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

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The solubility of carbon dioxide in aqueous mixtures of 2,2′-methyliminodiethanol (*N*-methyldiethanolamine, MDEA) and 1,4-diazacyclohexane (piperazine, PZ) was measured at low gas loadings (at stoichiometric molar ratios of carbon dioxide to (MDEA + PZ) between about 0.02 and 0.83) and consequently low partial pressures of carbon dioxide (from about (0.1 to 150) kPa) at three temperatures (313 K, 353 K, and 393 K) by headspace gas chromatography. The molality of MDEA in the aqueous mixture was varied between (2 and 8) mol·(kg of water)$^{-1}$ and the molality of piperazine was varied between (1 and 4) mol·(kg of water)$^{-1}$. The new experimental data supplement recently published high-pressure data for the same systems. Comparisons with prediction results from a formerly published thermodynamic model reveal that the set of model parameters from that previous publication should be revised.

Introduction

Absorption by aqueous solutions of (alkanol)amines is one of the most effective methods for the removal of sour gases, such as carbon dioxide and hydrogen sulfide, from gaseous effluents. For example, such absorption processes are used for the sweetening of natural gases, synthesis gases, and refinery gases. The “chemical” absorption of CO_2 in aqueous solutions of organic bases like amines and mixtures of amines, amino acids, and salts is currently discussed also for the removal of carbon dioxide from flue gas of fossil fueled power plants. In all such solutions, the sour gases are partially converted into ionic species via an acid−base buffer mechanism. Furthermore, CO_2 also reacts directly with primary and secondary amines by forming carbamates. Aqueous solutions of 2,2′-methyliminodiethanol (*N*-methyldiethanolamine, MDEA, [105-59-9]) as well as aqueous solutions of mixtures of MDEA with the modifier 1,4-diazacyclohexane (piperazine, PZ, [110-85-0])—so-called “activated MDEA” solution—are among the most applied absorption systems in particular when carbon dioxide and hydrogen sulfide are to be removed from gas streams.[1] MDEA is a tertiary amine and has a comparatively low enthalpy of reaction with the sour gases which leads to lower energy requirement for solvent regeneration in the stripper. As the reaction rate for the conversion of neutrally dissolved CO_2 to ionic species is slow, H_2S can be separated from CO_2 in a kinetically controlled process. Higher reaction rates are required for the removal of CO_2. Such higher reaction rates can be achieved by activating an aqueous solution of MDEA with piperazine. As a secondary amine piperazine has a high rate of reaction with CO_2. By using blends of such amines, energy efficiency and favorable kinetics can be combined.[1−4]

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 knowledge of the equilibrium properties. The vapor−liquid equilibrium (VLE), the chemical reaction equilibria, and the energies to vaporize and condense such mixtures have to be known, but that caloric information can be obtained from a thermodynamic model for the vapor−liquid equilibrium of such systems. The gas absorption typically takes place at around 310 K and elevated partial pressures of the sour gas, whereas the gas desorption in the stripper (solvent regeneration) occurs at elevated temperatures (around 400 K) and low partial pressures of that gas. Therefore, the aforementioned equilibrium properties need to be explored within relatively wide ranges of temperature, pressure, and amine and gas concentrations. A thermodynamic model that accurately describes the solubility of CO_2 and H_2S in aqueous solutions of (MDEA + PZ) can only be developed when sufficient and accurate experimental data on the solubility of (single) gases in aqueous solutions of the single amines and of the amine mixtures are available. During the past 15 years, our research group has been investigating in experimental and theoretical (modeling) work the solubility of CO_2 and/or H_2S at *high gas loadings* as well as at *low gas loadings* in those interesting subsystems, namely, (CO_2 + MDEA + H_2O),[5−8] (H_2S + MDEA + H_2O),[5,6,8] (CO_2 + PZ + H_2O),[9,10] and (H_2S + PZ + H_2O)[11] in mixtures of MDEA and PZ (CO_2 + MDEA + PZ + H_2O),[9,12] (H_2S + MDEA + PZ + H_2O),[11] and in (CO_2 + MDEA + H_2SO_4/$NaSO_4$ + H_2O),[13] (H_2S + MDEA + H_2SO_4/$NaSO_4$ + H_2O).[14] Although a lot of publications from various research groups exist for the solubility of CO_2 in aqueous solutions of MDEA or piperazine, only very little is known so far on the solubility of carbon dioxide in aqueous solutions of mixtures of (MDEA + PZ) at a temperature range between (300 and 400) K. Such information is required at high as well as at low gas loading, but different experimental techniques have to be employed for experimental work in both regions. Complementing recently published experimental data for the high gas loading region (Böttger et al.[12]) from a synthetic method, the present publication reports similar data for the low gas loading region that were measured by headspace gas chromatography.

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10.1021/je9003383 CCC: $40.75

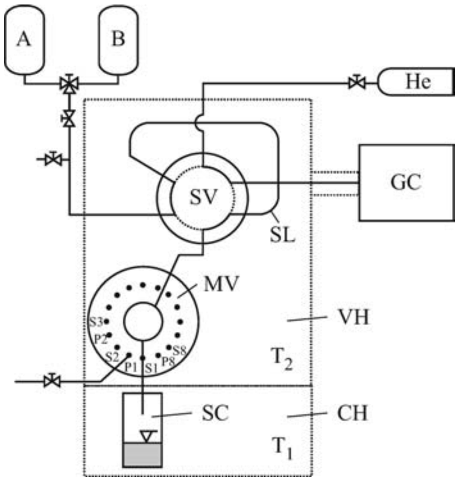

Figure 1. Scheme of the headspace chromatographic arrangement: CH, liquid-thermostatted cell holder (temperature T_1); VH, liquid-thermostatted valve holder (temperature $T_2 > T_1$); A, nitrogen tank (higher pressure); B, nitrogen tank (lower pressure); GC, gas chromatograph; He, Helium (carrier gas); SC, sample cell; MV, multiposition valve; S1 to S8, sample positions; P1 to P8, purge positions; SV, sample valve; SL, sample loop.

These data sets are currently used to extend and improve previously published thermodynamic models for the vapor−liquid equilibrium of the single amine systems (CO_2 + MDEA + H_2O)[7] and (CO_2 + PZ + H_2O)[10] in a wide range of amine concentrations, in particular also at higher piperazine concentrations and at elevated temperatures.

Experimental Section and Results

Apparatus and Method. Headspace gas chromatography was used in the present work to determine the solubility of CO_2 in aqueous solutions of (MDEA + PZ). That particular technique is well suited for the investigation of the solubility of gases in chemical solvents in the low partial pressure region. In the present investigation, the partial pressure of CO_2 ranged from about 0.1 kPa to nearly 150 kPa. The apparatus for the gas solubility experiments was the very same as that used in previous investigations on the solubility of CO_2 in aqueous solutions of both single amines MDEA[7] and piperazine[10] in the low gas loading region. The experimental arrangement and the experimental procedure have been described in detail before.[7] Therefore, only the main features are repeated here.

Experimental Technique. Figure 1 shows a scheme of the experimental arrangement. Its main components are a thermostatted cell holder, a thermostatted sample-valve holder (containing a multiposition valve and the sampling system), two large buffer tanks (volume ≈ 50 dm^3 each) filled with high-purity nitrogen, and a gas chromatograph {Agilent (type 6890), which is equipped with a capillary column (Alltech, type Heliflex AT-Q, 30m, 0.32 mm I.D.) and a thermal conductivity detector}.

In the experiments, eight sample cells (stainless steel vials, volume: either 11 cm^3 or 30 cm^3) are partially filled (to about 1/2 (vial volume: 11 cm^3) or to about 3/4 (vial volume: 30 cm^3) of the total volume) with a liquid mixture of (CO_2 + MDEA + PZ + H_2O) and mounted in the cell holder. Only one of those sample cells is shown in Figure 1. The composition of that liquid mixture is known from its gravimetric preparation (see below). The temperature is measured with a calibrated platinum resistance thermometer in the liquid bath that is used to control the temperature of the cell holder. The overall uncertainty of the temperature measurement is ± 0.1 K. During equilibration, very small amounts of the volatile components evaporate into the vapor phase (headspace). After equilibration, the cell is at first pressurized (from buffer tank A) with nitrogen to a constant pressure {(0.2, 0.26, and 0.45) MPa for the measurements at (313, 353, and 393) K, respectively} for 2 min. Second, the sample loop is filled from the vapor phase. This is achieved by connecting the vapor phase of the cell to buffer tank B. That tank is also pressurized to a constant pressure {(0.17, 0.2, and 0.37) MPa for the measurements at (313, 353, and 393) K, respectively}. The sample is then transferred to the gas chromatograph, and the sampling system is purged with nitrogen. A multiposition valve (Valco Instruments Co. Inc., type 2CSD16MWE-HC) allows one to connect each of the eight sample cells (by stainless steel capillaries, inner diameter: 0.25 mm) to the sample loop. The other eight positions of the multiposition valve are used for purging. The multiposition valve and the sample valve are both operated pneumatically by an electronic controller.

The temperature of the valve holder is kept at (15 to 20) K above the temperature of the cell holder. The line to the gas chromatograph is also kept at a higher temperature (to avoid condensation in the sampling system).

The primary data collected in the headspace chromatographic measurements are the peak areas of carbon dioxide. The peak area is proportional to the mass of the gas in the sample loop which again is proportional to the partial pressure of the gas in the cell. The relation between peak area and partial pressure in the cell is determined by calibration measurements with pure carbon dioxide and a high-precision pressure transducer (Schäfer Datametrics, Langen, Germany, type 590A-1000T-2Q1-V1X-4D). In that calibration, the pressure ranged from (7 to 70) kPa. In that pressure range, the peak area was proportional to the partial pressure. The maximum systematic uncertainty in the pressure measurement ranges from about ± 0.05 kPa at $p \approx 10$ kPa to about ± 0.15 kPa at $p \approx 70$ kPa. The maximum relative deviation between the measured pressures and the calibration line amounts to 2 %.

Materials and Sample Preparation. Carbon dioxide (4.5, volume fraction ≥ 0.99995) was purchased from Messer Griesheim GmbH, Krefeld, Germany. MDEA was either from Riedel-de Haën GmbH, Seelze, Germany (mass fraction ≥ 0.985) or from Sigma-Aldrich Chemie GmbH, Munich, Germany (mass fraction ≥ 0.99). Anhydrous piperazine (mass fraction ≥ 0.99) was purchased from Sigma-Aldrich Chemie GmbH, Munich, Germany. Both amines were degassed under vacuum before they were dissolved in water. That water was deionized, distilled, and degassed prior to use.

Typically, about 1.4 dm^3 of an aqueous solution of (MDEA + PZ) was gravimetrically prepared in an evacuated storage tank by dissolving known amounts of both amines in water. About 0.25 dm^3 of such an aqueous solution was then transferred to a smaller (also previously evacuated) storage tank (volume ≈ 0.3 dm^3). Known amounts of carbon dioxide were then added. The exact amount of mass of dissolved CO_2 was determined by weighing that storage tank before and after the addition of CO_2. The storage tank was shaken for about 5 h and finally stored for at least another 24 h. The vials of the headspace apparatus were then filled with the liquid mixture and mounted in the cell holder, where they were thermostatted to the experimental temperature for about 12 h. Corrections of the stoichiometric molalities of the solutes were applied to account for the transfer of CO_2 and water to the vapor (in both the second storage tank and the vials). The saturation pressures of MDEA and piperazine are low (almost negligible in the temperature range considered here). The vapor phase volumes in all

Table 1. Investigated Temperatures T, Stoichiometric Molalities $\bar{m}$, and Unloaded Mass Fractions w of MDEA and PZ in Aqueous Solutions and Loading α of CO_2

T	$\bar{m}_{MDEA}$	$\bar{m}_{PZ}$	w_{MDEA}	w_{PZ}	loading α_{CO_2}[a]	
K	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$			min	max
313.15	2.2	1.1	0.19	0.07	0.23	0.72
	2.2	2.1	0.18	0.13	0.23	0.83
	4.3	1.0	0.32	0.06	0.20	0.73
	4.0	2.0	0.29	0.10	0.28	0.71
	8.2	1.0	0.47	0.04	0.07	0.54
	8.3	2.1	0.46	0.08	0.18	0.60
353.15	2.2	2.1	0.18	0.13	0.10	0.56
	4.1	2.1	0.29	0.11	0.08	0.42
	3.8	3.8	0.25	0.18	0.15	0.44
	7.8	1.9	0.44	0.08	0.09	0.30
393.15	2.0	2.0	0.17	0.12	0.04	0.30
	4.1	2.0	0.29	0.11	0.02	0.23
	4.2	4.0	0.27	0.19	0.02	0.27
	7.7	1.9	0.44	0.08	0.02	0.17

[a] Loading $\alpha_{CO_2} = \bar{m}_{CO_2}/(\bar{m}_{MDEA} + \bar{m}_{PZ})$.

containers were estimated using the densities of the liquids. As all vapor phase volumes are small and the partial pressures of carbon dioxide and water (which were either calculated from a VLE model or known from the experiments) are also small, the corrections to the stoichiometric molality of all solutes are small (between 0.05 % and 1.5 % for CO_2 and negligible for MDEA and piperazine). The uncertainty in the stoichiometric molalities of MDEA and piperazine from the gravimetric preparation does not surmount ± 0.04 %. The total uncertainty in the amine molalities in the liquid phase in a vial is estimated to be smaller than ± 0.1 %. The relative uncertainty of the stoichiometric molality of carbon dioxide in such a liquid phase ranges from about ± 0.2 % up to about ± 1 %. It was estimated from the filling procedure described before including all corrections by means of a Gauss error propagation calculation.

Experimental Results

The solubility of carbon dioxide was measured in aqueous solutions of (MDEA + PZ) at three temperatures: 313 K, 353 K, and 393 K. The stoichiometric concentrations of MDEA and piperazine were between (2 and 8) molal and (1 and 4) molal, respectively. All reported molalities are moles per kilogram of water. The stoichiometric molar ratio of carbon dioxide to (MDEA + PZ) (i.e., the loading α_{CO_2}) ranged from $0.07 \le \alpha_{CO_2} \le 0.83$ for the experiments at 313 K and from $0.08 \le \alpha_{CO_2} \le 0.56$ ($0.02 \le \alpha_{CO_2} \le 0.30$) at 353 K (393 K). Table 1 gives an overview of the experimental conditions.

The experimental results are listed together with the corresponding uncertainties in Tables 2 to 4. The partial pressure of CO_2 ranges from about 0.1 kPa to about 150 kPa. The absolute uncertainty in the partial pressure of carbon dioxide was estimated from $\Delta p_{CO_2} = \pm (\Delta p^*_{CO_2} + 0.02 \cdot p_{CO_2})$. The first contribution $\Delta p^*_{CO_2}$ accounts for uncertainties in temperature as well as gas and amine molalities. It is determined from a Gauss error propagation calculation (by applying a VLE model). The second contribution results from the uncertainty of the calibration experiments. Each experimental data point was repeated 3 to 8 times. The absolute standard deviation from the average numerical value for the partial pressure of carbon dioxide ($\Delta p_{CO_2,repr}$) is also given in Tables 2 to 4. As expected, for almost all experimental data points, $\Delta p_{CO_2,repr}$ is less than Δp_{CO_2}. That finding supports the estimation of the experimental uncertainties.

Table 2. Solubility of Carbon Dioxide in Aqueous Solutions of (MDEA + PZ): Partial Pressure of Carbon Dioxide p_{CO_2} (and Its Standard Deviation $\Delta p_{CO_2,repr}$) above Aqueous Solutions (Composition Given by Stoichiometric Molalities of MDEA ($\bar{m}_{MDEA}$), PZ ($\bar{m}_{PZ}$), and Carbon Dioxide ($\bar{m}_{CO_2}$)) at $T = 313.15$ K ($\Delta T = \pm 0.1$ K, $\Delta\bar{m}_{MDEA}/\bar{m}_{MDEA} = \pm 0.1$ %, $\Delta\bar{m}_{PZ}/\bar{m}_{PZ} = \pm 0.1$ %)

$\bar{m}_{MDEA}$	$\bar{m}_{PZ}$	$\bar{m}_{CO_2}$	p_{CO_2}	$\Delta p_{CO_2,repr}$
$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	kPa	kPa
2.187	1.080	0.7566 ± 0.0006	0.31 ± 0.01	0.04
2.187	1.080	1.142 ± 0.001	1.42 ± 0.06	0.03
2.187	1.080	1.212 ± 0.001	1.73 ± 0.07	0.05
2.187	1.080	1.440 ± 0.002	3.40 ± 0.13	0.06
2.187	1.080	1.712 ± 0.004	6.72 ± 0.26	0.09
2.143	1.125	1.891 ± 0.005	9.83 ± 0.38	0.18
2.143	1.125	2.095 ± 0.009	16.1 ± 0.6	0.17
2.143	1.125	2.179 ± 0.011	20.3 ± 0.8	0.91
2.143	1.125	2.347 ± 0.016	28.9 ± 1.3	0.76
2.143	1.125	2.353 ± 0.017	30.5 ± 1.4	1.47
2.200	2.173	0.9989 ± 0.0007	0.11 ± 0.01	0.02
2.200	2.173	1.479 ± 0.001	0.43 ± 0.02	0.01
2.200	2.173	1.975 ± 0.001	1.51 ± 0.06	0.03
2.110	2.011	2.323 ± 0.003	5.09 ± 0.21	0.09
2.200	2.173	2.632 ± 0.004	7.04 ± 0.29	0.20
2.110	2.011	2.712 ± 0.007	12.3 ± 0.5	0.25
2.200	2.173	2.943 ± 0.008	14.0 ± 0.6	0.46
2.110	2.011	2.848 ± 0.010	16.5 ± 0.7	0.19
2.110	2.011	3.249 ± 0.025	42.6 ± 2.4	1.37
2.110	2.011	3.416 ± 0.035	58.3 ± 4.0	1.29
4.391	1.024	1.091 ± 0.001	0.95 ± 0.04	0.03
4.391	1.024	1.314 ± 0.001	1.60 ± 0.06	0.03
4.189	1.024	1.585 ± 0.002	2.99 ± 0.11	0.09
4.391	1.024	1.730 ± 0.002	3.73 ± 0.14	0.10
4.189	1.024	2.000 ± 0.004	6.15 ± 0.23	0.16
4.391	1.024	2.426 ± 0.007	10.8 ± 0.4	0.18
4.189	1.024	2.431 ± 0.007	11.6 ± 0.4	0.28
4.391	1.024	2.738 ± 0.011	16.5 ± 0.6	0.35
4.189	1.024	3.035 ± 0.017	25.2 ± 0.9	0.37
4.189	1.024	3.782 ± 0.042	61.8 ± 3.0	1.20
4.109	2.038	1.715 ± 0.001	0.81 ± 0.03	0.02
3.866	1.879	2.002 ± 0.001	1.85 ± 0.07	0.03
3.866	1.879	2.494 ± 0.003	4.55 ± 0.18	0.11
3.866	1.879	3.005 ± 0.007	10.1 ± 0.4	0.30
4.109	2.038	3.347 ± 0.008	12.3 ± 0.5	0.09
3.866	1.879	3.531 ± 0.015	21.9 ± 0.9	0.54
4.109	2.038	3.849 ± 0.017	23.8 ± 1.0	0.14
4.109	2.038	3.983 ± 0.020	28.9 ± 1.2	0.16
3.866	1.879	4.003 ± 0.029	41.8 ± 1.9	1.18
4.109	2.038	4.334 ± 0.032	45.1 ± 2.3	0.07
7.936	0.9601	0.6505 ± 0.0010	0.27 ± 0.01	0.01
7.936	0.9601	0.9853 ± 0.0011	0.71 ± 0.03	0.01
7.936	0.9601	1.465 ± 0.002	2.02 ± 0.08	0.07
7.936	0.9601	1.968 ± 0.004	4.41 ± 0.17	0.11
7.936	0.9601	2.105 ± 0.004	5.21 ± 0.20	0.20
8.425	1.073	3.429 ± 0.014	16.1 ± 0.6	0.47
8.425	1.073	3.890 ± 0.019	22.3 ± 0.8	0.55
8.425	1.073	4.422 ± 0.027	30.8 ± 1.1	1.00
8.425	1.073	4.569 ± 0.030	33.9 ± 1.2	1.63
8.425	1.073	5.110 ± 0.041	45.9 ± 1.6	1.57
8.519	2.138	1.909 ± 0.001	0.91 ± 0.04	0.01
8.519	2.138	3.031 ± 0.004	4.04 ± 0.16	0.02
8.519	2.138	4.109 ± 0.010	11.7 ± 0.5	0.12
8.113	2.148	4.551 ± 0.016	17.6 ± 0.7	0.98
8.519	2.138	5.253 ± 0.024	26.4 ± 1.0	0.09
8.113	2.148	5.213 ± 0.025	27.7 ± 1.1	0.50
8.519	2.138	5.354 ± 0.026	28.6 ± 1.1	0.53
8.113	2.148	5.723 ± 0.038	40.9 ± 1.5	1.81
8.113	2.148	5.945 ± 0.045	48.9 ± 1.8	1.52
8.113	2.148	6.132 ± 0.047	50.1 ± 1.9	2.21

The new experimental results for the partial pressure of CO_2 above aqueous solutions (with a nearly constant stoichiometric molality of piperazine of about 1 $mol \cdot (kg\ of\ water)^{-1}$ and stoichiometric molalities of MDEA of about 2 molal, about 4 molal, and about 8 molal, respectively) at 313 K are plotted versus α_{CO_2}, i.e., the stoichiometric molar ratio of CO_2 to (MDEA + PZ) in Figure 2.

Figure 2 reveals the typical behavior when a sour gas like carbon dioxide is dissolved in an aqueous solution of amines: the partial pressure of the sour gas at first only very slightly

Table 3. Solubility of Carbon Dioxide in Aqueous Solutions of (MDEA + PZ): Partial Pressure of Carbon Dioxide $p_{\mathrm{CO_2}}$ (and Its Standard Deviation $\Delta p_{\mathrm{CO_2,repr}}$) above Aqueous Solutions (Composition Given by Stoichiometric Molalities of MDEA ($\bar{m}_{\mathrm{MDEA}}$), PZ ($\bar{m}_{\mathrm{PZ}}$), and Carbon Dioxide ($\bar{m}_{\mathrm{CO_2}}$)) at $T = 353.15$ K ($\Delta T = \pm 0.1$ K, $\Delta\bar{m}_{\mathrm{MDEA}}/\bar{m}_{\mathrm{MDEA}} = \pm 0.1$ %, $\Delta\bar{m}_{\mathrm{PZ}}/\bar{m}_{\mathrm{PZ}} = \pm 0.1$ %)

$\bar{m}_{\mathrm{MDEA}}$	$\bar{m}_{\mathrm{PZ}}$	$\bar{m}_{\mathrm{CO_2}}$	$p_{\mathrm{CO_2}}$	$\Delta p_{\mathrm{CO_2,repr}}$
mol·kg^{-1}	mol·kg^{-1}	mol·kg^{-1}	kPa	kPa
2.402	2.232	0.4432 ± 0.0007	0.33 ± 0.01	0.002
2.402	2.232	0.8189 ± 0.0008	1.40 ± 0.05	0.02
2.059	1.991	0.982 ± 0.001	2.94 ± 0.11	0.07
2.402	2.232	1.422 ± 0.003	7.46 ± 0.28	0.24
2.402	2.232	1.868 ± 0.010	20.0 ± 1.0	0.24
2.059	1.991	1.701 ± 0.010	20.4 ± 0.8	0.21
2.402	2.232	2.149 ± 0.017	33.3 ± 1.3	1.20
2.059	1.991	2.057 ± 0.022	44.2 ± 1.7	0.79
2.059	1.991	2.202 ± 0.030	58.7 ± 2.2	1.92
2.059	1.991	2.247 ± 0.033	64.8 ± 2.5	0.74
4.232	2.136	0.4827 ± 0.0008	0.62 ± 0.02	0.01
4.232	2.136	0.6522 ± 0.0009	1.17 ± 0.05	0.02
4.232	2.136	0.872 ± 0.001	2.24 ± 0.09	0.04
4.030	2.057	1.049 ± 0.001	3.87 ± 0.15	0.09
4.232	2.136	1.443 ± 0.001	8.65 ± 0.32	0.16
4.232	2.136	1.782 ± 0.001	15.0 ± 0.6	0.57
4.030	2.057	1.949 ± 0.002	24.8 ± 0.9	0.42
4.030	2.057	2.121 ± 0.003	32.8 ± 1.2	0.58
4.030	2.058	2.370 ± 0.004	48.2 ± 1.8	1.55
4.030	2.057	2.394 ± 0.005	51.2 ± 1.9	1.89
4.030	2.058	2.535 ± 0.006	61.7 ± 2.3	2.90
3.778	3.746	1.133 ± 0.001	1.12 ± 0.04	0.02
3.778	3.746	1.216 ± 0.001	1.32 ± 0.05	0.01
3.822	3.798	1.544 ± 0.001	2.46 ± 0.09	0.03
3.778	3.746	1.797 ± 0.001	3.70 ± 0.14	0.08
3.778	3.746	2.163 ± 0.001	7.03 ± 0.27	0.18
3.778	3.746	2.368 ± 0.001	9.45 ± 0.36	0.38
3.822	3.798	2.687 ± 0.002	14.5 ± 0.6	0.12
3.778	3.746	2.913 ± 0.002	19.5 ± 0.7	0.33
3.822	3.798	3.135 ± 0.003	27.2 ± 1.0	0.68
3.822	3.798	3.365 ± 0.004	38.1 ± 1.4	0.90
7.643	1.971	0.892 ± 0.001	3.59 ± 0.13	0.16
7.598	1.892	1.107 ± 0.001	6.13 ± 0.23	0.16
7.913	1.952	1.133 ± 0.001	6.53 ± 0.24	0.04
7.915	1.952	1.291 ± 0.001	10.3 ± 0.4	0.11
7.913	1.952	1.370 ± 0.002	10.5 ± 0.4	0.36
7.913	1.952	1.425 ± 0.002	11.3 ± 0.4	0.15
7.643	1.971	1.507 ± 0.002	12.7 ± 0.5	0.12
7.913	1.952	1.708 ± 0.002	13.2 ± 0.5	0.43
7.599	1.892	1.561 ± 0.002	14.6 ± 0.5	0.50
7.643	1.971	1.901 ± 0.003	22.9 ± 0.8	0.23
7.599	1.892	2.138 ± 0.004	32.0 ± 1.2	0.92
7.644	1.971	2.529 ± 0.006	50.4 ± 1.8	1.27
7.643	1.971	2.903 ± 0.008	71.4 ± 2.6	3.03

Table 4. Solubility of Carbon Dioxide in Aqueous Solutions of (MDEA + PZ): Partial Pressure of Carbon Dioxide $p_{\mathrm{CO_2}}$ (and Its Standard Deviation $\Delta p_{\mathrm{CO_2,repr}}$) above Aqueous Solutions (Composition Given by Stoichiometric Molalities of MDEA ($\bar{m}_{\mathrm{MDEA}}$), PZ ($\bar{m}_{\mathrm{PZ}}$), and Carbon Dioxide ($\bar{m}_{\mathrm{CO_2}}$)) at $T = 393.15$ K ($\Delta T = \pm 0.1$ K, $\Delta\bar{m}_{\mathrm{MDEA}}/\bar{m}_{\mathrm{MDEA}} = \pm 0.1$ %, $\Delta\bar{m}_{\mathrm{PZ}}/\bar{m}_{\mathrm{PZ}} = \pm 0.1$ %)

$\bar{m}_{\mathrm{MDEA}}$	$\bar{m}_{\mathrm{PZ}}$	$\bar{m}_{\mathrm{CO_2}}$	$p_{\mathrm{CO_2}}$	$\Delta p_{\mathrm{CO_2,repr}}$
mol·kg^{-1}	mol·kg^{-1}	mol·kg^{-1}	kPa	kPa
2.013	2.018	0.1670 ± 0.0007	1.29 ± 0.05	0.04
2.013	2.018	0.2035 ± 0.0007	1.85 ± 0.07	0.01
2.013	2.018	0.2139 ± 0.0007	2.36 ± 0.08	0.08
2.015	2.008	0.3271 ± 0.0007	4.05 ± 0.14	0.03
2.015	2.008	0.4140 ± 0.0008	6.45 ± 0.23	0.33
2.013	2.018	0.5379 ± 0.0009	10.2 ± 0.4	0.26
2.015	2.008	0.666 ± 0.001	16.4 ± 0.6	0.27
2.015	2.008	0.827 ± 0.002	26.3 ± 0.9	0.30
2.013	2.018	0.827 ± 0.002	26.8 ± 0.9	1.04
2.015	2.008	1.178 ± 0.004	66.2 ± 2.3	1.32
4.011	1.999	0.1416 ± 0.0009	1.43 ± 0.05	0.06
4.011	1.999	0.2216 ± 0.0008	2.76 ± 0.10	0.11
4.052	2.002	0.3476 ± 0.0009	6.17 ± 0.22	0.14
4.011	1.999	0.399 ± 0.001	7.67 ± 0.27	0.33
4.234	2.137	0.481 ± 0.001	9.67 ± 0.34	0.21
4.234	2.137	0.649 ± 0.002	17.1 ± 0.6	0.22
4.234	2.137	0.867 ± 0.003	30.6 ± 1.1	0.36
4.011	1.999	0.858 ± 0.004	48.6 ± 1.7	1.83
4.052	2.002	1.119 ± 0.005	61.5 ± 2.1	0.74
4.052	2.002	1.235 ± 0.007	83.3 ± 2.9	3.78
4.011	1.999	1.361 ± 0.008	99.8 ± 3.5	2.09
4.406	4.099	0.1454 ± 0.0009	0.60 ± 0.02	0.02
3.930	3.859	0.2723 ± 0.0009	1.53 ± 0.06	0.02
3.930	3.859	0.369 ± 0.001	2.09 ± 0.08	0.07
3.930	3.859	0.620 ± 0.001	5.45 ± 0.19	0.15
4.406	4.099	0.840 ± 0.001	9.24 ± 0.33	0.23
3.930	3.859	0.923 ± 0.001	11.3 ± 0.4	0.14
4.406	4.099	1.287 ± 0.002	21.1 ± 0.8	0.63
4.406	4.099	1.564 ± 0.003	30.9 ± 1.1	0.81
4.406	4.099	1.643 ± 0.003	35.3 ± 1.3	0.84
3.930	3.859	1.712 ± 0.004	42.9 ± 1.5	1.69
3.930	3.859	1.789 ± 0.004	48.3 ± 1.7	0.70
4.406	4.099	2.258 ± 0.006	63.6 ± 2.3	2.25
7.680	1.953	0.166 ± 0.001	3.00 ± 0.11	0.08
7.680	1.953	0.243 ± 0.001	5.33 ± 0.19	0.07
7.680	1.953	0.362 ± 0.001	10.4 ± 0.4	0.30
7.680	1.953	0.437 ± 0.002	13.6 ± 0.5	0.23
7.602	1.893	0.535 ± 0.002	18.7 ± 0.7	0.14
7.680	1.953	0.576 ± 0.002	21.7 ± 0.8	0.27
7.602	1.893	0.648 ± 0.003	29.5 ± 1.0	0.82
7.602	1.893	0.746 ± 0.004	35.6 ± 1.2	0.22
7.647	1.972	0.883 ± 0.004	45.9 ± 1.6	1.16
7.681	1.953	0.947 ± 0.005	55.0 ± 1.9	0.77
7.602	1.893	1.091 ± 0.007	75.2 ± 2.6	2.12
7.917	1.953	1.117 ± 0.008	75.3 ± 2.6	1.95
7.917	1.953	1.347 ± 0.011	111.8 ± 3.8	5.88
7.602	1.893	1.530 ± 0.015	146.8 ± 5.0	1.25

increases with increasing numbers for the molar ratio of gas to amines (i.e., increasing stoichiometric molality of the gas in the liquid). This is due to the basic character of the amines. The sour gas is at first predominantly dissolved chemically (i.e., in nonvolatile ionic form, here as bicarbonate, carbamates, and carbonate) resulting in very small partial pressures of the sour gas at low gas loadings. However, when all amine has been spent by chemical reactions, a sour gas can no longer be absorbed "chemically" but has to be dissolved "physically".

Figures 3 and 4 show the new experimental results for the partial pressure of CO_2 above the other investigated solvent compositions (different molalities of MDEA and PZ) at 313 K, 353 K, and 393 K. The general features of these figures are the same as the features shown in Figure 2.

Comparison with Predictions. A thermodynamic model for the solubility of CO_2 in aqueous solutions of the single amines MDEA (Ermatchkov et al.[7]) and piperazine (Ermatchkov et al.[10]) was described and parametrized in previous publications. 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 molalities $\{2 < \bar{m}_{\mathrm{MDEA}} < 8; 1 < \bar{m}_{\mathrm{PZ}} < 4\}$ and molar ratios of CO_2 to amine from below 0.003 to above 1.4 but were restricted to data for aqueous solutions of the single amines. The model uses the extended Henry's law on the molality scale to describe the partial pressure of CO_2 above the aqueous solution. The extended Henry's law requires the "true" molality of (neutral) CO_2 as well as the activity coefficient of that species, but only a small part of the totally dissolved carbon dioxide is present in neutral form, as most CO_2 is converted to ionic species. The speciation is determined by reversible chemical reactions (chemical equilibrium). The important deviations from ideal mixing behavior in the aqueous, electrolyte solutions are considered through activity coefficients (of the true solutes). These activity coefficients 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 all solute species. The model

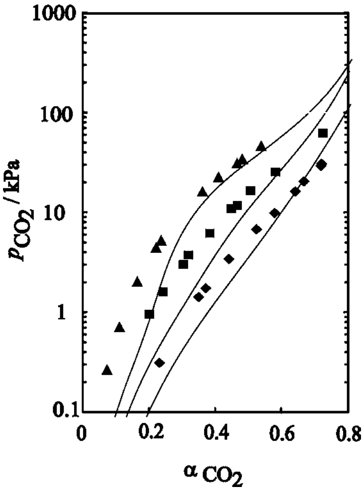

Figure 2. Partial pressure of CO_2 above aqueous solutions of (MDEA +PZ) at 313.15 K with $\bar{m}_{\mathrm{PZ}} \approx 1$ mol·kg^{-1}: new experimental results (◆, $\bar{m}_{\mathrm{MDEA}} \approx 2.2$ mol·kg^{-1}; ■, $\bar{m}_{\mathrm{MDEA}} \approx 4.3$ mol·kg^{-1}; ▲, $\bar{m}_{\mathrm{MDEA}} \approx 8.2$ mol·kg^{-1}) compared to prediction results (—).

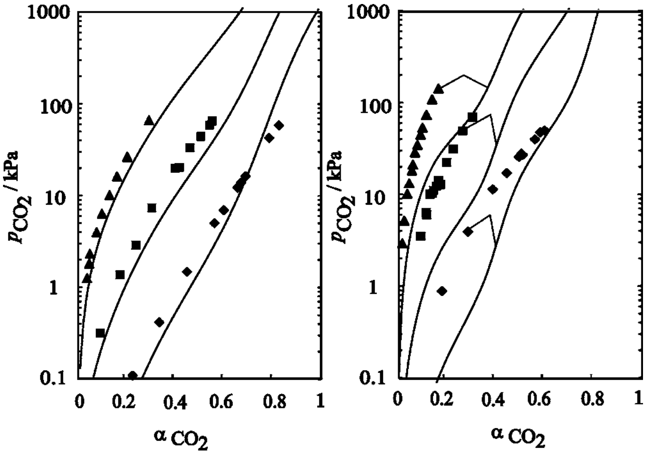

Figure 3. Partial pressure of CO_2 above aqueous solutions of (MDEA + PZ). Left diagram: New experimental results {◆, ($\bar{m}_{\mathrm{MDEA}} \approx 2.2$ mol·kg^{-1} + $\bar{m}_{\mathrm{PZ}} \approx 2.1$ mol·kg^{-1}) at 313 K; ■, ($\bar{m}_{\mathrm{MDEA}} \approx 2.2$ mol·kg^{-1} + $\bar{m}_{\mathrm{PZ}} \approx 2.1$ mol·kg^{-1}) at 353 K; and ▲, ($\bar{m}_{\mathrm{MDEA}} \approx 2.0$ mol·kg^{-1} + $\bar{m}_{\mathrm{PZ}} \approx 2.0$ mol·kg^{-1}) at 393 K} compared to prediction results (—). Right diagram: New experimental results {◆, ($\bar{m}_{\mathrm{MDEA}} \approx 8.3$ mol·kg^{-1} + $\bar{m}_{\mathrm{PZ}} \approx 2.1$ mol·kg^{-1}) at 313 K; ■, ($\bar{m}_{\mathrm{MDEA}} \approx 7.8$ mol·kg^{-1} + $\bar{m}_{\mathrm{PZ}} \approx 1.9$ mol·kg^{-1}) at 353 K; ▲, ($\bar{m}_{\mathrm{MDEA}} \approx 7.7$ mol·kg^{-1} + $\bar{m}_{\mathrm{PZ}} \approx 1.9$ mol·kg^{-1}) at 393 K} compared to prediction results (—).

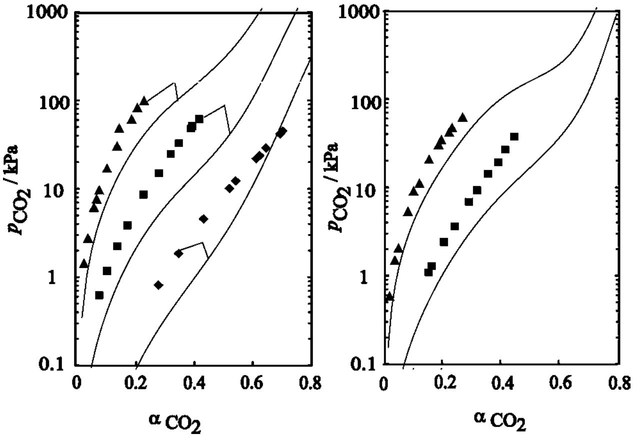

Figure 4. Partial pressure of CO_2 above aqueous solutions of (MDEA + PZ). Left diagram: New experimental results {◆, ($\bar{m}_{\mathrm{MDEA}} \approx 4.0$ mol·kg^{-1} + $\bar{m}_{\mathrm{PZ}} \approx 2.0$ mol·kg^{-1}) at 313 K; ■, ($\bar{m}_{\mathrm{MDEA}} \approx 4.1$ mol·kg^{-1} + $\bar{m}_{\mathrm{PZ}} \approx 2.1$ mol·kg^{-1}) at 353 K; ▲, ($\bar{m}_{\mathrm{MDEA}} \approx 4.1$ mol·kg^{-1} + $\bar{m}_{\mathrm{PZ}} \approx 2.0$ mol·kg^{-1}) at 393 K} compared to prediction results (—). Right diagram: New experimental results { ■, ($\bar{m}_{\mathrm{MDEA}} \approx 3.8$ mol·kg^{-1} + $\bar{m}_{\mathrm{PZ}} \approx 3.8$ mol·kg^{-1}) at 353 K; ▲, ($\bar{m}_{\mathrm{MDEA}} \approx 4.2$ mol·kg^{-1} + $\bar{m}_{\mathrm{PZ}} \approx 4.0$ mol·kg^{-1}) at 393 K} compared to prediction results (—).

for the system (CO_2 + MDEA + H_2O) was combined with the corresponding model for the system (CO_2 + PZ + H_2O)—with model parameters corresponding to "sets II" by Ermatchkov et al.[7,10]—to predict the pressure that is required to dissolve CO_2 in aqueous solutions of (MDEA + PZ). However, as the parametrization was based only on experimental data for the solubility of CO_2 in the (single amine + water) systems, all parameters for interactions between species that are only present either in aqueous solutions of (MDEA + CO_2) or in aqueous solutions of (PZ + CO_2) were neglected. Some of these parameters (for example, the binary interaction parameter between MDEA on one side and protonated piperazine ($PIPH_3^+$) on the other side, and the ternary parameter for interactions between HCO_3^-, MDEA, and $PIPH_3^+$) are expected to have a strong influence on the prediction results. The predicted solubility pressures are generally smaller than the experimental results (cf. Figures 2 to 4). As shown by the diagram on the left side of Figure 3, the deviations between predicted and experimentally determined partial pressures of CO_2 are small (order of magnitude: 10 %) as long as the amine concentrations are low. The deviations increase with increasing stoichiometric molalities of MDEA and PZ. Similar to prediction results in the high gas loading region (see Böttger et al.[12]) also in the low gas loading region, and particularly at low temperatures and high amine molalities, the predictions for the solubility pressure deviate considerably from the experimental results. The deviations can reach 1 order of magnitude (cf. right side of Figure 3).

Comparison with Literature Data. The direct comparison with literature data is difficult as the experimental conditions (such as temperature and stoichiometric amine concentration in the aqueous solvent mixture) are mostly different, and a reasonable inter- and extrapolation of the experimental data is not possible without a well-parametrized model for the solubility of CO_2 in aqueous mixtures of MDEA and PZ. Therefore, a detailed comparison with literature data has to be postponed (see also Conculsions). Furthermore, some literature data describe the amine content of the solvent using the molarity scale (i.e., moles per volume), sometimes even without clearly stating if the reported numbers for the molarities are valid for the temperature of preparing the solvents or the temperature of the actual gas solubility experiment. In 2003, Pérez-Salado Kamps et al.[9] compared the experimental results by Xu et al. (1998),[16] Liu et al. (1999),[17] and Bishnoi and Rochelle (2002)[18] with their own experimental data that were measured with a synthetic technique at pressures between (0.2 and 6.4) MPa (i.e., in the high gas loading region). Therefore, here the comparison is mostly restricted to results from more recent publications. Si Ali and Aroua (2004)[19] described the influence of small amounts of PZ (molarity $\bar{c}_{\mathrm{PZ}} \le 0.1$ mol·dm^{-3}) on the solubility of CO_2 in aqueous solutions of MDEA (molarity $\bar{c}_{\mathrm{MDEA}} \sim 2$ mol·dm^{-3}) at (40, 60, and 80) °C and partial pressures of CO_2 up to nearly 100 kPa. Jenab et al. (2005)[20] {cf. also Matin et al. (2007)[21]} 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 between 0.17 and 1.55) at (40, 50, 55, and 70) °C for partial pressures of CO_2 between about (0.03 and 4) MPa. Derks (2006)[22] reported experimental data for the partial pressure of CO_2 (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 molarities of

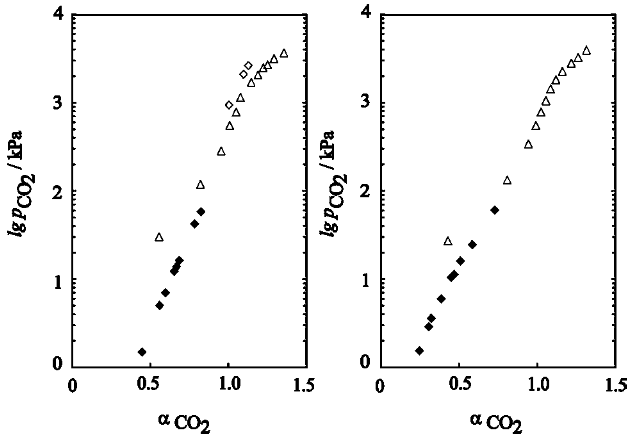

Figure 5. Partial pressure of carbon dioxide above aqueous solutions of (MDEA + PZ) at 313 K. Left diagram: New experimental results {◆, ($\bar{m}_{MDEA} \approx 2.2\ mol\cdot kg^{-1} + \bar{m}_{PZ} \approx 2.1\ mol\cdot kg^{-1}$)} compared to previous experimental results {◇, Böttger et al.[12] ($\bar{m}_{MDEA} \approx 2.2\ mol\cdot kg^{-1} + \bar{m}_{PZ} \approx 2.0\ mol\cdot kg^{-1}$); Δ, Jenab et al.[20] ($\bar{m}_{MDEA} \approx 3.0\ mol\cdot kg^{-1} + \bar{m}_{PZ} \approx 2.0\ mol\cdot kg^{-1}$)}. Right diagram: New experimental results {◆, ($\bar{m}_{MDEA} \approx 4.3\ mol\cdot kg^{-1} + \bar{m}_{PZ} \approx 1.0\ mol\cdot kg^{-1}$)} compared to previous experimental results {Δ, Jenab et al.[20] ($\bar{m}_{MDEA} \approx 3.8\ mol\cdot kg^{-1} + \bar{m}_{PZ} \approx 1.3\ mol\cdot kg^{-1}$)}.

(MDEA + PZ) were (4 + 0.6) $mol\cdot dm^{-3}$, (2.8 + 0.7) $mol\cdot dm^{-3}$, and (0.5 + 1.5) $mol\cdot dm^{-3}$, respectively. Recently, Jang et al. (2008)[23] published experimental data for the absorption of carbon dioxide in aqueous solutions of (MDEA + PZ) at (40, 60, and 80) °C and pressures up to nearly 5 MPa. Figure 5 shows on the left side the new experimental results for an aqueous solvent with ($\bar{m}_{MDEA} \approx 2.2\ mol\cdot kg^{-1} + \bar{m}_{PZ} \approx 2.1\ mol\cdot kg^{-1}$) of the present work at 313 K together with the experimental results of Böttger et al.[12] ($\bar{m}_{MDEA} \approx 2.2\ mol\cdot kg^{-1} + \bar{m}_{PZ} \approx 2.0\ mol\cdot kg^{-1}$) and of Jenab et al.[20] ($\bar{c}_{MDEA} \approx 2.0\ mol\cdot dm^{-3} + \bar{c}_{PZ} \approx 1.36\ mol\cdot dm^{-3}$)—these molarities were converted to molalities as described in the Appendix resulting in ($\bar{m}_{MDEA} \approx 3.0\ mol\cdot kg^{-1} + \bar{m}_{PZ} \approx 2.0\ mol\cdot kg^{-1}$). The right side of Figure 5 shows a comparison of the new experimental results for an aqueous solvent with ($\bar{m}_{MDEA} \approx 4.3\ mol\cdot kg^{-1} + \bar{m}_{PZ} \approx 1.0\ mol\cdot kg^{-1}$), of the present work at 313 K together with the experimental results of Jenab et al.[20] ($\bar{c}_{MDEA} \approx 2.5\ mol\cdot dm^{-3} + \bar{c}_{PZ} \approx 0.86\ mol\cdot dm^{-3}$)—these molarities were converted to molalities as described in the Appendix resulting in ($\bar{m}_{MDEA} \approx 3.8\ mol\cdot kg^{-1} + \bar{m}_{PZ} \approx 1.3\ mol\cdot kg^{-1}$). The results from the present investigation complement the literature data, but the investigated gas loading ranges do not overlap—the literature data are mostly for $\alpha_{CO_2} > 0.75$, whereas the new experimental data were taken for $\alpha_{CO_2} < 0.75$. However, the transition from the literature data to the new experimental data is generally smooth. Only some data points reported by Jenab et al.[20] at the lowest α_{CO_2}-numbers strongly deviate from the results of the present work. In that region, the partial pressures of CO_2 reported by Jenab et al.[20] are about twice as large as the experimental results from the present investigation. Figure 6 shows a comparison of the new experimental results for the partial pressure of carbon dioxide above aqueous solutions of ($\bar{m}_{MDEA} \approx 8.2\ mol\cdot kg^{-1}$ and $\bar{m}_{PZ} \approx 1.0\ mol\cdot kg^{-1}$) at 313 K with the data from Bishnoi and Rochelle[18] and Derks[22] for ($\bar{c}_{MDEA} \approx 2.5\ mol\cdot dm^{-3} + \bar{c}_{PZ} \approx 0.86\ mol\cdot dm^{-3}$)—these molarities were also converted to molalities as described in the Appendix resulting in ($\bar{m}_{MDEA} \approx 7.7\ mol\cdot kg^{-1} + \bar{m}_{PZ} \approx 1.2\ mol\cdot kg^{-1}$). The results of these three investigations overlap in a rather broad gas loading range ($0.15 < \alpha_{CO_2} < 0.55$). In that region, the results of all three research groups agree well, although the compositions of the aqueous amine solutions are slightly different.

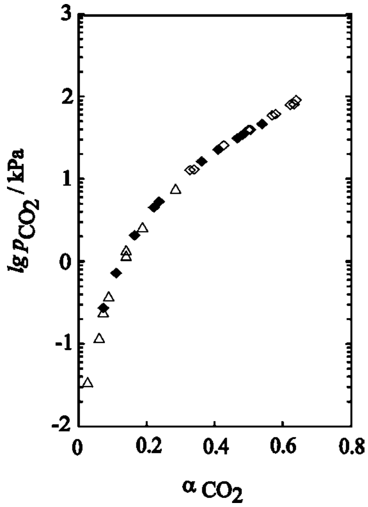

Figure 6. Partial pressure of carbon dioxide above aqueous solutions of (MDEA + PZ) at 313 K. New experimental results {◆, ($\bar{m}_{MDEA} \approx 8.2\ mol\cdot kg^{-1} + \bar{m}_{PZ} \approx 1.0\ mol\cdot kg^{-1}$)}; ◇, experimental results from Derks;[22] Δ, experimental results from Bishnoi and Rochelle,[18] both for ($\bar{m}_{MDEA} \approx 7.7\ mol\cdot kg^{-1} + \bar{m}_{PZ} \approx 1.2\ mol\cdot kg^{-1}$).

Conclusions

Complementing a recently published study on the solubility of carbon dioxide in aqueous solutions of (MDEA + PZ) in the high-pressure (high gas loading) region (Böttger et al.[12]), this contribution presents similar experimental results in the low pressure (low gas loading) region. The database available from both investigations considerably supplements and extends the experimental database for the vapor−liquid equilibrium of the industrially important system (CO_2 + MDEA + PZ + H_2O). The database is currently being used to parametrize a previously published thermodynamic model for the solubility of CO_2 in such aqueous solutions over a wide range of temperatures, gas loading, and amine concentrations. Caused by the conversion of the neutral solutes (CO_2, MDEA, and PZ) to a large number of ionic species, one cannot expect to reliably predict the solubility of carbon dioxide in the aqueous solutions of (MDEA +PZ) from models that describe the solubility of carbon dioxide in aqueous solutions of the single amines. Therefore, at least some model parameters have to be fitted to experimental data for the solubility of CO_2 in the aqueous solution of (MDEA + PZ).

Appendix

Conversion of Experimental Results on the "Molarity Scale" to the "Molality Scale".

Literature data for the solubility of CO_2 in aqueous solutions of (MDEA + PZ) which reported the composition of the gas-free aqueous amine solutions on the molarity scale were converted to the molality scale by

$$\frac{\bar{m}_i}{\bar{m}^0} = \frac{\bar{c}_i/\bar{c}^0}{\dfrac{\rho}{g\cdot cm^{-3}} - \sum_j \dfrac{\bar{c}_j}{\bar{c}^0}\dfrac{M_j}{1000}} \qquad i, j = MDEA, PZ$$

where $\bar{m}_i$ ($\bar{c}_i$) is the stoichiometric molality (molarity) of amine i in the aqueous solution at 293.15 K; $\bar{m}^0 = 1\ mol\cdot(kg\ H_2O)^{-1}$ and $\bar{c}^0 = 1\ mol\cdot(dm^3\ solvent)^{-1}$; ρ is the specific density of the gas-free solvent mixture also at 293.15 K; and

Table A1. Experimental Results for the Specific Density ρ of Aqueous Solutions of (MDEA + PZ) at 293.15 K[a]

$\bar{m}_{\mathrm{MDEA}}$ / $\mathrm{mol \cdot kg^{-1}}$	$\bar{c}_{\mathrm{MDEA}}$ / $\mathrm{mol \cdot dm^{-3}}$	$\bar{m}_{\mathrm{PZ}}$ / $\mathrm{mol \cdot kg^{-1}}$	$\bar{c}_{\mathrm{PZ}}$ / $\mathrm{mol \cdot dm^{-3}}$	ρ / $\mathrm{g \cdot cm^{-3}}$
1.8666	1.5496	-	-	1.0148
4.1177	2.8441	-	-	1.0296
6.1887	3.7001	-	-	1.0388
8.1861	4.3295	-	-	1.0448
10.032	4.7915	-	-	1.0486
12.099	5.2102	-	-	1.0516
-	-	0.2628	0.2568	0.9991
-	-	0.4689	0.4506	0.9998
-	-	0.7153	0.6743	1.0008
-	-	0.9675	0.8947	1.0018
-	-	1.2676	1.1464	1.0031
-	-	1.4477	1.2923	1.0040
2.1347	1.7195	0.0982	0.0791	1.0172
1.9335	1.5767	0.1798	0.1466	1.0160
2.0076	1.6120	0.3158	0.2536	1.0169
2.0673	1.6417	0.4086	0.3245	1.0177
2.0150	1.5984	0.4956	0.3931	1.0176
1.9969	1.5756	0.6039	0.4765	1.0178
3.9955	2.7528	0.2085	0.1437	1.0294
4.0175	2.7317	0.4207	0.2861	1.0301
4.0333	2.7126	0.6007	0.4040	1.0306
4.0002	2.6651	0.8217	0.5475	1.0310
4.0066	2.6448	0.9868	0.6514	1.0314
4.0236	2.6226	1.2075	0.7870	1.0321
6.1549	3.6342	0.3085	0.1822	1.0392
5.8659	3.4793	0.6041	0.3583	1.0386
6.0334	3.4884	0.9219	0.5330	1.0398
5.9558	3.4124	1.2241	0.7014	1.0400
5.9889	3.3782	1.5246	0.8600	1.0407
5.9889	3.3381	1.7899	0.9977	1.0411
8.0369	4.2150	0.4020	0.2108	1.0449
7.9747	4.1274	0.8007	0.4144	1.0451
7.1858	3.8402	1.1205	0.5988	1.0436
7.9823	4.0124	1.5034	0.7557	1.0459
8.2182	4.0215	1.8539	0.9072	1.0467
7.7262	3.8189	2.2749	1.1244	1.0462
8.6698	3.9095	3.3955	1.5312	1.0487
9.2092	4.5166	0.4434	0.2175	1.0474
9.5110	4.5041	0.9344	0.4425	1.0484
10.035	4.5209	1.5528	0.6996	1.0495
10.211	4.4855	2.0117	0.8837	1.0499
9.8780	4.3318	2.5195	1.1049	1.0499
9.9080	4.2654	3.0019	1.2923	1.0501
11.665	5.0032	0.7062	0.3029	1.0512
11.907	4.9521	1.2755	0.5305	1.0517
11.975	4.8820	1.7756	0.7239	1.0518
11.132	4.6295	2.3325	0.9700	1.0511
10.788	4.4833	2.8236	1.1734	1.0509
11.444	4.5431	3.3148	1.3159	1.0517

[a] $\Delta T = \pm\ 0.1$ K, $\Delta \bar{m}_{\mathrm{MDEA}} \leq \pm\ 0.0004\ \mathrm{mol \cdot kg^{-1}}$, $\Delta \bar{m}_{\mathrm{PZ}} \leq \pm\ 0.0004\ \mathrm{mol \cdot kg^{-1}}$, $\Delta \rho \leq \pm\ 0.0005\ \mathrm{g \cdot cm^{-3}}$.

Table A2. Coefficients of Equation A-1 for the Specific Density ρ of Aqueous Solutions of (MDEA + PZ) at 293.15 K

A_0	0.9982
A_1	$9.58 \cdot 10^{-3}$
A_2	$9.86 \cdot 10^{-4}$
A_3	$-1.65 \cdot 10^{-4}$
A_4	$3.03 \cdot 10^{-3}$
A_5	$1.85 \cdot 10^{-3}$
A_6	$5.72 \cdot 10^{-4}$
A_7	$-1.72 \cdot 10^{-4}$
A_8	$1.11 \cdot 10^{-3}$
A_9	$-3.34 \cdot 10^{-4}$
A_{10}	$-1.76 \cdot 10^{-4}$
A_{11}	$1.44 \cdot 10^{-5}$

M_j is the relative molecular mass of amine j. The density of aqueous solutions of (MDEA + PZ) was determined at (293.15 ± 0.1) K with a vibrating-tube densimeter (model DMA 602 HP, Anton Paar GmbH, Graz, Austria) with an uncertainty of less than $\pm\ 0.0005\ \mathrm{g \cdot cm^{-3}}$. The solvent mixtures were prepared gravimetrically with an uncertainty of less than $\pm\ 0.0004\ \mathrm{mol \cdot (kg\ H_2O)^{-1}}$. The experimental results are given in Table A1. The experimental results were correlated by the empirical relation

$$\frac{\rho}{\mathrm{g \cdot cm^{-3}}} = A_0 + A_1 \cdot \left(\frac{\bar{c}_{\mathrm{MDEA}}}{\bar{c}^0}\right) + A_2 \cdot \left(\frac{\bar{c}_{\mathrm{MDEA}}}{\bar{c}^0}\right)^2 + A_3 \cdot \left(\frac{\bar{c}_{\mathrm{MDEA}}}{\bar{c}^0}\right)^3 + \left[A_4 + A_5 \cdot \left(\frac{\bar{c}_{\mathrm{MDEA}}}{\bar{c}^0}\right) + A_6 \cdot \left(\frac{\bar{c}_{\mathrm{MDEA}}}{\bar{c}^0}\right)^2 + A_7 \cdot \left(\frac{\bar{c}_{\mathrm{MDEA}}}{\bar{c}^0}\right)^3\right] \cdot \left(\frac{\bar{c}_{\mathrm{PZ}}}{\bar{c}^0}\right) + \left[A_8 + A_9 \cdot \left(\frac{\bar{c}_{\mathrm{MDEA}}}{\bar{c}^0}\right) + A_{10} \cdot \left(\frac{\bar{c}_{\mathrm{MDEA}}}{\bar{c}^0}\right)^2 + A_{11} \cdot \left(\frac{\bar{c}_{\mathrm{MDEA}}}{\bar{c}^0}\right)^3\right] \cdot \left(\frac{\bar{c}_{\mathrm{PZ}}}{\bar{c}^0}\right)^2 \quad \text{(A-1)}$$

Coefficient A_0 (i.e., the density of pure water) was taken from Saul and Wagner.[24] All other coefficients A_i were fitted to the experimental density data given in Table A1. The coefficients are given in Table A2. The correlation equation represents the experimental with a standard (maximum) deviation of 0.0001 (0.0006) $\mathrm{g \cdot cm^{-3}}$.

Derks et al. (2008)[25] reported experimental data of the density of aqueous solutions containing both MDEA and piperazine at 293.15 K ($\bar{c}_{\mathrm{MDEA}} = (1, 2, 3, 4)\ \mathrm{mol \cdot dm^{-3}}$; $\bar{c}_{\mathrm{PZ}}$ is varying from (0 to 1) $\mathrm{mol \cdot dm^{-3}}$). These results agree well the new data. The the average relative difference between both data sets is less than 0.03 % and the maximum absolute deviation is 0.0008 $\mathrm{g \cdot cm^{-3}}$.

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Received for review April 7, 2009. Accepted June 8, 2009.

JE9003383