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Solubility of Hydrogen Sulfide in Aqueous Solutions of Piperazine in the Low Gas-Loading Region

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ABSTRACT: The solubility of hydrogen sulfide in 2 *m* (about 0.146 mass fraction) aqueous solutions of 1,4-diazacyclohexane (piperazine, $PIPH_2$) was measured at low gas loadings (at stochiometric molar ratios of hydrogen sulfide to $PIPH_2$ between about 0.14 and 1.04) and low partial pressures of hydrogen sulfide (from about (1.3 to 98.7) kPa) at (313.5 and 392.2) K by headspace gas chromatography. The new experimental results are a supplement to previously published data in the high gas-loading region. The new experimental data are compared to prediction results from a thermodynamic model that was based only on gas solubility data in the high gas-loading area. That thermodynamic model for describing the vapor−liquid equilibrium uses Pitzer's molality-based equation for the excess Gibbs energy of the aqueous solution. The average relative deviation between the new experimental results and the predictions for the partial pressure of hydrogen sulfide amounts to 10 %.

INTRODUCTION

The sour gases hydrogen sulfide and carbon dioxide are major impurities in natural, refinery, and synthesis gases. "Chemical" absorption by aqueous solutions of (alkanol)amines is one of the most effective industrial methods for the removal of such sour gases from gaseous effluents. Aqueous solutions of (alkanol)-amines absorb acid gases at around ambient temperatures, almost completely converting the sour gases into ionic species via an acid−base buffer mechanism. The sour gases are released (and the solvent is regenerated) at higher temperatures where the chemical reaction equilibrium is shifted from ionic to neutral species (of sour gases and amines). Aqueous solutions of *N*-methyldiethanolamine (MDEA) and aqueous solutions of mixtures of MDEA with piperazine, so-called "activated MDEA" solutions, are among the most applied absorption systems, in particular when carbon dioxide and hydrogen sulfide are to be removed from gas streams.[1] Aqueous solutions of the single tertiary amine MDEA are often used in kinetically controlled processes for the selective removal of H_2S in the presence of CO_2. Hydrogen sulfide reacts quickly with the amine to sulfides, whereas the conversion of neutrally dissolved carbon dioxide to ionic species is slow. Therefore, H_2S can be separated from CO_2. Higher reaction rates are required for the removal of CO_2. Such higher reaction rates are achieved by "activating" an aqueous solution of MDEA with piperazine. Aqueous solutions of $(MDEA + PIPH_2)$ are often used when both acid gases $(H_2S + CO_2)$ have to be removed simultaneously.

The competitive chemical absorption of hydrogen sulfide and carbon dioxide is kinetically controlled. However, deviation from equilibrium provides the driving force in that kinetically controlled process. Therefore, thermodynamic equilibrium properties play an essential role in basic engineering of such adsorption and desorption processes. The design and the optimization of such separation equipment require the knowledge of the equilibrium properties: vapor−liquid equilibrium (VLE), chemical reaction equilibrium, and the energies to vaporize and condense those mixtures. The information on the heat requirements can be obtained from a reliable thermodynamic model for the vapor−liquid equilibrium. However, reliable methods for the correlation and prediction of the vapor−liquid equilibrium for the simultaneous solubility of H_2S and CO_2 in aqueous solutions of $(MDEA + PIPH_2)$ can only be developed when at least sufficient and accurate experimental data on the solubility of the single gases in aqueous solutions of the single amines and of the amine mixtures are available in a wide range of temperature and pressure. Our research group has already published a lot of experimental data as well as thermodynamic models in that area $[(H_2S + MDEA + H_2O)$,[2−4,7] $(H_2S + PIPH_2 + H_2O)$,[5,9] $(H_2S + MDEA + PIPH_2 + H_2O)$,[5] $(H_2S + MDEA + H_2SO_4/NaSO_4 + H_2O)$,[6] $(CO_2 + MDEA + H_2O)$,[2−4,7] $(CO_2 + PIPH_2 + H_2O)$,[8,9] $(CO_2 + MDEA + PIPH_2 + H_2O)$,[8,10,11] and $(CO_2 + MDEA + H_2SO_4/NaSO_4 + H_2O)$[12]$]$. At first, the thermodynamic models for the vapor−liquid equilibrium were based only on experimental information in the high gas-loading region. These measurements were performed by a synthetic method where the total pressure was determined that is required to dissolve a known amount of sour gas in a known amount of liquid at a given temperature and solvent composition. That synthetic technique is not well-suited for investigations at low pressures (below about 2 MPa) because the experimental results for the total pressure in the low gas-loading region are subject to high experimental uncertainties mainly caused by the unavoidable presence of small amounts of other dissolved gases and uncertainties of the vapor pressure of the amines. Thermodynamic models which are based only on experimental data from the high gas-loading region can be used to predict the gas solubility in the

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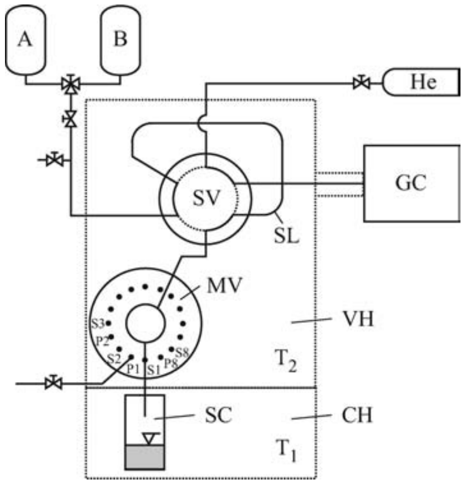

Figure 1. Scheme of the headspace chromatographic arrangement: CH, liquid-thermostatted cell holder (temperature T_1); VH, liquid-thermostatted sampling valve holder (temperature $T_2 > T_1$); A, buffer tank (high pressure); B, buffer tank (low pressure); GC, gas chromatograph; He, helium (carrier gas);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

low gas-loading region. However, it is rather difficult to estimate the uncertainties of such predictions. Therefore, for the assessment and for the development of improved models, it is necessary to have reliable experimental data for the solubility in the low gas-loading area.

■ EXPERIMENTAL SECTION AND RESULTS

Apparatus and Method. A headspace gas chromatographic technique was used to determine the solubility of hydrogen sulfide in an aqueous solution of piperazine. That particular technique is well-suited for the investigation of gas solubility in chemical solvents in the low partial pressure region. In the present investigation the partial pressure of hydrogen sulfide ranged from about 1.3 kPa to nearly 100 kPa. The equipment used for the gas solubility experiments was the same as in previous investigations on the solubility of CO_2 in aqueous solutions of the single amines MDEA[7] and piperazine[9] and some of their mixtures[10] in the low gas-loading region. The experimental arrangement and the experimental procedure have been described in detail before.[7] Therefore, only the main features are repeated here.

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

In an experiment eight sample cells (vials of volume: 30 cm^3, made of hastelloy or stainless steel and coated with a protection layer, Sulfinert by Restek Corporation) are partially filled (to about 75 % of the total volume) at room temperature with the loaded solution (H_2S + piperazine + H_2O) and mounted in the cell holder. Only one of those sample cells is shown in Figure 1. The composition of the liquid mixture is known from its gravimetric preparation (see below). The temperature is measured with a calibrated platinum resistance thermometer in the liquid bath that is used to control the temperature of the cell holder. The overall uncertainty of the temperature measurement is ± 0.1 K. During equilibration, very small amounts of the volatile components evaporate into the vapor phase (headspace). After equilibration the cell is at first pressurized (from buffer tank A) with nitrogen to a constant pressure [(0.2 and 0.45) MPa for the measurements at (313 and 393) K, respectively] for 2 min. Secondly, the sample loop is filled from the vapor phase. This is achieved by connecting the vapor phase of the cell to buffer tank B. That tank is also pressurized to a constant pressure [(0.17 and 0.37) MPa for the measurements at (313 and 393) K, respectively]. The sample is then transferred to the gas chromatograph, and the sampling system is purged with pure nitrogen. A multiposition valve (Valco Instruments Co., Inc., type 2CSD16MWE-HC) allows the connection of each of the eight sample cells (by stainless steel capillaries, that were also coated with the above-mentioned protection layer) to the sample loop. The other eight positions of the multiposition valve are used for purging. The multiposition valve and the sample valves (Valco Instruments Co., Inc., type ZVIC6WE-HC) are operated pneumatically via an electronic controller.

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

The primary data collected in a headspace chromatographic experiment indicate the peak area of hydrogen sulfide. This peak area is proportional to the mass of the gas in the sample loop which again is proportional to the partial pressure of the gas in the cell. The relation between the peak area and the partial pressure in the cell was determined by calibration measurements with pure hydrogen sulfide and a high-precision (absolute) pressure transducer (MKS Instruments, Inc., type MKS-Baratron 690A). In the calibration, the pressure ranged from (1 to 90) kPa. Caused by a small adsorption of H_2S on the metal surfaces, the peak area was not proportional to the partial pressure of H_2S as long as that pressure was below about 20 kPa. Therefore, the results of the calibration measurements were described by a third-order relation between the peak area and the partial pressure. At pressures above 20 kPa, the effect of adsorption is relatively small, and the calibration gives a linear relation between the peak area and the partial pressure of H_2S. The maximum relative uncertainty for the experimental results for the partial pressure of H_2S is about ± 3 % (for $1 \le p_{H_2S}$/kPa ≤ 20) and decreases to about 2 % (for $20 < p$/kPa ≤ 90).

Materials and Sample Preparation. Hydrogen sulfide (2.0, mass fraction ≥ 0.99) was purchased from Air Liquide Deutschland GmbH, Krefeld, Germany. Anhydrous piperazine (mass fraction ≥ 0.99) was purchased from Sigma-Aldrich Chemie GmbH, Munich, Germany. The solid, scaly piperazine anhydride was degassed under vacuum before it was dissolved in water. That water was deionized, distilled, and degassed prior to use.

Typically, about 1.4 dm^3 of an aqueous solution of piperazine was gravimetrically prepared in an evacuated storage tank of glass by dissolving known amounts of piperazine in water. About 0.25 dm^3 of such an aqueous solution was then transferred to a smaller (also previously evacuated) storage tank (volume ≈ 0.3 dm^3) and charged with known amounts of hydrogen sulfide. The exact amount of mass of dissolved H_2S was determined by weighing that storage tank before and after the addition of the sour gas. The charged storage tank was shaken for about 5 h, and finally stored for at least another 24 h to reach thermodynamic equilibrium. The vials of the headspace apparatus were then filled at room temperature with the liquid mixture and mounted in the cell holder, where they were thermostatted to the experimental temperature for another 12 h. Corrections of the stoichiometric molalities of the solutes were applied to account for the transfer of H_2S and water to the vapor phase (in both the second storage tank and the vials). As the saturation pressure of piperazine is low,[13] the transfer of $PIPH_2$ into the vapor phase was neglected. The vapor phase volumes in all containers were estimated using experimental data for the volumes of the containers and for the density of the solvent mixtures. As all vapor phase volumes are small and the partial pressures of hydrogen sulfide and water (which were either calculated from the previously published thermodynamic model or known from the experiments) are also small, the corrections to the stoichiometric molality of all solutes are small (between 0.1 % and 1.3 % for H_2S). The uncertainty in the stoichiometric molalities of piperazine from the gravimetric preparation does not surmount ± 0.04 %. The total uncertainty of the molality of $PIPH_2$ in the liquid phase in a vial is estimated to be smaller than ± 0.1 %. The relative uncertainty of the stoichiometric molality of hydrogen sulfide in such a liquid phase ranges from about ± 0.1 % up to about ± 0.5 %. It was estimated from the filling procedure described before including all corrections by means of a Gauss error propagation calculation.

■ EXPERIMENTAL RESULTS

The solubility of hydrogen sulfide in an aqueous solutions of piperazine ($_{\mathrm{PIPH}_2} \approx 2\ \mathrm{mol \cdot kg^{-1}}$) was measured at two temperatures: (313.5 and 392.2) K. The experimental results are listed together with the corresponding uncertainties in Table 1. The stoichiometric molar ratio of hydrogen sulfide to $PIPH_2$ (i.e., the loading α_{H_2S}) ranged from $0.52 \leq \alpha_{H_2S} \leq 1.04$ for the experiments at 313.5 K and from $0.14 \leq \alpha_{H_2S} \leq 0.79$ at 392.2 K. All molalities are moles per kilogram of water. The experimental results for the partial pressure of H_2S range from about 1.26 kPa to about 98.7 kPa. The absolute uncertainty for that partial pressure was estimated from $\Delta p_{H_2S} = \pm (\Delta p_{H_2S}^* + a_{\mathrm{Cal}} \cdot p_{H_2S})$. The first contribution $\Delta p_{CO_2}{}^*$ accounts for uncertainties in temperature as well as in the composition of the liquid mixture (i.e., in gas and amine molalities). It is determined from a Gauss error propagation calculation (by applying the thermodynamic model). The second contribution results from the uncertainty of the calibration experiments ($a_{\mathrm{cal}} = 0.03$ for $1 \leq p_{H_2S}/\mathrm{kPa} \leq 20$ and $a_{\mathrm{cal}} = 0.02$ for $20 < p_{H_2S}/\mathrm{kPa} \leq 90$).

Each experiment was repeated three to five times. The absolute standard deviation from the average numerical value for the partial pressure of hydrogen sulfide ($\Delta p_{H_2S,\mathrm{repr}}$) is also given. As expected, for most experimental data points $\Delta p_{H_2S,\mathrm{repr}}$ is less than Δp_{H_2S}. That finding supports the estimation for the experimental uncertainties.

The new experimental results for the partial pressure of hydrogen sulfide above aqueous solutions of $PIPH_2$ at 313.5 K and 392.2 K are plotted versus the stoichiometric molar ratio of H_2S to $PIPH_2$, α_{H_2S}, in Figure 2. The left side of Figure 2 shows the partial pressure of H_2S (in a linear scale plotted versus α_{H_2S}) in comparison with predictions by the thermodynamic model; the right side shows the same data together with the experimental results by Xia et al.[5] for similar temperatures and molalities of $PIPH_2$ in a logarithmic pressure scale again compared with calculation results.

Table 1. Experimental Results for the Solubility of Hydrogen Sulfide in Aqueous Solutions of Piperazine: Partial Pressure of Hydrogen Sulfide p_{H_2S} (and Its Standard Deviation $\Delta p_{H_2S,\mathrm{repr}}$) above Aqueous Solutions[a]

T K	$_{\mathrm{PIPH}_2}$ $\mathrm{mol \cdot kg^{-1}}$	$_{\mathrm{H_2S}}$ $\mathrm{mol \cdot kg^{-1}}$	p_{H_2S} kPa	$\Delta p_{H_2S,\mathrm{repr}}$ kPa
313.5	1.990	1.035 ± 0.002	1.26 ± 0.05	0.01
	1.951	1.361 ± 0.001	3.61 ± 0.14	0.17
	1.990	1.492 ± 0.001	3.84 ± 0.17	0.02
	1.951	1.547 ± 0.002	5.27 ± 0.23	0.21
	1.990	1.761 ± 0.002	10.9 ± 0.57	0.18
	1.990	1.813 ± 0.002	13.2 ± 0.76	0.18
	2.039	1.920 ± 0.002	21.1 ± 1.11	0.38
	2.039	2.041 ± 0.003	51.4 ± 3.69	1.08
	2.039	2.081 ± 0.005	73.7 ± 5.85	1.45
	1.990	2.063 ± 0.005	86.0 ± 7.42	4.03
392.2	2.026	0.292 ± 0.001	2.00 ± 0.07	0.10
	1.991	0.412 ± 0.001	3.99 ± 0.15	0.18
	2.026	0.461 ± 0.001	5.43 ± 0.20	0.21
	1.951	0.524 ± 0.002	6.97 ± 0.26	0.34
	1.951	0.608 ± 0.002	10.3 ± 0.38	0.37
	1.991	0.745 ± 0.001	14.0 ± 0.52	0.26
	2.026	0.814 ± 0.002	16.8 ± 0.63	0.34
	1.951	0.914 ± 0.002	24.7 ± 0.69	0.14
	1.991	1.032 ± 0.002	28.1 ± 0.84	0.46
	2.026	1.159 ± 0.002	38.4 ± 1.17	0.84
	2.026	1.278 ± 0.004	50.1 ± 1.70	1.37
	2.026	1.319 ± 0.002	55.3 ± 1.76	1.18
	1.951	1.328 ± 0.002	61.8 ± 2.04	1.77
	1.991	1.485 ± 0.003	82.7 ± 2.98	2.79
	1.951	1.538 ± 0.003	98.7 ± 3.82	1.76

[a] Composition is given by stoichiometric molalities of piperazine ($_{\mathrm{PIPH}_2}$), and hydrogen sulfide ($_{\mathrm{H_2S}}$) ($\Delta T = \pm 0.1$ K, $\Delta_{\mathrm{PIPH}_2}/_{\mathrm{PIPH}_2} = \pm 0.1$ %).

Figure 2 reveals the typical behavior when a sour gas is dissolved in an aqueous amine solution: the partial pressure of the sour gas at first only very slightly increases with increasing molar ratio of gas to amine (i.e., increasing stoichiometric molality of the gas in the liquid). This is due to the basic character of the amine. The sour gas is at first predominantly dissolved chemically (i.e., in nonvolatile ionic form, here as bisulfide (hydrosulfide) and sulfide) resulting in very small partial pressures of the sour gas at low gas loadings. However, when the amine has been spent by chemical reactions, newly added sour gas can no longer be absorbed "chemically" but has to be dissolved "physically". At high temperature the chemical reaction equilibrium is shifted in favor of neutrally dissolved sour gas, resulting in a higher partial pressure of hydrogen sulfide at constant gas loading.

Comparison with Predictions from a Thermodynamic Model of the Vapor−Liquid Equilibrium. The thermodynamic model for the solubility of hydrogen sulfide in aqueous solutions of piperazine was described and parametrized in previous publications (Xia et al.[5] and Ermatchkov et al.[9]). A detailed description of the model can be found there. In addition, all further thermodynamic properties were reported by Kuranov et al.[2] and Pérez-Salado et al.[4] The parametrization of the model

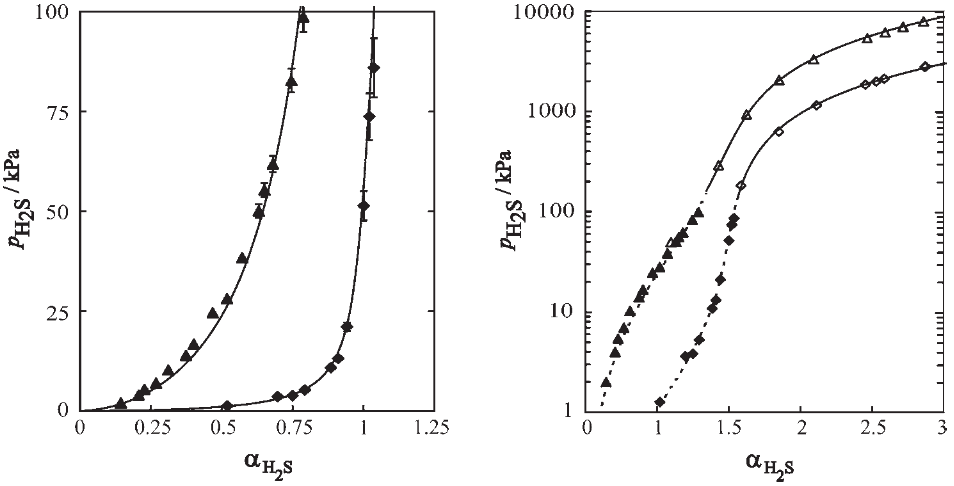

Figure 2. Partial pressure of hydrogen sulfide above aqueous solutions of piperazine with $_{PIPH_2} \approx 2$ mol·(kg water)$^{-1}$. Left diagram: new experimental results, this work: ◆, $T \approx 313.5$ K; ▲, $T \approx 392.2$ K, compared to prediction results of the model (solid line). Right diagram: experimental results for the calculated partial pressure of H_2S from Xia et al. (also Ermatchkov et al.), for: ◇, T ≈ 313.75 K; Δ, T ≈ 395.0 K, compared to correlation results (solid line). The new experimental results, this work: ◆, $T \approx 313.5$ K; ▲, $T \approx 392.2$ K, compared to prediction results of the model (dotted line). Error bars are only given when the experimental uncertainty is larger than the size of the symbol.

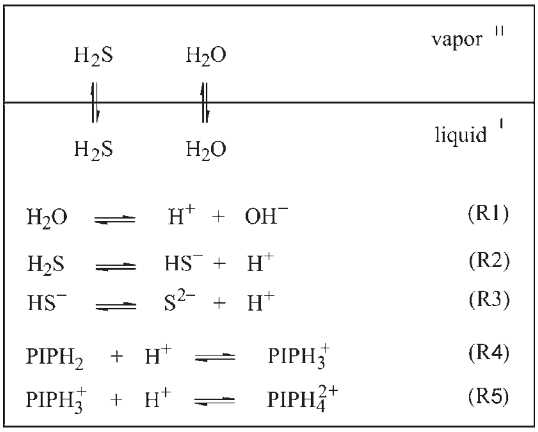

Figure 3. ($H_2S + PIPH_2 + H_2O$): model for the vapor—liquid equilibrium.

was based on experimental data for the total pressure above 2 *m* and 4 *m* aqueous solutions of piperazine at temperatures from 313 K to 393 K in the high gas-loading region ($0.6 < \alpha_{H_2S} < 3.1$) and partial pressures of H_2S between about 43 kPa and about 13000 kPa. Figure 3 shows a scheme of this model. The model neglects the volatility of piperazine.

Caused by chemical reactions in the liquid phase, hydrogen sulfide is dissolved not only in neutral, volatile form but also in nonvolatile, ionic form (dominantly as hydrosulfide HS^-), and piperazine is protonated. The following reversible chemical reactions (chemical equilibrium) are taken into account: the autoprotolyses of water (R1), the formation of hydrosulfide (bisulfide) and sulfide (R2, R3), and the first and second protonation of piperazine (R4, R5). The temperature dependent chemical reaction equilibrium constants on molality scale (K1 to K5) were adopted from previous publications.[2,4] The condition for chemical equilibrium for a chemical reaction R (= 1, ..., 5) is:

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

The balanced equation for the amounts of substance of a component i in the liquid phase is:

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

where ξ_R is the extent of reaction R. Solving this set of equations for given temperatures and stoichiometric amounts of substances $_i$ of components H_2O, $PIPH_2$, and H_2S results in the speciation, that is, the "true" composition, of the liquid phase (the amount of substance n_i of all species present).

The model uses the extended Henry's law on the molality scale to describe the partial pressure of H_2S above the aqueous solution.

$$k_{H,H_2S} \exp\left[\frac{v_{H_2S}^{\infty}(p - p_W^s)}{RT}\right] a_{H_2S} = y_{H_2S}\, p\, \phi_{H_2S} \tag{3}$$

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

$$p_W^s \phi_W^s \exp\left[\frac{v_W(p - p_W^s)}{RT}\right] a_W = y_W\, p\, \phi_W \tag{4}$$

The important deviation from ideal mixing behavior of molecular as well as of the ionic species in the aqueous, electrolyte solutions is considered through activity coefficients (of the true solutes). The activity coefficients are calculated from a modification of the Pitzer's equation for the excess Gibbs energy of aqueous electrolyte solutions. That equation requires binary and ternary parameters for interactions between all solute species. These interaction parameters were adopted from Ermatchkov et al.[9] They are given in Table 2.

Figure 2 shows a good agreement between the new experimental results and the prediction results. The average relative (absolute) deviation between the new experimental data and the prediction of the model for the partial pressure of H_2S amounts to 8.8 % (2.8 kPa) at 313.5 K and 11.6 % (2.6 kPa) at 392.2 K.

Figure 4 shows calculation results for the speciation in a 2 *m* aqueous solution of piperazine at 313 K (full lines) and 393 K (dotted lines), when hydrogen sulfide is added. As long as the

Table 2. (H_2S + Piperazine + H_2O): Interaction Parameters for Pitzer's Equation for the Excess Gibbs Energy from Ermatchkov et al.[9]

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

			T
parameter	q_1	q_2	K
$\beta_{H_2S,\ H_2S}^{(0)a}$	−0.26156	69.751	283 to 453
$\beta_{H_2S,\ HS^-}^{(0)}$	0.0096582	−18.988	313 to 413
$\beta_{H_2S,\ PIPH_3^+}^{(0)}$	0.16812	−48.836	313 to 393
$\beta_{PIPH_3^+,HS^-}^{(0)}$	0.027680		
$\beta_{PIPH_3^+,HS^-}^{(1)}$	1.4921	−469.89	
$\beta_{PIPH_4^{2+},HS^-}^{(0)}$	0.33892	97.698	
$\beta_{PIPH_4^{2+},HS^-}^{(1)}$	0.93222		
$\mu_{H_2S,PIPH_3^+,HS^-}$	−0.0089545	2.1507	
$\mu_{H_2S,\ H_2S,PIPH_3^+}$	0.0062141		

[a] Based on experimental results for the solubility of H_2S in water by Kuranov et al.[3]

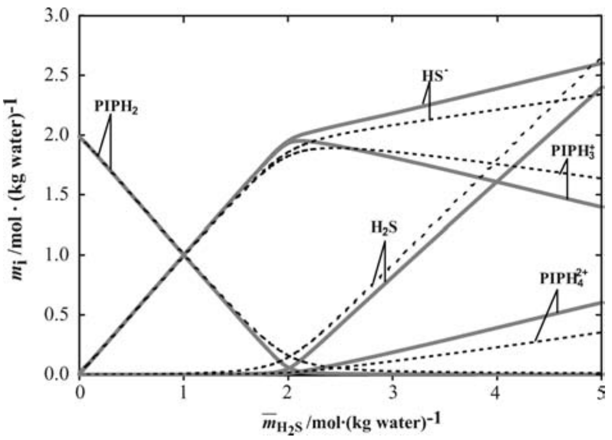

Figure 4. Predicted species distribution in the system (H_2S + $PIPH_2$ + H_2O) at 313.15 K (solid line) and 393.15 K (dotted line) for $_{PZ}$ = 2 mol·(kg water)$^{-1}$.

gas-loading α_{H_2S} < 1, hydrogen sulfide is almost completely dissolved as hydrosulfide (HS^-). Conversely, the base piperazine is protonated. The concentration of singly protonated piperazine ($PIPH_3^+$) is very close to the concentration of hydrosulfide (HS^-). When the gas loading increases beyond α_{H_2S} = 1, the concentration of neutrally dissolved H_2S nearly linearly increases with α_{H_2S}, and as the solution becomes more acidic, some of the singly protonated piperazine is converted into its diprotonated form. That conversion is stronger at 313 K than at 393 K.

■ CONCLUSIONS

Complementing previously published data and a thermodynamic model for the solubility of hydrogen sulfide in aqueous solutions of piperazine in the high-pressure (high gas-loading) region (Xia et al.[5] and Ermatchkov et al.[9]), this contribution presents similar experimental results for 2 *m* aqueous solutions of piperazine in the low pressure (low gas-loading) region. The database available from the three investigations extends the experimental database for the vapor−liquid equilibrium of the industrial important system (H_2S + CO_2 + MDEA + $PIPH_2$ + H_2O).

The previously parametrized thermodynamic model predicts the new experimental results for the partial pressure of hydrogen sulfide within about 10 %.

This new data for the solubility of hydrogen sulfide in an aqueous solution of piperazine as well as the results of ongoing experiments on the solubility of H_2S in (MDEA + H_2O) and (MDEA + $PIPH_2$ + H_2O) in the low gas-loading region should allow a further improvement in the description of the simultaneous solubility of hydrogen sulfide and carbon dioxide in aqueous solutions of MDEA that are activated by piperazine.

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