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Dilute SO_2 Absorption Equilibria in Aqueous HCl and NaCl Solutions at 298.15 K

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The solubility of dilute SO_2 in aqueous HCl and NaCl solutions was determined at 298.15 K as a function of ionic strength up to 3 mol·L^{-1}, in the partial pressure range between (0.075 and 1.8) kPa. Measurements were carried out by a saturation method using a laboratory batch reactor. Equations to correlate the apparent Henry's law constant, H_m, and the apparent first dissociation constant, K_{m1}, were obtained as a function of ionic strength. Comparisons between experimental results and theoretical predictions were also made. A model based on the classical Sechenov equation was tested, and a new value for the SO_2 gas-specific parameter was obtained to calculate H_m. Two different models were considered for calculating the activity coefficients to determine K_{m1}. An extended version of the Debye−Hückel theory described the experimental results for ionic strengths below 0.1 mol·L^{-1}. The Pitzer model was in good agreement with the experimental data in the ionic strength range between (0 and 3) mol·L^{-1}. The close fit between measured and calculated data showed that the selected models can be successfully used for estimating the solubility of SO_2 in salt solutions at low partial pressures.

Introduction

Sulfur dioxide is an important atmospheric contaminant. Its main source is stack gas due to burning of fuels with high sulfur content. SO_2 can be removed either during or immediately after combustion. In the latter case, the flue gas may be washed with an alkaline slurry or solution. Knowledge of the equilibrium data is an indispensable requirement for the design of the absorption and desorption processes. Several methods for flue gas desulfurization have been employed according to whether the reagent will be recycled or not. Seawater washing has been identified as an option among the nonregenerative processes, since it provides a natural alkaline phase. Such a process offers potential advantages for power stations located nearby the coast, since it is of simple design, requires no bulk chemicals, and has low capital and operating costs.[1] Seawater is a complex liquid phase, with NaCl being its main component and with bicarbonate and sulfate species being responsible for seawater alkalinity. The electrolyte composition of the liquid phase plays an important role in the absorption equilibrium, since it determines the nonideal behavior of the solution by means of the activity coefficients. Frequently, experimental measurements on single-electrolyte solutions, for instance NaCl solutions, are used to test methods for the estimation of the activity coefficients. The absorption equilibrium of SO_2 in aqueous NaCl solutions has already been studied at a pressure around 100 kPa,[2] but few literature data are available in the low partial pressure range of SO_2. The low concentration range of SO_2 is of interest in the purification of large amounts of waste gases and in the food industry where SO_2 is used as a preservative.

Thermodynamic constants for the SO_2 absorption equilibria in NaCl solutions can be described as follows:

(1) The gas/liquid equilibrium:

$$SO_2(g) \leftrightarrow SO_2(aq)$$

$$H_m^\circ = \frac{\hat{\phi}_{SO_2} P_{SO_2}}{\gamma_{SO_2} m_{SO_2}} = \frac{\hat{\phi}_{SO_2}}{\gamma_{SO_2}} H_m \tag{1}$$

where H_m° is the Henry's law constant, H_m is the apparent Henry's law constant, $\hat{\phi}_{SO_2}$ represents the fugacity coefficient, γ_{SO_2} represents the activity coefficient, P_{SO_2} represents the partial pressure of SO_2, and m represents the molal concentration. The subscript m refers to molal concentration.

(2) The first dissociation of SO_2(aq):

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

$$K_1 = \frac{\gamma_{H^+}\gamma_{HSO_3^-}}{\gamma_{SO_2} a_{H_2O}} \frac{m_{H^+} m_{HSO_3^-}}{m_{SO_2}} = Q_\gamma K_{m1} \tag{2}$$

where K_1 is the first dissociation constant and K_{m1} is the apparent first dissociation constant. Q_γ represents a term that includes the activity coefficients of the different species involved, and a_{H_2O} is the activity of water.

The influence of the electrolyte concentration on the gas−liquid equilibrium has been studied for many gaseous solutes and salt solutions.[3−9] With increasing salt concentration, gas solubility is nearly always found to decrease ("salting out" effect). At moderately high salt concentration, the solubility of a sparingly soluble gas compared to that one in pure water could be described by the classical Sechenov equation:

$$\log \frac{H_c}{H_c^\circ} = k_c C_s \tag{3}$$

where H_c is the apparent Henry's law constant, C_s is the salt molar concentration, the superscript zero refers to pure

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water, and the subscript c refers to molar concentration. The proportionality constant k_c, the Sechenov molar constant, is specific to the gas and salt and depends partially on temperature. There are several empirical models for the estimation of k_c. Recently, Schumpe,[7] Hermann et al.,[8] and Weisenberger and Schumpe[9] have suggested a model considering individual salting-out effects of the ions,

$$\log\frac{H_c}{H_c^\circ} = \sum_i (h_i + h_G)C_i \qquad (4)$$

Here h_i and h_G are the ion-specific and gas-specific parameters, respectively, and C_i represents molar concentration of the ion i. For a single salt, the relationship between the Sechenov constant and Schumpe parameters is

$$k_c = \sum_i (h_i + h_G)n_i \qquad (5)$$

where n_i is the index of the ion i in the salt formula.

With regard to the activity coefficients, Robinson and Stokes[10] developed a simple thermodynamic model using an extended version of the Debye−Hückel theory, valid for dilute electrolyte solutions. The model equation is given by

$$\log \gamma_i = A\left[\frac{-z_i^2\sqrt{I}}{1 + B\sigma_i\sqrt{I}} + \beta_i I\right] \qquad (6)$$

where I is the ionic strength, A is the constant in the Debye−Hückel equation, B is the Debye−Hückel parameter, z is the charge number, σ is the minimum approach distance, and β is the specific interaction parameter.

More recently, Pitzer et al.[11−17] developed methods to estimate the activity coefficients of solutes in complex concentrated electrolyte solutions. The standard definitions and thermodynamic transformations yield the following equation for the activity coefficients:

$$\ln \gamma_i = f^{\gamma} z_i^2 + 2\sum_j \lambda_{ij} m_j + \frac{z_i^2}{2}\sum_j\sum_k \lambda'_{jk} m_j m_k + 3\sum_j\sum_k \mu_{ijk} m_j m_k \qquad (7)$$

The first term on the right of the equation is an extended form of the Debye−Hückel parameter. The quantity λ_{ij} represents the short-range interaction between solute particles i and j in the presence of the solvent. This binary interaction parameter, or second virial coefficient, does not depend itself on the composition of neutral species, but in the case of ions it is dependent on the ionic strength. It does depend on the particular solute species i and j and on temperature and pressure. The equivalent quantity for triple interactions is μ_{ijk}; in principle, it might be ionic strength dependent, but with a single possible exception[16] there is no evidence of this. On the other hand, λ' is the partial derivative of λ with respect to the ionic strength.

The purpose of the present paper is to test several models used to predict the activity coefficients for the absorption of SO_2 into aqueous solutions at low partial pressures. An experimental study was carried out to evaluate the effect of the electrolyte concentration on the thermodynamic equilibrium involved in the absorption process. The solubility of dilute SO_2 in several electrolyte solutions was determined along with the values of the apparent Henry's law constant and the apparent first dissociation constant. To study independently the effect of the electrolyte concentration on the gas−liquid equilibrium, the dissociation of SO_2(aq), eq 2, was inhibited by using different acid solutions.

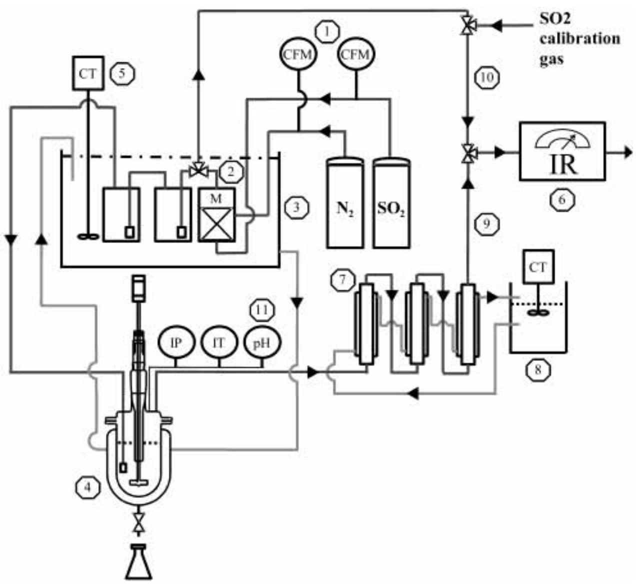


Figure 1. Experimental installation: (1) calibrated mass-flow controllers; (2) mixing unit; (3) thermostatic bath; (4) jacketed vessel; (5) temperature controller agitator; (6) IR SO_2 analyzer; (7) dehumidification unit; (8) cooler box; (9) main gas fluid; (10) additional gas fluid; (11) digital pH meter.

Experimental Section

(a) Materials. The sulfur dioxide and nitrogen used in the present work had purities higher than 99.9 vol % (Air Liquide). Sodium chloride was an analytical grade reagent (Merck) with a purity higher than 99 mass %. Hydrogen chloride, iodine, and sodium thiosulfate solutions were prepared from standard Tritisol ampules (Merck). The water used to prepare each solution was distilled and deionized with a Milli-Q Plus device to 18 MΩ·cm (Millipore).

(b) Experimental Procedure. Experiments were carried out at 298.15 K and 97.6 kPa, using $SO_2 + N_2$ mixtures in several electrolyte solutions in the SO_2 partial pressure range between (0.075 and 1.8) kPa. The electrolyte solutions used were NaCl(aq) (0 to 3) $mol\cdot L^{-1}$, HCl(aq) (0.5 to 1) $mol\cdot L^{-1}$, and HCl + NaCl mixtures (1 to 4) $mol\cdot L^{-1}$ total ionic strength.

The solubility of sulfur dioxide in aqueous solution was determined by a saturation method where the gas was bubbled through the liquid phase. The apparatus used is shown in Figure 1. The aqueous solutions were located in a jacketed vessel, and the temperature inside the solution could be regulated within ±0.1 K by circulating water from a thermostatic bath (Haake). Thermometers with subdivisions of ±0.1 K were used to monitor the bath and solution temperatures. A control valve adjusted the total pressure inside the vessel with ±0.05 kPa accuracy.

$SO_2 + N_2$ mixtures were prepared from pure gases with calibrated mass-flow controllers (Brooks Instruments). The accuracies of the mass-flow controllers were $\pm 10^{-5}$ and $\pm 10^{-3}$ $mol\cdot min^{-1}$ for SO_2 and N_2, respectively. From the total pressure and temperature, the partial pressure of SO_2 was calculated as follows:

$$P_{SO_2} = (P - P_W)\frac{G_{SO_2}}{G_{SO_2} + G_{N_2}} \qquad (8)$$

where P is the total pressure, P_W is the vapor pressure of water at the operation temperature, and G_{SO_2} and G_{N_2} are the molar flow of 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 500 Pa, an infrared SO_2 analyzer (ADC) directly measured the SO_2 molar fraction. The accuracy in the SO_2 partial pressure measurement was ±3 Pa.

The sulfur(IV) concentration was determined, once equilibrium was reached, by adding a known volume of solution from the vessel to a known volume of standard iodine. The excess iodine was back-titrated with standard sodium thiosulfate. The overall uncertainty in the determination of the sulfur(IV) concentration was estimated to be ±1%. Measurements of pH were carried out using a combined electrode (Ingold), located in 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. To determine the concentration of H^+ from the pH measurements, the electrode response was calibrated in the NaCl media using solutions with known concentrations of HCl. For each NaCl medium, an experimental correlation between the electrode response and the H^+ concentration was obtained. The overall uncertainty in the determination of the H^+ concentration was less than ±2%. In the solutions, the SO_2 concentration was calculated from the experimental data of sulfur(IV) and H^+ concentrations by means of the sulfur balance and the electroneutrality condition, as follows:

$$m_{S(IV)} = m_{SO_2} + m_{HSO_3^-}$$
$$m_{HSO_3^-} = m_{H^+}$$
$$m_{SO_2} = m_{S(IV)} - m_{H^+} \qquad (9)$$

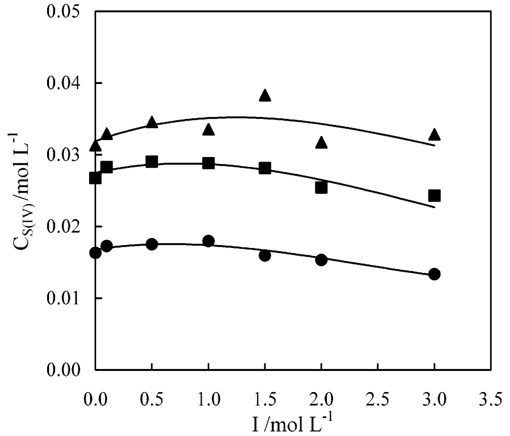
When the dissociation of SO_2(aq) was inhibited, the total sulfur(IV) concentration, $m_{S(IV)}$, equals the SO_2 concentration, m_{SO_2}.

Discussion and Results

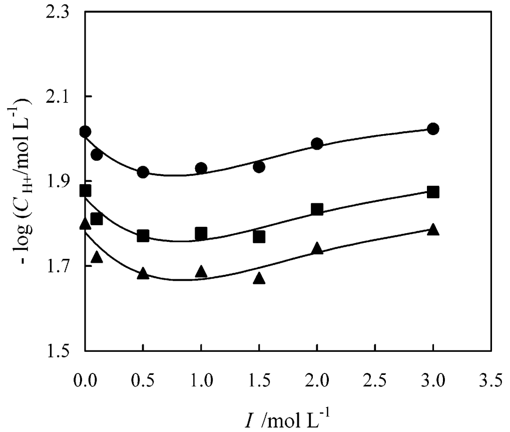
(a) SO_2 Solubility in Aqueous NaCl Solutions. Measurements at 298.15 K allowed the effect of ionic strength on the SO_2 solubility to be evaluated. Figure 2 shows the experimental solubility of SO_2 and H^+ concentration as a function of ionic strength for three SO_2 partial pressures. Values of the apparent Henry's law constant and the apparent first dissociation constant, determined from SO_2 equilibration measurements, are given in Table 1.

Since this study concerns only low pressures, the fugacity coefficient of SO_2 can be set equal to unity. In accordance with eq 1, H_m/H_m° gives the SO_2 activity coefficient, and the superscript zero denotes the value in pure water. The γ_{SO_2} values were correlated through a Sechenov type equation as follows:

$$\log \gamma_{SO_2} = \log \frac{H_m}{H_m^\circ} = 0.0188I/\text{mol·kg}^{-1} \qquad (10)$$



(a) Total solubility



(b) H^+ concentration

Figure 2. Experimental results in NaCl solutions for three SO_2 partial pressures: (▲) 0.5 kPa; (■) 1.0 kPa; (●) 1.5 kPa; (a) total solubility; (b) H^+ concentration.

Table 1. Experimental Values of the Apparent Henry's Law Constant and the Apparent First Dissociation Constant in SO_2 + NaCl Solutions at 298.15 K and P = 97.6 kPa

I		H_m				
mol·L^{-1}	mol·kg^{-1}	kPa·mol^{-1}·kg	r^2 [a]	K_{m1}	r^2 [a]	N[b]
water		82.9	0.999	0.0114	0.986	16
0.1	0.10	82.7	0.997	0.0200	0.991	19
0.5	0.51	86.6	0.998	0.0255	0.996	14
1.0	1.02	85.4	0.994	0.0250	0.984	20
1.5	1.55	91.2	0.982	0.0299	0.980	15
2.0	2.09	94.4	0.987	0.0220	0.983	10
3.0	3.21	91.7	0.999	0.0182	0.994	10

[a] r^2: correlation coefficient. [b] N: number of experimental data.

The value of H_m° (82.9 kPa·kg·mol^{-1}) has been discussed in a previous work.[18] Literature data on the Henry's law constant of sulfur dioxide in water are extensive. The correlations of Edwards et al.[19] and Goldberg and Parker,[20] based on selected data, give values at 298.15 K of 80.8 and 81.3 kPa·kg·mol^{-1}, respectively, which are in good agreement with our experimental result and with the values reported by Rabe and Harris[21] (84.6 kPa·kg·mol^{-1}) and Rumpf and Maurer[22] (85.2 kPa·kg·mol^{-1}). Some differences are observed with other literature data, such as those reported by Renon[23] (88.7 kPa·kg·mol^{-1}), as cited by Hunger et al.,[24] Camacho et al.[25] (74.3 kPa·kg·mol^{-1}), and Millero et al.[2] (89.7 kPa·kg·mol^{-1}). In relation to the Sechenov constant of SO_2 in NaCl(aq), few literature data are available. Chang and Rochelle[26] cited a molar constant of 0.076 L·mol^{-1}, taken from Harned and Owen.[27] Millero et al.[2] measured the solubility of SO_2 in NaCl solutions, giving a molal constant of 0.0246 kg·mol^{-1} at 298.15 K,

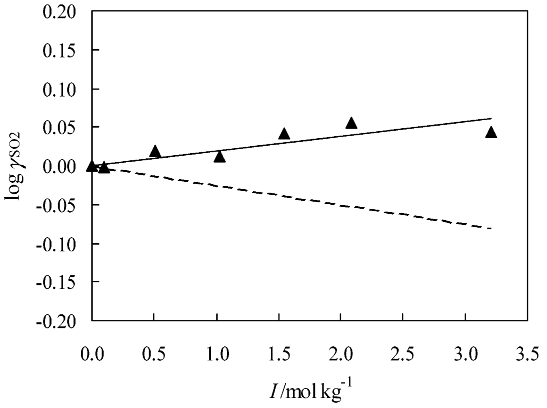


Figure 3. Activity coefficient of SO_2 in NaCl solutions as a function of ionic strength: (▲) experimental; (- - -) Schumpe model.[9]

similar to that obtained in the present work (0.0188 kg·mol^{-1}). The application of the Schumpe model,[9] eq 4, with $h_{Na^+} = 0.1143$ L·mol^{-1}, $h_{Cl^-} = 0.0318$ L·mol^{-1}, and $h_{SO_2} = -0.0817$ L·mol^{-1}, leads to a Sechenov molar constant of -0.0173 L·mol^{-1}, equivalent to a molal constant of -0.0249 kg·mol^{-1}. Figure 3 shows the experimental values of γ_{SO_2} as a function of the ionic strength, together with the values predicted by the Schumpe model. Although the ionic strength effect is small, it can be noted that the experimental results are contrary to the predictions of the model. Since the ion-specific parameters for Na^+ and Cl^- have been widely used in the literature with other gases but not with SO_2, the gas-specific parameter given for SO_2 may not be valid in NaCl solutions. For this reason, some additional experiments were done with acid solutions, to evaluate the gas−liquid equilibrium separately. The results are discussed in section b.

The apparent first dissociation constant of SO_2(aq) was determined from experimental data of H^+ and SO_2 concentrations. The values shown in Table 1 were correlated as follows:[2]

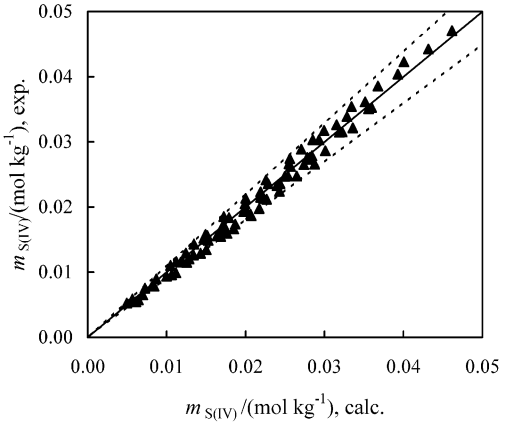
$$\mathrm{p}K_{m1} = 1.94 - 0.74\sqrt{I/\mathrm{mol{\cdot}kg^{-1}}} + 0.35I/\mathrm{mol{\cdot}kg^{-1}} \quad (11)$$

where pK_{m1} is ($-\log K_{m1}$). In this equation, the value 1.94 is the pK_1, correspondent to the thermodynamic constant K_1 at 298.15 K, and the sum of the other terms on the right side corresponds to ($\log Q_\gamma$) defined by eq 2. Literature data on thermodynamic constants for the dissociation of SO_2(aq) in water are extensive, and some of them have been discussed in a previous work.[18] The pK_1 obtained at 298.15 K is in reasonable agreement with the correlations of Edwards et al.[19] and Goldberg and Parker,[20] which give values of 1.89 and 1.87, respectively, and with the data of Millero et al.,[2] who reported the value of 1.86. Some differences are observed with other data, such as those reported by Renon[23] (pK_1 = 1.76), as cited by Hunger et al.[24] and Camacho et al.[25] (pK_1 = 1.73).

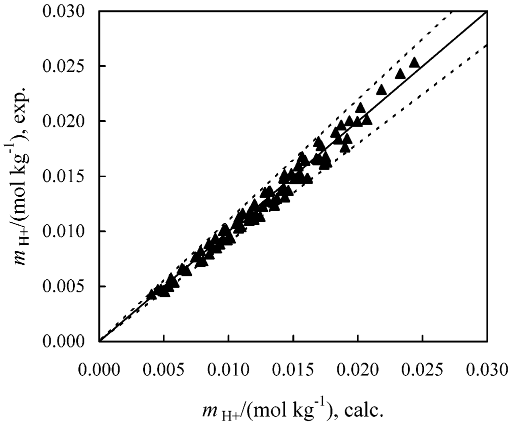
To obtain semiempirical expressions that allow the total solubility of SO_2 and the H^+ concentration to be estimated as a function of the SO_2 partial pressure, eqs 1, 2, and 9 were combined to give

$$m_{S(IV)} = \frac{P_{SO_2}}{H_m} + \sqrt{\frac{K_{m1}}{H_m}P_{SO_2}} \quad (12)$$

$$m_{H^+} = \sqrt{\frac{K_{m1}}{H_m}P_{SO_2}} \quad (13)$$



(a) Total solubility



(b) H^+ concentration

Figure 4. Comparison of experimental and calculated values in NaCl solutions: (▲) experimental; (- - -) (diagonal ±10%) deviation; (a) total solubility; (b) H^+ concentration.

By considering eqs 10 and 11, using the value of the Henry's law constant in pure water, the following equations are derived:

$$m_{S(IV)}/\mathrm{mol{\cdot}kg^{-1}} = 10^{-(4.919+0.0188I/\mathrm{mol{\cdot}kg^{-1}})}P_{SO_2}/\mathrm{Pa} + 10^{-(3.430-0.37\sqrt{I/\mathrm{mol{\cdot}kg^{-1}}}+0.185I/\mathrm{mol{\cdot}kg^{-1}})}\sqrt{P_{SO_2}/\mathrm{Pa}} \quad (14)$$

$$m_{H^+}/\mathrm{mol{\cdot}kg^{-1}} = 10^{-(3.430-0.37\sqrt{I/\mathrm{mol{\cdot}kg^{-1}}}+0.185I/\mathrm{mol{\cdot}kg^{-1}})}\sqrt{P_{SO_2}/\mathrm{Pa}} \quad (15)$$

Figure 4 shows the correlation between the experimental data, for H^+ and total sulfur(IV), and those calculated by eqs 14 and 15. As can be observed, these equations allow the estimation of the SO_2 + NaCl(aq) equilibrium with an overall uncertainty of ±10% in the ranges studied.

(b) SO_2 Solubility in Acid Solutions. Solubility measurements were made at 298.15 K with different acid solutions inhibiting SO_2 dissociation in order to study the effect of the electrolyte concentration on the gas−liquid equilibrium. All the liquid phases used showed that the dissociation of SO_2 was less than 5%. The apparent Henry's law constant and the activity coefficient of SO_2, given in Table 2, were calculated from experimental solubility data. In that table, C_s represents the molar concentration of the electrolyte solution.

A value for the SO_2 gas-specific parameter was obtained by minimizing the following function:

Table 2. Experimental Values of the Apparent Henry's Law Constant for SO$_2$ in Acid Solutions at 298.15 K

liquid phase	C_s / mol·L^{-1}	I / mol·L^{-1}	H_c / kPa·mol^{-1}·L	H_m / kPa·mol^{-1}·kg	r^2	$\log \gamma^c_{SO_2}$
HCl	0.5	0.5	75.9	75.1	0.999	−0.0394
	1.0	1.0	74.8	73.2	0.999	−0.0457
HCl + NaCl	0.5 + 0.5	1.0	78.5	76.2	0.999	−0.0247
	0.5 + 1.5	2.0	80.9	76.8	0.999	−0.0117
	0.5 + 3.5	4.0	85.7	77.7	0.999	0.0134

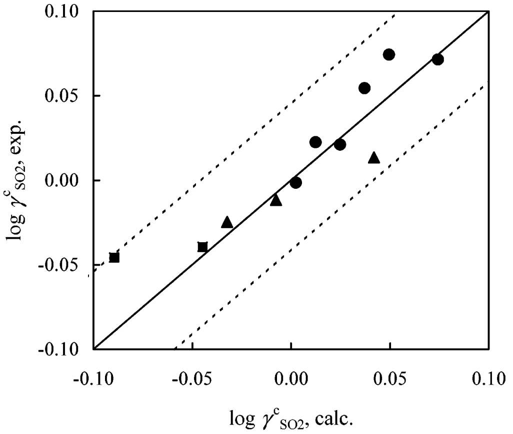


Figure 5. Comparison of experimental and calculated values of $\log \gamma^c_{SO_2}$: (▲) HCl + NaCl; (■) HCl; (●) NaCl; (- - -) ($\gamma^c_{SO_2}$ ±10%) deviation.

$$[\log(\gamma^c_{SO_2})_{exp} - \log(\gamma^c_{SO_2})_{calc}]^2 \quad (16)$$

In this function, $\log(\gamma^c_{SO_2})_{calc}$ is obtained by means of the Schumpe model, eq 4, assuming that the fugacity coefficient for SO$_2$, $\hat{\phi}_{SO_2}$, is equal to unity; then $\gamma^c_{SO_2}$ is given by H_c/H°_c. The ion-specific parameters for Cl$^-$, Na$^+$, and H$^+$ were fitted to those reported in the literature[9] ($h_{Cl^-} = 0.0318$ m^3·kmol^{-1}, $h_{Na^+} = 0.1143$ m^3·kmol^{-1}, $h_{H^+} = 0$ m^3·kmol^{-1}), and then h_{SO_2} was varied. The optimized parameter is

$$h_{SO_2} = -0.0607 \text{ m}^3\text{·kmol}^{-1}$$

This value is different from that reported in the literature[9] ($h_{SO_2} = -0.0817$ m^3·kmol^{-1}). Figure 5 shows the correlation between the experimental and calculated values of $\log(\gamma^c_{SO_2})$, using the new value obtained for h_{SO_2}. As can be observed, this new value allows us to represent the experimental data of $\gamma^c_{SO_2}$ within a deviation of ±10%. The regression coefficient and the standard deviation were 0.835 and 0.012, respectively.

(c) Thermodynamic Models for the SO$_2$(aq) Dissociation Equilibrium in NaCl Solutions. For the evaluation of the activity coefficients of solutes and the water activity, two different models were considered. The first one used a water activity equal to unity and eq 6 for the activity coefficients of solutes. The model parameters are shown in Table 3.

The second one was the Pitzer model,[11−17] where the activity coefficients for H$^+$ and HSO$_3^-$ in NaCl solutions are given by

$$\ln \gamma_H = z_H^2 f^\gamma + 2m_{Cl}(\lambda_{HCl} + EC_{HCl}) + 2m_{HSO_3}\lambda_{HHSO_3} + m_{Na}m_{Cl}(\lambda'_{NaCl} + C_{NaCl}) + m_H m_{Cl}(\lambda'_{HCl} + C_{HCl}) + m_{Na}m_{HSO_3}(\lambda'_{NaHSO_3} + C_{NaHSO_3}) + m_H m_{HSO_3}\lambda'_{HHSO_3} + m_{Na}(2\theta_{HNa} + m_{Cl}\Psi_{HNaCl}) \quad (17)$$

Table 3. Parameters in the Robinson and Stokes Equation, Eq 6

A/kg$^{1/2}$·mol$^{-1/2}$	0.5085
10^{-10} B/kg$^{1/2}$·mol$^{-1/2}$·m^{-1}	0.3281
$10^{10}\sigma_{H^+}$/m	9.0
$10^{10}\sigma_{HSO_3^-}$/m	4.0
β_{H^+}/kg·mol^{-1}	0.4
$\beta_{HSO_3^-}$/kg·mol^{-1}	0.0

$$\ln \gamma_{HSO_3} = z_{HSO_3}^2 f^\gamma + 2m_{Na}(\lambda_{NaHSO_3} + EC_{NaHSO_3}) + 2m_H\lambda_{HHSO_3} + m_{Na}m_{Cl}(\lambda'_{NaCl} + C_{NaCl}) + m_H m_{Cl}(\lambda'_{HCl} + C_{HCl}) + m_{Na}m_{HSO_3}(\lambda'_{NaHSO_3} + C_{NaHSO_3}) + m_H m_{HSO_3}\lambda'_{HHSO_3} \quad (18)$$

For systems containing a single salt MX, for example NaCl, the model parameters are given by

$$f^\gamma = -A^\phi\left[\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + \left(\frac{2}{1.2}\right)\ln(1 + 1.2\sqrt{I})\right] \quad (19)$$

$$\lambda_{MX} = \beta^{(0)}_{MX} + \left(\frac{2\beta^{(1)}_{MX}}{4I}\right)[1 - (1 + 2\sqrt{I})\exp(-2\sqrt{I})] \quad (20)$$

$$\lambda = \frac{\beta^{(1)}_{MX}}{2I^2}[-1 + (1 + 2\sqrt{I} + 2I)\exp(-2\sqrt{I})] \quad (21)$$

$$C_{MX} = \frac{C^{(\phi)}_{MX}}{2|z_M z_X|^{1/2}} \quad (22)$$

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

where A^ϕ represents the Debye−Hückel parameter for the osmotic coefficient (0.392 kg$^{1/2}$·mol$^{-1/2}$). The parameters $\lambda_{i,j}$, $\lambda'_{i,j}$, and $C^{(\phi)}_{MX}$ describe the thermodynamic properties of a pure electrolyte; λ and λ' represent measurable combinations of second virial coefficients, which arise from binary interactions given by $\beta^{(0)}_{MX}$ and $\beta^{(1)}_{MX}$, while $C^{(\phi)}_{MX}$ represents third virial coefficients and considers tertiary interactions of the type M−M−X and M−X−X.

The additional parameter θ_{MN}, introduced for electrolyte mixtures, represents the difference between the second virial coefficients for ions M and N of the same sign and interactions between the average second virial coefficients M−M and N−N. Because second virial coefficients are determined mainly by short-range interactions and ions of equal sign are seldom close together, θ_{MN} is expected to be small. Pitzer and Kim[15] include further mixing parameters ψ arising from differences in third virial coefficients, but these terms are smaller than θ and are negligible for single electrolytes.

The parameters $\beta^{(0)}_{MX}$ and $\beta^{(1)}_{MX}$ and $C^{(\phi)}_{MX}$ were evaluated for a large number of electrolytes by Pitzer and Mayorga[14] and Pitzer and Kim,[15] but few activity coefficient data

Table 4. Single-Electrolyte Solutions and Mixing Parameters at 298.15 K

electrolyte	$\beta^{(0)}_{MX}$	$\beta^{(1)}_{MX}$	$C^{(\phi)}_{MX}$	ref
HCl	0.1775	0.2945	0.0008	17
NaCl	0.0765	0.2644	0.00127	17
$HHSO_3$	0.15	0.40		24
$NaHSO_3$	0.0249	0.2455	0.0004	28
$\theta_{HNa} = 0.036$; $\psi_{HNaCl} = -0.004$				17

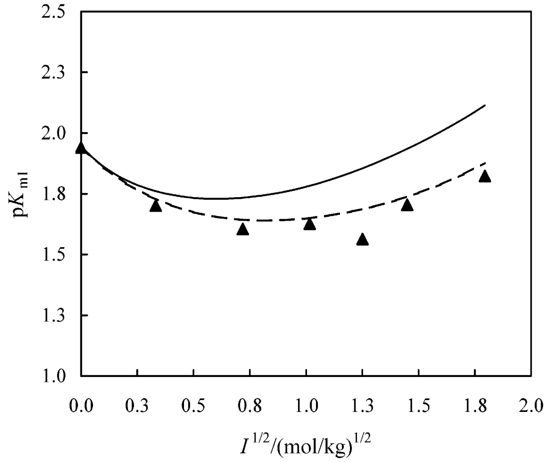


Figure 6. Comparison of experimental and calculated values of pK_{m1} for the dissociation of SO_2(aq) in NaCl solutions: (▲) experimental; (- - -) Pitzer model (with Rosenblatt's parameters); (—) Robinson and Stokes equation.

are available for SO_2 and $NaHSO_3$ solutions. Values of $\beta^{(0)}_{NaHSO_3}$, $\beta^{(1)}_{NaHSO_3}$, and $C^{(\phi)}_{NaHSO_3}$ were estimated by Rosenblatt,[28] from the effect of the ions on the structure of liquid water. Hungers et al.[24] modeled the thermodynamic equilibrium of dilute SO_2 absorption into Na_2SO_4 or H_2SO_4 electrolyte solutions and estimated the values of $\beta^{(0)}_{NaHSO_3}$ and $\beta^{(1)}_{NaHSO_3}$, in accordance with Rosenblatt's theories. In addition, Millero et al.[2] determined the values of $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, and $C^{(\phi)}_{MX}$ for $NaHSO_3$ and Na_2SO_3 from experimental measurements of the SO_2 solubility in NaCl solutions. The whole set of parameter values used in this work is listed in Table 4.

The water activity was calculated by the general Pitzer procedure compiled by Rumpf and Maurer:[29]

$$\begin{aligned}\ln a_{H_2O} = M_{H_2O}\Big\{ & 2A^{\phi}\frac{I^{1.5}}{1 + 1.2\sqrt{I}} - \\ & 2[m_H m_{Cl}(\beta^{(0)}_{HCl} + \beta^{(1)}_{HCl}\exp(-2\sqrt{I})) + \\ & m_H m_{HSO_3}(\beta^{(0)}_{HHSO_3} + \beta^{(1)}_{HHSO_3}\exp(-2\sqrt{I})) + \\ & m_{Na} m_{Cl}(\beta^{(0)}_{NaCl} + \beta^{(1)}_{NaCl}\exp(-2\sqrt{I})) + \\ & m_{Na} m_{HSO_3}(\beta^{(0)}_{NaHSO_3} + \beta^{(1)}_{NaHSO_3}\exp(-2\sqrt{I}))] - \\ & (m_H + m_{Na} + m_{Cl} + m_{HSO_3})\Big\}\end{aligned} \qquad (24)$$

Figure 6 shows a comparison between the experimental pK_{m1} data obtained in this work and the corresponding values calculated using the above thermodynamic models. The Robinson−Stokes equation is in good agreement with experimental data for ionic strengths below 0.1 mol·L^{-1}, but a deviation is observed at higher ionic strengths. By contrast, the Pitzer model is satisfactory in the studied range of ionic strength when Rosenblatt's parameters for Na−HSO_3 interactions are used.

Conclusions

The equilibrium distribution of SO_2 between a gaseous phase and several electrolyte solutions was studied experimentally at 298.15 K and 97.6 kPa in a partial pressure range between (0.075 and 1.8) kPa. Equations were derived to correlate the apparent Henry's law constant, H_m, and the apparent first dissociation constant, K_{m1}, as a function of the ionic strength, which ranged between (0 and 3) mol·L^{-1}. Comparisons between experimental results and theoretical predictions were also made. With regard to H_m, the Schumpe model,[7−9] based on the classical Sechenov equation, was used and a new value for the SO_2 gas-specific parameter, h_{SO_2}, was obtained. With regard to K_{m1}, two different models were tested to calculate the activity coefficients. The simplest one, an extended version of the Debye−Hückel theory valid for dilute electrolyte solutions, described the experimental results for ionic strengths below 0.1 mol·L^{-1}. The second one, a Pitzer model, was in good agreement with experimental data in the ionic strength range between (0 and 3) mol·L^{-1}. In this case, Rosenblatt's parameters[28] were used to characterize Na−HSO_3 interactions. The close agreement between the measured and calculated data showed that the selected models could successfully be used to estimate the solubility of dilute SO_2 in HCl and NaCl solutions.

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