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Chemical equilibrium constants for the formation of carbamates in (carbon dioxide + piperazine + water) from ¹H-NMR-spectroscopy

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Abstract

¹H-NMR spectroscopic investigations were performed on aqueous solutions of carbon dioxide and piperazine at temperatures ranging from (283 to 333) K to determine quantitatively the speciation. The experimental results were used to determine the chemical equilibrium constants for the formation of piperazine carbamate, piperazine dicarbamate and protonated piperazine carbamate.

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Keywords: Chemical reacting aqueous electrolyte solutions; Chemical equilibrium constants; Carbon dioxide; Piperazine; Carbamate

1. Introduction

Aqueous solutions of *N*-methyldiethanolamine (MDEA) are widely used for the sweetening of sour gases, particularly for the selective removal of carbon dioxide and/or hydrogen sulfide from gaseous effluents (*e.g.*, natural gases). In such solutions the sour gases are partially converted to ionic species while MDEA is protonated. As the absorption of carbon dioxide is hindered by slow kinetics, it is possible to favor

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the absorption of hydrogen sulfide over that of carbon dioxide. Process modifications attempt to improve the selective absorption of hydrogen sulfide by adding modifiers (usually primary or secondary amines) to the aqueous MDEA solution. Piperazine (PIPH₂) is a commonly used modifier.

The reliable design of such separation equipment requires equilibrium data as deviation from equilibrium provides the driving force in that kinetically controlled process. Correlating and predicting the (vapor + liquid) equilibrium for the simultaneous solubility of CO_2 and H_2S in aqueous solutions of MDEA and piperazine at first requires reliable information on the solubility of the single gases in water and in the aqueous solutions of the single amines as well as information on the equilibrium constants of the chemical reactions.

In previous work [1,2], the solubility of the single gases carbon dioxide and hydrogen sulfide in aqueous MDEA solutions was investigated at temperatures ranging from (313 to 413) K, for MDEA molalities up to 8 mol \cdot kg⁻¹ of water, and pressures up to about 8 MPa. New experimental results were recently presented for the solubility of hydrogen sulfide in aqueous solutions of piperazine at temperatures between (313 and 393) K, for piperazine molalities up to 4 mol \cdot kg⁻¹ of water, and pressures up to about 9 MPa [3]. Furthermore, the protonation of *N*-methyldiethanolamine in aqueous solution was investigated at temperatures from (278 to 368) K [4].

Piperazine is protonated and diprotonated in aqueous solutions in the presence of a sour gas. Furthermore, carbon dioxide and piperazine react in aqueous solutions to form (three) carbamate species: piperazine carbamate, piperazine dicarbamate and protonated piperazine carbamate. The chemical equilibrium constants for the protonation of piperazine are available in the literature [5], whereas only rough estimates have been published recently for the chemical equilibrium constants for the formation of the three carbamates [6,7].

In the present work the chemical reaction equilibrium for the formation of the three carbamate species is studied by ¹H-NMR spectroscopy. The experimental results are evaluated to determine species concentrations which furthermore are used to determine the chemical equilibrium constants for the formation of piperazine carbamate, piperazine dicarbamate and protonated piperazine carbamate. The NMR-investigations were carried out at temperatures ranging from (283 to 333) K at various overall concentrations of piperazine and carbon dioxide.

2. Experimental

¹H-NMR spectroscopy was applied to investigate solutions of (carbon dioxide + piperazine + deuterium oxide) to determine quantitatively the speciation. A Bruker DPX 400 NMR spectrometer (proton resonance frequency of 400.13 MHz) was used for the experiments. Measurements were performed at T = (283, 298, 313, and 333) K for piperazine molalities ranging from (0.1 to 1.5) mol \cdot kg⁻¹ of water. The aqueous solutions (with fixed piperazine molality) were loaded with up to one mol of carbon dioxide per mol of piperazine. Altogether 121 experiments were performed.

The aqueous piperazine solutions were prepared in a storage tank by dissolving known amounts of piperazine in pure deuterium oxide (D₂O). The stoichiometric molality of piperazine was determined gravimetrically with a relative uncertainty ranging from about ± 0.01 per cent (for the higher piperazine molalities) up to about ± 0.1 per cent (for the lower piperazine molalities). Carbon dioxide was volumetrically charged to an aqueous piperazine solution by means of a high precision displacement pump. The mass of carbon dioxide filled into the cell was calculated, assuming it was an ideal gas, with the experimental temperature and pressure ($T \approx 293$ K, $p \approx 0.1$ MPa). The stoichiometric molality of carbon dioxide is known with a relative uncertainty of at maximum ± 0.3 per cent. The liquid solutions were filled into NMR pyrex tubes which were evacuated before. The charged cells were sealed by means of a glass blowing burner. The cells were thermostated in a water bath for about 24 h before they were immersed into the spectrometer, which was kept at the same temperature. That temperature was controlled with an accuracy of about ± 0.1 K.

Carbon dioxide (mole fraction ≥ 0.99995) was purchased from Messer–Griesheim, Ludwigshafen, Germany. It was used without further purification. Piperazine (anhydrous, mass fraction ≥ 0.99 , Fluka Feinchemikalien GmbH, Neu-Ulm, Germany) and D₂O (mole fraction ≥ 0.999 , Sigma–Aldrich, Deisenhofen, Germany) were separately degassed under vacuum.

Figure 1 shows the molecular structure of the piperazine compounds present in (carbon dioxide + piperazine + deuterium oxide). When piperazine is dissolved in deuterium oxide, the protons (*i.e.*, the hydrogen atoms) bound in the NH amine groups are exchanged by deuterium atoms, producing a single peak in the water region ($\delta \approx 5$ ppm, cf. Chamberlain [8] where δ is the chemical shift). Figure 2 shows a typical ¹H-NMR spectrum of an aqueous solution of CO₂ and piperazine taken in the present work. All peaks in figure 2 result from protons bound in CH₂ groups in piperazine carbamate (PIPD₂⁺COO⁻), peak 2 is assigned to protons bound in CH₂ groups in molecular piperazine (PIPD₂⁺), and peak 3 is assigned to protons bound in CH₂ groups in piperazine (PIPD₂⁺), and peak 3 is assigned to protons bound in CH₂ groups in piperazine (PIPD₂⁺).

This assignment results from the assumption, that any protonation (by deuterium) of a molecule does not affect the chemical NMR environment of the H-atoms bound in those CH₂ groups. In order to confirm that assumption, we performed some ¹H-NMR measurements on (deuterium chloride + piperazine + deuterium oxide), for molar ratios of DCl to piperazine up to about two. Those solutions contain piperazine in molecular, in protonated as well as in diprotonated form. But – as expected – always only one additional peak appeared at $\delta \approx 2.8$ ppm.

The peak areas (the intensities) are proportional to the number of corresponding protons (*i.e.*, protons with same NMR chemical environment) in the solution (cf. *e.g.*, Chamberlain [8]). Therefore, the following equation must hold:



FIGURE 1. Molecular structure of piperazine species in (carbon dioxide + piperazine + deutrium oxide).



FIGURE 2. ¹H-NMR spectrum of (carbon dioxide + piperazine + deuterium oxide) at T = 298 K ($\bar{n}_{\text{PIPH}_2} \approx 1.5$ mol, $\bar{n}_{\text{CO}_2} \approx 0.8$ mol, $\tilde{\vec{m}}_{\text{D}_2\text{O}} = 1$ kg).

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$$A_i = k \sum_j N_{i,j} n_j, \tag{1}$$

where A_i is the peak area corresponding to protons with environment *i*, $N_{i,j}$ is the number of protons with environment *i* in component *j*, n_j the number of moles of component *j*, and *k* is a proportionality constant, which is independent of the proton with environment *i*. This constant has the same numerical value for all peak areas in a given spectrum, but has different values in different spectra.

Applying equation (1) to our system leads to the following equations:

$$A_1 = 4k(n_{\text{PIPDCOO}^-} + n_{\text{PIPD}^+_{\text{-}}\text{COO}^-}), \qquad (2)$$

$$A_2 = 8k(n_{\rm PIPD_2} + n_{\rm PIPD_2^+} + n_{\rm PIPD_4^{2+}}), \tag{3}$$

$$A_3 = 8kn_{\text{PIP}(\text{COO}^-)_2},\tag{4}$$

and

$$A_4 = 4k(n_{\text{PIPDCOO}^-} + n_{\text{PIPD}^+_2\text{COO}^-}).$$
(5)

No calibration is necessary in order to obtain the proportionality constant k. It follows from the mass balance for piperazine, and by addition of equations 2 to 5 and was determined for every single spectrum:

$$k = \frac{(A_1 + A_2 + A_3 + A_4)}{8\bar{n}_{\text{PIPH}_2}}.$$
(6)

From equations 2 to 6, the mole numbers of piperazine species corresponding to the peak areas can be calculated and listed into tables 1–4. The moles of piperazine carbamate and protonated piperazine carbamate may be calculated from the peak areas A_1 or A_4 . We calculated them from the sum of both areas:

$$A_1 + A_4 = 8k(n_{\rm PIPDCOO^-} + n_{\rm PIPD^+_{3}COO^-}).$$
⁽⁷⁾

In order to estimate the experimental uncertainty, the mean relative deviation in these sum of mole numbers, following whether from equations (2) or (5), or from equation (7) were calculated. This uncertainty amounts to about (2 ± 1.9) per cent. But, when an experiment was repeated several times, the difference in the calculated mole numbers (or sum of mole numbers), corresponding to the different peak areas (or sum of peak areas) was never higher than one per cent.

As an example, figure 3 shows the experimentally determined amount-of-substances of piperazine species plotted versus the stoichiometric mole number of carbon dioxide in an about one molal aqueous piperazine solution at T = 298 K.

The experimentally determined species concentrations were used to determine the equilibrium constants for the formation of piperazine carbamate, dicarbamate and protonated carbamate. The evaluation procedure is explained in the following chapter.

Speciation in (carbon dioxide + piperazine + water) from ¹H-NMR measurements at T = 283.15K and $\tilde{m}_{D_2O} = 1$ kg where \bar{n} and n are the stoichiometric and the true number of moles of species *i*, respectively

$\bar{n}_{\mathrm{PIPH}_2}$	\bar{n}_{PIPH_2} \bar{n}_{CO_2} $\sum_i n_i$			
(mol)	(mol)	(mol)		
		$i = \text{PIPD}_2, \text{PIPD}_3^+, \text{PIPD}_4^{2+}$	$i = \text{PIPDCOO}^-, \text{PIPD}_2^+\text{COO}^-$	$i = \operatorname{PIP}(\operatorname{COO}^{-})_2$
1.4489	1.3974	0.4119	0.9905	0.0465
1.4687	1.2260	0.4967	0.8734	0.0986
1.4687	0.9824	0.6858	0.6619	0.1211
1.4775	0.8166	0.8203	0.5628	0.0945
1.4489	0.6810	0.8973	0.4812	0.0704
1.4489	0.5087	0.9923	0.4198	0.0368
1.4489	0.3418	1.1303	0.3052	0.0133
1.4489	0.2845	1.1748	0.2658	0.0082
0.9998	0.9651	0.3107	0.6566	0.0325
0.9996	0.8179	0.3931	0.5425	0.0639
0.9996	0.7425	0.4478	0.4779	0.0739
0.9996	0.6455	0.5030	0.4243	0.0723
0.9998	0.4881	0.6164	0.3384	0.0450
0.9998	0.3386	0.7172	0.2616	0.0210
0.9998	0.2361	0.7894	0.1993	0.0111
0.4990	0.5040	0.1846	0.3064	0.0080
0.4630	0.3917	0.2016	0.2428	0.0186
0.4630	0.3149	0.2353	0.2026	0.0251
0.4990	0.2555	0.3145	0.1651	0.0193
0.4630	0.2076	0.3063	0.1430	0.0136
0.4990	0.1684	0.3684	0.1229	0.0077
0.5122	0.1077	0.4220	0.0871	0.0031
0.2858	0.2611	0.1349	0.1451	0.0058
0.2858	0.1888	0.1652	0.1079	0.0127
0.2858	0.1255	0.1986	0.0804	0.0069
0.2858	0.0590	0.2411	0.0431	0.0016
0.2160	0.1695	0.1191	0.0892	0.0077
0.2160	0.1225	0.1366	0.0711	0.0083
0.2160	0.0734	0.1633	0.0494	0.0032
0.2160	0.0352	0.1888	0.0264	0.0008
0.1033	0.0732	0.0684	0.0324	0.0025
0.1033	0.0498	0.0745	0.0272	0.0016
0.1033	0.0235	0.0890	0.0140	0.0003

3. Correlation

Due to chemical reactions, carbon dioxide is dissolved in an aqueous solution of piperazine not only in neutral, but also in non-volatile, ionic form. The following chemical reactions are considered: the autoprotolysis of water (reaction I), the protonation and diprotonation of piperazine (reactions II, III), the formation and dissociation of bicarbonate (reactions IV, V), and the formations of piperazine carbamate, piperazine dicarbamate and protonated piperazine carbamate (reactions VI, VII, and VIII):

Speciation in the (carbon dioxide + piperazine + water) system from ¹H-NMR measurements at T = 298.15 K and $\tilde{m}_{D_2O} = 1$ kg where \bar{n} and n are the stoichiometric and the true number of moles of species *i*, respectively

$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\bar{n}_{\mathrm{PIPH}_2}$	$\bar{n}_{\rm CO_2}$	$\sum_{i} n_i$		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	(mol)	(mol)			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			$i = \text{PIPD}_2, \text{PIPD}_3^+, \text{PIPD}_4^{2+}$	$i = \text{PIPDCOO}^-, \text{PIPD}_2^+\text{COO}^-$	$i = \text{PIP}(\text{COO}^-)_2$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.4489	1.3974	0.5096	0.9393	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.4687	1.2260	0.5651	0.8080	0.0957
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.4687	0.9824	0.7465	0.6087	0.1134
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.4775	0.8166	0.8711	0.5156	0.0909
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.4489	0.6810	0.9347	0.4493	0.0649
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.4489	0.5087	1.0446	0.3703	0.0340
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.4489	0.3418	1.1676	0.2673	0.0140
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.4489	0.2845	1.2276	0.2130	0.0082
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.9998	0.9651	0.4220	0.5777	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.9996	0.8179	0.4398	0.4983	0.0615
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.9996	0.7425	0.4888	0.4432	0.0676
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.9996	0.6455	0.5481	0.3843	0.0672
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.9998	0.4881	0.6485	0.3093	0.0420
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.9998	0.3386	0.7434	0.2371	0.0192
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.9998	0.2361	0.8135	0.1777	0.0086
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.4990	0.5040	0.2346	0.2644	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.4630	0.3917	0.2361	0.2107	0.0162
	0.4630	0.3149	0.2708	0.1700	0.0222
0.4630 0.2076 0.3235 0.1267 0.0127 0.4990 0.1684 0.3820 0.1099 0.0071 0.5122 0.1077 0.4339 0.0755 0.0027 0.2858 0.2611 0.1472 0.1333 0.0053 0.2858 0.1888 0.1672 0.1091 0.0096 0.2858 0.1255 0.2006 0.0796 0.0056 0.2858 0.0590 0.2393 0.0452 0.0013 0.2160 0.0352 0.1915 0.0240 0.0005 0.2160 0.0734 0.1664 0.0473 0.0022	0.4990	0.2555	0.3299	0.1519	0.0172
0.49900.16840.38200.10990.00710.51220.10770.43390.07550.00270.28580.26110.14720.13330.00530.28580.18880.16720.10910.00960.28580.12550.20060.07960.00560.28580.05900.23930.04520.00130.21600.03520.19150.02400.00050.21600.07340.16640.04730.0022	0.4630	0.2076	0.3235	0.1267	0.0127
0.5122 0.1077 0.4339 0.0755 0.0027 0.2858 0.2611 0.1472 0.1333 0.0053 0.2858 0.1888 0.1672 0.1091 0.0096 0.2858 0.1255 0.2006 0.0796 0.0056 0.2858 0.0590 0.2393 0.0452 0.0013 0.2160 0.0352 0.1915 0.0240 0.0005 0.2160 0.0734 0.1664 0.0473 0.0022	0.4990	0.1684	0.3820	0.1099	0.0071
0.2858 0.2611 0.1472 0.1333 0.0053 0.2858 0.1888 0.1672 0.1091 0.0096 0.2858 0.1255 0.2006 0.0796 0.0056 0.2858 0.0590 0.2393 0.0452 0.0013 0.2160 0.0352 0.1915 0.0240 0.0005 0.2160 0.0734 0.1664 0.0473 0.0022	0.5122	0.1077	0.4339	0.0755	0.0027
0.2858 0.1888 0.1672 0.1091 0.0096 0.2858 0.1255 0.2006 0.0796 0.0056 0.2858 0.0590 0.2393 0.0452 0.0013 0.2160 0.0352 0.1915 0.0240 0.0005 0.2160 0.0734 0.1664 0.0473 0.0022	0.2858	0.2611	0.1472	0.1333	0.0053
0.2858 0.1255 0.2006 0.0796 0.0056 0.2858 0.0590 0.2393 0.0452 0.0013 0.2160 0.0352 0.1915 0.0240 0.0005 0.2160 0.0734 0.1664 0.0473 0.0022	0.2858	0.1888	0.1672	0.1091	0.0096
0.2858 0.0590 0.2393 0.0452 0.0013 0.2160 0.0352 0.1915 0.0240 0.0005 0.2160 0.0734 0.1664 0.0473 0.0022	0.2858	0.1255	0.2006	0.0796	0.0056
0.2160 0.0352 0.1915 0.0240 0.0005 0.2160 0.0734 0.1664 0.0473 0.0022	0.2858	0.0590	0.2393	0.0452	0.0013
0.2160 0.0734 0.1664 0.0473 0.0022	0.2160	0.0352	0.1915	0.0240	0.0005
	0.2160	0.0734	0.1664	0.0473	0.0022
0.2160 0.1225 0.1420 0.0686 0.0053	0.2160	0.1225	0.1420	0.0686	0.0053
0.2160 0.1695 0.1274 0.0828 0.0057	0.2160	0.1695	0.1274	0.0828	0.0057
0.1033 0.0235 0.0905 0.0126 0.0002	0.1033	0.0235	0.0905	0.0126	0.0002
0.1033 0.0498 0.0785 0.0239 0.0010	0.1033	0.0498	0.0785	0.0239	0.0010
0.1033 0.0732 0.0698 0.0321 0.0014	0.1033	0.0732	0.0698	0.0321	0.0014

(I)
(II)
(III)
(IV)

$$\mathrm{HCO}_{3}^{-} \rightleftharpoons \mathrm{CO}_{3}^{2-} + \mathrm{H}^{+}, \tag{V}$$

Speciation in (carbon dioxide + piperazine + water) from ¹H-NMR measurements at T = 313.15 K and $\tilde{m}_{D_2O} = 1$ kg where \bar{n} and n are the stoichiometric and the true number of moles of species *i*, respectively

$\bar{n}_{\mathrm{PIPH}_2}$	$\bar{n}_{\rm CO_2}$	$O_2 \qquad \sum_i n_i$			
(mol)	(mol)	(mol)			
		$i = \text{PIPD}_2, \text{PIPD}_3^+, \text{PIPD}_4^{2+}$	$i = \text{PIPDCOO}^-, \text{PIPD}_2^+\text{COO}^-$	$i = \text{PIP}(\text{COO}^-)_2$	
1.4489	1.3974	0.6118	0.8371		
1.4687	1.2260	0.5995	0.7514	0.1178	
1.4687	0.9824	0.8194	0.5444	0.1049	
1.4775	0.8166	0.8666	0.5190	0.0919	
1.4489	0.6810	0.9359	0.4420	0.0710	
1.4489	0.5087	1.0300	0.3775	0.0414	
1.4489	0.3418	1.1660	0.2665	0.0165	
1.4489	0.2845	1.1899	0.2481	0.0109	
0.9998	0.9651	0.4570	0.5428		
0.9996	0.8179	0.4526	0.4676	0.0794	
0.9996	0.7425	0.4909	0.4333	0.0754	
0.9996	0.6455	0.5213	0.4122	0.0661	
0.9998	0.4881	0.6323	0.3184	0.0491	
0.9998	0.3386	0.7335	0.2430	0.0233	
0.9998	0.2361	0.7994	0.1884	0.0119	
0.4990	0.5040	0.2968	0.2021		
0.4630	0.3917	0.2511	0.1942	0.0176	
0.4630	0.3149	0.2780	0.1660	0.0190	
0.4990	0.2555	0.3298	0.1499	0.0192	
0.4630	0.2076	0.3202	0.1324	0.0104	
0.4990	0.1684	0.3756	0.1141	0.0093	
0.5122	0.1077	0.4232	0.0869	0.0020	
0.2858	0.2611	0.1711	0.1147		
0.2858	0.1888	0.1783	0.0980	0.0095	
0.2858	0.1255	0.2064	0.0739	0.0055	
0.2858	0.0590	0.2435	0.0408	0.0015	
0.2160	0.1695	0.1395	0.0717	0.0047	
0.2160	0.1225	0.1474	0.0631	0.0055	
0.2160	0.0734	0.1674	0.0461	0.0025	
0.2160	0.0352	0.1895	0.0261	0.0004	
0.1033	0.0732	0.0734	0.0284	0.0015	
0.1033	0.0498	0.0802	0.0223	0.0009	
0.1033	0.0235	0.0904	0.0127	0.0002	

$PIPH_2 + HCO_3^- \rightleftharpoons PIPHCOO^- + H_2O_3$ (V	V]	I)
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$$PIPHCOO^{-} + HCO_{3}^{-} \rightleftharpoons PIP(COO^{-})_{2} + H_{2}O, \qquad (VII)$$

and

$$PIPHCOO^{-} + H^{+} \rightleftharpoons PIPH_{2}^{+}COO^{-}.$$
 (VIII)

The condition for chemical equilibrium yields the following equation for the equilibrium constant *K*:

Speciation in (carbon dioxide + piperazine + water) from ¹H-NMR measurements at T = 333.15K and $\tilde{m}_{D_2O} = 1$ kg where \bar{n} and n are the stoichiometric and the true number of moles of species *i*, respectively

$\bar{n}_{\mathrm{PIPH}_2}$	$\bar{n}_{\rm CO_2}$	$\sum_i n_i$		
(mol)	(mol)	(mol)		
		$i = \text{PIPD}_2, \text{PIPD}_3^+, \text{PIPD}_4^{2+}$	$i = \text{PIPDCOO}^-, \text{PIPD}_2^+\text{COO}^-$	$i = \text{PIP}(\text{COO}^-)_2$
1.4489	1.3974	0.7412	0.7077	
1.4687	1.2260	0.6714	0.6859	0.1114
1.4687	0.9824	0.7664	0.4337	0.2686
1.4775	0.8166	0.9874	0.3032	0.1870
1.4489	0.6810	1.0083	0.3679	0.0727
1.4489	0.5087	1.0906	0.2885	0.0698
1.4489	0.3418	1.1693	0.2557	0.0239
1.4489	0.2845	1.2301	0.1982	0.0206
0.9998	0.9651	0.5169	0.4828	
0.9996	0.8179	0.6594	0.1815	0.1587
0.9996	0.7425	0.6505	0.2019	0.1471
0.9996	0.6455	0.5487	0.2448	0.2061
0.9998	0.4881	0.7039	0.2526	0.0433
0.9998	0.3386	0.7770	0.1842	0.0385
0.9998	0.2361	0.8259	0.1514	0.0225
0.4990	0.5040	0.2919	0.2071	
0.4630	0.3917	0.2491	0.1195	0.0944
0.4630	0.3149	0.3024	0.1012	0.0594
0.4990	0.2555	0.3652	0.0998	0.0340
0.4630	0.2076	0.3661	0.0690	0.0278
0.4990	0.1684	0.3982	0.0894	0.0114
0.5122	0.1077	0.4384	0.0709	0.0029



FIGURE 3. Speciation in (carbon dioxide + piperazine + deuterium dioxide) at T = 298 K resulting from ¹H-NMR measurements at $(\bar{n}_{\text{PIPH}_2} \approx 1 \text{ mol and } \tilde{\tilde{m}}_{D_2O} = 1 \text{ kg})$ compared with the correlation. \blacktriangle , PIP(COO⁻)₂; \blacksquare , (PIPDCOO⁻ + PIPD₂⁺COO⁻); and \blacklozenge , (PIPD₂ + PIPD₃⁺ + PIPD₄²⁺).

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$$K_R(T) = \prod_i a_i^{v_{i,R}},\tag{8}$$

where $v_{i,R}$ is the stoichiometric coefficient of species *i* in reaction *R* and a_i is the activity of species *i*. The balance equations for the number of moles of a species *i* in the liquid phase is:

$$n_i = \bar{n}_i + \sum_R v_{i,R} \xi_R,\tag{9}$$

where ξ_R is the extent of reaction *R*. Solving this set of equations for a given temperature and given stoichiometric numbers \bar{n}_i of mixed components (*i.e.*, CO₂, piperazine, and H₂O) results in the "true" composition of the liquid phase, *i.e.*, the mole numbers of all neutral and ionic species. The calculation requires an activity coefficient model for aqueous electrolyte solutions (*e.g.*, Pitzer [9]), and the knowledge of the temperature dependent chemical equilibrium constants K_I to K_{VIII} (on the molality scale, if Pitzer's G^E equation is used).

Constants K_{I} to K_{V} were taken from literature. Details on the correlation equations for those reactions were given by Pérez–Salado Kamps *et al.* [2] and Xia *et al.* [3]. Temperature dependent constants K_{VI} to K_{VIII} were simultaneously fitted to the ¹H-NMR speciation data on the system (carbon dioxide + piperazine + water). For that purpose, two assumptions were applied: on one hand, in Pitzer's G^{E} equation only the modified Debye–Hückel term was considered (*e.g.*, Pérez–Salado Kamps *et al.* [2]), that is all interaction parameters were set to zero – the ionic strength was always less than one molal. On the other hand, the reaction enthalpies of reactions VI to VIII were assumed to be temperature independent, and the temperature dependency of the equilibrium constants for these reactions was described with a two parameter equation:

$$\lg K_R(T) = A_R + \frac{B_R}{T}.$$
(10)

The optimization was performed as follows. In a first step, the protonation constant of piperazine carbamate ($K_{\rm VIII}$) was estimated (*i.e.*, parameters $A_{\rm VIII}$ and $B_{\rm VIII}$ of equation (10) were set to a reasonable starting number). According to this assumption, numbers for $K_{VI,i}$ and $K_{VII,i}$ can be calculated from every single experimental speciation data point i (i = 1, 2, ..., 121, with the exception of data points where no piperazine dicarbamate was detected). The resulting numbers for $\lg K_{VLi}$ (and $\lg K_{\text{VII},i}$) were regressed according to equation (10). Finally, a variation of parameters A_{VIII} and B_{VIII} was performed in order to minimize the average relative deviation between $\lg K_{\text{VI},i}$ and $\lg K_{\text{VII},i}$ and the corresponding linearily regressed equations for $\lg K_{\rm VI}$ and $\lg K_{\rm VII}$. Although the optimization was repeated starting from very different numerical values for $A_{\rm VIII}$ and $B_{\rm VIII}$, it always led to the same results. The resulting numerical values for the coefficients of equation (10) are given in table 5. Figure 4 shows the results of that correlation, including standard deviations in $\lg K_{\text{VI}}$ and $\lg K_{\text{VII}}$. At T = (283, 298, 313, and 333) K the following numerical values (and standard deviations) are found for $\lg K_{VI}$: (1.80 ± 0.09), (1.52 ± 0.08) , (1.26 ± 0.11) , and (0.96 ± 0.16) , and for $\lg K_{VII}$: (0.44 ± 0.21) , (0.34 ± 0.18) , (0.25 ± 0.16) , and (0.14 ± 0.26) .

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TABLE 5 Equilibrium constants for chemical reactions VI to VIII (on the molality scale) ($\lg K_R = A + B/(T/K)$) and temperature range of validity

Reaction	A	В	T/K
VI	-3.750	1570.4	283 to 333
VII	-1.587	574.2	283 to 333
VIII	4.354	1517.0	283 to 333



FIGURE 4. Experimental results for the chemical equilibrium constants *K* for the carbamate formations in (carbon dioxide + piperazine + water), and comparison with literature data. Δ , This work reaction VI; \Box , this work reaction VII; \bigcirc , this work reaction VIII, —, correlation, this work; --- and -·--, references [6,7].

The molar Gibbs free energy and the molar enthalpy of reaction of reactions VI to VIII can be calculated from equation (10) (with coefficients given in table 5) applying the well-known thermodynamic relations:

$$\Delta_r G_{\rm m} = -R \cdot T \cdot \ln K \tag{11}$$

and

$$\Delta_{\rm r} H_{\rm m} = -R \cdot \frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)}.\tag{12}$$

At standard state ($T^0 = 298.15 \text{ K}$) the results are (on the molality scale): $\Delta_r G_m^\circ = -8.66 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_r H_m^\circ = -30.07 \text{ kJ} \cdot \text{mol}^{-1}$ for reaction VI; $\Delta_r G_m^\circ = -1.93 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_r H_m^\circ = -10.99 \text{ kJ} \cdot \text{mol}^{-1}$ for reaction VII; and $\Delta_r G_m^\circ = -53.90 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_r H_m^\circ = -29.04 \text{ kJ} \cdot \text{mol}^{-1}$ for reaction VIII.

4. Discussion

With the new correlation equations for the three carbamate formation constants the model is able to reliably describe the speciation in (carbon dioxide + piperazine + deuterium oxide) resulting from ¹H-NMR measurements. A typical example is shown in figure 3 for an aqueous about one molal piperazine solution at T =298 K. As expected (up to this point all interaction parameters were neglected), deviations between experimental data and the correlation become larger with increasing piperazine and carbon dioxide concentration, *i.e.* with increasing ionic strength.

As already mentioned, the chemical equilibrium constants for the formation of the three carbamates have been estimated recently by Bishnoi and Rochelle [6,7]. Bishnoi and Rochelle [6] orginaly fitted these constants to some experimental results for the partial pressure of carbon dioxide above aqueous 0.6 M piperazine solutions at T = (313 and 343) K (17 data points) and some ¹H-NMR speciation data at T = 298 K (2 data points). They arbitrarily assumed that the reaction enthalpies in reactions VI and VII do not differ. In a second estimation [7], some additional experimental carbon dioxide partial pressures above aqueous 0.6 M piperazine and 4 M MDEA solutions at T = (313 and 343) K (13 data points) were included in the fitting. The results from these publications differ considerably, in particular for K_{VI} and K_{VII} , from the results presented here, as shown in figure 4.

Figure 5 gives the speciation in an aqueous one molal piperazine solution at T = 298 K, when up to 1.2 mol of carbon dioxide were added (per kg of water), as predicted by the model presented before. The new correlation equations for K_{VI}



FIGURE 5. Predicted species distribution in (carbon dioxide + piperazine + water) at T = 298 K with $(\bar{m}_{\text{PIPH}_2} = 1 \text{ mol} \cdot \text{kg}^{-1})$.

to K_{VIII} were considered, and all interaction parameters in Pitzer's model were set to zero. Considerable amounts of all carbon dioxide and piperazine species can be expected in those solutions. In order to extend the existing thermodynamic model for describing phase equilibria for (carbon dioxide + hydrogen sulphide + MDEA + water) [1,2] allowing for the presence of piperazine, in a next step, parameters describing interactions between carbon dioxide and piperazine (and all their species) will have to be determined from experimental solubility data of carbon dioxide in aqueous piperazine solutions. This work is now in progress.

5. Conclusions

Sour gas sweetening is often achieved by absorption in aqueous solutions of amines. The basic design of such absorption processes requires a thermodynamic model for the solubility of sour gases, *e.g.*, carbon dioxide and hydrogen sulfide, in aqueous solutions of one or more amines, *e.g.*, 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 [1,2], as well as on the solubility of hydrogen sulfide in aqueous solutions of piperazine [3], and on the protonation of MDEA in aqueous solution [4]. The equilibrium constants for the formation of piperazine carbamate, dicarbamate and protonated carbamate were determined from ¹H-NMR spectroscopic investigations of (carbon dioxide +piperazine + water). Those chemical equilibrium constants are required in order to enable an extension of the thermodynamic model for describing phase equilibria for (carbon dioxide + hydrogen sulphide + MDEA + water) allowing for the presence of piperazine.

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