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CO_2 Absorption in Aqueous Piperazine Solutions: Experimental Study and Modeling

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ABSTRACT: In this work, new solubility data of CO_2 in aqueous piperazine (Pz) solutions were measured over a temperature range from $T = (287.1 \text{ to } 313.1)$ K and for amine concentrations from $m = (0.10 \text{ to } 2.00)$ mol·kg^{-1}. The CO_2 partial pressure was kept within $P_{CO_2} = (0.11 \text{ to } 525.17)$ kPa using a vapor−liquid equilibrium (VLE) apparatus based on a static-synthetic method. These experimental data and those found in the literature for the ternary system Pz−CO_2−H_2O were correlated using a model combining the virial equation of state to calculate the fugacity coefficients with a modified Pitzer's thermodynamic model for the activity coefficients. With the new extended interaction parameters $\beta^0_{i,j}$ and $\beta^1_{i,j}$ that cover a wide range of temperature, CO_2 partial pressure, and amine concentration, the model is able to correlate satisfactorily the available reliable experimental solubility data.

1. INTRODUCTION

In the past few years, large human emission of greenhouse gases has become one of the most discussed environmental issues around the world. This has motivated intensive research on CO_2 capture where new and more energy-efficient absorbents are essential. For technical, economical, and environmental concerns, actual industrial CO_2 absorption processes use aqueous solutions of alkanolamines. This technique is widely applied for acid gases (CO_2, H_2S) removal during natural gas sweetening as well as for CO_2 capture from fossil-fuel-fired power plants or from other important industries such as chemical and petrochemical, steel, aluminum, and cement production.

Industrially more often used alkanolamines are monoethanolamine (MEA), diethanolamine (DEA), *N*-methyldiethanolamine (MDEA), and 2-amino-2-methyl-1-propanol (AMP).[1] The choice of a certain amine is mainly based on the absorption capacity, reaction kinetics, and regenerative potential and facility. The use of blended alkanolamine solutions has also recently become very attractive because of the combination of each amine advantages: a fast reactivity from a primary or secondary amine coupled with the high absorption capacity and low solvent regeneration cost from a tertiary or sterically hindered alkanolamine (SHA).

In our laboratory, extensive studies of CO_2 capture in membrane contactors using piperazine (Pz)-activated aqueous SHA solutions are in progress. A set of four SHA was chosen to study the hindered effect on the absorbent properties.[2] It concerns AMP, a simple hindrance form of MEA, and three SHA derived from AMP: 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD), and 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD). On the basis of these solution kinetics,[2−5] equilibrium data,[6−9] and their regenerative capacity,[10] it appeared that the Pz-AHPD mixture may be an interesting alternative to conventional amine solutions. The development of a model describing this solution thermodynamic equilibrium would be of great interest as the deviation from equilibrium provides the driving force in kinetically controlled absorption. Such work was reported in a previous paper:[11] a thermodynamic model based on the Pitzer's equations for the activity coefficients coupled with the truncated virial equation of state for representing the nonideality of the vapor phase was used to predict the CO_2 solubility in the CO_2−Pz−AHPD−H_2O system with the assumption that the interaction parameters describing the ternary subsystem (CO_2−Pz−H_2O and CO_2−AHPD−H_2O) are necessary to describe the quaternary system CO_2−Pz−AHPD−H_2O. The resulting model prediction showed a large deviation (average relative deviation of 37 %) with our experimental data. This was believed to come from the fact that 49 % of our quaternary experimental data was obtained at temperatures lower than 313.1 K, the lowest reported temperature of the interaction parameters available in the literature[12] for the system CO_2−Pz−H_2O.

In this work, new solubility data of CO_2 in aqueous piperazine solutions were obtained over a temperature range from $T = (287.1 \text{ to } 313.1)$ K and for amine concentrations from $m = (0.10 \text{ to } 2.00)$ mol·kg^{-1} using a vapor−liquid equilibrium (VLE) apparatus based on a static-synthetic method. These data will be used (i) to increase the very scarce reliable database of CO_2 solubility in aqueous Pz solutions below 313 K and (ii) along with all reliable data found in the literature for CO_2−Pz−H_2O at all temperatures, to revise and extend the available interaction parameters for this subsystem.

2. EXPERIMENTAL SECTION

2.1. Reagents. All aqueous piperazine solutions used in this work were prepared with degassed distilled water and piperazine (CAS No. 110-85-0). The amine (from Laboratoire MAT, Quebec, Canada) was supplied with a mass fraction of 0.999 and was used without further purification. CO_2 gas bottle was of

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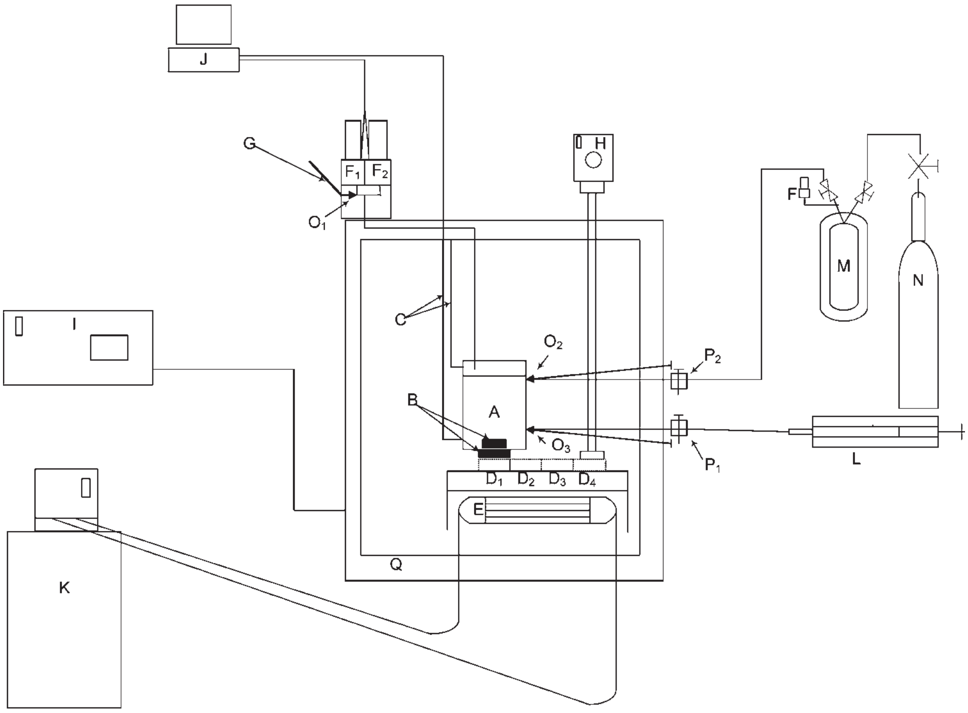

Figure 1. Schematic diagram of the solubility apparatus: A, equilibrium cell; B, magnetic rod; C, platinum resistance thermometer; D_i, gears; E, coil; F, pressure transducer (F_1, low pressure values; F_2, high pressure values); G, valve; H, stirrer; I, temperature controller; J, computer; K, circulating bath; L, variable volume press for liquid introduction; M, small gas cylinder; N, gas cylinder; O_i, needle valve; P_i, valves; Q, laboratory oven.

commercial grade with a minimum purity of 99.5 % and was supplied by Praxair.

2.2. Apparatus and Procedures. The experimental setup for the CO_2 solubility measurements used in this work is shown in Figure 1. As the same setup and procedures were used in our previous work,[11] only the main details will be mentioned here. The VLE cell (from Armines, France) is made of TA6 V titanium and has an internal volume of about $1.15 \cdot 10^{-4}$ m^3. The cell is agitated with a magnetic rod and is located in a modified XU027 laboratory oven from France Etuves, which allows a temperature control of ± 0.1 K. A special feature of this apparatus, compared to similar ones, is the addition in the oven of a coil refrigerated with a thermostatted bath (K-12108-10 from Cole-Palmer). This coil allowed us to make solubility measurements under room temperature (273.15 to 303.15 K) with the same temperature precision. Pressure in the cell was measured by one of the two installed absolute pressure transducers (Druck PTX-611, (0 to 100) kPa and (0 to 16 000) kPa) according to the pressure range with a precision of 0.08 %. Liquid introduction inside the equilibrium cell was made with a variable volume press (stainless steel 316, internal diameter of $3.002 \cdot 10^{-2}$ m) equipped with a linear encoder (Heidenhain, LS487C) which allowed knowing the exact longitudinal position of the piston in press with an accuracy of $\pm 2 \cdot 10^{-6}$ m. Gas introduction inside the equilibrium cell was made by a thermostatted small gas cylinder with an internal volume of about $7 \cdot 10^{-5}$ m^3. This small gas cylinder was equipped with a Druck PTX-611 (0 to 16 000) kPa absolute pressure transducer.

A standard CO_2 solubility experiment consisted of a sequence of successive step. First, the piperazine aqueous solution was prepared to its specific concentration, m = (0.10 to 2.00) $mol \cdot kg^{-1}$, by a gravimetric method. A Mettler Toledo AE204 balance with a precision of ± 0.001 g was used. The solution was then degassed, put inside the variable volume press, and subsequently transferred with the piston in the equilibrium cell. All of these steps were made under vacuum. The equilibrium cell was next heated to the desired temperature, and the solution was agitated. At this stage, the vapor pressure of the solution was measured by the low pressure transducer. This was followed by the introduction of the CO_2 in the equilibrium cell via the small gas cylinder. The introduced CO_2 mole number was calculated by using the cylinder volume and its temperature as well as the observed pressure drop in the cylinder after the gas introduction. The system equilibrium was reached when the pressure inside the equilibrium cell was varying less than 0.5 % for at least 30 min. The remaining CO_2 mole number in the cell was calculated based on the temperature, the equilibrium pressure, and the head space volume and was corrected by the compressibility factor. The difference between the introduced and the remaining gas mole number in the head space of the equilibrium cell was then calculated which lead to the concentration of absorbed gas in the solution.

3. THERMODYNAMIC MODELING OF THE VLE

3.1. Chemical Equilibrium in the Liquid Phase. When CO_2 is absorbed in piperazine solutions, many chemical reactions happen in the liquid phase. The model applied to correlate/predict the solubility of carbon dioxide in this solution considers the following equilibriums for the chemical species in the liquid phase: the formation and dissociation of bicarbonate (reactions 1 and 2), the autoprotolysis of water (reaction 3), the protonation and diprotonation of piperazine (reactions 4 and 5), and the formation of piperazine carbamate, piperazine dicarbamate, and protonated piperazine

Table 1. Chemical Equilibrium Constant for the Chemical Reaction *R*, Expressed on the Molality Scale, and Temperature Range of Validity[a]

K_R	A	B	C	$10^2\cdot D$	$10^{-5}\cdot E$	T/K	ref
K_1	−1203.01	68359.6	188.444	−20.6424	−47.1291	273.1 to 673.1	13
K_2	175.360	−7230.6	−30.6509	1.31478	−3.72805	273.1 to 523.1	14
K_3	140.932	−13445.9	−22.4773	-	-	273.1 to 498.1	15
K_4	14.119	3814.44	-	−1.5096	-	273.1 to 323.1	16
K_5	10.113	2192.3	-	−1.7396	-	273.1 to 323.1	16
K_6	−8.635	3616.0	-	-	-	283.1 to 333.1	17
K_7	−3.654	1322.1	-	-	-	283.1 to 333.1	17
K_8	10.025	3493.0	-	-	-	283.1 to 333.1	17

[a]
$$\ln K_R = A + \frac{B}{(T/\mathrm{K})} + C\cdot\ln(T/\mathrm{K}) + D\cdot(T/\mathrm{K}) + \frac{E}{(T/\mathrm{K})^2}$$

carbamate (reactions 6 to 8).

$$CO_2 + H_2O \overset{K_1}{\leftrightarrow} HCO_3^- + H^+ \qquad (1)$$

$$HCO_3^- \overset{K_2}{\leftrightarrow} CO_3^{2-} + H^+ \qquad (2)$$

$$H_2O \overset{K_3}{\leftrightarrow} H^+ + OH^- \qquad (3)$$

$$Pz + H^+ \overset{K_4}{\leftrightarrow} PzH^+ \qquad (4)$$

$$PzH^+ + H^+ \overset{K_5}{\leftrightarrow} PzH_2^{2+} \qquad (5)$$

$$Pz + HCO_3^- \overset{K_6}{\leftrightarrow} PzCOO^- + H_2O \qquad (6)$$

$$PzCOO^- + HCO_3^- \overset{K_7}{\leftrightarrow} Pz(COO^-)_2 + H_2O \qquad (7)$$

$$PzCOO^- + H^+ \overset{K_8}{\leftrightarrow} PzH^+COO^- \qquad (8)$$

The condition for chemical equilibrium for a chemical reaction *R* is:

$$K_R(T) = \prod_i a_i^{\nu_{i,R}} \quad \text{where } R = (1 \text{ to } 8) \qquad (9)$$

Constants for the calculation of the various K_R as a function of temperature as well as their sources are given in Table 1.

In addition to the above equilibrium equations, overall Pz and CO_2 concentrations ($\mathrm{mol}\cdot\mathrm{kg}^{-1}$) as well as charge balance must be satisfied. In the balance equations for Pz and carbon dioxide in the liquid phase (eqs 10 and 11) $\tilde{m}_{Pz}$ denotes the stoichiometric concentration of Pz ($\mathrm{mol}\cdot\mathrm{kg}^{-1}$), and α denotes the CO_2 loading in the solutions, expressed as total moles of CO_2 absorbed both chemically and physically per mole of amine.

$$\tilde{m}_{Pz} = m_{Pz} + m_{PzH^+} + m_{PzH_2^{2+}} + m_{PzCOO^-} + m_{Pz(COO^-)_2} + m_{PzH^+COO^-} \qquad (10)$$

$$\alpha\cdot\tilde{m}_{Pz} = m_{CO_2} + m_{HCO_3^-} + m_{CO_3^{2-}} + m_{PzCOO^-} + 2m_{Pz(COO^-)_2} + m_{PzH^+COO^-} \qquad (11)$$

$$m_{H^+} + m_{PzH^+} + 2m_{PzH_2^{2+}} = m_{OH^-} + m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{PzCOO^-} + 2m_{Pz(COO^-)_2} \qquad (12)$$

Solving this set of 11 independent equations (eqs 9 to 12) for a given temperature, Pz overall concentration, and CO_2 loading results in the true (equilibrium) composition of the liquid phase, expressed as the molality of each species ($\mathrm{mol}\cdot\mathrm{kg}^{-1}$), needed for solving the VLE equations.

3.2. VLE.

In this study, only water is treated as a solvent species. Carbon dioxide, piperazine, and the several ions are treated as solute species. The reference state for the chemical potential of water is the pure liquid and defined as a 1 *m* solution in pure water for the solute species, both at the system temperature and pressure.

The condition of VLE is applied to calculate the total pressure and the composition of the gas phase. The extended Raoult's law is used to express the VLE for water (eq 13), and the extended Henry's law is used to express the equilibrium for carbon dioxide (eq 14). It was assumed that the presence of piperazine in the gas phase could be neglected.

$$P_w^{sat}\varphi_w^{sat}\exp\left[\frac{V_w(P - P_w^{sat})}{RT}\right]a_w = Py_w\varphi_w \qquad (13)$$

$$m_{CO_2}\gamma_{CO_2}^{*,m}H_{CO_2,H_2O}^m(T, P_w^{sat})\exp\left[\frac{V_{CO_2,H_2O}^{\infty}(P - P_w^{sat})}{RT}\right] = Py_{CO_2}\varphi_{CO_2} \qquad (14)$$

The VLE calculation requires the knowledge of the following properties:

(i) Henry's constants for the solubility of carbon dioxide in pure water on the molality scale, $H_{CO_2,H_2O}^m(T,P_w^{sat})$, were taken from Rumpf and Maurer.[18]

(ii) The vapor pressure P_w^{sat} and the molar volume V_w of pure water were taken from Saul and Wagner.[19]

(iii) The fugacity coefficients φ_i were calculated using a truncated virial equation of state. Pure component second virial coefficients B_{H_2O,H_2O} and B_{CO_2,CO_2} for water and carbon dioxide, respectively, were calculated on the basis of the data given by Dymond and Smith.[20] The mixed second virial coefficients B_{CO_2,H_2O} were calculated according to the correlations of Hayden and O'Connell.[21]

(iv) The partial molar volumes V_{CO_2,H_2O}^{∞} of carbon dioxide dissolved at infinite dilution in water were calculated as recommended by Brelvi and O'Connell[22] and correlated as a function of temperature.

3.3. Pitzer's G^E Model for Activity Coefficients.

In this paper, activity coefficients of both neutral and ionic species were

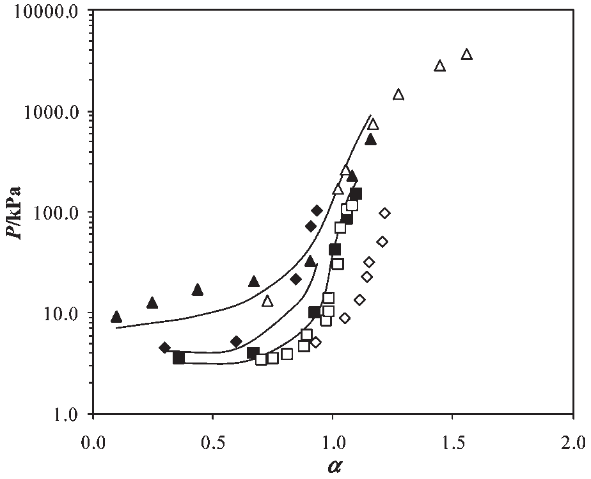

Figure 2. Comparison of various solubility data of CO_2 (1) in piperazine (2) aqueous solutions of concentration m_2/mol·kg^{-1} at temperature T/K: ■, $m_2 = 0.60$ and $T = 298.1$; □, $m_2 = 0.60$ and $T = 298.1$, ref 24; ◆, $m_2 = 0.60$ and $T = 303.1$; ◇, $m_2 = 0.60$ and $T = 303.1$, ref 29; ▲, $m_2 = 2.00$ and $T = 313.1$; △, $m_2 = 2.00$ and $T = 313.1$, ref 28; lines, model correlation.

calculated using a modified Pitzer[23] model for the excess Gibbs energy of aqueous electrolyte solutions (eq 15). Only the main equations of this model are recalled here. More details can be found in our previous publication.[11]

$$\frac{G^{E}}{RTn_{w}M_{w}} = f_1(I) + \sum_{i\neq w}\sum_{j\neq w} m_i m_j \lambda_{ij}(I) + \sum_{i\neq w}\sum_{j\neq w}\sum_{k\neq w} m_i m_j m_k \tau_{ijk} \qquad (15)$$

$f_1(I)$ is a modified Debye–Hückel term depending on ionic strength (I), temperature, and solvent (water) properties. $\lambda_{ij}(I)$ is the ionic strength dependent second virial coefficient:

$$\lambda_{ij}(I) = \beta_{ij}^{(0)} + \beta_{ij}^{(1)}[(2/x^2)(1-(1+x)e^{-x})] \qquad (16)$$

where $x = 2(I)^{1/2}$.

The influence of temperature on the binary interaction parameters $\beta_{ij}^{(0)}$ and $\beta_{ij}^{(1)}$ is approximated by the relation:

$$\beta_{ij}^{(0)} \text{ or } \beta_{ij}^{(1)} = q_0 + \frac{q_1}{T/\mathrm{K}} \qquad (17)$$

The ternary interaction parameters τ_{ijk} are considered independent of temperature.

The equation for the activity coefficients of dissolved species follows from the appropriate derivative of G^{E}, and water activity is calculated from the Gibbs–Duhem equation:

$$\ln \gamma_i^{*,m} = -A_{\phi} z_i^2 \left(\frac{\sqrt{I}}{1+1.2\sqrt{I}} + \frac{2}{1.2}\ln(1+1.2\sqrt{I})\right) + 2\sum_{j\neq w} m_j \lambda_{ij}(I) - z_i^2 \sum_{j\neq w}\sum_{k\neq w} m_j m_k \frac{\beta_{jk}^{(1)}}{Ix^2}\left[1-\left(1+x+\frac{x^2}{2}\right)e^{-x}\right] + 3\sum_{j\neq w}\sum_{k\neq w} m_j m_k \tau_{ijk} \qquad (18)$$

$$\ln a_w = M_w\left(2A_{\phi}\frac{I^{1.5}}{1+1.2\sqrt{I}} - \sum_{i\neq w}\sum_{j\neq w} m_i m_j(\beta_{ij}^{(0)} + \beta_{ij}^{(1)}e^{-x})\right) - M_w\left(2\sum_{i\neq w}\sum_{j\neq w}\sum_{k\neq w} m_i m_j m_k \tau_{ijk} + \sum_{i\neq w} m_i\right) \qquad (19)$$

3.3.1. Interaction Parameters for the System CO_2–Pz–H_2O. Interaction parameters for the ternary system CO_2–Pz–H_2O were determined on the basis of experimental data taken from the literature and from the present work, as it will be explained in Section 4.1. In this system, 11 species are present in the liquid phase: CO_2, HCO_3^-, CO_3^{2-}, Pz, PzH^+, PzH_2^{2+}, $PzCOO^-$, $Pz(COO^-)_2$, PzH^+COO^-, H^+, and OH^-. Because of the very low concentration of H^+ and OH^- with respect to the other species, their interactions with all other species were ignored, and therefore, the corresponding interaction parameters were set to zero. On the basis of the results of Derks et al.,[24] all of the interaction parameters associated with PzH_2^{2+} were also neglected. The second pK_a of piperazine, which is 5.3 at 298 K, is too low considering the pH range of interest for the CO_2 absorption. Therefore, PzH_2^{2+} concentration is supposed to be very small and interactions with this ion can be neglected. Another simplification can be made concerning the CO_3^{2-} interactions considering that the CO_2 absorption decreases the pH, lowering considerably the carbonate concentration.[24] To additionally reduce the number of parameters, all binary and ternary interaction parameters involving species with the same sign of charge were neglected. Only the parameters which were found to have a significant influence on the liquid phase species distribution were optimized based on the experimental data: $\beta_{CO_2,HCO_3^-}^{(0)}$, $\beta_{CO_2,PzH^+}^{(0)}$, $\beta_{CO_2,PzH^+COO^-}^{(0)}$, $\beta_{HCO_3^-,PzH^+}^{(0)}$, $\beta_{Pz,PzCOO^-}^{(0)}$, $\beta_{PzH^+,PzH^+COO^-}^{(0)}$, $\beta_{PzH^+,PzCOO^-}^{(0)}$, $\beta_{PzH^+,Pz(COO^-)_2}^{(0)}$, $\beta_{PzH^+COO^-,PzH^+COO^-}^{(0)}$, $\beta_{HCO_3^-,PzH^+}^{(1)}$, and $\beta_{PzH^+COO^-,PzH^+COO^-}^{(1)}$. Parameters q_0 and q_1 were fitted simultaneously to the selected experimental data.

4. RESULTS AND DISCUSSION

4.1. CO_2–Pz–H_2O Solubility Database. In addition to obtaining CO_2 solubility data in piperazine aqueous solution at temperatures lower than 313 K, it was imperative to gather from literature all other reliable solubility data for this system to get interaction coefficient parameters set for the model, able to cover large temperature, pressure, and amine composition ranges. A survey of the literature shown that five other independent research groups[24,28−32] reported solubility data for the CO_2–Pz–H_2O system. A comparison of our data with some of these sources is made in Figure 2. In this figure, good agreement between our data and those of two of these five independent groups was found: Derks et al.[24] and Pérez-Salado Kamps et al.,[28] respectively, for piperazine molalities of (0.60 and 2.00) mol·kg^{-1} and at temperatures of (298.1 and 313.1) K.

However, quite large deviations appear between our data and those of Aroua and Mohd Salleh,[29] as for example, for a piperazine molality of 0.60 mol·kg^{-1} and 303.1 K (Figure 2). In general, data reported in that work[29] are constantly right-shifted comparatively to ours: for a given CO_2 partial pressure, equilibrium loading given by Aroua and Mohd Salleh[29] is much higher. Similar disagreements were also reported by Ermatchkov et al.[12]

Table 2. Number of Reliable Data of CO_2 (1) Solubility in Aqueous Solution of Piperazine (2) and Their Source

		T	m_2	
source	N	K	mol·kg^{-1}	α
this work	64	287.1 to 313.1	0.10 to 2.00	0.10 to 2.68
ref 24	58	298.1 to 343.1	0.2 to 0.64	0.36 to 1.23
ref 12	52	313.1 to 393.1	1.0 to 4.4	0.05 to 0.95
ref 32	42	313.1 to 343.1	0.3 to 1.4	0.92 to 2.77
ref 30	17	313.1 to 343.1	0.64	0.16 to 0.96
ref 28	92	314.1 to 395.1	2.00 to 3.96	0.50 to 1.64
ref 31	29	313.1 to 333.1	2.0 to 8.0	0.26 to 0.86

Table 3. Solubility of CO_2 (1) in Aqueous Solution of Piperazine (2) at T = 287.1 K ($\Delta T = \pm$ 0.1 K)

m_2	Δm_2			P	ΔP		
mol·kg^{-1}	mol·kg^{-1}	α	Δα	kPa	kPa	y_1	Δy_1
0.10	0.002	1.37	0.12	68.29	0.05	0.978	0.002
0.10	0.002	1.89	0.31	181.1	0.1	0.992	0.002
0.10	0.002	2.68	0.57	338.7	0.3	0.995	0.002
0.50	0.0005	0.316	0.004	2.130	0.002	0.257	0.002
0.50	0.0005	0.65	0.01	2.822	0.002	0.441	0.002
0.50	0.0005	0.92	0.02	18.61	0.01	0.915	0.002
0.50	0.0005	1.05	0.06	93.90	0.08	0.983	0.002
1.00	0.0003	0.248	0.002	1.931	0.002	0.218	0.002
1.00	0.0003	0.563	0.003	2.581	0.002	0.418	0.002
1.00	0.0003	0.89	0.01	6.327	0.005	0.764	0.002
1.00	0.0003	1.05	0.03	86.55	0.07	0.983	0.002
1.00	0.0003	1.10	0.04	157.2	0.1	0.991	0.002

Table 4. Solubility of CO_2 (1) in Aqueous Solution of Piperazine (2) at T = 293.1 K ($\Delta T = \pm$ 0.1 K)

m_2	Δm_2			P	ΔP		
mol·kg^{-1}	mol·kg^{-1}	α	Δα	kPa	kPa	y_1	Δy_1
0.100	0.002	1.15	0.13	44.52	0.04	0.948	0.002
0.100	0.002	1.32	0.25	81.34	0.07	0.972	0.002
0.100	0.002	1.49	0.42	135.4	0.1	0.983	0.002
0.50	0.0005	0.421	0.004	2.504	0.002	0.079	0.002
0.50	0.0005	0.79	0.01	3.201	0.003	0.282	0.002
0.50	0.0005	1.02	0.03	33.66	0.03	0.932	0.002
0.50	0.0005	1.07	0.05	70.52	0.06	0.967	0.002
0.50	0.0005	1.17	0.10	161.7	0.1	0.986	0.002
1.09	0.0002	0.330	0.002	2.716	0.002	0.173	0.002
1.09	0.0002	0.619	0.004	3.261	0.003	0.315	0.002
1.09	0.0002	0.82	0.01	6.148	0.005	0.638	0.002
1.09	0.0002	0.93	0.01	33.28	0.03	0.933	0.002
1.09	0.0002	0.98	0.03	94.66	0.08	0.977	0.002
1.09	0.0002	1.04	0.06	195.0	0.2	0.989	0.002

Table 5. Solubility of CO_2 (1) in Aqueous Solution of Piperazine (2) at T = 298.1 K ($\Delta T = \pm$ 0.1 K)

m_2	Δm_2			P	ΔP		
mol·kg^{-1}	mol·kg^{-1}	α	Δα	kPa	kPa	y_1	Δy_1
0.10	0.002	0.45	0.01	3.256	0.003	0.034	0.002
0.10	0.002	1.00	0.05	13.93	0.01	0.775	0.002
0.10	0.002	1.12	0.11	41.15	0.03	0.924	0.002
0.10	0.002	1.24	0.19	73.40	0.06	0.957	0.002
0.63	0.0004	0.357	0.002	3.519	0.003	0.118	0.002
0.63	0.0004	0.665	0.005	4.049	0.003	0.236	0.002
0.63	0.0004	0.92	0.01	10.204	0.008	0.698	0.002
0.63	0.0004	1.01	0.02	42.81	0.03	0.928	0.002
0.63	0.0004	1.06	0.04	86.96	0.07	0.965	0.002
0.63	0.0004	1.10	0.07	150.8	0.1	0.980	0.002
1.00	0.0003	0.236	0.002	3.410	0.003	0.089	0.002
1.00	0.0003	0.494	0.003	3.793	0.003	0.184	0.002
1.00	0.0003	0.713	0.005	4.983	0.004	0.381	0.002
1.00	0.0003	0.87	0.01	22.00	0.02	0.860	0.002
1.00	0.0003	0.92	0.02	61.73	0.05	0.950	0.002
1.00	0.0003	0.95	0.03	102.30	0.08	0.970	0.002

Table 6. Solubility of CO_2 (1) in Aqueous Solution of Piperazine (2) at T = 303.1 K ($\Delta T = \pm$ 0.1 K)

m_2	Δm_2			P	ΔP		
mol·kg^{-1}	mol·kg^{-1}	α	Δα	kPa	kPa	y_1	Δy_1
0.10	0.002	0.66	0.02	4.485	0.004	0.058	0.002
0.10	0.002	1.00	0.05	14.49	0.01	0.708	0.002
0.10	0.002	1.09	0.12	37.46	0.03	0.887	0.002
0.10	0.002	1.18	0.19	63.87	0.05	0.934	0.002
0.10	0.002	1.33	0.29	104.67	0.08	0.960	0.002
0.63	0.0004	0.298	0.002	4.540	0.004	0.080	0.002
0.63	0.0004	0.596	0.005	5.202	0.004	0.200	0.002
0.63	0.0004	0.85	0.01	21.75	0.02	0.809	0.002
0.63	0.0004	0.91	0.03	73.04	0.06	0.943	0.002
0.63	0.0004	0.93	0.04	104.74	0.08	0.960	0.002
1.00	0.0003	0.193	0.002	4.769	0.004	0.128	0.002
1.00	0.0003	0.428	0.003	5.516	0.004	0.249	0.002
1.00	0.0003	0.65	0.01	6.561	0.005	0.371	0.002
1.00	0.0003	0.86	0.01	12.95	0.01	0.683	0.002
1.00	0.0003	0.97	0.03	74.28	0.06	0.945	0.002

Concerning the two remaining independent sources, Rochelle's research group[30,31] and Kadiwala et al.,[32] data of the former were verified in Ermatchkov's work,[12] and Kadiwala et al.[32] compared their data against those of Pérez-Salado Kamps et al.[28] and found good agreements. Therefore, all data from these two sources were considered reliable and were added to the databank used in the parameter regression. A total of 354 data points was finally included in the databank. Table 2 summarizes the origin and the number of data used in this work the parameter estimation.

4.2. Solubility Measurements. CO_2 solubility measurements were made, following the procedure described in Section 2.2, in aqueous piperazine solutions over a temperature range from T = (287.1 to 313.1) K and for amine concentrations from m = (0.10 to 2.00) mol·kg^{-1}. The CO_2 partial pressure was kept within P_{CO_2} = (0.11 to 525.17) kPa using a VLE apparatus based on a static-synthetic method. The validity of the apparatus and procedure were verified in our previous work.[11] All of the results are shown in Tables 3 to 7 along with their experimental

Table 7. Solubility of CO_2 (1) in Aqueous Solution of Piperazine (2) at T = 313.1 K ($\Delta T = \pm 0.1$ K)

m_2	Δm_2			P	ΔP		
$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	α	Δα	kPa	kPa	y_1	Δy_1
2.00	0.0001	0.097	0.001	9.34	0.01	0.238	0.002
2.00	0.0001	0.247	0.002	12.81	0.01	0.447	0.002
2.00	0.0001	0.436	0.002	17.26	0.01	0.592	0.002
2.00	0.0001	0.671	0.003	20.79	0.02	0.664	0.002
2.00	0.0001	0.907	0.005	33.17	0.03	0.791	0.002
2.00	0.0001	1.08	0.02	229.0	0.2	0.970	0.002
2.00	0.0001	1.16	0.04	532.0	0.4	0.987	0.002

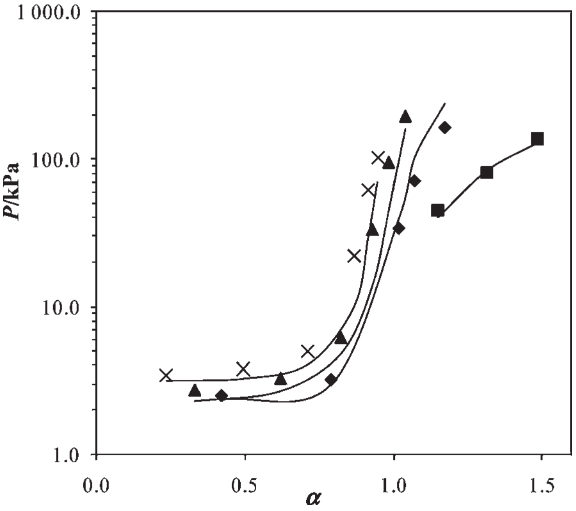

Figure 3. Equilibrium pressure above aqueous solutions of CO_2 (1) + piperazine (2) at concentration $m_2/mol \cdot kg^{-1}$ and temperature T/K as a function of solution CO_2 loading (α): ■, m_2 = 0.10 and T = 293.1; ◆, m_2 = 0.50 and T = 293.1; ▲, m_2 = 1.09 and T = 293.1; ×, m_2 = 1.00 and T = 298.1; lines, model correlation.

Table 8. Interaction Parameters in Pitzer's G^E Equation for the Ternary CO_2−Pz−H_2O System as in eq 17 for a Temperature Range of (287.1 to 395.1) K

parameters	q_0	q_1
$\beta_{CO_2,HCO_3^-}^{(0)}$	5.8194	−2201.7
$\beta_{CO_2,PzH^+}^{(0)}$	−5.2153	1911.2
β_{CO_2,PzH^+COO^-}	−0.3542	184.13
$\beta_{PzH^+,HCO_3^-}^{(0)}$	0.4900	−179.00
$\beta_{PzH^+,HCO_3^-}^{(1)}$	2.5000	−870.92
$\beta_{Pz,PzCOO^-}^{(0)}$	0.1500	−21.00
$\beta_{PzH^+,PzCOO^-}^{(0)}$	0.0200	55.344
$\beta_{PzH^+,Pz(COO^-)_2}^{(0)}$	5.0011	−1480.00
$\beta_{PzH^+,PzH^+COO^-}^{(0)}$	−1.7999	580.00
$\beta_{PzH^+COO^-,PzH^+COO^-}^{(0)}$	0.4001	−221.99
$\beta_{PzH^+COO^-,PzH^+COO^-}^{(1)}$	2.2000	−580.00

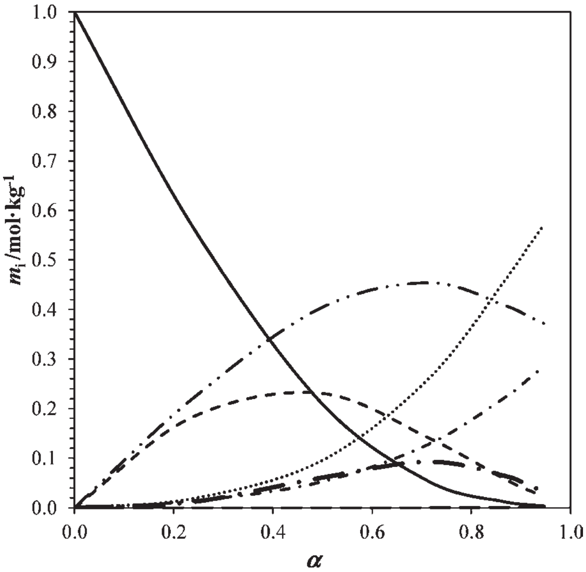

Figure 4. Species distribution in the aqueous CO_2 (1) + Pz (2) system at 298.1 K ($m_2/mol \cdot kg^{-1}$ = 1.00) as a function of solution CO_2 loading: —, Pz; — ·· —, PzH^+; - - -. $PzCOO^-$; ···, PzH^+COO^-; — · —, $Pz(COO^-)_2$; - · -, HCO_3^-; − −, CO_2.

uncertainties. In these tables, y_1 is the mole fraction of CO_2 in the gas phase.

In Figure 3 as well from Tables 3 to 7 and considering the uncertainties, it can be shown that at a constant amine concentrations and CO_2 partial pressure an increase in temperature leads to a decrease of the CO_2 loading capacity. Furthermore, as expected and also observed in other works,[25−27] at a fixed temperature, an increase in piperazine concentration leads to a decrease of the solution CO_2 loading.

The equilibrium CO_2 partial pressure increases at first very slowly with respect to the loading during the chemical absorption when the gas is mostly dissolved in nonvolatile ionic form. Then, at a loading near the unity, all further CO_2 absorption in the equilibrium cell can be related to physical absorption: the pressure increases sharply as the loading increases.

4.3. Modeling Results. All 354 selected experimental data for the system CO_2−Pz−H_2O, covering a large range of amine concentrations, temperature, and solution loading, were correlated together with our regressed set of interaction parameter (Table 8) with a pressure average relative deviation of 26.1 %. This percentage is quite satisfying, taking into account the wide range of amine concentrations, temperature, and solution loading in the solubility database considered for parameter estimation. Generally, higher deviations were obtained at very large amine concentrations and very high ionic strengths or at very low solution loading (very low CO_2 true molality in the liquid phase). In these regions, the addition of more ionic strength dependent parameters and some amine−water interaction parameters[17,33] might lead to the increase of the modeling accuracy. Figures 2 and 3 show a comparison between some of our data and the model correlation.

On the basis of the equilibrium model, an example of the speciation of several ions and of their activity coefficient in an aqueous Pz solution is shown respectively in Figures 4 and 5. The concentration profiles are represented as a function of the CO_2 loading for a Pz aqueous solution with a concentration of 1.00 $mol \cdot kg^{-1}$ at 298.1 K. Because H^+, OH^-, and PzH_2^{2+} concentrations are much lower than the concentrations of all other species, the corresponding curves were not represented. The piperazine concentration decreases rapidly at CO_2 loadings up to about 1 $mol \cdot mol^{-1}$ of amine, while the protonated amine PzH^+ and the amine carbamate $PzCOO^-$ concentrations show a fast increase. When the CO_2 stoichiometric concentration is less than

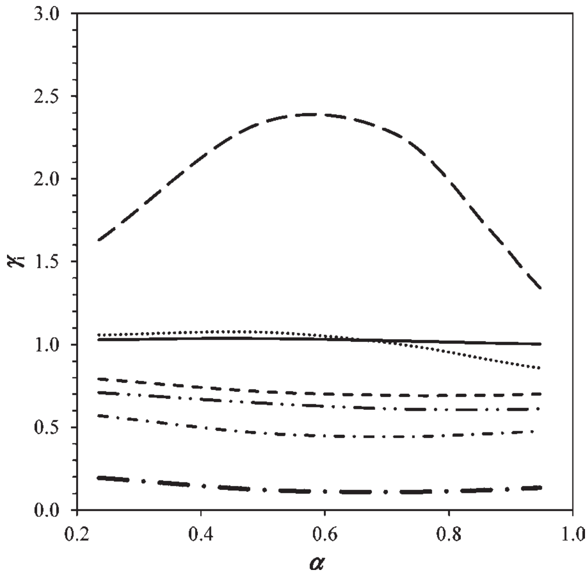

Figure 5. Calculated activity coefficients in the aqueous CO_2 (1) + Pz (2) system at 298.1 K (m_2/mol·kg^{-1} = 1.00) as a function of solution CO_2 loading: —, Pz; — ·· —, PzH^+; - - -, $PzCOO^-$; ···, PzH^+COO^-; — · —, $Pz(COO^-)_2$; - · · -, HCO_3^-; — —, CO_2.

that of piperazine, CO_2 is practically completely chemically dissolved (this is observed on the entire CO_2 loading range shown) and mainly converted into piperazine carbamate, piperazine dicarbamate, and protonated piperazine species. The same behavior was observed for other amine concentrations.[24,28]

5. CONCLUSIONS

In the present work, new data concerning the solubility of CO_2 in aqueous piperazine (Pz) solutions were obtained for a temperature range of T = (287.1 to 313.1) K and for amine concentrations from m = (0.10 to 2.00) mol·kg^{-1}. The CO_2 partial pressure was kept within P_{CO_2} = (0.11 to 525.17) kPa using a VLE apparatus based on a static-synthetic method. On the basis of these experimental data and from selected data from literature, 354 data values for the ternary system CO_2−Pz−H_2O were satisfactorily correlated with an mean average deviation of 26.1 % using a modified Pitzer's thermodynamic model for the activity coefficients combined with the virial equation of state for representing the fugacity coefficients. A new set of interaction parameters for this system was found in this work to cover a wider range of temperature, pressure, and amine concentration.

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■ LIST OF SYMBOLS

a_i	activity of species i
A_ϕ	Debye−Hückel parameter for the osmotic coefficient
$B_{i,j}$	second virial coefficients between species i and j
I	ionic strength
K_R	equilibrium constant for the chemical reaction R, expressed on the molality scale
$H^m_{CO_2,H_2O}(T,P_w^{sat})$	Henry's constant for the solubility of carbon dioxide in pure water on the molality scale
M_w	molar mass of water (kg·mol^{-1})
m_i	true molality of species i in solution
$\tilde{m}_i$	stoichiometric molality of component i
n	number of moles
P	pressure
q_0, q_1	coefficients, as defined in eq 17
P_w^{sat}	saturated vapor pressure of water
R	universal gas constant
T	absolute temperature (K)
V	(partial) molar volume
y	vapor phase mole fraction
z_i	charge of ion i

■ GREEK LETTERS

α	CO_2 loading, mol CO_2/mol amine
$\beta_{i,j}^{(0)}$, $\beta_{i,j}^{(1)}$	binary interaction parameters between species i and j in Pitzer's equation
$\nu_{i,R}$	stoichiometric coefficient of component i in the reaction R
φ_i	fugacity coefficient of component i
$\gamma_i^{*,m}$	activity coefficient of component i normalized to infinite dilution, on molality scale
$\lambda_{ij}(I)$	second virial coefficient in Pitzer's equation
τ_{ijk}	ternary interaction parameter in Pitzer's equation

■ SUBSCRIPTS AND SUPERSCRIPTS

R	reaction R
∞	infinite dilution in pure water
m	molality
w	water

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