Solubility of HBr in H_2SO_4/H_2O and $HNO_3/H_2SO_4/H_2O$ Solutions

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The solubility of HBr in H_2SO_4/H_2O and $HNO_3/H_2SO_4/H_2O$ solutions was determined by measuring the HBr vapor pressure over stirred bulk solutions using tunable diode laser spectrometry. The experimental results for the solubility of HBr in sulfuric acid solutions show good agreement with experimental literature data. However, there is a factor 2−6 discrepancy between experimental and model values. The solubility of HBr in sulfuric acid was parameterized as a function of the H_2SO_4 concentration and temperature in the range 53−75 wt % H_2SO_4 and 195−250 K, respectively. The solubility of HBr in ternary $HNO_3/H_2SO_4/H_2O$ solutions was determined for the first time. An increase in the solubility was observed on exchanging H_2SO_4 by HNO_3 at constant water weight fraction. This observation is in qualitative agreement with model calculations, however, the observed solubility change was much larger than predicted by the model calculations. The solubility of HBr in ternary solutions was parameterized as a function of both the concentration of HNO_3/H_2SO_4 and the temperature. The relations derived can be used for atmospheric modeling of the influence of heterogeneous HBr reactions on atmospheric ozone destruction.

1. Introduction

During the past decade it has been demonstrated that halogen activating heterogeneous reactions on surfaces of polar stratospheric clouds (PSC) play an important role in the destruction of stratospheric ozone.[1,2] In addition, similar reactions may be involved in the observed ozone destruction in the lower polar troposphere at sunrise.[3] The rates of some of these reactions, however, have been found to be strongly dependent on the aerosol composition[4−6] caused, e.g., by the changing solubility of involved halogen species HX in the aerosol.

Although the stratospheric bromine concentration of ∼20 ppt is much lower than that of chlorine, heterogeneous reactions leading to bromine activation may be important, since these reactions are much faster compared to chlorine reactions.[7] This fact could compensate the lower abundance of bromine. It has been calculated that heterogeneous bromine reactions can result in a 30% increase in stratospheric ozone depletion during periods of volcanic activity.[8] In model calculations it is assumed that heterogeneous hydrolysis of $BrONO_2$ is the most important bromine activating reaction since HBr concentrations are too low in these models.[8,9] However, recent field observations show much higher stratospheric HBr concentrations in the range 1−2 ppt[10,11] compared to the models. Therefore, it can be concluded that there might be either some unknown HBr sources such as the reaction of BrO with OH[12] or that HBr sinks were overestimated. Accordingly, bromine activating heterogeneous reactions involving the reservoir species HBr could also be of importance for the destruction of ozone.

Besides the determination of reaction probabilities, exact knowledge of the solubility of HBr in the aerosol solutions important for the atmosphere is needed to calculate the influence of bromine activating reactions on the ozone depletion. While the stratospheric background aerosol consists of ∼60−80 wt % H_2SO_4,[13] it is assumed that polar stratospheric clouds of type 1b are liquid ternary solutions of H_2O, H_2SO_4, and HNO_3.[14] In addition, polar tropospheric aerosols with sulfuric acid concentrations up to 70 wt % have been observed.[15,16] However, very few data are available for the solubility of HBr in sulfuric acid,[17−19] and no data exist for the solubility of HBr in ternary solutions. Recently, several complex thermodynamic activity coefficient models have been developed with which the HBr solubility can be calculated for these solutions.[20−22] However, deviations of the models from existing data for the solubility of HBr in sulfuric acid are significant under certain conditions leading to the conclusions that (i) the existing data set has to be improved and (ii) the existing models have to be adapted to this data set. Accordingly, in a very recent study[23] the model of Carslaw et al.[22] was revised using the available data for the solubility of HBr in H_2SO_4, leading to much better agreement between model and experiments. However, for the solubility of HBr in ternary solutions experimental data are needed to validate these models. In addition, the revised data have to be converted into a simple empirical formula suitable for use in atmospheric models as has been done in the study of Luo et al.[21]

Accordingly, the aim of the present study was a detailed study of the solubility of HBr in H_2SO_4/H_2O and $HNO_3/H_2SO_4/H_2O$ solutions as a function of composition and temperature, including a simple parameterization of the data.

2. Experimental Section

The solubility of HBr in H_2SO_4/H_2O and $HNO_3/H_2SO_4/H_2O$ solutions was determined by measuring the vapor pressure of HBr over stirred bulk solutions with known liquid-phase concentrations.

The HBr vapor pressure was monitored by tunable diode laser spectrometry (TDL) using long path absorption in a 436 L reactor equipped with a White mirror system with an optical path length of 47.7 m. The absorption cross sections of two HBr lines at 2634.891 and 2635.297 cm^{-1} were calibrated (i) by vapor pressure measurements of pure HBr in a 15 cm cell and (ii) by injection of different diluted HBr solutions of known

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mass and concentration into the 436 L reactor. Details of the diode laser spectrometer are reported elsewhere.[24]

The acid mixtures were added to a 1 L glass container that could be cooled to ~190 K in a thermostated ethanol bath (see Figure 1). The container was connected with the 436 L reactor by a glass tube of 4 cm diameter equipped with a Teflon valve. Typically, 125 mL of the acid mixture was prepared by mixing different acids of well-known concentration at low temperatures (<250 K) in the glass container. To avoid the formation of a temperature gradient, the mixtures were stirred with a Teflon stirrer driven by an electrical motor that was separated from the glass container by a magnetic clutch. The temperature of the mixture was monitored with a calibrated thermocouple with an accuracy of better than ±0.5 K. The experimental setup is shown in Figure 1.

After the reactor was evacuated to $\sim 10^{-2}$ mbar the Teflon valve of the preevacuated acid container was opened and the increase of the HBr vapor pressure was monitored as a function of time by the diode laser. The concentration time profile of HBr effusing from the container into the 436 L reactor was described by a first-order process with a rate constant k_{increase}. After the equilibrium between the gas and liquid phase was established, the valve was again closed and the first-order HBr wall loss rate constant, k_{wall}, was determined. To account for the deviation of the gas-phase concentration caused by wall losses, the measured HBr concentration under equilibrium conditions was corrected by using the measured k_{increase} and k_{wall} coefficients:

$$[\mathrm{HBr}]_{\mathrm{corr}} = [\mathrm{HBr}]_{\mathrm{eq}}(1 + k_{\mathrm{wall}}/k_{\mathrm{increase}}) \tag{1}$$

Under typical conditions k_{increase} was found to be much larger than k_{wall} ($\sim 10^{-1}$ compared to $\sim 10^{-3}$ min^{-1}), therefore, the corrections were of the order of only a few percent. Except for total pressures >0.2 mbar, which were obtained at high temperature and low acid concentration, the correction caused by the decrease in k_{increase} became significant and thus limited the concentration and temperature range of the experiments.

Effective Henry's law constants, K_{H}^{*}, were determined from the corrected HBr vapor pressure p (atm) and the HBr liquid concentration c_{lq} (mol L^{-1}) according to

$$K_{\mathrm{H}}^{*} = \frac{c_{\mathrm{lq}}}{p_{\mathrm{g}}} \tag{2}$$

Since HBr dissociates in the solution according to

$$\mathrm{HBr} \rightleftharpoons \mathrm{H}^{+} + \mathrm{Br}^{-} \tag{3}$$

c_{lq} reflects the sum of the concentrations of solvated HBr and Br^{-}.

For the experimental conditions applied, H^{+} concentrations resulting from the dissociation of HBr were much lower than those of the solvents H_2SO_4 and HNO_3. In this case the HBr gas-phase concentration is directly proportional to the liquid concentration c_{lq}; therefore, Henry's law (eq 2) is applicable for the experimental conditions applied.

During a typical experiment the solubility of HBr was determined for a given acid mixture as a function of the temperature. Since HBr in the 436 L reactor was lost to the vacuum system, after each gas-phase measurement the liquid concentration c_{lq} of HBr decreased during the experiment. Accordingly, c_{lq} was calculated from the initial liquid concentration, the measured gas-phase concentration and the estimated wall losses. However, for most conditions, i.e., high solubility and high HBr liquid concentration, changes in c_{lq} could be neglected.

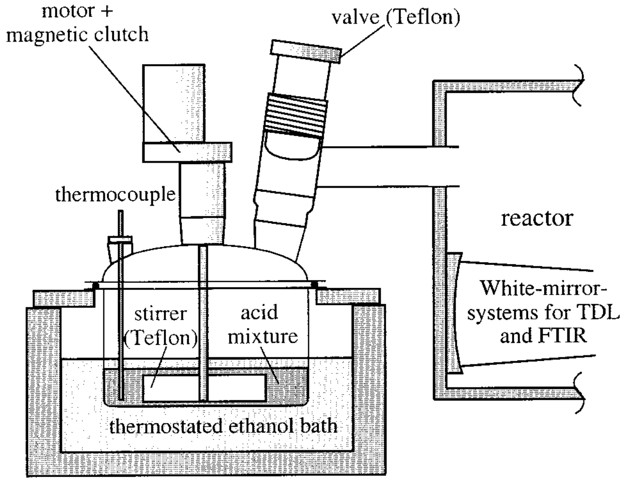

Figure 1. Experimental setup.

The acid concentrations of single HBr, HNO_3 and H_2SO_4 solutions and those of the acid mixtures after the experiments were determined by standard titration with 1 N NaOH. The acid concentration after the experiment was in good agreement with the theoretical value. In addition, the density of the mixture was determined after the experiment, which was also in agreement with the theoretical value. Accordingly, volume contraction of the mixtures and changes of the acid concentration during the experiments were neglected. For the conversion of the acid concentration from mol L^{-1} to wt % the density at 298.15 K of the different acids was taken from the literature.[22,25,26] The accuracy of the acid concentration was estimated to be better than 0.5 wt %.

For a better comparison with literature data the effective Henry's law constants are given in units of mol L^{-1} atm^{-1}. However, since the temperature dependence of the density of the mixtures was unknown, the volume of the mixture was assumed to be independent of temperature, a simplification that leads only to small errors of a few percent in the calculated values.

The uncertainty of the measured effective Henry's law constants was estimated to be better ±40% for typical experimental conditions and are given by the error bars in the fiures. Only for low acid concentrations and high temperatures, for which wall losses became more important, was the uncertainty estimated to be only better than a factor of 2.

3. Results and Discussion

3.1. Solubility of HBr in H_2SO_4. The solubility of HBr in H_2SO_4 was determined for different temperatures in the range 197−243 K and H_2SO_4 concentrations between 45 and 72 wt %. The temperature range for a given acid mixture was limited (i) by the total pressure to <0.2 mbar (see Experimental Section) and (ii) by the freezing point of the mixture. It was found that the mixtures were often supercooled by up to 40 K before they froze.

It was observed that the solubility increased with decreasing H_2SO_4 concentration and decreasing temperature (see Figure 2). The first observation can be explained by (i) salting out of HBr by H_2SO_4 and (ii) by the equilibrium (3), which is shifted toward HBr with increasing acidity. The temperature dependence of the effective Henry's law constant (K_{H}^{*}) can be described by

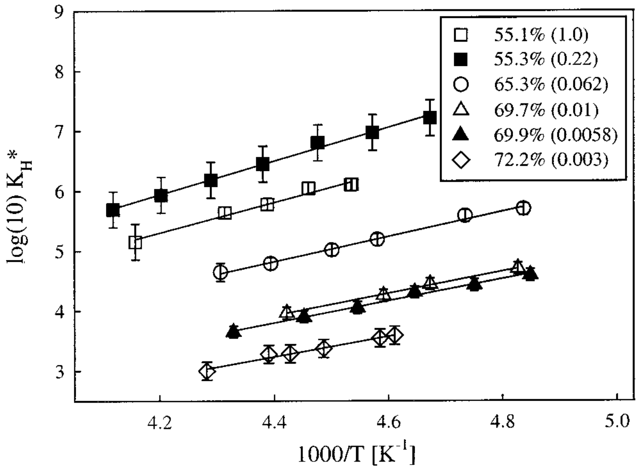

Figure 2. Plots of the logarithm of the effective Henry's law constant (K^*_H) as a function of the inverse temperature for different H_2SO_4 concentrations. The numbers in the inset show the H_2SO_4 concentration (wt %) while the numbers in brackets give the HBr concentration (mol L^{-1}).

the van't Hoff equation:

$$\ln K^*_{H(x)} = -\Delta H/RT + \Delta S/R \qquad (4)$$

in which T denotes the absolute temperature, ΔH the enthalpy, and ΔS the entropy of solution and dissociation, respectively. However, in eq 4 $K^*_{H(x)}$ is defined as the mole fraction of HBr in H_2SO_4 assuming a standard state of 1 atm for HBr in the gas phase, in contrast to this study where K^*_H is calculated according to eq 2 in mol L^{-1} atm^{-1}. Accordingly, for the calculation of ΔS from our experimental data the concentration of the solvent H_2SO_4 in mol L^{-1} was taken into consideration, similar to the study of Williams et al.[17] For low HBr concentration the Henry's law constant in eq 4 can be replaced by

$$K^*_{H(x)} = K^*_{H(eq\ 2)}[\text{solvent}]^{-1} \qquad (5)$$

Therefore, from a plot of $\log(10)K^*_H$ against $1000/T$ (see Figure 2), the entropy change can be calculated by

$$\Delta S = (\text{intercept} - \log(10)[\text{solvent}]) \times 8.314 \times \ln 10 \qquad (6)$$

From the experimental temperature dependence, as exemplified in Figure 2, the enthalpy and the entropy of solution and dissociation was calculated for the different H_2SO_4 concentrations. Both thermodynamic values are listed in Table 1 together with literature values for the solubility of HBr in pure water[27] assuming complete dissociation (eq 3). The given errors represent only the statistical precision (2σ). The values of ΔH were observed to continuously increase with decreasing H_2SO_4 concentration in the range 0−72 wt % (see Table 1). This is caused by the decreasing degree of solvation with decreasing water weight fraction. In contrast, the values of ΔS are constant within the experimental errors (see Table 1). However, since the errors of ΔS are very large, single values for the different H_2SO_4 concentrations have to be treated with caution. Accordingly, a weighted mean value of $\Delta S = -116 \pm 7$ J mol^{-1} K^{-1} was derived from all experiments, which is in excellent agreement with the value for pure water[27] of -116 ± 6 J mol^{-1} K^{-1} (see Table 1).

TABLE 1: Enthalpy (ΔH) and Entropy (ΔS) of Solution and Dissociation Calculated from the Temperature Dependence of K^*_H (Eq 4) for Different H_2SO_4 Concentrations[a]

$c_{H_2SO_4}$ (wt %) [c_{HBr} (mol L^{-1})]	$c_{H_2SO_4(corr)}$ (wt %) corrected for HBr	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
0^b	0^b	−85.1 ± 1.9	−116± 6
45.3 (1.80)	53.4	−56.3± 2.1	−135 ± 9
55.3 (0.217)	56.3	−53.7± 3.1	−129 ± 14
57.5 (0.217)	58.5	−53.0 ± 7.3	−134 ± 32
55.1 (1.00)	59.6	−43.7± 4.5	−99 ± 40
60.4 (0.132)	61.0	−49.9± 6.9	−130 ± 29
62.5 (0.072)	62.8	−44.2 ± 0.7	−112± 3
62.4 (0.144)	63.0	−41.5 ± 2.5	−102 ± 11
62.8 (0.14)	63.4	−46.8 ± 1.5	−125 ± 7
64.1 (0.058)	64.4	−43.6 ± 2.3	−115± 9
65.1 (0.10)	65.5	−45.9 ± 6.5	−129 ± 31
65.3 (0.062)	65.5	−41.4 ± 2.7	−110 ± 12
66.9 (0.058)	67.2	−40.4 ± 2.9	−113 ± 13
69.7 (0.01)	69.7	−35.9 ± 5.4	−105 ± 25
69.9 (0.005)	69.9	−38.7 ± 1.9	−118 ± 8
70.6 (0.005)	70.6	−37.8 ± 3.4	−116 ± 13
72.2 (0.003)	72.2	−32.6 ± 4.6	−102 ± 21

[a] $c_{H_2SO_4(corr)}$ reflects the acid concentration assuming infinitely diluted HBr solutions (see text). ΔS was calculated from the intercept of eq 4 taking into consideration the concentration of the solvent H_2SO_4 (see text). [b] For pure water, literature data from ref 27 were used.

According to Henry's law, the solubility should be almost independent of the HBr liquid-phase concentrations in the case of diluted solutions. This was indeed observed for the low HBr concentrations used for high H_2SO_4 acidity (see Figure 2, 69.9 wt % H_2SO_4). However, for low H_2SO_4 acidity higher HBr liquid concentrations had to be applied in the experiments in order to keep the HBr gas-phase concentration above the detection limit. Under these conditions a significant influence of K^*_H on the HBr concentration was observed. From Figure 2 it is evident that for the experiments with 55 wt % H_2SO_4 the solubility of HBr decreased with increasing HBr content. This observation can be explained by the fact that the H^+ activity of the solutions is caused to a large extent by the added HBr for low H_2SO_4 and high HBr concentration. In this case equilibrium (3) is shifted more to HBr, leading to a decreasing effective solubility with increasing HBr liquid-phase concentration. Hence, HBr liquid-phase concentrations in the experiments should be as low as possible since atmospheric aerosol concentrations are also expected to be extremely low. Williams et al.[17] estimated that the HBr concentration in stratospheric background aerosols is ~10^{-8} mol L^{-1} at 210 K and 66 wt % H_2SO_4. However, since it was not possible to carry out HBr measurements in the gas phase with HBr concentrations prevailing in the stratosphere the effect of the HBr concentration on the measured effective Henry's law constants had to be corrected. Since the H^+ activity of the different solutions can only be estimated by complex models (e.g., Carslaw et al.[22]), the activity was replaced by the concentration for the correction. Similar to other studies (e.g., Tabazadeh et al.[20]) it was estimated that sulfuric acid is completely dissociated at low temperature and acid concentration, i.e., conditions for which deviations from the ideal Henry's law were found to be significant. To correct the data to infinite dilution of HBr, the H^+ concentration of HBr was added to that of H_2SO_4, leading to an increased H_2SO_4 concentration, $c_{H_2SO_4(corr)}$. The correction was found to be significant for high HBr and low H_2SO_4 concentrations (see Table 1).

To describe the solubility of HBr as a function of both the temperature and the H_2SO_4 concentration, the thermodynamic data obtained from the temperature dependence (4) were parameterized as a function of the corrected H_2SO_4 concentration. However, the errors determined for the entropy change ΔS were found to be very large due to the limited temperature range of the experiments (see Table 1). Accordingly, the

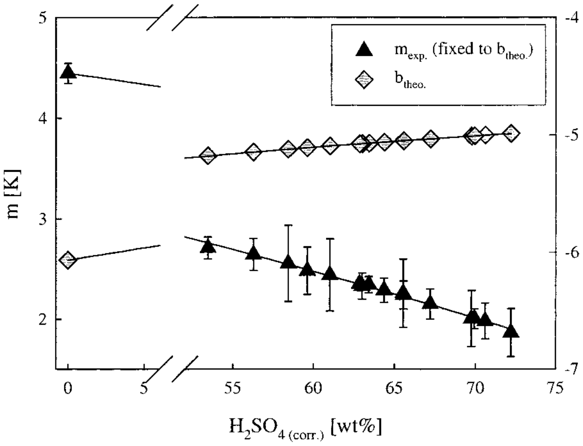

Figure 3. Reevaluated slope and intercept of the temperature dependence of the solubility of HBr in H_2SO_4: $\log(10)K_H^* = m \times 1000/T + b$, obtained by fixing the intercept to the theoretical value calculated with ΔS for pure water[27] corrected for the concentration of the solvent H_2SO_4. The solid lines reflect quadratic fits from which eq 7 was derived.

experimental data were reevaluated by fixing the intercept of the temperature dependence of $\log(10)K_H^* = m \times 1000/T + b$, to the theoretical value calculated with ΔS for pure water corrected for the concentration of the solvent H_2SO_4 (see above). The reevaluated values of m and b are shown in Figure 3 as a function of the corrected H_2SO_4 concentration, including the values for pure water.[27] Both values were parameterized by quadratic functions of the H_2SO_4 concentration, leading to an equation from which the effective Henry's law constant can be calculated as a function of both temperature T (K) and the corrected H_2SO_4 concentration, $c_{H_2SO_4(corr)}$ (wt %):

$$\log(10)K_H^* = m_{H_2SO_4(corr)} \times 1000/T + b_{H_2SO_4(corr)} \qquad (7)$$

The H_2SO_4 dependence of $m_{H_2SO_4(corr)}$ and $b_{H_2SO_4(corr)}$ is well described by

$$m_{H_2SO_4(corr)} = m_1 \times c_{H_2SO_4(corr)}^{\;2} + m_2 \times c_{H_2SO_4(corr)} + m_3\,(K)$$

$$b_{H_2SO_4(corr)} = b_1 c_{H_2SO_4(corr)}^{\;2} + b_2 c_{H_2SO_4(corr)} + b_3$$

with the following values for the parameters $m_1 - m_3$ and $b_1 - b_3$:

$$m_1 = -1.977 \times 10^{-4}\,(\text{wt \%}^{-2}\,\text{K}),$$

$$b_1 = -8.979 \times 10^{-5}\,(\text{wt \%}^{-2})$$

$$m_2 = -2.096 \times 10^{-2}\,(\text{wt \%}^{-1}\,\text{K}),$$

$$b_2 = 2.141 \times 10^{-2}\,(\text{wt \%}^{-1})$$

$$m_3 = -4.445\,(\text{K}), \qquad b_3 = -6.067$$

From the parameter $m_{H_2SO_4(corr)}$ the enthalpy of solution and dissociation for HBr in H_2SO_4 can be calculated: $\Delta H = -m_{H_2SO_4(corr)} \times 8.314 \times \ln 10$ (kJ mol^{-1}). With eq 7 all individual experimental data points can be calculated with an accuracy of better than a factor of 2 (see Figure 4) and an average deviation of ±17%.

The experimental results for the solubility of HBr in sulfuric acid solutions are in good agreement with experimental literature data.[17−19] The results of Williams et al.,[17] Abbatt et al.,[18] and those of Abbatt and Nowak[19] agree at least within a factor of ~2 with the data calculated using eq 7 (see Figure 5). For the study of Williams et al.[17] only the direct vapor pressure measurements were taken into account for 54, 60, and 66 wt %, since their values determined from the kinetic uptake measurements are up to a factor of ~5 higher. The diffusion constant of HBr in H_2SO_4 has to be known for the calculation

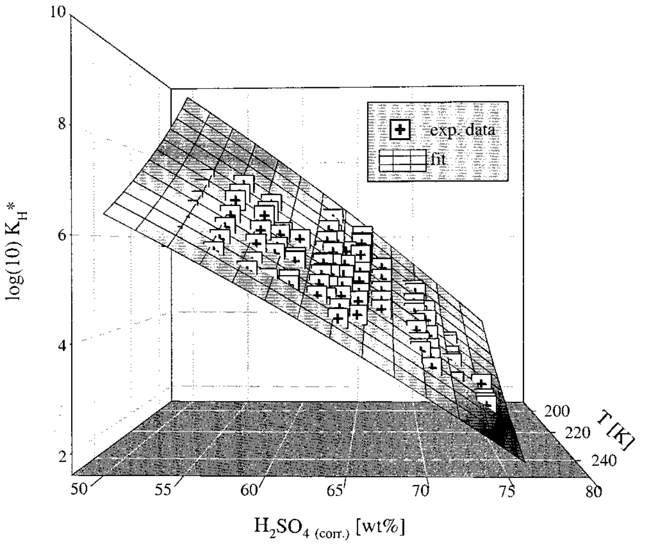

Figure 4. Comparison of the experimental solubility of HBr in H_2SO_4 with values calculated with eq 7 as a function of the corrected sulfuric acid concentration and temperature.

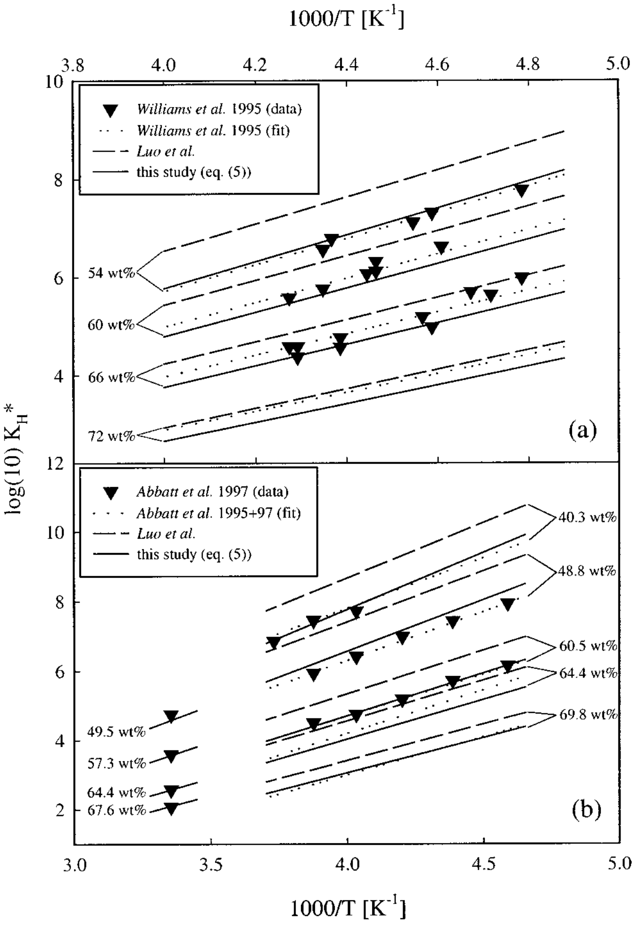

Figure 5. Comparison of the calculated solubility of HBr in H_2SO_4 (eq 7) with model calculations of Luo et al.,[21] (a) with data of Williams et al.[17] and (b) with data of Abbatt et al.[18] and Abbatt and Nowak.[19]

of the solubility from kinetic uptake measurements. Accordingly, it might be possible that this discrepancy is caused by an error in the diffusion constants used.[28]

It is interesting to note that values calculated with eq 7 are in excellent agreement with the study of Abbatt and Nowak[19] who investigated the solubility of HBr in H_2SO_4 over a larger temperature and concentration range compared to the present study. The agreement for room temperature and for H_2SO_4 concentration <53 wt % and low temperature is excellent (see Figure 5b). Therefore, it is assumed that eq 7 can be used for atmospheric modeling in the complete concentration and temperature range of atmospheric interest.

While comparing the experimental results of this study with the model of Luo et al.,[21] which is based on the activity coefficient model of Carslaw et al.,[22] much higher deviations were observed (see Figure 5). Values calculated with eq 7 are factors of 2−6 lower than those calculated by the model of Luo et al.[21] The discrepancy increases with decreasing acid concentration in contrast to the recommended concentration range of the model. The observed trend is also evident when the experimental values of the other studies are compared with the model (see Figure 5). Deviations of the experimental data from, e.g., the study of Williams et al.[17] for 54 wt % H_2SO_4 can reach nearly 1 order of magnitude compared to the model. The model of Carslaw et al.,[22] on which the study of Luo et al.[21] is based, was very recently revised by Massucci et al.[23] for HBr leading to much better agreement with experimental studies. However, since the activity coefficient models are very complex, the parameterization from the present study (7) can be adapted much easier for atmospheric modeling.

3.2. Solubility of HBr in $H_2SO_4/HNO_3/H_2O$ Solutions. Similar to the experiments with pure H_2SO_4/H_2O solutions, the solubility of HBr was also determined in $HNO_3/H_2SO_4/H_2O$ mixtures. For simplification of the interpretation, three sets of experiments were performed in which the water weight fraction of the mixture was held almost constant, while H_2SO_4 was replaced stepwise by HNO_3. In these experiments ~62, ~65, and ~70 wt % total acid concentration was used. The concentration range was limited, since for higher acidity reactions of impurities caused significant changes in the HBr liquid-phase concentration. For lower acid concentration, where high solubility was found, too high HBr liquid-phase content had to be used. For this condition the effective solubility was again affected by the H^+ activity of HBr (see section 3.1).

In the experiments with $HBr/H_2SO_4/HNO_3/H_2O$ mixtures the formation of products such as BrNO from the reaction of HBr with impurities was observed by FTIR spectrometry. Accordingly, the HBr liquid-phase concentration, which was calculated from the initially added amount of HBr and which was corrected for gas-phase losses to the vacuum system after every gas-phase measurement, could have changed during the experiments as a result of these reactions. This would lead to systematic errors of the effective Henry's law constants. To establish whether the liquid-phase concentration of HBr had significantly changed during the duration of an experiment that was up to 12 h, the effective Henry's law constant was measured for similar conditions at the beginning and the end of the experiment. The similar results obtained for the effective Henry's law constants indicate that HBr losses caused by reactions can be neglected for the experimental condition applied, i.e., for 62−70 wt % acid concentration and ~195−240 K.

TABLE 2. Enthalpy (Δ*H*) and Entropy (Δ*S*) of Solution and Dissociation Calculated from the Temperature Dependence of K_H^* (Eq 4) for Different HNO_3 and H_2SO_4 Concentrations and Different c_{acid}[a]

$c_{HNO_3}/c_{H_2SO_4}$ (wt %) (c_{HBr} (mol L^{-1}))	$c_{HNO_3(corr.)}/c_{H_2SO_4(corr.)}$	Δ*H* (kJ mol^{-1})	Δ*S* (J mol^{-1} K^{-1})
(a) $c_{acid} \approx 62$ wt %			
0.0/62.4 (0.144)	0.0/63.0	−41.5 ± 2.5	−102 ± 11
0.0/62.5 (0.073)	0.0/62.8	−44.2 ± 0.7	−112 ± 3
7.2/55.0 (0.144)	7.3/55.6	−46.0 ± 1.0	−116 ± 4
7.2/54.5 (0.36)	7.4/56.0	−42.6 ± 2.9	−104 ± 13
14.6/47.0 (0.36)	15.0/48.3	−42.6 ± 1.9	−100 ± 8
24.7/36.6 (0.36)	25.4/37.7	−44.6 ± 2.3	−101 ± 11
24.4/36.1 (0.72)	25.8/38.2	−44.7 ± 1.5	−105 ± 7
40.2/20.0 (0.72)	42.6/21.2	−45.4± 2.9	−100 ± 13
59.7/0.0 (0.72)	63.5/0.0	−47.1 ± 8.8	−101 ± 37
(b) $c_{acid} \approx 65$ wt %			
0.0/65.1 (0.100)	0.0/65.5	−45.9 ± 6.5	−128 ± 31
0.0/64.1 (0.058)	0.0/64.4	−43.6 ± 2.3	−115 ± 9
0.0/65.3 (0.062)	0.0/65.5	−41.4 ± 2.7	−110 ± 12
9.6/55.6 (0.058)	9.6/55.8	−40.9 ± 11.9	−99 ± 54
9.6/55.6 (0.058)	9.6/55.8	−49.1 ± 4.2	−134 ± 19
19.5/45.6 (0.058)	19.6/45.8	−49.5 ± 5.7	−130 ± 26
24.3/40.5 (0.143)	24.5/40.9	−48.0 ± 1.9	−121 ± 8
34.7/28.3 (0.36)	35.6/29.1	−62.7 ± 4.6	−173± 21
(c) $c_{acid} \approx 70$ wt %			
0.0/69.7 (0.0102)	0.0/69.7	−35.9 ± 5.4	−105 ± 25
0.0/69.9 (0.0051)	0.0/69.9	−38.7 ± 1.9	−118 ± 8
0.0/70.6 (0.005)	0.0/70.6	−37.8 ± 3.4	−116 ± 13
10.0/59.7 (0.050)	10.1/59.9	−40.1 ± 1.5	−113 ± 7
20.4/49.0 (0.099)	20.5/49.3	−37.4 ± 2.1	−93 ± 11
31.2/38.2 (0.099)	31.5/38.4	−35.7 ± 2.3	−80 ± 11
42.3/26.7 (0.141)	42.8/27.0	−33.7 ± 3.8	−70 ± 17
48.4/21.0 (0.099)	48.7/21.2	−38.2 ± 7.7	−87 ± 34
69.3/0.0 (0.100)	69.9/0.0	−57.1 ± 15.7	−158 ± 69

[a] $c_{HNO_3(corr.)}$ and $c_{H_2SO_4(corr.)}$ reflect the acid concentrations assuming infinitely diluted HBr solutions (see text). Δ*S* was calculated from the intercept of eq 4 taking into consideration the concentration of the solvent (see text).

In Table 2 the different acid compositions used in the experiments are listed together with the thermodynamic data obtained from the temperature dependence of the solubility (eq 4). Again, for calculating ΔS from our experimental data the concentration of the solvent, i.e., sum of $[H_2SO_4] + [HNO_3]$, was taken into consideration according to eq 6. Although the values of Δ*S* were again found to have large errors caused by the limited temperature range, a weighted mean value of $\Delta S = -111 \pm 12$ J mol^{-1} K^{-1} was determined for all experiments, which is again in good agreement with the literature value for pure water.[27]

It was observed that the solubility of HBr increased with increasing HNO_3 concentration for a given water weight fraction (see Figure 6). For a quantitative comparison of the data for similar total acid content two problems occurred: (i) the acid content, i.e., the sum of $[HNO_3]$ and $[H_2SO_4]$, showed a small variability for a given set of experiments, which had a significant effect on the solubility (see section 3.1), and (ii) again, similar to the experiments with H_2SO_4, the added HBr caused significant variations of the Henry's law constant (see top of Figure 6).

In order to overcome these two problems, first the effect of the HBr concentration on the Henry's law constant was corrected. Again, it was assumed that HNO_3 and H_2SO_4 were completely dissociated. In order to extrapolate the data to infinite dilution of HBr, the H^+ concentration of HBr was added to that of HNO_3 and H_2SO_4, according to their relative H^+ content. This correction leads to increasing acid concentrations (see Table 2). Second, the measured Henry's law constants were normalized to an acid concentration, i.e., the sum of the corrected concentrations of HNO_3 and H_2SO_4, of exactly 62, 65, and 70 wt % for the different sets of experiments. It was assumed that relative changes in the solubility caused by variations in the

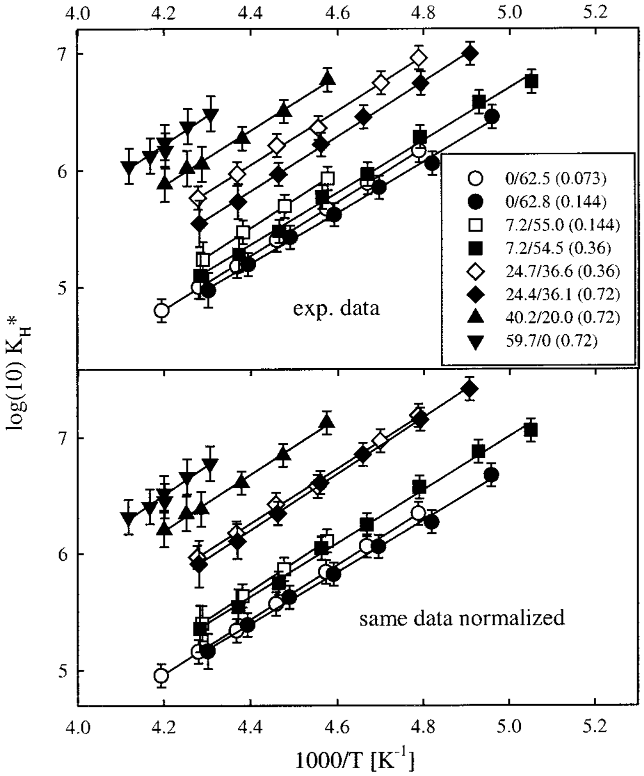

Figure 6. Effective Henry's law constant of HBr in $HNO_3/H_2SO_4/H_2O$ mixtures. Numbers in the inset represent the HNO_3/H_2SO_4 concentrations (wt %), while the numbers in brackets give the HBr concentration (mol L^{-1}). The top figure shows the original data, while the bottom figure shows the same data after normalization for infinitely diluted HBr solutions and for an acid concentration of 62 wt % (see text).

acid concentration of HNO_3 and H_2SO_4 are similar to those for pure H_2SO_4. Accordingly, the solubility was normalized to equal acid concentration by taking the acid dependence of K_H^* for pure H_2SO_4 from eq 7, in which the sulfuric acid concentration $c_{H_2SO_4}$ was replaced by $c_{acid} = c_{H_2SO_4} + c_{HNO_3}$. In order to establish whether the applied normalizations were reasonable, the HBr concentration was varied for three different acid mixtures. The experimental data clearly show that the Henry's law constants decrease again with increasing HBr concentration, similar to the observations for pure H_2SO_4 (see top of Figure 6). After normalization to an infinitely diluted HBr solution and equal acid content, the corrected Henry's law constants were equal within the experimental errors (see bottom of Figure 6), indicating the validity of the corrections.

In order to describe the solubility of HBr as a function of all variables, i.e., T, $c_{H_2SO_4}$, and c_{HNO_3}, the thermodynamic data obtained from the temperature dependence (4) were again parameterized. Again, since the errors for ΔS were found to be very large, the experimental data were reevaluated by fixing the intercept of the temperature dependence, $\log(10)K_H^* = m \times 1000/T + b$, to the theoretical value calculated with ΔS for pure water corrected for the concentration of the solvents H_2SO_4 and HNO_3 (see above). The reevaluated values of m and b were plotted as a function of the corrected HNO_3 concentration for each set of experiments, i.e., for acid concentrations of 62, 65, and 70 wt %, respectively. Both values were parameterized by quadratic functions of the HNO_3 concentration for each set. The intercepts of these quadratic functions, i.e., the values obtained for pure H_2SO_4 of 62, 65, and 70 wt %, were fixed to the values obtained by eq 7, for which an extended data set was available. Since the remaining parameters, which are dependent on the HNO$_3$ concentration, did not show a systematic trend with the acid concentration for the different sets of experiments, mean values were derived. Therefore, the following equation was obtained, from which the effective Henry's law constant can be calculated as a function of the temperature T (K), the acid concentration, $c_{acid} = c_{H_2SO_4} + c_{HNO_3}$ (wt %), and the HNO_3 concentration, c_{HNO_3} (wt %):

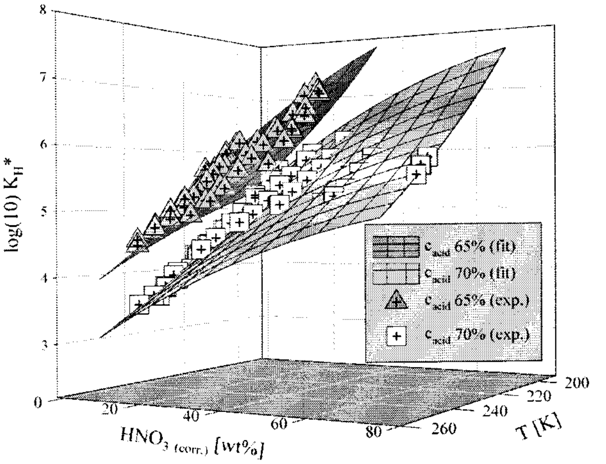

Figure 7. Comparison of the experimental solubility of HBr in $HNO_3/H_2SO_4/H_2O$ mixtures with values calculated with eq 8 as a function of the corrected nitric acid concentration and temperature. The experimental solubility was normalized to infinitely diluted HBr solutions with an acid concentration of 65 and 70 wt %, respectively (see text).

$$\log(10)K^*_{\mathrm{H}\ \mathrm{H_2SO_4,HNO_3},T} = m_{\mathrm{H_2SO_4,HNO_3},T} \times 1000/T + b_{\mathrm{H_2SO_4,HNO_3},T} \qquad (8)$$

The slope and the intercept of eq 8 are given by

$$m_{\mathrm{H_2SO_4,HNO_3},T} = m_1 c_{\mathrm{HNO_3}}^{\ 2} + m_2 c_{\mathrm{HNO_3}} + m_{\mathrm{acid}}\ (\mathrm{K})$$

$$b_{\mathrm{H_2SO_4,HNO_3},T} = b_1 c_{\mathrm{HNO_3}}^{\ 2} + b_2 c_{\mathrm{HNO_3}} + b_{\mathrm{acid}}$$

The values of m_{acid} and b_{acid} are equal to the values $m_{H_2SO_4}$ and $b_{H_2SO_4}$ obtained from eq 7, respectively, except that $c_{H_2SO_4}$ was replaced by $c_{acid} = c_{H_2SO_4} + c_{HNO_3}$. The following mean values of m_1, m_2, b_1, and b_2 were derived for the description of the solubility of HBr in $HNO_3/H_2SO_4/H_2O$ mixtures:

$$m_1 = 4.726 \times 10^{-5}\ (\mathrm{wt}\ \%^{-2}\ \mathrm{K}) \qquad m_2 = 9.421 \times 10^{-3}\ (\mathrm{wt}\ \%^{-1}\ \mathrm{K})$$

$$b_1 = -1.018 \times 10^{-5}\ (\mathrm{wt}\ \%^{-2}) \qquad b_2 = 2.842 \times 10^{-3}\ (\mathrm{wt}\ \%^{-1})$$

From the parameter $m_{H_2SO_4,HNO_3,T}$ the enthalpy of solution and dissociation for HBr in $H_2SO_4/HNO_3/H_2O$ mixtures can be calculated by $\Delta H = -m_{H_2SO_4(corr)} \times 8.314 \times \ln 10$ (kJ mol^{-1}). Equation 8 describes all individual experimental data points of the $HNO_3/H_2SO_4/H_2O$ mixtures with an accuracy of better than a factor of 2 and a mean deviation of ±28%. In Figure 7 the experimental data points for $c_{acid} = 65$ and 70 wt % are shown in comparison with values calculated by eq 8. It should be emphasized that eq 8 is equal to eq 5 for pure H_2SO_4, leading to the same good agreement as already explained above.

The observed trend of increasing solubility of HBr when exchanging H_2SO_4 by HNO_3 at constant water weight fraction

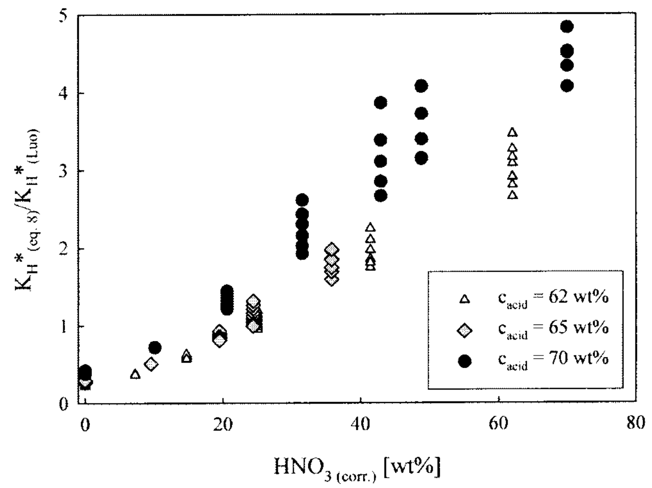

Figure 8. Ratio of K_H^* calculated with eq 8 and values calculated with the model of Luo et al.[21] as a function of the HNO_3 concentration for all data points of the present study.

is qualitatively in good agreement with the prediction of model calculations by Luo et al.[21] The observation could be explained by the decreasing H^+ activity of the solution. Decreasing H^+ activity results in a shift of equilibrium (3) to the right side, leading to higher effective solubility. However, for the experimental conditions applied, the observed trend is quantitatively much more pronounced compared to the model calculations.[21] Accordingly, for higher HNO_3 concentrations, the solubility calculated with eq 8 is higher than that of the model (see Figure 8), whereas the values of the present study for pure H_2SO_4 are lower (see also section 3.1).

Because of experimental problems, the data from the present study unfortunately do not include conditions typically expected for polar stratospheric clouds of type 1b. Tabazadeh et al.,[20] for example, calculated that the acid concentration of PSC type 1b formed below ~195 K is <50 wt %. Although extrapolation of eq 8 beyond the experimental range is prone to error, we have compared the model of Luo et al.[21] with eq 8 also for these conditions. For 195 K, 10 ppbv HNO_3, 5 ppmv H_2O, 0.036 mg m^{-3} H_2SO_4, and 100 mbar total pressure Tabazadeh et al.[20] calculated a concentration of ~40 wt % HNO_3 and ~5 wt % H_2SO_4 in ternary solutions. For these conditions we found that the solubility of HBr is in good agreement with the value calculated by the model of Luo et al.[21] This can be explained by the lower solubility found for H_2SO_4 and the more pronounced HNO_3 dependence compared to the model. Both trends seem to compensate one another under these conditions.

4. Summary and Conclusion

In the present study the solubility of HBr was determined for the solution in H_2SO_4/H_2O and $HNO_3/H_2SO_4/H_2O$ mixtures as a function of temperature and acid concentration over a wide range of conditions. The experimental results were parameterized as a function of both the concentration of HNO_3/H_2SO_4 and of the temperature, respectively. All the experimental data points including the solubility of HBr in pure water are in excellent agreement with this parameterization.

The solubility of HBr in sulfuric acid was found to be in good agreement with existing literature data. All the experimental results of the existing studies can be calculated with the parameterization to within a factor of ~2. However, much lower Henry's law constants were found compared to the model calculations of Luo et al. The deviation increased with decreasing H_2SO_4 concentration.

For ternary $HNO_3/H_2SO_4/H_2O$ solutions, an increase in the solubility of HBr was observed on exchanging H_2SO_4 by HNO_3 at constant water weight fraction. This trend is qualitatively in good agreement with model calculations. However, the observed trend is much larger compared with the model calculations, leading to higher solubility than expected in HNO_3 rich ternary solutions.

The data set now available for the solubility of HBr in H_2SO_4/H_2O and $HNO_3/H_2SO_4/H_2O$ may be used to test the validity of existing models and to further improve the models. In addition, the simple parameterization of the solubility can be used for modeling the effect of heterogeneous HBr reactions on atmospheric ozone destruction.

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