

# Solubility of Carbon Dioxide in Aqueous Solutions of *N*-Methyldiethanolamine and Piperazine in the High Gas Loading Region

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A synthetic technique was used to measure the solubility of carbon dioxide in three aqueous solutions of 2,2'-methyliminodiethanol (*N*-methyldiethanolamine, MDEA) and piperazine (PZ) at around (313, 333, 353, and 393) K and pressures between about (0.2 and 10) MPa. The molalities of (MDEA + PZ) in the aqueous solutions were (2.2 + 1.97), (4.22 + 2.01), and (7.83 + 2.07), respectively. The loading of the amines by carbon dioxide (i.e., the molar ratio of (MDEA + PZ) and CO<sub>2</sub>) varied between 0.2 and 2.0. The new experimental results are to supplement previously published experimental data of our research group for a single solution of both amines {molalities of (MDEA + PZ) in the aqueous solutions: (2.0 + 2.0)}. The new experimental results are compared to predictions from a model that combines previously published models for (CO<sub>2</sub> + MDEA + H<sub>2</sub>O) and (CO<sub>2</sub> + PZ + H<sub>2</sub>O).

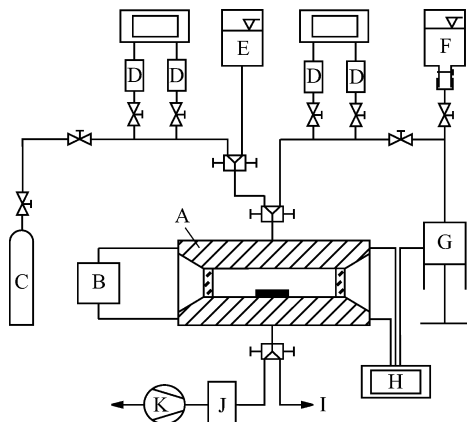
## Introduction

Sour gases like carbon dioxide and hydrogen sulfide are commonly removed from natural or synthesis gas by “chemical” absorption in aqueous solutions of organic bases like, for example, single amines, amine mixtures, or mixtures of an amine and a salt of an amino acid. Among the most widely used chemical absorbents are aqueous solutions of alkanolamines, e.g., MDEA (= 2,2'-methyliminodiethanol = *N*-methyldiethanolamine), and aqueous solutions of amine mixtures, e.g., (MDEA + PZ). The competitive chemical absorption of carbon dioxide and hydrogen sulfide is kinetically controlled. However, deviation from equilibrium provides the driving force in a kinetically controlled process. Hence, the reliable design and optimization of the separation equipment require the knowledge of the equilibrium properties, in particular the chemical reaction equilibrium and the vapor–liquid equilibrium (VLE), as well as information on the energy to vaporize/condense the mixtures. The gas absorption takes place at low temperatures (typically around room temperature) and (often) elevated pressures (up to about 4 MPa or more), whereas the gas desorption (i.e., the solvent regeneration in the stripper) occurs at elevated temperatures (around 400 K) and low pressures (in particular at low partial pressures of the gas). Therefore, the aforementioned equilibrium properties need to be explored within relatively wide ranges of temperature, pressure, as well as amine and gas concentrations.

During the last 15 years, our research group has been investigating in experimental and modeling work the phase equilibrium when carbon dioxide and/or hydrogen sulfide are captured in aqueous solutions of MDEA<sup>1–3</sup> and in aqueous solutions of PZ.<sup>4–6</sup> Previous extensions of this research dealt with the solubility of those single sour gases in aqueous solutions of sulfuric acid and sodium sulfate<sup>7–9</sup> and in aqueous solutions of MDEA and PZ.<sup>4,5</sup> Such phase equilibria have also attained attention by other research groups. The experimental results by

Xu et al. (1998),<sup>10</sup> Liu et al. (1999),<sup>11</sup> and Bishnoi and Rochelle (2002)<sup>12</sup> were already compared to model predictions in 2003 by Pérez-Salado Kamps et al.<sup>5</sup> More recently, experimental data by Si Ali and Aroua (2004)<sup>13</sup> describe the influence of small amounts of PZ (molarity  $\bar{c}_{\text{PZ}} \leq 0.1$  molar) on the solubility of CO<sub>2</sub> in aqueous solutions of MDEA (molarity  $\bar{c}_{\text{MDEA}} \sim 2$  molar) at (40, 60, and 80) °C and partial pressures of CO<sub>2</sub> up to nearly 100 kPa. Jenab et al. (2005)<sup>14</sup> {cf. also Matin et al. (2007)<sup>15</sup>} reported experimental results for the solubility of carbon dioxide in (1.35 to 4.77) molar aqueous solutions of MDEA that contained also PZ (molarity 0.17 to 1.55) at (40, 50, 55, and 70) °C for partial pressures of CO<sub>2</sub> between about (0.03 and 4) MPa. Derks (2006)<sup>16</sup> reported experimental data for the partial pressure of CO<sub>2</sub> (in the range between about (0.25 and 110) kPa) above three aqueous solutions of (MDEA + PZ) at temperatures between (298 and 323) K. The molalities of (MDEA + PZ) of the three solvent mixtures were (4 + 0.6), (2.8 + 0.7), and (0.5 + 1.5), respectively. Recently, Jang et al. (2008)<sup>17</sup> published experimental data for the absorption of carbon dioxide in aqueous solutions of MDEA and PZ at (40, 60, and 80) °C and pressures up to nearly 5 MPa. Experimental results that are also related to the topic of the present work were presented by Böttinger et al. (2008).<sup>18</sup> These authors studied the speciation in aqueous solutions of MDEA (about 30 mass percent) and PZ (about 10 mass percent) and molar ratios of carbon dioxide to amines between about 0.06 and 0.78 by NMR spectroscopy at (20, 40, and 60) °C. The present contribution primarily aims to extend the experimental database created in previous work by our research group for the solubility of CO<sub>2</sub> in aqueous solutions of such amine mixtures at elevated pressures and to evaluate a formerly published thermodynamic model<sup>5</sup> by comparing predictions with the new experimental data. The extension of the experimental data covers (a) the temperature range for aqueous solutions that contain only small amounts of both amines (molalities of MDEA and PZ:  $\bar{m}_{\text{MDEA}} = \bar{m}_{\text{PZ}} \sim 2$  molal)<sup>5</sup> from 353 K to 313 K and 393 K, respectively, and (b) the amine concentrations that were

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**Figure 1.** Apparatus for measuring the solubility of a single gas in a solvent at elevated pressures: A, cylindrical high-pressure equilibrium view cell with two sapphire windows and magnetic stirrer; B, thermostat; C, container for the gas; D, pressure transducers; E, tank for rinsing water; F, tank for solvent mixture; G, high-pressure spindle press; H, AC-bridge with three platinum resistance thermometers; I, solution outlet; J, cooling trap; K, vacuum pump.

increased to ( $\bar{m}_{\text{MDEA}} + \bar{m}_{\text{PZ}} < 10$  molal) at temperatures from about 313 K to about 393 K.

## Experimental Section and Results

**Apparatus and Method.** The synthetic method was applied for the gas solubility experiments. The apparatus was the very same, and the experimental procedures remained similar to those during previous investigations.<sup>19–22</sup> Therefore, we restrict to the main features and amend the specific differences that result from the particular systems investigated. The procedure consists of measuring the pressure required to dissolve a precisely known amount of gas in an also precisely known amount of solvent that fills a high-pressure view cell. Figure 1 shows a scheme of the apparatus. Its central component is a cylindrical, high-pressure view cell (cell volume about 30 cm<sup>3</sup>) with two sapphire windows on each end. The view cell is thermostatted by a liquid that flows through an annular jacket. That jacket is much longer than the view cell. The jacket is well insulated so that temperature differences within the thermostating liquid in the annular jacket are smaller than the uncertainty of the temperature measurement (cf. below). The evacuated cell is charged with the solvent and the gas so that a homogeneous liquid phase exists at a pressure that is somewhat above the solubility pressure. Then, very small amounts (volume expansion of about 0.012 cm<sup>3</sup>) of the liquid mixture are withdrawn step by step until the first (very small) stable gas bubbles appear. The pressure at which the degassing starts is the solubility pressure of the mixture. That pressure is calculated as the arithmetic average of the pressures before and after that last step. The mass of carbon dioxide in the view cell was between (1.5 and 7) g. It was determined gravimetrically by weighing a condenser (from which the cell is charged) before and after the charging process on a high precision balance. Gravimetric uncertainties amount to  $\pm 0.01$  g. The solvent mixtures were prepared gravimetrically. The experimental uncertainty of the stoichiometric molalities (defined as the number of moles per kilogram of water) is less than  $\pm 0.002$  molal for MDEA as well as for PZ. The amount of mass of the solvent filled into the cell was calculated from the volume displacement in a calibrated spindle press (from which the solvent is charged into the cell) and the solvent density. The density of the solvent was determined in separate measurements with a vibrating tube densimeter (model

**Table 1.** Experimental Results for the Specific Density of Aqueous Solutions of (MDEA + PZ)

$\bar{m}_{\text{MDEA}}$ mol·kg <sup>-1</sup>	$\bar{m}_{\text{PZ}}$ mol·kg <sup>-1</sup>	$T$ K	$\rho$ g·cm <sup>-3</sup>		
2.227	1.966	289.0	1.026		
		291.0	1.025		
		293.0	1.024		
		295.1	1.023		
		297.1	1.023		
		299.1	1.022		
		301.1	1.021		
		303.1	1.020		
		4.216	2.010	289.0	1.037
				291.0	1.036
				293.0	1.035
295.1	1.034				
297.1	1.033				
299.1	1.032				
301.1	1.031				
303.1	1.030				
7.831	2.072			289.0	1.049
				291.0	1.047
				293.0	1.046
		295.1	1.045		
		297.1	1.044		
		299.1	1.042		
		301.1	1.041		
		303.1	1.040		

DMA 60/DMA 602 HAT, Anton Paar GmbH, Graz, Austria) with an uncertainty of less than  $\pm 0.001$  g·cm<sup>-3</sup>. The results of the density measurements are given in Table 1.

The relative uncertainty of the mass of solvent (as well as of the mass of water) in the view cell is about 0.14 %. The relative uncertainty of the stoichiometric molality of carbon dioxide in the solvent decreases from  $\pm 1$  % at the lowest molality ( $\bar{m}_{\text{CO}_2} \sim 2$  molal) to  $\pm 0.3$  % at the highest molality ( $\bar{m}_{\text{CO}_2} \sim 11$  molal). Two calibrated platinum resistance thermometers in the thermostatted jacket of the view cell were used to determine the temperature with an uncertainty below  $\pm 0.1$  K. The solubility pressure was measured with two precise pressure transducers (WIKA GmbH, Klingenberg, Germany; full scale (2.5 and 10) MPa, respectively) in connection with a mercury barometer (Lambrecht, Göttingen, Germany). All pressure transducers were calibrated against a high-precision pressure balance (Desgranges & Huot, Aubervilliers, France) before and after each measurement series. The maximum uncertainty in the solubility pressure measurement results from the intrinsic uncertainty of the pressure transducers (i.e., 0.1 % of the transducer's full scale), an additional contribution of about  $\pm 0.01$  MPa from a small temperature drift inside the isolated (high-pressure) tubes filled with the solvent, that connect the view cell with the pressure transducers and the difference of the pressure transducer's readings before and after the last expansion step.

**Materials and Sample Pretreatment.** Carbon dioxide (4.5, volume fraction  $\geq 0.99995$ ) was purchased from Messer Griesheim GmbH, Krefeld, Germany. Water was bidistilled and degassed, and MDEA and PZ were bought from Honeywell Riedel-de Haën GmbH, Seelze, Germany and Sigma-Aldrich Chemie GmbH, Munich, Germany, respectively. The guaranteed upper limit for the content of impurities was 1.5 mass % for MDEA and 1.0 mass % for PZ. Both amines were only degassed but otherwise used without further purification.

**Experimental Results.** The solubility of carbon dioxide was measured in three aqueous solutions of MDEA and PZ at temperatures between about (313 and 393) K. The stoichiometric molality of PZ was kept at around 2 molal, and that of MDEA was about (2, 4, and 8) moles per kilogram of water {mass

**Table 2. Solubility of CO<sub>2</sub> in Aqueous Solutions of MDEA and PZ** { $\bar{m}_{\text{MDEA}}/(\text{mol}\cdot\text{kg}^{-1}) = (2.227 \pm 0.001)$ ;  $\bar{m}_{\text{PZ}}/(\text{mol}\cdot\text{kg}^{-1}) = (1.966 \pm 0.001)$ }

<i>T</i>	$\bar{m}_{\text{CO}_2}$	<i>p</i>
K	mol·kg <sup>-1</sup>	MPa
313.0 ± 0.1	4.237 ± 0.019	0.953 ± 0.014
	4.623 ± 0.019	2.109 ± 0.014
	4.749 ± 0.020	2.651 ± 0.014
	4.847 ± 0.020	3.603* ± 0.014
	8.229 ± 0.030	8.060* ± 0.020
393.1 ± 0.1	1.902 ± 0.017	0.518 ± 0.011
	2.708 ± 0.017	1.512 ± 0.014
	2.985 ± 0.018	1.988 ± 0.014
	3.517 ± 0.018	3.660 ± 0.014
	3.579 ± 0.018	3.965 ± 0.014
	3.757 ± 0.019	4.797 ± 0.020
	3.939 ± 0.019	6.002 ± 0.020
	4.101 ± 0.019	7.229 ± 0.020
	4.193 ± 0.019	8.186 ± 0.020
	4.306 ± 0.019	9.353 ± 0.020

**Table 3. Solubility of CO<sub>2</sub> in Aqueous Solutions of MDEA and PZ** { $\bar{m}_{\text{MDEA}}/(\text{mol}\cdot\text{kg}^{-1}) = (4.216 \pm 0.002)$ ;  $\bar{m}_{\text{PZ}}/(\text{mol}\cdot\text{kg}^{-1}) = (2.010 \pm 0.001)$ }

<i>T</i>	$\bar{m}_{\text{CO}_2}$	<i>p</i>	
K	mol·kg <sup>-1</sup>	MPa	
313.3 ± 0.1	5.393 ± 0.023	0.218 ± 0.011	
	5.697 ± 0.024	0.344 ± 0.011	
	6.458 ± 0.025	3.814* ± 0.014	
	6.821 ± 0.026	8.525* ± 0.020	
	5.278 ± 0.023	0.561 ± 0.011	
333.2 ± 0.1	5.708 ± 0.024	1.001 ± 0.014	
	6.034 ± 0.024	1.600 ± 0.014	
	6.350 ± 0.025	2.846 ± 0.014	
	6.607 ± 0.025	4.347 ± 0.020	
	6.775 ± 0.026	5.392 ± 0.020	
	6.932 ± 0.026	6.692 ± 0.020	
	7.069 ± 0.026	8.172 ± 0.020	
	7.230 ± 0.027	10.26 ± 0.02	
	353.3 ± 0.1	4.560 ± 0.022	0.722 ± 0.014
		5.107 ± 0.023	1.225 ± 0.014
5.493 ± 0.024		1.918 ± 0.014	
5.765 ± 0.024		2.677 ± 0.014	
6.051 ± 0.025		3.646 ± 0.014	
6.381 ± 0.025		5.686 ± 0.020	
6.610 ± 0.026		7.414 ± 0.020	
6.659 ± 0.026		7.781 ± 0.020	
6.811 ± 0.026		9.682 ± 0.020	
7.010 ± 0.026		11.88 ± 0.02	
393.2 ± 0.1	2.575 ± 0.020	0.783 ± 0.011	
	3.460 ± 0.021	1.604 ± 0.014	
	3.793 ± 0.021	2.107 ± 0.014	
	4.259 ± 0.022	3.095 ± 0.014	
	4.591 ± 0.023	4.005 ± 0.014	
	4.810 ± 0.023	4.811 ± 0.020	
	5.237 ± 0.024	6.640 ± 0.020	
	5.541 ± 0.024	8.519 ± 0.020	
	5.692 ± 0.024	9.748 ± 0.020	

fraction of MDEA  $\approx (0.185, 0.30, \text{ and } 0.44)$ . The mass fraction of PZ in the solvent was about 0.12, 0.10, and 0.085, respectively. The stoichiometric molar ratio of carbon dioxide to (MDEA + PZ) ranged from about 0.45 to 2.0 (for the solvent with  $\bar{m}_{\text{MDEA}} \approx 2$  molal) and from about 0.3 to 1.2 for both other solvent mixtures. The solubility pressure was between about (0.2 and 12) MPa. The experimental results are given together with their uncertainties in Tables 2 to 4. At 313 K, the formation of a solid phase was observed when the molar ratio of carbon dioxide to amine surmounted about 0.5. Schwarzenbach<sup>23</sup> and Freeman et al.<sup>24</sup> described the precipitation of piperazine hexahydrate from aqueous solutions at low temperatures. Bishnoi and Rochelle<sup>12</sup> also observed such precipitations. However, as in the current experiments, the precipitation was

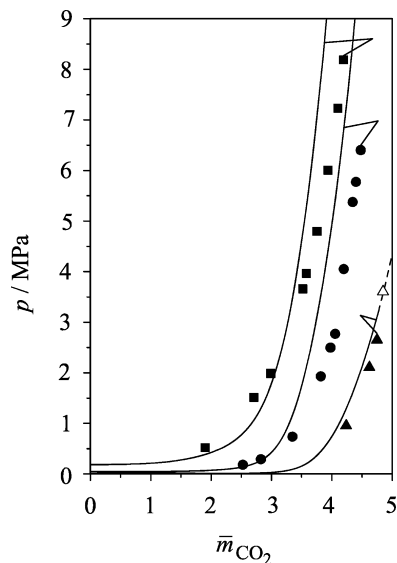
**Table 4. Solubility of CO<sub>2</sub> in Aqueous Solutions of MDEA and PZ** { $\bar{m}_{\text{MDEA}}/(\text{mol}\cdot\text{kg}^{-1}) = (7.831 \pm 0.002)$ ;  $\bar{m}_{\text{PZ}}/(\text{mol}\cdot\text{kg}^{-1}) = (2.072 \pm 0.002)$ }

<i>T</i>	$\bar{m}_{\text{CO}_2}$	<i>p</i>	
K	mol·kg <sup>-1</sup>	MPa	
333.1 ± 0.1	6.676 ± 0.028	0.294 ± 0.011	
	7.635 ± 0.030	0.634 ± 0.011	
	8.268 ± 0.031	1.032 ± 0.014	
	8.958 ± 0.032	1.851 ± 0.014	
	9.76 ± 0.034	3.651 ± 0.014	
	9.79 ± 0.034	3.834 ± 0.014	
	10.14 ± 0.035	5.013 ± 0.020	
	10.31 ± 0.035	6.024 ± 0.020	
	10.53 ± 0.035	7.500 ± 0.020	
	10.73 ± 0.036	8.997 ± 0.020	
	353.1 ± 0.1	5.390 ± 0.027	0.457 ± 0.011
		6.145 ± 0.028	0.711 ± 0.014
		7.090 ± 0.029	1.254 ± 0.014
		7.731 ± 0.030	1.825 ± 0.014
		8.470 ± 0.032	2.975 ± 0.014
9.035 ± 0.033		4.466 ± 0.014	
9.375 ± 0.033		5.657 ± 0.020	
9.621 ± 0.034		6.826 ± 0.020	
9.916 ± 0.034		8.832 ± 0.020	
2.974 ± 0.024		0.889 ± 0.014	
393.1 ± 0.1	3.800 ± 0.025	1.393 ± 0.014	
	4.864 ± 0.026	2.485 ± 0.014	
	5.356 ± 0.027	3.200 ± 0.014	
	5.650 ± 0.027	3.726 ± 0.014	
	6.213 ± 0.028	4.866 ± 0.020	
	6.730 ± 0.029	6.240 ± 0.020	
	7.008 ± 0.029	7.179 ± 0.020	
	7.407 ± 0.030	8.729 ± 0.020	

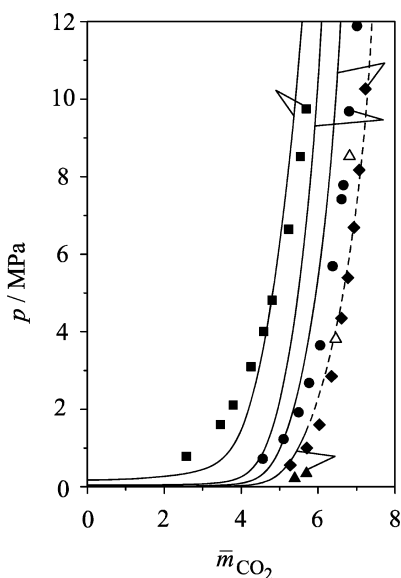
induced by large amounts of CO<sub>2</sub>, and it is assumed that a complex of piperazine and carbon dioxide (that might also contain some water) precipitated. Freeman et al.<sup>24</sup> shortly mentioned the precipitation of a piperazine carbamate complex at high gas loadings. The corresponding data points are marked with an asterisk in Tables 2 and 3.

Figures 2, 3, and 4 show the new experimental results for the solubility pressure for the investigated three mixed solvent mixtures without those results where a precipitation was observed. As common for chemical solvents for carbon dioxide, the partial pressure of CO<sub>2</sub> (and consequently also the solubility pressure) remains very small as long as the molar ratio of carbon dioxide and the chemical solvent is low. This holds particularly at low temperatures. That phenomenon is caused by the conversion of volatile CO<sub>2</sub> to nonvolatile ionic species such as bicarbonate and piperazine carbamates (cf. Pérez-Salado Kamps et al.<sup>5</sup>), and the amount of true (molecular) CO<sub>2</sub> in the liquid remains small. However, when that molar ratio is above one (i.e., when the stoichiometric molality of CO<sub>2</sub> is larger than the sum of the stoichiometric molalities of MDEA and PZ), there is a strong increase in the solubility pressure with increasing molality of carbon dioxide. In that region, the physical solubility dominates the solubility pressure as additional carbon dioxide is dissolved predominantly in molecular form in an aqueous electrolyte solution.

**Comparison with Predictions.** In previous publications thermodynamics models for the solubility of CO<sub>2</sub> in aqueous solutions of the single amines MDEA (Ermatchkov et al.<sup>3</sup>) and PZ (Ermatchkov et al.<sup>6</sup>) were described and parametrized. The models apply the extended Henry's law on the molality scale to describe the partial pressure of CO<sub>2</sub> above the aqueous solution. But as only some of the CO<sub>2</sub> is dissolved in neutral (molecular) form, it also takes into account the chemical reaction equilibrium in the liquid phase. The important deviations from ideality in the aqueous, electrolyte solutions (expressed by the

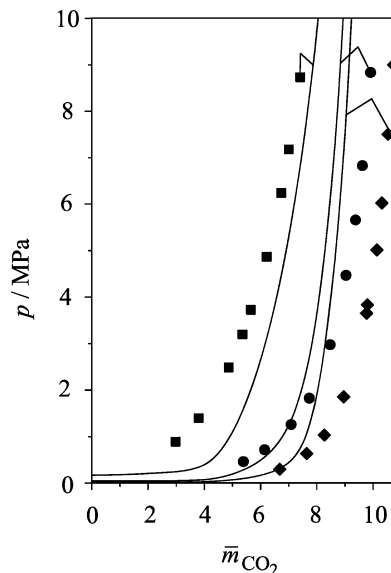


**Figure 2.** Solubility of CO<sub>2</sub> in aqueous solutions of (MDEA + PZ). New experimental results for ( $\bar{m}_{\text{MDEA}} = 2.227 \text{ mol}\cdot\text{kg}^{-1} + \bar{m}_{\text{PZ}} = 1.966 \text{ mol}\cdot\text{kg}^{-1}$ ) at  $\blacktriangle, \triangle$ , 313 K (without and with precipitating solids, respectively); and  $\blacksquare$ , 393 K compared to experimental results from Pérez-Salado Kamps et al.<sup>5</sup> (after applying a small temperature correction, cf. Appendix) for ( $\bar{m}_{\text{MDEA}} = 1.975 \text{ mol}\cdot\text{kg}^{-1} + \bar{m}_{\text{PZ}} = 1.966 \text{ mol}\cdot\text{kg}^{-1}$ ) at  $\bullet$ , 354 K and to prediction results (—).



**Figure 3.** Solubility of CO<sub>2</sub> in aqueous solutions of (MDEA + PZ) ( $\bar{m}_{\text{MDEA}} = 4.216 \text{ mol}\cdot\text{kg}^{-1} + \bar{m}_{\text{PZ}} = 2.010 \text{ mol}\cdot\text{kg}^{-1}$ ). New experimental results {(without and with precipitating solids, respectively)  $\blacktriangle, \triangle$ , 313 K;  $\blacklozenge$ , 333 K;  $\bullet$ , 353 K; and  $\blacksquare$ , 393 K} compared to prediction results (—).

activity coefficients of the true solutes) are described by a modification of Pitzer's equation for the Gibbs excess energy of aqueous electrolyte solutions. That equation requires binary and ternary parameters for interactions between solute species. The parametrization of the model was based on experimental gas solubility data at temperatures from (313 to 393) K that cover a wide range of amine concentrations  $\{2 < (\text{molality of MDEA}) < 8; 1 < (\text{molality of PZ}) < 4\}$  and molar ratios of CO<sub>2</sub> to amine from below 0.01 to above 1.2 but were restricted to data for aqueous solutions of the single amines. These models (with model parameters corresponding to "sets II" by Ermachkov et al.<sup>3,6</sup>) were combined for estimating the solubility pressure when CO<sub>2</sub> is dissolved in an aqueous solution of (MDEA + PZ). The prediction results are also shown in Figures



**Figure 4.** Solubility of CO<sub>2</sub> in aqueous solutions of (MDEA + PZ) ( $\bar{m}_{\text{MDEA}} = 7.831 \text{ mol}\cdot\text{kg}^{-1} + \bar{m}_{\text{PZ}} = 2.072 \text{ mol}\cdot\text{kg}^{-1}$ ). New experimental results  $\{\blacklozenge, 333 \text{ K}; \bullet, 353 \text{ K}; \text{and } \blacksquare, 393 \text{ K}\}$  compared to prediction results (—).

2 to 4. The predictions for the solubility pressure deviate considerably from the experimental results. At low loading of the amines, the predictions lie below the experimentally determined solubility pressures, whereas at high amine loadings, the predictions for the solubility pressure are too high. As the parametrization was based only on experimental data for the solubility of CO<sub>2</sub> in the (single amine + water) systems, the combined model lacks any parameters for interactions between such species that are only present in aqueous solutions of (MDEA + CO<sub>2</sub>) or in aqueous solutions of (PZ + CO<sub>2</sub>). For example, there are no parameters for binary interactions between the protonated species of MDEA (MDEAH<sup>+</sup>) and piperazine carbamate anions (PIPHCOO<sup>-</sup>) or for ternary interactions between CO<sub>2</sub>, MDEAH<sup>+</sup>, and PIPHCOO<sup>-</sup>. In all experiments, carbon dioxide was predominantly absorbed in ionic form, but the solubility pressure is dominated by the amount of molecular (neutral) carbon dioxide in the aqueous solution. A crude estimate (just applying Henry's law for the solubility of CO<sub>2</sub> in water<sup>25</sup>) reveals that in an aqueous (6 molal CO<sub>2</sub> + 4.22 molal MDEA + 2.0 molal PZ) solution at 353 K less than 8 % of all CO<sub>2</sub> is dissolved in molecular form. In other words, the share of neutrally dissolved CO<sub>2</sub> has to be predicted with an accuracy of better than 0.8 % (related to the total amount of dissolved CO<sub>2</sub>) when the solubility pressure is to be predicted with an uncertainty of 10 %. Therefore, we cannot expect to find a good agreement between prediction results and experimental data for the solubility pressure. A good agreement can only be achieved when some model parameters are fitted to experimental results for the solubility of CO<sub>2</sub> in aqueous solutions of the mixed amine system. However, the determination of a new set of model parameters should be based both on high pressure as well as on low pressure gas solubility data. Experimental work (by headspace gas chromatography) in the low pressure region is now in progress at our institution. A correlation will be performed (i.e., a new set of model parameters will be determined) when the results of these investigations become available.

## Conclusions

Modeling the solubility of CO<sub>2</sub> in aqueous solutions of MDEA that are activated by piperazine requires a reliable and

extensive experimental database on the solubility of CO<sub>2</sub> in aqueous solutions of the single amines as well as on the solubility of CO<sub>2</sub> in aqueous solutions of (MDEA + PZ). The experimental data should cover the high gas loading region (molar ratio of CO<sub>2</sub> to amines around 0.5 to 1.2) as well as the lower gas loading region that is of great interest for the regeneration of the amine-containing solvent mixtures. Both loading ranges are hard to investigate with the same experimental technique. The “synthetic gas solubility method” is an appropriate technique for investigations in the high-gas loading range, whereas the “headspace gas chromatographic technique” has been successfully used for investigations in the low gas loading range. The present work reports experimental results for the solubility of CO<sub>2</sub> in aqueous solutions of (MDEA + PZ) in the high gas loading range. Currently, the solubility in the low gas-loading range is being investigated by headspace gas chromatography. When the results of both investigations will be completed, a new parametrization of a thermodynamic framework will be done.

## Appendix

### Corrected Experimental Results from Pérez-Salado Kamps et al.<sup>5</sup> for the System (CO<sub>2</sub> + MDEA + piperazine + H<sub>2</sub>O).

As recently mentioned,<sup>6</sup> the platinum resistance thermometers used in the work by Pérez-Salado Kamps et al.<sup>5</sup> were recalibrated straight after those experimental results had been published, showing that a small correction had to be applied to the temperature values. The correct temperature is 354.35 K (instead of 353.15 K). The corrected experimental results for the solubility of carbon dioxide in (MDEA + piperazine + H<sub>2</sub>O) from Pérez-Salado Kamps et al.<sup>5</sup> are given in Table A1.

**Table A1. Solubility of Carbon Dioxide in Aqueous Solutions of MDEA and Piperazine: Experimental Results from Pérez-Salado Kamps et al.<sup>5</sup> (after Correcting the Temperature)**

$T$ K	$\bar{m}_{\text{MDEA}}$ mol·kg <sup>-1</sup>	$\bar{m}_{\text{PZ}}$ mol·kg <sup>-1</sup>	$\bar{m}_{\text{CO}_2}$ mol·kg <sup>-1</sup>	$P$ MPa
354.35	1.975	1.966	2.526	0.1807
			2.826	0.2896
			3.347	0.7345
			3.817	1.929
			3.977	2.496
			4.054	2.768
			4.198	4.050
			4.347	5.375
			4.399	5.773
			4.478	6.400

## Literature Cited

- (1) Kuranov, G.; Rumpf, B.; Smirnova, N. A.; Maurer, G. Solubility of single gases carbon dioxide and hydrogen sulfide in aqueous solutions of N-methyldiethanolamine in the temperature range 313–413 K at pressures up to 5 MPa. *Ind. Eng. Chem. Res.* **1996**, *35*, 1959–1966.
- (2) Pérez-Salado Kamps, A.; Balaban, A.; Jödecke, M.; Kuranov, G.; Smirnova, N. A.; Maurer, G. Solubility of single gases carbon dioxide and hydrogen sulfide in aqueous solutions of N-methyldiethanolamine at temperatures from 313 to 393 K and pressures up to 7.6 MPa: New experimental data and model extension. *Ind. Eng. Chem. Res.* **2001**, *40*, 696–706.
- (3) Ermatchkov, V.; Pérez-Salado Kamps, A.; Maurer, G. Solubility of carbon dioxide in aqueous solutions of N-methyldiethanolamine in the low gas loading region. *Ind. Eng. Chem. Res.* **2006**, *45*, 6081–6091.
- (4) Xia, J.; Pérez-Salado Kamps, A.; Maurer, G. Solubility of H<sub>2</sub>S in (H<sub>2</sub>O + piperazine) and in (H<sub>2</sub>O + MDEA + piperazine). *Fluid Phase Equilib.* **2003**, *207*, 23–34.
- (5) Pérez-Salado Kamps, A.; Xia, J.; Maurer, G. Solubility of CO<sub>2</sub> in (H<sub>2</sub>O + piperazine) and in (H<sub>2</sub>O + MDEA + piperazine). *AIChE J.* **2003**, *49*, 2662–2670.
- (6) Ermatchkov, V.; Pérez-Salado Kamps, A.; Speyer, D.; Maurer, G. Solubility of carbon dioxide in aqueous solutions of piperazine in the low gas loading region. *J. Chem. Eng. Data* **2006**, *51*, 1788–1796.
- (7) Pérez-Salado Kamps, A.; Rumpf, B.; Maurer, G.; Anoufrikov, Y.; Kuranov, G.; Smirnova, N. A. Solubility of CO<sub>2</sub> in H<sub>2</sub>O + N-methyldiethanolamine + (H<sub>2</sub>SO<sub>4</sub> or Na<sub>2</sub>SO<sub>4</sub>). *AIChE J.* **2002**, *48*, 168–177.
- (8) Anoufrikov, Y.; Pérez-Salado Kamps, A.; Rumpf, B.; Smirnova, N. A.; Maurer, G. Solubility of H<sub>2</sub>S in H<sub>2</sub>O + N-methyldiethanolamine + (H<sub>2</sub>SO<sub>4</sub> or Na<sub>2</sub>SO<sub>4</sub>). *Ind. Eng. Chem. Res.* **2002**, *41*, 2571–2578.
- (9) Kuranov, G.; Rumpf, B.; Maurer, G.; Smirnova, N. A. VLE modelling for aqueous systems containing methyldiethanolamine, carbon dioxide and hydrogen sulfide. *Fluid Phase Equilib.* **1997**, *136*, 147–162.
- (10) Xu, G.-W.; Zhang, C.-F.; Qin, S.-J.; Gao, W.-H.; Liu, H.-B. Gas-liquid equilibrium in a CO<sub>2</sub>-MDEA-H<sub>2</sub>O system and the effect of piperazine on it. *Ind. Eng. Chem. Res.* **1998**, *37*, 1473–1477.
- (11) Liu, H.-B.; Zhang, C.-F.; Xu, G.-W. A study of equilibrium solubility for carbon dioxide in methyldiethanolamine-piperazine-water solution. *Ind. Eng. Chem. Res.* **1999**, *38*, 4032–4036.
- (12) Bishnoi, S.; Rochelle, G. T. Thermodynamics of piperazine/methyldiethanolamine/water/carbon dioxide. *Ind. Eng. Chem. Res.* **2002**, *41*, 604–612.
- (13) Si Ali, B.; Aroua, M. K. Effect of piperazine on CO<sub>2</sub> loading in aqueous solutions of MDEA at low pressure. *Int. J. Thermophys.* **2004**, *25*, 1863–1870.
- (14) Jenab, M. H.; Abdi, M. A.; Najibi, S. H.; Vahidi, M.; Matin, N. S. Solubility of carbon dioxide in aqueous mixtures of N-methyldiethanolamine + piperazine + sulfolane. *J. Chem. Eng. Data* **2005**, *50*, 583–586.
- (15) Matin, N. S.; Goharrokhi, M.; Vahidi, M.; Jenab, M. H.; Abdi, M. A.; Najibi, S. H. Solubility of CO<sub>2</sub> in aqueous solutions of N-methyldiethanolamine + piperazine using extended Debye-Hückel model. *J. Chem. Eng. Jpn.* **2007**, *40* (4), 1–11.
- (16) Derks, P. W. J. Carbon dioxide absorption in piperazine activated N-methyldiethanolamine. PhD Dissertation, University of Twente, The Netherlands, **2006**.
- (17) Jang, W. J.; Yoon, Y. I.; Park, S. D.; Rhee, Y. W.; Baek, I. H. Absorption of CO<sub>2</sub> using mixed aqueous solution of N-methyldiethanolamine with piperazine for pre-combustion CO<sub>2</sub> capture. *J. Korean Ind. Eng. Chem.* **2008**, *19* (6), 645–651.
- (18) Böttinger, W.; Maiwald, M.; Hasse, H. Online NMR spectroscopic study of species distribution in MDEA - H<sub>2</sub>O - CO<sub>2</sub> and MDEA - PIP - H<sub>2</sub>O - CO<sub>2</sub>. *Ind. Eng. Chem. Res.* **2008**, *47*, 7917–7926.
- (19) Rumpf, B. Untersuchungen zur Löslichkeit reagierender Gase in Wasser und salzhaltigen wässrigen Lösungen. Doctoral Dissertation, University of Kaiserslautern, Germany, 1992.
- (20) Rumpf, B.; Maurer, G. Solubilities of hydrogen cyanide and sulfur dioxide in water at temperatures from 293.15 to 413.15 K and pressures up to 2.5 MPa. *Fluid Phase Equilib.* **1992**, *81*, 241–260.
- (21) Pérez-Salado Kamps, A.; Tuma, D.; Xia, J.; Maurer, G. Solubility of CO<sub>2</sub> in the ionic liquid [bmim][PF<sub>6</sub>]. *J. Chem. Eng. Data* **2003**, *48*, 746–749.
- (22) Kumelan, J.; Pérez-Salado Kamps, A.; Tuma, D.; Maurer, G. Solubility of CO<sub>2</sub> in the ionic liquid [hmim][Tf<sub>2</sub>N]. *J. Chem. Thermodyn.* **2006**, *38*, 1396–1401.
- (23) Schwarzenbach, D. Structure of piperazine hexahydrate. *J. Chem. Phys.* **1968**, *48* (9), 4134–4140.
- (24) Freeman, S. A.; Dugas, R.; Van Wagener, D.; Nguyen, T.; Rochelle, G. T. Carbon dioxide capture with concentrated, aqueous piperazine. *Energy Procedia* **2008**, (GHGT-9), in press.
- (25) Rumpf, B.; Maurer, G. An experimental and theoretical investigation on the solubility of carbon dioxide in aqueous solutions of strong electrolytes. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 85–97.

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