Solubility of Carbon Dioxide in Aqueous Solutions of Piperazine in the Low Gas Loading Region

Viktor Ermatchkov, Álvaro Pérez-Salado Kamps, Dirk Speyer, and Gerd Maurer*

Applied Thermodynamics, University of Kaiserslautern, P.O. Box 30 49, D-67653 Kaiserslautern, Germany

The solubility of carbon dioxide in aqueous solutions of piperazine was determined at low gas loadings (stoichiometric molar ratios of carbon dioxide to piperazine between about 0.05 and 0.95) and temperatures between (313 and 393) K by means of headspace gas chromatography. The stoichiometric molality of piperazine amounted to about (1 and 2) mol·(kg of water)$^{-1}$ {mass fraction of piperazine ≈ (8 and 15) %} at $T \approx 313$ K and to about (2 and 4) mol·(kg of water)$^{-1}$ {mass fraction of piperazine ≈ (15 and 26) % } at $T \approx (353$ and $393)$ K. The partial pressure of carbon dioxide was between about (0.1 and 95) kPa. A thermodynamic model for describing the vapor−liquid equilibrium (which applies Pitzer's molality scale based equation for describing the Gibbs excess energy of the aqueous phase) is revised and extended using the new data.

Introduction

Sour gases such as carbon dioxide and hydrogen sulfide are often removed from natural or synthesis gases by "chemical" absorption in aqueous solutions of single amines (in many cases alkanolamines, such as 2,2′-methyliminodiethanol = *N*-methyldiethanolamine = MDEA) or amine mixtures (e.g., MDEA + piperazine). The competitive chemical absorption of carbon dioxide and hydrogen sulfide is kinetically controlled. However, deviation from equilibrium provides the driving force in such kinetically controlled processes. Hence, the reliable design and optimization of the separation equipment at first requires 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 (around or somewhat above room temperature) and 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 390 K or more) 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, and amine and gas concentrations.

To develop a thermodynamic model to describe the simultaneous solubility of carbon dioxide and hydrogen sulfide in aqueous solutions of MDEA + piperazine, at first reliable experimental information on the solubility of the single gases in aqueous solutions of the single amines is required. The present work concentrates on one of those interesting subsystems, namely, (CO_2 + piperazine + H_2O). The solubility of carbon dioxide in aqueous solutions of piperazine at *high* gas loadings was already investigated in a previous work[1] applying a well-proven and very reliable technique based on the synthetic method.[2−5] That technique allows for the determination of the total pressure required to dissolve a known amount of gas in a known amount of liquid at given temperature and solvent composition. A temperature range from $T \approx (313$ to $393)$ K was covered, stoichiometric piperazine molalities amounted to about (2 and 4) mol·(kg of water)$^{-1}$, and total pressures ranged up to about 9.6 MPa. However, this experimental technique is only suited for investigations at pressures above $p \approx 0.2$ MPa, that is, it is restricted to the so-called high gas loading (elevated pressure) region. Based alone on these experimental results at high gas loadings, a thermodynamic model describing the VLE of the system (CO_2 + piperazine + H_2O) was developed in a previous work.[1] This model is able to predict the gas solubility in the low gas loading region. Prediction results agree favorably with the few (reliable) experimental data found in the literature.[6,7] However, the industrial need persists to assess the prediction results by comparison with more and accurate experimental information in the low gas loading region, in particular also at higher piperazine concentrations and at higher temperatures.

Recently,[8] we applied a headspace gas chromatography technique[9,10] for the reliable determination of the solubility of carbon dioxide in aqueous solutions of MDEA at low gas loadings (cf. also refs 5 and 11). In the present work, these investigations are extended to the solubility of carbon dioxide in aqueous solutions of piperazine at low gas loadings at temperatures $T \approx (313, 353,$ and $393)$ K. The stoichiometric molality of piperazine amounts to about (1 and 2) mol·(kg of water)$^{-1}$ at $T \approx 313$ K and to about (2 and 4) mol·(kg of water)$^{-1}$ at $T \approx (353$ and $393)$ K. Partial pressures of carbon dioxide range from about (0.1 to 95) kPa.

Experimental Section

The experimental arrangement of the headspace gas chromatograph and the experimental procedure have been described in detail before;[8] therefore, no descriptions are given here.

Substances. Carbon dioxide (mole fraction ≥ 99.995 %) was purchased from Messer-Griesheim, Ludwigshafen, Germany. Piperazine (anhydrous, mass fraction ≥ 99 %) was purchased from Sigma-Aldrich (Deisenhofen, Germany) and was degassed under vacuum. Deionized water was degassed by vacuum distillation.

Sample Preparation. The aqueous piperazine solutions (about 1 L) were gravimetrically prepared in a storage tank by

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* Corresponding author. Tel.: +49 631 205 2410. Fax: +49 631 205 3835. E-mail: gmaurer@rhrk.uni-kl.de.

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dissolving known amounts of the amine in water (under vacuum). To avoid the precipitation of solid piperazine, the solutions were thermostated up to $T \approx 323$ K. A known amount of that aqueous piperazine solution (about 0.25 L) was then transferred to a second (evacuated) storage tank (volume ≈ 0.3 L), then charged with carbon dioxide, shaken for a few minutes, and finally thermostated to the respective temperature for about 1 day. The sample cells {stainless steel vials, volume ≈ (11 to 30) cm^3} were then partially filled with that liquid mixture and mounted in the cell holder, where they were thermostated to the desired experimental temperature for about 12 h. As it was confirmed in a series of pre-experiments, this procedure ensured the attainment of thermodynamic equilibrium in both the second storage tank and the sample cells. (Systematic) corrections of the stoichiometric molalities of the gas and the amine were applied to account for the transfer of the sour gas and water to the vapor (in both the second storage tank and the sample cells). Since the vapor phase volumes in those tanks (which were estimated) and the partial pressures of carbon dioxide and water (which were either calculated from the previous VLE model[1] or known from the experiment) are small, the correction of the stoichiometric molality of carbon dioxide is also small {(0.003 to 1.7) %}, and the correction of the stoichiometric molality of piperazine is insignificant (and only due to the vaporization of water, as the saturation pressure of pure piperazine is almost negligible in the temperature range considered here).[12] The relative gravimetrical uncertainty in the stoichiometric molality of piperazine does not surmount ± 0.03 %. The total uncertainty in that molality is estimated to be smaller than ± 0.1 %. The relative uncertainty in the stoichiometric molality of carbon dioxide ranges from about ± 0.04 % (for the higher piperazine and carbon dioxide molalities) up to about ± 0.3 % (for the lower piperazine and carbon dioxide molalities). It was estimated from the filling procedure described before (including all corrections) by means of a Gauss error propagation calculation.

Results

The solubility of carbon dioxide in aqueous solutions of piperazine (PIPH_2) was measured at stoichiometric molalities of piperazine in water of $\tilde{m}_{\text{PIPH}_2} \approx (1 \text{ and } 2)\ \text{mol·kg}^{-1}$ {mass fraction of piperazine ≈ (8 and 15) %} at $T \approx 313$ K and of $\tilde{m}_{\text{PIPH}_2} \approx (2 \text{ and } 4)\ \text{mol·kg}^{-1}$ {mass fraction of piperazine ≈ (15 and 26) %} at $T \approx (353 \text{ and } 393)$ K. The stoichiometric molar ratio of carbon dioxide to piperazine ($\tilde{m}_{\text{CO}_2}/\tilde{m}_{\text{PIPH}_2}$) ranged from about 0.05 to about 0.95. The partial pressure of carbon dioxide (p_{CO_2}) was between about (0.1 and 95) kPa.

The experimental results are listed in Tables 1 to 3. The listings include the experimental uncertainties. The absolute uncertainty in the partial pressure of carbon dioxide is estimated from $\Delta p_{\text{CO}_2} = \pm (\Delta p_{\text{CO}_2}{}^* + 0.02 p_{\text{CO}_2})$. The first contribution accounts for uncertainties in temperature as well as gas and amine molalities. It is determined from a Gauss error propagation calculation (by applying the VLE model described in the next section). The second contribution is the uncertainty of the calibration experiments.[8]

To check the reproducibility of the experimental technique, each experimental data point given in Tables 1 to 3 was repeated 3 to 8 times. Only the averaged experimental results are reported together with the absolute standard deviation from that average numerical value for the partial pressure of carbon dioxide ($\Delta p_{\text{CO}_2,\text{repr}}$). For almost all investigated points, $\Delta p_{\text{CO}_2,\text{repr}}$ is (well) below the estimated experimental uncertainty of the partial pressure of carbon dioxide (Δp_{CO_2}), confirming the reliability of that estimation.

Table 1. Solubility of Carbon Dioxide (2) in Aqueous Solutions of Piperazine (1) at $T = 313.1$ K ($\Delta T = \pm 0.1$ K, $\Delta\tilde{m}_1/\tilde{m}_1 = \pm 0.1$ %)

$\tilde{m}_1$ / mol·kg^{-1}	$\tilde{m}_2$ / mol·kg^{-1}	p_2 / kPa	$\Delta p_{2,\text{repr}}$ / kPa
1.167	0.742 4 ± 0.000 6	0.57 ± 0.02	0.01
1.167	0.785 0 ± 0.000 6	0.85 ± 0.03	0.03
1.167	0.841 4 ± 0.000 6	1.49 ± 0.05	0.11
0.989 0	0.732 4 ± 0.000 5	1.67 ± 0.06	0.04
0.989 0	0.790 2 ± 0.000 6	3.30 ± 0.12	0.12
0.989 0	0.848 1 ± 0.000 8	6.55 ± 0.27	0.05
0.989 0	0.889 ± 0.001	12.62 ± 0.63	0.29
0.989 0	0.911 ± 0.002	17.50 ± 1.08	0.22
1.167	1.103 ± 0.003	30.09 ± 2.43	0.64
1.167	1.105 ± 0.003	30.17 ± 2.49	0.99
2.750	1.319 8 ± 0.000 6	0.115 ± 0.004	0.007
2.750	1.792 9 ± 0.000 7	0.72 ± 0.02	0.02
2.091	1.455 1 ± 0.000 6	1.14 ± 0.04	0.04
2.091	1.642 6 ± 0.000 8	3.60 ± 0.12	0.07
2.750	2.301 ± 0.001	8.67 ± 0.28	0.24
2.044	1.801 ± 0.003	20.41 ± 0.79	0.33
2.091	1.887 ± 0.003	20.56 ± 1.02	0.45
2.044	1.870 ± 0.003	24.22 ± 1.33	0.19
2.044	1.932 ± 0.006	48.42 ± 3.70	1.78

Table 2. Solubility of Carbon Dioxide (2) in Aqueous Solutions of Piperazine (1) at $T = 353.15$ K ($\Delta T = \pm 0.1$ K, $\Delta\tilde{m}_1/\tilde{m}_1 = \pm 0.1$ %)

$\tilde{m}_1$ / mol·kg^{-1}	$\tilde{m}_2$ / mol·kg^{-1}	p_2 / kPa	$\Delta p_{2,\text{repr}}$ / kPa
2.281	0.306 3 ± 0.000 7	0.111 ± 0.003	0.001
2.281	0.702 2 ± 0.000 6	0.87 ± 0.02	0.02
2.281	1.146 0 ± 0.000 7	3.58 ± 0.10	0.14
2.156	1.169 6 ± 0.000 8	5.60 ± 0.16	0.24
2.156	1.347 ± 0.001	10.82 ± 0.33	0.22
2.156	1.466 ± 0.002	18.36 ± 0.60	0.30
1.969	1.425 ± 0.003	25.62 ± 0.99	0.49
1.969	1.450 ± 0.003	28.42 ± 1.16	0.42
1.969	1.504 ± 0.004	37.95 ± 1.78	0.90
3.950	0.611 7 ± 0.000 6	0.154 ± 0.004	0.009
3.950	1.090 1 ± 0.000 8	0.48 ± 0.01	0.01
3.950	1.586 9 ± 0.000 7	1.53 ± 0.04	0.06
4.168	2.197 6 ± 0.000 8	4.47 ± 0.13	0.15
4.168	2.400 ± 0.001	6.86 ± 0.20	0.11
4.168	2.571 ± 0.001	10.15 ± 0.29	0.42
4.199	2.874 ± 0.002	19.85 ± 0.59	0.15
4.199	3.039 ± 0.004	31.40 ± 0.98	1.34
4.199	3.391 ± 0.010	77.63 ± 3.64	2.06

Table 3. Solubility of Carbon Dioxide (2) in Aqueous Solutions of Piperazine (1) at $T = 393.15$ K ($\Delta T = \pm 0.1$ K, $\Delta\tilde{m}_1/\tilde{m}_1 = \pm 0.1$ %)

$\tilde{m}_1$ / mol·kg^{-1}	$\tilde{m}_2$ / mol·kg^{-1}	p_2 / kPa	$\Delta p_{2,\text{repr}}$ / kPa
2.046	0.193 6 ± 0.000 6	1.15 ± 0.03	0.01
2.013	0.412 2 ± 0.000 6	4.81 ± 0.13	0.02
2.013	0.550 5 ± 0.000 7	8.93 ± 0.23	0.14
2.046	0.674 5 ± 0.000 9	13.94 ± 0.37	0.08
2.046	0.890 ± 0.002	29.14 ± 0.81	0.61
2.013	0.973 ± 0.002	41.23 ± 1.22	0.15
3.837	0.199 4 ± 0.000 6	0.534 ± 0.013	0.002
4.443	0.324 7 ± 0.000 7	0.90 ± 0.02	0.02
3.972	0.503 8 ± 0.000 7	2.18 ± 0.05	0.01
3.972	0.884 1 ± 0.000 7	5.99 ± 0.14	0.02
3.837	1.130 8 ± 0.000 9	10.94 ± 0.27	0.16
4.443	1.787 ± 0.001	25.32 ± 0.62	0.16
3.837	1.841 ± 0.002	42.93 ± 1.14	0.60
4.443	2.177 ± 0.003	46.93 ± 1.23	0.85
3.972	2.337 ± 0.006	95.30 ± 3.05	3.32

In Figure 1 as well as in Figures 2a and 3a, the experimental results for the partial pressure of carbon dioxide (open symbols) are plotted versus the stoichiometric molar ratio of carbon dioxide to piperazine at preset temperature and stoichiometric piperazine molality of approximately (1, 2, and 4) mol·(kg of water)$^{-1}$, respectively. When the sour gas carbon dioxide is

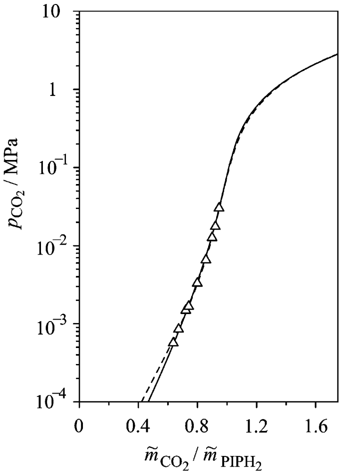

Figure 1. Partial pressure of carbon dioxide above liquid mixtures of (CO_2 + piperazine + H_2O), $\tilde{m}_{PIPH_2} \approx 1$ mol·kg^{-1}, $T = 313.1$ K: △, experimental results, this work; —, correlation results (parameter set II); - - -, prediction results (parameter set I).

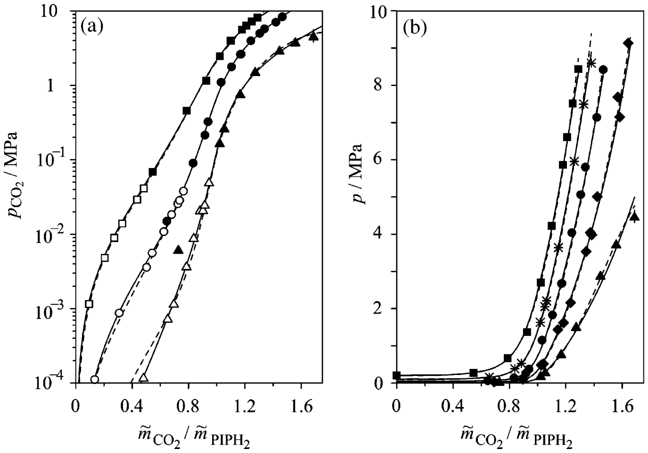

Figure 2. Partial pressure of carbon dioxide (a) and total pressure (b) above liquid mixtures of (CO_2 + piperazine + H_2O), $\tilde{m}_{PIPH_2} \approx 2$ mol·kg^{-1}. Experimental results, this work: △, $T = 313.1$ K; ○, $T = 353.15$ K; □, $T = 393.15$ K. Experimental results from Pérez-Salado Kamps et al.[1] (after applying a small temperature correction, cf. Appendix): ▲, $T = 313.75$ K {solid triangle with vertical bar denotes one experimental point where the precipitation of a solid phase was observed}; ◆, $T = 334.05$ K; ●, $T = 354.35$ K; ∗, $T = 374.65$ K; ■, $T = 395$ K. —, correlation results (parameter set II). - - -, correlation/prediction results (parameter set I).

added to an aqueous solution of piperazine, the total pressure at first only very slightly increases with increasing amount of the gas in the liquid. This is due to the basic character of piperazine as well as to the negligibly small saturation pressure of the pure amine. In particular, the partial pressure of carbon dioxide at first (i.e., for low gas loadings $\tilde{m}_{CO_2}/\tilde{m}_{PIPH_2}$) is very small, that is, carbon dioxide is almost completely dissolved chemically (i.e., in nonvolatile ionic form). But it increases rapidly (for higher gas loadings) when, in the liquid phase, piperazine has been spent by chemical reactions, and the sour gas can no longer be absorbed chemically but has to be dissolved physically (cf. also ref 1).

Thermodynamic Modeling of the Vapor−Liquid Equilibrium

A detailed description of the model applied to correlate and predict the solubility of carbon dioxide in aqueous solutions of piperazine can be found in a previous publication.[1] Only a short outline is repeated here.

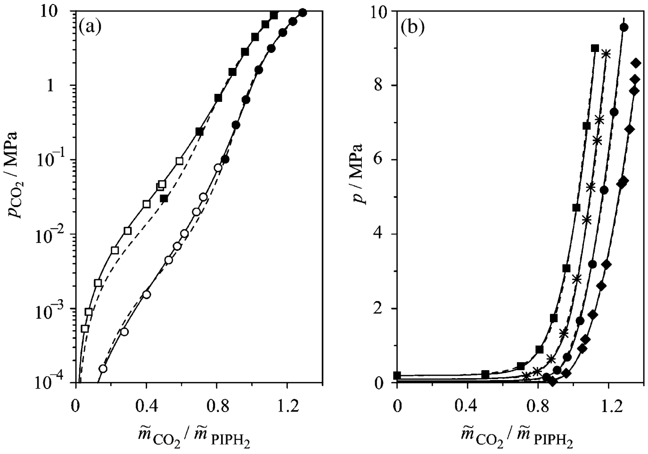

Figure 3. Partial pressure of carbon dioxide (a) and total pressure (b) above liquid mixtures of (CO_2 + piperazine + H_2O), $\tilde{m}_{PIPH_2} \approx 4$ mol·kg^{-1}. Experimental results, this work: ○, $T = 353.15$ K; □, $T = 393.15$ K. Experimental results from Pérez-Salado Kamps et al.[1] (after applying a small temperature correction, cf. Appendix): ◆, $T = 334.05$ K; ●, $T = 354.35$ K; ∗, $T = 374.7$ K; ■, $T = 395$ K. —, correlation results (parameter set II). - - -, correlation/prediction results (parameter set I).

Due to chemical reactions, the liquid phase contains carbon dioxide and piperazine not only in volatile (i.e., neutral) but also in nonvolatile, ionic form. The following (reversible) chemical reactions are considered in the liquid phase:

autoprotolysis of water:

$$H_2O \rightleftharpoons H^+ + OH^- \tag{I}$$

formation of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}):

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \tag{II}$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \tag{III}$$

first protonation and second protonation of piperazine:

$$PIPH_2 + H^+ \rightleftharpoons PIPH_3^+ \tag{IV}$$

$$PIPH_3^+ + H^+ \rightleftharpoons PIPH_4^{2+} \tag{V}$$

and formation of three carbamate species (piperazine carbamate, piperazine dicarbamate, and protonated piperazine carbamate):

$$PIPH_2 + HCO_3^- \rightleftharpoons PIPHCOO^- + H_2O \tag{VI}$$

$$PIPHCOO^- + HCO_3^- \rightleftharpoons PIP(COO^-)_2 + H_2O \tag{VII}$$

$$PIPHCOO^- + H^+ \rightleftharpoons PIPH_2^+COO^- \tag{VIII}$$

The condition for chemical equilibrium for a chemical reaction r (= I, ..., VIII) is

$$K_r(T) = \prod_i a_i^{\nu_{i,r}} \tag{1}$$

The influence of pressure on a chemical reaction equilibrium constant (K_r) is neglected. The term a_i is the activity of species i. Only water is treated as a solvent species. Piperazine, carbon dioxide, and the ions are treated as solute species. The reference state for the chemical potential of water is the pure liquid at systems temperature and pressure, whereas for the chemical potential of a solute species it is the one molal solution of that solute in pure water at systems temperature and pressure, the solute experiencing the same interactions as infinitely diluted in pure water. $\nu_{i,r}$ is the stoichiometric factor of reactant i in reaction r ($\nu_{i,r} > 0$ for a product and $\nu_{i,r} < 0$ for an educt).

The balance equation for the amounts of substance (the number of moles) of a species i in the liquid solution is

$$n_i = \tilde{n}_i + \sum_r \nu_{i,r}\xi_r \qquad (2)$$

where ξ_r is the extent of reaction r. Solving this set of equations for a given temperature and given stoichiometric amounts of substances (number of moles) $\tilde{n}_i$ of components H_2O, $PIPH_2$, and CO_2 results in the speciation, that is, the "true" composition of the liquid phase (the amount of substance n_i of all species present).

The VLE condition results in the extended Henry's law for carbon dioxide:

$$k_{H,CO_2} \exp\left[\frac{\upsilon^{\infty}_{CO_2}(p - p^{s}_{W})}{RT}\right] a_{CO_2} = y_{CO_2}\, p\phi_{CO_2} \qquad (3)$$

and in the extended Raoult's law for water:

$$p^{s}_{W}\phi^{s}_{W} \exp\left[\frac{\upsilon_{W}(p - p^{s}_{W})}{RT}\right] a_{W} = y_{W}\, p\phi_{W} \qquad (4)$$

$k_{H,CO_2}(T)$ is Henry's constant of carbon dioxide in pure water (based on the molality scale) at the vapor pressure of pure water $\{p^{s}_{W}(T)\}$. $\upsilon^{\infty}_{CO_2}(T)$ and $\upsilon_W(T)$ are the partial molar volume of carbon dioxide infinitely diluted in water and the molar volume of pure liquid water, respectively. The influence of pressure on these properties is neglected here. (R is the universal gas constant.) The virial equation of state, which was truncated after the second virial coefficient, was used to calculate the vapor phase fugacity coefficient of component i, ϕ_i.

In principle, piperazine might also be present in the vapor phase. However, as the saturation pressure of pure piperazine is small in the temperature range considered here,[12] its presence in the vapor phase is neglected. From eqs 3 and 4, the total pressure p and the vapor phase composition (y_i is the vapor phase mole fraction of component i) are calculated (after the speciation in the liquid has been calculated).

Activities are calculated from Pitzer's molality scale based equation for the excess Gibbs energy (G^{E}) of aqueous electrolyte solutions[13,14] (cf. Appendix I to Ermatchkov et al.[8]). The activity of a solute species i follows from

$$a_i = \frac{m_i}{m^{\circ}}\gamma_i \qquad (5)$$

where m_i is the molality of solute species i (i.e., the number of moles n_i of this species i per kg of water):

$$\frac{m_i}{m^{\circ}} = \frac{n_i}{M^{*}_{W} n_W} \qquad (6)$$

and $m^{\circ} = 1\ \mathrm{mol{\cdot}kg^{-1}}$. $M_W{}^*$ is the relative molar mass of water divided by 1000 ($M_W{}^* = 0.018\,015\,28$), and n_W is the true number of moles of water.

The activity coefficient of a solute species γ_i (on the molality scale) is directly calculated from that G^{E} equation, whereas the activity of water a_W is calculated from the activity coefficients of all solute species by applying the Gibbs−Duhem equation.

As it was already mentioned in previous work,[8,15,16] when Pitzer's G^{E} equation is applied to chemical reacting systems, it is much easier to use the general equations for the activity coefficient of a solute species (and for the activity of water) as a function of the interaction parameters $\beta^{(0)}_{ij}$, $\beta^{(1)}_{ij}$, $\beta^{(2)}_{ij}$, and μ_{ijk} rather than using rearranged equations as a function of comprehensive parameters (e.g., C^{ϕ}_{MX}, $B^{(0)}_{G,MX}$, $\Gamma_{G,MX,MX}$, $\Gamma_{G,G,MX}$, cf. Appendix I to ref 8). This does not increase the amount of independent parameters and drastically simplifies the computer codes. Such a procedure was also applied in the present work.

Required Thermodynamic Properties. Chemical reaction equilibrium constants (on the molality scale) were adopted from the literature (K_{I} from ref 17, K_{II} from ref 18, K_{III} from ref 19, K_{IV} and K_{V} from ref 20, and K_{VI} to K_{VIII} from ref 21). Henry's constant for carbon dioxide in water $k_{H,CO_2}(T)$ (on the molality scale) was taken from ref 3. The vapor pressure of water was taken from ref 22. The molar volume of liquid water was approximated by the molar volume of saturated liquid water, which was also taken from ref 22. The partial molar volume of carbon dioxide infinitely diluted in water, $\upsilon^{\infty}_{CO_2}$, was calculated as recommended by Brelvi and O'Connell[23] (cf. also ref 24). Pure component second virial coefficients B_{CO_2,CO_2} and B_{H_2O,H_2O} were calculated from a correlation based on data recommended by Dymond and Smith.[25] The mixed second virial coefficient B_{CO_2,H_2O} was calculated as recommended by Hayden and O'Connell.[26] Details on all required thermodynamic properties were given previously.[24,27,28]

Interaction Parameters in Pitzer's G^{E} Model

Binary Systems ($CO_2 + H_2O$) and (Piperazine + H_2O). When one of the single components CO_2 or piperazine is dissolved in pure water, with the exception of very dilute solutions, chemical reactions can be neglected. Thus, from experimental results on the VLE of an aqueous solution of one of the mentioned solute components, only parameters describing interactions between the single neutral solute components (either CO_2 or piperazine) in water can be determined. However, in the pressure region of interest in the absorption/desorption processes, parameters for interactions between CO_2 in water can be neglected.[3] Furthermore, all parameters for interactions between piperazine in water were neglected because their influence on the partial pressure of carbon dioxide above liquid mixtures of (CO_2 + piperazine + H_2O) in the low gas loading region as well as on the total pressure above those mixtures in the high gas loading region is insignificant—at least in the amine concentration regions, which are important for the absorption/desorption processes.

Ternary System (CO_2 + Piperazine + H_2O). In previous work[21] we presented experimental results from ^{1}H NMR spectroscopic investigations on aqueous solutions of carbon dioxide and piperazine at temperatures ranging from (283 to 333) K. The investigated aqueous solutions with fixed stoichiometric piperazine molality {ranging from 0.1 to 1.5 mol·(kg of water)$^{-1}$} were loaded with up to 1 mol of carbon dioxide per mol of piperazine. The experimental results for the speciation {i.e., for the amounts of substance of (molecular piperazine + protonated piperazine + diprotonated piperazine), (piperazine carbamate + protonated piperazine carbamate), and piperazine dicarbamate} were used to determine the (temperature dependent) chemical equilibrium constants for the formation of piperazine carbamate, piperazine dicarbamate and protonated piperazine carbamate. For that purpose and because the molal ionic strength was always less than one, in Pitzer's G^{E} equation only the modified Debye−Hückel term was considered (i.e., all interaction parameters were set to zero). Under these premises, the model was able to reproduce the experimental results for the number of moles of (molecular piperazine +

protonated piperazine + diprotonated piperazine), (piperazine carbamate + protonated piperazine carbamate), and piperazine dicarbamate in 1 kg of water with an average absolute (relative) deviation of (0.019, 0.024, and 0.014) mol {(4, 9.9, and 25.5) %}, respectively. In particular, the concentrations of piperazine and carbon dioxide in water were rather low in those spectroscopic investigations. In that low concentration region, Pitzer's parameters do not have an essential influence on the evaluation results for the chemical equilibrium constants for the carbamate formations. Therefore, these results are adopted here without any re-evaluation.

However, the partial pressure of carbon dioxide above a liquid mixture of (CO_2 + piperazine + H_2O) is proportional to the activity (i.e., to the product of the true molality and the activity coefficient) of carbon dioxide in that liquid (cf. eqs 3 and 5). Consequently, that activity is not only strongly influenced by the chemical reaction equilibrium, but also by the physical interactions between the solute species (in particular between molecular carbon dioxide on one side and the other solute species on the other side). Therefore, the gas solubity data can be used to determine the interaction parameters in Pitzer's equation. And it is preferable to experimentally investigate the solubility of carbon dioxide in aqueous solutions of piperazine at relative high stoichiometric amine molalities (up to 4 $mol\cdot kg^{-1}$ at the higher temperatures) not only because such high piperazine concentrations are common in the absorption/desorption processes but also because the interaction parameters can much more reliably be determined at those high concentrations.

Predictions from the Previous Model. As it was already mentioned, the previous model[1] for the VLE of the system (CO_2 + piperazine + H_2O) was based alone on experimental gas solubility data at high gas loadings from Pérez-Salado Kamps et al.[1] {at $\tilde{m}_{PIPH_2} \approx$ (2 and 4) $mol\cdot kg^{-1}$}. However, a recalibration of the platinum resistance thermometers used in that work showed that a small correction had to be applied to the temperature values. The corrected temperatures are calculated from $T = T_{old} + \Delta T$, where $\Delta T \approx$ (0.6, 0.9, 1.2, 1.5, and 1.8) K at $T_{old} \approx$ (313.15, 333.15, 353.15, 373.15, and 393.15) K, respectively. Therefore, in the previous model, a small correction had to be applied also to the temperature-dependent interaction parameters in Pitzer's G^E equation. For better clarity, both the corrected experimental results for the solubility of carbon dioxide in (piperazine + H_2O) by Pérez-Salado Kamps et al.[1] and the corrected interaction parameters of the previous model for the VLE of the system (CO_2 + piperazine + H_2O) are listed in the Appendix. That corrected parameter set is here referred to as parameter set I. {The experimental results for the solubility of hydrogen sulfide in (piperazine + H_2O) reported by Xia et al.[29] had to be corrected as well and are also listed in that Appendix together with the corrected interaction parameters of the previous model for the VLE of the system (H_2S + piperazine + H_2O).}

In Figure 2b and Figure 3b, the corrected experimental results for the total pressure by Pérez-Salado Kamps et al.[1] are plotted versus the stoichiometric molar ratio of carbon dioxide to piperazine ($\tilde{m}_{CO_2}/\tilde{m}_{PIPH_2}$) at preset temperature and stoichiometric piperazine molality of about (2 and 4) $mol\cdot(kg\ of\ water)^{-1}$, respectively. In addition, and just to visually corroborate the consistency of the whole database in both the high and the low gas loading regions, Figure 2a and Figure 3a include the partial pressures of carbon dioxide in the high gas loading region {at $T \approx$ (313.7, 354.4, and 395) K}, as calculated from the (corrected) experimental total pressures[1] by subtracting the (small) partial pressure of water, as predicted from the model.

Table 4. Interaction Parameters (Set II) in Pitzer's G^E Equation for the System (CO_2 + Piperazine + H_2O):[a]

$$f(T) = q_1 + \frac{q_2}{(T/K)}$$

parameter	q_1	q_2	T/K
$\beta^{(0)}_{PIPH_3^+,HCO_3^-}$	0.28872	−120.03	313−393
$\beta^{(1)}_{PIPH_3^+,HCO_3^-}$	3.9469	−1 343.3	
$\beta^{(0)}_{PIPH_2^+COO^-,PIPH_2^+COO^-}$	1.0378	−397.18	
$\beta^{(1)}_{PIPH_2^+COO^-,PIPH_2^+COO^-}$	3.1375	−858.12	
$\beta^{(0)}_{PIPH_3^+,PIPHCOO^-}$	−0.19873	125.37	
$\beta^{(0)}_{PIPH_3^+,PIP(COO^-)_2}$	4.9494	−1422.8	
$\beta^{(0)}_{PIPH_3^+,PIPH_2^+COO^-}$	−1.2915	445.15	
$\beta^{(0)}_{CO_2,PIPH_3^+}$	−0.77195	211.23	
$\beta^{(0)}_{CO_2,PIPH_2^+COO^-}$	1.9421	−611.22	
$\beta^{(0)}_{PIPH_2,PIPHCOO^-}$	0.34964	−83.169	

[a] The parameter set is based on CO_2 gas solubility data in (piperazine + H_2O) from ref 1 (after applying a small temperature correction, cf. Appendix) and from this work.

As can be seen from Figures 1 to 3, the previous model (parameter set I, dashed curves) is able to predict the new experimental results for the partial pressure of carbon dioxide above (CO_2 + piperazine + H_2O) in the low gas loading region. The average relative (absolute) deviation between experimental and prediction results for p_{CO_2} amounts to 18.4 % (3.7 kPa) {3.5 % (0.16 kPa), 13.6 % (1.6 kPa), and 33 % (8.3 kPa) at $\tilde{m}_{PIPH_2} \approx$ (1, 2, and 4) $mol\cdot kg^{-1}$, respectively}.

New Correlation. However, to achieve an even better agreement between the new experimental results and the model calculation results for the partial pressure of carbon dioxide above (CO_2 + piperazine + H_2O) in the low gas loading region, in particular at the higher amine concentrations and at the highest investigated temperature (see Figure 3a), a new set of interaction parameters was determined (parameter set II, cf. Table 4). It was adjusted to the gas solubility data in both the low gas loading region (data from the present work) and the high gas loading region (corrected data by Pérez-Salado Kamps et al.[1]). In an optimization procedure, the difference between experimental and calculated results for the partial pressure of carbon dioxide and for the total pressure above (CO_2 + piperazine + H_2O) (in the low and high gas loading regions, respectively) was minimized. The model accurately (almost within the estimated experimental uncertainty) describes the experimental results for the solubility of CO_2 in aqueous solutions of piperazine for low as well as high gas loadings (cf. Figures 1 to 3, full curves). With parameter set II, the average relative (absolute) deviation between experimental and correlation results for p_{CO_2} (at low gas loadings) amounts to 5.1 % (0.72 kPa) {3.1 % (0.37 kPa), 6.8 % (0.82 kPa), and 4 % (0.76 kPa) at $\tilde{m}_{PIPH_2} \approx$ (1, 2, and 4) $mol\cdot kg^{-1}$, respectively}. The agreement between experimental and correlation results for the total pressure p (at high gas loadings) is as good as with parameter set I. With parameter set II, the average relative (absolute) deviation between experimental and correlation results for p (disregarding data points at pressures below 0.2 MPa with relatively high experimental uncertainties as well as one experimental point, where the precipitation of a solid phase was observed)[1] amounts to 3.0 % (86 kPa) {3.4 % (94 kPa) and 2.4 % (76 kPa) at $\tilde{m}_{PIPH_2} \approx$ (2 and 4) $mol\cdot kg^{-1}$, respectively}, whereas, with parameter set I, those deviations amount to 3.0 % (100 kPa) {3.1 % (103 kPa) and 2.9 % (96 kPa) at $\tilde{m}_{PIPH_2} \approx$ (2 and 4) $mol\cdot kg^{-1}$, respectively} (see also Table 5).

Table 5. Comparison between Experimental Data from the Literature for the Total and/or Partial Pressure above Aqueous Solutions of Piperazine (1) and Carbon Dioxide (2) and Calculation Results from the Present Model

		experimental ranges					mean relative deviations							
							parameter set II				parameter set I			
		T	$\tilde{m}_1$	$\tilde{m}_2$	p	p_2	$\|\Delta p/p\|$	$\|\Delta p\|$	$\|\Delta p_2/p_2\|$	$\|\Delta p_2\|$	$\|\Delta p/p\|$	$\|\Delta p\|$	$\|\Delta p_2/p_2\|$	$\|\Delta p_2\|$
source	N	K	mol·kg^{-1}	mol·kg^{-1}	kPa	kPa	%	kPa	%	kPa	%	kPa	%	kPa
						Correlation								
ref 1[a]	95	314−395	2.0−4.0	0−5.4	13−9 560		3.0[b]	86[b]			3.0[b]	100[b]		
this work	52	313−393	1.0−4.4	0.2−3.4		0.1−95.3			5.1	0.72				
						Prediction								
this work	52	313−393	1.0−4.4	0.2−3.4		0.1−95.3							18.4	3.7
ref 6	17	313−343	0.63	0.1−0.6		0.03−40			17.6	1.13			18.3	1.11
ref 30	140	293−323	0.1−1.1	0.1−1.4		0.9−95.6			1265	166			1216	158
ref 7	58	298−343	0.2−0.63	0.1−0.7		0.3−111			25.4	3.9			31.6	4.4

[a] A small temperature correction was applied to the experimental data by Pérez-Salado Kamps et al.,[1] cf. Appendix. [b] Only the data at $p > 0.2$ MPa (with no solid-phase precipitation) were considered for calculating those mean relative deviations.

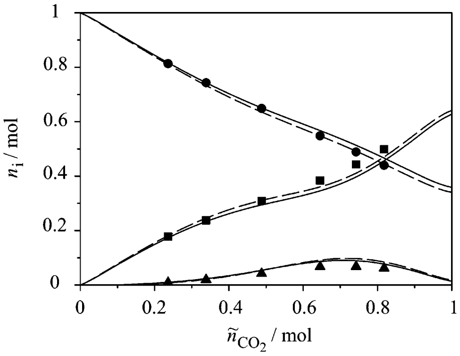

Figure 4. Speciation in mixtures of (CO_2 + piperazine + deuterium oxide) at $T = 298$ K ($\tilde{n}_{PIPH_2} \approx 1$ mol and the stoichiometric amount of mass of water was 1 kg). Symbols denote results from ^1H NMR measurements by Ermatchkov et al.:[21] ●, molecular piperazine + protonated piperazine + diprotonated piperazine; ■, piperazine carbamate + protonated piperazine carbamate; ▲, piperazine dicarbamate. - - -, correlation results from Ermatchkov et al.[21] (based on the Debye−Hückel term alone). —, calculation results (parameter set II).

It might also be noted that, by applying parameter set II, the model reproduces the experimental results for the speciation {number of moles of (molecular piperazine + protonated piperazine + diprotonated piperazine), (piperazine carbamate + protonated piperazine carbamate), and piperazine dicarbamate in 1 kg of water} from the aforementioned spectroscopic investigations with an average absolute (relative) deviation of (0.023, 0.031, and 0.014) mol {(4.3, 11.4, and 25.8) %}, respectively (cf. also Figure 4). (The deviations are about the same if parameter set I is used: (0.028, 0.036, and 0.014) mol {(5.4, 14.6, and 24.5) %, respectively.) As expected, those deviations are only insignificantly lower, when all interaction parameters are set to zero.

Comparison with Literature Data

Table 5 reports mean relative and absolute deviations between experimental results for the total pressure and/or the partial pressure of carbon dioxide above liquid mixtures of (CO_2 + piperazine + H_2O) taken from the literature[1,6,7,30] as well as from the present work and correlation/prediction results from the present model (parameter set II) as well as from the previous model (parameter set I). Table 5 also reports the experimental ranges (for the temperature, the stoichiometric molalities of piperazine and carbon dioxide, and the partial pressure of carbon dioxide) of all those investigations. Apart from our own data (ref 1 and this work), not very much experimental information for the solubility of carbon dioxide in aqueous piperazine solutions is available in the open literature.[6,7,30] These investigations cover a temperature range from (293 to 343) K and are all restricted to the low amine loading (low pressure) region. However, the stoichiometric molality of piperazine in the investigated solutions is rather low (0.63 mol·kg^{-1} in ref 6, (0.1 to 1.09) mol·kg^{-1} in ref 30, and (0.2 to 0.63) mol·kg^{-1} in ref 7). The solubility data by Bishnoi and Rochelle[6] and by Derks et al.[7] reasonably agree with prediction results from our model (with both parameter sets) (see also Figure 5). The solubility data reported in ref 30 extremely disagree with all other literature data and with prediction results from our model.

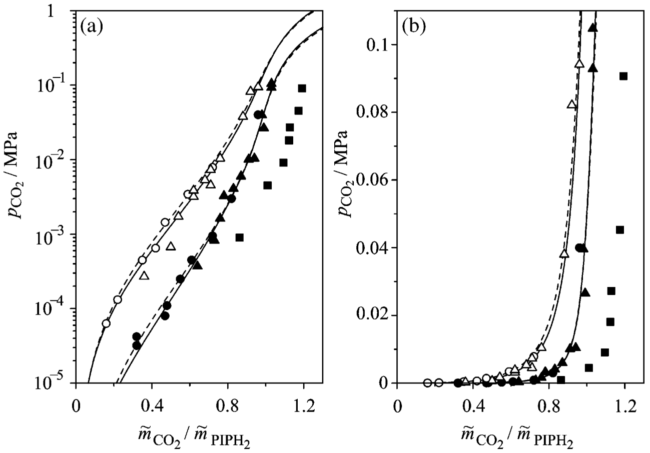

Figure 5. Partial pressure of carbon dioxide above liquid mixtures of (CO_2 + piperazine + H_2O), $\tilde{m}_{PIPH_2} \approx 0.63$ mol·kg^{-1}. Experimental results: Bishnoi and Rochelle:[6] ●, $T = 313$ K; ○, $T = 343$ K. Aroua and Mohd Salleh:[30] ■, $T = 313.15$ K. Derks et al.:[7] ▲, $T = 313.15$ K; △, $T = 343.15$ K. —, prediction results (parameter set II). - - -, prediction results (parameter set I).

Conclusions

Modeling the phase equilibrium for the simultaneous solubility of carbon dioxide and hydrogen sulfide in aqueous solutions of MDEA + piperazine requires a reliable and extensive experimental database on the solubility of the single gases in aqueous solutions of the single amines. However, for the subsystem (CO_2 + piperazine + H_2O), there was very little experimental information for the gas solubility available in the open literature. In an attempt to extend that database, the solubility of carbon dioxide in aqueous solutions of piperazine was investigated in previous work[1] by means of a technique based on the synthetic method. A temperature range from ≈ (313.7 to 395) K was covered, piperazine molalities amounted to ≈ (2 and 4) mol·(kg of water)$^{-1}$, and total pressures ranged from ≈ (0.2 to 9.6) MPa. That method is restricted to the *high* gas loading/elevated pressure region ($p > 0.2$ MPa). In the present work headspace gas chromatography is applied for the reliable determination of the solubility of carbon dioxide in aqueous solutions of piperazine at *low* gas loadings. The temperature ranges from $T \approx (313 \text{ to } 393)$ K. The stoichiometric molality of piperazine reaches up to about 4 mol·(kg of water)$^{-1}$. Partial pressures of carbon dioxide range from about (0.1 to 95) kPa.

A previously presented thermodynamic model for describing the phase equilibrium of the system (CO_2 + piperazine + H_2O), which was solely based on the gas solubility data in the high gas loading region,[1] is now extended allowing for the new experimental results in the low gas loading region.

Appendix

(I) Corrected Experimental Results from Ref 1 for the System (CO_2 + Piperazine + H_2O). The corrected experimental results for the solubility of CO_2 in (piperazine + H_2O) and the corrected interaction parameters of the previous model for the VLE of that system are given in Tables 6 and 7, respectively.

Table 6. Solubility of Carbon Dioxide (2) in Aqueous Solutions of Piperazine (1)[a]

T	$\tilde{m}_1$	$\tilde{m}_2$	p	$\tilde{m}_2$	p
K	mol·kg^{-1}	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa
313.75	1.995	1.452	0.0133	2.540	1.486
		2.037	0.1707	2.884	2.859
		2.102	0.2652	3.107	3.702
		2.328	0.7535	3.366	4.446[b]
334.05	1.995	1.380	0.0308	2.462	2.158
		1.785	0.1016	2.681	3.533
		2.077	0.5144	2.762	3.978
		2.361	1.616	3.157	7.147
334.05	2.035	2.088	0.4820	2.897	5.007
		2.327	1.435	3.194	7.683
		2.796	4.039	3.342	9.131
354.35	1.995	1.289	0.0630	2.339	2.678
		1.661	0.1385	2.480	4.038
		1.830	0.2627	2.606	5.062
		1.874	0.3736	2.671	5.801
		2.058	1.151	2.834	7.137
		2.205	1.827	2.924	8.421
		2.333	2.670		
374.65	2.035	1.336	0.1556	2.164	2.206
		1.704	0.3851	2.335	3.636
		1.801	0.5257	2.564	5.952
		2.073	1.630	2.700	7.492
		2.140	2.053	2.811	8.592
395.0	2.035	0	0.2021	2.239	4.222
		1.109	0.2740	2.400	5.859
		1.602	0.6650	2.464	6.605
		1.882	1.370	2.540	7.510
		2.080	2.699	2.623	8.433
334.05	3.964	3.495	0.0428	5.047	5.346
		3.805	0.2575	5.093	5.435
		4.165	0.9225	5.229	6.820
		4.235	1.170	5.332	7.852
		4.400	1.832	5.349	8.160
		4.592	2.609	5.369	8.598
		4.708	3.185		
354.35	3.964	3.359	0.1487	4.395	3.187
		3.600	0.3404	4.656	5.182
		3.827	0.6899	4.882	7.279
		4.114	1.666	5.102	9.560
374.7	3.950	2.895	0.1756	4.250	4.384
		3.144	0.3054	4.337	5.258
		3.450	0.6459	4.483	6.523
		3.735	1.331	4.535	7.080
		4.028	2.787	4.683	8.846
395.0	3.950	0	0.1876	3.794	3.076
		1.981	0.2325	4.017	4.712
		2.772	0.4472	4.249	6.906
		3.192	0.8936	4.436	8.999
		3.514	1.741		

[a] Experimental results from ref 1 (after applying a small temperature correction) [b] The precipitation of a solid phase was observed.

Table 7. Interaction Parameters (Set I) in Pitzer's G^{E} equation for the System (CO_2 + Piperazine + H_2O):[a]

$$f(T) = q_1 + \frac{q_2}{(T/\mathrm{K})}$$

parameter	q_1	q_2	T/K
$\beta^{(0)}_{\mathrm{CO_2,HCO_3^-}}$[b]	−0.016 572	49.690	313−413
$\beta^{(0)}_{\mathrm{PIPH_3^+,HCO_3^-}}$	−0.078 520	41.644	313−393
$\beta^{(1)}_{\mathrm{PIPH_3^+,HCO_3^-}}$	15.211	−4 616.7	
$\beta^{(0)}_{\mathrm{PIPH_2^+COO^-,PIPH_2^+COO^-}}$	0.45950	−185.51	
$\beta^{(1)}_{\mathrm{PIPH_2^+COO^-,PIPH_2^+COO^-}}$	−2.7955	1 042.7	
$\beta^{(0)}_{\mathrm{PIPH_3^+,PIPHCOO^-}}$	−3.5012	1 345.9	
$\beta^{(0)}_{\mathrm{PIPH_3^+,PIP(COO^-)_2}}$	3.7694	−699.54	
$\beta^{(0)}_{\mathrm{PIPH_3^+,PIPH_2^+COO^-}}$	−2.5491	814.39	
$\beta^{(0)}_{\mathrm{CO_2,PIPH_3^+}}$	1.6742	−702.62	
$\beta^{(0)}_{\mathrm{CO_2,PIPH_2^+COO^-}}$	−0.33897	122.49	

[a] The parameter set is based on CO_2 gas solubility data in (piperazine + H_2O) from ref 1 (after applying a small temperature correction). [b] Parameter adopted from Ermatchkov et al. (parameter set I in that work).[8]

Table 8. Solubility of Hydrogen Sulfide (3) in Aqueous Solutions of Piperazine (1)[a]

T	$\tilde{m}_1$	$\tilde{m}_3$	p	$\tilde{m}_3$	p
K	mol·kg^{-1}	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa
313.75	1.981	2.151	0.1892	4.131	2.131
		2.672	0.6358	4.690	2.804
		3.195	1.161	4.704	2.825
		3.871	1.863	5.568	2.849[b]
		4.019	1.999	5.878	2.862[b]
334.05	1.981	2.156	0.3051	3.890	2.810
		2.221	0.4000	4.421	3.678
		2.848	1.250	4.524	3.877
		3.580	2.312	4.806	4.280[b]
		3.855	2.737	5.513	4.299[b]
354.4	1.982	1.865	0.1363	4.125	4.333
		2.087	0.3560	4.671	5.661
		2.259	0.6198	4.815	6.033
		2.676	1.365	4.911	6.245[b]
		3.326	2.659	5.589	6.248[b]
		3.888	3.803		
374.65	1.982	1.513	0.1543	4.007	5.169
		1.837	0.2701	4.642	7.027
		2.065	0.5329	4.771	7.536
		2.415	1.233	5.083	8.593[b]
		3.337	3.372	6.154	8.604[b]
		3.645	4.164		
395.0	1.991	0	0.2002	3.916	5.701
		1.188	0.2502	4.165	6.516
		1.849	0.4949	4.409	7.325
		2.237	1.150	4.417	7.356
		2.689	2.302	4.697	8.358
		3.170	3.585		
334.05	3.945	3.909	0.1586	5.999	2.271
		4.067	0.2795	6.878	3.232
		4.153	0.3673	7.424	3.945
		5.179	1.353	8.508	4.334[b]
		5.457	1.649	8.893	4.330[b]
		5.807	2.006		
354.4	3.945	3.782	0.2395	7.111	5.201
		4.132	0.5291	7.153	5.262
		4.399	0.808 7	7.597	6.081
		4.927	1.415	7.635	6.057
		5.305	2.011	8.470	6.216[b]
		6.263	3.645	8.629	6.228[b]
374.7	3.974	3.158	0.1976	5.843	3.926
		3.606	0.3024	6.848	6.270
		4.022	0.6260	7.669	8.179
		4.687	1.514	8.999	8.732[b]
		4.959	2.036	9.406	8.748[b]
395.0	3.974	0	0.1916	5.124	3.067
		2.404	0.2645	5.705	4.343
		3.398	0.4782	6.158	5.647
		4.100	1.083	7.042	7.752
		4.204	1.242	7.326	8.721
		4.911	2.611		

[a] Experimental results from ref 29 (after applying a small temperature correction). [b] The appearance of a second liquid "hydrogen sulfide-rich" phase was observed.

Table 9. Interaction Parameters in Pitzer's G^E equation for the System (H_2S + Piperazine + H_2O):[a]

$$f(T) = q_1 + \frac{q_2}{(T/\mathrm{K})}$$

parameter	q_1	q_2	T/K
$\beta^{(0)}_{H_2S,H_2S}$[b]	−0.261 56	69.751	283−453
$\beta^{(0)}_{H_2S,HS^-}$[c]	0.009 658 2	−18.988	313−413
$\beta^{(0)}_{H_2S,PIPH_3^+}$	0.168 12	−48.836	313−393
$\beta^{(0)}_{PIPH_3^+,HS^-}$	0.027 680		
$\beta^{(1)}_{PIPH_3^+,HS^-}$	1.492 1	−469.89	
$\beta^{(0)}_{PIPH_4^{2+},HS^-}$	0.338 92	−97.698	
$\beta^{(1)}_{PIPH_4^{2+},HS^-}$	0.932 22		
$\mu_{H_2S,PIPH_3^+,HS^-}$	−0.008 9545	2.1507	
$\mu_{H_2S,H_2S,PIPH_3^+}$	0.006 2141		

[a] The parameter set is based on H_2S gas solubility data in (piperazine + H_2O) from ref 29 (after applying a small temperature correction). [b] Parameter is based on H_2S gas solubility data in pure water and was adopted from ref 27. [c] Parameter was adopted from ref 8.

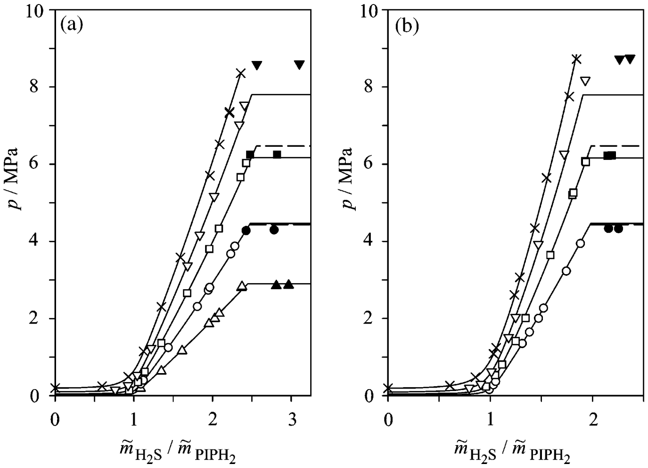

Figure 6. Total pressure above liquid mixtures of (H_2S + piperazine + H_2O), $\tilde{m}_{PIPH_2} \approx 2$ mol·kg^{-1} (a), 4 mol·kg^{-1} (b). Experimental results from Xia et al.[29] (after applying a small temperature correction, cf. Appendix): △, ▲, $T = 313.75$ K; ○, ●, $T = 334.05$ K; □, ■, $T = 354.4$ K; ▽, ▼, $T \approx 374.7$ K; ×, $T = 395$ K. The filled symbols denote experimental points where a second hydrogen sulfide-rich liquid phase was observed. —, correlation results, this work; — and - - - denote two different approaches to estimate the VLLE equilibrium pressure (cf. Xia et al.[29]).

The experimental data for the total pressure above (CO_2 + piperazine + H_2O) by ref 1 (after applying the temperature correction and disregarding data points at pressures below 0.2 MPa with relatively high experimental uncertainties as well as one experimental point, where the precipitation of a solid phase was observed) are correlated with an average relative deviation of 3.0 % {3.1 % and 2.9 % at $\tilde{m}_{PIPH_2} \approx$ (2 and 4) mol·kg^{-1}, respectively} (cf. also Figures 2b and 3b).

(II) Corrected Experimental Results from Ref 29 for the System (H_2S + Piperazine + H_2O). The corrected experimental results for the solubility of H_2S in (piperazine + H_2O) and the corrected interaction parameters of the previous model for the VLE of that system are given in Tables 8 and 9, respectively. The experimental data for the total pressure above (H_2S + piperazine + H_2O) by ref 29 (after applying the temperature correction and disregarding data points at pressures below 0.2 MPa with relatively high experimental uncertainties as well as data points, where the appearance of a second "hydrogen sulfide-rich" liquid phase was observed) are correlated with an average relative deviation of 2.0 % {1.6 % and 2.5 % at $\tilde{m}_{PIPH_2} \approx$ (2 and 4) mol·kg^{-1}, respectively} (cf. also Figure 6).

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