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Solubility of dilute sulfur dioxide in binary mixtures of ethylene glycol and tetraethylene glycol dimethyl ether

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ABSTRACT

Solubility data of dilute SO_2 in binary mixtures of ethylene glycol (EG) and tetraethylene glycol dimethyl ether (TEGDME) were measured by the isothermal gas–liquid equilibrium experiments at temperatures ranging from 293.15 K to 313.15 K with SO_2 partial pressure below 120 Pa. The results show that the solubility of SO_2 increases with the increasing mass fraction of TEGDME in the mixtures. When the mass fraction of TEGDME is up to 80.00%, the mixture exhibits the greatest solubility. Henry's law constants (H'), enthalpy changes (ΔH), entropy changes (ΔS) and Gibbs free energies (ΔG) of the absorption processes were also calculated. According to the obtained thermodynamic parameters, the absorption processes are physical absorptions, which obey Henry's law within the investigated SO_2 partial pressure region. Furthermore, the addition of TEGDME shows significant improvement over pure EG in absorption solubility, and the mixtures after SO_2 absorption can be regenerated by heating and N_2 bubbling. The binary mixtures have a potential application in SO_2 removal.

1. Introduction

Sulfur dioxide (SO_2), one of the most significant contaminants, is the main causes of several environment problems, *e.g.*, acid rain, polluted rivers, corroded architectures, and human health problems. Especially, it plays an important role in the formation of particulate matters 2.5 (PM 2.5), which has spread across China in the past few years [1,2]. Nowadays, the control of SO_2 emission has become a serious problem.

The most effective way to control the SO_2 in flue gas emitted from combustion of fossil fuels is flue gas desulfurization (FGD). The conventional flue–gas desulfurization (FGD) technique is based on limestone. However, there are some inherent drawbacks, such as high capital investment and operating cost, useless byproducts ($CaSO_4$ and $CaSO_3$), and waste water [3,4]. Considering that SO_2 is a kind of useful chemical material, regeneration of the SO_2 after absorption is desirable. Thus, organic solvents [5,6], ionic liquids (ILs) [7–11], and SO_2-binding organic liquids [12–14], which can be regenerated by reducing pressure or increasing temperature, turn to be alternatives to the conventional method.

Due to the favorable absorption and desorption properties of acid gases and their excellent fluid properties, organic solvents, including alcohols, amines, amides, sulfoxides, and ethers, have caught the attention of researchers for many years [4,6,15–28]. Ethylene glycol (EG) and its aqueous solutions are considered to be a kind of promising absorbent for SO_2 because of their advantages such as reversible absorption, low price, and non-toxic. Our previous work demonstrated that the absorption of SO_2 in EG is a physical absorption process, so the absorbent can be regenerated by either reducing pressure or increasing temperature [29,30]. However, the absorption capacities of dilute SO_2 in pure EG and its aqueous solutions are rather low, so an improvement is still required. Tetraethylene glycol dimethyl ether (TEGDME) is a polar solvent which has been applied in acid gases removal [19,28]. To the best of our knowledge, few solubility data of SO_2 in pure TEGDME and binary mixtures of EG and TEGDME can be found in literature.

In this work, we determined the solubilities of SO_2 in EG, TEGDME and their mixtures at temperatures from 293.15 K to 313.15 K under a constant pressure of 122.7 K to investigate the effect of the mixture composition on SO_2 absorption. In addition, further thermodynamic parameters, including Henry's law constants (H'), enthalpy changes (ΔH), entropy changes (ΔS) and Gibbs free energies (ΔG), were also calculated to investigate the mechanism of the absorption processes.

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2. Experimental

2.1. Materials

Ethylene glycol (EG) and tetraethylene glycol dimethyl ether (TEGDME) were purchased from Beijing Yili Fine Chemical Co., Ltd. and Alfa Aesar, respectively. All reagents were obtained in the highest purity grade possible, and directly used as received without further purification. (see Table 1) The standard dilute gas of SO_2 in N_2 ($\Phi_{SO_2} = 8 \times 10^{-3}$) employed in determination of gas–liquid equilibrium data of EG and TEGDME mixtures was supplied by Beijing Gas Center, Peking University. Chromatographic grade ethanol and distilled water were also used in present work.

Binary mixtures of EG and TEGDME were prepared by mass using an analytic balance (Sartorius BS 224S), of which the uncertainty is 0.0001 g. The uncertainty for each binary mixture is less than 0.01% in mass fraction.

2.2. Determination of SO_2 solubility in binary mixtures

Solubilities of dilute SO_2 in binary mixtures were obtained by determination of gas–liquid equilibrium data with a dynamic analytic method. Apparatus and process for the determination were identical to our previous report [31]. The gas phase (SO_2/N_2) was recycled in the absorption bottle by the gas circulatory pump in order to achieve the gas–liquid equilibrium. The SO_2 concentration in gas phase was determined by using an Agilent GC equipped with a 2 m × 3.2 mm Porapak Q packed column and an FPD detector. A calibration curve was detected with an external standard method to confirm the relationship between the concentration of SO_2 and the response value of GC. The calibration results showed that GC method presented high stability with the relative uncertainty of 1.0%. The SO_2 concentration in liquid phase was determined with indirect iodometric titration. The relative uncertainty of SO_2 molarity in the liquid phase was estimated to be 0.6%. During the experiment process, the system temperatures were controlled by a thermostatic bath and determined by a standard thermometer with an uncertainty of 0.01 K. System total pressures were inspected by a meter with accuracy of 0.1 kPa. All experiments were conducted at a constant pressure of 122.7 kPa, and for each mixture with a certain component, the gas–liquid equilibrium data were determined at temperatures ranging from 293.15 K to 313.15 K.

3. Results and discussion

3.1. Solubility of SO_2

All GLE data of SO_2 in binary mixtures were listed in Table 2 and plotted in Figs. 1–5 at different temperatures. In Table 2, w_1 is mass fraction of TEGDME in the mixture, p_{SO_2} is the partial pressure of SO_2 in GLE system, and C_{SO_2} denotes the molarity of SO_2 in the liquid phase.

As shown in Figs. 1–5, the solubility plots are similar to those in literature [32]. The results show that the solubility of SO_2 in each mixture increases linearly with the partial pressure of SO_2 in gas phase, which indicates that the absorptions of SO_2 in EG, TEGDME and their mixtures are typical physical processes under the investigated SO_2 partial pressure. After the absorption of SO_2, desorption experiment of the binary mixture with TEGDME mass fraction equal to 80.00% was conducted by bubbling N_2 at 80 °C with a constant flow of 200 mL/min, and the solvent can be totally regenerated in 30 min. (see Fig. 6) It means that the absorption process is reversible, and the mixture can be reused.

Furthermore, we can see from the figures that the solubility of SO_2 in pure EG is lower than pure TEGDME, and solubilities in different mixtures increase with the mass fraction of TEGDME. However, when the mass fraction of TGEDME is 80.00% (mole fraction of TEGDME is about 53%), the solubility of SO_2 is significantly greater than pure TEGDME, and the mixture exhibits the best absorption performance. It demonstrates that the addition of TEGDME to EG is beneficial for improving its absorption performance to absorb SO_2.

According to the literature, absorption of SO_2 by alcohols and ethers attributes to the interactions between S atom (in SO_2) and O atom (in alcohols or ethers), where the alcohols or ethers work as a Lewis base [9]. When EG and TEGDME are mixed together, the original hydrogen bond in pure EG is destroyed, and a new hydrogen bond appears by the interaction between hydroxyl groups in EG and the oxygen atoms in TEGDME. As a result, when the mole ratio of EG and TEGDME is equal to 1:1, a new supermolecule system is formed in the mixture, and the formed structure may have a stronger Lewis basicity. However, a further spectroscopy investigation of the mechanism is still needed.

3.2. Henry's law constant

For a physical absorption system, concentrations of SO_2 in gas phase and liquid phase obey Henry's law. Here, we take gas–liquid equilibrium data of mixture with the TEGDME mass fraction equal to 80.00% as an example. It can be seen in Fig. 7 that the curves of partial pressure of SO_2 (p_{SO_2}) *versus* the SO_2 concentration in liquid phase are linear, which indicates that the absorption processes of dilute SO_2 in TEGDME+ EG mixtures obeys Henry's law. Then, Henry's law constants were calculated by the following equations [33,34]

$$H_x(T,p) = \lim_{C_{SO_2}\to 0} \frac{f^L_{SO_2}(T,p)}{C_{SO_2}} = \lim_{C_{SO_2}\to 0} \frac{p\phi_{SO_2}(T,p)}{C_{SO_2}} \approx \frac{P_e}{C_{SO_2}} \quad (1)$$

where $H_x(T, p)$ is Henry's law constant based on the molarity, C_{SO_2} is the concentration of SO_2 in the liquid phase, $f^L_{SO_2}$ is the fugacity of SO_2, φ_{SO_2} is the fugacity coefficient, and p_e is the pressure of SO_2 at equilibrium. For a physical absorption process, Henry's law constants can be obtained by calculating the linear slope.

Table 1
Chemicals employed in the experiments.

Chemical used	Source	Purity (%)	Basis for purity
Ethylene glycol	Beijing Yili Fine Chemical Co., Ltd.	>99.0	Mass percent
Tetraethylene glycol dimethyl ether	Alfa Aesar	>98.0	Mass percent
$Na_2S_2O_3$	Sinopharm Chemical Reagent Co., Ltd.	>99.0	Mass percent
I_2	Sinopharm Chemical Reagent Co., Ltd.	>95.0	Mass percent
SO_2 gas[a]	Beijing Gas Center, Peking University	–	–
N_2 gas	Beijing Gas Center, Peking University	99.99	Volume percent

[a] SO_2 gas employed in present work is diluted by N_2 with the volume fraction of SO_2 equal to 0.8%.