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Solubility of Sulfur Dioxide in Aqueous Sulfuric Acid Solutions

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In this paper we describe a relatively simple apparatus for measuring gas solubilities in a corrosive solvent at various gas partial pressures, the main requirements for which are accurate pressure measuring devices. We summarize all the data for sulfur dioxide solubilities in aqueous sulfuric acid solutions available to us and present them in a form suitable for further comparison and possible applications. Finally we add to the data the results of our own work for two temperatures and a range of gas partial pressures for the acid concentration of 97.0 wt %.

Introduction

In this paper we assemble and evaluate the rather limited available data for SO_2 solubilities in aqueous sulfuric acid and report results of additional measurements.

Early data for the solubilities of SO_2 in sulfuric acid for a pressure of 101.3 kPa and for a temperature of 293.2 K, and for a range of acid concentrations from 55 to 98 wt %, were reported by Miles and Fenton (*1*). Solubilities at 101.3 kPa were reported for temperatures of 313.2 and 333.2 K for a range of acid concentrations of Cupr (*2*). A range of SO_2 partial pressures was utilized in a series of solubility experiments using a narrow range of acid concentrations by Lopatto and Savinaev (*3*). Conditions of very dilute acid were used in conjunction with very low equilibrium SO_2 concentrations in N_2 for data reported by Johnstone and Leppla (*4*) and also by Parkinson (*5*). Solubilities for a pressure of 101.3 kPa were reported for a range of temperatures and for two acid concentrations by Milbauer (*6*). Data are available from a paper by Miles and Carson (*7*) for SO_2 solubilities at 101.3 kPa pressure and several temperatures in fuming (SO_3-rich) sulfuric acid. A more recent paper, of Domka et al. (*8*), contains solubility data for a range of pressures from 101.3 kPa to 2.03 MPa for a gas containing 6% SO_2 in N_2 in temperatures from 293 to 373 K and for an acid concentration of 96.5 wt %.

In this work we report data for SO_2 solubilities for a range of pressures from 101.3 to 405.2 kPa and temperatures of 298.2 and 323.2 K in 97.0 wt % sulfuric acid. In addition, for these two temperatures and composition of acid, we also report solubilities with reduced concentrations or SO_2 partial pressures in N_2.

Difficulties of accurate solubility measurements for gases containing SO_2 and for aqueous sulfuric acid solutions may be anticipated. When the available data are examined, it is readily evident that there is a good deal of inconsistency even in the regions where overlap occurs. As a result it is not possible to recommend solubility values for the whole spectrum of variables. Instead, we must conclude that additional experiments, accurately performed, are required to fully elucidate the solubility behavior in this complex system.

The solubilities appearing in the literature have been reported in units essentially of mass ratio, grams of SO_2 per 100 g of aqueous sulfuric acid solution. Utilizing these units, the SO_2 solubility shows a minimum value corresponding approximately to 85 wt % H_2SO_4. It was indicated by Miles and Fenton (*1*) that the minimum occurred at the equimolar concentration of H_2SO_4 and water. It is of interest to present these same data using the more conventional method for expressing solubility, the mole fraction H_2SO_4 in the aqueous solvent solution, and mole fraction SO_2 in the combined solute–solvent solution. Using these concentrations, it is possible to directly compare the SO_2 solubilities in sulfuric acid solutions with solubilities in other solvents.

Experimental Section

The method utilized for measuring SO_2 solubilities in sulfuric acid involved observing the pressure changes as a result of the dissolution process, in a gas supply reservoir of known volume. A diagram of the apparatus is shown in Figure 1. Two vessels were required: one was a stainless steel gas reservoir, 303 cm^3 in volume, and the other was the flanged stainless steel dissolution cell, 105 cm^3 in volume. Both vessels needed to be small in volume so that pressure changes resulting from the dissolution of the gas could be accurately measured. The dissolution cell was a pressure cell which could be opened as required, containing a 25-cm^3 beaker for the acid solvent. From 5 to 10 g of acid was used in the experiments. Pressure transducers from Data Instruments were used to measure the pressures and were readable to 0.07 kPa. The internal volume of the interconnecting tubing and transducers was included in the volume measurement of the respective systems.

The *PVT* behavior of SO_2 as described by Kang and McKetta (*9*) was used in determining the compressibilities that applied for the various temperatures and pressures utilized. A computer program allowed the evaluation of the gas compressibilities from a BWR-type of equation of state. The same equation of state was used to calibrate the internal volumes of the two systems by determining the mass of gas confined in each system at a known temperature and pressure. Determination of the gas molar volumes by means of the second virial coefficients for SO_2 based on Pitzer's correlation gave almost identical values (*10*). The SO_2 gas and SO_2–N_2 mixtures were purchased from Air Products with the purity of the former gas specified as 99.9%.

The acid concentration was indirectly determined by means of an Anton Paar digital densitometer (DMA 60) calibrated by using the known densities of dried N_2 gas and distilled water. The densities at 298.15 and 323.15 K of 1831.3 and 1807.1 kg/m^3, respectively, correspond to an acid concentration of 97.0 wt % H_2SO_4 as tabulated by Perry (*11*).

The experimental procedure involved accurately weighing the beaker and magnetic stirrer before and after charging the beaker with approximately 7 g of acid. The beaker was then placed inside the dissolution vessel. The acid was deaerated under vacuum while being stirred. It was considered that the amount evaporated was negligible because of the very low vapor pressure of the acid. The vapor pressure of 97.0 wt % acid is listed as 4.3×10^{-4} kPa for a temperature of 323 K (*11*). It would have been possible to determine the amount of gas dissolved by using the known free volume in the dissolution cell and connecting tubing as well as the volume and pressure change of the gas reservoir. However, it was found that, after charging the dissolution cell to the desired pressure, the pressure remained constant until the stirrer was started. It was apparent that the dissolution process required the use of the stirrer and that the amount of gas dissolved during the initial charging period was negligibly small. Hence the determination of the quantity of gas dissolved was simplified. Only the volume

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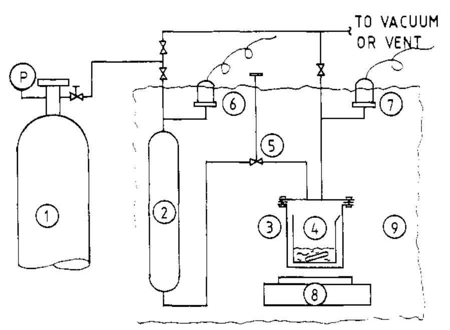

Figure 1. Schematic diagram of the solubility apparatus: 1. gas supply cylinder; 2. gas reservoir; 3. dissolution cell; 4. glass beaker, 25 cm^3, with stirrer; 5. needle valve; 6, 7. pressure transducers; 8. magnetic stirrer, variable speed; 9. constant temperature bath.

Table I. Solubility of Pure SO_2 Gas in 97.0 wt % H_2SO_4

gas press., kPa	solubility, g of SO_2/100 g of aq H_2SO_4	mole fracn SO_2, x_p
	For 298.15 K	
101.3^a		0.039
102.6	2.95	0.0384
152.2	4.69	0.0596
185.2	6.03	0.0753
203.0	6.86	0.0848
247.8	8.48	0.103
	For 323.15 K	
101.3^a		0.0203
113.6	1.82	0.0242
152.9	2.25	0.0295
209.6	2.93	0.0381
262.9	3.79	0.0487
306.9	4.45	0.0567
356.8	5.36	0.0675
407.6	6.33	0.0788

^{a} Extrapolated by using Figure 4.

and pressure change in the gas reservoir was required. The gas reservoir was charged to a pressure of about 275 kPa. Subsequently, with the stirrer in the acid beaker shut off, the dissolution cell was slowly charged by regulating the needle valve in the gas supply tubing to the pressure of the experiment or 101.3 ± 0.03 kPa. The resulting initial pressure in the supply reservoir was recorded, and the stirrer was started. After the stirrer was started, the solution rate was initially very high so that a significant flow of gas was required to keep the gas pressure in the dissolution cell constant. Although it was not possible to keep the pressure completely constant initially, the pressure could be maintained to ±0.14 kPa when equilibrium was approached. After an elapsed time of at least 1 h when the pressure was completely constant (to within ±0.03 kPa), the final reservoir pressure was recorded. The temperature was controlled to ±0.02 K.

The second phase of the experiments involved measuring solubilities above 101.3 kPa pressure. These measurements were made using an incremental addition of gas for increasing equilibrium pressures. The gas supply reservoir was charged to a relatively high initial pressure. After the quantity of gas required to saturate the acid at approximately 101.3 kPa pressure was determined, the pressure in the dissolution cell was increased to a higher level, and the incremental amount of gas required to saturate the solvent at the higher pressure was determined. Thus, the total amount of gas required to saturate the acid at the higher pressure was determined. Although it was possible to make all the measurements for increasing pressures with one charge of acid, the solubility experiments were repeated with fresh solvent to avoid the possible accumulation of experimental errors for the results at the highest pressures. It is estimated that these solubility results are accurate to at least ±3%, the major source of error being the precision of the pressure measurements.

The third phase of these experiments involved measuring the solubilities of SO_2 in sulfuric acid at reduced partial pressures of SO_2 for which the gas was diluted with N_2. Mixed gas, having compositions of SO_2 in N_2 of 7.10 and 15.30 vol % SO_2, was purchased from Air Products Inc. and used as received. The procedure was modified to permit the measurement of the SO_2 solubility without requiring the analysis of the gas phase at the equilibrium conditions. This was accomplished by pressurizing the evacuated dissolution cell with a single charge of mixed gas and observing the drop in pressure after stirring was begun. The initial pressure was chosen so that the drop in pressure was significantly less than 7.1% when the mixed gas containing 7.1% SO_2 in N_2 was used and less than 15.3% when the feed composition containing 15.3% SO_2 in N_2 was used. This procedure required the accurate measurement of the initial and final pressures, and allowed for a good estimate of the final equilibrium concentration or partial pressure of SO_2 in the gas mixture. It was assumed that, in comparison with the high solubility of SO_2, the solubility of N_2 in the acid was negligible; thus the total change in pressure was considered to be the result of the dissolution of SO_2 from the gas phase, the quantity of which could be readily determined.

The solubility of N_2 in 95.6% sulfuric acid has been reported for 293 K in terms of an Ostwald coefficient of 1.672 by Battino in the *Solubility Data Series* volume for nitrogen (*12*). This can be converted to a solubility of 0.0011 g/100 g of acid for a pressure of 101.3 kPa. It is apparent that, even though N_2 is the major component in the gas phase, its solubility will not significantly alter the solubility of the much more soluble SO_2 gas. For these experiments one charge of acid was sufficient for two or more experiments when the solvent was thoroughly degassed for the removal of SO_2 after each completed experiment. The final weight of acid was compared with that initially charged and found to be only negligibly different. Because of the additional procedures involved while using SO_2–N_2 gas, it is considered that the accuracy is less than that for pure gas and is estimated to be ±4%. Higher accuracies may be possible by analysis of the gas and liquid phases in equilibrium.

Results and Discussion

The results of our experiments for the solubilities of pure SO_2 in 97.0 wt % acid and temperatures of 298.15 and 323.15 K for pressures of 101.3 kPa and up to 405.2 kPa are shown in Table I. The results for the solubility measurements using SO_2 and N_2 gas mixtures in acid of the same concentration and various total, and hence partial pressures of SO_2, are shown in Table II.

The unusual solubility characteristics of SO_2 for a pressure of 101.3 kPa as a function of acid concentration are shown in Figure 2. Data for the SO_2 solubility in pure water are from the *Solubility Data Series* edited by Young (*13*). The data of Miles and Fenton (*1*) and Cupr (*2*) are for a range of acid concentrations. The data of Milbauer (*6*) are for only two concentrations, 62.0% and 90.8% acid, as a function of temperature as shown in Figure 3. The combined, smoothed data of Miles and Fenton (*1*), Cupr (*2*), and Miles and Carson (*7*) were interpolated to obtain an estimate of the solubility in 97.0 wt % acid as shown in Figure 3 and indicated as from the literature. These latter data have also been interpolated as required for comparison in Figure 2. Similarly, some of the data of Lopatto and Savinaev (*3*) for low gas partial pressures have been consistent enough to allow extrapolation to atmospheric pressure. These extrapolated data are also shown in Figure 2. The data for solubilities of SO_2 in fuming (SO_3-rich) sulfuric acid of Miles and Carson (*7*) include data in the concentrated

Table II. Solubility of SO_2 from Dilute Solutions of Nitrogen and SO_2 Gases for Higher Pressures

temp, K	total press., kPa	gas composn, mol % SO_2	SO_2 partial press, kPa	solubility, g of SO_2/100 g of acid	solubility, mole fracn SO_2, x_p
298.15	269.9	0.0386	10.4	0.307	0.004 13
	386.9	0.0368	14.2	0.464	0.006 23
	514.2	0.0473	24.3	0.625	0.008 37
323.15	200.4	0.1134	22.7	0.319	0.004 29
	303.5	0.0422	12.8	0.215	0.002 90
	395.0	0.1098	43.4	0.687	0.009 20
	399.5	0.0518	20.7	0.311	0.004 18
	508.4	0.0493	25.1	0.477	0.006 00

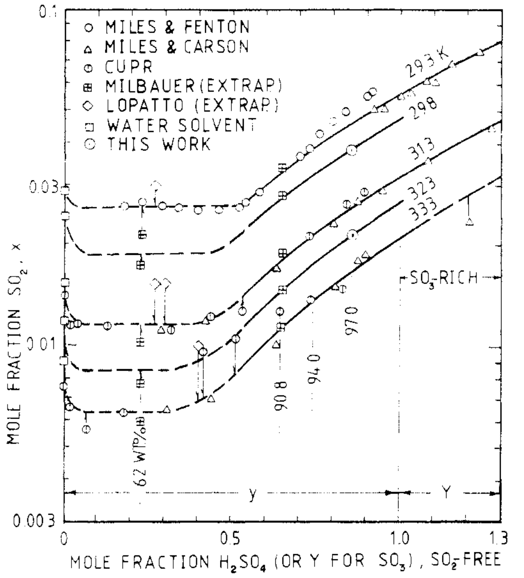

Figure 2. Solubility of SO_2 at 101.3 kPa pressure as a function of sulfuric acid or SO_3 concentration.

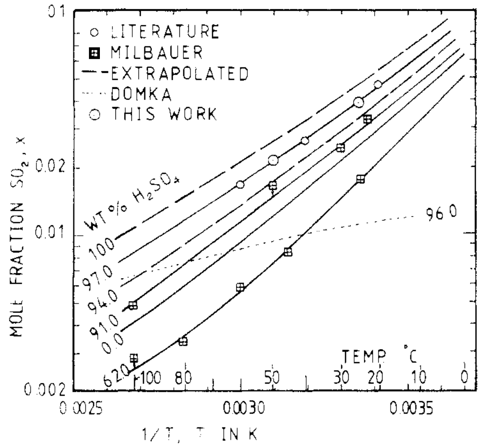

Figure 3. Solubility of SO_2 at 101.3 kPa pressure in various concentrations of sulfuric acid as a function of temperature.

H_2SO_4 region as well as that in the fuming acid region and, hence, are most useful for comparison. Finally, the solubilities as measured in this work are also shown. There appears to be a drop in SO_2 solubility for very low acid concentrations, below that in water. Subsequently, as the acid concentration is increased above about 40–50 mol % H_2SO_4, a steady increase is observed with increasing acid concentrations. Most peculiar is the fact that the solubility of SO_2 continues to increase even for fuming acid solutions containing increasing quantities of free, dissolved SO_3. In essence, the solubility of SO_2 for this situation corresponds approximately to that in liquefied SO_3 solvent since no free water molecules are available.

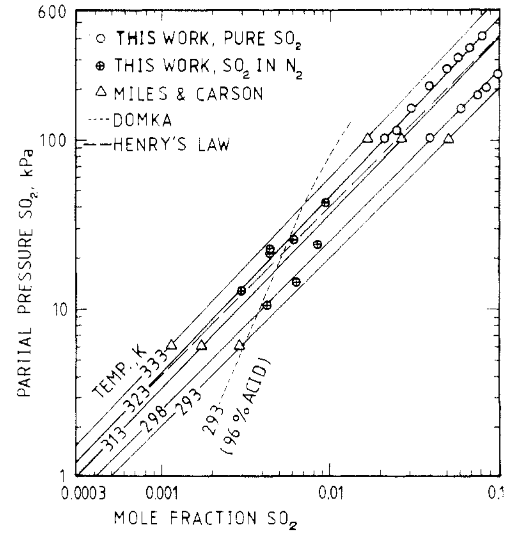

Figure 4. Solubility of SO_2 in 97.0 wt % sulfuric acid as a function of gas partial pressure.

Perhaps of most use for equipment design purposes are the SO_2 solubilities in sulfuric acid as a function of SO_2 partial pressure. All the solubility data in 97.0% acid, obtained for partial pressures from 10.1 to 405 kPa as obtained in this work, are summarized using log scales for the mole fraction solubility and gas partial pressure in Figure 4. The data of Miles and Carson (*7*) are quite consistent with ours, suggesting that solubilities for other temperatures and partial pressures may also be estimated. The data of Domka et al., however, appear inconsistent and are considered in serious error, the reason for which we cannot ascertain. It is noted that Henry's law appears to be followed for temperatures of 293 and 298 K but deviations occur with increasing temperatures.

It is useful to be able to extrapolate SO_2 solubilities to lower or higher gas partial pressures. It is, of course, not appropriate to assume that Henry's law will be obeyed. A method for describing data over a large range of partial pressure is very successfully handled using log scales for the partial pressure and mole fraction solubility as discussed in an earlier *Solubility Data Series* publication by Hayduk (*14*).

Henry's law expressed using log scales is as follows

$$p = hx_p \tag{1}$$

$$\log p = \log h + \log x_p \tag{2}$$

or

$$P = H + X \tag{3}$$

If Henry's law is obeyed, H is constant and P is directly proportional to X. Thus the slope of a graph of P versus X for a gas that obeys Henry's law will be unity. Extrapolations are usually relatively easy even for pressure intervals of factors of 10 or more when the form of the relationship is established. This relation is often linear even though Henry's law is not obeyed. We have arbitrarily defined an acid concentration in the fuming sulfuric acid region as a mole ratio of SO_3 to H_2SO_4 (Y), as shown in Figure 2. Some of the data of Miles and Carson were recalculated by using this concentration and are shown in Figure 2.

The solubility at 101.3 kPa pressure as a function of temperature is shown in Figure 3. Although some of the data, such as those of Milbauer, are shown directly, some of the lines are simply interpolations of the available data as obtained from Figure 2. If we compare Figure 2 with Figure 3, it may be observed that the SO_2 solubility values of Milbauer in 62.0% acid may be too low when compared with data of other workers. More particularly, the recently published results of Domka et al. (*8*) appear not to conform in magnitude or in slope to those of other workers, and for these reasons appear to be in significant error. A further comparison of additional data by Domka et al. for various SO_2 partial pressures again indicates serious discrepancies when compared with our work and that of Miles and Carson. Figure 3 shows a consistent pattern for SO_2 solubilities in various concentrations of acid, and in water, as a function of temperature.

Glossary

h	Henry's law constant, kPa/mole fraction
H	log h
p	partial pressure of gas, kPa
P	log p
T	absolute temperature, K
x	mole fraction dissolved gas at a gas partial pressure of 101.3 kPa: moles of SO_2/(moles of H_2SO_4 + moles of SO_2 + moles of water)
x_p	mole fraction dissolved gas at a gas partial pressure $p \neq 101.3$ kPa
X	log x_p
y	mole fraction H_2SO_4 in solvent solution
Y	concentration of dissolved SO_3 in fuming sulfuric acid; mole ratio, moles of SO_3/mole of H_2SO_4

Registry No. SO_2, 7446-09-5; H_2SO_4, 7664-93-9.

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Viscosities and Densities of Some Binary Liquid Mixtures of Esters at 303.15 and 313.15 K

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Viscosities and densities have been measured as a function of mole fraction at 303.15 and 313.15 K for binary liquid systems of benzene + *n*-propyl acetate and benzene + ethyl butyrate and carbon tetrachloride + *n*-propyl acetate, + *n*-butyl acetate, and + ethyl butyrate. The mixture viscosities were fitted to an empirical equation proposed by Katti and Chaudhri. It was found that the equation predicts the mixture viscosities reasonably well at both the temperatures and the agreement between the experimental and calculated viscosities is satisfactory.

Introduction

This investigation is a part of the authors research program (*1-5*) on the thermodynamic and transport properties of binary liquid mixtures of esters. Continued interest in the thermodynamic and transport properties of binary liquid mixtures containing esters (*6-9*) makes it desirable to study systematically the influence of esters and the chemical structure of the other component upon the viscosities. In addition, the present study of viscosities was undertaken to test further the validity of the Katti and Chaudhri equation at higher temperatures. As a contribution toward a more comprehensive description along these lines, we report in this paper the measurements of viscosities and densities for binary liquid mixtures of benzene + *n*-propyl acetate and benzene + ethyl butyrate and carbon tetrachloride + *n*-propyl acetate, + *n*-butyl acetate, and + ethyl butyrate at 303.15 and 315.15 K.

Experimental Section

Materials. The solvents benzene, carbon tetrachloride, and *n*-butyl acetate, all analytical grade (BDH), were purified as per the standard procedure given by Riddick and Bunger (*10*). *n*-Propyl acetate (Fluka AG) and ethyl butyrate (Fluka AG) with a reported purity of >99% were used without further treatment. *n*-Butyl acetate (AR, BDH) was dried and fractionally distilled. All the chemicals were distilled before use. Further the purities were checked by measuring their refractive indexes at 303.15 K (Table I).

Measurements. Densities were measured with a pycnometer having a bulb volume of about 20 cm^3 and internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 303.15 and 313.15 K with doubly distilled water and benzene. The temperature of the thermostat was maintained constant to within ±0.005 K at the desired value and

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