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# Absorption Equilibria of Dilute $SO_2$ in Seawater

**Juan Rodríguez-Sevilla,* Manuel Álvarez, María C. Díaz, and María C. Marrero**

Departamento de Ingeniería Química, Facultad de Química, Universidad de La Laguna, Avda. Astrofísico Francisco Sánchez, s/n. 38200 La Laguna, Spain

The solubility of dilute $SO_2$ in seawater, from mixtures $SO_2 + N_2$, was determined in a temperature range between (278.15 and 318.15) K and a $SO_2$ partial pressure range between (0.050 and 1.5) kPa. Measurements were carried out by a saturation method using a laboratory-stirred batch reactor. Equations to correlate experimental data were obtained as a function of temperature and $SO_2$ partial pressure. Comparisons between experimental results, literature data, and theoretical predictions were also made at different temperatures. Two different models were considered to evaluate the activity coefficients of ionic species. Theoretical calculations were made using both an extended version of the Debye−Hückel theory and the Pitzer ion-interaction model. Both models led to similar predictions and were in good agreement with the experimental results. The reasonable fitting between measured and calculated data showed that the selected models can be successfully used for predicting the absorption equilibria of dilute sulfur dioxide in seawater at different temperatures.

## Introduction

Sulfur dioxide is an important atmospheric contaminant. Its main source is flue gases from the burning of fuels with a high sulfur content. $SO_2$ can be removed either during or immediately after combustion. In the latter case, the $SO_2$ may be absorbed by an alkaline slurry or solution. Several methods for flue gas desulfurization (FGD) have been employed according to whether the reagent will be regenerated or not. Seawater scrubbing has been identified as an option among the FGD nonregenerative processes, since it provides a natural alkaline phase. Such a process offers potential advantages for power stations located nearby the coast, since it has a simple design, requires no bulk chemicals, and has low capital and operating costs.

Knowledge of the equilibrium data involving the sulfur dioxide−seawater system is an indispensable requirement for the design and operation of the absorption process. Bromley and Read[1] reported a few experimental and estimated data on solubility of sulfur dioxide in seawater. Abdulsattar et al.[2] proposed a simplified chemical model using an extended version of the Debye−Hückel theory for electrolyte solutions developed by Bromley.[3] This model predicts the solubility of sulfur dioxide seawater in a temperature range between (283.15 and 298.15) K and a $SO_2$ concentration range between ($10^{-5}$ and 1) mol·kg$^{-1}$. A comparison of the predicted $SO_2$ solubility in seawater with that one in freshwater indicated that sulfur dioxide is about two or three times more soluble in seawater than in freshwater. The higher solubility in seawater can be explained by the presence of alkaline components in seawater (mainly $HCO_3^-$ and $SO_4^{2-}$). Douabul and Riley[4] measured the solubility of sulfur dioxide in distilled water and decarbonated seawater at a $SO_2$ pressure of 101.3 kPa in the temperature range between (278.95 and 303.15) K and a salinity range between (0 and 40) g·kg$^{-1}$. The measurements showed that the $SO_2$ solubility was lower in decarbonated seawater than in distilled water, decreasing slightly with the increase of seawater salinity. Recently, Al-Enezi et al.[5] measured the $SO_2$ solubility in distilled water and seawater, from mixtures of $SO_2 + N_2$, at a $SO_2$ partial pressure of 22.4 Pa in the temperature range between (283.15 and 313.15) K and a salinity range between (5 and 65.1) g·kg$^{-1}$. They provided a second-order equation to correlate the $SO_2$ solubility as a function of temperature and initial salinity. Their results indicated a $SO_2$ solubility data lower than those predicted by Abdulsattar et al.[2] and an increase in the $SO_2$ solubility at higher initial salinity, which is the opposite effect to that found by Douabul and Riley.[4]

As shown above, limited data on solubility of sulfur dioxide in seawater are found in the literature, and some discrepancies are even observed among those data. Hence, the present work is focused on to provide new equilibrium measurements at low partial pressures and different temperatures. Low partial pressure range is of interest in FGD by seawater scrubbing. The performance at different temperatures is necessary to simulate variations in the operational conditions of $SO_2$ absorbers. Also, the experimental results will allow testing several thermodynamics models in order to predict equilibrium data for the absorption of sulfur dioxide in seawater.

## Experimental Section

***(a) Materials.*** The purity of sulfur dioxide and nitrogen used in the present work was higher than 99.9 volume % (Air Liquide). Natural seawater was collected from the supply stream of a Flakt-Hydro seawater FGD plant situated in a coastal power station located at the Canary Islands, Spain. The ionic composition of the seawater was measured according to the Standard Methods;[6] results are shown in Table 1. Artificial seawater samples were prepared according to the procedure of Lyman and Fleming, as cited by Riley and Skirrow.[7] The ionic composition of those samples is also shown in Table 1. Chemicals used for preparing artificial seawater were analytical-grade

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* To whom correspondence should be addressed. E-mail: jrguezs@ull.es. Telephone: +34 922 318058. Fax: +34 922 318004.

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**Table 1. Composition of the Seawater Samples**

| | natural seawater: pH = 7.79; $S = 36.87\ \mathrm{g{\cdot}kg^{-1}}$; $I = 0.775\ \mathrm{mol{\cdot}kg^{-1}}$ | | artificial seawater: pH = 7.92; $S = 35.00\ \mathrm{g{\cdot}kg^{-1}}$; $I = 0.732\ \mathrm{mol{\cdot}kg^{-1}}$ | |
|---|---|---|---|---|
| ion | $C_i/\mathrm{mol{\cdot}L^{-1}}$ | $m_i/\mathrm{mol{\cdot}kg^{-1}}$ | $m_i/\mathrm{mol{\cdot}kg^{-1}}$ | $C_i/\mathrm{mol{\cdot}L^{-1}}$ |
| $Cl^-$ | 0.5628 | 0.5700 | 0.5600 | 0.5663 |
| $SO_4{}^{2-}$ | 0.0306 | 0.0310 | 0.0291 | 0.0288 |
| $HCO_3{}^-$ | 0.00326 | 0.00330 | 0.00282 | 0.00279 |
| $Br^-$ | | | 0.00085 | 0.00084 |
| $F^-$ | 0.00042 | 0.00043 | 0.00007 | 0.00007 |
| $Na^+$ | 0.5061 | 0.5126 | 0.4857 | 0.4803 |
| $Mg^{2+}$ | 0.0640 | 0.0648 | 0.0553 | 0.0555 |
| $K^+$ | 0.0129 | 0.0131 | 0.00927 | 0.00917 |
| $Ca^{2+}$ | 0.0116 | 0.0117 | 0.0154 | 0.0152 |
| $Sr^{2+}$ | | | 0.00016 | 0.00016 |
| B | 0.00056 | 0.0057 | 0.00045 | 0.00045 |

reagents (Merck) with purities higher than 99 mass %. Iodine and sodium thiosulfate solutions were prepared from standard Tritisol ampules (Merck). The water used to prepare all solutions was distilled and deionized with a Milli-Q Plus device, 18 MΩ·cm (Millipore).

***(b) Experimental Procedure.*** Experiments were carried out at a total pressure of 97.6 kPa, using $SO_2 + N_2$ mixtures in the $SO_2$ partial pressure range between (0.050 and 1.5) kPa. The solubility of sulfur dioxide in aqueous solution was determined by a saturation method where the gaseous mixture was bubbled through the liquid phase. The installation used has been described in previous works.[8,9]

$SO_2 + N_2$ mixtures were prepared from pure gases with calibrated mass-flow controllers (Brooks Instruments). The uncertainties of the molar flow rate measurements were $\pm 10^{-5}$ and $\pm 10^{-3}$ mol·min$^{-1}$, for $SO_2$ and $N_2$, respectively. The overall uncertainty in the $SO_2$ partial pressure adjustment was estimated to be ±2%. For $SO_2$ partial pressures below 0.5 kPa, an infrared $SO_2$ analyzer (ADC) directly measured the $SO_2$ gaseous molar fraction with an uncertainty in the $SO_2$ partial pressure measurement of ±0.003 kPa. A control valve adjusted the total pressure inside the vessel with an uncertainty of ±0.05 kPa.

Seawater samples were located in a stirred jacketed vessel, and the temperature inside the solution was regulated within ±0.1 K by circulating water from a thermostatic bath (Haake). Thermometers with subdivisions of ±0.1 K were used to monitor both the bath and solution temperatures. Measurements of pH were carried out using a combined electrode (Ingold), located into the vessel solution, and a digital pH-meter (Radiometer). Buffer solutions of pH 1.68 ± 0.01 (Radiometer), 4.00 ± 0.02 (Merck), and 7.00 ± 0.02 (Merck) were used for the instrument calibration.

Before starting the measurements, the vessel of about 0.5 L of capacity was filled with deionized water and the installation was purged with nitrogen until steady-state conditions were obtained for temperatures and gas flow rate. Once steady-state conditions were achieved, the vessel was emptied, dried with the nitrogen flow, and filled again with 0.350 L of a fresh seawater sample. An additional time was required to stabilize temperatures again. During this time and through each experimental run, the nitrogen flow was saturated with water at the operation temperature, and pH and temperature of the seawater sample were continuously monitored. When a constant temperature was reached, a $SO_2$ flow at the required rate was injected into the nitrogen main flow and the $SO_2 + N_2$ mixture was bubbled through the seawater sample.

The sulfur dioxide was absorbed until saturation conditions were attained. At that point, the pH of the water leveled off at a constant value and the $SO_2$ concentration in the gas stream was the same in the outlet and in the inlet. Once equilibrium was reached, the total sulfur (IV) concentration in the liquid was determined by adding a known volume of seawater sample from the vessel to a known volume of standard iodine. The excess iodine was back titrated with the standard sodium thiosulfate. The overall uncertainty in the determination of the sulfur (IV) concentration was estimated to be ±1%.

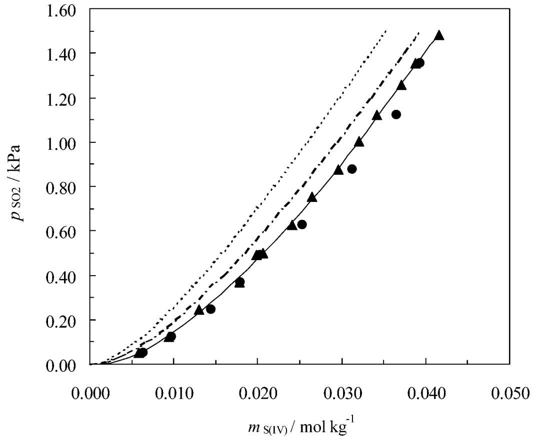

**Figure 1.** Solubility of sulfur dioxide in aqueous solutions at 298.15 K: dotted line, distilled water; dot-dashed line, 0.75 mol·kg$^{-1}$ NaCl solution; ▲, artificial seawater; ●, natural seawater.

## Discussion and Results

***(a) $SO_2$ Solubility in Seawater.*** Measurements at 298.15 K with natural and artificial seawater allowed comparing the total absorption capacity of both solutions. Figure 1 shows the experimental data of sulfur (IV) concentration in seawater as a function of the $SO_2$ partial pressure, together with experimental correlations for the $SO_2$ solubility in distilled water[8] and NaCl solutions with similar ionic strength.[9] Small differences (less than 5%) can be observed between the total absorption capacity of the natural and artificial seawater samples. However, the $SO_2$ solubility in artificial seawater increases within (20−60)% in relation to distilled water and within (6−30)% in relation to NaCl solutions. The higher differences are observed at the lower partial pressures of $SO_2$.

To establish the effect of temperature, measurements at 278.15 K and 318.15 K were also carried out with artificial seawater. Experimental data of pH and total solubility of

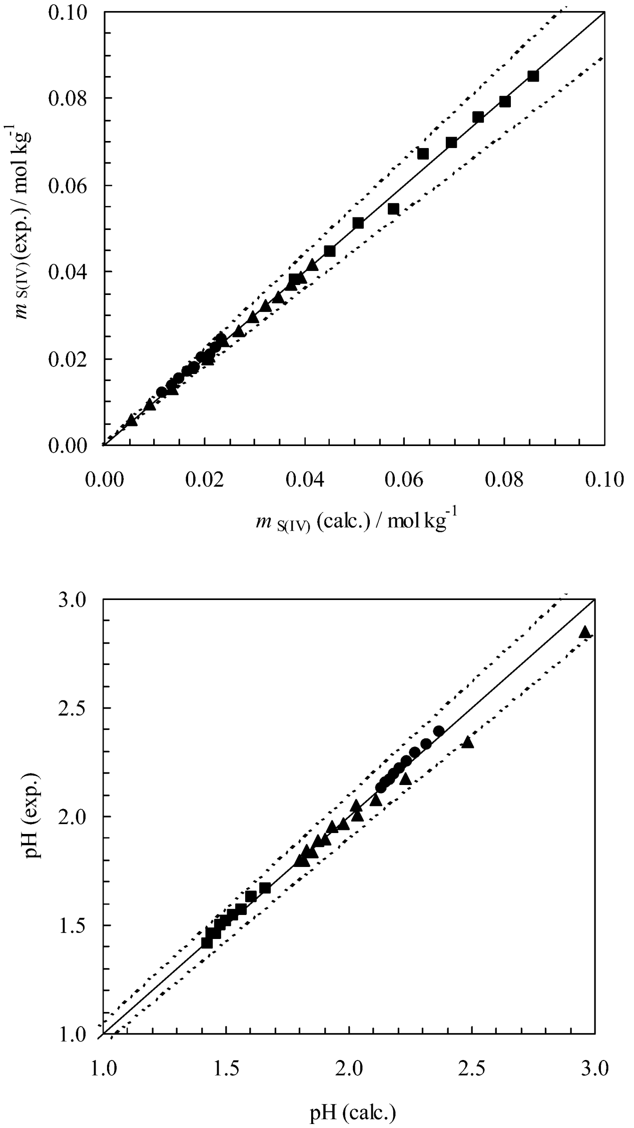

**Figure 2.** Comparison of experimental and calculated values of total solubility, $m_{S(IV)}$, and pH in artificial seawater: ●, 278.15 K; ▲, 298.15 K; ■, 318.15 K; dotted line, diagonal ±5% deviation.

$SO_2$ were correlated as functions of temperature and partial pressure of $SO_2$ as follows

$$\mathrm{pH} = A(T) + \frac{9.6876}{\ln(p_{SO_2}/\mathrm{Pa})}$$

$$A(T) = 5.589 - \frac{1526}{(T/\mathrm{K})} \quad (1)$$

$$m_{S(IV)}/\mathrm{mol\cdot kg^{-1}} = B(T)(p_{SO_2}/\mathrm{Pa}) + C(T)(p_{SO2}/\mathrm{Pa})^{1/2}$$

$$\frac{1}{B(T)} = 1.10847 \times 10^{6} - \frac{2.9917 \times 10^{8}}{(T/\mathrm{K})}$$

$$C(T) = 5.2302 \times 10^{-3} - 1.51407 \times 10^{-5}(T/\mathrm{K}) \quad (2)$$

The $R^2$ values for the above correlations were 0.991 and 0.998, respectively; the root-mean-square deviations from the fitted curves were 0.036 and 0.0010 $\mathrm{mol\cdot kg^{-1}}$, respectively (Figure 2). The validity ranges are a salinity of 35.00 $\mathrm{g\cdot kg^{-1}}$, a temperature between (278.15 and 318.15) K, and a $SO_2$ partial pressure between (0.050 and 1.5) kPa. Both equations can be combined to derive the following correlation between total $SO_2$ solubility, pH, and temperature

**Table 2. Fitting Constants of Eq 4, $a_1$, $a_2$, $a_3$, $a_4$, and $a_5$, to Correlate Literature Data of $SO_2$ Solubility in Seawater**

| constants | Douabul and Riley[4] | Al-Enezi et al.[5] |
|---|---|---|
| $a_1$ | 148.23507 | $2.669204 \times 10^{-2}$ |
| $a_2$ | −0.941699 | $-1.607938 \times 10^{-4}$ |
| $a_3$ | $3.314327 \times 10^{-4}$ | $1.045986 \times 10^{-5}$ |
| $a_4$ | $1.50622 \times 10^{-3}$ | $2.445612 \times 10^{-7}$ |
| $a_5$ | $4.525683 \times 10^{-6}$ | $1.295351 \times 10^{-7}$ |
| validity range: | $p_{SO_2} = 101.3$ kPa;<br>pH = 0.8;<br>$T = (278.15-303.15)$ K;<br>$S = (0$ to $40)$ $\mathrm{g\cdot kg^{-1}}$ | $p_{SO_2} = 0.022431$ kPa;<br>pH = (2.5−2.6);<br>$T = (283.15-313.15)$ K;<br>$S = (0$ to $40)$ $\mathrm{g\cdot kg^{-1}}$ |

$$m_{S(IV)}/\mathrm{mol\cdot kg^{-1}} = A(T)\exp\left[\frac{9.6876}{\mathrm{pH} - C(T)}\right] + B(T)\exp\left[\frac{4.8438}{\mathrm{pH} - C(T)}\right] \quad (3)$$

$$\frac{1}{A(T)} = 1.10847 \times 10^{6} - \frac{2.9917 \times 10^{8}}{(T/\mathrm{K})}$$

$$B(T) = 5.2302 \times 10^{-3} - 1.51407 \times 10^{-5}(T/\mathrm{K})$$

$$C(T) = 5.589 - \frac{1526}{(T/\mathrm{K})}$$

The validity ranges are a salinity of 35.00 $\mathrm{g\cdot kg^{-1}}$, a pH between (1.5 and 3.0), and a temperature between (278.15 and 318.15) K.

As it was mentioned in the Introduction, experimental data for the $SO_2$ + seawater system are scarce in the literature.[1,2,4,5] Data from Bromley and Read,[1] as were reported by Abdulsattar et al.,[2] provide equilibrium values of total solubility and pH at 12.8 °C and 33.9 $\mathrm{g\cdot kg^{-1}}$ in salinity but do not provide values of partial pressure of $SO_2$. Data from Douabul and Riley[4] and Al-Enezi et al.[5] are given only at a single $SO_2$ pressure of 101.3 kPa and 0.022431 kPa, respectively. Al-Enezi et al. correlated their experimental results in the temperature range between (283.15 to 313.15) K and a salinity range between (0 to 65.1) $\mathrm{g\cdot kg^{1}}$ by a function of the form

$$m_{S(IV)}/\mathrm{mol\cdot kg^{-1}} = a_1 + a_2(T/\mathrm{K}) + a_3(S/\mathrm{g\cdot kg^{-1}}) + a_4(T/\mathrm{K})^2 + a_5(S/\mathrm{g\cdot kg^{-1}})^2 \quad (4)$$

where S is salinity. The original data were given in molar concentrations, and the fitting constants have been recalculated using the seawater density, by means of the international equation of state of seawater.[10] Values of the constants for molal concentrations are shown in Table 2. Solubility data of Douabul and Riley were obtained in the temperature range between (278.15 and 303.15) K and a salinity range between (0 and 40) $\mathrm{g\cdot kg^{-1}}$. They have been also correlated by a function of the form as eq 4, showing Table 2 the set of fitting constants.

Table 3 compares, at 285.95 K, solubility calculated by eq 3 and experimental data from Bromley and Read[1,2] and Al-Enezi et al.[5] in the pH range between (1.5 and 3.0). Data from Bromley and Read are close to those calculated by eq 3, but a significant lower solubility is observed for the datum at pH 2.55, from Al-Enezi et al., compared both with the calculated value and the experimental value at pH 2.5. This low solubility was observed even by the authors themselves in their own solubility data in distilled water.

**Table 3. Comparison between the $SO_2$ Solubility in Seawater Calculated by Eq 3, $m_{s(IV)}$ (Eq 3), and Experimental Data from Literature, $m_{S(IV)}$ (exp), at 285.95 K**

| pH | $m_{S(IV)}$ (eq 3)/mol·kg$^{-1}$ | $m_{S(IV)}$ (exp)/mol·kg$^{-1}$ | ref |
|---|---|---|---|
| 1.5 | 0.082 | 0.07 | 1, 2 |
| 2.0 | 0.019 | 0.025 | 1, 2 |
| 2.5 | 0.0090 | 0.0096 | 1, 2 |
| 2.55 | 0.0085 | 0.0012 | 5 |
| 2.7 | 0.0074 | 0.0067 | 1, 2 |
| 3.0 | 0.0056 | 0.0046 | 1, 2 |

**Table 4. Selected Expressions for the Henry's Law Constant, $H_m°$, and the Equilibrium Constants $K_1$, $K_2$, $K_3$, and $K_4$, from $T$ = 278.15 K to 318.15 K**

| constants | expression | ref |
|---|---|---|
| $H_m°$/kPa·mol$^{-1}$·kg | = exp [14.642 − 3058/($T$/K)] | 8 |
| $K_1$/mol·kg$^{-1}$ | = exp [2335/($T$/K) − 12.319] | 8 |
| $K_2$/mol·kg$^{-1}$ | = exp [−358.57 + 5477.1/($T$/K) + 65.31 ln($T$/K) − 0.1624($T$/K)] | 11 |
| $K_3$/mol·kg$^{-1}$ | = exp [2825.27($T$/K) − 14.0321] | 14 |
| $K_4$/mol·kg$^{-1}$ | = exp [(−6723.67/($T$/K) − 9.72048)] | 16 |

***(b) Thermodynamic Models.*** A simplified chemical model, proposed by Abdulsattar et al.[2] and used by Al-Enezi et al.,[5] has been applied to predict the equilibrium solubility of sulfur dioxide in seawater in the temperature range between (278.15 and 318.15) K. The model considers the presence of eight species (apart from water): $SO_2$ (g), $SO_2$ (aq), $HSO_3^-$, $SO_3^{2-}$, $HSO_4^-$, $SO_4^{2-}$, $H^+$, and $OH^-$. The following equilibria are involved

$$SO_2(g) \leftrightarrow SO_2(aq) \qquad H_m° = \frac{\hat{\phi}_{SO_2} p_{SO_2}}{\gamma_{SO_2} m_{SO_2}} \tag{5}$$

$$SO_2(aq) + H_2O \leftrightarrow H^+ + HSO_3^-$$

$$K_1 = \frac{\gamma_{H^+}\gamma_{HSO_3^-}}{\gamma_{SO_2} a_{H_2O}} \frac{m_{H^+} m_{HSO_3^-}}{m_{SO2}} \tag{6}$$

$$HSO_3^- \leftrightarrow H^+ + SO_3^{2-} \qquad K_2 = \frac{\gamma_{H^+}\gamma_{SO_3^{2-}} m_{H^+} m_{SO_3^{2-}}}{\gamma_{HSO_3^-} \quad m_{HSO_3^-}} \tag{7}$$

$$HSO_4^- \leftrightarrow H^+ + SO_4^{2-} \qquad K_3 = \frac{\gamma_{H^+}\gamma_{SO_4^{2-}}}{\gamma_{HSO_4^-}} \frac{m_{H^+} m_{SO_4^{2-}}}{m_{HSO_4^-}} \tag{8}$$

$$H_2O \leftrightarrow H^+ + OH^- \qquad K_w = \frac{\gamma_{H^+}\gamma_{OH^-}}{a_{H_2O}} m_{H^+} m_{OH^-} \tag{9}$$

Here, $H_m°$ is the Henry's law constant in molal unit, $\hat{\phi}_{SO_2}$ is the fugacity coefficient, $K$ is the equilibrium constant, $\gamma$ is the activity coefficient, $m$ is the molal concentration, and $a_{H_2O}$ is the water activity. Since this study concerns only low pressures, the fugacity coefficient can be set equal to unity.

Chemical equilibria involving inorganic carbon species ($CO_2$, $HCO_3^-$, and $CO_3^{2-}$) have been omitted since the low pH values are dominant at equilibrium and $CO_2$ would be desorbed from the liquid phase. As no $CO_2$(g) is present in the gas, which is composed only by $N_2$ and $SO_2$, the desorbed $CO_2$ will be removed from the installation and inorganic carbon species are assumed not to be present in the equilibrated system.

Table 4 reports the selected expressions for the variation of $H_m°$ and the equilibrium constants with temperature. The correlations for $H_m°$ and $K_1$ were established previously[8] under the same experimental conditions as the present work and fits well with data from Goldberg and Parker[11] and Siddiqi et al.[12] The correlation for $K_2$[11] is frequently used as a reference correlation for the $H_2SO_3$ second dissociation constant.[13] The correlation for $K_3$[14] fits also very well with literature data.[15]

**Table 5. Schumpe ($h$) and Bromley ($B$) Specific Parameters at 298.15 K**

| ion or gas | $h_i$/L·mol$^{-1}$ | $B_i$/kg·mol$^{-1}$ |
|---|---|---|
| $Cl^-$ | 0.0318 | 0.156 |
| $SO_4^{2-}$ | 0.1117 | −0.009 |
| $HSO_3^-$ | 0.0549 | −0.013 |
| $SO_3^{2-}$ | 0.127 | −0.087 |
| $HSO_4^-$ |  | −0.013 |
| $OH^-$ | 0.0839 |  |
| $H^+$ | 0 | 0.087 |
| $Na^+$ | 0.1143 | −0.035 |
| $K^+$ | 0.0922 | −0.087 |
| $Ca^{2+}$ | 0.1762 | −0.035 |
| $Mg^{2+}$ | 0.1694 | 0.043 |
| $SO_2$ | −0.0607 |  |

The model uses $p_{SO_2}$ as an independent variable. Then, 7 concentrations and 7 activity coefficients are unknown, and 14 independent equations are needed to solve the system for each temperature. The equilibrium relationships, eqs 5−9, are completed with seven equations for the activity coefficients and two ionic balances:

Total S(VI) balance

$$m_{S(VI)}° = m_{HSO_4^-} + m_{SO_4^{2-}} \tag{10}$$

Hydrogen balance

$$m_{H^+} = \frac{10^{-pH°}}{\gamma_{H^+}} + m_{HSO_3^-} + 2m_{SO_3^{2-}} - m_{HSO_4^-} \tag{11}$$

Here, $m_{S(VI)}°$ and pH° are the initial concentration of $SO_4^{2-}$ and the initial pH of the seawater, respectively.

The activity coefficient for $SO_2$ (aq) has been estimated by the equation proposed by Schumpe,[17] considering the fugacity coefficient of $SO_2$ equal to unity

$$\log \gamma_{SO_2} = \sum_i (h_i + h_{SO_2}) C_i \tag{12}$$

Here, $h_i$ is the specific parameter of the ion $i$, $h_{SO_2}$ is the gas-specific parameter of the $SO_2$, and $C_i$ is the molar concentration of the ion $i$. Values for the different $h_i$ at 298.15 K were taken from Weisenberger and Schumpe;[18] the value for $h_{SO_2}$ at 298.15 K was proposed in a previous work;[9] those data are shown in Table 5. The temperature influence on the specific parameters was considered as gas specific, assuming a linear function in the range of (283.15 to 363.15) K given by[18]

$$(h_{SO_2} - h_{SO_2}°)/\text{m}^3\cdot\text{kmol}^{-1} = 0.275 \times 10^{-3}(T/\text{K} - 298.15) \tag{13}$$

where $h_{SO_2}°$ is the value at 298.15 K.

Activity coefficients for the ionic species involved in eqs 6−9 have been evaluated by two different sets of equations:

(1) Bromley's equations.[3] This model considers an extended version of the Debye−Hückel theory to estimate the single ion activity coefficients as a function of the ionic strength, $I$, and the liquid-phase composition. Ionic strength is defined as

$$I = \frac{1}{2}\sum_i m_i z_i^2 \tag{14}$$

Bromley equations are for a generic anion X

$$\log \gamma_{\mathrm{X}} = -\frac{A_\gamma z_{\mathrm{X}}{}^2 I^{1/2}}{1 + I^{1/2}} + B_{\mathrm{X}} \sum_{\mathrm{M}} m_{\mathrm{M}} + \sum_{\mathrm{M}} B_{\mathrm{M}} m_{\mathrm{M}} \quad (15)$$

and for a generic cation M

$$\log \gamma_{\mathrm{M}} = -\frac{A_\gamma z_{\mathrm{M}}{}^2 I^{1/2}}{1 + I^{1/2}} + B_{\mathrm{M}} \sum_{\mathrm{X}} m_{\mathrm{X}} + \sum_{\mathrm{X}} B_{\mathrm{X}} m_{\mathrm{X}} \quad (16)$$

Subscripts X and M denote anions and cations, respectively, $z$ is the ion charge, $A_\gamma$ is the constant of the Debye−Hückel equation, and the terms $B_i$ are individual ion parameters.

For water as solvent, temperature dependence of $A_\gamma$ in the range between (273.15 to 328.15) K is given by[19]

$$A^\phi/\mathrm{kg}^{1/2}\mathrm{mol}^{-1/2} = \frac{A_\gamma}{3} = 1.134 + 1.4052 \times 10^{-3}(T/\mathrm{K} - 273.15) + 1.122 \times 10^{-5}(T/\mathrm{K} - 273.15)^2 \quad (17)$$

where $A^\phi$ is the Debye−Hückel constant for the osmotic coefficient.

$B_i$ values[2] at 298.15 K are also given in Table 5. Values at other temperatures were estimated by assuming that variations in individual $B_i$ values would follow the variations of overall $B$ for the sea salt as a whole.[2] Bromley et al.[20] reported the temperature dependence of $B_{\mathrm{seasalt}}$. From this information, the following temperature dependence for $B_i$ has been derived

$$B_i(T/\mathrm{K}) = B_{\mathrm{seasalt}}(T/\mathrm{K}) - [B_{\mathrm{seasalt}}(298.15\ \mathrm{K}) - B_i(298.15\ \mathrm{K})]$$

$$B_{\mathrm{seasalt}}(T/\mathrm{K}) = 1.94357 + 0.031102 \ln\left(1 - \frac{243}{T/\mathrm{K}}\right) - \frac{78.565}{T/\mathrm{K}} - 0.27491 \ln(T/\mathrm{K}) \quad (18)$$

(2) Pitzer's equations.[21−23] This model is used frequently for the prediction of activity coefficients in multielectrolyte solutions with ionic strengths between (0−6) mol·kg$^{-1}$. Equations for single ion activity coefficients and for the water activity are derived from the formulation of the total excess Gibbs energy of the solution.

For an anion X

$$\ln \gamma_{\mathrm{X}} = z_{\mathrm{X}}{}^2 F + \sum_c 2m_c(B_{c\mathrm{X}} + EC_{c\mathrm{X}}) + \sum_a m_a\Big(2\Phi_{\mathrm{X}a} + \sum_c m_c \Psi_{c\mathrm{X}a}\Big) + \sum_c \sum_{<c'} m_c m_{c'} \Psi_{cc'\mathrm{X}} + |z_{\mathrm{X}}| \sum_c \sum_a m_c m_a C_{ca} + 2\sum_n m_n \lambda_{n\mathrm{X}} + \ldots \quad (19)$$

For a cation M

$$\ln \gamma_{\mathrm{M}} = z_{\mathrm{M}}{}^2 F + \sum_a 2m_a(B_{\mathrm{M}a} + EC_{\mathrm{M}a}) + \sum_c m_c\Big(2\Phi_{\mathrm{M}c} + \sum_a m_a \Psi_{\mathrm{M}ca}\Big) + \sum_a \sum_{<a'} m_a m_{a'} \Psi_{\mathrm{M}aa'} + |z_{\mathrm{M}}| \sum_c \sum_a m_c m_a C_{ca} + 2 \sum_n m_n \lambda_{n\mathrm{M}} + \ldots \quad (20)$$

For the water activity

$$\ln a_{\mathrm{H_2O}} = M_{\mathrm{H_2O}}\Bigg\{\frac{2A^\phi I^{3/2}}{1 + bI^{1/2}} - 2\Big[\sum_c \sum_a m_c m_a(B^\phi_{ca} + 2EC_{ca}) + \sum_c \sum_{<c'} m_c m_{c'}\Big(\Phi^\phi_{cc'} + \sum_a m_a \Psi_{cc'a}\Big) + \sum_a \sum_{<a'} m_a m_{a'}\Big(\Phi^\phi_{aa'} + \sum_c m_c \Psi_{caa'}\Big) + \sum_n \sum_c m_n m_c \lambda_{nc} + \sum_n \sum_a m_n m_a \lambda_{na} + \ldots.\Big] - \sum_i m_i\Bigg\} \quad (21)$$

where $M_{\mathrm{H_2O}}$ is the molecular mass of water (0.018 kg·mol$^{-1}$).

In the above equations, the third virial terms for neutral solutes are omitted. The subscripts $a$, $a'$ and $c$, $c'$ denote anions and cations different to X and M, respectively; the subscript $n$ denotes neutral solutes; $a < a'$ and $c < c'$ indicate that the sums are over the various anions $a$, $a'$ and cations $c$,$c'$, respectively.

The quantity F includes the Debye−Hückel's parameter for the osmotic coefficient, $A^\phi$, and other terms as follows

$$F = -A^\phi\left[\frac{\sqrt{I}}{1 + b\sqrt{I}} + \left(\frac{2}{b}\right) \ln(1 + b\sqrt{I})\right] + \sum_c \sum_a m_c m_a B'_{ca} + \sum_c \sum_{<c'} m_c m_{c'} \Phi'_{cc'} + \sum_a \sum_{<a'} m_a m_{a'} \Phi'_{aa'} \quad (22)$$

Here, $b$ is a constant with the value 1.2 kg$^{1/2}$·mol$^{-1/2}$ and $B'$ and $\Phi'$ are the ionic strength derivatives of $B$ and $\Phi$, respectively.

The quantity $E$ is given by

$$E = \frac{1}{2} \sum_i m_i |z_i| \quad (23)$$

The terms $C_{\mathrm{MX}}$ are related to the empirical parameters $C_{\mathrm{MX}}{}^\phi$ by the expression

$$C_{\mathrm{MX}} = \frac{C^\phi_{\mathrm{MX}}}{2|z_+ z_-|^{1/2}} \quad (24)$$

The terms $B$ and $B'$ include the specific parameters of the electrolyte MX, $\beta_{\mathrm{MX}}{}^{(0)}$, $\beta_{\mathrm{MX}}{}^{(1)}$, and $\beta_{\mathrm{MX}}{}^{(2)}$, and depend on the ionic strength as follows

$$B_{\mathrm{MX}}{}^\phi = \beta_{\mathrm{MX}}{}^{(0)} + \beta_{\mathrm{MX}}{}^{(1)} \exp(-\alpha_1 I^{1/2}) + \beta_{\mathrm{MX}}{}^{(2)} \exp(-\alpha_2 I^{1/2})$$

$$B_{\mathrm{MX}} = \beta_{\mathrm{MX}}{}^{(0)} + \beta_{\mathrm{MX}}{}^{(1)} g(\alpha_1 I^{1/2}) + \beta_{\mathrm{MX}}{}^{(2)} g(\alpha_2 I^{1/2})$$

$$B_{\mathrm{MX}}{}' = \frac{\beta_{\mathrm{MX}}{}^{(1)} g'(\alpha_1 I^{1/2}) + \beta_{\mathrm{MX}}{}^{(2)} g'(\alpha_2 I^{1/2})}{I} \quad (25)$$

The functions $g$ and $g'$ are given by

$$g(x) = \frac{2[1 - (1 + x) \exp(-x)]}{x^2}$$

$$g'(x) = \frac{-2[1 - (1 + x + x^2/2) \exp(-x)]}{x^2} \quad (26)$$

where the independent variable $x$ is $\alpha I^{1/2}$. For electrolytes with one monovalent ion, at 298.15 K, $\alpha_1$ and $\alpha_2$ take the values 2.0 kg$^{1/2}$·mol$^{-1/2}$ and 0, respectively; for 2-2 electrolytes at 298.15 K, the optimum values are (1.4 and 12) kg$^{1/2}$·mol$^{-1/2}$, respectively. For many applications, those

**Table 6. Available Single Electrolyte Solution Parameters $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, and $C_{MX}^{\phi}$ for the $SO_2$ + Seawater System at 298.15 K**

| cation M | anion X | $\beta_{MX}^{(0)}$ | $\beta_{MX}^{(1)}$ | $\beta_{MX}^{(2)}$ | $C_{MX}^{\phi}$ | ref |
|---|---|---|---|---|---|---|
| $H^+$ | $HSO_3^-$ | 0.15 | 0.4 | | | 19 |
| $H^+$ | $HSO_4^-$ | 0.2065 | 0.5556 | | | 22, 23 |
| $H^+$ | $SO_4^{2-}$ | 0.0298 | | | 0.0438 | 22, 23 |
| $H^+$ | $Cl^-$ | 0.1775 | 0.2945 | | 0.0008 | 22, 23 |
| $Na^+$ | $HSO_3^-$ | 0.0249 | 0.2455 | | 0.0004 | 22, 23 |
| $Na^+$ | $SO_3^{2-}$ | 0.021 | 1 | | | 19 |
| $Na^+$ | $OH^-$ | 0.0864 | 0.253 | | 0.0044 | 22, 23 |
| $Na^+$ | $HSO_4^-$ | 0.0454 | 0.398 | | | 22, 23 |
| $Na^+$ | $SO_4^{2-}$ | 0.0196 | 1.1130 | | 0.00497 | 22, 23 |
| $Na^+$ | $Cl^-$ | 0.0765 | 0.2644 | | 0.00127 | 22, 23 |
| $Mg^{2+}$ | $HSO_3^-$ | 0.49 | 1.804 | | | 19 |
| $Mg^{2+}$ | $SO_3^{2-}$ | 0.2 | 3.00 | −41 | | 19 |
| $Mg^{2+}$ | $HSO_4^-$ | 0.4746 | 1.729 | | | 22, 23 |
| $Mg^{2+}$ | $SO_4^{2-}$ | 0.221 | 3.343 | −37.23 | 0.0025 | 22, 23 |
| $Mg^{2+}$ | $Cl^-$ | 0.35235 | 1.6815 | | 0.00519 | 22, 23 |
| $K^+$ | $HSO_3^-$ | −0.096 | 0.2481 | | | 19 |
| $K^+$ | $SO_3^{2-}$ | 0.065 | 1 | | | 19 |
| $K^+$ | $OH^-$ | 0.1298 | 0.32 | | 0.0041 | 22, 23 |
| $K^+$ | $HSO_4^-$ | −0.0003 | 0.1735 | | | 22, 23 |
| $K^+$ | $SO_4^{2-}$ | 0.04995 | 0.7793 | | | 22, 23 |
| $K^+$ | $Cl^-$ | 0.03 | 0.2122 | | 0.0084 | 22, 23 |
| $Ca^{2+}$ | $HSO_3^-$ | 0.438 | 1.76 | | | 19 |
| $Ca^{2+}$ | $SO_3^{2-}$ | 0.18 | 2.38 | −61.3 | | 19 |
| $Ca^{2+}$ | $OH^-$ | −0.1747 | −0.2303 | −5.72 | | 22, 23 |
| $Ca^{2+}$ | $HSO_4^-$ | 0.2145 | 2.53 | | | 22, 23 |
| $Ca^{2+}$ | $SO_4^{2-}$ | 0.2 | 3.1973 | −55.7 | | 22, 23 |
| $Ca^{2+}$ | $Cl^-$ | 0.3159 | 1.614 | | 0.00034 | 22, 23 |

**Table 7. Available Mixing Parameters, $\theta_{ij}$ and $\psi_{ijk}$,[22,23] and Ion−Neutral Interaction Parameters, $\lambda_{ni}$,[24] for the $SO_2$ + Seawater System at 298.15 K**

| | | | $\psi_{ijk}$ | | | | |
|---|---|---|---|---|---|---|---|
| $i$ | $j$ | $\theta_{ij}$ | $k = Na^+$ | $k = K^+$ | $k = Ca^{2+}$ | $k = Mg^{2+}$ | $k = H^+$ |
| $Cl^-$ | $SO_4^{2-}$ | 0.030 | 0.000 | −0.005 | −0.002 | −0.008 | 0.013 |
| $Cl^-$ | $HSO_4^-$ | −0.006 | −0.006 | | | | |
| $Cl^-$ | $OH^-$ | −0.05 | −0.006 | −0.006 | −0.025 | | |
| $SO_4^{2-}$ | $HSO_4^-$ | | −0.0094 | −0.0677 | | −0.425 | |
| $SO_4^{2-}$ | $OH^-$ | −0.013 | −0.009 | −0.05 | | | |

| | | | $\psi_{ijk}$ | | |
|---|---|---|---|---|---|
| $i$ | $j$ | $\theta_{ij}$ | $k = Cl^-$ | $k = SO_4^{2-}$ | $k = HSO_4^-$ |
| $Na^+$ | $K^+$ | −0.012 | −0.0018 | −0.010 | |
| $Na^+$ | $Ca^{2+}$ | 0.07 | −0.007 | −0.055 | |
| $Na^+$ | $Mg^{2+}$ | 0.07 | −0.012 | −0.015 | |
| $Na^+$ | $H^+$ | 0.036 | −0.004 | | −0.0129 |
| $K^+$ | $Ca^{2+}$ | 0.032 | −0.025 | | |
| $K^+$ | $Mg^{2+}$ | 0 | −0.022 | −0.048 | |
| $K^+$ | $H^+$ | 0.005 | −0.011 | 0.0197 | −0.0265 |
| $Ca^{2+}$ | $Mg^{2+}$ | 0.007 | −0.012 | 0.024 | |
| $Ca^{2+}$ | $H^+$ | 0.092 | −0.015 | | |
| $Mg^{2+}$ | $H^+$ | 0.010 | −0.011 | | −0.0178 |

| $n$ | $i$ | $\lambda_{ni}$ |
|---|---|---|
| $SO_2$ | $Na^+$ | 0.0283 |
| $SO_2$ | $Mg^{2+}$ | 0.085 |
| $SO_2$ | $Cl^-$ | 0 |

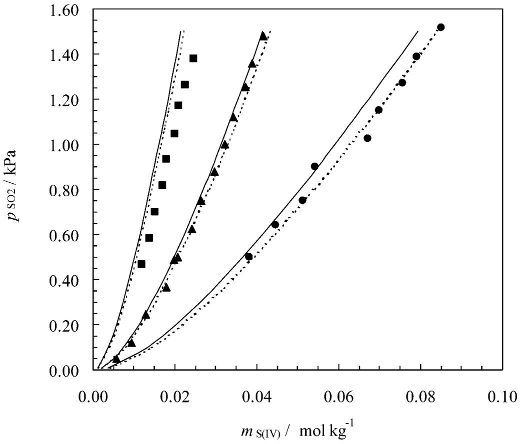

**Figure 3.** Comparison of experimental solubility against model predictions for the $SO_2$ + seawater system: ●, 278.15 K; ▲, 298.15 K; ■, 318.15 K; dotted line, Bromley's model; solid line, Pitzer's model.

values may be assumed as independent of pressure and temperature.

The terms Φ, Φ′, and Ψ take into account interactions between ions of the same sign, which arise only for multielectrolyte solutions. For solubility calculations, the following considerations are usually assumed

$$\Phi_{ij} \approx \Phi_{ij}^{\phi} \approx \theta_{ij} \qquad \Phi_{ij}' \approx 0 \tag{27}$$

where $\theta_{ij}$, arising from short-range forces, is taken as a constant for any particular anion *a, a′* or cation *c, c′* at a given pressure and temperature.

Thus, the Pitzer's ion-interaction model provides an expression for the activity coefficients in multielectrolyte solutions in terms of seven types of empirical parameters: $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, $C_{MX}^{\phi}$, $\theta_{ij}$, $\Psi_{ijk}$, and $\lambda_{ni}$. No data for all those parameters are available in the literature, particularly the $C^{\phi}$ , $\theta$, $\Psi$, and $\lambda$ parameters. Tables 6 and 7 list data found at 298.15 K[19,21−24] for solutes involved in equilibria 6−9. Temperature dependencies are only available for some of those parameters.

Previous calculations have found a relative insensitivity of the calculated activity coefficients to moderate changes in $\beta^{(0)}$ and $\beta^{(1)}$ by temperature. Also Rosenblatt[19] estimated that the only temperature-dependent quantity that changes significantly in the range (273.15 to 323.15) K is $A^{\phi}$, given by eq 17. Thus, in the studied temperature range, no temperature dependency of the interaction parameters has been considered. However, temperature effects should be taken into account to achieve significantly greater accuracy than the present work estimates, particularly at a temperature around 323.15 K or higher.

Model calculations for each temperature were carried out assuming an initial value of ionic strength, $I$, and hydrogen concentration, $m_H$. Then, values of species concentrations and activity coefficients were calculated from the equation system by an iterative procedure with two nested loops. In the inner loop, a new value of $m_H$ was generated from eq 11 until convergence within ±0.1%. In the outer loop, a new value of $I$ was generated from eq 14 until convergence within ±0.1%.

Calculations of $SO_2$ solubility were made at different temperatures using both Bromley and Pitzer activity coefficient equations. Water activity was calculated by eq 21 when Pitzer's equations were used, while it was set equal to unity when Bromley's equations were used. Figure 3 shows the experimental data together with the model predictions. As it can be observed, both Bromley and Pitzer equations lead to similar predictions. Experimental results at 298.15 K are fairly well represented by the models. Results at 318.15 K show more differences between experimental data and theoretical values. Those differences could be attributed to both the large decrease in the gas solubility and the assumptions used for taking into account the temperature effect on the specific interaction parameters.

## Conclusions

The solubility of $SO_2$ in seawater, from mixtures of $SO_2$ + $N_2$, has been studied experimentally in the temperature range between (278.15 and 318.15) K and a $SO_2$ partial pressure range between (0.050 and 1.5) kPa. Low partial pressure range is of interest in flue gas desulfurization by seawater scrubbing, and different temperatures are necessary to simulate variations in the operational conditions of $SO_2$ absorbers. Measurements at 298.15 K with natural and artificial seawater allowed comparing the total absorption capacity of both solutions. Small differences (less than 5%) could be observed between the total absorption capacity of the natural and artificial seawater samples. However, the $SO_2$ solubility in artificial seawater increased within (20−60)% in relation to distilled water, and within (6−30)% in relation to NaCl solutions of similar ionic strength. To establish the effect of temperature on solubility and pH at equilibrium, measurements at 278.15 K and 318.15 K were also carried out with artificial seawater. Correlation equations were derived as a function of the $SO_2$ partial pressure and temperature, and comparisons with literature data were also made. Experimental results allowed testing several thermodynamic models in order to predict the solubility of $SO_2$ in seawater at low partial pressures and different temperatures. Two different models were considered to evaluate activity coefficients of ionic species. Calculations were made at different temperatures using an extended version of the Debye−Hückel theory and the Pitzer ion-interaction model. Both models led to similar predictions and were in good agreement with the experimental results. The reasonable fitting between measured and calculated data show that the selected models can be successfully used to estimate equilibrium data for the absorption of sulfur dioxide in seawater.

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