Solubility of CO_2 in H_2O+*N*-Methyldiethanolamine +(H_2SO_4 or Na_2SO_4)

Álvaro Pérez-Salado Kamps, Bernd Rumpf, and Gerd Maurer
Lehrstuhl für Technische Thermodynamik, Universität Kaiserslautern, D-67653 Kaiserslautern, Germany

Yuri Anoufrikov, George Kuranov, and Natalia A. Smirnova
Dept. of Chemistry, St. Petersburg State University, St. Petersburg, Russia

The solubility of carbon dioxide in aqueous solutions of methyldiethanolamine (MDEA) sulfate (1 m), in aqueous solutions of MDEA and MDEA sulfate (2 m and 1 m, respectively), and in aqueous solutions of MDEA and sodium sulfate (2 m and 1 m, respectively) was measured at 313 K to 413 K and total pressures up to 10.6 MPa. The experimental results were used to extend and test a model for the thermodynamic equilibrium encountered in the solubility of carbon dioxide in such aqueous solutions.

Introduction

Aqueous solutions of 2,2′-methyliminodiethanol (*N*-methyldiethanolamine; MDEA) are widely used for the sweetening of sour gases, particularly for the selective removal of hydrogen sulfide from gaseous effluents which also contain carbon dioxide. In such solutions the sour gases are partially converted to ionic species (that is, to bisulfide, bicarbonate, and carbonate), while MDEA is protonated. The loaded absorbents are regenerated thermally as, at elevated temperatures, the chemical reaction equilibrium is shifted to the molecular nonionic species, that is, volatile gases and nonvolatile MDEA. As the absorption of carbon dioxide is hindered by slow kinetics, it is possible to favor the absorption of hydrogen sulfide over that of carbon dioxide. Process modifications attempt to improve the selective absorption of hydrogen sulfide by adding modifiers to the aqueous MDEA solution. Piperazine is a commonly used modifier (Chakma and Meisen, 1987; Xu et al., 1998).

The gaseous effluents which have to be sweetened often contain some sulfur trioxide. In aqueous solutions sulfur trioxide is converted to sulfuric acid. Sulfuric acid blocks MDEA as it reacts with MDEA in aqueous solution to MDEA sulfate, thus reducing the absorption capacity of the solution. Furthermore, MDEA sulfate might also have an influence on the thermodynamic equilibrium, as it reduces—like any other strong electrolyte—the gas solubility (salting-out). Thermal regeneration is usually not sufficient to desorb sulfur trioxide, that is, MDEA sulfate cannot be converted to MDEA and volatile sulfur trioxide in a desorption process at higher temperatures. Therefore, sodium hydroxide is added in some processes to convert MDEA sulfate to sodium sulfate and MDEA. The absorption medium is then an aqueous solution of MDEA and sodium sulfate. A reliable computer-assisted design of such ab-/desorption equipment requires, on the one hand, the knowledge of transport and reaction kinetics; on the other hand, a reliable model for the thermodynamic equilibrium, that is, the phase equilibrium and the chemical reaction equilibria, as deviation from equilibrium provides the driving force for the kinetics. The development of such models has to be based on experimental data.

The present article aims to achieve two goals. At first, it aims to provide reliable experimental data on the solubility of carbon dioxide in aqueous solutions of MDEA sulfate (1 *m*), of MDEA + MDEA sulfate (2 *m* and 1 *m*, respectively), and of MDEA + sodium sulfate (also 2 *m* and 1 *m*, respectively) at temperatures from 313 K to 413 K and total pressures up to about 10 MPa for the one molal MDEA sulfate solutions, and up to about 5 MPa for the MDEA and salt containing solutions. At second, that experimental data is used together with literature data for the phase equilibrium in binary and ternary subsystems (such as $CO_2 + H_2O$, $H_2SO_4 + H_2O$, $Na_2SO_4 + H_2O$, $CO_2 + MDEA + H_2O$, $CO_2 + Na_2SO_4 + H_2O$) to extend and test a thermodynamic model for the solubility of carbon dioxide in aqueous solutions of MDEA (Kuranov et al., 1996; Pérez-Salado Kamps et al., 2001). An extension of that work is in progress to include the solubility of hydrogen sulfide in such aqueous solutions of

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Correspondence concerning this article should be addressed to G. Maurer.

MDEA and the strong electrolytes MDEA-sulfate and sodium sulfate. Thus, a method to calculate the vapor-liquid equilibrium of the industrial important system $CO_2 + H_2S + MDEA + H_2SO_4 + Na_2SO_4 + H_2O$ will become available.

Experimental Studies

The experimental equipment and procedure are basically the same as in previous investigations (cf., Rumpf and Maurer, 1993); therefore, only a few essentials 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 aqueous 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 mass of the charged gas (up to about 2.4 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 by measuring the position of the high-pressure displacer piston before and after each experiment. The mass of the solvent is calculated—with a relative uncertainty of max. 0.7%—from its known density (from separate measurements with a vibrating tube densimeter). Three pressure transducers (WIKA GmbH, Klingenberg, Germany) for pressures ranging to 0.6 MPa, to 4 MPa, and to 11 MPa 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 ± 0.1K.

The aqueous solutions were prepared in a storage tank by dissolving known amounts of MDEA and (H_2SO_4 or Na_2SO_4) in pure water. The molalities of MDEA and Na_2SO_4 in the aqueous solution were determined gravimetrically with relative uncertainties smaller than $\pm 0.1\%$. The relative uncertainty in the molality of H_2SO_4 was less than $\pm 0.1\%$, as it was taken from a Fixanal-tube.

Substances

Carbon dioxide (≥ 99.995 mol %) was purchased from Messer-Griesheim, Ludwigshafen, Germany. It was used without further purification. *N*-methyldiethanolamine (≥ 98 mass %, Merck-Griesheim, Ludwigshafen, Germany) was degassed under vacuum. Sulfuric acid (Fixanal, 0.5 mol, Riedel de Haën AG, Seelze, Germany) was used without further purification. Sodium sulfate (≥ 99.0 mass %, Riedel de Haën AG, Seelze, Germany) was degassed and dried under vacuum. Deionized water was degassed by vacuum distillation.

Table 1. CO_2 Solubility in Aqueous Solutions of MDEA at 313 K ($\overline{m}_{MDEA} = 1.949$ mol/kg)

T (K)	$\overline{m}_{CO_2}$ (mol/kg)	p (MPa) Exp.	p (MPa) Model by Pérez-Salado Kamps et al. (2001)
313.15	2.065	0.8374	0.7911
313.14	2.224	1.510	1.478
313.15	2.373	2.308	2.246
313.15	2.522	3.131	3.117
313.13	2.757	4.883	4.739

Experimental Results

To check the experimental arrangement and procedure, the solubility of carbon dioxide in an aqueous 2 m MDEA solution was measured at 313 K. The molality of CO_2 was about 2.8 mol/kg at maximum, resulting in total pressures up to about 5 MPa. As usual, throughout the article, molality is used for the number of mols per kilogram of water. The new experimental results are compared to results calculated with the model of Pérez-Salado Kamps et al. (2001) in Table 1. That correlation is based on recent experimental data (Kuranov et al., 1996; Pérez-Salado Kamps et al., 2001). The correlation gives that data for the total pressure above an aqueous 2 m MDEA solution at 313 K with an average relative deviation of 3.2%. The new data for the total pressure agree with the correlation with an average relative deviation of 2.9%.

Table 2 gives an overview of the experiments of the present work for the solubility of carbon dioxide in aqueous solutions of MDEA and one of the single strong electrolytes sulfuric acid and sodium sulfate. In a first series of measurements the solubility of CO_2 was measured in about 2 m MDEA + 1 m H_2SO_4 aqueous solutions (for temperatures from 313 to 413 K, cf. Table 3). As the strong (sulfuric) acid is completely dissociated, in such solutions the weak base MDEA is completely protonated; therefore, the solvent can be treated as a 1 m aqueous solution of the strong electrolyte $(MDEAH)_2SO_4$. The experimental results for the total pressure above that solution are plotted in Figure 1 vs. the molality of carbon dioxide. Carbon dioxide is salted-out by $(MDEAH)_2SO_4$, that is, the total pressure above the salt-

Table 2. Experimental Conditions of This Investigation

Strong Electrolyte M_2X	$\overline{m}_{MX}$ (mol/kg)	$\overline{m}_{MDEA}$ (mol/kg)	$\overline{m}_{CO_2}^{(max)}$ (mol/kg)	T (K)	$p^{(max)}$ (MPa)
H_2SO_4	1	2	1.02	313	7.88
			0.94	333	9.98
			0.72	373	10.05
			0.70	393	10.61
			0.63	413	9.81
H_2SO_4	1	4	2.53	313	3.35
			2.18	353	3.32
			1.62	393	4.21
Na_2SO_4	1	2	2.40	313	3.85
			2.29	333	4.29
			2.06	373	4.37
			1.57	413	4.54

Table 3. CO_2 Solubility in Aqueous Solutions of MDEA and H_2SO_4 ($\bar{m}_{MDEA} = 1.989$ mol/kg; $\bar{m}_{H_2SO_4} = 0.9936$ mol/kg)

T (K)	$\bar{m}_{CO_2}$ (mol/kg)	p (MPa)
313.15	0.4135	2.290
313.15	0.4707	2.682
313.15	0.6019	3.620
313.15	0.7292	4.611
313.15	0.8228	5.532
313.15	0.9750	7.137
313.14	1.020	7.879
333.14	0.3165	2.392
333.14	0.4985	4.081
333.15	0.5270	4.368
333.15	0.6418	5.554
333.15	0.7303	6.721
333.14	0.8683	8.827
333.14	0.9360	9.979
373.14	0.2174	2.479
373.14	0.3584	4.242
373.15	0.4816	5.926
373.15	0.4859	5.998
373.15	0.4883	6.008
373.16	0.5976	7.695
373.16	0.6822	9.277
373.14	0.7230	10.049
393.15	0.0	0.1905
393.15	0.0	0.1906
393.15	0.0	0.1890
393.15	0.2008	2.626
393.16	0.3682	4.872
393.15	0.3736	4.972
393.16	0.4690	6.452
393.15	0.5856	8.377
393.15	0.6681	9.901
393.15	0.7040	10.607
413.15	0.0	0.3497
413.15	0.0	0.3500
413.15	0.0	0.3478
413.15	0.1800	2.706
413.15	0.3066	4.437
413.15	0.3983	5.833
413.15	0.5257	7.866
413.15	0.6314	9.810

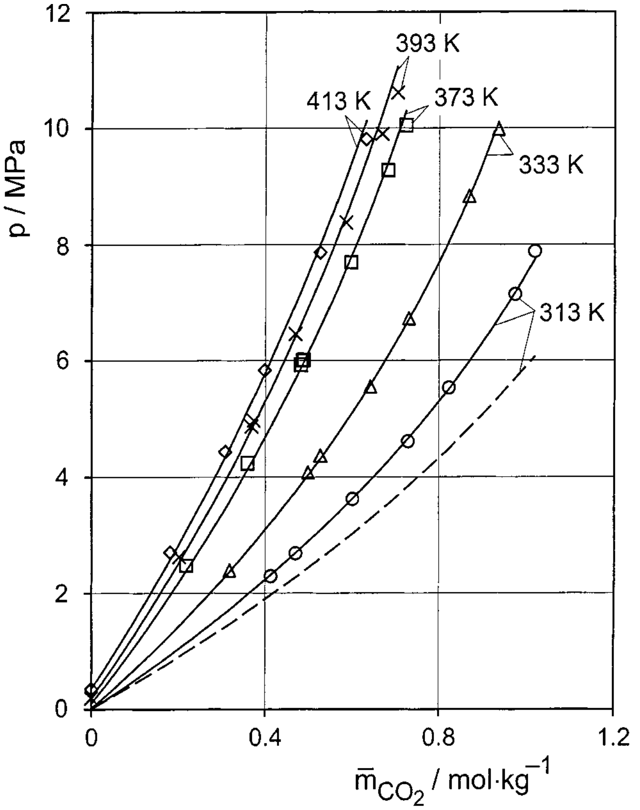

Figure 1. Total pressure in the system CO_2 + $(MDEAH)_2\ SO_4 + H_2O$ ($\bar{m}_E \approx 1$ mol/kg).

(○, △, □, ×, ◇) exp. results, this work; (—) correlation, this work; (– – –) solubility of CO_2 in water at 313 K.

containing solution is larger than that above the salt-free solution. This is shown in Figure 1 for the 313 K isotherm.

The solubility of CO_2 was also measured in about 4 m MDEA + 1 m H_2SO_4 [that is, 2 m MDEA + 1 m $(MDEAH)_2SO_4$] aqueous solutions at temperatures of 313, 353 and 393 K (cf. Table 4). The experimental results for the total pressure above those solutions are plotted in Figure 2 vs. the overall carbon dioxide molality.

Furthermore, the solubility of CO_2 was measured in about 2 m MDEA + 1 m Na_2SO_4 aqueous solutions at temperatures of 313, 333, 373 and 413 K. The experimental results for the total pressure above those solutions are given in Tables 5 and 6. The number of phases π_P in the equilibrium cell are also given, as, in some experiments, the precipitation of solid sodium bicarbonate was observed. The appearance of this salt was confirmed experimentally by analyzing the solid phase withdrawn from the cell after the completion of a series of measurements. The experimental results for the total pressure are plotted in Figure 3 vs. the overall molality of carbon dioxide. The behavior of the quaternary system CO_2 + MDEA + Na_2SO_4 + H_2O is very similar to that observed for the salt-free system (see Pérez-Salado Kamps et al., 2001).

Table 4. CO_2 Solubility in Aqueous Solutions of MDEA and H_2SO_4 ($\bar{m}_{MDEA} = 3.992$ mol/kg; $\bar{m}_{H_2SO_4} = 0.9862$ mol/kg)

T	$\bar{m}_{CO_2}$	p (MPa)	
(K)	(mol/kg)	Exp.	Pred.
313.16	1.734	0.1959	0.1717
313.15	1.969	0.4784	0.4527
313.16	2.146	1.056	1.035
313.15	2.317	1.935	1.912
313.15	2.391	2.437	2.359
313.16	2.530	3.354	3.294
353.17	0.9264	0.2512	0.2525
313.15	1.193	0.4021	0.3985
353.15	1.568	0.8213	0.8116
353.16	1.734	1.197	1.168
353.15	1.903	1.777	1.745
353.14	2.032	2.451	2.404
353.17	2.179	3.323	3.441
393.14	0.1720	0.3407	0.3285
393.14	0.5898	0.8734	0.8424
393.16	0.8674	1.413	1.372
393.15	1.132	2.124	2.092
393.15	1.315	2.745	2.766
393.13	1.501	3.570	3.649
393.14	1.617	4.207	4.335

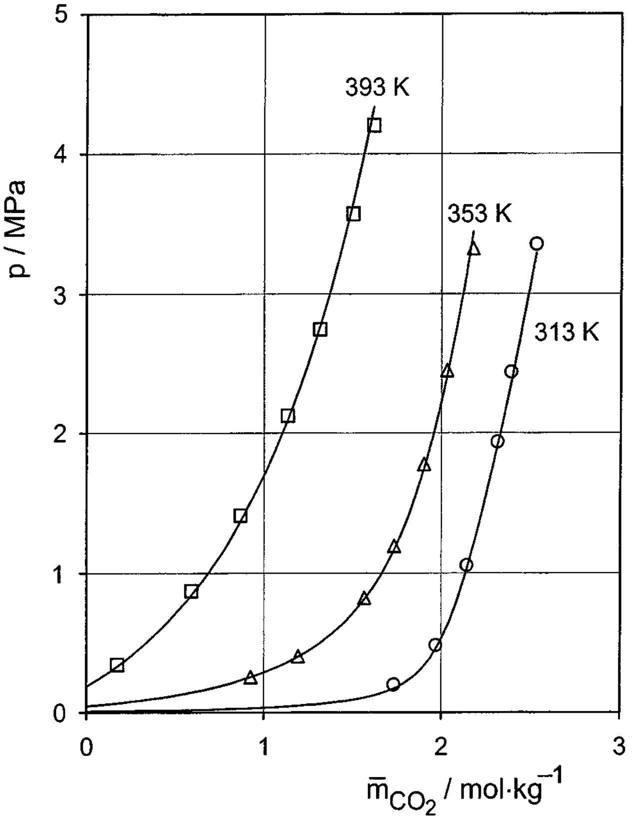

Figure 2. Total pressure in the system CO_2 + MDEA + H_2SO_4 + H_2O.

($\overline{m}_{MDEA} \approx 4$ mol/kg; $\overline{m}_{H_2SO_4} \approx 1$ mol/kg): (○, △ □) exp. results, this work; (—) prediction, this work.

As a typical example, the results at $T = 313$ K are shortly discussed. Adding carbon dioxide to an MDEA- and Na_2SO_4-containing aqueous solution at this temperature at first only slightly increases the total pressure above the solution, as, in that range, the sour gas is mostly dissolved in nonvolatile, ionic form. When the overall molality of the sour gas surmounts the overall molality of MDEA, the total pressure increases steeply as MDEA has been spent by the chemical reactions and additional sour gas can no longer be absorbed chemically, that is, in nonvolatile ionic form, but has to be dissolved physically. Qualitatively, the same behavior is observed for the other isotherms.

The new experimental results will be compared to correlations/predictions in the following chapters.

Modeling

Figure 4 shows a scheme of the model applied to correlate the solubility of carbon dioxide in aqueous solutions of MDEA and the strong electrolytes sulfuric acid and sodium sulfate. The vapor-liquid equilibrium is described by the extended Raoult's law for water

$$p_w^s \cdot \varphi_w^s \cdot \exp\left(\frac{v_w \cdot (p - p_w^s)}{R \cdot T}\right) \cdot a_w = y_w \cdot p \cdot \varphi_w'' \qquad (1)$$

Table 5. CO_2 Solubility in Aqueous Solutions of MDEA and Na_2SO_4 at 313 and 333 K ($\overline{m}_{MDEA} = 1.968$ mol/kg; $\overline{m}_{Na_2SO_4} = 1.009$ mol/kg)

T (K)	$\overline{m}_{CO_2}$ (mol/kg)	p (MPa) Exp.	p (MPa) Pred.*	p (MPa) Pred.†	π_P Exp.	π_P Pred.*	π_P Pred.†
313.15	1.781	0.1287	0.1059	0.1052	2	3	3
313.15	1.878	0.2395	0.1906	0.1871	2	3	3
313.14	1.947	0.4021	0.3423	0.3286	3	3	3
313.16	1.983	0.5048	0.4822	0.4566	3	3	3
313.14	2.050	0.9528	0.8610	0.7947	3	3	3
313.15	2.131	1.556	1.459	1.330	3	3	3
313.15	2.173	1.901	1.804	1.640	3	3	3
313.15	2.185	1.939	1.902	1.728	3	3	3
313.16	2.197	2.175	2.007	1.822	3	3	3
313.12	2.204	2.228	2.066	1.874	3	3	3
313.14	2.208	2.301	2.106	1.910	3	3	3
313.16	2.240	2.529	2.394	2.168	3	3	3
313.15	2.262	2.517	2.602	2.354	3	3	3
313.14	2.286	2.756	2.839	2.566	3	3	3
313.13	2.290	2.799	2.873	2.597	3	3	3
313.13	2.309	3.253	3.068	2.771	3	3	3
313.16	2.344	3.337	3.426	3.089	3	3	3
313.15	2.396	3.852	4.004	3.603	3	3	3
333.14	1.650	0.1976	0.1905	0.1878	2	2	2
333.15	1.746	0.2963	0.2747	0.2674	2	2	2
333.16	1.824	0.4190	0.3968	0.3784	2	2	2
333.16	1.937	0.7472	0.7795	0.6967	2	3	2
333.17	1.981	0.9877	1.037	0.8999	2	3	2
333.14	2.026	1.326	1.377	1.160	2	3	2
333.14	2.051	1.652	1.606	1.332	2	3	2
333.14	2.068	1.632	1.768	1.453	2	3	3
333.13	2.133	2.269	2.484	1.985	2	3	3
333.12	2.194	3.077	3.263	2.558	2	3	3
333.14	2.214	3.053	3.534	2.755	2	3	3
333.13	2.293	4.294	4.744	3.627	2	3	3

*$\tau_{CO_2Na^+,HCO_3^-} = 0$.
†τ_{CO_2,Na^+,HCO_3^-} according to Eq. 22 and Table 8.

Table 6. CO_2 Solubility in Aqueous Solutions of MDEA and Na_2SO_4 at 373 and 413 K ($\overline{m}_{MDEA} = 1.952$ mol/kg; $\overline{m}_{Na_2SO_4} = 0.9933$ mol/kg)

T (K)	$\overline{m}_{CO_2}$ (mol/kg)	p (MPa) Exp.	p (MPa) Pred.†	p (MPa) Pred.‡	π_P Exp.	π_P Pred.†	π_P Pred.‡
373.15	1.012	0.3315	0.2968	0.2950	2	2	2
373.16	1.133	0.4169	0.3762	0.3725	2	2	2
373.15	1.232	0.5120	0.4616	0.4549	2	2	2
373.14	1.376	0.7029	0.6342	0.6186	2	2	2
373.14	1.527	0.9802	0.9143	0.8753	2	2	2
373.17	1.578	1.047	1.048	0.9939	2	2	2
373.12	1.589	1.151	1.078	1.020	2	2	2
373.13	1.746	1.761	1.702	1.540	2	2	2
373.13	1.851	2.416	2.380	2.060	2	2	2
373.15	1.892	2.686	2.730	2.314	2	2	2
373.15	1.984	3.538	3.717	2.996	2	2	2
373.15	2.056	4.372	4.737	3.662	2	2	2
413.17*	0.1396	0.3774	0.3514	0.3514	2	2	2
413.19*	0.3496	0.5006	0.4444	0.4441	2	2	2
413.14	0.6547	0.8321	0.7580	0.7528	2	2	2
413.15	0.8892	1.305	1.218	1.194	2	2	2
413.14	1.080	1.873	1.794	1.730	2	2	2
413.15	1.198	2.329	2.273	2.160	2	2	2
413.14	1.408	3.384	3.452	3.171	2	2	2
413.15	1.486	3.894	4.037	3.650	2	2	2
413.16	1.554	4.350	4.615	4.110	2	2	2
413.16	1.573	4.536	4.798	4.253	2	2	2

*$\overline{m}_{MDEA} = 1.900$ mol/kg; $\overline{m}_{Na_2SO_4} = 0.9566$ mol/kg.
†$\tau_{CO_2,Na^+,HCO_3^-} = 0$.
‡τ_{CO_2,Na^+,HCO_3^-} according to Eq. 22 and Table 8.

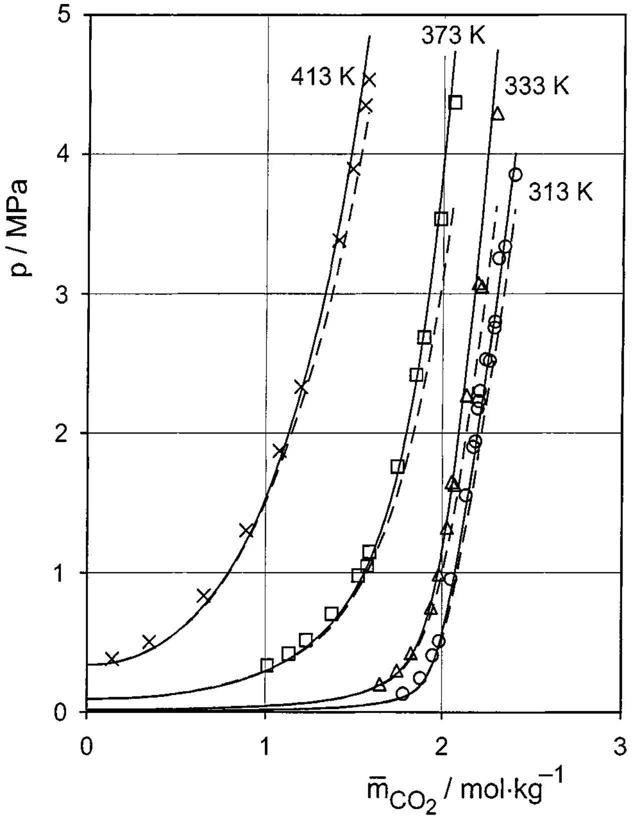

Figure 3. Total pressure in the system CO_2 + MDEA + Na_2SO_4 + H_2O.

($\bar{m}_{MDEA} \approx 2$ mol/kg; $\bar{m}_{Na_2SO_4} \approx 1$ mol/kg): (○, △, □, ×) exp. results, this work; (—) prediction 1 (with $\tau_{CO_2,Na^+,HCO_3^-} = 0$), this work; (---) prediction 2 (with τ_{CO_2,Na^+,HCO_3^-} according to Eq. 22 and Table 8), this work.

and by the extended Henry's law for carbon dioxide

$$H_{CO_2,w}(T,p_w^s)\cdot\exp\left(\frac{v_{CO_2,w}^{\infty}\cdot(p-p_w^s)}{R\cdot T}\right)\cdot a_{CO_2}=y_{CO_2}\cdot p\cdot\varphi_{CO_2}''' \qquad (2)$$

In principle, MDEA might also be present in the vapor phase. However, as the vapor pressure of pure MDEA is very small in the temperature range considered here (cf., Xu et al., 1991), the presence of MDEA in the vapor phase is neglected.

The molality of carbon dioxide in the liquid phase differs from the corresponding "overall" or stoichiometric molality as carbon dioxide reacts with MDEA. The model takes into account the following chemical reaction equilibria in the liquid phase: the formation and dissociation of bicarbonate (reactions *R*1 and *R*2), the autoprotolysis of water (reaction *R*3), the dissociation of protonated methyldiethanolamine (reaction *R*4), and the formation of bisulfate (reaction *R*5). Although reaction *R*5 is not significant in the concentration ranges considered in this work, it was included in the model in order to enable extrapolations/predictions in other concentration regions. It is assumed that the strong electrolytes sulfuric acid and sodium sulfate are fully dissociated in the aqueous phase. The condition for chemical equilibrium yields the following equation for a chemical reaction *R*

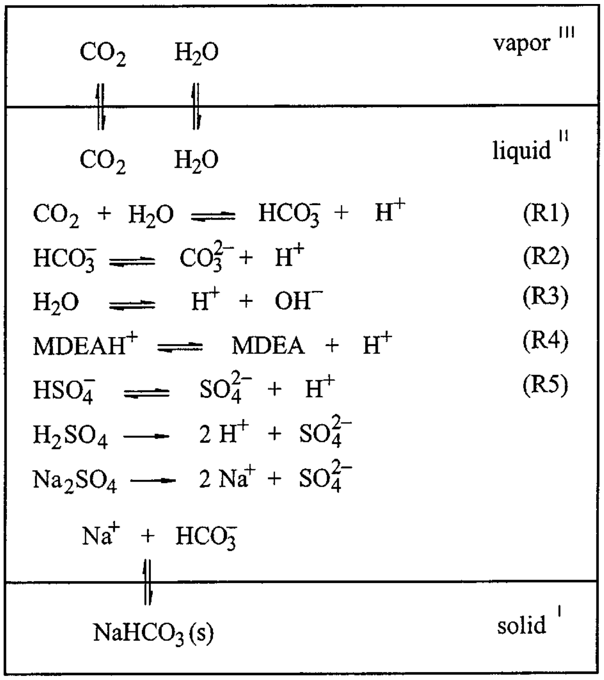

Figure 4. Vapor-liquid equilibrium and chemical reactions in the CO_2-MDEA-H_2SO_4-Na_2SO_4-H_2O system.

$$K_R(T)=\prod_i a_i^{\nu_{i,R}} \qquad (3)$$

where $\nu_{i,R}$ is the stoichiometric factor of component *i* in reaction *R* ($\nu_{i,R} > 0$ for a product and $\nu_{i,R} < 0$ for an educt). For any dissolved species (but not for the solvent water), the activity a_i is

$$a_i = m_i\gamma_i^* \qquad (4)$$

However, due to the chemical reactions, bicarbonate ions are also present, and, as the solubility of sodium bicarbonate in water is rather small, the formation of a solid phase (when Na_2SO_4 is the strong electrolyte) is also taken into account. The solid-liquid equilibrium is expressed by the solubility product

$$K_{NaHCO_3}^{(s)}(T,p) = a_{Na^+}\cdot a_{HCO_3^-} \qquad (5)$$

The precipitation of $NaHCO_3$ is neglected as long as $a_{Na^+}\cdot a_{HCO_3^-} < K_{NaHCO_3}^{(s)}$.

To determine the molalities of all (neutral and ionic) species in the liquid phase for given temperature and stoichiometric mol numbers of MDEA ($\bar{n}_{MDEA} = \bar{m}_{MDEA}$), carbon dioxide ($\bar{n}_{CO_2} = \bar{m}_{CO_2}$), water ($\bar{n}_w = 1/M_w$), sulfuric acid ($\bar{n}_{H_2SO_4} = \bar{m}_{H_2SO_4}$), and sodium sulfate ($\bar{n}_{Na_2SO_4} = \bar{m}_{Na_2SO_4}$) in the condensed phases, the equations for chemical reaction

Table 7. Partial Molar Volume for CO_2 at Infinite Dilution in Water and Mixed Second Virial Coefficient

T (K)	$v^{\infty}_{CO_2,w}$ (cm^3/mol)	$B_{CO_2,w}$ (cm^3/mol)
313.15	33.4	−163.1
333.15	34.7	−144.6
353.15	36.3	−129.0
373.15	38.3	−115.7
393.15	40.8	−104.3
413.15	43.8	−94.3

and solid-liquid equilibria have to be solved simultaneously with the mass balance equations

$$\bar{n}_w = n''_w + n''_{HCO_3^-} + n''_{CO_3^{2-}} + n''_{OH^-} + n'_{NaHCO_3} \tag{6}$$

$$\bar{n}_{CO_2} = n''_{CO_2} + n_{HCO_3^-} + n''_{CO_3^{2-}} + n'_{NaHCO_3} \tag{7}$$

$$\bar{n}_{MDEA} = n''_{MDEA} + n''_{MDEAH^+} \tag{8}$$

$$\bar{n}_{H_2SO_4} + \bar{n}_{Na_2SO_4} = n''_{SO_4^{2-}} + n''_{HSO_4^-} \tag{9}$$

$$2\bar{n}_{Na_2SO_4} = n''_{Na^+} + n'_{NaHCO_3} \tag{10}$$

and the condition for electroneutrality of the aqueous phase

$$n''_{MDEAH^+} + n''_{H^+} + n''_{Na^+} = n_{HCO_3^-} + 2n''_{CO_3^{2-}} + n''_{OH^-} + 2n''_{SO_4^{2-}} + n''_{HSO_4^-} \tag{11}$$

The model requires the following thermodynamic properties: (i) vapor pressure of water p_w^s. It was taken from Saul and Wagner (1987); (ii) molar volume of liquid water v_w, which was approximated by the molar volume of saturated liquid water v_w^s, which was also taken from Saul and Wagner (1987); (iii) Henry's constant (on molality scale) for the solubility of CO_2 in pure water. $H_{CO_2,w}$ was taken from Rumpf and Maurer (1993); (iv) partial molar volume of CO_2 at infinite dilution in water $v^{\infty}_{CO_2,w}$. It was taken from Brelvi and O'Connell (1972) (cf. Table 7); (v) fugacity coefficients (for saturated water φ_w^s and for water and carbon dioxide in the vapor phase φ_i''): They were calculated from the virial equation of state truncated after the second virial coefficient. Pure component virial coefficients were calculated from correlations given by Rumpf and Maurer (1993), which are based on the data collection by Dymond and Smith (1980). Mixed virial coefficients were estimated as recommended by Hayden and O'Connell (1975, cf. Table 7); (vi) chemical reaction equilibrium constants (on molality scale), $K_R(T,p)$ ($R \overset{\wedge}{=} R1, \ldots, R5$): K_{R1} and K_{R2} were taken from Patterson et al. (1982, 1984), K_{R3} from Edwards et al. (1978), K_{R4} from Pérez-Salado Kamps and Maurer (1996), while K_{R5} was obtained from Pitzer et al. (1977); (vii) the solubility product for $NaHCO_3$ in water (also on molality scale) was taken from Brewer (1982); (viii) activity of water a_w and activity coefficients γ_i^* of all solute species, which were calculated from a modified Pitzer (1973) model for the excess Gibbs energy G^E of aqueous solutions containing strong electrolytes. The resulting expressions are given, for example, by Pérez-Salado Kamps et al. (2001). As far as possible, interaction parameters ($\beta_{i,j}^{(0)}$, $\beta_{i,j}^{(1)}$, and $\tau_{i,j,k}$) for the interesting system $CO_2 + MDEA + H_2SO_4 + Na_2SO_4 + H_2O$ are taken from the literature on binary and ternary subsystems.

Interaction Parameters in Pitzer's G^E Model

From binary subsystems

$CO_2 + H_2O$ and $MDEA + H_2O$. When one of the single components CO_2 or MDEA 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 $\beta_{i,i}^{(0)}$ and $\tau_{i,i,i}$ (for i being CO_2 or MDEA) can be determined. However, in the concentration range being of interest in the present work all those parameters can be neglected (cf. Kuranov et al., 1996).

$H_2SO_4 + H_2O$. Interaction parameters for the system $H_2SO_4 + H_2O$ were taken from Pitzer et al. (1977). They are valid for temperatures around 298 K, but they were adopted also for temperatures up to 413 K. Although they are not significant in the concentration ranges considered in this work (very small amounts of H^+ ions), they were included in the model in order to enable extrapolations/predictions to other concentration regions.

$Na_2SO_4 + H_2O$. Interaction parameters for the system $Na_2SO_4 + H_2O$ were taken from Rogers and Pitzer (1981) for temperatures from 303 to 473 K.

$NaHCO_3 + H_2O$. Interaction parameters for the system $NaHCO_3 + H_2O$ were taken from Xia et al. (1999). They were derived from data given by Peiper and Pitzer (1982) and from experimental results for the solubility of $NaHCO_3$ in water at temperatures between 270 and 373 K.

$Na_2CO_3 + H_2O$. The correlation reported by Peiper and Pitzer (1982) for the interaction parameters in the system $Na_2CO_3 + H_2O$ was adopted in the present work. It was derived from experimental data at temperatures between 273 K and 323 K. This correlation was adopted also for temperatures up to 413 K.

$NaOH + H_2O$. Interaction parameters for this system (for temperatures from 273 to 623 K) were taken from Pabalan and Pitzer (1987). The pressure is approximated by the saturation pressure of water. They are actually not significant in the concentration ranges considered in this work (very small amounts of OH^- ions), but are included here in order to enable extrapolations/predictions to other concentration regions.

From ternary subsystems

$CO_2 + MDEA + H_2O$. Pérez-Salado Kamps et al. (2001) described experimental results for the solubility of carbon dioxide in aqueous solutions of MDEA ($m_{MDEA} \le 8$ m) in the temperature range from 313 to 413 K and for pressures up to 7.6 MPa applying Pitzer's expression for the excess Gibbs energy of the aqueous solution. The set of parameters was adopted here.

$CO_2 + (MDEAH)_2SO_4 + H_2O$. To describe the new experimental solubility pressures of carbon dioxide above aqueous 1 m solutions of $(MDEAH)_2SO_4$ (cf., Table 3) with Pitzer's equation, parameters from the binary subsystems

Table 8. Additional Interaction Parameters for Pitzer's Equation for the Systems $CO_2 + (MDEAH)_2SO_4 + H_2O$ and $CO_2 + NaOH + H_2O$ (This Work) $f(T) = q_1 + \frac{q_2}{T} + \frac{q_3}{T^2}$

Parameter	q_1	q_2	q_3	T(K)	
$B^{(0)}_{CO_2,(MDEAH)_2SO_4}$	1.1274	−826.6	155,960	313−413	Fitted
$B^{(0)}_{CO_2,NaHCO_3}$	−0.2499	274.1055	−49,880	313−433	Predicted
$\Gamma_{CO_2,NaHCO_3,NaHCO_3}$	0.2544	−219.507	42,637		Fitted

$CO_2 + H_2O$ and $(MDEAH)_2SO_4 + H_2O$ have to be taken into account. As already mentioned, however, parameters for the binary subsystem $CO_2 + H_2O$ ($\beta^{(0)}_{CO_2,CO_2}$ and $\tau_{CO_2,\,CO_2,\,CO_2}$) can be neglected. Furthermore, no experimental data are available for the binary subsystem $(MDEAH)_2SO_4 + H_2O$; therefore, interaction parameters for that subsystem ($\beta^{(0)}_{MDEAH^+,SO_4^{2-}}$, $\beta^{(1)}_{MDEAH^+,SO_4^{2-}}$ and $C^{\phi}_{(MDEAH)_2SO_4}$) had to be neglected.

The three parameters $B^{(0)}_{CO_2,(MDEAH)_2SO_4}$, $\Gamma_{CO_2,(MDEAH)_2SO_4,(MDEAH)_2SO_4}$, and $\Gamma_{CO_2,CO_2,(MDEAH)_2SO_4}$ might be considered in order to describe the new experimental results for the ternary system $CO_2 + (MDEAH)_2SO_4 + H_2O$. However, with $B^{(0)}_{CO_2,(MDEAH)_2SO_4}$ alone, the experimental results for the total pressure can be correlated with an average relative deviation of 1.6%. No remarkable improvement could be achieved by considering ternary parameters. The maximum relative deviation in the total pressure is 4.8%, occurring at $T = 413.15$ K, and $p = 2.706$ MPa, where the calculated pressure is too small by about 0.13 MPa. $B^{(0)}_{CO_2,(MDEAH)_2SO_4}$ is given in Table 8. The results of the correlation are shown in Figure 1.

$CO_2 + Na_2SO_4 + H_2O$. Interaction parameters for that system ($B^{(0)}_{CO_2Na_2SO_4}$ and $\Gamma_{CO_2,Na_2SO_4,Na_2SO_4}$) were taken from Rumpf and Maurer (1993). They are valid for temperatures from 313 to 433 K.

$CO_2 + (NH_4)_2SO_4 + H_2O$. This system is obviously not a subsystem of the interesting system $CO_2 + MDEA + H_2SO_4 + Na_2SO_4 + H_2O$. However, the interaction parameters for this system ($B^{(0)}_{CO_2,(NH_4)_2SO_4}$ and $\Gamma_{CO_2,(NH_4)_2SO_4,(NH_4)_2SO_4}$, given by Rumpf and Maurer (1993) for temperatures from 313 to 433 K) were taken into account, in order to follow the same conventions as in previous work

$$\beta_{G,NH_4^+} = 0 \tag{12}$$

$$\tau_{G,M,M} = \tau_{G,X,X} = 0 \tag{13}$$

$$\tau_{G,G,NH_4^+} = 0 \tag{14}$$

Therefore (Pérez-Salado Kamps et al., 2001)

$$\beta^{(0)}_{CO_2,SO_4^{2-}} = B_{CO_2,(NH_4)_2SO_4} \tag{15}$$

$$\beta^{(0)}_{CO_2,Na^+} = \frac{1}{2}\left[B^{(0)}_{CO_2,Na_2SO_4} - B^{(0)}_{CO_2,(NH_4)_2SO_4}\right] \tag{16}$$

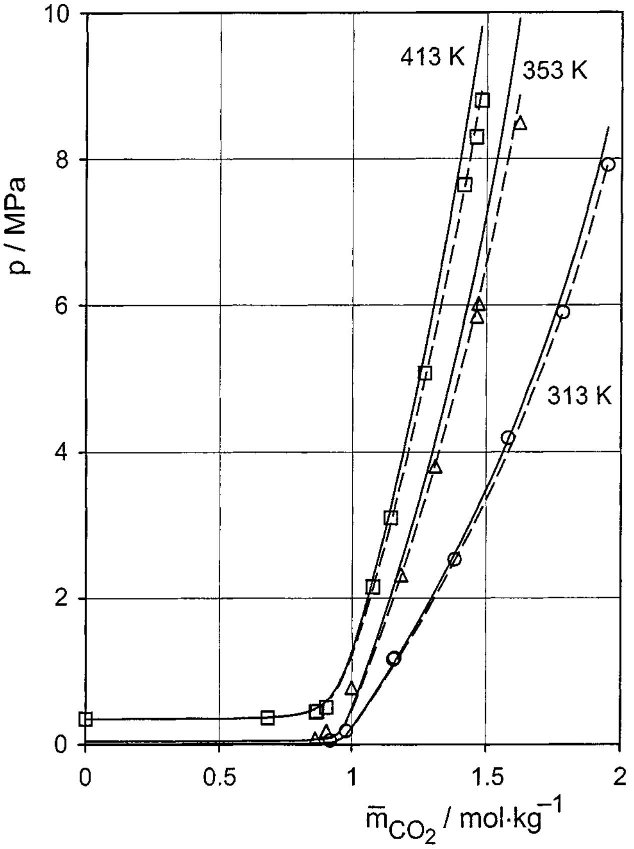

Figure 5. Total pressure in the system $CO_2 + NaOH + H_2O$ ($\bar{m}_{NaOH} \approx 1$ mol/kg).

(○, △, □) exp. results, Rumpf et al. (1998); (—) prediction, this work; (−−−) correlation, this work.

$$\tau_{CO_2,Na^+,SO_4^{2-}} = \frac{1}{4}\Gamma_{CO_2,Na_2SO_4,Na_2SO_4} \tag{17}$$

$$\beta^{(0)}_{CO_2,MDEAH^+} = \frac{1}{2}\left[B^{(0)}_{CO_2,(MDEAH)_2SO_4} - B^{(0)}_{CO_2,(NH_4)_2SO_4}\right] \tag{18}$$

$$\beta^{(0)}_{CO_2HCO_3^-} = B^{(0)}_{CO_2,MDEAHHCO_3} - \beta^{(0)}_{CO_2,MDEAH^+} \tag{19}$$

$$\beta^{(0)}_{CO_2,CO_3^{2-}} = B^{(0)}_{CO_2(MDEAH)_2CO_3} - 2\beta^{(0)}_{CO_2,MDEAH} \tag{20}$$

$CO_2 + NaOH + H_2O$. Rumpf et al. (1998) measured the solubility of carbon dioxide in about 1 *m* aqueous solutions of sodium hydroxide for temperatures from 313 to 433 K and pressures up to about 10 MPa. Some of those experimental results are shown in Figure 5. In order to predict (or correlate) the data given by Rumpf et al. (1998) with Pitzer's equation following the procedure given by those authors, parameters given above describing interactions: (1) between the neutral solute carbon dioxide (system $CO_2 + H_2O$); (2) between charged species (systems $NaHCO_3 + H_2O$, $Na_2CO_3 + H_2O$, and $NaOH + H_2O$); and (3) between neutral solute carbon dioxide and charged species (parameters $\beta^{(0)}_{CO_2,Na^+}$, $\beta^{(0)}_{CO_2,HCO_3^-}$ and $\beta^{(0)}_{CO_2,CO_3^{2-}}$) were taken into account. In 1 *m* aqueous NaOH solutions, and for overall carbon dioxide molalities up to about 1 *m*, CO_2 is practically completely dissolved in ionic form (as HCO_3^- and CO_3^{2-}). While the "true" molality of CO_3^{2-} is neglectable for higher overall carbon dioxide molali-

ties, the "true" molality of HCO_3^- is constant and equal to 1 *m*. That is, additionally added CO_2 is no longer being dissolved chemically, but physically. The experimental results in this concentration region can therefore be used to fit interaction parameters of the system $CO_2 + NaHCO_3 + H_2O$. $B^{(0)}_{CO_2,NaHCO_3}$, $\Gamma_{CO_2,NaHCO_3,NaHCO_3}$, and $\Gamma_{CO_2,CO_2,NaHCO_3}$ might be considered. However, $B^{(0)}_{CO_2,NaHCO_3}$ can be predicted from $\beta^{(0)}_{CO_2,Na^+}$ and $\beta^{(0)}_{CO_2,HCO_3^-}$

$$B^{(0)}_{CO_2,NaHCO_3} = \beta^{(0)}_{CO_2,Na^+} + \beta^{(0)}_{CO_2,HCO_3^-} \qquad (21)$$

Setting $\Gamma_{CO_2,NaHCO_3,NaHCO_3}$ and $\Gamma_{CO_2,CO_2,NaHCO_3}$ to zero, this set of parameters allows a prediction of the solubility of carbon dioxide in aqueous solutions of sodium hydroxide. A comparison between predicted and experimentally determined total pressures is shown in Figure 5 (full lines). The experimental results for the total pressure above $CO_2 + NaOH + H_2O$ are predicted with an average relative deviation of 8.7%. (This is if one neglects data points with $\bar{m}_{CO_2} \leq 1.1\ \bar{m}_{NaOH}$, where the total pressure is nearly not changed by the addition of carbon dioxide, and where the relative uncertainty in the pressure readings can reach up to 5%). By fitting $\Gamma_{CO_2,NaHCO_3,NaHCO_3}$ to that experimental data (see Figure 5, dashed lines), this average relative deviation is reduced to 3.9%. $B^{(0)}_{CO_2,NaHCO_3}$ and $\Gamma_{CO_2,\ NaHCO_3,NaHCO_3}$ are given in Table 8. Therefore (Pérez-Salado Kamps et al., 2001)

$$\tau_{CO_2,Na^+,NHCO_3^-} = \frac{1}{2}\Gamma_{CO_2,NaHCO_3,NaHCO_3} \qquad (22)$$

Predictions for Quaternary Systems

$CO_2 + MDEA + (MDEAH)_2SO_4 + H_2O$. The new experimental data (cf. Table 4) are used to assess predictions from the thermodynamic model previously presented. Parameters in Pitzer's equation describing interactions: (1) between the neutral solute carbon dioxide (from $CO_2 + H_2O$); (2) between charged species (from $H_2SO_4 + H_2O$); and (3) between neutral solutes carbon dioxide or MDEA and charged species (from $CO_2 + (NH_4)_2SO_4 + H_2O$, $CO_2 + (MDEAH)_2SO_4 + H_2O$, $CO_2 + MDEA + H_2O$) were taken into account. Calculated total pressures are given in Table 4. The total pressures were successfully predicted with an average relative deviation of 2.8%. The maximum relative deviation in the total pressure is 12.3% (at $T = 313.16$ K, and $p = 0.1959$ MPa, that is, in the low-pressure region, where the calculated pressure is too small by about 0.0242 MPa). The results of the prediction are compared to the experimental results in Figure 2.

$CO_2 + MDEA + Na_2SO_4 + H_2O$. The new experimental data (cf. Tables 5 and 6) are also used to assess predictions from the thermodynamic model presented above. Two prediction runs were performed: In a first run (prediction 1), parameters given above for interactions: (1) between the neutral solute carbon dioxide (from $CO_2 + H_2O$) and between the neutral solute MDEA (from $MDEA + H_2O$); (2) between charged species (from $H_2SO_4 + H_2O$, $Na_2SO_4 + H_2O$, $NaHCO_3 + H_2O$, $Na_2CO_3 + H_2O$, and $NaOH + H_2O$); and (3) between neutral solutes carbon dioxide or MDEA and charged species (systems $CO_2 + (NH_4)_2SO_4 + H_2O$, $CO_2 + Na_2SO_4 + H_2O$, $CO_2 + (MDEAH)_2SO_4 + H_2O$, and $CO_2 + MDEA + H_2O$) were taken into account. That is, the ternary parameter τ_{CO_2,Na^+,HCO_3^-} describing interactions in the system $CO_2 + NaOH + H_2O$ was neglected. The predictions for the total pressure deviate from the experimental data by about 6.6% (average relative deviation). In a second run (prediction 2), the parameter τ_{CO_2,Na^+,HCO_3^-} was also taken into account. In this case, the average relative deviation in the total pressures grew up to 11.4%. (Calculated total pressures for both runs are given in Tables 5 and 6, and are shown in Figure 3—full and dashed lines give predictions 1 and 2, respectively.) Thus, parameter τ_{CO_2,Na^+,HCO_3^-} has a large influence on the calculated total pressures in the system $CO_2 + MDEA + Na_2SO_4 + H_2O$. Figure 6 shows predictions for "true" molalities of all solute species present in the liquid phase (except H^+, OH^-, and HSO_4^-) for the aqueous 2 *m* MDEA and 1 *m* Na_2SO_4 solution at 313 K, when carbon dioxide is added. (For that calculation, τ_{CO_2,Na^+,HCO_3^-} was set to zero.) As expected, adding carbon dioxide to an MDEA solution reduces the amount of neutral MDEA, thereby producing protonated MDEA, bicarbonate, and carbonate ions. Furthermore, the number of mols of solid $NaHCO_3$ per kg of water is shown. When the solubility limit of $NaHCO_3$ is surpassed, the increase in the concentration of HCO_3^- is damped. For the experimental data points at high molalities of carbon dioxide, that is, in the region where the increase in the total pressure curve is steep, the total pressure is dominated by the amount of neutrally dissolved carbon dioxide. As that amount is small in comparison to the overall amount of dissolved carbon dioxide, that is, in ionic or neutral form, or in the precipitated salt, very small absolute deviations in that amount result in large deviations in the total pressure. This example demonstrates that even very small uncertainties in predictions for the composition of the liquid phase or in the amount of the precipitated salt—resulting, for example, from different values for parameter τ_{CO_2,Na^+,HCO_3^-}—lead to a large uncertainty in the predictions of the concentration of neutrally dissolved carbon dioxide and consequently also for the pres-

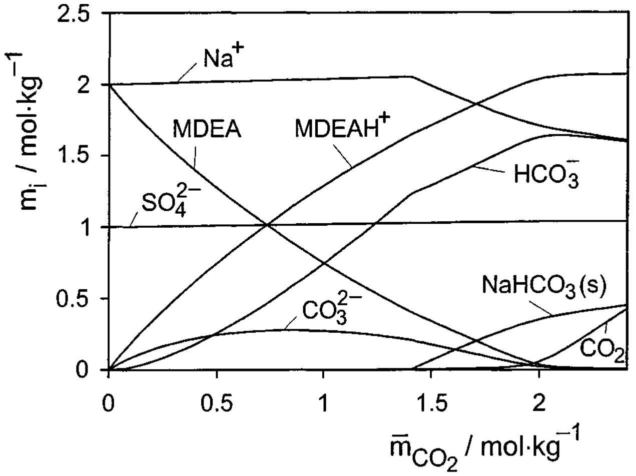

Figure 6. Predicted species distribution in the $CO_2 + MDEA + Na_2SO_4 + H_2O$ system at 313 K.

($\bar{m}_{MDEA} = 2$ mol/kg; $\bar{m}_{Na_2SO_4} = 1$ mol/kg).

sures. However, there are many more other parameters that may influence the predicted total pressures in this system—such as $\tau_{\mathrm{Na}^+,\mathrm{MDEAH}^+,\mathrm{HCO}_3^-}$, $\tau_{\mathrm{Na}^+,\mathrm{MDEAH}^+,\mathrm{SO}_4^{2-}}$—which were neglected due to the lack of experimental information. Nevertheless, the predictions for the total pressure agree reasonably with the experimental data.

Conclusions

The solubility of carbon dioxide in aqueous solutions of MDEA (2 *m*) and sulfuric acid (1 *m*) was measured in the temperature range from 313 K to 413 K at total pressures up to 10.6 MPa. Interaction parameters for Pitzer's G^E-equation were determined from the new experimental results. A thermodynamic model is presented—based on Pitzer's equation for the Gibbs excess energy—allowing for predictions of vapor-liquid and vapor-liquid-solid equilibrium data in aqueous MDEA solutions containing the strong electrolytes sulfuric acid and sodium sulfate. The model is based on investigations of binary and ternary subsystems. The solubility of carbon dioxide in aqueous solutions of MDEA (4 *m*) and sulfuric acid (1 *m*), as well as in aqueous solutions of MDEA (2 *m*) and sodium sulfate (1 *m*), was measured at temperatures from 313 K to 413 K and total pressures up to 4.5 MPa, in order to assess model predictions. The model is able to quantitatively predict the new experimental results for the total pressure. The calculated results for the pressure in the system containing sodium sulfate can be improved by fitting some additional interaction parameters. Such a procedure might be reasonable for some applications, but, from a more general point of view, is not recommended, as the influence of different parameters cannot be separated in such a multicomponent system.

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Notation

a_i = activity of component *i*
$B_{i,j}$ = second virial coefficient for interactions between components *i* and *j*
$B^{(r)}_{G,MX}$ = effective second osmotic virial coefficient in Pitzer's equation for interactions between a gas *G* and a salt *MX* ($r = 0, 1$)
f = function
G^E = excess Gibbs energy
H_{i,CO_2} = Henry's constant for the solubility of CO_2 *i* in pure water (on molality scale)
K_R = equilibrium constant for chemical reaction *R* (on molality scale)
$K_i^{(s)}$ = solubility product for salt *i* in water (on molality scale)
m_i = true molality of component *i*
$\overline{m}_i$ = overall (stoichiometric) molality of component *i*
M_w = molar mass of water in kg/mol
M = cation *M*
n_i = true number of moles of component *i*
$\bar{n}_i$ = overall (stoichiometric) number of mols 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
X = anion *X*
y = vapor phase mol fraction
$\beta^{(0)}, \beta^{(1)}$ = binary interaction parameters in Pitzer's equation
Γ = third osmotic virial coefficient in Pitzer's equation
γ_i^* = activity coefficient of component *i* normalized to infinite dilution (on molality scale)
$\nu_{i,R}$ = stoichiometric coefficient of component *i* in reaction *R*
π_P = number of phases
τ = third virial coefficient in Pitzer's equation
Γ = third osmotic virial coefficient in Pitzer's equation
φ = fugacity coefficient

Subscripts

exptl = experimental
i,j,k = component *i*, *j*, *k*
MX = strong electrolyte
pred = prediction
R = reaction *R*
w = water

Superscripts

max = maximum
s = saturation
$*$ = normalized to infinite dilution
∞ = infinite dilution in pure water
$'$ = solid phase
$''$ = liquid phase
$'''$ = vapor phase

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