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Measurement and Correlation of Solubility Data for CO_2 in $NaHCO_3$ Aqueous Solution

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ABSTRACT: To investigate the influence of $NaHCO_3$ on the CO_2 absorption in aqueous solution, the solubility of CO_2 in $NaHCO_3$ aqueous solutions [(0, 0.05, 0.1, 0.5, and 1.0) $mol\cdot kg^{-1}$] was measured in the temperature range from (313 to 333) K with pressure range from (0.3 to 2.0) MPa by employing a new designed batch apparatus. The results showed that the solubility data for CO_2 in $NaHCO_3$ aqueous solutions agreed well with Henry's law, and the Henry constant appeared to be a function of temperature and the concentration of $NaHCO_3$. Two thermodynamic models were proposed for correlating the experimental data, that is, the modified Setschenow and Peng−Robinson (PR)-Duan equations. It was proved that the models fitted well in with the experimental data, and the average relative deviations were (4.06 and 3.90) %, respectively. In addition, the Henry constant in pure water can be basically predicted at a certain temperature range. The influence of $NaHCO_3$ on the solubility of CO_2 is interpreted by "salting-out effect" which is usual for the salt-containing solutions.

INTRODUCTION

The carbonation of aqueous sodium chromate is an attractive alternative to the conventional acidification route for the manufacturing of sodium dichromate which is extensively used in leather, textile, and other industries.[1−3] This process involves the absorption of carbon dioxide in aqueous sodium chromate solution.[4,5] However, with taking byproduct $NaHCO_3$ unceasingly, the carbonation will be affected because $NaHCO_3$ plays a negative role during the absorption of CO_2, that is, $NaHCO_3$ obviously decreased the solubility of CO_2 in the carbonization solutions.[6,7] The objective of this work is to investigate the system CO_2−water in the presence of $NaHCO_3$ to get enough experimental data to validate a rational thermodynamic model for describing this system. Therefore, it was decided to measure the solubility of CO_2 in aqueous solutions of $NaHCO_3$ (0, 0.05, 0.1, 0.5, and 1.0 $mol\cdot kg^{-1}$) within the temperature range from (313 to 333) K and for pressure range from (0.3 to 2.0) MPa. The conditions selected were determined by the carbonization process. For the correlation of the experimental data, two thermodynamic models—modified Setchenow and Peng Robinson (PR)-Duan equations—were proposed.

A large number of experimental studies have been conducted with different techniques to measure the solubility of CO_2 in pure water and more complex aqueous solutions. Table 1 reports the solubility of CO_2 in different aqueous solutions at various temperatures, pressures, and concentrations presented in literature. Among these studies, the solubility of CO_2 in NaCl aqueous solutions was widely studied, such as the data from Koschel et al.,[8] Takenouchi and Kennedy,[9] Nighswander et al.,[10] Rumpf et al.,[11] Drummond,[12] and Gehrig.[13] However, the data are scarce on the solubility of CO_2 in other systems. Portuga et al.[14] measured the solubility of CO_2 in aqueous solutions of potassium glycinate with a stirred reactor. Ferrentino et al.[15] used two different setups (semicontinuous equipment and batch equipment) to measure the solubility of CO_2 in NaH_2PO_4 aqueous solutions. Bermejo et al.[16] determined the solubility of CO_2 in pure water and aqueous solutions of Na_2SO_4 with a Cailletet apparatus. Kamps et al.[17] reported the simultaneous solubility of NH_3 and CO_2 in aqueous solutions of NH_4Cl, NH_4NO_3, and $NaNO_3$. Kamps et al.[18] used a high-pressure view-cell technique based on the synthetic method to determine the solubility of CO_2 in aqueous solutions of KCl and K_2CO_3. Prutton and Savage[19] determined the solubility of CO_2 in aqueous solutions $CaCl_2$. Gao et al.[20] and Wong and Ya[21]determined the solubility of CO_2 in aqueous solutions of $NaHCO_3$ using the equilibrium liquid sampling method and a coulometric technique, respectively.

Modeling of the gas−liquid phase equilibria which has been widely studied can basically be subdivided into four approaches: (1) the empirical approaches, such as Setchenow's salting-out equation[22] and Kent and Eisenberg's KE equation;[23] (2) the application of the activity coefficient model, which forms the basis for the electrolyte NRTL (nonrandom two-liquid) model[24] and Li−Mather[25−27] equation; (3) the use of an equation of state (EOS) model, which is a fairly new development, finding application in recent publications. Kiepe et al.[28] successfully

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Table 1. Solubility of CO_2 in Different Aqueous Solutions

authors	aqueous solution	m_s/mol·kg^{-1}	T/K	P/MPa
Koschel et al.[8]	NaCl	1−3	323−373	0−20
Takenouchi and Kennedy[9]	NaCl	0−4.28	423−723	10−140
Nighswander et al.[10]	NaCl	0−0.17	353−473	2−10
Rumpf et al.[11]	NaCl	4−6	313−433	0.1−10
Drummond[12]	NaCl	0−6.5	290−673	3.5−40
Gehrig[13]	NaCl	1−4.3	408−800	3−280
Portuga et al.[14]	NH_2CH_2COOK	0.1−3.0	293−351	0−0.06
Ferrentino et al.[15]	NaH_2PO_4	0.02−0.40	288−368	7.58−13.10
Bermejo et al.[16]	Na_2SO_4	0.25−1	288−368	0−14
Kamps et al.[17]	NH_4Cl+ NH_4NO_3+ $NaNO_3$	4	313−393	0−0.7
Kamps et al.[18]	KCl	2−4	313−433	0−9.4
Kamps et al.[18]	K_2CO_3	0.43−1.7	313−393	0.27−9.2
Prutton and Savage[19]	$CaCl_2$	0−3.9	348−394	1−70
Gao et al.[20]	$NaHCO_3$	0.2−0.8	323−403	5−50
Wong and Ya[21]	$NaHCO_3$	0.1−0.5	278−298	

predicted the gas solubility in the NaCl aqueous solution system by coupling the predictive Soave−Redlich−Kwong (PSRK) EOS with the group contribution model LIFAC. Duan and Sun[29−32] established a sound thermodynamic model based on a specific particle interaction approach for the chemical potential of CO_2.[33,34] The fourth approach is the application of the statistical mechanics, for example, scaled particle theory[35,36] successfully applied for calculating the solubility of nonpolar gas in KOH aqueous solutions (10 to 50 wt %),[37] or the molecular thermodynamic model[38−41] established by Hu et al. for predicting the Henry's constants of gases in electrolyte solutions based on the first-order perturbation theory and a simplified radial distribution function.

■ EXPERIMENTAL SECTION

Materials. CO_2 had a mole fraction purity of 0.999; $NaHCO_3$ had a mass fraction purity of 0.998, and deionized water had an electrical conductivity of no more than 0.079 μs·cm^{-1}. $NaHCO_3$ aqueous solutions were prepared for the concentrations of (0, 0.05, 0.1, 0.5, and 1.0) mol·kg^{-1}.

Apparatus. The solubility was measured at ambient pressure by using a static approach which was described in literature.[14,15,42,43] A new designed batch apparatus applied for the experiment is shown in Figure 1. Here a gas mass-flow controller was innovatively used which is more convenient and precise to take place of storing vessel for acquiring CO_2 quantity added to the reactor, n_0. The apparatus consists of a gas cylinder; a GCF equilibrium still (947.21 ± 5.29 mL by calibration), which could bear the high pressure of 30 MPa; a 2XZ-4 vacuum pump, the limited pressure is 6·10^{-2} Pa; a Mettler Toledo AL104 electronic balance with an accuracy of 0.0001 g; a CH2015 thermostatic bath, with an accuracy of ± 0.05 K; a SevenStar CS200 gas mass-flow controller, with an uncertainty of ± 1 mL·min^{-1}; and a CYB-36 pressure transducer with an accuracy of ± 0.05 % of full scale (6 MPa).

Procedure. First, a known volume (400 mL) of fresh $NaHCO_3$ aqueous solutions, m_{sol}, V_{sol}, previously degassed was injected into the equilibrium still, V_t. The thermostatic bath was started which was used to adjust the temperature in the still to the desired value. Then, the still was purged by operating the vacuum pump to make it completely empty and remove the remaining air. The values were turned on: V1, V2, and V3. A certain amount of gas was pushed into the still, which was recorded by gas mass-flow controller, V_0. Value V$_3$ was turned off. Then, the stirring system was started until the equilibrium of the gas−liquid achieved, which happened when the pressure recorded, P_{eq}, in the equilibrium still became constant. The solubility of CO_2 in $NaHCO_3$ aqueous solutions was computed as eqs 1 to 6.

$$n_0 = \frac{V_0 \cdot \rho(CO_2)}{M(CO_2)} \tag{1}$$

Here, $\rho(CO_2)$ and $M(CO_2)$ represent the density and molar mass of CO_2, respectively.

The amount of CO_2, n_{eq}, remaining in the gas phase when the equilibrium happened was calculated by the Peng−Robinson cubic equation of state[44,45] with the CO_2 partial pressure in the gas phase, P_{CO_2}, temperature, T, volume of gas phase in the still, V_g, and the volume per mole of CO_2, V_m. Here P_{CO_2} was computed by assuming that the gas phase obeyed Dalton's law and the partial pressure of water in vapor mixture,P_{H_2O}, is the same as the saturation pressure of pure water. Therefore, n_{eq} was obtained as follows,

$$P_{CO_2} = P_{eq} - P_{H_2O} \tag{2}$$

$$V_g = V_t - V_{sol} \tag{3}$$

$$P_{CO_2} = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)} \tag{4}$$

$$n_{eq} = \frac{V_g}{V_m} \tag{5}$$

The solubility of CO_2 in $NaHCO_3$ aqueous solutions, m_{ex}, was then acquired,

$$m_{ex} = \frac{n_0 - n_{eq}}{m_{sol}} \tag{6}$$

The uncertainty of m_{ex} was determined from the uncertainty in temperature, pressure, and volume, which were ± 0.1, ± 0.05,

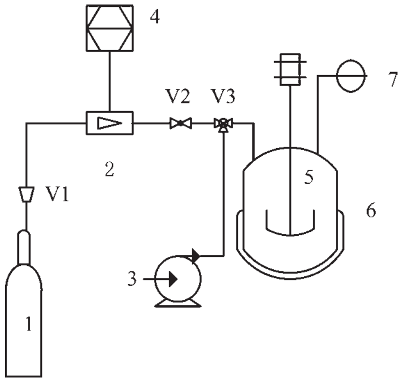

Figure 1. Schematic diagram of the experimental equipment: 1, gas cylinder; 2, gas mass-flow controller; 3, vacuum pump; 4, computer; 5, equilibrium still; 6, thermostatic bath; 7, pressure transducer; V1∼V3, vales.

Table 2. Solubility of CO_2 in Pure Water Compared with Literature at T = 323 K

	P_{CO_2} MPa	m_{CO_2} $mol \cdot kg^{-1}$
experiment	0.105	0.0208
	2.502	0.5111
literature[46]	0.1	0.0196
	2.5	0.5187

and ± 1 %, respectively, to give the estimated maximum uncertainty of ± 4 %.

RESULTS

To demonstrate the accuracy and precision of CO_2 solubility equipment and measurement procedures, the experimental results for the solubility of CO_2 in pure water were compared with the values presented in the literature.[46] Table 2 reports the experimental values of the solubility of CO_2 in pure water at 323 K.

It can be concluded from Table 2 that the experiment values differ from the literature values by 1.1 % and −1.5 % at (0.1 and 2.5) MPa, respectively. Therefore, it indicates that this equipment is able to reproduce the accurate solubility results which were very close to the experimental values of the solubility of CO_2 in pure water reported in previously published works.

Table 3 reports the experimental values of the solubility of CO_2 in $NaHCO_3$ aqueous solutions (0, 0.05, 0.1, 0.5, 1.0 $mol \cdot kg^{-1}$) at a temperature range from (313 to 333) K with a pressure range from (0.3 to 2) MPa.

THERMODYNAMIC MODELS

Modified Setschenow Equation. From the solubility data presented in Table 3, it can be seen that a linear equilibrium relationship between CO_2 concentration and the equilibrium CO_2 partial pressure is obvious, which is described as Henry's law. For simplicity, the nonideality for gas phase is neglected in this work, because calculation is limited in the low-medium pressures, consequently, using P_{CO_2} to replace the fugacity of CO_2, f_{CO_2}, as eq 7,

$$P_{CO_2} = H \cdot m_{CO_2} \tag{7}$$

Table 3. Solubility of CO_2 in $NaHCO_3$ Aqueous Solutions

	T = 313 K		T = 323 K		T = 333 K	
m_{NaHCO_3} $mol \cdot kg^{-1}$	P_{CO_2} MPa	m_{CO_2} $mol \cdot kg^{-1}$	P_{CO_2} MPa	m_{CO_2} $mol \cdot kg^{-1}$	P_{CO_2} MPa	m_{CO_2} $mol \cdot kg^{-1}$
0	0.369	0.1006	0.392	0.0673	0.380	0.0598
	0.792	0.1798	0.798	0.1487	0.784	0.1281
	1.204	0.2751	1.196	0.2330	1.209	0.1948
	1.595	0.3916	1.602	0.3204	1.602	0.2626
	1.993	0.4736	1.997	0.4014	2.000	0.3198
0.05	0.357	0.0806	0.579	0.1091	0.369	0.0565
	0.708	0.1595	0.939	0.1745	0.762	0.1196
	0.913	0.2104	1.292	0.2447	1.363	0.2157
	1.289	0.3014	1.695	0.3223	1.592	0.2539
	1.990	0.4604	1.975	0.3816	1.792	0.2756
0.1	0.310	0.0725	0.362	0.0655	0.378	0.0471
	0.856	0.1950	0.793	0.1440	0.822	0.1117
	1.200	0.2720	1.210	0.2257	1.185	0.1670
	1.605	0.3608	1.599	0.3024	1.593	0.2268
	1.901	0.4344	2.017	0.3866	1.988	0.2997
0.5	0.371	0.0725	0.399	0.0769	0.404	0.0516
	0.824	0.1617	0.807	0.1417	0.790	0.0984
	1.221	0.2349	1.188	0.2010	1.191	0.1460
	1.605	0.3082	1.605	0.2682	1.598	0.1963
	1.990	0.3900	1.993	0.3363	2.016	0.2564
1.0	0.376	0.0793	0.346	0.0667	0.342	0.0418
	0.826	0.1529	0.830	0.1331	0.853	0.0964
	1.222	0.2161	1.204	0.1816	1.200	0.1277
	1.619	0.2806	1.603	0.2380	1.595	0.1663
	2.035	0.3462	1.958	0.2884	1.955	0.1959

Therefore, as soon as Henry's constant, H, is predicted by building a credible thermodynamic model and the ambient pressure is given, the solubility of CO_2 in $NaHCO_3$ aqueous solutions will be known. It is well-known that the Setschenow equation[47] is applied for describing the relationship between the concentrations of aqueous solution and gas solute when the ambient pressure is certain. The modified Setchenow equation is proposed in this work for calculating H, which is determined by the concentration of the salt solutions, m_s, and T, as eq 8,

$$\log H = k_s \cdot m_s + k_0 \tag{8}$$

Combined eqs 7 and 8, it obtain eq 9,

$$\log \frac{P_{CO_2}}{m_{CO_2}} = k_s \cdot m_s + k_0 \tag{9}$$

To calculate the solubility of CO_2 as a function of T, P_{CO_2}, and m_s, it needs to determine the parameters, k_s and k_0, which are dependent upon T. Following Li and Mather,[26] the parameters are selected as eq 10,

$$f(T) = a \ln T + b/T + c \tag{10}$$

Equations 9 and 10 form the basis of parametrization for the model; the objective function for regression is as eq 11,

$$F_{obj} = \sum \left| \frac{m_{ex} - m_{CO}}{m_{ex}} \right| \tag{11}$$

Table 4. Fitted Values for Henry's Constants of the $CO_2-NaHCO_3-H_2O$ System

	a	*b*	*c*
k_s	96.5800	30934.3165	−653.6629
k_0	19.1934	5295.9216	−126.5809

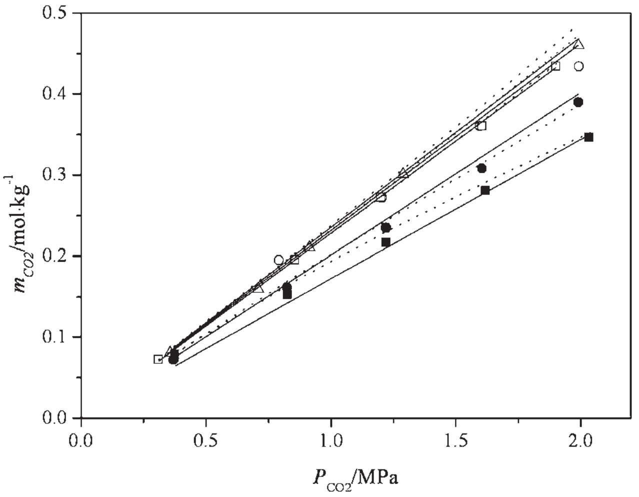

Figure 2. Solubility of CO_2 in $NaHCO_3$ aqueous solutions as a function of P_{CO_2} at $T = 313$ K. The points show the experimental data. The solid and dot lines show the modified Setschenow equation and PR-Duan equation correlated values, respectively. ○, 0 mol·kg^{-1}; △, 0.05 mol·kg^{-1}; □, 0.1 mol·kg^{-1}; ●, 0.5 mol·kg^{-1}; ■, 1.0 mol·kg^{-1} $NaHCO_3$ aqueous solutions.

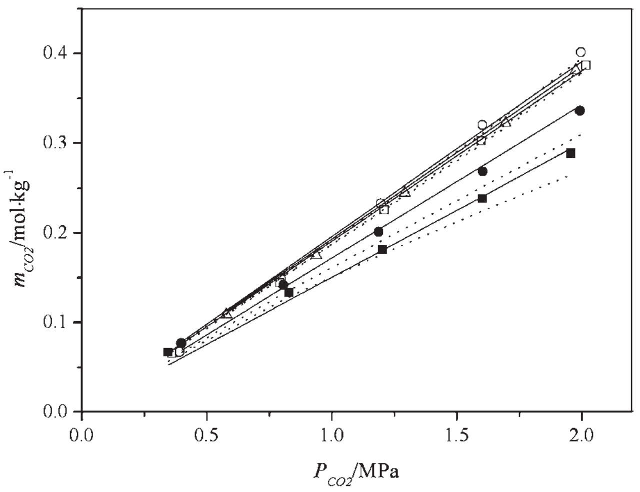

Figure 3. Solubility of CO_2 in $NaHCO_3$ aqueous solutions as a function of P_{CO_2} at $T = 323$ K. The points show the experimental data. The solid and dot lines show the modified Setschenow equation and PR-Duan equation correlated values, respectively. ○, 0 mol·kg^{-1}; △, 0.05 mol·kg^{-1}; □, 0.1 mol·kg^{-1}; ●, 0.5 mol·kg^{-1}; ■, 1.0 mol·kg^{-1} $NaHCO_3$ aqueous solutions.

Here m_{CO} represents the correlated solubility of CO_2 by equation. Results of the parameters are listed in Table 4, and the correlation results are shown in Figures 2 to 4. The average relative deviation for the solubility of CO_2 from experimental data is 4.06 %.

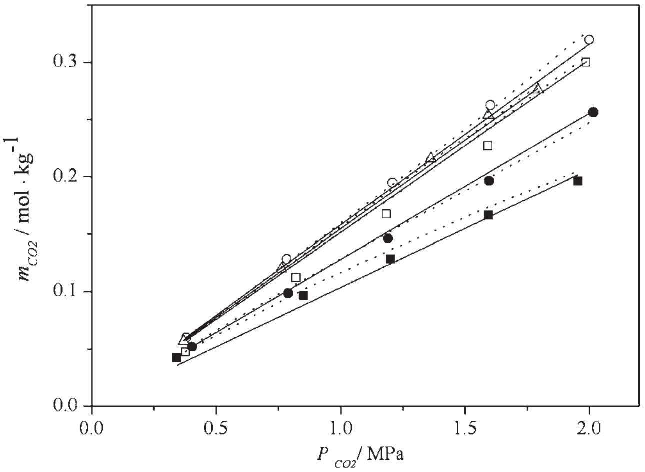

Figure 4. Solubility of CO_2 in $NaHCO_3$ aqueous solutions as a function of P_{CO_2} at $T = 333$ K. The points show the experimental data. The solid and dot lines show the modified Setschenow equation and PR-Duan equation correlated values, respectively. ○, 0 mol·kg^{-1}; △, 0.05 mol·kg^{-1}; □, 0.1 mol·kg^{-1}; ●, 0.5 mol·kg^{-1}; ■, 1.0 mol·kg^{-1} $NaHCO_3$ aqueous solutions.

PR-Duan Equation. The solubility of CO_2 in aqueous solutions is determined from the balance of chemical potential between in the liquid phase, $\mu^{l}{}_{CO_2}$, and in the gas phase, $\mu^{g}{}_{CO_2}$. The chemical potential can be expressed in terms of fugacity, f_{CO_2}, in the gas phase and activity, a_{CO_2}, in the liquid phase, as eqs 12 and 13,

$$\begin{aligned}\mu^{l}{}_{CO_2}(T,P,m) &= \mu^{l(0)}{}_{CO_2}(T,P) + RT\ln a_{CO_2}(T,P,m)\\ &= \mu^{l(0)}{}_{CO_2}(T,P) + RT\ln m_{CO_2} + RT\ln \gamma_{CO_2}(T,P,m)\end{aligned} \tag{12}$$

$$\begin{aligned}\mu^{g}{}_{CO_2}(T,P,m) &= \mu^{g(0)}{}_{CO_2}(T) + RT\ln f_{CO_2}(T,P,y)\\ &= \mu^{g(0)}{}_{CO_2}(T) + RT\ln P_{CO_2} + RT\ln \varphi_{CO_2}(T,P,y)\end{aligned} \tag{13}$$

At equilibrium, $\mu^{l}{}_{CO_2} = \mu^{g}{}_{CO_2}$, to obtain eq 14,

$$\ln \frac{P_{CO_2}}{m_{CO_2}} = \frac{\mu^{l(0)}{}_{CO_2}(T,P) - \mu^{l(0)}{}_{CO_2}(T)}{RT} - \ln \varphi_{CO_2}(T,P,y) + \ln \gamma_{CO_2}(T,P,m) \tag{14}$$

where $\mu^{l(0)}{}_{CO_2}$ and $\mu^{g(0)}{}_{CO_2}$ are the standard chemical potential of CO_2 in the ideal liquid phase ($m_{CO_2} = 1$ mol·kg^{-1}) and that in the ideal gas phase ($P_{CO_2} = 1$ MPa), respectively. The difference between $\mu^{l(0)}{}_{CO_2}$ and $\mu^{g(0)}{}_{CO_2}$ is defined as $\Delta G^{0}{}_{m,CO_2}$ for the CO_2 absorption process.

$\ln \varphi_{CO_2}$ can be acquired from the PR equation for pure CO_2, because the fugacity coefficient of CO_2, φ_{CO_2}, in the gas phase of CO_2-H_2O mixtures differs little from that of pure CO_2 at the experimental region. $\ln \varphi_{CO_2}$ can be calculated by eqs 15 and 16,

$$\ln \varphi_i = \frac{1}{RT}\int_{V_m}^{\infty}\left[\left(\frac{\partial P}{\partial n_i}\right) T, V, n_j - \left(\frac{RT}{V_i}\right)\right] dV_i - \ln Z \tag{15}$$

Table 5. T and P_{CO_2} Dependence of Parameters for the PR-Duan Equation

	$\Delta G^0_{m,CO_2}/RT$	λ_{CO_2-Na}	$\varsigma_{CO_2-Na-HCO_3}$
c_1	8.5921	1.0646	−0.2418
c_2	−2239.6877	−285.6020	
c_3	−0.0591	0.06984	

Peng and Robinson[48] defined the parameters A and B. Therefore, eq 16 for calculating $\ln \varphi_{CO_2}$ can be acquired,

$$A = \frac{aP}{(RT)^2} \quad B = \frac{bP}{RT} \quad Z = \frac{PV_m}{RT}$$

$$\ln \varphi_{CO_2} = Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \ln\left[\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B}\right] \tag{16}$$

$\ln \gamma_{CO_2}$ can be obtained from the Pitzer[34,49,50] and Duan[29−32] equations, as eq 17,

$$\ln \gamma_{CO_2} = \sum_c 2\lambda_{CO_2-c} m_a + \sum_a 2\lambda_{CO_2-a} m_a + \sum_c \sum_a \varsigma_{CO_2-a-c} m_c m_a \tag{17}$$

where c and a represent cations and anions, respectively. λ and ς are the second-order and third-order interaction parameters, respectively. Substituting eq 17 in eq 14, we obtain eq 18,

$$\ln \frac{P_{CO_2}}{m_{CO_2}} = \frac{\Delta G^0{}_{m,CO_2}}{RT} - \ln \varphi_{CO_2} + \sum_c 2\lambda_{CO_2-c} m_c + \sum_a 2\lambda_{CO_2-c} m_a + \sum_c \sum_a \varsigma_{CO_2-a-c} m_c m_a \tag{18}$$

In the above equation, $\lambda_{CO_2-HCO_3}$ is set to zero; because measurements can only be made in electronically neutral solutions ($m_c = m_a$), one of the λ parameters can be deleted. Therefore, to calculate the solubility of CO_2 in $NaHCO_3$ aqueous solutions, the parameters, λ_{CO_2-Na}, $\varsigma_{CO_2-Na-HCO_3}$, and $\Delta G^0{}_{m,CO_2}/RT$ need to be determined, which are all dependent upon T and P_{CO_2}. Following Pitzer et al.[51] and Li and Mather,[26] eq 19 for the parameters is selected,

$$f(T, P_{CO_2}) = c_1 + c_2/T + c_3 P_{CO_2} \tag{19}$$

Equations 18 and 19 form the basis of parametrization for the model. According to the objective function—eq 11, the term $\Delta G^0{}_{m,CO_2}/RT$ was first evaluated by using the CO_2 solubility data in pure water with an average relative deviation of 3.85 %. Then, λ_{CO_2-Na} and $\varsigma_{CO_2-Na-HCO_3}$ were evaluated simultaneously by fitting eq 18 using the CO_2 solubility data in $NaHCO_3$ aqueous solutions with average relative deviation of 3.90 %. T and P_{CO_2} dependence of parameters are listed in Table 5, and the deviations of correlation for the solubility of CO_2 from experimental data are shown in Figures 2 to 4. The model, which is calculated by use of the PR equation in the gas phase and described by Duan's specific interaction model[29−33] in the liquid phase, is an application of the EOS approach and defined as the PR-Duan equation in this work.

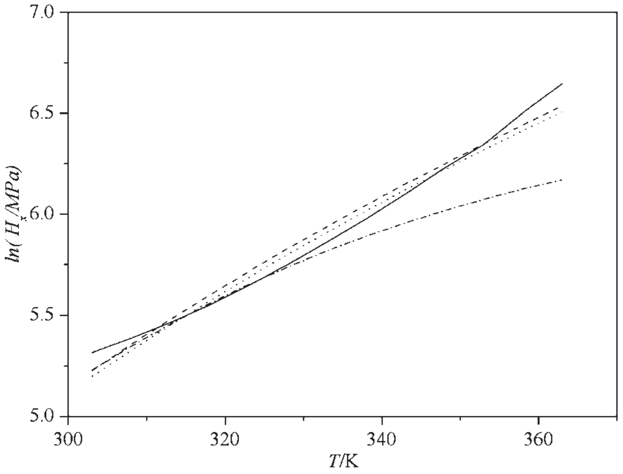

Figure 5. Correlated Henry constants for CO_2 in pure water as a function of T. The solid, dash, dot, and dash-dot lines show the eq 20, Lelieveld, Lide, and Harvey results, respectively.

DISCUSSION

Experimental data in Table 3 and curves in Figures 2 to 4 demonstrate the influence of $NaHCO_3$ on the solubility of CO_2. Comparing the results with the solubility of CO_2 in pure water ($0\ mol \cdot kg^{-1}$ $NaHCO_3$), these values were lower and decreased with the increase of salt concentration in the solutions at a certain temperature and pressure. It can be interpreted by hydration. Because so much salt $NaHCO_3$ joins in the water, there will be a significant quantity of H_2O coming forth to associate with the ions in solutions as ionic hydration. Furthermore, with increasing the concentration of the saline solution, the water bonded to ions Na^+ and $HCO_3{}^-$ is increasing, while the free water for dissolving CO_2 is decreasing. Therefore, a given total volume of water will dissolve a smaller concentration of CO_2 at equilibrium. The phenomenon—the effect of decreasing the solubility of molecular species by increasing salt concentration—is known as the "salting-out effect", which in most case is not concerned with the composition in the aqueous solution.[52,53]

The modified Setchenow equation is also applicable to the prediction of the Henry constant of CO_2 in pure water, H_0, at a certain situation. According to eqs 9 and 10, H_0 can be obtained,

$$\log H_0 = k_0 \tag{20}$$

H_0 calculated by this model was compared with literature values which were reported by Harvey,[54] Lide and Frederikse,[55] and Lelieveld and Crutzen[56] as Figure 5. Here, the unit of H_0 is expressed as mole fraction based on Harvey's model.

It can be seen from Figure 5 that H_0 calculated by eq 20 basically approach the values which were correlated by Lide and Frederikse and Lelieveld and Crutzen in the temperature range from (303 to 363) K. By comparison, the difference between Harvey and eq 20 is small in the temperature range from (303 to 338) K and becomes a little obvious in the higher temperature range, because the measurements are only carried out at three temperatures. Therefore, it indicates that eq 20 is able to predict Henry constant of CO_2 in pure water in a certain temperature range.

CONCLUSION

The solubility of CO_2 in pure water and $NaHCO_3$ aqueous solution was measured within the temperature range from (313 to 333) K and pressure range from (0.3 to 2.0) MPa by using a new designed static setup. Two thermodynamic models—the modified Setchenow and PR-Duan equations—were proposed with average relative deviation of (4.06 and 3.90) %, respectively. In addition, the Henry constant can be basically predicted at a certain temperature range. The influence of $NaHCO_3$ on the solubility of CO_2 is obvious, and it can be interpreted by "salting-out effect" which is usual for the salt-containing solutions.

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