Solubility of CO_2 in (H_2O+Piperazine) and in (H_2O+MDEA+Piperazine)

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A thermodynamic model for describing the phase equilibrium for the system CO_2 + methyldiethanolamine + water has been extended, allowing for the presence of piperazine. Model parameters are estimated from new experimental results for the solubility of carbon dioxide in aqueous solutions of piperazine (for piperazine molalities up to 4 mol per kilogram of water, temperatures between 313 and 393 K, and pressures up to about 9.6 MPa). The model is tested by comparing predicted and experimental carbon dioxide solubilities in aqueous mixtures of both amines (2 molal MDEA + 2 molal piperazine, at 353 K, and pressures up to about 6.4 MPa).

Introduction

Aqueous solutions of *N*-methyldiethanolamine (MDEA) and piperazine ($PIPH_2$) are widely used for selectively removing hydrogen sulfide from gaseous effluents containing carbon dioxide (such as natural gases). In such amine solutions, the sour gases are physically and (predominantly) chemically absorbed. The selectivity is mainly due to large differences in chemical-reaction rates and/or mass-transfer rates. In order to design the separation equipment, a model for describing the thermodynamic equilibrium (that is, chemical and phase equilibrium) is required, as deviation from equilibrium provides the driving force in a kinetically controlled process.

In previous work (Kuranov et al., 1996; Pérez-Salado Kamps et al., 2001), a thermodynamic model is extended for describing the solubility of the single gases carbon dioxide and hydrogen sulfide in aqueous MDEA solutions was developed. The model parameters were based on experimental data on the protonation constant of MDEA (Pérez-Salado Kamps and Maurer, 1996), and on gas solubility data covering a temperature range from 313 K to 413 K. MDEA molality range is up to 8 mol per kilogram of water, and the pressure range is up to about 8 MPa. More recently, a model for describing the solubility of hydrogen sulfide in aqueous solutions of piperazine, based on experimental results at temperatures between 313 K and 393 K, piperazine molalities up to 4 mol per kilogram of water, and pressures up to about 9 MPa has been developed (Xia et al., 2003).

In the present contribution, the model is extended for describing the solubility of carbon dioxide in aqueous solutions of piperazine. The model is based, on the one hand, on recently published results for the chemical equilibrium constants for the formation of piperazine carbamate, piperazine dicarbamate, and protonated piperazine (Ermatchkov et al.,

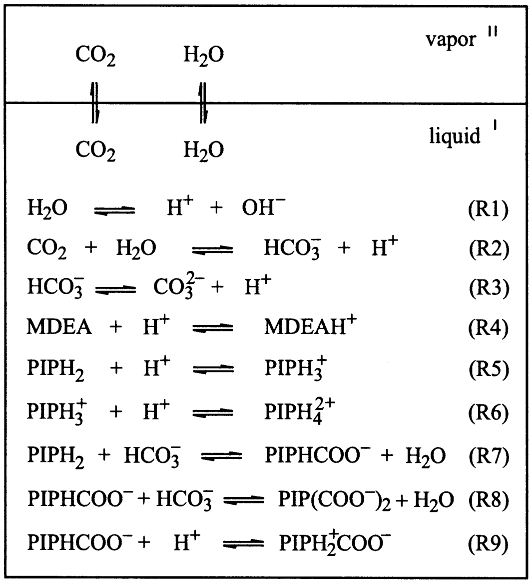

Figure 1. VLE and chemical reactions in the CO_2 + MDEA+piperazine+H_2O system.

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2003), and on the other hand, on new experimental solubility data at temperatures between 313 K and 393 K, piperazine molalities up to 4 mol per kilogram of water, and pressures up to about 9.6 MPa.

The thermodynamic models describing the solubility of a single gas (CO_2 or H_2S) in aqueous solutions of the single amines (MDEA or piperazine) can be combined in order to predict the phase equilibrium of the higher systems up to CO_2–H_2S–MDEA–piperazine–H_2O. Following this procedure, Xia et al. (2003) were able to accurately predict some limited experimental VLE data of the H_2S–MDEA–piperazine–H_2O system. The model is now further tested by comparing some new experimental results for the solubility of carbon dioxide in aqueous mixtures of both amines (2 molal MDEA + 2 molal piperazine, at 353 K, and pressures up to about 6.4 MPa) with predictions.

Modeling

Figure 1 shows a scheme of the model applied to correlate (predict) the solubility of carbon dioxide in aqueous solutions of MDEA or (and) piperazine.

Chemical equilibrium in the aqueous phase

Due to chemical reactions in the liquid phase, carbon dioxide is dissolved predominantly in nonvolatile, ionic form. The following chemical reactions are considered in the liquid phase: the autoprotolysis of water (reaction R1), the formation and dissociation of bicarbonate (reactions R2, R3), the protonation of methyldiethanolamine (reaction R4), the protonation and diprotonation of piperazine (reactions R5, R6), and the formations of piperazine carbamate, piperazine dicarbamate, and protonated piperazine carbamate (reactions R7, R8, R9).

The condition for chemical equilibrium for a chemical reaction, R, results in

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

The balance equation for the number of moles of a species i in the liquid phase is

$$n_i' = \bar{n}_i + \sum_R \nu_{i,R}\,\xi_R \tag{2}$$

Solving this set of equations for a given temperature, and given stoichiometric mole numbers $\bar{n}_i$ of mixed components (that is, CO_2, MDEA, piperazine, and H_2O), results in the "true" composition of the liquid phase, that is, the molalities of all neutral and ionic species.

Activity coefficients of both molecular and ionic solute species were calculated from a modified Pitzer's equation for the excess Gibbs energy of aqueous electrolyte solutions (Pitzer, 1977) (see, for example, Pérez-Salado Kamps et al., 2001). The activity of water was calculated from the Gibbs-Duhem equation.

The calculation requires the knowledge of the temperature-dependent chemical equilibrium constants K_1–K_9 (on the molality scale). K_1 was taken from Edwards et al. (1978), K_2 and K_3 from Patterson et al. (1982, 1984), K_4 from Pérez-Salado Kamps and Maurer (1996), K_5 and K_6 from Hetzer et al. (1968), and K_7–K_9 from Ermatchkov et al. (2003). Details of the correlation equations for the chemical equilibrium constants are given in Table 1.

Vapor–liquid equilibrium

The extended Raoult's law is used to express the vapor–liquid equilibrium for water

$$p^s_{H_2O}\varphi^s_{H_2O}\exp\left(\frac{\upsilon_{H_2O}\left(p - p^s_{H_2O}\right)}{RT}\right)a_{H_2O} = y_{H_2O}\,p\,\varphi''_{H_2O}, \tag{3}$$

while the extended Henry's law is applied for expressing that equilibrium for CO_2:

$$H^{(m)}_{CO_2,H_2O}\left(T, p^s_{H_2O}\right)\exp\left(\frac{\upsilon^{\infty}_{CO_2,H_2O}\left(p - p^s_{H_2O}\right)}{RT}\right)m_{CO_2}\gamma^*_{CO_2} = y_{CO_2}\,p\,\varphi''_{CO_2} \tag{4}$$

Throughout the article, molality (that is, number of moles per kilogram of water) is used for describing the solute concentration. In principle, MDEA and piperazine might also be present in the vapor phase. However, because, on the one hand, the vapor pressure of both amines is very small in the temperature range considered here [see, for example, Xu et al. (1991, 1998)], and on the other hand, the concentration of both amines (in molecular form) in the liquid is low to very low in the pressure region investigated in the present work, their presence in the vapor phase is neglected.

Details on all required thermodynamic properties (Henry's constant $H^{(m)}_{CO_2,H_2O}(T, p^S_{H_2O})$ for carbon dioxide in pure water (on the molality scale); the vapor pressure $p^s_{H_2O}$ and molar volume υ_{H_2O} of pure water; the partial molar volume of car-

Table 1. Chemical Equilibrium Constants (on the Molality Scale) $\ln K_R = A + B/(T/K) + C\cdot\ln(T/K) + D\cdot(T/K) + E/(T/K)^2$

Reaction	A	B	C	$10^2\cdot D$	E	T/K
R1	140.932	−13445.9	−22.4773	—	—	273–498
R2	−1203.01	68359.6	188.444	−20.6424	$-4.71291\cdot10^6$	273–673
R3	175.360	−7230.6	−30.6509	1.31478	$-3.72805\cdot10^5$	273–523
R4	79.474	819.7	−10.9756	—	—	278–422
R5	14.119	3814.4	—	−1.5096	—	273–323
R6	10.113	2192.3	—	−1.7396	—	273–323
R7	−8.635	3616.1	—	—	—	283–333
R8	−3.655	1322.3	—	—	—	283–333
R9	10.026	3493.1	—	—	—	283–333

Table 2. Interaction Parameters in Pitzer's G^E Equation $f(T) = q_1 + q_2/(T/K)$

Parameter	q_1	q_2	T/K	Subsystem
$\beta^{(0)}_{CO_2,HCO_3^-}$	0.23042	$-0.22012 \cdot 10^2$	313–413	$CO_2 + MDEA + H_2O$*
$\beta^{(0)}_{CO_2,MDEAH^+}$	-0.13952	$-0.44825 \cdot 10^1$		
$\tau_{CO_2,MDEAH^+,HCO_3^-}$	$-0.61812 \cdot 10^{-3}$	—		
$\beta^{(0)}_{MDEA,HCO_3^-}$	$-0.46353 \cdot 10^{-2}$	$0.49422 \cdot 10^2$		
$\beta^{(0)}_{MDEA,CO_3^{2-}}$	$0.21287 \cdot 10^{-1}$	—		
$\beta^{(0)}_{MDEAH^+,HCO_3^-}$	0.31729	$-0.90860 \cdot 10^2$		
$\beta^{(1)}_{MDEAH^+,HCO_3^-}$	-0.68478	$0.29029 \cdot 10^3$		
$\tau_{MDEAH^+,HCO_3^-,HCO_3^-}$	$-0.55509 \cdot 10^{-2}$	$0.15327 \cdot 10^1$		
$\beta^{(0)}_{MDEAH^+,CO_3^{2-}}$	$0.22476 \cdot 10^{-1}$	—		
$\beta^{(1)}_{MDEAH^+,CO_3^{2-}}$	0.58421	—		
$\tau_{MDEAH^+,CO_3^{2-},CO_3^{2-}}$	$0.28235 \cdot 10^{-2}$	—		
$\beta^{(0)}_{PIPH_2^+COO^-,PIPH_2^+COO^-}$	$0.96213 \cdot 10^{-1}$	$-0.72200 \cdot 10^2$	313–393	$CO_2 + PIPH_2 + H_2O$
$\beta^{(1)}_{PIPH_2^+COO^-,PIPH_2^+COO^-}$	-0.83929	$0.32479 \cdot 10^3$		
$\beta^{(0)}_{PIPH_3^+,HCO_3^-}$	0.55489	$0.20459 \cdot 10^1$		
$\beta^{(1)}_{PIPH_3^+,HCO_3^-}$	$-0.18949 \cdot 10^1$	$0.77648 \cdot 10^3$		
$\beta^{(0)}_{CO_2,PIPH_3^+}$	0.14624	$-0.18724 \cdot 10^3$		
$\beta^{(0)}_{CO_2,PIPH_2^+COO^-}$	0.55705	$-0.19684 \cdot 10^3$		
$\beta^{(0)}_{PIPH_3^+,PIPH_2^+COO^-}$	$-0.13044 \cdot 10^1$	$0.44098 \cdot 10^3$		
$\beta^{(0)}_{PIPH_3^+,PIPHCOO^-}$	$-0.20678 \cdot 10^1$	$0.77643 \cdot 10^3$		
$\beta^{(0)}_{PIPH_3^+,PIP(COO^-)_2}$	$-0.10966 \cdot 10^1$	$0.64679 \cdot 10^3$		

* *Source:* from Pérez-Salado Kamps et al. (2001).

bon dioxide, infinitely diluted in liquid water $v^{\infty}_{CO_2,H_2O}$; and information on the vapor phase nonideality) were given recently (Pérez-Salado Kamps et al., 2001).

Interaction parameters in Pitzer's G^E model

Binary Aqueous Subsystems. When one of the single components, CO_2, MDEA, 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 vapor–liquid equilibrium of an aqueous solution of the mentioned components, only interaction parameters between the single solutes (either CO_2, MDEA, or piperazine) can be determined.

$CO_2 + H_2O$ System. In the pressure range of interest in the present work, parameters for interactions between CO_2 can be neglected (see Rumpf and Maurer, 1993).

MDEA + H_2O and Piperazine + H_2O Systems. All parameters were neglected, as they are not important in the amine loading region investigated in the present work.

CO_2 + MDEA + H_2O Ternary Subsystem. The parameters were taken from a previous publication (Pérez-Salado Kamps et al., 2001; see Table 2).

CO_2 + Piperazine + H_2O Ternary Subsystem. In order to determine interaction parameters for this system, reliable experimental information is required on the solubility of carbon dioxide in aqueous solutions of piperazine. Only very limited experimental information on this solubility can be found in the literature (Bishnoi and Rochelle, 2000). Therefore, experiments were performed to determine that solubility.

Experimental Studies

A description of the experimental equipment and procedure, as well as details on the chemicals used (manufacturers, purities, pretreatment) can be found in previous publications [see, for example, Rumpf and Maurer (1993); Pérez-Salado Kamps et al. (2002); and Xia et al. (2003)]. Therefore, only the basic experimental technique and experimental uncertainties are given here.

In an experiment, a thermostated high-pressure cell (material = Hastelloy C4; volume = about 30 cm^3) with two sapphire windows is partially filled with a known amount of the aqueous solvent. A known amount of gas is added to the cell from a storage tank. Step by step, more solvent is added to the cell by a calibrated high-pressure displacer, until the gas is completely dissolved in the liquid phase. The amount of solvent charged to the cell is only slightly above the minimum amount needed to dissolve the gas completely. After equilibration, very small amounts of the liquid mixture are withdrawn stepwise from the cell until the first very small stable bubbles appear. That pressure is the equilibrium pressure to dissolve the charged amount of the gas in the charged amount of solvent at the fixed temperature.

The aqueous solutions were prepared in a storage tank by dissolving known amounts of piperazine in pure water. The molality of piperazine in the aqueous solution was determined gravimetrically with a relative uncertainty smaller than ±0.1%. The mass of the charged gas (up to about 5 g) is determined by weighing with an uncertainty of ±0.008 g. The volume of the aqueous solvent needed to dissolve the gas is determined in each experiment. The mass of the solvent is calculated—with a maximum relative uncertainty of ±0.7%—from its volume and known density (from separate measurements with a vibrating tube densimeter). Two pressure transducers (WIKA GmbH, Klingenberg, Germany) for pressures ranging to 4 MPa and to 10 MPa, respectively, were used to determine the solubility pressure. Before and after each series of measurements, the transducers were calibrated against a high precision pressure gauge (Desgranges & Huot, Aubervilliers, France). The maximum uncertainty in the pressure measurement is ±0.1% of each transducer's maximum reading. The temperature is determined with two calibrated platinum resistance thermometers placed in the heating jacket of the cell with an uncertainty below ±0.1 K.

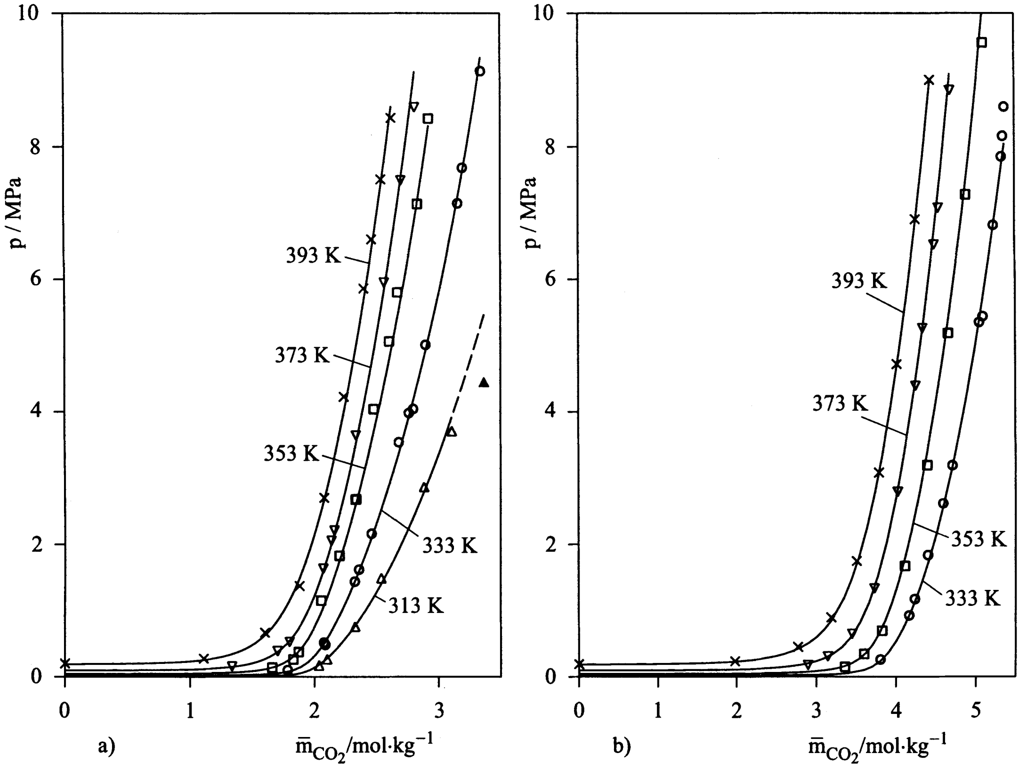

Figure 2. Total pressure above aqueous solutions of (CO_2+piperazine).

(a) $\bar{m}_{PIPH_2} \approx 2$ mol/kg, (b) $\bar{m}_{PIPH_2} \approx 4$ mol/kg: (△, ○, □, ▽, ×) exptl results, this work; (——) correlation, this work; (– – –) extrapolation into VLSE region.

The solubility of carbon dioxide was measured in about 2 molal (and 4 molal) aqueous piperazine solutions at temperatures from 313 K to 393 K, in 20 K intervals. The experimental results for the total pressure above those solutions given in Table 3 are plotted in Figure 2 vs. the stoichiometric molality of the gas.

The behavior of the CO_2 + piperazine + H_2O system is very similar to that of the CO_2 + MDEA + H_2O system (see, for example, Pérez-Salado Kamps et al., 2001). Adding a sour gas to a piperazine-containing aqueous solution at first only slightly increases the total pressure above the solution, as the gas is mostly dissolved in nonvolatile, ionic form. When the stoichiometric molality of the sour gas exceeds that of the base piperazine, the total pressure increases steeply, as piperazine has been spent by the chemical reactions and more sour gas can no longer be absorbed chemically, that is, in nonvolatile ionic form, but has to be dissolved physically.

The precipitation of a salt (probably piperazine bicarbonate) was observed at high carbon dioxide molalities in the aqueous 2-molal piperazine solution at 313 K. The experimental result, where this additional solid phase appeared, is characterized by a full symbol in Figure 2. In principle, the formation of a solid phase might be taken into account by the model (by means of the solid–liquid equilibrium condition). But, as precipitation was only observed in a single experiment, and as the precipitate could not be analyzed, no attempt was made to take precipitation into account.

Figure 3 shows calculations for the speciation in an aqueous 4-molal piperazine solution at 353 K, when carbon dioxide is added. As long as the stoichiometric molality of carbon dioxide is less than that of piperazine, the sour gas is almost completely dissolved chemically, that is, it is mainly converted to the three coexisting piperazine carbamate species on the one side, and to bicarbonate (and carbonate, which is present only in very small amounts) on the other side. Simultaneously, piperazine is protonated. When the stoichiometric molality of the sour gas exceeds that of the base piperazine, the sour gas can no longer be absorbed chemically, but has to be dissolved physically, that is, as neutral carbon dioxide in

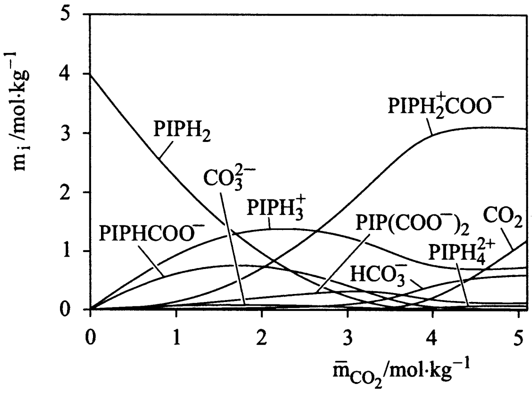

Figure 3. Predicted species distribution in the CO_2+ piperazine+H_2O system at 353 K ($\bar{m}_{PIPH_2}$ = 4 mol/kg).

an aqueous electrolyte solution. Therefore, as the aqueous solution becomes more and more acidic, the concentration of molecular carbon dioxide increases practically linearly, and only very small changes in the concentrations of all other species (including the diprotonated piperazine, which is present only in very small amounts) are observed.

In the "high" pressure/"high" amine loading region ($\overline{m}_{CO_2}/\overline{m}_{PIPH_2} > 1$), the liquid can be regarded as an aqueous mixture of the strong electrolyte $PIPH_3HCO_3$, where two neutral species [CO_2 and the protonated piperazine carbamate ($PIPH_2{}^+COO^-$), which is a zwitterion] are physically dissolved. The high-pressure solubility data for this system might therefore be described with parameters for interactions that also occur in the binary subsystems $CO_2 + H_2O$, $PIPH_2{}^+COO^- + H_2O$, and $PIPH_3HCO_3 + H_2O$, and in the ternary subsystems $CO_2 + PIPH_3HCO_3 + H_2O$, $CO_2 + PIPH_2{}^+COO^- + H_2O$, and $PIPH_2{}^+COO^- + PIPH_3HCO_3 + H_2O$. In the "middle" amine loading region ($0.5 < \overline{m}_{CO_2}/\overline{m}_{PIPH_2} < 1$), the liquid can be regarded as an aqueous mixture of the strong electrolytes $PIPH_3PIPHCOO$, $(PIPH_3)_2PIP(COO)_2$, and $PIPH_3HCO_3$, where two neutral species [molecular piperazine and protonated piperazine carbamate ($PIPH_2{}^+COO^-$)] are physically dissolved. Because—within this concentration region—the influence of piperazine on the vapor pressure is negligible (and was therefore neglected by our model), solubility data might be described with interaction parameters only from the binary subsystems $PIPH_2{}^+COO^- + H_2O$, $PIPH_3PIPHCOO + H_2O$, $(PIPH_3)_2PIP(COO)_2 + H_2O$, and $PIPH_3HCO_3 + H_2O$. However, interaction parameters for the binary subsystems $PIPH_2{}^+COO^- + H_2O$, $PIPH_3PIPHCOO + H_2O$, $(PIPH_3)_2PIP(COO)_2 + H_2O$, and $PIPH_3HCO_3 + H_2O$, as

Table 3. Solubility of Carbon Dioxide in Aqueous Solutions of Piperazine

$T = 313.13$ K		$T = 333.14$ K		$T = 333.14$ K	
$\overline{m}_{PIPH_2} =$ 1.995 mol/kg		$\overline{m}_{PIPH_2} =$ 1.995 mol/kg		$\overline{m}_{PIPH_2} =$ 2.035 mol/kg	
$\overline{m}_{CO_2}$/mol/kg	p/MPa	$\overline{m}_{CO_2}$/mol/kg	p/MPa	$\overline{m}_{CO_2}$/mol/kg	p/MPa
1.452	0.0133	1.380	0.0308	2.088	0.4820
2.037	0.1707	1.785	0.1016	2.327	1.435
2.102	0.2652	2.077	0.5144	2.796	4.039
2.328	0.7535	2.361	1.616	2.897	5.007
2.540	1.486	2.462	2.158	3.194	7.683
2.884	2.859	2.681	3.533	3.342	9.131
3.107	3.702	2.762	3.978		
3.366	4.446*	3.157	7.147		

$T = 353.16$ K		$T = 373.15$ K		$T = 393.15$ K	
$\overline{m}_{PIPH_2} =$ 1.995 mol/kg		$\overline{m}_{PIPH_2} =$ 2.035 mol/kg		$\overline{m}_{PIPH_2} =$ 2.035 mol/kg	
$\overline{m}_{CO_2}$/mol/kg	p/MPa	$\overline{m}_{CO_2}$/mol/kg	p/MPa	$\overline{m}_{CO_2}$/mol/kg	p/MPa
1.289	0.0630	1.336	0.1556	0	0.2021
1.661	0.1385	1.704	0.3851	1.109	0.2740
1.830	0.2627	1.801	0.5257	1.602	0.6650
1.874	0.3736	2.073	1.630	1.882	1.370
2.058	1.151	2.140	2.053	2.080	2.699
2.205	1.827	2.164	2.206	2.239	4.222
2.333	2.670	2.335	3.636	2.400	5.859
2.339	2.678	2.564	5.952	2.464	6.605
2.480	4.038	2.700	7.492	2.540	7.510
2.606	5.063	2.811	8.592	2.623	8.433
2.671	5.801				
2.834	7.137				
2.924	8.421				

$T = 333.16$ K		$T = 353.14$ K		$T = 373.16$ K		$T = 393.15$ K	
$\overline{m}_{PIPH_2} = 3.964$ mol/kg		$\overline{m}_{PIPH_2} = 3.964$ mol/kg		$\overline{m}_{PIPH_2} = 3.950$ mol/kg		$\overline{m}_{PIPH_2} = 3.950$ mol/kg	
$\overline{m}_{CO_2}$/(mol/kg)	p/MPa	$\overline{m}_{CO_2}$/(mol/kg)	p/MPa	$\overline{m}_{CO_2}$/(mol/kg)	p/MPa	$\overline{m}_{CO_2}$/(mol/kg)	p/MPa
3.495	0.0428	3.359	0.1487	2.895	0.1756	0	0.1876
3.805	0.2575	3.600	0.3404	3.144	0.3054	1.981	0.2325
4.165	0.9225	3.827	0.6899	3.450	0.6459	2.772	0.4472
4.235	1.170	4.114	1.666	3.735	1.331	3.192	0.8936
4.400	1.832	4.395	3.187	4.028	2.787	3.514	1.741
4.592	2.609	4.656	5.182	4.250	4.384	3.794	3.076
4.708	3.185	4.882	7.279	4.337	5.258	4.017	4.712
5.047	5.346	5.102	9.560	4.483	6.523	4.249	6.906
5.093	5.435			4.535	7.080	4.436	8.999
5.229	6.820			4.683	8.846		
5.332	7.852						
5.349	8.160						
5.369	8.598						

* The precipitation of a solid phase was observed.

Table 4. Solubility of Carbon Dioxide in Aqueous Solutions of MDEA and Piperazine

$T = 353.14$ K
$\overline{m}_{\mathrm{MDEA}} = 1.975$ mol/kg
$\overline{m}_{\mathrm{PIPH_2}} = 1.966$ mol/kg

$\overline{m}_{\mathrm{CO_2}}$/(mol/kg)	p/MPa
2.526	0.1807
2.826	0.2896
3.347	0.7345
3.817	1.929
3.977	2.496
4.054	2.768
4.198	4.050
4.347	5.375
4.399	5.773
4.478	6.400

well as for the ternary subsystems $CO_2 + PIPH_3HCO_3 + H_2O$, $CO_2 + PIPH_2{}^+COO^- + H_2O$, and $PIPH_2{}^+COO^- + PIPH_3HCO_3 + H_2O$, are not available. The new experimental data for the solubility of CO_2 in $PIPH_2 + H_2O$, which cover the middle and high amine loading regions, were therefore used to determine some of those parameters. The experimental point, where an additional solid phase appeared, was excluded from the fitting runs. Altogether, nine additional interaction parameters had to be considered (see Table 2). The new experimental results are compared with correlations in the following section.

In addition, the solubility of CO_2 was measured in about 2 molal MDEA + 2 molal piperazine aqueous solutions at 353 K (see Table 4). The experimental results for the total pressure above those solutions are plotted in Figure 4 vs. the stoichiometric molality of the gas. Those experimental results are compared with predictions in the following section.

Discussion

CO_2 + Piperazine + H_2O System

The experimental data for the total pressure above aqueous solutions of piperazine and carbon dioxide (disregarding data points at pressures below 0.1 MPa, where the experimental uncertainty can reach up to 10%, and disregarding the data point where a precipitation of a salt was observed) are correlated with an average relative deviation of 4% (4.3 and 3.5%, at 2 and 4 molal piperazine, respectively). Figure 2 shows a comparison between experimental and calculated total pressures (for preset temperature and stoichiometric molality of piperazine and the sour gas) above aqueous 2- and 4-molal solutions of piperazine.

The model does not consider the precipitation of a salt. Therefore, in Figure 2, the calculated carbon dioxide solubility pressure curve above the aqueous 2 molal piperazine solution at 313 K just gives an extrapolation for pressures above about 4 MPa, which is characterized by a dashed line. In reality, when the solubility limit of the salt is reached, a sudden change in the slope is to be expected in that curve.

CO_2 + MDEA + Piperazine + H_2O System

The solubility of carbon dioxide in aqueous solutions of both MDEA and piperazine can be predicted from the model described before when one assumes that only such parameters are of essential influence that were required to describe the solubility of CO_2 in the aqueous solutions of the single amines. Predictions for the total pressure (for given temperature and stoichiometric composition of the liquid phase) are compared with the new experimental results (at $T = 353.14$ K, $\overline{m}_{\mathrm{MDEA}} = 1.975$ mol/kg, $\overline{m}_{\mathrm{PIPH_2}} = 1.966$ mol/kg) in Figure 4. Deviations amount to about 35%. But, for example, at a pressure of 5 MPa, this rather large deviation in the pressure corresponds to a deviation in the stoichiometric molality of carbon dioxide of only about 5% ($\overline{m}_{\mathrm{CO_2}} \approx (4.1 \pm 0.2)$ mol/kg). Some parameters for obviously important interactions between species of MDEA on the one side and species of piperazine on the other side, or between the sour gas, MDEA, and piperazine (and their species), were neglected. These interactions seem to influence the chemical reaction equilibrium in such a way that the (small) amount of molecular carbon dioxide is overestimated. As shown in Figure 5, at $\overline{m}_{\mathrm{CO_2}} \approx 4.1$ mol/kg only about 15% of the dissolved carbon dioxide is present in molecular form. An error in predicting the chemically bound carbon dioxide by about 6% results in deviations in the total pressure of approximately 35%.

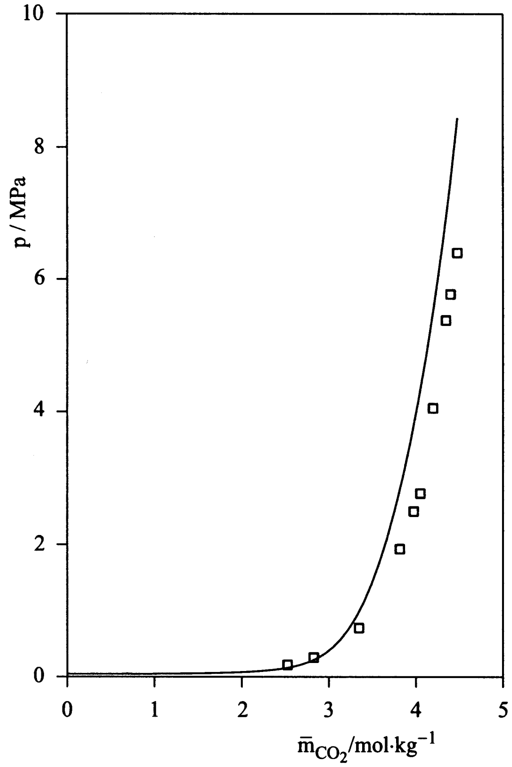

Figure 4. Total pressure above aqueous solutions of (CO_2 + MDEA + piperazine).

$T = 353.14$ K; $\overline{m}_{\mathrm{MDEA}} = 1.975$ mol/kg; $\overline{m}_{\mathrm{PIPH_2}} = 1.966$ mol/kg: (□) exptl results, this work; (——) prediction, this work (with interaction parameters from CO_2 + MDEA + H_2O and CO_2 + piperazine + H_2O).

Apart from the experimental results given in the present work, little information can be found in the open literature on the solubility of carbon dioxide in mixtures of MDEA and piperazine (Xu et al., 1998; Liu et al., 1999; and Bishnoi and Rochelle, 2002). Because the experimental phase-equilibrium database on this system is very limited, it is very difficult to

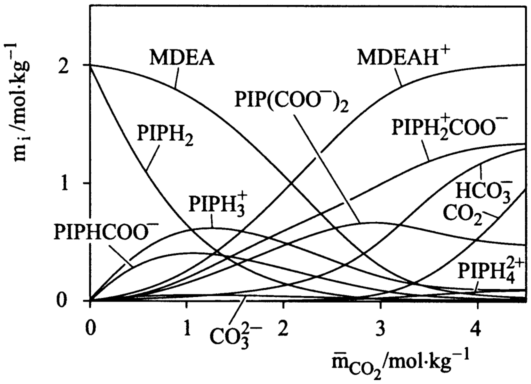

Figure 5. Predicted species distribution in the CO_2 + MDEA + piperazine + H_2O system at 353 K ($\bar{m}_{MDEA} = 2$ mol/kg; $\bar{m}_{PIPH_2} = 2$ mol/kg).

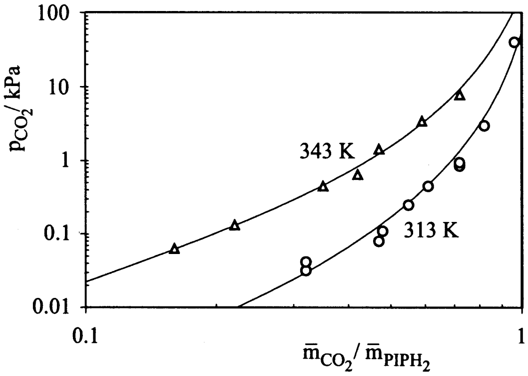

Figure 6. Carbon dioxide partial pressure above aqueous solutions of (CO_2 + piperazine).

$\bar{m}_{PIPH_2} = 0.63$ mol/kg: (○, △) exptl results, Bishnoi and Rochelle (2000); (——) prediction, this work.

identify and exclude inconsistent data, and it is not possible to reliably determine up-to-now neglected interaction parameters. Therefore, no attempt was made to correlate the experimental data on the phase equilibrium of this quaternary system. Nevertheless, the model predictions were used for comparison with those experimental data.

Comparison with Literature Data

Comparison with the data in the literature reveals another problem. Some authors used the molarity scale to give concentrations of MDEA and piperazine. However, they did not report the temperature at which the solutions were prepared. In such cases, it was assumed that the temperature was 293.15 K, and new experimental data for the density of aqueous solutions of MDEA and piperazine were used to convert molarities into molalities.

CO_2 + Piperazine + H_2O System

Bishnoi and Rochelle (2000) measured the solubility of carbon dioxide in 0.6 M (0.63 molal) piperazine solutions at 313 and 343 K at low and middle amine loading ($0.16 \leq \bar{m}_{CO_2}/\bar{m}_{PIPH_2} \leq 0.96$). In the low amine loading region ($\bar{m}_{CO_2}/\bar{m}_{PIPH_2} < 0.5$), the liquid can be regarded as an aqueous mixture of the strong electrolyte $PIPH_3PIPHCOO$ and the two neutral species (molecular) piperazine and protonated piperazine carbamate ($PIPH_2^+COO^-$) (see Figure 3). In this concentration region molecular piperazine may have an essential influence on the very low vapor pressure of the mixture. Nevertheless, as can be seen from Figure 6, model predictions for the partial pressure of carbon dioxide agree well with the experimental results by Bishnoi and Rochelle (2000). The average relative deviation between experiment and prediction amounts to 22%, but no systematic deviation is observed.

It may be worthwhile to mention, that, according to predictions from our model, the solubility of carbon dioxide is much higher in aqueous solutions of piperazine than it is in aqueous solutions of MDEA (at a given temperature and a given stoichiometric amine molality)—especially in the low and middle amine loading regions—which on the one hand is due to the somewhat higher basic character of aqueous piperazine solutions, and on the other hand can be attributed to the formation of carbamate species in this system, that is, to the higher capability of dissolving the sour gas chemically. For example, dissolving 2 moles of carbon dioxide in an aqueous 4 molal MDEA (piperazine) solution at 353 K results in a carbon dioxide partial pressure of about 260 kPa (4 kPa).

CO_2 + MDEA + Piperazine + H_2O System

In a more recent publication, Bishnoi and Rochelle (2002) report experimental results for the partial pressure of carbon dioxide (13 experimental points) above aqueous 4 M (7.74 molal) MDEA and 0.6 M (1.16 molal) piperazine solutions at 313 and 343 K in the low amine loading region. The partial pressure of carbon dioxide ranges from 0.033 kPa to 7.48 kPa. They estimated the uncertainty of the experimental data to ±30%. As can be seen from Figure 7, predictions for the partial pressure of carbon dioxide are systematically lower (by nearly one order of magnitude) than the experimental data.

Xu et al. (1998) reported 11 experimental data points for the partial pressures of carbon dioxide above aqueous 4.28 M MDEA and 0.103, 0.257, and 0.515 M piperazine solutions—that is, 8.14 molal MDEA + 0.196 molal piperazine, 8.34 molal MDEA + 0.500 molal piperazine, and 8.69 molal MDEA + 1.046 molal piperazine, respectively—at 343 K. Those data cover only the low amine loading region. The partial pressure of carbon dioxide ranges from about 3.8 kPa to 76.8 kPa. In this region the predictions for the partial pressure of carbon dioxide lie systematically below the experimental data by about 60% (see Figure 7).

Liu et al. (1999) reported 80 experimental results for the partial pressure of carbon dioxide above aqueous MDEA and piperazine solutions—covering a temperature range from 303 K to 363 K—at various concentrations of both amines: 1.53 M (1.87 molal) MDEA + 0.17 M (0.21 molal) piperazine, 1.35 M (1.64 molal) MDEA + 0.35 M (0.43 molal) piperazine, 3.15 M (5.00 molal) MDEA + 0.35 M (0.56 molal) piperazine, 2.8 M (4.38 molal) MDEA + 0.7 M (1.09 molal) piperazine, 4.77 M (10.93 molal) MDEA + 0.53 M (1.21 molal) piperazine, and 3.75 M (8.03 molal) MDEA + 1.55 M (3.32 molal) piperazine. The partial pressure of carbon dioxide ranges from about 13 kPa to 935 kPa. In this region the predictions for the partial

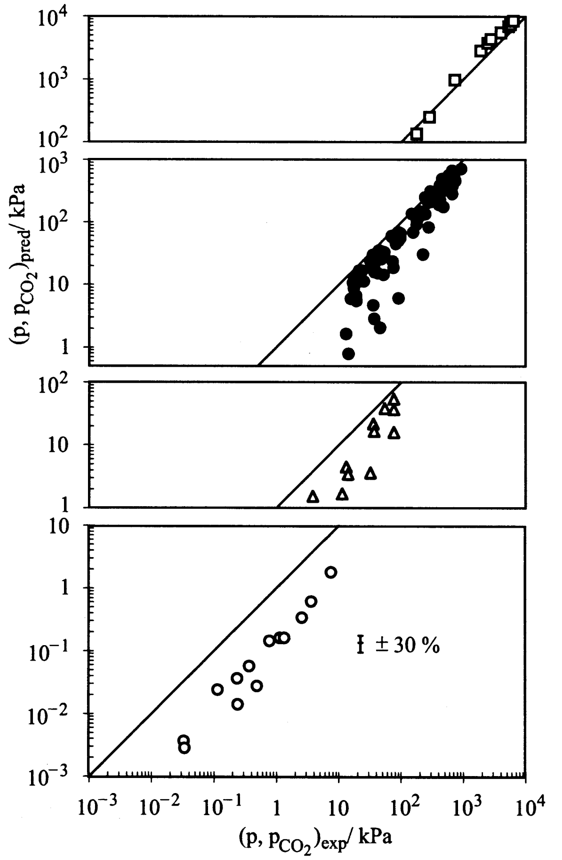

Figure 7. Comparison of experimental and predicted (total or carbon dioxide partial) pressures above aqueous solutions of (CO_2+MDEA+piperazine).

(○) Bishnoi and Rochelle (2002; p_{CO_2}); (△) Xu et al. (1998; p_{CO_2}); (●) Liu et al. (1999; p_{CO_2}); (□) this work (p).

pressure of carbon dioxide again in most cases fall below the experimental data (on average by about 40%) (see Figure 7). Those deviations increase with increasing stoichiometric concentrations of MDEA and piperazine, and with increasing stoichiometric mole ratios of piperazine to MDEA (from about 15% above the aqueous 1.87 molal MDEA + 0.21 molal piperazine solutions to about 78% above the aqueous 8.03 molal MDEA + 3.32 molal piperazine solutions).

Finally, Figure 7 includes a comparison of the experimental results for the total pressure above aqueous 1.975 molal MDEA + 1.966 molal piperazine solutions ($T = 353$ K) presented in this work (10 experimental points) with predictions from our model. The total pressure ranges from about 181 kPa to 6,400 kPa.

Conclusions

Sour gas sweetening is often achieved by absorption in aqueous solutions of amines. The basic design of these absorption processes requires a thermodynamic model for the single and simultaneous solubility of sour gases, for example, carbon dioxide and hydrogen sulfide, in aqueous solutions of one or more amines, for example, methyldiethanolamine (MDEA) and piperazine. The present work is an extension of previous work on the solubility of the single gases carbon dioxide and hydrogen sulfide in aqueous solutions of MDEA (Kuranov et al., 1996; Pérez-Salado Kamps et al., 2001), and on the solubility of hydrogen sulfide in aqueous solutions of piperazine (Xia et al., 2003). New experimental results are presented for the solubility of carbon dioxide in aqueous solutions of piperazine. The previously presented thermodynamic model for describing phase equilibria for the CO_2 + MDEA + H_2O system has been extended, allowing for the presence of piperazine. New VLE data on the CO_2 + MDEA + piperazine + H_2O system are used to assess model predictions. The existing experimental database on the phase equilibrium of this quaternary system is very limited. Additional information is required in order to develop a thermodynamic model with predictive character.

Notation

a_i = activity of component i
f = function
$H^{(m)}$ = Henry's constant (on the molality scale)
K_R = equilibrium constant for chemical reaction R (on the molality scale)
m_i = true molality of component i
$\overline{m}_i$ = stoichiometric molality of component i
n_i = true number of moles of component i
$\overline{n}_i$ = stoichiometric number of moles of component i
p = pressure
p_i = partial pressure of component i
q_i = coefficients
R = universal gas constant
T = absolute temperature
v = (partial) molar volume
y = vapor-phase mole fraction

Greek letters

$\beta^{(0)}, \beta^{(1)}$ = binary interaction parameters in Pitzer's equation
γ_i^* = activity coefficient of component i normalized to infinite dilution in pure water (on the molality scale)
$\nu_{i,R}$ = stoichiometric coefficient of component i in reaction R
ξ_R = extent of reaction R
τ = third virial coefficient in Pitzer's equation
φ = fugacity coefficient

Subscripts and superscripts

R = reaction R
exp = experimental
pred = predicted
s = saturation
∞ = infinite dilution in pure water
$'$ = liquid phase
$''$ = vapor phase

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