Solubility and thermodynamic properties of sulfuryl fluoride in water

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A B S T R A C T

The solubility of sulfuryl fluoride in water was experimentally measured over the pressure from $P = (0$ to $600)$ kPa and $T = (283.15$ to $308.15)$ K using isochoric saturation method. Results show that SO_2F_2 solubility increases with increasing pressure and decreases with increasing temperature. Using the experimental solubility data, Henry's law constants and the thermodynamic properties such as the standard Gibbs free energy, enthalpy, and entropy changes of SO_2F_2 solvation were obtained. Henry's law constant based on mole fraction and molality of SO_2F_2 in water vary from $(432.21$ to $1052.96)$ MPa and $(7.78$ to $18.96)$ MPa at $T = (283.15$ to $308.15)$ K, respectively.

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1. Introduction

Sulfuryl fluoride (SO_2F_2), an alternative fumigant to methyl bromide (CH_3Br), has been widely used to fumigate the timber, buildings, construction materials, soils, vehicles, foods, *etc.* [1–5], owing to its several advantages, including easy dispersal on a structure, rapid penetration into materials, almost no residue formation, and ready dissipation after aeration [6]. However, the toxicity and greenhouse effect of sulfuryl fluoride has recently aroused much attention. SO_2F_2 gas is considered as an inhalation hazardous material, which can cause damage to human's central nervous system and inhalation system after long term exposure [7]. In addition, the atmospheric lifetime and global warming potentials (100 year time horizon, relative to carbon dioxide) of SO_2F_2 are approximately 36 years and 4780, respectively [8].

Since 1978 SO_2F_2 has been accumulated in the global atmosphere with a growth rate of $5 \pm 1\%$ per year [9]. The treatment of SO_2F_2 after fumigation has been investigated for reducing the concentration of SO_2F_2 in the atmosphere [10–12]. Especially, the chemical absorption of SO_2F_2 by aqueous NaOH solution is regarded as a promising method for the industrial treatment of SO_2F_2 after fumigation. Meanwhile, Henry's law constants in water are essential to the research of chemical absorption of SO_2F_2 by aqueous NaOH solution. However, the data on Henry's law constants of SO_2F_2 in water are lacked. Furthermore, little data on the solubility of SO_2F_2 in water are available for theoretical study on chemical's environmental and atmospheric loss processes [13].

In present paper, we reported the solubility of SO_2F_2 in water at $P = (0$ to $600)$ kPa and $T = (283.15$ to $308.15)$ K, since the fact that chemical absorption of SO_2F_2 by aqueous NaOH solution was usually performed at room temperature [11,12]. Furthermore, Henry's law constants at $T = (283.15$ to $308.15)$ K were calculated using the solubility data. The related thermodynamic property changes accompanying the dissolution were also presented.

2. Experimental section

2.1. Material

The specifications and sources of the chemicals used in this work are summarized in table 1.

2.2. Apparatus and procedure

Since the fact that SO_2F_2 is slightly soluble in water without hydrolysis in neutral and acidic conditions [14], SO_2F_2 solubility determination was performed using isochoric saturation method [15]. The stainless steel apparatus is illustrated in figure 1. The details of the experimental method for the measurement of gas solubility were previously presented and are briefly described here [16,17]. The steel stainless apparatus consists of a gas equilibrium cell (EC, 10) with a magnetic stirrer, a gas reservoir (GR, 5) and pressure transmitters (6, 11). The volumes of the EC and GR were 141.61 and 370.99 cm³, respectively. During the experimental procedure, the EC and GR were immersed in two separated temperature-constant water-baths. The weight of water in the EC was measured using an electronic balance (Mettler–Toledo

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TABLE 1
Specifications and sources of chemicals used in this work.

Chemical name	Molecular formula	CAS no.	Molecular weight $M/(g \cdot mole^{-1})$	Purity	Source
Sulfuryl flouride	SO_2F_2	2699-79-8	102.06	0.999[a]	Hangzhou Maoyu Electronic Chemicals
Water	H_2O	7732-18-5	18.02		Distilled in laboratory

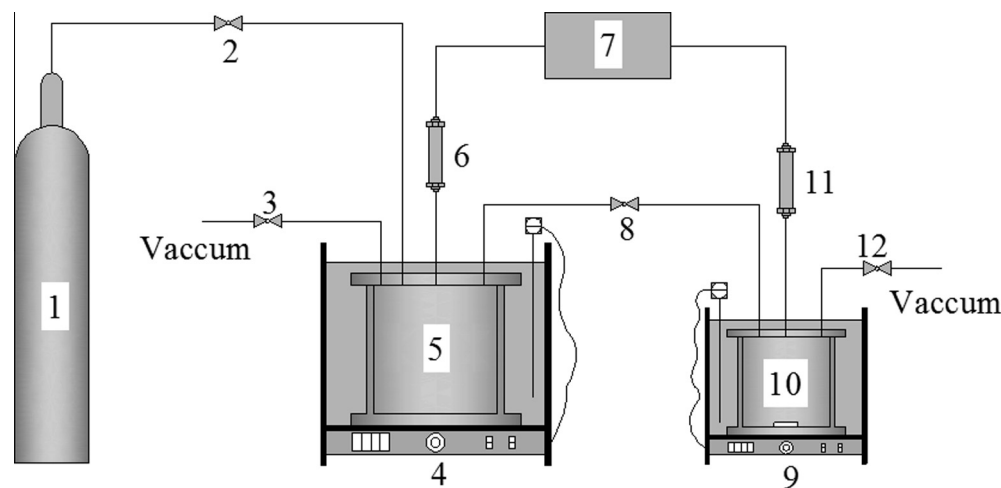[a] Mass fraction purity (as stated by the supplier).

FIGURE 1. The schematic diagram of the SO_2F_2 solubility apparatus 1 – SO_2F_2 cylinder; 2, 3, 8, 12 – stainless steel valve; 4, 9 – temperature-constant water-bath; 5 – gas reservoir; 6, 11 – pressure transmitter; 7 – pressure monitor; 10 – gas equilibrium cell.

AL204) with the uncertainty of ±0.0002 g. The pressure was monitored using a pressure transmitter (Fujian WIDEPLUS Precision Instruments Co., Ltd, WIDEPLUS-8, (0 to 600) kPa, with the accuracy of 0.1% full scale).

The total number of moles of SO_2F_2 gas injected into the gas equilibrium cell was calculated using the procedure adopted by Park and Sandall [18] and Jenab et al. [19]:

$$n_b = \frac{V_{GR}}{RT_a}\left(\frac{P_{a1}}{Z_{a1}} - \frac{P_{a2}}{Z_{a2}}\right) \qquad (1)$$

where V_{GR} denotes the volume of the gas reservoir, R is the universal gas constant, Z_{a1} and Z_{a2} are the compressibility factors corresponding to the initial and final pressures, P_{a1} and P_{a2}, respectively, in the gas reservoir before and after transferring gas, and T_a is the temperature of water bath, which is equal to that of the gas reservoir. Compressibility factors were calculated using the Soave–Redlich–Kwong (SRK) equation of state. Equilibration between liquid and vapor phases inside the gas equilibrium cell was reached after the pressure of the system being constant for 2 h, and the partial pressure of SO_2F_2 at equilibrium in the gas equilibrium cell, P_b^e, was calculated as follows:

$$P_b^e = P_T - P_R \qquad (2)$$

where P_T and P_R denote the total pressure at equilibrium and residual pressure at the beginning of experiment, respectively. However, the residual pressure must be subtracted from the total pressure to obtain the equilibrium partial of SO_2F_2. The gas phase volume, V_g, was calculated as follows:

$$V_g = V_{EC} - V_w = V_{EC} - \frac{m_w}{\rho_w} \qquad (3)$$

where V_{EC} denotes the volume of the gas equilibrium cell, V_w is the volume of water in the gas equilibrium cell, m_w and ρ_w are the weight and density of water in the gas equilibrium cell, respec-

tively. The density of water was obtained from the National Institute of Standards and Technology (NIST) database [20]. The mole number of remaining SO_2F_2 gas in the gas phase, n_b^g, was determined using the following equation:

$$n_b^g = \frac{V_g P_b^e}{Z_b R T_b} \qquad (4)$$

where T_b is the equilibrium temperature of the gas equilibrium cell, Z_b is the compressibility factor of SO_2F_2 gas at temperature T_b and pressure P_b^e. The number of moles of SO_2F_2 in the liquid phase, n_b^l, was then determined as follows:

$$n_b^l = n_b - n_b^g \qquad (5)$$

The molality and mole fraction of the loaded SO_2F_2 in the liquid phase were defined as

$$m_b = 10^3 \frac{n_b^l}{m_w} \qquad (6)$$

$$x_b = \frac{n_b^l}{n_b^l + \frac{m_w}{M_w}} \qquad (7)$$

where M_w is molecular weight of water.

The parameters of SO_2F_2 used in SRK equation of state to calculate compressibility factors and fugacity coefficients are listed in table 2 [7].

2.3. The Soave–Redlich–Kwong (SRK) cubic equation of state

For a pure substance the SRK equation of state expressed in pressure [21] is

$$P = \frac{RT}{\upsilon - b} - \frac{a(T,\omega)}{\upsilon(\upsilon + b)} \qquad (8)$$