

Solubility of sulphur dioxide in aqueous electrolyte solutions at higher ionic strengths - Chloride and bromide containing systems

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Abstract

The absorption of sulphur dioxide in chloride and bromide containing electrolyte solutions was measured up to ionic strengths of 5 mol/dm³. The thermodynamic equilibrium of the gas phase and the liquid phase was characterized by UV spectroscopy. UV spectra analysis gave strong evidence for SO₂X⁻ complexes existing in the solutions. Consequently, these compounds were implemented in the reaction scheme for absorption.

For thermodynamic modelling the activity coefficient model of Pitzer was used. The Pitzer parameters of some important ion pairs and, as a very effective extension, the Sechenov constant for dissolved molecular sulphur dioxide were fitted to laboratory data. This work demonstrates that fitting Sechenov's constant improves the model performance very much. With the extended model we find a good agreement between model prediction and experimental data over the entire range of concentrations.

Keywords

sulphur dioxide, solubility, UV spectroscopy, activity coefficient model, Sechenov's constant

Introduction

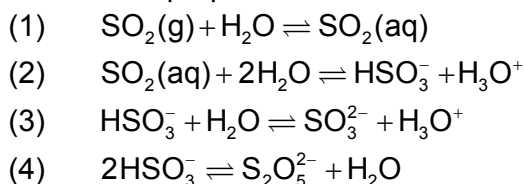
Understanding the absorption behaviour of sulphur dioxide in aqueous electrolyte solutions is of major interest for the design of flue gas desulphurization processes, as for example wet flue gas desulphurization of coal fired power plants or municipal solid waste incineration plants.

A very important species dissolved in the aqueous phase of these scrubber systems is chloride from HCl co-absorption which is enriched in power plant scrubbers up to a concentration of 30 – 40 g/dm³ (0,85 – 1,1 mol/kg) because of scrubber solution recycling.

The presence of chloride ions affects the process in different ways:

- 1.) High electrolyte concentrations change the activity coefficients of the scrubber solution compounds and thus affect the absorption capacity of SO₂ from the gas phase (physorption).
- 2.) If chloride participates in chemical reactions, these reactions also influence the SO₂ removal (chemisorption).

As a basis to describe the chemical reactions during SO₂ absorption the following chemical model is proposed:

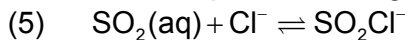


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Up to now only few experimental and theoretical investigations on these systems are reported. Most data are available for the binary system $\text{SO}_2/\text{H}_2\text{O}$, e.g. Johnstone and Leppla [1]; Rabe and Harris [2]; Rumpf and Maurer [3]; Krissmann et al. [4] and Goldberg and Parker [5].

Krissmann [4,6] measured and modelled the ternary system $\text{HCl}/\text{SO}_2/\text{H}_2\text{O}$ at 25°C up to a HCl concentration of 1 mol/kg and a SO_2 partial pressure of 0.73 kPa using Pitzer's activity coefficient model. The measurement data indicate that at given SO_2 partial pressure the solubility of SO_2 decreases up to a HCl molality of about 0.5 mol/kg , and then moderately increases between 0.5 und 1.0 mol/kg HCl . From a multivariate analysis of the UV spectra recorded from the aqueous phase Krissmann et al. conclude that this behaviour results from the formation of an ion complex corresponding to the chloride concentration.

Other experiments proved that addition of calcium chloride (0.5 M CaCl_2 instead of 1 M HCl) has the same effect on the spectra as addition of HCl (Siddiqi et al. [7]). Therefore the formation of a complex according to



was implemented in the model. The ion complex SO_2Cl^- is described by Wedzicha and Webb [8] as well as by Salama and Wasif [9].

In flue gas cleaning units downstream of combustion plants also fluoride, bromide, and iodide are detected, but in much smaller concentrations compared to the chloride. In presence of $\text{SO}_2(\text{aq})$ at flue gas desulphurization a complex formation reaction analogously to reaction (5) may be considered on principle also for these halides.

In this work bromide containing systems were included to compare the bromide effects to the chloride behaviour and find evidence for the existence of these ion complexes. The complex formation reaction proposed for the bromide ion is

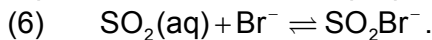


Figure 1 shows the complete reaction scheme included in the model.

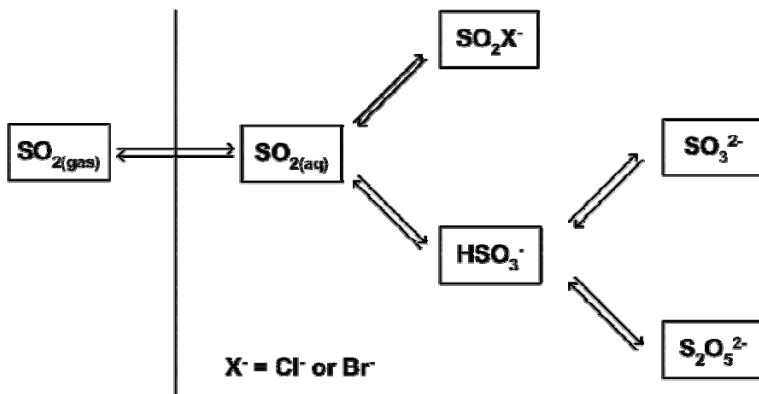


Fig. 1 Reaction scheme for sulphur compounds at SO_2 absorption

This work represents an investigation of the systems $\text{HCl}/\text{SO}_2/\text{N}_2/\text{H}_2\text{O}$, $\text{NaCl}/\text{SO}_2/\text{N}_2/\text{H}_2\text{O}$, $\text{HBr}/\text{SO}_2/\text{N}_2/\text{H}_2\text{O}$ und $\text{NaBr}/\text{SO}_2/\text{N}_2/\text{H}_2\text{O}$ covering an electrolyte concentration up to 5 mol/dm^3 and a broad range in pH value (pH 0-4). Concentrations of SO_2 in the gas and aqueous phase were measured by UV spectroscopy. For thermodynamic equilibrium calculations the K value method including the activity coefficient model of Pitzer was used.

Maurer et al. [10] and Rodriguez-Sevilla et al. [11] investigated the system $\text{NaCl}/\text{SO}_2/\text{N}_2/\text{H}_2\text{O}$ with regard to other system conditions (temperature, pressure) and used another method of modelling.

Burow [12], Woodhouse and Norris [13], Salama et al. [9], Witekowa [14], and Milanova and Benoit [15] measured the stability of the complexes SO_2X^- ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in dimethyl sulfoxide (DMSO) and acetonitrile (ACN) by UV spectroscopy. They found the bromide complex being more stable than the chloride complex in all experiments. In the spectra the authors observed a pronounced bathochromic shift of the peak maxima in the sequence SO_2Cl^- , SO_2Br^- , and SO_2I^- . Successful work on these complexes in aqueous systems is not reported. According to the authors this may result from a higher instability of the complexes in the presence of water.

The bathochromic shift measured for bromide and iodide in systems containing DMSO and ACN suggests the spectroscopic investigation of similar aqueous systems to verify the existence of the ion complexes SO_2X^- as proposed by the reaction model (Figure 1). Aqueous systems containing SO_2X^- should also exhibit a distinct bathochromic shift of the peak maxima, for example for $\text{X} = \text{Br}$ compared to $\text{X} = \text{Cl}$.

Experimental

The experiments were carried out in an apparatus designed to establish and measure thermodynamic equilibria in systems with a liquid and a gas phase. Main components are a reaction cell with an immersed optical probe, a gas cycle with a gas mixing chamber, a membrane pump to circulate the gas phase and a vacuum pump. In order to reduce temperature fluctuations and condensation phenomena the assembly was installed in a heated box.

Analytical methods

The concentration of sulphur dioxide in the gas phase was determined by UV spectroscopy using a diode array photometer X-dap (*Polytec*), which was connected to the optical cell by fiberoptic cables. The molality of total absorbed sulphur dioxide $m(\text{SO}_2)_{\text{tot}}$ and the equilibrium partial pressure were calculated from the difference between the concentrations at the beginning and at equilibrium.

For the measurement of UV active sulphur species in the aqueous phase ($\text{SO}_2(\text{aq})$ and SO_2X^-) a UV/VIS photometer UV2 (*Unicam*) was used. The photometer was equipped with an immersion probe connected by fibreoptic cables.

The extinctions at 280 nm (E_{280}) in the liquid phase were used for model calculations, and the spectral range from 240 – 360 nm was evaluated by multivariate analysis (principal component analysis, PCA).

Modelling

Modelling makes use of the electrolyte activity coefficient model of Pitzer [16] and starts with the ion interaction parameters proposed by Rosenblatt [17], Hunger et al. [18] and Krissmann [4]. For better prediction of gas solubility the model was extended by Sechenov's approach according to Schumpe [19]. For modelling the thermodynamic equilibrium the K-value method [20] was used. For simultaneous fitting of model parameters like Pitzer's interaction parameters a modified simplex procedure according to Nelder and Mead [24] was used.

Fitting the interaction parameters of the ions HSO_3^- , SO_3^{2-} and $\text{S}_2\text{O}_5^{2-}$ did not improve the model considerably. For that reason these parameters were not changed. Following parameters were fitted or determined for the first time:

Pitzer's interaction parameters β^0 and β^1 for the ion pairs $\text{H}^+/\text{SO}_2\text{Cl}^-$, $\text{Na}^+/\text{SO}_2\text{Cl}^-$, $\text{H}^+/\text{SO}_2\text{Br}^-$ und $\text{Na}^+/\text{SO}_2\text{Br}^-$

- The standard free enthalpy of formation $\Delta_f G^\circ$ für SO_2Br^- , the extinction coefficient $\epsilon(\text{SO}_2\text{Br}^-)_{280}$ at 280 nm
- Sechenov's constant for $\text{SO}_2(\text{aq})$

The new parameters are summarized in tables 1 and 2. Consideration of ternary Pitzer's parameters C^ϕ for the ion pairs did not improve the model any more.

Results and discussion

UV spectroscopy

Results from UV spectroscopy give important evidence about the existence of the ion complexes SO_2X^- as proposed in Figure 1. Figure 3 shows a pronounced bathochromic peak maxima shift and an extinction coefficient increase for the spectra in water, chloride solutions, and bromide solutions, respectively. This indicates that besides dissolved molecular SO_2 there is a compound with a much higher extinction coefficient influencing the spectrum.

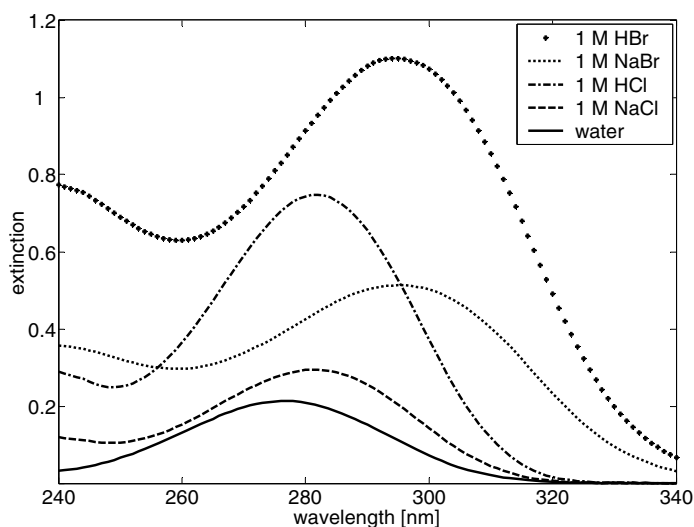


Fig. 3 UV spectra of aqueous phase for the absorption of 0.6 vol.-% SO_2 in water, 1 M NaCl, 1 M HCl, 1 M NaBr and 1 M HBr

Systems $\text{HCl}/\text{SO}_2/\text{N}_2/\text{H}_2\text{O}$ and $\text{HBr}/\text{SO}_2/\text{N}_2/\text{H}_2\text{O}$

The SO_2 solubility was measured in these systems at different HCl and HBr concentrations between 0 and 5 mol/dm³ and different initial SO_2 concentrations up to about 1 vol.-%. Because of the presence of the acids the pH value in these solutions was $\text{pH} < 1$.

Figures 4 and 5 represent the model prediction compared to experimental data after fitting. The plots show the partial pressure of $\text{SO}_2(\text{g})$ versus total molality of absorbed SO_2 (i.e. $\text{SO}_2(\text{aq})$, SO_2X^-). The results for the fitting of the extinction at 280 nm in the liquid phase are not shown here, but are at least as good as the fitting of the partial pressure, if not better.

The concentration of halide ions and protons strongly influences the sulphur dioxide solubility. In the lower HX concentration range (up to 1 M HX) there is a solubility decrease with rising HX molarity because the equilibria in equations (2) and (3) shift to the left hand side. This results in a higher concentration of $\text{SO}_2(\text{aq})$ and a corresponding higher partial pressure of sulphur dioxide in the gas phase. Compared to this chemical effect controlled

by low pH (pH 0-1) superposed physical effects of increasing halide and proton concentration are not apparent.

The measurement and the fitting of the extinction at 280 nm illustrate that the pH controlled trend reverts at higher HX molarities (3 and 5 M HX). Because of missing data in this concentration range it was not evident until now whether this reversal results from interaction forces between dissolved species (physical effect) or can be attributed to the formation of new halide-sulphur complexes (chemical effect). The chemical effect may be explained by the formation of a compound SO_2X^- according to equations (5) and (6), which reduces the concentration of $\text{SO}_2(\text{aq})$ at higher halide molarities.

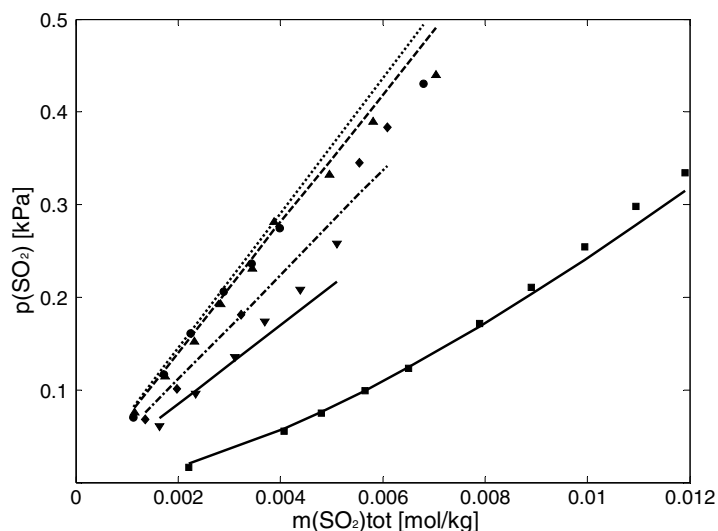


Fig. 4 SO_2 partial pressure vs. molality of total absorbed SO_2 at different HCl concentrations

■ H_2O , exp., – H_2O , calc., ● 0,5 M, exp., ····· 0,5 M, calc., ▲ 1 M, exp.,
 – – – 1 M, calc., ◆ 3 M, exp., - - - 3 M, calc., ▼ 5 M, exp., – 5 M, calc.

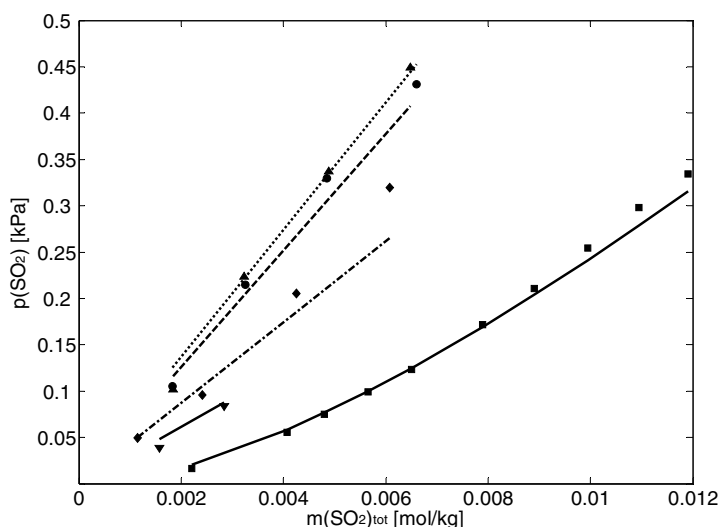


Fig. 5 SO_2 partial pressure vs. molality of total absorbed SO_2 at different HBr concentrations

■ H_2O , exp., – H_2O , calc., ● 0,5 M, exp., ····· 0,5 M, calc., ▲ 1 M, exp.,
 – – – 1 M, calc., ◆ 3 M, exp., - - - 3 M, calc., ▼ 5 M, exp., – 5 M, calc.

Systems $\text{NaCl}/\text{SO}_2/\text{N}_2/\text{H}_2\text{O}$ and $\text{NaBr}/\text{SO}_2/\text{N}_2/\text{H}_2\text{O}$

In these systems the SO_2 solubility was measured up to a NaCl and NaBr concentration of 5 mol/dm^3 , while the SO_2 concentration varied again up to 1 vol.-%. The initial pH value of the solutions was between 4 and 5. After absorption pH dropped down to pH 1 - 3 depending on the amount of SO_2 absorbed.

Figures 6 and 7 compare model results and experimental data.

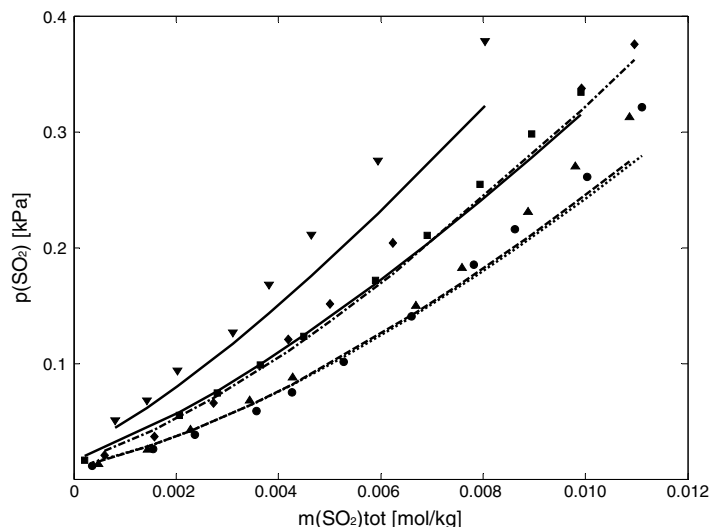


Fig. 6 SO_2 partial pressure vs. molality of total absorbed SO_2 at different NaCl concentrations

■ H_2O , exp., – H_2O , calc., ● 0,5 M, exp., ····· 0,5 M, calc., ▲ 1 M, exp.,
 - - - 1 M, calc., ◆ 3 M, exp., - - - 3 M, calc., ▼ 5 M, exp., - 5 M, calc.

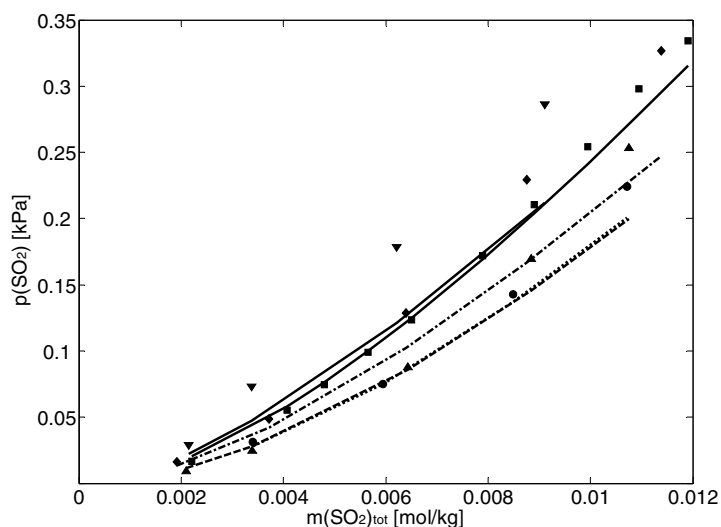


Fig. 7 SO_2 partial pressure vs. molality of total absorbed SO_2 at different NaBr concentrations

■ H_2O , exp., – H_2O , calc., ● 0,5 M, exp., ····· 0,5 M, calc., ▲ 1 M, exp.,
 - - - 1 M, calc., ◆ 3 M, exp., - - - 3 M, calc., ▼ 5 M, exp., - 5 M, calc.

The presence of NaX exerts a strong influence on the SO_2 solubility in water. With increasing NaX molarity the solubility first increases (the partial pressure decreases) and

then declines below the solubility in pure water. This behaviour is completely different from the observations in presence of HX. The formation of SO_2X^- (equations (5) and (6)) is much less important because due to higher pH value (pH 1-3) the molarity of $\text{SO}_2(\text{aq})$ is much smaller in favour of HSO_3^- . Calculation with the Pitzer model point out that in the presence of NaX a strong physical effect appears which is dominated by the interaction between the sodium ion and HSO_3^- . Given the amount of total SO_2 absorbed, the activity coefficient of HSO_3^- is smaller than in pure water up to a NaX molarity of about 1 mol/dm^3 . There is a salting-in effect for SO_2 absorption.

At NaX molarities from about 3 mol/dm^3 the activity coefficient of HSO_3^- is larger than in pure water, resulting in a salting-out effect.

New model parameters

Model parameters after fitting are tabulated in tables 1 and 2.

For all systems investigated in this work, fitting only Pitzer's parameters is not sufficient to come to a satisfying prediction of measurement data by the model. Only when Sechenov's constant is implemented and fitted a good model performance is achieved.

Comparing the complex formation constants $K(\text{SO}_2\text{X}^-)$ it becomes evident that SO_2Br^- is slightly more stable than SO_2Cl^- as predicted from different authors [9,16,17,18]. The extinction coefficient at 280 nm $\varepsilon(\text{SO}_2\text{X}^-)_{280}$ is a little lower for the bromide complex because of the peak maximum shift from 280 nm to about 300 nm. The interaction parameters are in the same order of magnitude for all ion pairs.

Tab. 1 New model parameters

	chloride system		bromide system
	this work	references [7,9]	this work
$K(\text{SO}_2\text{X}^-)$	0.148	0.148	0.2963
$\Delta_r g^\circ(\text{SO}_2\text{X}^-)$	-426.96 kJ/mol	-426.96 kJ/mol	-401.4479 kJ/mol
$\varepsilon(\text{SO}_2\text{X}^-)_{280}$	$3112 \text{ dm}^3/(\text{mol}\cdot\text{cm})$	$3112 \text{ dm}^3/(\text{mol}\cdot\text{cm})$	$2875 \text{ dm}^3/(\text{mol}\cdot\text{cm})$
$\beta^0(\text{H}^+/\text{SO}_2\text{X}^-)$	0.14338	0.1694	0.11468
$\beta^1(\text{H}^+/\text{SO}_2\text{X}^-)$	0.79291	0.5386	0.87248
$\beta^0(\text{Na}^+/\text{SO}_2\text{X}^-)$	0.05940	-	0.14559
$\beta^1(\text{Na}^+/\text{SO}_2\text{X}^-)$	0.56515	-	-0.04592

Tab. 2 New Sechenov's constants

h_i bzw. h_G	H^+	Na^+	Cl^-	Br^-	SO_2
Schumpe [22]	0	0.1143	0.0318	0.0269	-0.0817
this work	0	0.1143	0.0318	0.0269	-0.0221

Principal component analysis

In order to further review the suggestion of a complex formation the UV spectra were evaluated by principal component analysis (PCA) [22]. This method allows for a characterization of the impact of different absorbing compounds on a spectrum. Examination of the spectra from the systems under investigation in this work brought out two principal components PC1 and PC2 in each case. These compounds were able to explain the largest proportion of data variance.

The score plots display the results for chloride containing systems (Figure 8), and for bromide systems (Figure 9). The scores in Figures 12 and 13 are a measure for the influence of a compound on the spectrum and therefore they stand for the concentration of the species absorbing in the solution.

The principal component 1 (PC1) probably corresponds to $\text{SO}_2(\text{aq})$ while PC2 stands for SO_2X^- . The ions HSO_3^- and SO_3^{2-} do not absorb in the analyzed spectral range from 240 bis 400 nm [23,27]. Any impact of $\text{S}_2\text{O}_5^{2-}$ can be excluded from model calculations because this ion does not appear to be important for equilibria at $\text{pH} < 4$.

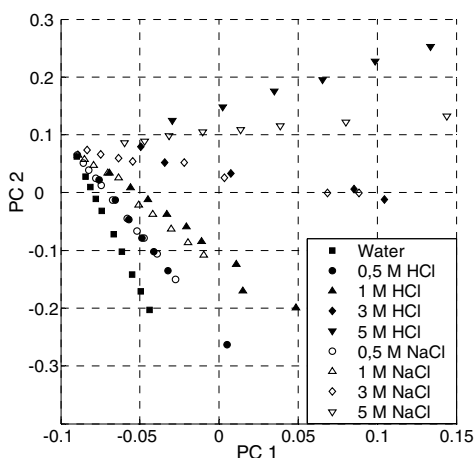


Fig. 8 PCA score plot of liquid phase spectra in HCl and NaCl

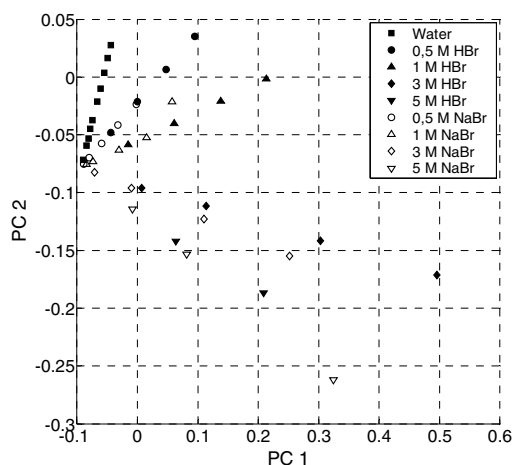


Fig. 9 PCA score plot of liquid phase spectra in HBr and NaBr

According to equations (5) and (6) there must be a correlation between $\text{SO}_2(\text{aq})$ and SO_2X^- , which is determined only by halide molarity. PCA can prove this correlation: If the scores for all spectra with equal halide molarity are on the same straight line, the slope in the score plot is a function of halide molarity. In Figure 8 this applies to experiments at the same halide molarity of 0.5 mol/dm^3 , 1 mol/dm^3 and 3 mol/dm^3 in NaCl and in HCl. In Figure 9 this effect can be observed even for all experiments. Thus, the score plots show a correlation between $\text{SO}_2(\text{aq})$ and SO_2X^- which is based on the halide molarity. Consequently this correlation can be described by equations (5) and (6), respectively.

However, the pH value of the solutions containing NaX and HX is very different. So the PCA proves also that pH is not a factor determining the correlation.

For the 5 M solutions of HCl and NaCl the scores are not on the same line but on two different neighboured lines. Possibly the description of reality by the chemical model (Figure 1) is not sufficient any more at this high ionic strength, because there are other reactions coming up to be important which lead to different chemical species. One reaction may be a protonation of SO_2Cl^- to HOSOCI at very low pH in 5 M HCl. For 5 M HBr and NaBr there

scores are on the same straight line. Maybe protonation of SO_2Br^- is more difficult because this complex is more stable than the chloride complex.

Conclusion

This work describes the impact of high halide concentrations on sulphur dioxide absorption over a broad range of pH and up to high electrolyte concentrations. The thermodynamic equilibrium between the species in the gas and the aqueous phase was measured.

As predicted in the literature the UV spectra display a pronounced bathochromic effect in the sequence from water over chloride systems to bromide systems. This is a strong evidence for SO_2X^- complexes existing also in aqueous systems. Another strong indication for these complexes was gained by a principal component analysis of the liquid phase UV spectra. The analysis proved a clear and distinct correlation between two principal components (supposed to be $\text{SO}_2(\text{aq})$ and SO_2X^-) based on the halide concentration. These findings justify the implementation of the SO_2X^- complexes in the chemical model.

For modelling the thermodynamic equilibrium Pitzer's parameters of the ion pairs $\text{H}^+/\text{SO}_2\text{Cl}^-$, $\text{Na}^+/\text{SO}_2\text{Cl}^-$, $\text{H}^+/\text{SO}_2\text{Br}^-$ und $\text{Na}^+/\text{SO}_2\text{Br}^-$ as well as Sechenov's constant for $\text{SO}_2(\text{aq})$ were fitted to experimental data.

While for the system $\text{HCl}/\text{SO}_2/\text{N}_2/\text{H}_2\text{O}$ - already well described by Krissmann [7,9] - still little improvement could be achieved, for the system $\text{NaCl}/\text{SO}_2/\text{N}_2/\text{H}_2\text{O}$ only the new parameter set enables a good model performance. For the systems $\text{HBr}/\text{SO}_2/\text{N}_2/\text{H}_2\text{O}$ and $\text{NaBr}/\text{SO}_2/\text{N}_2/\text{H}_2\text{O}$ several parameters have been fitted for the first time. Additionally to fitting Pitzer's parameters the implementation of Sechenov's constant turned out to be important to significantly reduce deviations.

Now the new model always achieves a satisfying, in most cases even a good or very good agreement with experimental data over the total concentration range up to ionic strengths of 5 mol/dm^3 .

Experimental work was done in the laboratory of the Chair for Thermodynamics at Duisburg-Essen university (Prof. B. Atakan) with kind support from the staff.

Literature

- [1] H. F. Johnstone, P. W. Leppla, J. Am. Chem. Soc, 56 (1934) 2233 - 2238.
- [2] A. E. Rabe, J. F. Harris, J. Chem. Eng. Data, 8 (1936) 333 - 336.
- [3] B. Rumpf, G. Maurer, Fluid Phase Equilib., 81 (1992) 241 – 260.
- [4] J. Krissmann, Ma. A. Siddiqi, K. Lucas, Fluid Phase Equilib., 169(2) (2000) 223-236.
- [5] R. N. Goldberg, V. B. Parker, J. Res. NBS, 90 (1985) 341 - 358.
- [6] J. Krissmann, Komplexe Phasen- und Reaktionsgleichgewichte bei der nassen Rauchgasreinigung. VDI-Fortschritt-Bericht, Reihe 3: Verfahrenstechnik, Nr. 598, VDI-Verlag, Düsseldorf, 1999.
- [7] M. A. Siddiqi, J. Krissmann, K. Lucas, Fluid Phase Equilib., 136 (1997) 185 – 195.
- [8] B. L. Wedzicha, P. P. Webb, Food Chem., 55(4) (1996) 337-341.
- [9] a) A. Salama, S. B. Salama, M. Sobeir, S. Wasif, J. Chem. Soc. (A), (1971) 1112-1117.
b) S. B. Salama, S. Wasif, J. Chem. Soc. Dalton Trans., (1975) 151-153.
c) S. B. Salama, S. Wasif, M. M. Omer, J. Chem. Soc. Dalton Trans., (1978) 918-920.
- [10] J. Xia, B. Rumpf, G. Maurer, Fluid Phase Equilib., 165 (1999) 99-119.
- [11] J. Rodriguez-Sevilla, M. Alvarez, G. Limiñana, M. C. Diaz, J. Chem. Eng. Data, 47 (2002) 1339-1345.
- [12] D. F. Burow, Inorg. Chem., 11(3) (1972) 573-583.
- [13] E. J. Woodhouse, T. H. Norris, Inorg. Chem., 10(3) (1971) 614-619.

- [14] S. Witekowa, Z. Chem., 2 (1962) 315 – 316.
- [15] E. Milanova, R. L. Benoit, Can. J. Chem., 55 (1977) 2807-2812.
- [16] K. S. Pitzer, J. Phys. Chem., 77 (1973) 268 – 277.
- [17] G. M. Rosenblatt, AIChE J., 27 (1981) 619.
- [18] T. Hunger, F. Lapique, A. Storck, J.Chem.Eng.Data, 35 (1990) 453-463.
- [19] S. Weisenberger, A. Schumpe, AIChE J., 42(1) (1996) 298 – 300.
- [20] M. Luckas, J. Krissmann, *Thermodynamik der Elektrolytlösungen*, Springer-Verlag, Berlin, 2001.
- [21] J. A. Nelder, R. Mead, Computer J. 6 (1965) 308.
- [22] J. Bortz, Statistik, 6. Auflage, Springer Medizin Verlag Heidelberg, 2005.
- [23] A. Huss, Jr., C. A. Eckert, J. Phys. Chem., 81(24) (1977) 2268-2270.
- [24] E. Hayon, A. Treinin, J. Wilf, J. Am. Chem. Soc., 94(1) (1972) 47-57.