for heptane the value is about 5.9 MPa/K. 2,2,4-Trimethylpentane shows a significantly higher value (6.5 MPa/K), whereas methylcyclopentane is close to the heptane value. Evidently, high-pressure phase equilibria are more sensitive to differences in molecular structure than equilibria at ambient pressure.

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Registry No. Methanol, 67-56-1; 2,2,4-trimethylpentane, 540-84-1; methylcyclopentane, 96-37-7.

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Thermodynamic Equilibrium of Diluted SO_2 Absorption into Na_2SO_4 or H_2SO_4 Electrolyte Solutions

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An investigation of the thermodynamics of SO_2 absorption into aqueous sulfate or sulfuric acid solutions is reported. The study has been conducted on SO_2 scrubbing under industrial practice and its possible further oxidation into sulfate compounds. Low-cost electrolytes—sodium sulfate or sulfuric acid—have been considered below 2 M, and the flue-gas partial pressure was varied between 10^{-4} and 0.1 atm. Temperatures were fixed at 25 and 50 °C. Available data relative to SO_2 solubility in the selected electrolytes were surveyed. The results, obtained by the theoretical approach, have been expressed in the form of the pH evolution vs the total amount of tetravalent sulfur, present either in molecular or ionized form, which still has to be converted through a further process, i.e. electrochemical or chemical. The performance of the various models proposed for the estimation of activity coefficients is discussed in this paper; for the parameter ranges investigated here, most calculations could be carried out with a sufficient accuracy with the help of the "macroscopic" relations suggested by Meissner or Bromley. Experimental saturation of electrolyte solution with diluted SO_2 could validate the models used.

Introduction

SO_2 absorption is of major interest for solving pollution problems arising predominantly in industrial areas and represents therefore an important domain of technological interest. Sulfur dioxide can be scrubbed, for example, into molten salts at fairly high temperature or dissolved into various kinds of electrolytes. Among the various existing processes of mentionable relevance in the literature are some which involve a further treatment of dissolved sulfur dioxide through chemical oxidation (see for instance the papers of Goto and Smith (*1*) or Berrutti et al. (*2*)) or via an electrooxidation process (*3*, *4*). This oxidation of the dissolved sulfur dioxide yields sulfate ions, which, depending on the nature of the process, can lead either to dilute or highly concentrated sulfuric acid. In order to reduce the number of species present in the saturated electrolyte, one can make use of sulfate compounds, on one hand, as an absorption medium and, on the other hand, as a supporting electrolyte. Therefore, sodium sulfate and sulfuric acid can be selected for scrubbing media. Moreover, the moderate cost of such a supporting electrolyte is an additional criterion for the feasibility of an industrial scale process for flue-gas desulfurization.

The present work concerns thermodynamic aspects of the absorption of SO_2-containing flue gas produced by industrial operations. The overall pressure is close to 1 atm, and the simulated pollutant mole fraction is varied from low concentrations up to concentrations of several percent. For the sake of the design and mounting of an oxidizing scrubber installation, the maximal amount of pollutant to be converted can be attained through the thermodynamics of the system SO_2/electrolyte. SO_2 is a fairly strong acid and when dissolved in aqueous medium, can dissociate into HSO_3^- and SO_3^{2-}. The extent of both dissociations is a function of the pH of the electrolyte. Thus, the further treatment of the dissolved flue gas will largely depend on the overall amount of sulfur dioxide already absorbed in the liquid phase, present either in molecular or ionized form. This study has been conducted to render available a data source useful in the removal of sulfur dioxide through a chemical or electrochemical operation; it allows the prediction of the chemical composition of sulfate solutions saturated with sulfur dioxide under various operating conditions.

In a general manner, dissolution of the considered flue gas into sulfate electrolytes is accompanied by the partial dissociations of both sulfur dioxide and the supporting electrolyte. The saturated electrolyte containing a numerous amount of important chemical species involves a fairly complex thermodynamical approach, differing significantly from the more pure and academic manner taken into consideration up to now. The thermodynamics of the systems $SO_2/H_2O/H_2SO_4$ and $SO_2/H_2O/Na_2SO_4$ does not seem to have been studied previously. Experimental data of SO_2 solubility in various sulfate electrolytes (*5*) or theoretical work for the system SO_2/H_2O (*6*, *7*) exists in relevant literature publications for which realistic models for

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the Gibbs excess free energy and activity coefficients have been suggested and tested. Their contributions for modeling of electrolyte solutions are generally developed for the simplified problem involving a reduced number of dissolved species; besides, the examples chosen are often rather far from industrial practice of gas absorption. Furthermore, the use of such sophisticated models is very often hindered additionally by the nonavailability of physical parameters of less classical chemical compounds; in these cases the required numerical values can often be estimated with the help of "empirical" rules such as the ones proposed, e.g., by Rosenblatt (*8*) for the case of sulfite-sulfate electrolyte.

For the reasons stated above, a theoretical approach was developed by using rather simple models for the expressions for excess enthalpy and activity coefficients: some parameters, being of minor significance such as third-order virial coefficients or ternary parameters for triple-body interactions, have been neglected for the calculations. The relevant data to SO_2 solubility and to the various equilibrium constants are surveyed and presented here. The electrolytes considered were aqueous solutions of sodium sulfate or sulfuric acid of concentrations below 2 M. The electrolyte chemical compositions under thermodynamical equilibrium have been determined with the help of two models for activity coefficients and the results compared for various conditions of temperature, ionic strength, and SO_2 partial pressure. In addition, the assumptions done and the models used were validated by experimental trials of sulfur dioxide absorption and the dosage of the saturated electrolyte solutions.

SO_2 Solubility

The gas solubility in an electrolyte can be expressed by Henry's constant, *H*, linking molality of the molecular solute species with its corresponding partial pressure. Henry's constant largely depends on temperature and is weakly altered by pressure. The following correlation proposed by Krichevsky and Kasarnovsky (*9*), incorporating the reference value $H°$, was used in this study:

$$y_{SO_2} f_{SO_2} P = m_{SO_2} g_{SO_2} H°_{SO_2} \exp\left[\frac{v_{b,SO_2}(P - P_w^s)}{RT}\right] \quad (1)$$

where y_{SO_2} is the vapor mole fraction of SO_2, f_{SO_2} is its fugacity coefficient, and *m* denotes the molality of the dissolved species. In the present case, the total gas pressure is close to 1 bar and the temperature range is that appliable for scrubbing processes of flue gas into aqueous media; the exponential correcting factor differs from unity by less than 1%. SO_2 absorption into pure water has been extensively studied, and various relations between Henry's constant and temperature have been proposed (*6*, *7*). Table I gives a brief survey.

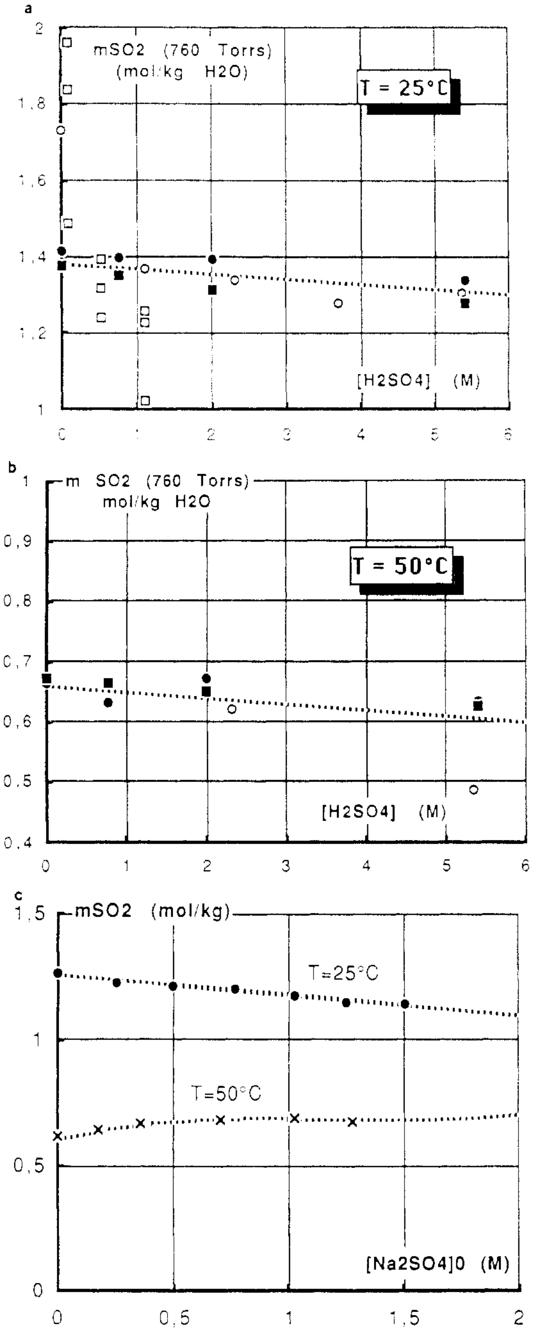

Figure 1. Solubility of SO_2 in aqueous solution of Na_2SO_4 at 25 (a) and 50 °C (b): (···) suggested numerical law; (●) Kuznecov, 760 Torr; (○) Millett, 45 Torr; (■) Kuznecov, 45 Torr; (□) Johnstone and Leppla, below 10 Torr. (c) Solubility of SO_2 in aqueous solution of H_2SO_4 at 25 and 50 °C: (···) suggested numerical law; (●, ×) data reported in ref 5.

SO_2 solubility was measured in various sulfate mediums, and most of the data are summarized in Gmelin's handbook (*10*) or in Landolt-Börnstein tables (*5*). The absorption of sulfur dioxide in diluted sulfuric acid was investigated by Kuznecov (*11*), Millett (*12*), and Johnstone and Leppla (*13*); data relevant to sodium sulfate solution were provided by Fox (*14*) and Hudson (*15*). Most of the available data are expressed in the form of the volume of gas-phase SO_2 dissolved per mass unit of electrolyte; in addition most results concern absorption of weakly diluted flue-gas mixtures. For each supporting electrolyte, all data have been treated to be representative of pure SO_2 scrubbing under the assumption that the molality of molecular sulfur dioxide, m_{SO_2}, was a linear function of the SO_2 partial pressure considered: conclusions reported in Gmelin's book allow us use of such an assumption between 0 and 1 atm. In this report the values obtained have been expressed as the variation of m_{SO_2} versus supporting electrolyte concentration; molality values could be deduced from concentration values by means of conversion tables listed in the *Handbook of Chemistry and Physics*.

Literature data were summarized for two temperature values: 25 and 50 °C. The numerous experimental values for a sulfuric medium could be plotted in a satisfactory manner (Figure 1) as Henry's law seems to be valid for all flue-gas pressures below 1 bar; nevertheless, data relative to diluted sulfur dioxide are fairly widespread, and the observed dispersion likely stems from experimetnal uncertainties involved by diluted gas assays of weak SO_2 concentrations. For both temperatures, m_{SO_2} slightly decreases with the rise in concentration of sulfuric acid introduced in the liquid phase. By contrast, the variation of SO_2 molality with sodium sulfate concentration depends largely on

Table I. SO_2 Solubility in Selected Electrolytes

condition	expression	ref
pure water	$H^\circ = \exp[-5578.8/T - 8.7612 \ln T + 68.418]$	7
	$H^\circ = \exp[-5160.4/T - 7.61 \ln T + 60.538]$	28
25 °C, Na_2SO_4	$m_{SO_2} = [1 - 0.065[Na_2SO_4]_0]/0.80$	present work
25 °C, H_2SO_4	$m_{SO_2} = [1 - 0.01[H_2SO_4]_0]/0.725$	present work
25 °C	$H^\circ = 0.808\,16$	7
	$H^\circ = 0.872\,17$	28
50 °C, Na_2SO_4	$m_{SO_2} = [1 + 0.38[Na_2SO_4]_0 - 0.25[Na_2SO_4]_0^2 + 0.10[Na_2SO_4]_0^3]/1.653$	present work
50 °C, H_2SO_4	$m_{SO_2} = [1 - 0.015[H_2SO_4]_0]/1.515$	present work
50 °C	$H^\circ = 1.697\,41$	7
	$H^\circ = 1.817\,53$	28

temperature: larger decreases are observed below 20 °C, and the saturation molality remains next to constant as the temperature exceeds 40 °C (*5*). Table I reports the numerical laws deduced from literature data. Under the assumptions that both the activity coefficient and the fugacity coefficient are equal to unity, it can be expected that limiting values for the supporting electrolyte at zero concentration corresponds to the inverse of Henry's constant: the accordance holds firm for sodium sulfate concentration with a deviation of 5%, but a less satisfactory consistency between the various values is observed for the case of sulfuric acid. The observed deviation may be caused by the assumption of ideal behavior of the gas and dissolved sulfur dioxide.

Ion Equilibria in Solution

The dissociations of dissolved sulfur dioxide in aqueous solutions yield ionic species according to the following reactions:

$$SO_2 + H_2O \leftrightarrow H^+ + HSO_3^- \quad (2)$$

$$HSO_3^- \leftrightarrow H^+ + SO_3^{2-} \quad (3)$$

Reaction 2 corresponds to the hydrolysis of absorbed SO_2. The forward rate constant for the reaction has been measured as 3.4×10^6 s^{-1} by Eigen (*16*), and the reaction can be regarded as instantaneous. H^+ appearing in relations 2 and 3 can be the protonated species resulting from water dissociation: in fairly concentrated acidic medium, H^+ only exists under the form H_3O^+ and two H_2O molecules are required for each dissociation.

Sulfuric acid is a very strong acid and generates bisulfate and sulfate ions:

$$H_2SO_4 + H_2O \leftrightarrow H_3O^+ + HSO_4^- \quad (4)$$

$$HSO_4^- + H_2O \leftrightarrow H_3O^+ + SO_4^{2-} \quad (5)$$

The first dissociation of H_2SO_4 is generally treated as being complete; however, the molecular form exists to a significant extent above 2 M, and, at high concentrations, the acid may be said to be the solvent and the water the solute. The second dissociation, the decomposition of bisulfate, prevails only in very low acid concentrations. The concentrations of the various sulfate species were measured by Raman spectroscopy (*17*), whose experimental results could provide estimates for the amount of the molecular form in sulfuric media. Their experimental results could be expressed through the following relationship:

$$[H_2SO_4] = 0.046[H_2SO_4]_0^{1.41} \quad (6)$$

where $[H_2SO_4]_0$ denotes the concentration of sulfuric acid introduced. Sodium sulfate is totally dissociated into Na^+ and $NaSO_4^-$. Although the $NaSO_4^-$ ion is ignored for many thermodynamical calculations, its presence has been proved by several studies, as early as 1930 (*18*). Its partial dissociation is written as

$$NaSO_4^- \leftrightarrow Na^+ + SO_4^{2-} \quad (7)$$

whereby the sulfate ions can be protonated, according to eq 5, leading to bisulfate ions. The values of the equilibrium constants can be obtained from the difference of free formation enthalpy and formation entropy, as often provided by literature data. Table II reports the selected expressions for the variation of *K* with the electrolyte temperature. The chosen correlation concerning sulfuric acid second dissociation proposed by Pitzer (*19*) fits very well with the data from NBS Tables, $K_{HSO_4} = 0.010\,144$ at 25 °C. Similarly, the selected relation for $NaSO_4^-$ dissociation stems from experimental measurements of cell potential and correctly validates the constant value at 25 °C proposed by both NBS Tables and Russian thermodynamic data compilations equal to 0.185 86 and 0.198 51, respectively (*20*).

Table II. Selected Expressions for Equilibrium Constants (*K*)

equilibrium	constant expression (mol, kg)	ref
$H_2O/H^+, OH^-$	$\exp[-13445.9/T - 22.443 \ln (T) + 140.932]$	28
SO_2/HSO_3^-	$\exp[-3768/T - 20 \ln (T) + 122.53]$	28
HSO_3^-/SO_3^{2-}	$\exp[1333.4/T - 21.274]$	28
HSO_4^-/SO_4^{2-}	$\exp[2825.2/T - 14.0321]$	19
$NaSO_4^-/SO_4^{2-}$	$\exp[1329.2/T - 6.0794]$	30

The orders of magnitude of the equilibria and Henry's constants make it possible to deduce that the absorption of SO_2 into a next to neutral solution will lead to a solution possessing acidic properties. The OH^- and SO_3^{2-} can thus be neglected for further calculations with regard to both electrolyte solutions.

Assumptions and Equations of the Model

The model described has been developed for a reference temperature of 25 °C; the theoretical investigation of two-phase thermodynamics at other temperatures is a simple extension of the method suggested, taking into account the changes of solubility and equilibrium constants as well as the temperature-dependence law for activity coefficients.

Calculations were performed on the basis of the following assumptions.

(i) The partial pressure of SO_2 is constant and fixed to an arbitrary value. This assumption coresponds to an isobaric absorption device provided with the gas inlet and outlet pressure at 1 atm. The kinetics of absorption is disregarded, and the liquid phase is saturated with tetravalent sulfur species.

(ii) SO_2 partial pressure was varied from 10^{-4} atm up to 0.1 atm.

(iii) Diluted electrolytes only were investigated. Sodium sulfate concentration could be a priori varied from 0 M up to its saturation concentration, i.e. 1.957 M at 25 °C under the form $Na_2SO_4 \cdot 10H_2O$ (*21*); however, the concentration range in this study will be limited to 0–1 M, although the concentration should exceed 0.1 M in a technical process in order to ensure a sufficient electrical conductivity for a further electrochemical SO_2 oxidation. With regards to sulfuric acid, its concentration was maintained below 2 M (17% w/w). The moderate ranges investigated correspond to a low-cost electrolyte for which a simplified model for calculation of activity coefficients might be successfully used. In addition, the possible extension of H_2SO_4 concentration range will be discussed.

(iv) Although the water molecule is involved through several hydrolysis reactions, its consumption will be neglected in the mass balances.

(v) The extent of the first-dissociation H_2SO_4 cannot be calculated in an accurate manner, since it is known that when passing from dilute sulfuric acid solutions to concentrated ones, the ionic composition changes substantially. The concentration of SO_4^{2-} ions becomes negligible, the HSO_4^- ions dominate the solution, hydrogen ions solvated by sulfuric acid ($H_3SO_4^+$) appear, the activity of hydrogen ions grows sharply, and the activity of water decreases. Additionally SO_2 absorption into aqueous sulfuric medium tends to increase its pH to a moderate extent and could thereafter involve a certain decrease of molecular H_2SO_4 concentration: for the present case, $[H_2SO_4]$ should lay between 0 and the value deduced from relation 6. Two limiting scenarios were therefore considered: molecular sulfuric acid is neglected in the calculations (the assumption is so much more correct when the amount of acid introduced is weak); the concentration of molecular sulfuric acid is estimated regardless of the influence of dissolved sulfur dioxide by relation 6. It can be observed that (6) yields a maximal molecular concentration of 0.12 for $[H_2SO_4]_0 = 2$ M, and therefore both scenarios are expected to provide comparable results.

(vi) The amounts of dissolved sulfur dioxide, expressed in the form of m_{SO_2} were estimated as functions of flue-gas partial pressure and the initial composition of the electrolyte, with the help of the relations reported in Table I.

The following species were considered: in the gas phase, H_2O, SO_2, and inert gas; in the liquid phase, H_2O, SO_2, H^+ or H_3O^+, Na^+, HSO_3^-, HSO_4^-, SO_4^{2-}, and eventually H_2SO_4 or $NaSO_4^-$. As explained above, m_{SO_2} and $m_{H_2SO_4}$ are given values taken from simulated operating conditions. The concentrations of ionic species are correlated with the following relations: electroneutrality equation; mass balances for sulfate compounds in the case of a sulfuric medium and for both sodium and sulfate species for the absorption into Na_2SO_4 electrolyte; expressions for the constants of equilibria 2 and 5 for the example of H_2SO_4 electrolyte and equilibria 2, 5, and 7 for sodium sulfate solutions:

$$K_{SO_2} = \frac{\gamma_{HSO_3^-} m_{HSO_3^-} \gamma_{H^+} m_{H^+}}{\gamma_{SO_2} m_{SO_2} a_{H_2O}} \quad \text{or} \quad \frac{\gamma_{HSO_3^-} m_{HSO_3^-} \gamma_{H_3O^+} m_{H_3O^+}}{\gamma_{SO_2} m_{SO_2} a_{H_2O}^2} \tag{8}$$

$$K_{HSO_4^-} = \frac{\gamma_{SO_4^{2-}} m_{SO_4^{2-}} \gamma_{H^+} m_{H^+}}{\gamma_{HSO_4^-} m_{HSO_4^-} a_{H_2O}} \quad \text{or} \quad \frac{\gamma_{SO_4^{2-}} m_{SO_4^{2-}} \gamma_{H_3O^+} m_{H_3O^+}}{\gamma_{HSO_4^-} m_{HSO_4^-} a_{H_2O}^2} \tag{9}$$

$$K_{NaSO_4^-} = \frac{\gamma_{SO_4^{2-}} m_{SO_4^{2-}} \gamma_{Na^+} m_{Na^+}}{\gamma_{NaSO_4^-} m_{NaSO_4^-}} \tag{10}$$

All equations are functions of molalities of the various chemical species, and the activity coefficients involved are calculated through two different models, which will be described later. Concentrations of supporting electrolyte had to be converted into molalities with the following relationship:

$$m_i = \frac{C_i}{\rho - \sum C_j M_{0j}} \tag{11}$$

where the subscripts i and j are relative to the various compounds, differing from water in the studied system. In the present case a possible change of the total specific weight of the solution arising from the dissolved sulfur dioxide, either in molecular or ionized form, has been neglected and conversions have been done on the basis of solutions of sodium sulfate or sulfuric acid; values of specific weight as a function of the supporting electrolyte amount introduced were provided from literature data.

The calculation procedure relies upon an iterative method: postulated values for the various species molalities provide preliminary estimates of activity coefficients; these estimates can lead to a new set of values for the molalities with the help of equations involving electroneutrality, mass balances, and equilibrium constants, and a substitution technique made it possible to reduce the dimension of the nonlinear system. Obtained values for molalities yielded new approximations of the activity coefficients. Calculations were followed through until a definite desired precision was attained.

Fugacity and Activity Coefficients

The fugacity coefficient for the gas-phase SO_2 was estimated from the results of Nakamura et al. (*22*). This coefficient depends on SO_2 partial pressure and on several parameters; the values of which are given by Nakamura. Preliminary calculations show that the fugacity equals unity ±1%, whatever the operating conditions in the ranges of pressure and concentration investigated.

(1) Approximated Relation for Activity Coefficients. With regard to activity coefficients, most calculations have been done with the help of "simple" methods suggested either by Meissner (*23–26*) or by Bromley (*27*). According to their theory, a reduced activity coefficient, Γ, is related to the mean molal activity coefficient of a strong electrolyte as follows:

$$\Gamma = \gamma_{\pm}^{1/z_+z_-} \tag{12}$$

Both theories proposed rely upon an extended Debye and Hückel law for the calculations of activity coefficients, which represents reality in a fairly wide range of ionic strength with the help of one unique parameter, B or q, depending on the nature of the salt. The resulting expressions for the reduced activity coefficient are reported in Appendix 1. For the present study, we assumed that the expressions for the activity coefficients of all ionic species were relations derived from the reduced coefficient calculated on the basis of a pure Na_2SO_4 (or H_2SO_4) solution and taking into account the ion charge z_i and the overall ionic strength I:

$$\log \gamma_i = z_i^2 \log \Gamma \tag{13}$$

These models generally provide good results for strong electrolytes of ionic strengths up to 6 m, but their performance can be affected to a certain degree by the nature of the considered salt (*20*) and to a greater part by its dissociation; in particular, it was found that sulfate species cannot be investigated totally in a satisfactory manner through any of the proposed models (i.e. lack of additional parameters introduced in an additional version of Bromley's equation to compensate for strong ion association of unsymmetrical 1–2 salts). Activity coefficients in sodium sulfate medium were studied with Meissner's method for which $q = 0.19$ at 25 °C. By contrast, sulfuric acid does not obey their fitting (*26*), and the model proposed by Bromley was thereafter preferred: B parameter was fixed to 0.0606 at 25 °C.

Although the water activity could be estimated through Meissner's results, the water activity and the activity coefficients for SO_2 and H_2SO_4 were postulated to be equal to unity for simplification reasons.

(2) Pitzer's Model Modified by Beutler and Renon (6, 28). The overall formalism used for further application was introduced by Beutier and Renon and has been clearly described (*20*) for the example of the SO_2/H_2O system. Their methodology was applied for this investigation for which a larger number of chemical species had to be considered. In a general manner, activity of every component is an exponential function of several contributions: Debye–Hückel term, ion–ion interactions with use of standard Pitzer notations and concepts, ion–molecule interaction coefficients from dielectric effects, and molecule–molecule interactions. This approach differs from the one suggested by Pitzer (*29*) in that they considered that short-range forces in binary interactions were due to ions only whereas Beutier considered that molecules should also be included. However, in this study no ternary parameters were used because of the lack of available data for the complex

Table III. Interaction Parameters β_0 and β_1 for Cation i and for Anion j[a]

	i	$j = 1$	$j = 2$	$j = 3$	$j = 4$
$\beta_0(i,j)$	1	0.15*	0.2103	0.25*	0.0027
	2	0.0249	0.0554	0.21*	0.0196
$\beta_1(i,j)$	1	0.40*	0.4711	0.53*	0.0
	2	0.2455	0.2755	0.47*	1.113

[a] Values marked with an asterisk are estimated values in accordance with Rosenblatt's postulations.

Table IV. Volumes V_b[a] and V_c (dm^3/kg of H_2O) and Ionic Radius r (Å)

compd	subscript	V_b	V_c	r	assumptions made
SO_2	2	0.0413			none
H^+	3	−0.0047	0.138 44	3.8	none
Na^+	4	0.0134	0.039 42	2.5	Na^+ equivalent to NH_4^+
HSO_3^-	5	0.035	0.049 66	2.7	none
HSO_4^-	6	0.0265	0.049 66	2.7	V_c and r: values for HSO_3^-
$NaSO_4^-$	7	0.035	0.068	3.0	estimated values
SO_4^{2-}	8	0.0197	0.055 38	2.8	SO_4^{2-} equivalent to SO_3^{2-}

[a] V_b corresponds to infinite dilution (*7*, *31*).

electrolytes considered; it should be noted that some authors (i.e. Edwards) estimate that, due to the large uncertainties arising from the binary parameters, it is essentially impossible to justify a meaningful determination of ternary parameters obtained from experimental data.

The formalism deduced from Beutier and Renon's model used in this study is reported in Appendix 2. This method requires an appreciable number of parameters such as partial molar volumes, ionic volumes, coefficients for binary interactions, etc. Most of the data could be taken from literature (*8*, *19*); the remaining values were estimated in accordance with Rosenblatt's theories: the practicability of the model from these estimated values was tested through numerical tests. The whole set of the parameter values is given in Appendix 2 (Tables III and IV).

Experimental Technique for the Study of SO_2 Absorption

(*1*) ***Experimental Apparatus.*** The solubility apparatus used here is shown schematically in Figure 2. The complete solubility device was mounted in a large fume hood. The absorption reactor was a water-jacketed steel reactor, having an inner diameter of 7.8 cm and a total volume of 382 cm^3. A water bath maintained the absorption liquid at a constant temperature. Three equally spaced vertical baffles, each being 1/12th of the vessel diameter in width, were attached to the inner wall of the vessel. The liquid stirrer was a propeller-type Rushton. In order to measure the evolution of the pH without disturbing the equilibrium system, a glass electrode (Tacussel PHN 81) was directly inserted into the absorbing vessel. The total pressure existing over the solution was controlled and measured by a manometer (Protais) with 0.01 bar accuracy.

(*2*) ***Chemicals.*** Anhydrous sodium sulfate was purchased from Fluka Chemicals, having a minimum purity of 99%. Sulfuric acid was diluted from 1 N standardized solutions. Sulfur dioxide and nitrogen, used as an inert gas, were purchased from Prodair: the minimum species purities were 99.9 and 99.99 mol %, respectively. The water used was the usual grade of laboratory conductivity water, however being filtered additionally through microporous filter cartridges (Millipore): its final resistivity was over 18 MΩ cm, and its pH was found to be 7-7.2 after CO_2 removal.

(*3*) ***Procedure.*** A 300 cm^3 amount of the solution, at the desired concentration of sodium sulfate or sulfuric acid, respectively, was prepared with purified water and placed in the absorption vessel. A saturating vessel was used to saturate the gas before it entered the stirred absorption chamber. After both vessels were brought to thermal equilibrium, the solution was degassed by letting oxygen-free nitrogen pass through while stirring gently. Once the solution was sufficiently degassed, the desired concentration in ppm, corresponding to a definite partial pressure of SO_2, was attained by adjusting the flow rates of nitrogen and SO_2 by means of flow meters (Tylan). SO_2 concentration was measured by an one-canal UV analyzer (Binos BIN 4b.1). This procedure allowed SO_2 partial pressure to be controlled with 2% accuracy. Once the concentration was constant the gas was passed into the reactor with the help of a three-way valve. During the saturation period, the excess gas was vented via the gas analyzer. The passage of the gas was continued for several hours with gentle stirring. During the final stages of the equilibrium, the pH electrode was taken from the reactor, calibrated with two acidic buffer solutions, and reinserted into the absorption chamber. Once the outlet gas concentration was constant and equal to the inlet concentration ± 10 ppm, the inlet valve was closed and the pH measured. Sampling of the saturated solution was carried out by opening a large valve (inner diameter 8 mm) at the bottom of the reactor and by letting the liquid flow into a small piece of a flexible tube having two valves attached to it. The tube and the valves were weighed, and afterward the solution was flowed directly into a prepared iodine solution of known concentration. The amount of tetravalent sulfur was determined by back-titrating the excess iodine with a fresh thiosulfate solution using a starch indicator.

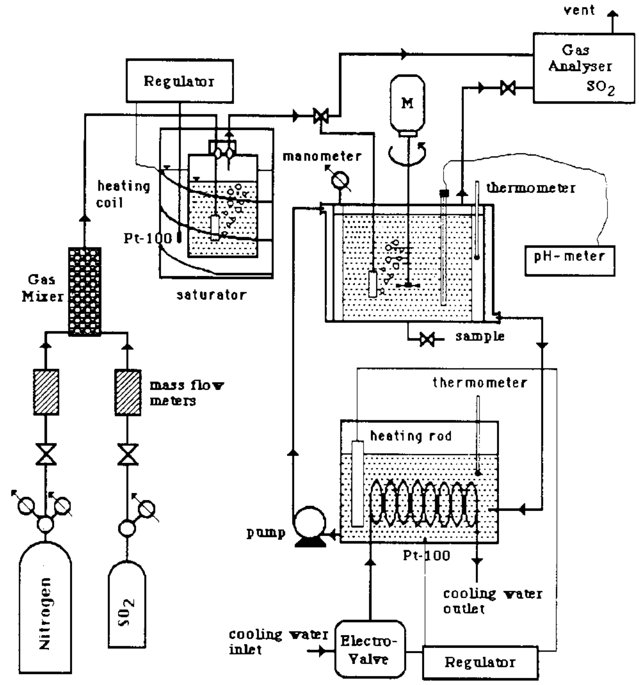

Figure 2. Schematic view of the experimental device for the investigation of gas–liquid equilibrium.

Equilibrium of $SO_2/Na_2SO_4/H_2O$

Calculations were performed for different values of SO_2 partial pressure and concentrations of the supporting electrolyte. Due to the principle of the numerical solution used, the case of zero concentration for Na_2SO_4 could not be treated directly: equilibria values for different concentrations of SO_2/H_2O in the absence of a supporting electrolyte were thereby calculated through a specific reduced equation set, disregarding sodium sulfate concentration.

Because of the partial hydrolysis of sulfur dioxide, the total amount of sulfur dioxide, denoted S(IV), seemed to us to represent a key variable. In addition, another numerical value of

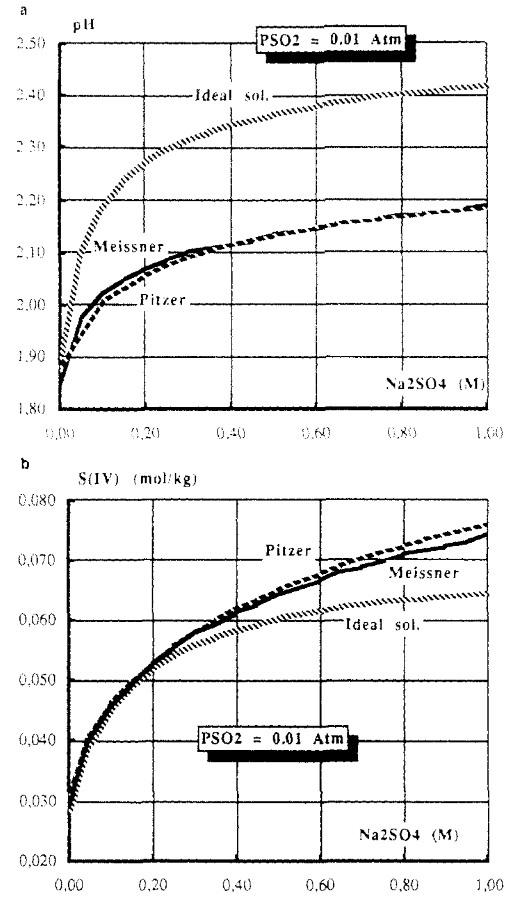

Figure 3. Thermodynamics of $SO_2/Na_2SO_4/H_2O$ at P_{SO_2} = 0.01 atm and T = 25 °C for various models for activity coefficients: (a) variation of pH solution; (b) variation of S(IV) molality.

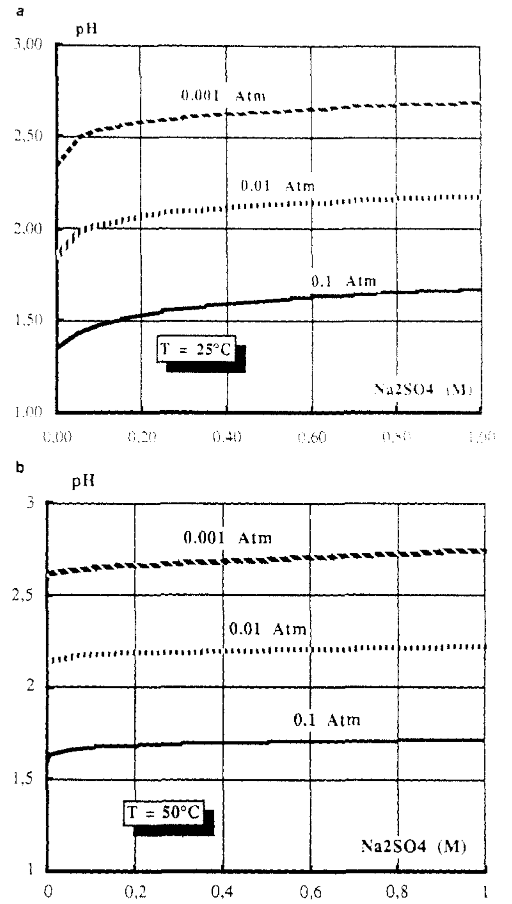

Figure 4. pH of a Na_2SO_4 solution in equilibrium with SO_2 at 25 (a) or 50 °C (b).

importance relative to ionic tetravalent sulfur can be expressed in the form of the ratio of S(IV) to the dissolved SO_2 concentration.

(*1*) *Influence of the Activity Coefficient Model*. The formalism suggested by Renon et al. was only tested for the example of SO_2 absorption into a sodium sulfate electrolyte: the estimated values of some parameters relative to ion-ion interaction were modified by ±10% and the calculations repeated; for most trials, the model results were altered by the numerical procedure by less than 1%.

As an example, the variations of the pH solution and of the S(IV) concentration in dependence of the supporting electrolyte concentration are plotted in Figure 3 for a SO_2 partial pressure of 0.01 atm and 25 °C by using three different models describing interactions between solvated species. As can be seen from Figure 3a, very similar results are obtained through Meissner's and Pitzer's procedure: a very good agreement is observed especially for the highest ionic strength considered, i.e. over 0.4 M, and the maximal pH deviation between the two models was noticed to be below 0.02 at a sulfate concentration of 0.1 M. The values for the total amount of tetravalent sulfur predicted by the two models differ only by 3% for the most concentrated solutions, as shown in Figure 3b. The main contribution for the deviations observed is likely due to the fact that the SO_2 activity coefficient was assumed to be equal to unity (due to the relatively small partial pressure of SO_2 involved); cross-checking Pitzer's model however yields values of γ_{SO_2} up to 1.17 for 1 M Na_2SO_4, and the nature of the method considered should affect the extent of sulfur dioxide dissociation and thereby the pH values for the various concentrations, as a consequence. By contrast, water activity varies only between 0.97 and 1 under the investigated conditions. Nevertheless, although γ_{SO_2} can differ from unity to a certain extent, it should be stated that a compensation effect, emanating from the dependent nature of the set of equations interlinked with one another, strongly reduces the effect of one parameter on the results and thereby allows a satisfactory accordance between both methods.

Finally it was shown that, assuming an ideal behavior of the considered electrolyte solution, drastic errors result in estimation of the pH value for various concentrations of the supporting electrolyte. The calculated pH value is largely higher than corresponding values stemming from Meissner's and Pizer's model.

(*2*) *Influence of Other Parameters*. The variations of the electrolyte pH are plotted in Figure 4a,b for three simulated SO_2 pressures -10^{-3}, 10^{-2}, and 10^{-1} atm—and for sodium sulfate concentration varied between 0 and 1 M. As expected, the pH ranges between 1 and 3, whatever the operating conditions, which validates the assumptions with regard to OH^- and SO_3^{2-} concentrations. Electrolyte pH largely depends on the partial pressure of SO_2: pH reduces nearly by 0.5 as the flue-gas pressure is increased by a factor of 10, due to the acidic character of SO_2. Increasing the support electrolyte concentration allows a slight enhancement of the solution pH: the presence of a large amount of sodium sulfate buffers the liquid and hinders to a certain degree the acidic character of the gas. For salt concentrations above 0.2 M, the pH is roughly constant; this effect is even more pronounced at higher temperature. In general it was found that the solution pH is a decreasing function of the temperature: the dependence of the equilibrium constants with temperature can be invoked, but the observed phenomenon is more likely due to the strong temperature dependence of the SO_2 solubility.

Figure 5 reports the variations of the tetravalent sulfur molality, in the range 0.001–0.30 mol/kg, as a function of different operating conditions. Temperature affects the overall molality

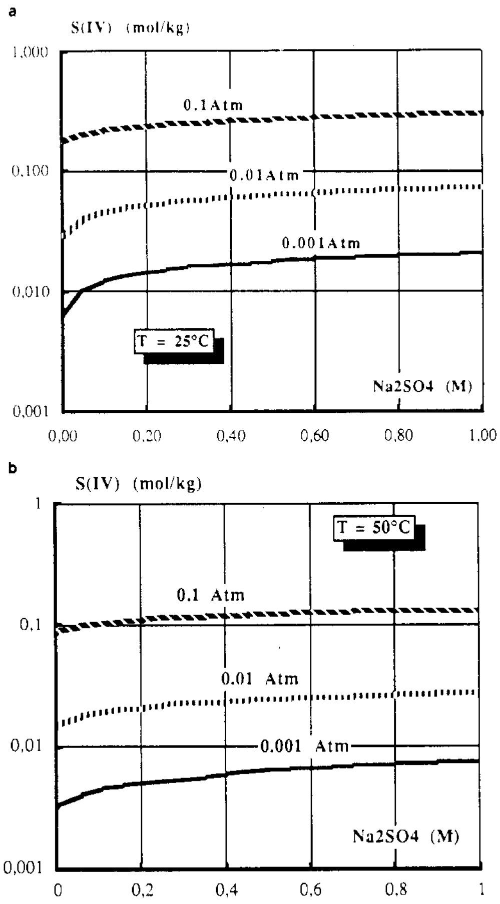

Figure 5. S(IV) molality in a Na_2SO_4 solution in equilibrium with SO_2 at 25 (a) or 50 °C (b).

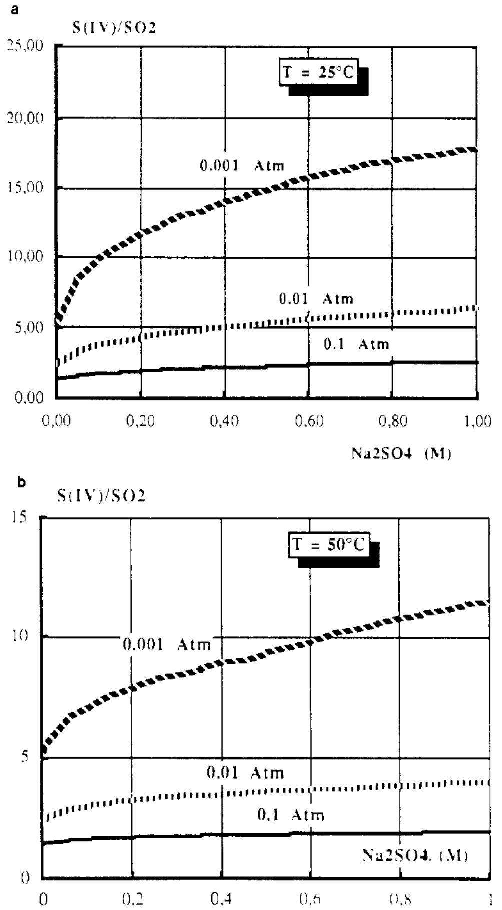

Figure 6. Ratio of molalities of S(IV) over molecular SO_2 in a Na_2SO_4 electrolyte in equilibrium with SO_2 at 25 (a) or 50 °C (b).

Table V. Thermodynamics of the Absorption of Diluted Gas-Phase SO_2 into Sodium Sulfate Solution: Comparison of Experimental Results to Predicted Values

SO_2 pressure, atm	variable	method	at various Na_2SO_4 concn (M) 0	0.05	0.50	1.00
10^{-2}	pH	model	1.845	1.974	2.135	2.190
		expt	1.84	1.93	2.14	2.19
	S(IV)	model	0.0293	0.0402	0.0642	0.0745
		expt	0.0302	0.0394	0.0615	0.0646
10^{-3}	pH	model	2.345	2.492	2.638	2.688
		expt	2.33	2.48	2.61	2.67
	S(IV)	model	0.006 28	0.010 36	0.017 93	0.020 85
		expt	0.006 2	0.009 3	0.016 2	0.020 7

because of the variation of Henry's constant. As explained above, *S*(IV) is the sum of two contributions. The molality of molecular SO_2 is a next to linear function of the flue-gas pressure and weakly depends on the ionic strength of the electrolyte; on the contrary, the amount of bisulfite ion is an increasing function of both SO_2 partial pressure and sodium sulfate concentration, due to reaction 2. As a consequence, the amount of tetravalent sulfur, to be converted through chemical or electrochemical process, is enhanced by both P_{SO_2} and sodium sulfate concentration, especially below 0.2 M.

As expected, the molal ratio $S(IV)/[SO_2]$ depends largely on the flue-gas pressure (Figure 6): for large values of SO_2 pressure,the ratio is fairly small, corresponding to a weak amount of sulfur dioxide dissociation in the aqueous medium. On the contrary, when very diluted gas mixtures are used, a significant increase in the molal ratio is observed, taking on values of up to almost 20 at 1 M Na_2SO_4. This increase in ratio is to a weaker extent dependent on the sodium sulfate concentration since the equilibrium of eq 2 toward the reactant side is to a certain degree enhanced by reassociation of protonated sulfate species, corresponding to eq 5. In addition, Figure 6 shows that increasing temperature leads to smaller extents of dissociation: despite the slight influence of electrolyte pH, it was observed that the dissociation constant is reduced by a factor close to 2 by varying the temperature from 25 to 50 °C.

(3) Comparison to Experimental Data. The aim of the experimental part was to verify the approach used here. The reproducibility and correct functioning of the solubility apparatus were checked by making measurements of sulfur dioxide in pure water at $P_{SO_2} = 0.01$ and 0.001 atm and at 25 °C. Three titrations were always taken for all runs, and the mean average was used as the final experimental value; these titrations gave coefficients of variation of 3% and 1.3%, respectively. Then, absorption experiments were carried out in various sodium sulfate solutions. Table V displays the comparison of practical measurements to the predicted values by Meissner's model for various amounts of sodium sulfate. Experimental pH values confirm the theory as the maximal deviation is generally below 0.04. The agreement is quite satisfactory with regard to *S*(IV) as the experimental amounts of *S*(IV) equal the predicted ones within an error range of only several percent. The deviations observed are likely due to experimental problems: apart from possible error committed in the sampling procedure, a certain amount of evaporation of the water could occur, considering the relatively large amount of gas passed through the reactor during the long-time gas absorption (up to 10 h) in spite of the saturation device mounted before the absorption chamber; concentrating sulfate solution could modify the specific weight and involve erratic estimation of the sample volume.

Equilibrium of $SO_2/H_2SO_4/H_2O$

The difference of the obtained results for the various models applied for the case of the supporting electrolyte being mo-

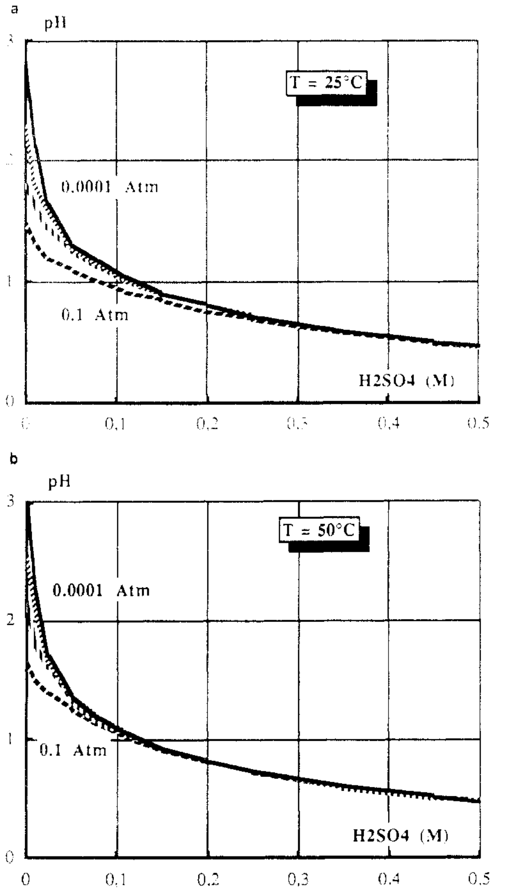

Figure 7. pH in a sulfuric acid electrolyte in equilibrium with SO_2 at 25 (a) or 50 °C (b). SO_2 partial pressure was equal to 10^{-4}, 10^{-3}, 10^{-2}, and 10^{-1} atm.

lecular sulfuric acid was first tested in the case of the SO_2 partial pressure being 10^{-2} atm, at 25 °C. The deviation obviously increases with the amount of H_2SO_4 introduced, and, with regard to pH solution, the maximal divergence is observed below 0.03 M. The maximal amount of molecular sulfuric acid, expressed by (6), which was considered, corresponds to a lower dissociation extent of H_2SO_4 and HSO_4^- and a slight reduction of H^+ concentration; as a consequence, relation 6 yields pH values slightly larger than those calculated under the assumption of total first dissociation. The results presented in the following text rely upon the assumption of entire dissociation of H_2SO_4.

Solution pH obviously decreases with the concentration of sulfuric acid introduced and can reach negative values when surpassing molal concentrations of 1.8 *m*. The partial pressure of sulfur dioxide has an almost negligible effect on the pH, especially for H_2SO_4 concentrations larger than 0.2 M, since the vast majority of the hydrogen ions originate from the first dissociation of sulfuric acid, which is considered to be complete (Figure 7). In the case of weak sulfuric acid concentrations, the pH decreases when partial pressure values for SO_2 are increased because of the acidic nature of sulfur dioxide; for instance a 0.05 M H_2SO_4 electrolyte exhibits pH values of 1.23 and 1.08 for flue-gas pressures of 10^{-4} and 0.1 atm, respectively. This dependence is dampened by an increase of temperature, due to a weaker SO_2 solubility. For the case of more concentrated electrolytes, approximate calculations can be done regardless of the partial pressure of SO_2: the dependence of the constant for the second dissociation of H_2SO_4 with temperature involves a small increase of pH as T is varied from 25 to 50 °C.

The dissociation of SO_2 in ionic species during its dissolution into an aqueous medium can only be observed in very dilute sulfuric acid electrolytes: consequently the molal amount of tetravalent sulfur is a next to linear function of P_{SO_2} as soon as $[H_2SO_4]_0$ exceeds 0.2 M (Figure 8). In general it can be said that SO_2 dissociation does exist to an appreciable extent, according to eqs 2 and 3, for H_2SO_4 concentrations below 0.05 M and for relatively high dilution rates of the flue gas.

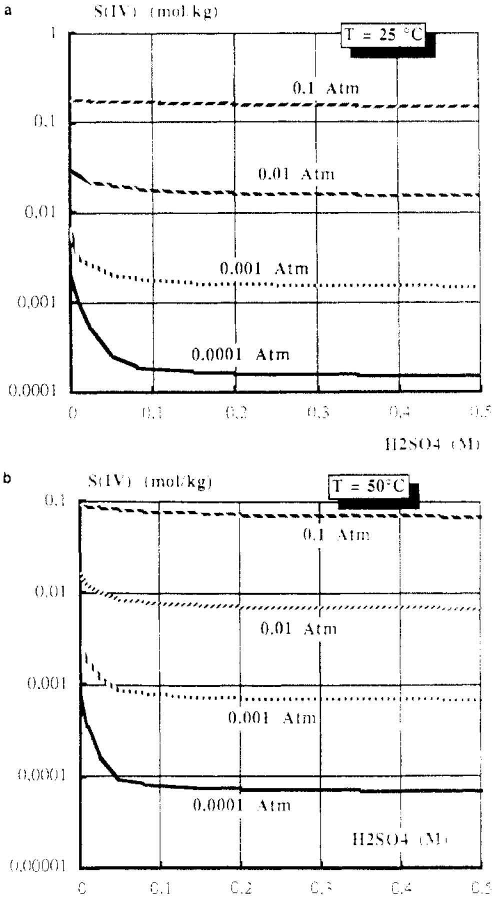

Figure 8. S(IV) molality in sulfuric acid electrolyte in equilibrium with SO_2 at 25 (a) or 50 °C (b). SO_2 partial pressure was equal to 10^{-4}, 10^{-3}, 10^{-2}, and 10^{-1} atm.

Table VI. Thermodynamics of the Absorption of Diluted Gas-Phase SO_2 into Sulfuric Acid Solution: Comparison of Experimental Results to Predicted Values

SO_2 pressure, atm	variable	method	at various H_2SO_4 concn (M) 0	0.01	0.20
10^{-2}	pH	model	1.845	1.652	0.780
		expt	1.84	1.61	0.77
	S(IV)	model	0.0293	0.0254	0.0146
		expt	0.0302	0.0212	0.0130
10^{-3}	pH	model	2.345	1.817	0.784
		expt	2.33	1.81	0.80
	S(IV)	model	0.006 28	0.003 12	0.001 45
		expt	0.006 2	0.002 83	0.001 66

The results given by theory and practice are compared in Table VI for two partial pressures and low amounts of sulfuric acid: the sulfuric acid concentration was maintained below or at 0.20 M to observe SO_2 dissociation and its influence on pH and on *S*(IV) molality. Experimental and theoretical values for a zero concentration of H_2SO_4 are obviously those relative to SO_2 absorption into pure water, reported in Table V. The pH, measured in the absorption device, verifies the model prediction and the deviation between theory and practice is of the order of magnitude of the pH meter accuracy. The agreement is less satisfactory for *S*(IV) molality, as deviations up to 15% can be seen in Table VI and two causes can be invoked: (i) due to the acidic nature of the solution, tetravalent sulfur is mainly in the form of SO_2, which could be desorbed to a weak extent in the sampling procedure; (ii) the low concentration of S(IV) in the acid solution decreases the accuracy of the volumetric dosage, especially for the lowest SO_2 pressure investigated.

Conclusion

The present study allows the prediction of the various species either in ionic or molecular form existing in an H_2SO_4 or Na_2SO_4 electrolyte solution in equilibrium with diluted SO_2 concentrations in the gas phase. The influence of temperature, flue-gas pressure, and the amount of sulfate introduced on pH and the extent of SO_2 dissociation has been described. For fairly dilute electrolyte solutions (below 2 M), the interactions between the various solutes can be expressed in a satisfactory manner with the help of rather simplified models, such as the ones suggested by Bromley or Meissner; slight deviations in nonideality of such neutral compounds as, i.e., SO_2 and H_2O in such concentration ranges can be neglected in a first approximation. The calculations presented were successfully verified by experimental investigation of SO_2 absorption carried out in a bench-scale device.

Calculations could be performed for much more rigorous experimental conditions (nonambiant temperature, high concentrations of the supporting electrolyte) but the presented method should be in such a case modified beforehand when such investigations are undertaken. With regard to temperature, most of the data available were measured at moderate temperature conditions and investigations in a larger temperature range, i.e. below 5 °C or above 80 °C for instance, necessitates experimental determination of SO_2 solubility in the selected electrolyte. However, a theoretical study of SO_2 absorption into higher concentrations of sulfuric acid could be easily done because of the following feasible approximations: (i) absorption of SO_2 leads to the only existing sulfur species, namely molecular SO_2; (ii) numerous data relevant to scrubbing into concentrated H_2SO_4 solutions are available; (iii) the influence of SO_2 on the thermodynamics of H_2O/H_2SO_4 can be neglected. It should be noted that the existence of molecular sulfuric acid should not be disregarded in any of these assumptions.

List of Symbols

a	activity (mol/kg)
A	Debye–Hückel constant's for activity coefficients
B	Bromley's interaction coefficient
B	coefficient in Meissner's relation (relation A1)
$B(i,j)$	second-order virial coefficient (interaction between cation i with anion j)
$B'(i,j)$	derived function of $B(i,j)$
$B_w(i,j)$	derived functions of $B(i,j)$
C	concentration (mol/L)
D	dielectric constant of water, equals 78.288 at 25 °C
d_0	density of water, equals 0.997 kg/dm^3 at 25 °C
e	electron charge, 4.8029×10^{-10} esu
f	fugacity coefficient of vapor
FAC	Debye–Hückel term for activity coefficient given by (A6)
g	number of grams of i, $i = 0$ for solvent
H	Henry's constant (atm/(mol/kg))
I	ionic strength (mol/kg)
k	Boltzmann's constant, 1.38045×10^{-16} erg/K
K	equilibrium constant (mol, kg)
L	dimensionless constant of dielectric contribution
m	molality (mol/kg)
M_0	molecular weight (kg/mol)
M_w	molecular weight of solvent, 0.01802 kg/mol in the present case
P	overall pressure (atm)
P_w^s	vapor pressure of pure water (atm)
q	Meissner's constant for activity coefficient
r	ionic cavity radius (Å)
R	gas constant, 82.06 cm^3 atm/(mol K)
T	temperature (K or °C)
T	contribution of interaction in activity coefficient formulas
v_b	partial molar volume (dm^3/mol)
v_c	volume of ionic cavity (dm^3/mol)
V_f	volume of real solution (dm^3/kg of H_2O)
V_m	volume of neutral solution excluding ions (dm/kg of H_2O)
V_{ic}	volume of ionic solution excluding neutral species (dm^3/kg of H_2O)
z	ion charge
α	dielectric coefficient of neutral solute (dm^3/mol)
β_0,β_1	parameters for second-order virial coefficients and derived functions
γ	activity coefficient
Γ	reduced activity coefficient introduced by Meissner
λ	binary self-interaction of neutral solute
ρ	specific weight (kg/m^3)

Appendix 1

(1) Meissner's Procedure (for Na_2SO_4 Electrolyte). The reduced activity coefficient, Γ, can be calculated at 25 °C by the following formula:

$$\Gamma = \Gamma^*[1 + B(1 + 0.1I)^q - B] \qquad \text{(A1)}$$

where

$$B = 0.75 - 0.065q$$

$$\log \Gamma^* = -0.5107I^{1/2}/(1 + CI^{1/2})$$

$$C = 1 + 0.055q\exp(-0.023I^3)$$

and $q = -0.19$ in the present case. The effect of temperature could be taken into account with the relation

$$\log \Gamma(T) = (1.125 - 0.005T)\log \Gamma(25\ °\mathrm{C}) - (0.125 - 0.005T)\log \Gamma_{\mathrm{ref}} \qquad \text{(A2)}$$

where T is expressed in Celsius and

$$\log \Gamma_{\mathrm{rel}} = -\frac{0.41I^{1/2}}{1 + I^{1/2}} + 0.039I^{0.92} \qquad \text{(A3)}$$

(2) Bromley's Method (H_2SO_4 Electrolyte). At the standard temperature, the various interactions can be expressed as follows:

$$\log \Gamma = \frac{-AI^{1/2}}{1 + I^{1/2}} + \frac{(0.06 + 0.6B)I}{\left(1 + \dfrac{1.5}{|z_+z_-|}I\right)^2} + \frac{BI}{|z_+z_-|} \qquad \text{(A4)}$$

The first term in (A4) is the Debye–Hückel relation for which the radius of various ion pairs is close to 3 Å; the Debye–Hückel coefficient is given by the expression

$$A = \frac{1}{2.303}\left[\frac{e}{(DkT)^{1/2}}\right]\left[\frac{2\pi d_0 N_A}{1000}\right]^{1/2} \qquad \text{(A5)}$$

$A = 0.511$ at 298.15 K. With regard to sulfuric acid, the value for the coefficient B is 0.0606. Estimation of activity coefficients at other temperatures can be done by means of relations A2 and A3 (*20*).

Appendix 2

Activity coefficient for every compound is an exponential function of several terms: Debye–Hückel term, ion–ion interactions with use of standard Pitzer notations and concepts, ion–molecule interaction coefficients from dielectric effects, and molecule–molecule interactions. The main parameters are briefly introduced and the corresponding assumptions as well. The model is described for the example of the $SO_2/Na_2SO_4/H_2O$ system. At last, the following notation was chosen for the sake of more convenient mathematical expressions: H_2O, 1; SO_2, 2; H^+, 3; Na^+, 4; HSO_3^-, 5; HSO_4^-, 6; $NaSO_4^-$, 7; SO_4^{2-}, 8.

(1) Debye-Hückel Term. This term, denoted FAC, is a derived expression of the classical Debye-Hückel expression; contrary to Bromley's theory, the ion diameter is not fixed to 3 Å, and the FAC expression is denoted as follows:

$$\mathrm{FAC} = -\frac{A'}{3}\left[\frac{I^{1/2}}{1 + 1.2I^{1/2}} + \frac{2}{1.2}\ln(1 + 1.2I^{1/2})\right] \qquad \text{(A6)}$$

where $A' = 2.303A$.

(2) Ion–Ion Interaction Term. Pitzer's theory makes it possible to estimate the effects of ion–ion interaction on excess free enthalpy and, as a consequence, on activity coefficient. The interactions are described through virial coefficients. Only interactions between anions and cations have been considered, and the third-order virial coefficients have been neglected. Calculations have been achieved with respect to interactions existing between two cations, H^+ and Na^+, and four anions, HSO_3^-, HSO_4^-, $NaSO_4^-$, and SO_4^{2-}; the various parameters used were defined by means of the following convention, independent of the above-cited notations: the first subscript, i, denotes the cation (1 for H^+ and 2 for Na^+); j is relative to the anion (1 for HSO_3^-, 2 for HSO_4^-, 3 for $NaSO_4^-$, and 4 for SO_4^{2-}).

The set of values for the required parameters is reported in Table III. Second-order virial coefficients, $B(i,j)$, and derived functions can be defined as functions of parameters β_0 and β_1 and of ionic strength as well:

$$B(i,j) = \beta_0(i,j) + \beta_1(i,j)[1 - (1 + 2I^{1/2})\exp(-2I^{1/2})]/(2I)$$

$$B'(i,j) = \beta_1(i,j)[1 - (1 + 2I^{1/2} + 2I)\exp(-2I^{1/2})] \qquad \text{(A7)}$$

$$B_w(i,j) = \beta_0(i,j) + \beta_1(i,j)\exp(-2I^{1/2})$$

Another extent can thereafter be introduced:

$$B_{\mathrm{sum}} = 2\sum_{i=1}^{2} m(i+2)\sum_{j=1}^{4} m(j+4)B'(i,j) \qquad \text{(A8)}$$

The whole set of parameters and functions allows the expression of the ion–ion interaction term:

cation ($k = i + 2$ and $i = 1, 2$)

$$T_{\mathrm{ion,ion}}(i+2) = -B_{\mathrm{sum}}/4I^2 + 2\sum_{j=1}^{4} m(j+4)B(i,j) \qquad \text{(A9)}$$

anion ($k = j + 4$ and $j = 1, 4$)

$$T_{\mathrm{ion,ion}}(j+4) = -z(j+4)^2 B_{\mathrm{sum}}/4I^2 + 2\sum_{i=1}^{2} m(i)\,B(i,j) \qquad \text{(A10)}$$

(3) Ion–Molecule Interaction Term. This contribution, relative to a shift of the dielectric constant of the solvent due to the presence of ionic species, can be estimated by means of several coefficients and parameters. At first some characteristic volumes, such as the volume of neutral solution, V_m, the volume of ionic solution, V_i, the volume of all ionic cavities, V_{cT}, and the volume of real solution, V_f, have to be calculated from the partial molar volumes and ionic cavities volumes, denoted $V_b(k)$ and $V_c(k)$, respectively. Values for volumes V_b and V_c are reported in Table IV.

$$V_m = 1/d_0 + m(2)\,V_b(2)$$

$$V_i = 1/d_0 + \sum_{k=3}^{8} m(k)\,V_b(k) \qquad \text{(A11)}$$

$$V_{cT} = \sum_{k=3}^{8} m(k)\,V_c(k)$$

$$V_f = V_i + m(2)\,V_b(2)$$

where d_0 is the density of water, equal to 0.997 kg/dm³ at 25 °C;

$$V_{fc} = V_f - V_{cT} \quad \text{and} \quad V_{ic} = V_i - V_{cT}$$

In addition, a dimensionless dielectric constant, DIV, is defined as the ratio of the dielectric constant of a solution without ions over the dielectric constant for pure water

$$\mathrm{DIV} = 1 + \frac{\alpha(2)\,m(2)}{V_m} \qquad \text{(A12)}$$

if $\alpha(2)$ is the dielectric coefficient of SO_2, the only neutral solute, equal to −0.030 dm³/mol (*28*). In order to simplify the activity coefficient equations, the two following terms are defined as

$$\Sigma L = \sum_{k=3}^{8} m(k)\,L(k) \qquad \text{(A13)}$$

and

$$L(k) = \frac{e^2 z(k)}{2r(k)kTD} \times 10^8$$

$$\mathrm{BRAC} = \mathrm{DIV}m(2)\left[\frac{-\alpha(2)}{V_m}\,\frac{V_i + 0.5V_{cT}}{V_{ic}} - \frac{1.5V_b(2)V_{cT}}{V_{ic}V_{fc}}\right] \qquad \text{(A14)}$$

if e is the electron charge, D is the dielectric constant of water, k is the Boltzmann constant, and $r(k)$ is the radius of k ion.

The ion–molecule interaction term for each species can be expressed as follows:

ions (species 3–8)

$$T_{\mathrm{ion\text{-}mol}}(k) = \mathrm{BRAC}\,L(k) + 1.5\Sigma L\left[\mathrm{DIV}\frac{V_f V_c(k) - V_{cT}V_b(k)}{V_{fc}^2} - \frac{V_i V_c(k) - V_{cT}V_b(k)}{V_{ic}^2}\right] \qquad \text{(A15a)}$$

SO_2

$$T_{\mathrm{ion\text{-}mol}}(2) = \Sigma L\,\mathrm{DIV}\left[\frac{-1.5V_b(2)V_{cT}}{V_{fc}^2} + \frac{V_f + 0.5V_{cT}}{V_{fc}}\left(\frac{V_b(2)}{V_m} - \frac{\mathrm{DIV}(V_b(2) + \alpha(2))}{V_m}\right)\right] \qquad \text{(A15b)}$$

H_2O

$$T_{\mathrm{ion\text{-}mol}}(1) = \frac{2AM_w}{3}\,\frac{I^{1.5}}{1 + 1.2I^{1/2}} - 2\sum_{i=1}^{2} m(i+2)\sum_{j=1}^{4} m(j+4) \times B_w(i,j) - \Sigma LM_w\left[\frac{-\alpha(2)\,m(2)\,\mathrm{DIV}^2}{d_0 V_m^2}\,\frac{V_f + 0.5V_{cT}}{V_{fc}} + \frac{1.5V_{cT}\mathrm{DIV}}{d_0 V_{fc}^2} - \frac{1.5V_{cT}}{d_0 V_{ic}^2}\right] \qquad \text{(A15c)}$$

where M_w is the molecular weight of water, equal to 0.01802 kg/mol.

(4) Molecule-Molecule Interaction Term. Due to the nature of these interactions, their contributions solely affect water activity and SO_2 activity coefficient. The order of magnitude of molecular sulfur dioxide in the electrolyte makes it possible to neglect the ternary self-interaction term. The contributions depend on the binary self-coefficient λ_{2-2}, equal to -0.05, and are given by the following expressions:

$$T_{\text{mol-mol}}(1) = -\lambda_{2-2}m^2(2)$$

$$T_{\text{mol-mol}}(2) = 2\lambda_{2-2}m(2) \qquad \text{(A16)}$$

The various expressions established for every contribution lead to the expressions of activity coefficients and water activity:

$$\text{H}_2\text{O} \quad a_{\text{H}_2\text{O}} = \exp[M_w\{T_{\text{mol-mol}}(1) - \sum_{k=2}^{8} m(k)\} + T_{\text{ion-mol}}(1)]$$

$$\text{SO}_2 \quad \gamma(2) = \exp[T_{\text{ion-mol}}(2) + T_{\text{mol-mol}}(2)]$$

$$\text{ions} \quad \gamma(k) = \exp[z(k)^2\text{FAC} + T_{\text{ion-ion}}(k) + T_{\text{ion-mol}}(\text{k})] \qquad \text{(A17)}$$

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Dielectric Constants and Excess Volumes of 2-Pyrrolidone + Water at Several Temperatures

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The dielectric constants and volumes of mixing of 2-pyrrolidone + water mixtures were measured at 25, 35, 45, and 55 °C over the entire composition range. The excess dielectric constants and the polarizations were calculated. The observed deviations from ideality, decreasing with increasing temperature, are interpreted in terms of hydrogen-bonding interactions.

Introduction

Recently, the petroleum industry has given much attention to the high density high boiling point, and high polarity solvents. This interest has resulted from their high efficiency in the extraction of monocyclic aromatic hydrcarbons (C_6–C_9) from petroleum products. 2-Pyrrolidone (C_4H_7ON) has the solvent properties that may make it an interesting extraction agent. 2-Pyrrolidone has a comparable selectivity (*1*) to *N*-formylmorpholine (*2*), glycol (*3*), and *N*-methylpyrrolidone (*4*) and less than that of sulfone (*5*). Cosolvents are used in the petroleum industry to increase the selectivity and solvent power of aromatic extractants; therefore we have initiated a program to study some thermodynamic properties of the binary mixtures containing aromatic extractants as a common solvent. The present work reports the density ρ (g cm^{-3}), refractive index n_D, dielectric constant ϵ, excess dielectric constant $\Delta\epsilon$, and excess molar volume V^E of 2-pyrrolidone + water mixtures at 25, 35, 45, and 55 °C.

Experimental Section

2-Pyrrolidone (Fluka AG pure grade) was purified as previously described (*6*). The water content, as determined by

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