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Solubility of Dilute SO_2 in Dimethyl Sulfoxide

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The solubility of SO_2 in dimethyl sulfoxide has been determined from 293.15 K to 313.15 K and at partial pressures of SO_2 from 0.15 kPa to 2.62 kPa. A solubility model is proposed, and the solubilities calculated by the model show good agreement with experimental data.

1. Introduction

An area of major interest in recent years is the control of sulfur dioxide emissions from power plants and industrial plants. Flue gases frequently contain dilute sulfur dioxide, and it is necessary to remove these acidic components. Many of the processes involve the absorption of sulfur dioxide into an alkaline solution and a chemical reaction with an amine. An alternate purification process is physical absorption with polar organic solvents. Physical absorption with a polar solvent provides a convenient and economical method for removing acid gases. In designing an absorption system to purify flue gases, it is necessary to know the solubilities of SO_2 in the absorbing solvents, but the fundamental data which have been published for dimethyl sulfoxide (DMSO) are only over a limited range of temperature and partial pressures of SO_2.[1−3] The solubilities of SO_2 in DMSO determined by Benon[1] and Lenoir[2] are at 25 °C; the solubility data reported by Kurochkin[3] are at one partial pressure of SO_2. It is necessary to have solubility data over wide temperature and partial pressure of SO_2 ranges. This work reports solubility data suitable for possible absorption processes. In the present study, the solubilities of sulfur dioxide in DMSO at temperatures from 293.15 K to 313.15 K and partial pressures of SO_2 from 0.15 kPa to 2.62 kPa have been measured. A solubility model is proposed, and the solubilities that have been calculated by the model agree with the experimental data to within ±4%.

2. Experimental Section

2.1. Materials and Analysis Method. Dimethyl sulfoxide was AR grade, and its purity was greater than 99%. It was degassed under vacuum. Water was purified by vacuum distillation and deionzation. The dilute SO_2 mixture was prepared by mixing sulfur dioxide and nitrogen. The sulfur dioxide and nitrogen had the purities $x(SO_2) > 0.999$ and $x(N_2) > 0.99999$, respectively. A SO_2 analyzer with a SO_2 sensor (type NTS 100, Nanjing, China) was used for the SO_2 analysis (=0.5% SO_2) of the gas phase. The uncertainty of the SO_2 analyzer was ±10 ppm. More than 0.5% SO_2 concentration was analyzed by iodometry. The two methods were calibrated before measuring SO_2 concentration.

2.2. Solubility Measurement. The solubility of SO_2 in DMSO was measured using the apparatus shown in Figure 1.[4]

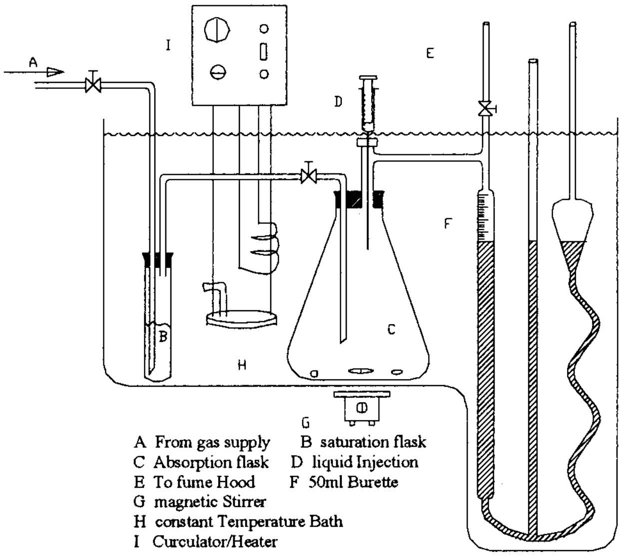

Figure 1. Solubility apparatus.

The principle for this method is to bring a known volume of liquid into contact with a gas in a closed system at a constant temperature and pressure. Equilibrium is reached by agitating the liquid for some time until no change in the volume of the gas is observed. The amount of gas absorbed is measured volumetrically; typical volumes were from 2 cm^3 to 40 cm^3, with an uncertainty of ±0.05 cm^3.

The procedure for making a solubility measurement is as follows. A gas saturated with the vapors of the absorbing liquid was passed through the system at a constant temperature long enough to completely purge the absorption flask. Then the inlet and outlet valves were closed. The height of the mercury in the three branches was leveled, ensuring that the pressure in the flask was atmospheric, and the position of the meniscus was recorded. An aliquot of degassed liquid that was kept at the same temperature of the experiments was weighed and injected into the absorption flask. The uncertainty of mass was ±0.000 01 g. The liquid sample was continuously agitated via an external magnetic stirrer. The height of the mercury in the three branches was leveled every few minutes to make sure that the gas phase was at atmospheric pressure. Equilibrium was reached when the height of the mercury in each branch was leveled and remained constant. The measured volume change was equal to the volume of liquid sample minus the volume of gas absorbed. The whole apparatus was kept at a constant temperature

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Table 1. Critical Properties, T_c and P_c, and Acentric Factors, ω, Used in the Equation of State

component	T_c/K	P_c/kPa	ω
SO_2	430.8[6]	7880[6]	0.256[6]
N_2	126.2[6]	3390[6]	0.039[6]
DMSO	707[7]	5850[7]	0.414[7]

Table 2. Binary Interaction Constants for the Modified Soave Equation, k_{ij}

system	k_{ij}	source	AAD %[a]
$SO_2 + N_2$	0.1628	this work	1.37
SO_2 + DMSO	0.0299	this work	
N_2 + DMSO	0.2831	this work	

[a] AAD % $= (100/n)\sum_{o=1}^{n} |(p_i^{\mathrm{exp}} - p_i^{\mathrm{calc}})/p_i^{\mathrm{exp}}|$; n = number of data points.

Table 3. Density, ρ, and Vapor Pressure of DMSO, P^S

expression	source	SD(ρ)[a]
$\rho/\mathrm{g{\cdot}cm^{-3}} = 1.1195 - 0.001(T/\mathrm{K} - 273.15)$	this work	0.000 99
$\lg P^S/\mathrm{kPa} = 25.62052 - 3539.32/(T/\mathrm{K}) - 6.00000 \lg(T/\mathrm{K})$	ref 9	

[a] SD(ρ) $= \{[\sum_{o=1}^{n}(p_i^{\mathrm{exp}} - p_i^{\mathrm{calc}})^2]/(n-1)\}^{1/2}$; n = number of data points.

Table 4. Comparison of Experimental Data for SO_2 Solubility in Water and Literature Data

T/K	S/mass %	S(lit.)[10]/mass %	$100(S - S(\mathrm{lit.}))/S$
293.15	10.15	9.61	5.32
298.15	8.61	8.33	3.25
303.15	7.24	7.23	0.14
308.15	6.11	6.10	0.16

inside a temperature-controlled bath. The uncertainty of temperature is ±0.05 K.

2.3. Data Reduction. The solubility of SO_2 and its equilibrium composition of the gas phase are calculated from material balance and equations of equilibrium for each component. Typically, there are two components in the system: (1) the gas phase, which includes SO_2, N_2, and solvent vapor, and (2) the liquid phase, which includes solvent and the dissolved sulfur dioxide.

The total moles in the gas phase in the cell (n_{inlet}/mol) can be calculated from the gas-phase analysis and modified SRK equations of state.[5]

The measured pure component constants are given in Table 1.[6,7]

The only parameter in the SRK equation that requires information other than the pure component data is k_{ij}. k_{ij} represents the interaction parameters. The optimum values of k_{ij} were determined by the least-squares method; the optimum values of k_{ij} and the quality of the fit are given in Table 2.

The inlet SO_2 moles in the gas phase in the cell ($n_{SO_2,1}$/mol) can be calculated from eq 1

$$n_{SO_2,1} = y_{SO_2,1} n_{\mathrm{inlet}} \tag{1}$$

where $y_{SO_2,1}$ is the inlet mole fraction of SO_2, which can be calculated from the inlet concentration of SO_2 in the gas phase, and n_{inlet} is the inlet total moles of components.

The volume of the SO_2 gas absorbed can be calculated from the measured volume change of the buret and the injected mass of the liquid sample. The moles of dissolved SO_2 ($n_{SO_2}/\mathrm{mol{\cdot}kg^{-1}}$) are calculated as follows:

$$n_{SO_2}/(\mathrm{mol{\cdot}kg^{-1}}) = \left(\frac{m/g}{1.1195 - 0.001(T/\mathrm{K} - 273.15)} - \Delta V/\mathrm{cm^3}\right)\rho_{SO_2}/(\mathrm{g{\cdot}dm^3})/(64m/g) \tag{2}$$

where n_{SO_2} is the SO_2 solubility, m represents the injected mass of the liquid sample, T is the absolute temperature, ΔV is the measured volume change of the buret, and ρ_{SO_2} represents the SO_2 density.

The equilibrium SO_2 moles in the gas phase ($n_{SO_2,2}$/mol) are equal to the inlet SO_2 moles minus the dissolved SO_2 moles.

$$n_{SO_2,2} = n_{SO_2,1} - n_{SO_2} c_1 \tag{3}$$

where $n_{SO_2,1}$ is the inlet SO_2 moles, n_{SO_2} is the SO_2 solubility in moles per kilogram, and C_1 is the unit conversion coefficient.

The equilibrium total moles in the gas phase (n/mol) can be calculated with eq 4

$$n = n_{\mathrm{inlet}} - n_{SO_2} c_1 \tag{4}$$

So the equilibrium mole fraction of SO_2 in the gas is

$$y_{SO_2} = \frac{n_{SO_2,2}}{n} \tag{5}$$

where y_{SO_2} is the equilibrium SO_2 mole fraction in the gas phase.

Since this study is concerned only with low pressures of SO_2, the fugacity coefficient for the gas is assumed to be equal to 1. So the equilibrium partial pressure of SO_2 (P_{SO_2}/kPa) is given as in eq 6

$$P_{SO_2} = y_{SO_2} P \tag{6}$$

where P represents the atmospheric pressure.

The densities of the pure solvent DMSO over the temperature range (293.15 to 343.15) K were determined using a 10 cm^3 gravity bottle with a specially made thermometer. The density was determined by mass using an analytical balance (type TG332A, China). The balance had a range of measurement up to 20 g with an accuracy of ±0.000 01 g. The temperature was controlled within ±0.05 K of the test temperature. These measurements were compared with data reported by Pacak.[8] Compared with the data of Pacak,[8] the standard deviation of the density was 0.000 99. The vapor pressure and density of the pure solvent as a function of temperature are listed in Table 3.[8,9]

2.4. Test of Apparatus. To ensure proper operation of the apparatus, the solubility of SO_2 in water was measured and compared with the values reported in the literature.[10] The experimental measurements agreed with the reported values with a mean relative deviation of 2.22%. The measured values are listed in Table 4.

3. Results and Discussion

3.1. Solubility of SO_2 in Dimethyl Sulfoxide. Solubility data are shown in Figure 2 and Table 5. In Table 5, $P^{\circ}_{SO_2}$/kPa is the inlet partial pressure of SO_2 in the gas phase. P_{SO_2}(cal)/kPa is the calculated partial pressure of

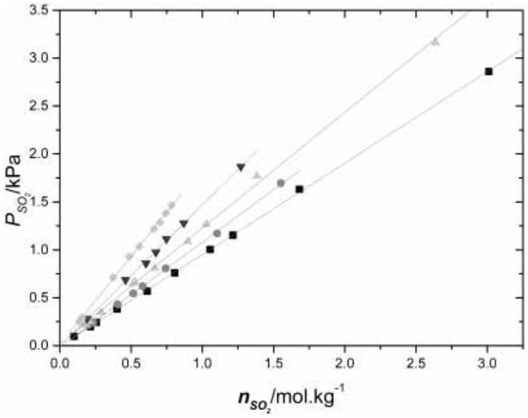

Figure 2. Phase equilibrium for (sulfur dioxide + DMSO) at low SO_2 concentration at different temperatures. Experimental data: ■, T/K = 293.15; ●, T/K = 298.15; ▲, T/K = 303.15; ▼, T/K = 308.15; ◆, T/K = 313.15; —, calculated.

Table 5. Solubility of SO_2 in DMSO at Different Temperatures

T K	n_{SO_2} mol·kg^{-1}	$P^{\circ}_{SO_2}$ kPa	P_{SO_2} kPa	H_i kPa·kg·mol^{-1}	P_{SO_2}(cal) kPa	rel dev %
293.33	0.216	0.337	0.197	0.914	0.203	−3.10
293.35	0.255	0.395	0.243	0.950	0.241	0.77
293.10	0.613	0.956	0.568	0.926	0.575	−1.31
293.45	0.806	1.25	0.759	0.942	0.761	−0.22
293.05	1.06	1.65	1.00	0.950	0.989	1.33
293.45	1.22	1.89	1.15	0.948	1.15	0.36
293.65	1.68	2.62	1.63	0.970	1.60	2.23
293.35	0.157	0.250	0.149	0.950	0.148	0.76
293.15	0.401	0.625	0.381	0.950	0.376	1.14
293.15	0.0996	0.155	0.0947	0.950	0.0936	1.15
298.55	0.202	0.341	0.216	1.07	0.214	0.93
297.95	0.235	0.395	0.240	1.02	0.246	−2.15
298.10	0.406	0.709	0.430	1.06	0.426	0.91
298.05	0.515	0.872	0.546	1.06	0.540	1.04
298.06	0.582	0.966	0.620	1.06	0.611	0.61
298.35	0.743	1.25	0.806	1.09	0.785	−0.61
298.35	1.10	1.89	1.17	1.06	1.17	0.24
298.35	1.55	2.62	1.69	1.09	1.64	−3.67
302.85	0.181	0.341	0.218	1.20	0.220	−0.95
303.05	0.207	0.394	0.254	1.23	0.252	0.69
303.05	0.291	0.546	0.348	1.20	0.355	−1.76
303.05	0.512	0.964	0.628	1.23	0.625	3.68
303.15	0.523	0.983	0.641	1.23	0.640	4.04
303.05	0.667	1.25	0.806	1.21	0.814	−0.95
303.05	0.898	1.691	1.09	1.21	1.10	−0.82
303.05	1.03	1.89	1.27	1.23	1.25	1.12
302.95	1.38	2.61	1.69	1.22	1.68	1.10
303.15	0.135	0.251	0.162	1.20	0.166	−2.07
308.25	0.190	0.394	0.279	1.47	0.282	−1.04
308.05	0.461	0.964	0.685	1.49	0.679	0.81
307.95	0.603	1.25	0.858	1.42	0.884	−3.08
308.05	0.674	1.43	0.974	1.45	0.992	−1.86
308.05	0.748	1.55	1.11	1.49	1.10	0.94
308.05	0.869	1.76	1.28	1.47	1.28	−0.23
308.00	1.27	2.62	1.87	1.47	1.87	−0.01
313.55	0.134	0.341	0.250	1.86	0.253	−1.28
313.05	0.153	0.393	0.289	1.90	0.281	3.11
313.15	0.373	0.964	0.710	1.90	0.690	2.84
313.20	0.487	1.26	0.929	1.91	0.903	2.79
313.05	0.557	1.43	1.03	1.86	1.03	0.91
313.05	0.659	1.68	1.22	1.85	1.21	0.54
313.05	0.702	1.77	1.28	1.83	1.29	−0.60
313.25	0.743	1.89	1.38	1.86	1.38	0.16
313.35	0.784	1.97	1.47	1.87	1.46	0.21

SO_2, and H_i is the corresponding proportionality constant, expressed as

$$H_i/(\text{kPa·kg·mol}^{-1}) = \frac{P_{SO_2}/\text{kPa}}{n_{SO_2}/(\text{mol·kg}^{-1})}$$

Table 6. Correlation Result of the Relation of the Equilibrium Partial Pressure of SO_2, P_{SO_2}, with the Molality of the Dissolved Sulfur Dioxide, n_{SO_2}

T K	H_i kPa.kg.mol^{-1}	SD(H_i)^a
293.15	0.9591	0.054 13
298.15	1.0787	0.057 22
303.15	1.2203	0.039 17
308.15	1.4661	0.046 57
313.15	1.8659	0.022 59

[a] SD(H_i) = $[\sum_{o=1}^{n}(H_i^{\text{exp}} - H_i^{\text{calc}})^2/(n-1)]^{1/2}$; n = number of data points.

Table 7. Correlation Result of the Relation between H_i and Temperature T

gas	a_i kPa·kg·mol^{-1}	b_i kPa·kg·mol^{-1}·K^{-1}	c_i kPa·kg·K·mol^{-1}
SO_2	−1027.32	154.58	43719.51
correlation coefficient	0.99716	0.9973	0.9989

3.2. Analysis and Discussion. (1) SO_2 Solubility at Different Partial Pressures. Since this study is concerned only with low partial pressures of SO_2, the fugacity coefficient for the gas is assumed to be equal to 1.0.

$$f_{SO_2} = y_{SO_2}\phi_{SO_2}P = y_{SO_2}P = P_{SO_2} = H_i n_{SO_2} \qquad (7)$$

It can be seen from Figure 2 that the curves of equilibrium partial pressure P_{SO_2} versus the dissolved sulfur dioxide concentration n_{SO_2} are linear, which indicates that the absorption of low amounts of SO_2 in DMSO obeys Henry's law.

Since the fugacity coefficient is equal to 1 in view of the low pressures, H_i is simply Henry's law constant.

The experimental H_i values of Table 5 are correlated with eq 7, and the standard deviations are less than 0.05722. The values of the parameter H_i in the correlation equation are presented in Table 6. The experimental H_i value at 298.15 K is 1.08 kPa·kg·mol^{-1}, compared with those of Benon[1] (0.840 kPa·kg·mol^{-1}) and Lenoir[2] (0.901 kPa·kg·mol^{-1}); the experimental data agree relatively well with literature values.

(2) Variation of Henry's Law Constant H_i and Temperature T. The relation of Henry's law constant H_i and temperature T can be expressed by the following semiempirical equation:[11]

$$\ln H_i/(\text{kPa·kg·mol}^{-1}) = a_i + b_i \ln T + c_i/T \qquad (8)$$

The experimental values of Table 5 are correlated with eq 8 using a least-squares criterion. The values of the parameters a_i, b_i, and c_i are presented in Table 7. The relation curve of Henry's law constant H_i and temperature T is shown in Figure 3.

(3) Correlation Model of SO_2 Solubility for a Dilute SO_2−DMSO System. According to gas−liquid-phase equilibrium theory, we use the above regressed parameters, which are obtained from experimental data, to predict the solubility of dilute SO_2 in the DMSO systems. The correlation model is shown in eq 9:

$$P_{SO_2}(\text{cal})/\text{kPa} = \exp(a_i + b_i \ln(T/\text{K}) + c_i/(T/\text{K}))n_{SO_2}/(\text{mol·kg}^{-1}) \qquad (9)$$

where a_i, b_i, and c_i are empirical constants and the values of these constants are listed in Table 7.

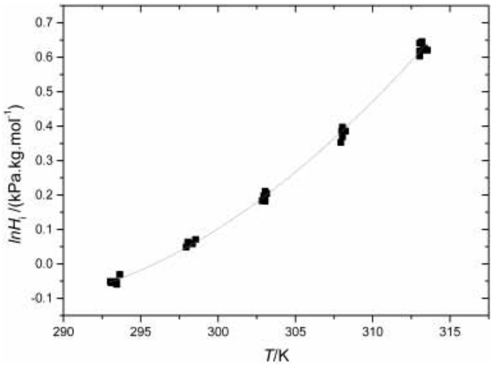

Figure 3. Relation of the coefficient of SO_2 solubility H_i/kPa·kg·mol^{-1} and temperature T/K: ■, experimental data of our own; —, calculated.

The equilibrium partial pressure calculated using eq 9, P_{SO_2}(cal), is listed in Table 5. The relative deviations are also listed in Table 5. Relative deviations are calculated according to eq 10.

$$\text{relative deviation (\%)} = \left(\frac{P_{SO_2} - P_{SO_2}(\text{cal})}{P_{SO_2}}\right) \times 100 \quad (10)$$

This model predicts the estimated values with less than 4% relative deviation. The excellent agreement between the measured and calculated partial pressures shows that the simple model is able to describe the gas–liquid equilibrium of (sulfur dioxide + DMSO) with sufficient accuracy.

4. Conclusions

(1) The solubility of dilute SO_2 in DMSO has been determined from 293.15 K to 313.15 K and at partial pressures of SO_2 from 0.15 kPa to 2.62 kPa with a suitable experimental method and solubility apparatus. The result shows there is great solubility for dilute SO_2 in DMSO, and the dissolving process of dilute SO_2 in DMSO obeys Henry's law.

(2) A solubility model based on gas–liquid-phase equilibrium principles is proposed. It appears the relative deviation among all these values does not exceed 4.04%, and the average relative deviation is 1.37%; the solubilities calculated by the model show good agreement with the experimental data.

(3) The experimental solubilities and correlation equation in this work can be used as essential data and as a model for process design of removal of SO_2 from flue gas.

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