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# Solubility of Carbon Dioxide in Aqueous HCl and $NaHCO_3$ Solutions from 278 to 298 K

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The solubility of carbon dioxide in aqueous HCl and $NaHCO_3$ solutions has been determined by the coulometric technique at ambient pressure and at 278, 283, 287, and 298 K. The maximum molality of HCl and $NaHCO_3$ solutions was 1 and 0.5 $mol\cdot kg^{-1}$, respectively. The error in $CO_2$ solubility in HCl solutions estimated from parallel experiments was about 0.3%. For bicarbonate solutions, the overall error was larger because the solubility is the difference between the determined dissolved inorganic carbon and sodium bicarbonate molality. Under investigated conditions, errors in solubility data varied from ±0.3% for dilute solutions to ±1.3% for 0.5 *m* sodium bicarbonate. Obtained data were treated by the Pitzer method. Pitzer parameters $\lambda_{CO_2,NaHCO_3}$ and $\lambda_{CO_2,HCl}$ were derived as a function of temperature.

## Introduction

The salting-out effect of electrolytes on the solubility of $CO_2$ and the reverse effect of dissolved $CO_2$ on the behavior of electrolyte solutions have been studied as a valuable step in developing reliable chemical models for technology and for many geological fluids, including seawater, hydrothermal water, and oil-field brines.[1−5] In these studies, the Pitzer method[6,7] was successfully used for the treatment of experimental data as well as for developing predictive models.

It is obvious that dissolved $CO_2$ gas may have an effect on the activity coefficients of carbon dioxide system species ($CO_2$(aq), $H^+$, $HCO_3^-$, and $CO_3^{2-}$) and as a result produce a shift in stoichiometric acid−base equilibrium. This possible effect was eliminated in classical experiments to determine the first ionization constants of carbonic acid by empirical extrapolation of $CO_2$ to zero content.[8] For investigations of the carbon dioxide system in seawater, this effect is negligible because of the very low molalities of dissolved $CO_2$, $H^+$, $HCO_3^-$, and $CO_3^{2-}$ ions in seawater and is not considered. However, for experiments involving the ocean disposal of fossil fuel $CO_2$[9] or for the study of carbon dioxide-rich hydrothermal fluids,[10] the effect of high $CO_2$ molality on activity coefficients of components of the carbon dioxide system may be appreciable and should be taken into account. The influence of dissolved $CO_2$ on carbon dioxide equilibrium in relation to liquid $CO_2$ disposal in the ocean can be taken into account by the Pitzer method if the needed Pitzer parameters are available at low temperatures. The most important parameters are $\lambda_{CO_2,CO_2}$ and $\lambda_{CO_2,H} + \lambda_{CO_2,HCO_3}$. The second virial coefficient $\lambda_{CO_2,CO_2}$ can be derived from high-pressure $CO_2$ solubility data in pure water.[4,11,12] The electroneutral combination of virial coefficients of interest ($\lambda_{CO_2,H} + \lambda_{CO_2,HCO_3}$) may be obtained from $CO_2$ solubility data in NaCl, HCl, and $NaHCO_3$ solutions at ambient pressure. There are accurate $CO_2$ solubility data in aqueous NaCl solutions at low temperatures[8] that were used to determine $\lambda_{CO_2,NaCl}$[12] as a function of temperature, but data are scarce on the solubility of $CO_2$ in HCl[5,13,14] and $NaHCO_3$[15] aqueous solutions at low temperatures.

Our aim in this work was to determine $CO_2$ solubility in aqueous HCl and $NaHCO_3$ solutions experimentally for molality ranges of 0.2 to 1 and 0.1 to 0.5 $mol\cdot kg^{-1}$, respectively, and at temperatures of 278, 283, 287, and 298 K. The Pitzer method was used to treat data for the evaluation of $\lambda_{CO_2,HCl}$ and $\lambda_{CO_2,NaHCO_3}$ parameters as a function of temperature.

## Experimental Procedures

Measurements of $CO_2$ solubility were carried out by the coulometric technique, which is commonly used to measure dissolved inorganic carbon.[16,17] A stock solution of HCl of approximately 1 $mol\cdot kg^{-1}$ was prepared from ACS-grade concentrated acid. The exact concentration was determined by the coulometric titration method. HCl solutions in other concentrations were prepared by diluting the stock solution. All experiments were carried out using a Mettler AT400 analytical balance, taking into account buoyancy corrections. Sodium bicarbonate (ACS grade) was used without any additional purification and was assayed by the Fisher Scientific Co. to be 100.1% $NaHCO_3$. Results of our titration were 100.12%, which agreed well with the value given by Fisher Scientific. Solutions of sodium bicarbonate were prepared by weight. Barometric pressures were measured by means of a digital pressure gage (Setra model 320 with a resolution of 0.01 mbar). High-purity $CO_2$ gas (99.99%) was saturated with water vapor by bubbling first through a chamber containing a test solution before being equilibrated with the same solution in a second chamber. Both chambers were immersed in a water bath at a temperature that was constant to within ±0.01 K. After bubbling $CO_2$ gas through the equilibration chamber for over 2 h, we drew about 2 g of the sample from the second chamber using a glass syringe. The sample was injected into a scrubber via a rubber septum and acidified ($NaHCO_3$ solutions) with $CO_2$-free orthophosphoric acid. The $CO_2$ in the solution was then purged, using ultra-high-purity

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**Table 1. Measured Solubility Coefficients of $CO_2$ ($\alpha$/mol·kg$^{-1}$·bar$^{-1}$) in $NaHCO_3$ and HCl Solutions**

| 278.15 K | | 283.15 K | | 288.15 K | | 293.15 K | | 298.15 K | |
|---|---|---|---|---|---|---|---|---|---|
| $m$ | $\alpha$ | $m$ | $\alpha$ | $m$ | $\alpha$ | $m$ | $\alpha$ | $m$ | $\alpha$ |
| mol·kg$^{-1}$ | mol·kg$^{-1}$·bar$^{-1}$ | mol·kg$^{-1}$ | mol·kg$^{-1}$·bar$^{-1}$ | mol·kg$^{-1}$ | mol·kg$^{-1}$·bar$^{-1}$ | mol·kg$^{-1}$ | mol·kg$^{-1}$·bar$^{-1}$ | mol·kg$^{-1}$ | mol·kg$^{-1}$·bar$^{-1}$ |
| $NaHCO_3$ Solutions | | | | | | | | | |
| 0.09973 | 0.0606 | 0.10333 | 0.0497 | 0.09957 | 0.0430 | 0.10314 | 0.0366 | 0.10843 | 0.0324 |
| 0.20017 | 0.0573 | 0.20179 | 0.0474 | 0.20046 | 0.0410 | 0.20110 | 0.0341 | 0.19909 | 0.0305 |
| 0.29874 | 0.0539 | 0.30049 | 0.0436 | 0.30001 | 0.0379 | 0.30064 | 0.0312 | 0.29908 | 0.0281 |
| 0.40523 | 0.0509 | 0.39971 | 0.0414 | 0.39899 | 0.0352 | 0.39754 | 0.0288 | 0.40206 | 0.0265 |
| 0.51435 | 0.0462 | 0.50043 | 0.0381 | 0.50885 | 0.0321 | 0.49825 | 0.0271 | 0.49876 | 0.0238 |
| HCl Solutions | | | | | | | | | |
| 0.19031 | 0.06231 | 0.19976 | 0.05220 | 0.20021 | 0.04439 | 0.20487 | 0.03832 | 0.19988 | 0.03339 |
| 0.40314 | 0.06171 | 0.40209 | 0.05181 | 0.40368 | 0.04411 | 0.40240 | 0.03816 | 0.39690 | 0.03329 |
| 0.61220 | 0.06092 | 0.61174 | 0.05153 | 0.61040 | 0.04392 | 0.61184 | 0.03796 | 0.59983 | 0.03314 |
| 0.81950 | 0.06069 | 0.84022 | 0.05139 | 0.81047 | 0.04384 | 0.80407 | 0.03791 | 0.81097 | 0.03310 |
| 1.09303 | 0.06032 | 1.09303 | 0.05104 | 1.09303 | 0.04361 | 1.09303 | 0.03756 | 1.09303 | 0.03301 |

nitrogen, and transferred into a coulometric cell where it was titrated. The exact amount of sample was determined by weighing the syringe before and after injection. Each of the samples was run a minimum of four times. The results of the first run were not used because they gave systematically lower values, as a rule, because of trapped air in the needle of the syringe, which was flushed out after the first injection. Analytical runs were continued until three runs agreed to within 0.15% of the total dissolved inorganic carbon (DIC). In the case of sodium bicarbonate solutions, molalities of dissolved $CO_2$ gas were calculated as the difference between total dissolved inorganic carbon (measured) and the prepared (calculated) molality of $NaHCO_3$. For all investigated solutions, determined molalities of $CO_2$ were normalized to standard $CO_2$ pressure, $P° = 0.1$ MPa. During our experiments, atmospheric pressure ($P_{tot}$) varied; therefore, solubility coefficients were calculated by means of the following equation

$$\alpha = \frac{m_{CO_2}}{P_{tot} - P_w^s} \tag{1}$$

where $m_{CO_2}$ is the measured molality of dissolved $CO_2$, $P_{tot}$ is atmospheric pressure, and $P_w^s$ is the vapor pressure of water. The solubility coefficients are expressed in mol·kg$^{-1}$·bar$^{-1}$ and are related to a standard pressure of 0.1 MPa. Each value is an average of three runs, and the results are listed in Table 1. DIC was determined to have a standard deviation of about ±0.07%. Therefore, the error in $CO_2$ solubility in HCl solutions is about 0.3% at the 0.99 confidence level. For bicarbonate solutions, the overall error is larger because the solubility is the difference between DIC and the sodium bicarbonate molality. This is the most important distinction of this $CO_2$ solubility study from other solution solubility studies. Under our conditions, errors in the solubility data varied from ±0.3% for dilute solutions to ±1.3% for 0.5 *m* sodium bicarbonate.

## Thermodynamic Treatment and Discussion

The experimental conditions for determining $CO_2$ solubility in HCl and $NaHCO_3$ aqueous solutions imply that there are two coexisting phases in equilibrium for the system under consideration. At vapor−liquid equilibrium, the chemical potential of $CO_2$ is the same in both phases, allowing us to write the following equation

$$\ln\left(\frac{y_{CO_2} P_{tot} \phi_{CO_2}}{k_{H,m} m^o}\right) + \int_{P^o}^{P_w^s} \frac{V_{CO_2}^{\infty}(T, P)}{RT}\, dP = \ln\left(\frac{m_{CO_2} \gamma_{CO_2}}{m^o}\right) \tag{2}$$

where $R$ is the gas constant, $T$ is the temperature in Kelvin, $m^o$ is the standard molality (1 mol·kg$^{-1}$), $\phi_{CO_2}$ is the fugacity coefficient of $CO_2$ for which values were calculated using Weiss's relationship,[18] $k_{H,m}$ is the Henry's law constant (molality scale), $\gamma_{CO_2}$ is the activity coefficient of $CO_2$ referenced to Henry's law (molality scale), $V_{CO_2}^{\infty}$ is the partial molar volume of $CO_2$ at infinite dilution, and $y_{CO_2}$ is the molar fraction of $CO_2$ in the gas phase and is calculated from the following relationship:

$$y_{CO_2} = 1 - \frac{P_w^s}{P} \tag{3}$$

$$P_w^s = P_w^o \exp(-M_A \varphi_m \textstyle\sum_i m_i) \tag{4}$$

Here, $P_w^o$ is the vapor pressure of pure water,[19] $\varphi_m$ is the osmotic coefficient, and $M_A$ is the molar mass of water. The osmotic coefficient has been calculated using the Pitzer method, where the Pitzer parameters for $NaHCO_3$ and HCl solutions have been taken from Millero[20] and Peiper.[21] The Pitzer method[7] for neutral species gives the equation for the activity coefficient of dissolved $CO_2$ as follows:

$$\ln(\gamma_{CO_2}) = 2m_{CO_2}\lambda_{CO_2,CO_2} + 2\sum_c m_c \lambda_{CO_2,c} + 2\sum_a m_a \lambda_{CO_2,a} + 6\sum_c \sum_a m_c m_a \zeta_{CO_2,c,a} \tag{5}$$

For single 1−1 electrolyte (our case) solutions, eq 5 yields

$$\ln(\gamma_{CO_2}) = 2m_{CO_2}\lambda_{CO_2,CO_2} + 2m(\lambda_{CO_2,c} + \lambda_{CO_2,a}) + 6m^2 \zeta_{CO_2,c,a} \tag{6}$$

where $m$ is the electrolyte molality ($NaHCO_3$ or HCl). Using Weiss's relationship for the solubility coefficient in seawater[18] and solubility data of liquid $CO_2$,[22] we[12] obtained empirical relations for $\lambda_{CO_2,CO_2}$ and for the solubility coefficient of $CO_2$ in seawater, $K_o^*$,

$$\lambda_{CO_2,CO_2}/\text{kg·mol}^{-1} = -0.2546 + 75.571/T - 5.428 \times 10^{-10} P/\text{Pa} \tag{7}$$

$$\ln(K_0^*/\mathrm{mol{\cdot}kg^{-1}{\cdot}bar^{-1}}) = -5.97508 \times 10^1 + 9.34517 \times 10^3\ \mathrm{K}/T + 2.33585 \times 10^1 \ln(T/100\ \mathrm{K}) - 3.2874 \times 10^{-3} T/\mathrm{K} + 5.380 \times 10^{-6} T^2/\mathrm{K}^2 + S[2.2843 \times 10^{-2} - 2.2534 \times 10^{-4} T/\mathrm{K} + 4.518 \times 10^{-7} T^2/\mathrm{K}^2] \quad (8)$$

where $S$ is the salinity of seawater, expressed as the mass fraction per mil.

The solubility coefficient $K_0^*$ corresponds to trace molalities of $CO_2$ in solution and relates to the Henry's law constant as follows:

$$\ln\{K_0^* k_{\mathrm{H,m}}\} = \int_{P^\circ}^{P_\mathrm{w}^\mathrm{s}} \frac{V_{\mathrm{CO_2}}^{\infty}(T, P)}{RT}\,\mathrm{d}P - k_{\mathrm{set}} S \quad (9)$$

Here, $k_{\mathrm{set}}$ is the Setschenow coefficient for seawater. From eqs 1, 2, 6, and 9, we have

$$\ln\left\{\frac{K_0^* \phi_{\mathrm{CO_2}}}{\alpha}\right\} = 2m_{\mathrm{CO_2}}\lambda_{\mathrm{CO_2,CO_2}} + 2(\lambda_{\mathrm{CO_2},c} + \lambda_{\mathrm{CO_2},a})m + 6\zeta_{\mathrm{CO_2},c,a} m^2 \quad (10)$$

When the electrolyte molality is less than 1, the contribution of the third term of eq 10 is not important, as a rule, and for ambient pressure conditions, the slope of the dependence $\ln(\alpha P^\circ/m^\circ)$ versus $m$ is roughly $2(\lambda_{\mathrm{CO_2,Na}} + \lambda_{\mathrm{CO_2,HCO_3}})$. This dependence, including all experimental points, is demonstrated in Figure 1. There is a curvature in the dependencies shown in Figure 1a despite there being comparatively low concentrations of sodium bicarbonate in the studied solutions. This gives evidence that the third term of eq 10 is important for sodium bicarbonate solutions. According to eq 10, we defined function $f$ as

$$f \equiv \ln\left[\frac{\phi_{\mathrm{CO_2}} m^\circ}{\alpha P^\circ}\right] - 2m_{\mathrm{CO_2}}\lambda_{\mathrm{CO_2,CO_2}} \quad (11)$$

Using this equation, we were able to determine extrapolated values of the solubility coefficients ($\alpha_o$) at zero molality using the least-squares method and two- and three-term statistical hypotheses. Relative deviations between values of $\alpha_o$ obtained from our experimental data for $NaHCO_3$ and $K_0^*$, calculated by eq 8, demonstrate better agreement when the three-term hypothesis was used (Figure 2). However, this improvement is not significant (<0.5%) for HCl solutions. Because our experimental data did not contradict the $K_0^*$ values, we were then able to evaluate the Pitzer parameters by including the solubility coefficients expressed by eq 8 in the function defined by eq 11. This function was then redefined as follows:

$$F \equiv \ln\left(\frac{\phi_{\mathrm{CO_2}} K_0^*}{\alpha}\right) - 2m_{\mathrm{CO_2}}\lambda_{\mathrm{CO_2,CO_2}} \quad (12)$$

The dependence of $F$ versus $m$ should then be a straight line for HCl solutions, with zero intercept and a slope equal to $2(\lambda_{\mathrm{CO_2,H}} + \lambda_{\mathrm{CO_2,HCO_3}})$. For $NaHCO_3$ solutions, the line is second order with zero intercept. Using our solubility data (Table 1), we calculated the $F$ values for $NaHCO_3$ and HCl solutions using eq 12 and present these data in Figure 3. The treatment of $F$ values by a least-squares method provides $(\lambda_{\mathrm{CO_2,H}} + \lambda_{\mathrm{CO_2,Cl}})$ parameters for HCl solutions. For $NaHCO_3$ solutions, we obtained two sets of parameters. One set is $(\lambda_{\mathrm{CO_2,Na}} + \lambda_{\mathrm{CO_2,HCO_3}})$ parameters that have been determined assuming that $\zeta_{\mathrm{CO_2,Na,HCO_3}} \equiv 0$. Another set is obtained by treating $F$ values, along with molalities, as a second-order line with zero intercept, which results in $(\lambda^*_{\mathrm{CO_2,Na}} + \lambda^*_{\mathrm{CO_2,HCO_3}})$ and $\zeta_{\mathrm{CO_2,Na,HCO_3}}$ parameters. These Pitzer parameters are listed in Table 2, along with their

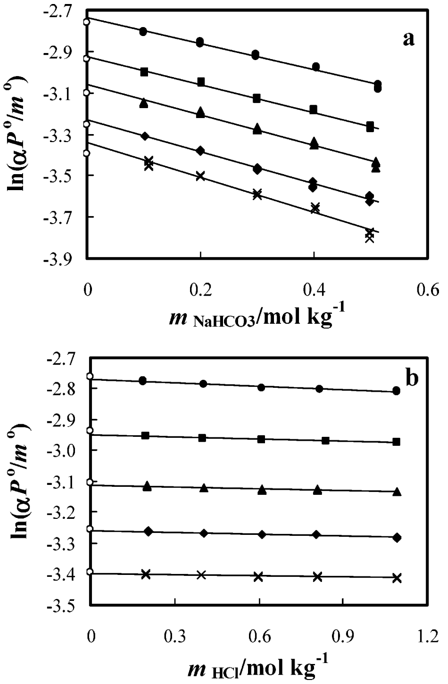

**Figure 1.** Logarithm of the solubility coefficient of carbon dioxide in (a) $NaHCO_3$ and (b) HCl solutions at the following temperatures: ●, 278.15 K; ■, 283.15 K; ▲, 288.15 K; ◆, 293.15 K; ×, 298.15 K. The solubility coefficients for pure water (○) were calculated using eq 8.

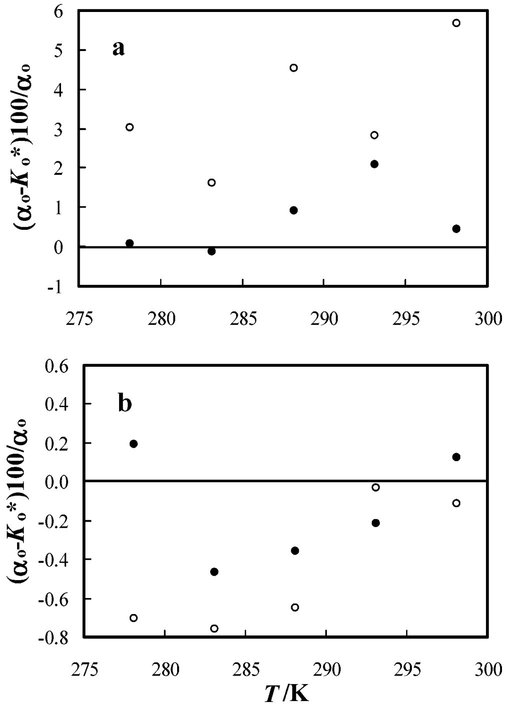

**Figure 2.** Relative deviations between extrapolated solubility coefficients of $CO_2$ in (a) $NaHCO_3$ and (b) HCl solutions to zero molality of electrolyte ($\alpha_o$) and calculated by means of eq 8. Two- and three-term statistical hypotheses used for the extrapolation procedure are marked by open and solid circles, respectively.

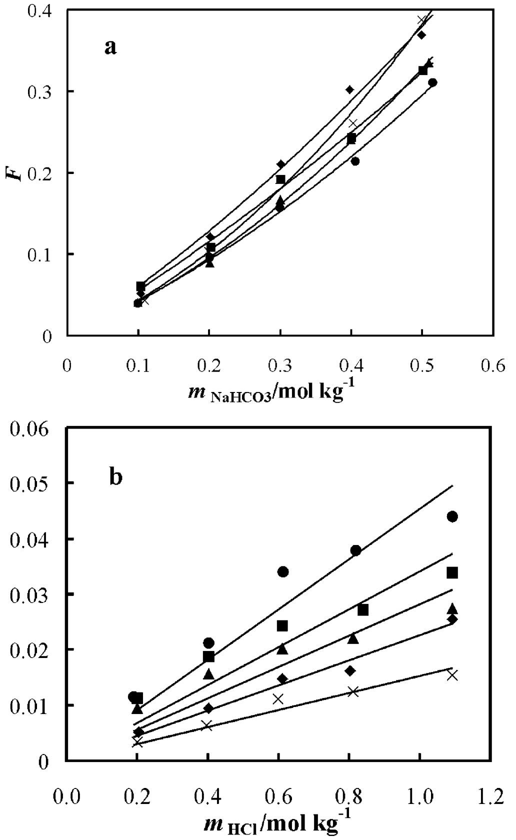

**Figure 3.** The Dependence function, $F$, defined by eq 12 vs molality of (a) $NaHCO_3$ and (b) HCl at the following temperatures: ●, 278.15 K; ■, 283.15 K; ▲, 288.15 K; ◆, 293.15 K; ×, 298.15 K.

**Table 2. Parameters of ($\lambda_{CO_2,Na} + \lambda_{CO_2,HCO_3}$)/kg·mol$^{-1}$ and ($\lambda_{CO_2,H} + \lambda_{CO_2,Cl}$)/kg·mol$^{-1}$ Determined from $CO_2$ Solubility Data for $NaHCO_3$ and HCl Solutions at Different Temperatures**

| $T$/K | 278.15 | 283.15 | 288.15 | 293.15 | 298.15 |
|---|---|---|---|---|---|
| ($\lambda_{CO_2,Na} + \lambda_{CO_2,HCO_3}$)/kg·mol$^{-1}$ | 0.2786 | 0.3129 | 0.3062 | 0.3499 | 0.3423 |
| SD | 0.0068 | 0.0044 | 0.0085 | 0.0066 | 0.0117 |
| ($\lambda^*_{CO_2,Na} + \lambda^*_{CO_2,HCO_3}$)/kg·mol$^{-1}$ | 0.1846 | 0.2688 | 0.1681 | 0.2358 | 0.1602 |
| SD | 0.0084 | 0.0096 | 0.0079 | 0.0148 | 0.0186 |
| $\zeta_{CO_2,Na,HCO_3}$/kg$^2$·mol$^{-2}$ | 0.0739 | 0.0345 | 0.1069 | 0.0907 | 0.1500 |
| SD | 0.0083 | 0.0096 | 0.0076 | 0.0149 | 0.0189 |
| ($\lambda_{CO_2,H} + \lambda_{CO_2,Cl}$)/kg·mol$^{-1}$ | 0.0225 | 0.0169 | 0.0141 | 0.0111 | 0.0074 |
| SD | 0.0008 | 0.0007 | 0.0006 | 0.0002 | 0.0003 |

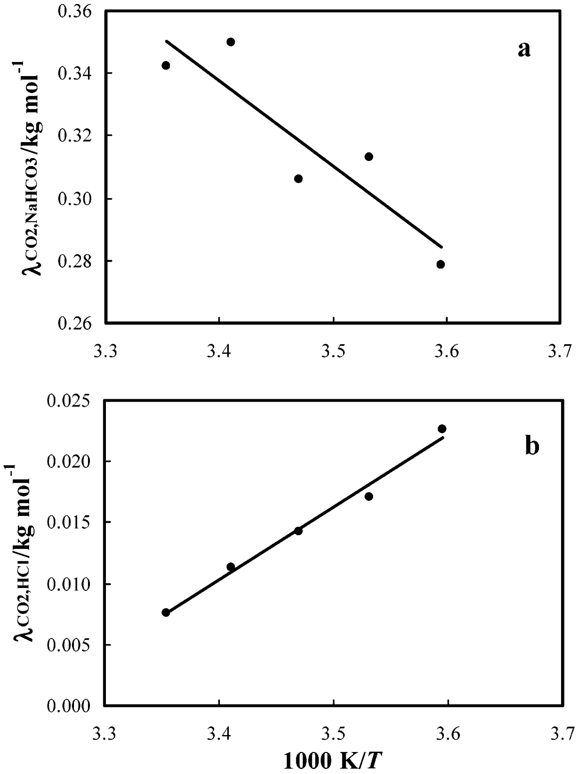

**Figure 4.** Dependence of (a) $\lambda_{CO_2,NaHCO_3}$ and (b) $\lambda_{CO_2,HCl}$ parameters vs $^1/_T$. Solid circles are calculated by the least-squares method using the $F$ function defined by eq 12. Solid lines are calculated by eqs 13 and 14.

standard errors. As seen from Table 2, including an additional parameter ($\zeta_{CO_2,Na,HCO_3}$) results in an increasing uncertainty of evaluation. Moreover, because of the large scatter in data points for ($\lambda^*_{CO_2,Na} + \lambda^*_{CO_2,HCO_3}$) and $\zeta_{CO_2,Na,HCO_3}$ parameters versus temperature, the inclusion of $\zeta_{CO_2,Na,HCO_3}$ to treat the $CO_2$ solubility data of $NaHCO_3$ solutions does not improve with the processing of data over the whole temperature range. For this reason, we did not evaluate the empirical temperature dependence of ($\lambda^*_{CO_2,Na} + \lambda^*_{CO_2,HCO_3}$) and $\zeta_{CO_2,Na,HCO_3}$.

For parameters ($\lambda_{CO_2,Na} + \lambda_{CO_2,HCO_3}$) and ($\lambda_{CO_2,H} + \lambda_{CO_2,HCO_3}$) listed in Table 2, again, using a least squares evaluation, we derived the following equations:

$$(\lambda_{CO_2,Na} + \lambda_{CO_2,HCO_3})/\text{kg·mol}^{-1} = 1.2674 - 273.414\ \text{K}/T \tag{13}$$

$$(\lambda_{CO_2,H} + \lambda_{CO_2,Cl})/\text{kg·mol}^{-1} = -0.1926 + 59.669\ \text{K}/T \tag{14}$$

Equations 13 and 14 describe the original Pitzer parameters with SDs of 0.014 and 0.0008, respectively, which are close to the standard deviations found in Table 2. The Pitzer parameters found in Table 2 and the calculated values from eqs 13 and 14 are presented in Figure 4.

From eqs 1 and 10, and assuming that $\zeta_{CO_2,Na,HCO_3} \equiv 0$, the solubility of $CO_2$ in $NaHCO_3$ and HCl solutions can be calculated at ambient total pressure by the equation

$$\ln\left(\frac{m_{CO_2}}{m^o}\right) = \ln\left(\frac{K^*_o\phi_{CO_2}(P^o - P^s_w)}{m^o}\right) - 2m_{CO_2,CO_2}\lambda_{CO_2,CO_2} - 2(\lambda_{CO_2,c} + \lambda_{CO_2,a})m \tag{15}$$

using empirical relationships 7, 8, 13, and 14. Because the right-hand side of eq 15 has the term containing the molality of $CO_2$, the calculation of solubility can then be carried out using the iteration procedure. In the first step, solubility was calculated ignoring the second term of the equation. The next step takes this term into account. Two cycles were enough because the third iteration gave results almost identical to the second. Figure 5 compares measured solubility data[5,13,14] with calculations using eq 15. The solubility data of He and Morse[5] were systematically lower than our calculations for 298 K. However, obtained deviations are comparable to experimental errors (precision ±1%) for 273 K. Geffcken's data[13] reasonably agree (within 2%) with our calculations. Robb and Zimmer's[14] data are systematically higher than our data by about 2% for 298 K. There are additional sources of solubility $CO_2$ data,[23] but they were obtained either using a different temperature range or are considered to be questionable. Therefore, we did not include them for comparison in Figure 5.

The obtained Pitzer parameters ($\lambda_{CO_2,Na} + \lambda_{CO_2,HCO_3}$) and ($\lambda_{CO_2,H} + \lambda_{CO_2,HCO_3}$) in this paper, eqs 13 and 14, can be used

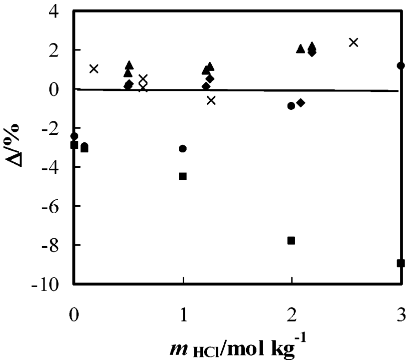

**Figure 5.** Relative deviations, Δ, between the measured solubility of $CO_2$ in HCl and that calculated by eq 15: Geffcken[13] at temperatures of ◆, 288 K and ▲, 298 K; Robb and Zimmer[14] at a temperature of ×, 298 K; He and Morse[5] at temperatures of ●, 273 K and ■, 298 K.

to estimate the effect of dissolved high $CO_2$ molality on the stoichiometric acid−base equilibrium in seawater.[15]

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