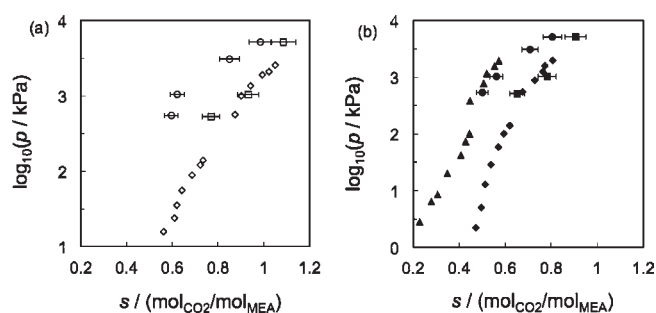
**Table 10.** Experimental Values for the Solubility of  $\text{CO}_2$  in Aqueous MEA Solutions ( $w = 0.1500$  and  $0.3000$ ) at 322.5 K and 372.9 K

$p$	$s$	$\delta s$	$p$	$s$	$\delta s$
MPa	(mol $\text{CO}_2$ /mol amine)		MPa	(mol $\text{CO}_2$ /mol amine)	
$w = 0.1500$			$w = 0.3000$		
$T = 322.5 \text{ K}$					
0.53	0.769	0.04	0.51	0.652	0.03
1.04	0.931	0.05	1.03	0.782	0.04
5.15	1.085	0.05	5.16	0.906	0.05
$T = 372.9 \text{ K}$					
0.55	0.595	0.03	0.54	0.500	0.03
1.05	0.621	0.03	1.03	0.561	0.03
3.08	0.849	0.04	3.07	0.708	0.04
5.19	0.984	0.05	5.13	0.805	0.04

for the regression, as it seems the enthalpy would remain constant in that domain (see discussion above). The enthalpy of solution estimated from this model<sup>43</sup> is supposed to be independent in the limits of the selected literature domain: temperatures from 313 K to 423 K, amine compositions between  $w = 0.015$  and  $w = 0.030$  wt %, and pressures between  $2 \cdot 10^{-6}$  MPa to 0.56 MPa. Within these approximations we calculated an enthalpy of solution,  $\Delta_{\text{sol}}H = -88 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$  of  $\text{CO}_2$ , in close agreement with our experimental average enthalpies  $\Delta_{\text{sol}}H^{\text{av}}$  regarding the experimental uncertainty.

**3.2. Solubility Data.** The calorimetric data were used for an indirect determination of the solubility limits of  $\text{CO}_2$  in the aqueous amine solutions. Numerical values were graphically determined from Figure 5; they are reported in Table 10 for the different conditions of temperature, pressure, and composition investigated in this study. Up to the saturation of the MEA solution the enthalpy expressed per mole of amine increases with loading until it reaches a plateau. The plateau indicates that no more carbon dioxide can be dissolved into the solution; the solution is saturated (two-phase region). The solubility limit corresponds thus to the point where the plateau is reached.

The experimental uncertainty depends on the identification precision of the first point of the plateau, and on the basis for the



**Figure 7.** Solubility of  $\text{CO}_2$  in MEA solutions vs total pressure. (a)  $w_{\text{MEA}} = 0.15$ ,  $\square$ , this work,  $T = 322.5 \text{ K}$ ;  $\circ$ , this work,  $T = 372.9 \text{ K}$ ;  $\diamond$ , Shen and Li,<sup>17</sup>  $T = 313 \text{ K}$ . (b)  $w_{\text{MEA}} = 0.30$ ,  $\blacksquare$ , this work,  $T = 322.5 \text{ K}$ ;  $\bullet$ , this work,  $T = 372.9 \text{ K}$ ;  $\blacklozenge$ , Shen and Li,<sup>17</sup>  $T = 313 \text{ K}$ ;  $\blacktriangle$ , Shen and Li,<sup>17</sup>  $T = 373 \text{ K}$ .

reproducibility of the measurements and possibility of systematic errors affecting the enthalpy of solution or the flow rates reliability of the pumps, it is expected that this method allows a determination of the solubility limit within 5 % and 9 %.

Limits of solubility of  $\text{CO}_2$  in the aqueous solutions of MEA were plotted versus the equilibrium total pressure  $p$  on a pressure–log scale in Figure 7 as well as literature values from Shen and Li.<sup>17</sup> A good agreement characterized by a deviation smaller than 5 % with their data on the solubility was observed.

The general tendency is a decrease of the  $\text{CO}_2$  solubility (expressed in mol of  $\text{CO}_2$  per mol of MEA) in aqueous MEA solutions with the composition of the absorbent (Table 10); this trend agrees with the other studies found in the literature. Indeed when increasing the amine concentration, the number of molecules of water necessary to solvate ions in solution also increases. Consequently, the number of molecules of water available to solvate  $\text{CO}_2$  decreases. One can also notice that, in the same conditions of composition and pressure, an augmentation of the temperature leads to a decrease of the solubility as the basicity of the amine also decreases.

As a final remark, the good consistency observed between solubility limits from this work and the literature, measured using methods specifically designed for solubility work, indicated that the mixture of  $\text{CO}_2$ –absorbent solution occurred properly during the calorimetric experiments. However, it was pointed out that our experimental technique was limited to reasonable differences of volume flow rates between gas and solution to prevent any mixing issue.

## 4. CONCLUSION

In this paper we provided new experimental enthalpy of solution data for the system  $\{\text{CO}_2 + \text{MEA} + \text{H}_2\text{O}\}$ . The solubility data derived from our enthalpy data were found to be consistent with the direct phase equilibria measurements from the literature within the estimated experimental uncertainty.

The enthalpy of solution,  $\Delta_{\text{sol}}H$  ( $/\text{kJ} \cdot \text{mol}^{-1}$  of  $\text{CO}_2$ ) was found to be constant at low  $\text{CO}_2$  loading within experimental uncertainty. In this domain an average enthalpy of solution,  $\Delta_{\text{sol}}H^{\text{av}}$ , was estimated for conditions of pressure and amine composition investigated. These values were used to discuss pressure, temperature, and absorbent composition effects on the enthalpy of solution. The enthalpies of solution of carbon dioxide

in aqueous solutions of MEA were observed to be independent of pressure within experimental uncertainty. However, the enthalpy obtained at the highest pressures and low loadings, above 2 MPa, seemed to be experimentally underestimated. This could be due to CO<sub>2</sub>–absorbent mixing difficulties. No significant temperature or composition effect was observed.

A simplified thermodynamic model<sup>43</sup> that does not take into account pressure, temperature, and absorbent composition effects was used to estimate the enthalpy of solution. Within these approximations the calculated enthalpy of solution was found to be quite close to our experimental average enthalpies,  $\Delta_{\text{sol}}H^{\text{av}}$ . However, this simplified thermodynamic model<sup>43</sup> was not able to describe the enthalpy of solution for loadings above  $\alpha = 0.5$  mol CO<sub>2</sub>/mol amine, where the dissolution process is not controlled anymore by the carbamate formation but by the carbon dioxide, which reacts with the amine to form a carbonate. In that case it would be helpful to use a rigorous thermodynamic model<sup>8</sup> to describe the change of energetic behavior observed around  $\alpha = 0.5$  where it seems to have a change of the governance for the chemical mechanisms involved in the CO<sub>2</sub> dissolution. For this purpose, the experimental enthalpies provided in this work could be used as consistent experimental data to develop such theoretical thermodynamic models and design new industrial process for gas treating operations.

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## NOMENCLATURE

$A, B, C, D$  : fitting parameters for eq 10

$K_{\text{CO}_2}$  : equilibrium constant defined in eq 8

$p$  : total pressure

$p_{\text{CO}_2}$  : partial pressure of CO<sub>2</sub>

$R$  : ideal gas constant

$s$  : limit of solubility

$T$  : temperature

$x_{\text{MEA}}^{\text{g}}$  : gas free amine mole fraction with  $x_{\text{MEA}}^{\text{g}} = \frac{\text{mol}_{\text{MEA}}}{\text{mol}_{\text{MEA}} + \text{mol}_{\text{H}_2\text{O}}}$

$x_{\text{CO}_2}$  : molar fraction of CO<sub>2</sub>

$\alpha$  : loading

$\delta_i$  : uncertainty on  $i$

$\delta_{\text{max}}$  : maximum uncertainty

$\Delta_{\text{sol}}H$  : enthalpy of solution

$\Delta_{\text{sol}}H^{\text{av}}$  : enthalpy of solution averaged for low loading

$\rho$  : density

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