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Solubility Properties and Spectral Characterization of Sulfur Dioxide in Ethylene Glycol Derivatives

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Solubilities of SO_2 in ethylene glycol derivatives were determined by dynamic isothermal gas-liquid equilibrium (GLE) experiments, and the thermodynamic parameters of the absorption processes were calculated. The GLE results indicated that the solubilities of SO_2 in ethylene glycol derivatives increase in the order: diols < monomethyl ethers < dimethyl ethers, with the enthalpy values ranging from –23.2 to –43.3 kJ/mol. The regeneration experiment found that the absorption of SO_2 in tetraethylene glycol dimethyl ether is reversible, and the solvents can be reused without a significant loss of absorption capacity. The interactions between SO_2 and ethylene glycol derivatives were investigated by UV, IR and NMR. In addition, a ^{1}H-NMR spectroscopy technique with external references was used to investigate the physical absorption process of SO_2 for the first time, in order to avoid the influence of deuterated solvents. Spectroscopic investigations showed that the interactions between SO_2 and ethylene glycol derivatives are based on both the charge-transfer interaction and hydrogen bond. Ethylene glycol derivatives with desirable absorption capacities and excellent regeneration abilities are promising alternatives to conventional sorbents in SO_2 separation.

1. Introduction

Sulfur dioxide (SO_2), mainly emitted from the combustion of fossil fuels, has been one of the most important air pollutions, which causes serious damage to the environment and human health.[1] Hence, the removal of SO_2 from flue gas has become a global concern. The conventional technology widely used over the past decades is limestone scrubbing.[2] However, it still has some drawbacks, including irreversible process, low efficiency and production of useless byproducts like waste water and $CaSO_4$. Accordingly, new sorbents which can absorb SO_2 efficiently, reversibly and selectively are still needed.

Due to their excellent properties, such as negligible vapor pressure, wide liquid temperature range, high thermal stability and tunable structure, ionic liquids have been broadly studied in absorption of SO_2.[3, 4] In 2004, 1,1,3,3-tetramethylguandinium lactate [TMG][L] was first noted for SO_2 removal, and the result showed that the ionic liquid can absorb about 1 mole SO_2 per mole IL at 1 bar with 8% SO_2 in gas phase.[5] Later, numerous ILs based on guanidinium,[6, 7] alkanolaminium,[8, 9] imidazolium,[10-12] pyridinium[13] and phosphonium[14] have been synthesized and applied in the SO_2 removal. Recently, ether-functionalized [15-21] and anion-functionalized task-specific ionic liquids [22-24] were discovered to improve the SO_2 absorption capacity, which is attributed to the multiple binding sites for SO_2 in the functionalized molecules. Nevertheless, the industrial applications of ionic liquids have been limited by their high expenses and viscosities.

High-boiling solvents with low vapor pressures and proper viscosities are valuable solvents for flue gas desulfurization. In previous work, solubilities of SO_2 in ethylene glycol and poly (ethylene glycol) have been determined, and the absorption mechanism was discussed.[25-28] However, as far as we know, few comparisons of the absorption capacity and interaction mechanism have been made among ethylene glycol derivatives. Besides that, an efficient way to explore the interactions between SO_2 and the solvents in the physical absorption process is still in demand.

In the work, solubilities of sulfur dioxide in ethylene glycol derivatives were determined by isothermal gas-liquid equilibrium experiment at the temperature ranging from 293.15 to 313.15 K, and a constant total pressure of 122.7 kPa. Thermodynamic parameters were calculated based on the GLE data to investigate the absorption processes. Desorption experiments were also conducted to study the regeneration property. In addition, UV and IR spectra of SO_2 in ethylene glycol derivates were recorded to study the interaction between SO_2 and solvents by comparing the spectral changes with the polarity of solvents. In conventional ^{1}H-NMR experiments, deuterated reagents are mixed with samples as the internal references, so the chemical absorption processes of SO_2 can be analyzed according to the chemical shifts of hydrogen atoms. However, the polar deuterated solvents (d^6-DMSO, $CDCl_3$, etc.) affect the physical absorption processes obviously because of their significant absorptions of acid gases. Here, we introduce a ^{1}H-NMR spectroscopy method with external references, which is employed in the investigation of interaction between SO_2 and physical sorbents for the first time.

2. Experimental section

2.1. Materials

Ethylene glycol derivatives, including ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), ethylene glycol monomethyl ether (EGME), diethylene glycol monomethyl ether (DEGME), ethylene glycol dimethyl ether (EGDME), diethylene glycol dimethyl ether (DEGDME), triethylene glycol dimethyl ether (TriEGDME), and tetraethylene glycol dimethyl ether (TetraEGDME), were selected in the study. TriEGDME and TetraEGDME were purchased from Tokyo Chemcal Industry CO. Ltd. and Alfa Aesar, respectively, while the other reagents were from Sinopharm Chemical Reagent Co. Ltd. All reagents were obtained in the highest purity grade possible, and directly used as received without further purification. Chromatographic grade Ethanol and distilled water were also used in this work. A certified standard gas SO_2 in N_2 ($\Phi_{SO2}=8\times10^{-3}$), supplied by Beijing Gas Center, Peking University (China), were employed to determine the GLE data of dilute SO_2 in ethylene glycol derivatives.

2.2. Solubility Measurements

Solubility data of dilute SO_2 in ethylene glycol derivatives were measured by isothermal gas-liquid equilibrium experiments at the temperature ranging from 293.15 K to 313.15 K and a constant total pressure of 122.7 kPa. The experimental instrument and process, including data process, were identical to the literature.[29, 30]

Measuring temperature was kept constant by a circulation water bath with ± 0.01 K uncertainty. The system pressure was determined by a pressure gauge with an accuracy of ± 0.1 kPa. The relative uncertainty of SO_2 concentration in the liquid phase was estimated to be ± 0.6%. The mass of samples were determined with an analytical balance (Sartorius BS 224S), and the uncertainty is ±0.0001 g.

2.3. Desorption Experiment

Desorption experiment, which was conducted to investigate the regeneration property of tetraethylene glycol dimethyl ether, was carried out by bubling N_2 gas in flow rate of 200 mL/min through the sample absorbed SO_2 (5 mL) at 343.15 K. The concentrations of SO_2 in liquid phase before and after desorption were determined with the iodometric method.

2.4. Spectral Measurements

Spectrometric methods, including UV, IR and ^{1}H-NMR, were used to investigate the mechanism of interactions between SO_2 and ethylene glycol derivatives. UV-vis spectra were acquired with a UV-vis spectroscopy (UV 2401PC Shimadzu). The IR spectra were recorded on a Bruker Vector 22 FT-IR spectrophotometer, in which a typical thin film method was performed at ambient condition, with the wavenumber ranging from 400 cm^{-1} to 4000 cm^{-1} and a resolution of 1 cm^{-1}. A 500 MHz Bruker Avance III spectrometer was used to conduct the ^{1}H-NMR experiments. The NMR experiments were performed with both of the internal and external references. For internal references, the sample was mixed in d^6-DMSO or $CDCl_3$. For external references, the samples and deuterated reagents were injected into capillary tubes (25 cm × 0.9 mm) and NMR tubes (17.8 cm × 5 mm), respectively. Then the capillary tube was inserted into the NMR tube to separate the samples from the solvents (deuterated regents).

3. Results and discussion

3.1. Solubility Data

A series of gas-liquid equilibrium (GLE) data of dilute SO_2 in ethylene glycol derivatives were measured, and the results are listed in Table S1 (in ESI†). In the table, C_{SO2} and p_{SO2} denote the concentration of SO_2 in liquid and the partial pressure of SO_2 in gas phase, respectively.

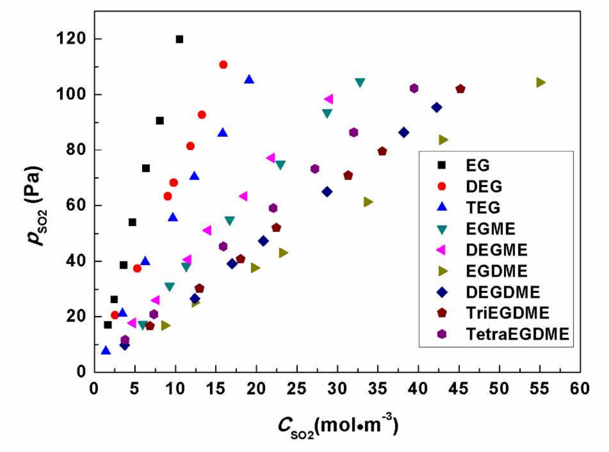


Fig. 1 Solubility plots of dilute sulfur dioxide in ethylene glycol derivatives at 293.15 K and 122.7 kPa.

The GLE data of SO_2 in ethylene glycol derivatives at 293.15 K are plotted in Fig. 1, with the partial pressure of SO_2 in gas phase ranging from 0 to 130 Pa. (Figures of GLE data at other temperatures are shown from Fig. S1 to Fig. S4 in ESI†) It displays that the partial pressure of SO_2 in gas phase is proportional to the concentration of SO_2 in liquid within the range of investigated partial pressure. And the linear extrapolation curves pass through the zero point for all ethylene glycol derivatives, which demonstrates that the absorptions of SO_2 in these solvents are typical physical processes and obey the Henry's law. In Figure 1, it's obvious that the solubilities of SO_2 in these solvents increase in the order: EG < DEG < TEG < DEGME < EGME < TetraEGDME < TriEGDME < DEGDME < EGDME. According to the results, we can divide these solvents into three categories: diols, monomethyl ethers and dimethyl ethers, and the solubility is improved *via* the substitution of hydroxyl group by methoxy group and the increasing numbers of ethylene glycol monomer (for diols and monomethyl ethers), which is consistent with the previous results of EG and PEG in literature.[26, 27] As a conclusion, ethers show better absorption abilities than alcohols.

Dimroth and Reichardt have proposed a parameter, $E_T(30)$, to estimate the solvent polarity based on the transition energy for the absorption band of Reachardt's dye. [31] The $E_T(30)$ values of EG, DEG, TEG, EGME, TriEGDME, DEGDME and EGDME are 56.3, 53.8, 52.8, 52.0, 38.9, 38.6 and 38.2 kcal/mol, respectively, which means the polarity decreases in the order. However, the solubilities of SO_2 in ethylene glycol derivatives are opposite to the changing trend of polarity. As a consequence, dipole-dipole interaction is not the mean factor of the absorption process, and hydrogen-bond and charge-transfer interaction should be taken into consideration.

3.2. Thermodynamical model

GLE data of dilute SO_2 in pure EGDME at different temperatures are plotted in Fig. 2 as an example to investigate the absorption property changing with the temperature, and the results are fitted linearly at each temperature. It indicated that the solubility of SO_2 in EGDME decreases with the increasing temperatures, which means heating can be used as an efficient method for the regeneration of solvents.

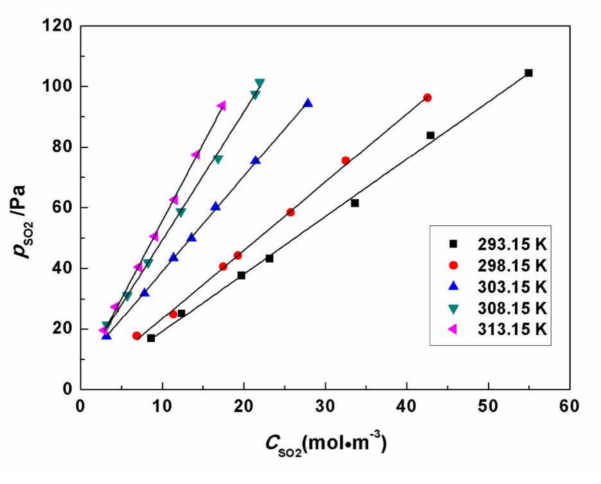


Fig. 2 Solubility curves of dilute sulfur dioxide in EGDME at temperatures ranging from 293.15 K to 313.15 K and a constant pressure of 122.7 kPa.

Considering that the absorptions of SO_2 in ethylene glycol derivatives are typical physical processes as mentioned above, Henry's law constant (H'), Gibbs free energy (ΔG), enthalpy changes (ΔH) and entropy changes (ΔS) were calculated based on the GLE data with the data treatment method in literature.[30] (See Table S2 in ESI†) All thermodynamic parameters are listed in Table 1. It demonstrates that the absorptions are exothermic and enthalpy driving at investigated condition. The values of enthalpy are between -20 kJ/mol and -45 kJ/mol, and increase in the order: diols < monomethyl ethers < dimethyl ethers, which are consistence with the solubility results. As in literature[28], the absorption process of SO_2 in EG or PEG is based on both of the charge-transfer interaction and hydrogen bonding. The entire process can be divided into two steps: first, the absorption of SO_2 induces the deposition of intermolecular hydrogen bond in pure EG or PEG; then SO_2 molecules interact with EG or PEG molecules. Comparing the enthalpy of SO_2 absorbed in diethers with in diols, it indicates that the existence of hydrogen bond (or hydroxyl group) is unfavorable for the absorption, mainly owing to the deposition energy of hydrogen bonds in the first step. *At the temperature of 293.15 K.

Table 1 Thermodynamic parameters of dilute SO_2 absorbed in ethylene glycol derivatives at the pressure of 122.7 kPa

	ΔG/kJ·mol^{-1} *	ΔH/kJ·mol^{-1}	ΔS/J·mol^{-1}·K^{-1}
EG	-13.0	-33.1	-68.6
DEG	-14.3	-23.2	-29.9
TEG	-14.9	-23.3	-28.3
EGME	-16.2	-32.1	-55.4
DMGME	-16.0	-34.9	-64.2
EGDME	-17.5	-37.3	-67.5
DEGDME	-17.0	-43.3	-89.4
TriEGDME	-17.1	-38.8	-74.1
TetraEGDME	-16.7	-34.7	-61.7

*At the temperature of 293.15 K.

3.3. Desorption Result

After the absorption of SO_2, desorption of the high-boiling EG derivative, TetraEGDME, was conducted by heating and N_2 bubbling. The desorption result shows that the 100% SO_2 molecules can be regenerated in 30 min under the given condition, which means that the SO_2 absorbed can be recycled, and the solvent can be reused. To evaluate the recyclability of the solvent, five cycles of absorption and desorption were conducted with the regenerated solvent without further purification. (see Fig. S5 in ESI†) The result demonstrates that the solvent shows favorable recyclability, and is a promising alternative in industrial.

3.4 UV Spectroscopy Analyses

Absorption spectra of SO_2 absorbed in ethylene glycol derivatives were measured. For each spectrum, solvents with increasing concentrations of SO_2 absorbed were detected, with the pure solvent as a reference. Since it's difficult to measure the SO_2 absorption spectrum in gas phase, a spectrum of SO_2 in n-C_6H_{14} was measured instead, working as a reference to investigate the spectral changes caused by physical intermolecular interactions between SO_2 and polar ethylene glycol derivatives.

Absorptions of SO_2 in n-C_6H_{14} and typical ethylene glycol derivatives were shown in Fig. 3. Two characteristic absorption bands are observed, which belong to the electronic transition of $\pi \rightarrow \pi^*$ for SO_2 or $n \rightarrow \sigma^*$ for oxygen atom in derivatives (shorter wavelength band) and $n \rightarrow \pi^*$ for SO_2 (longer wavelength band), and the intensities of both the bands increase with the concentration of SO_2. The position of shorter wavelength band moves to long wavelength with the increasing concentrations of SO_2, which is more significant when the ratio of hydroxyl group goes up in the derivative. It's attribute to the bathochromic shift of $n \rightarrow \sigma^*$transition with the formation of hydrogen bond between sulfur dioxide and hydroxyl group in diols.[32, 33]

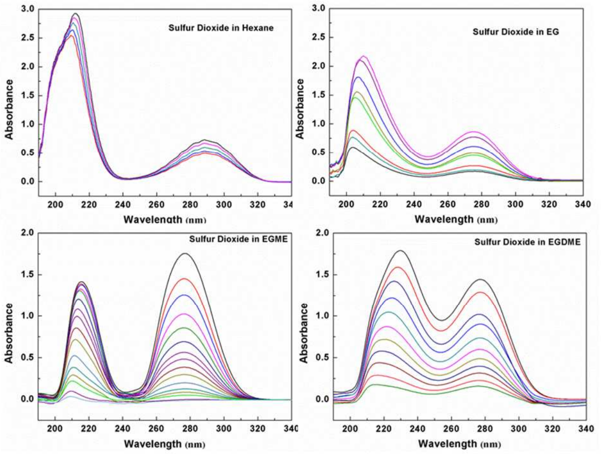
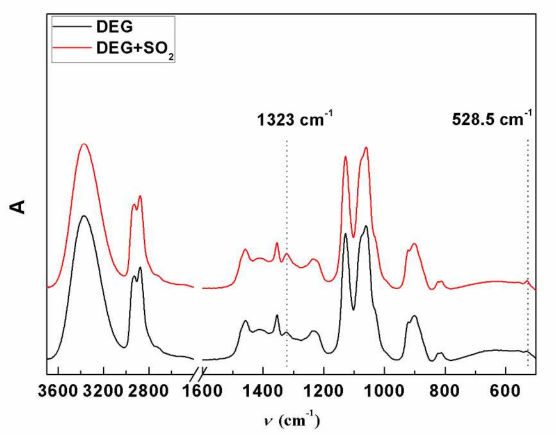


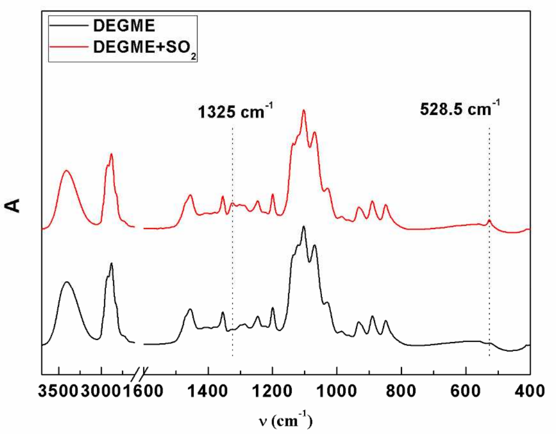
Fig. 3 UV spectra of SO_2 in hexane, EG, EGME and EGDME with different concentrations of SO_2.

In contrast to the apolar solvents (n-C_6H_{14}), relative band intensity of $n \rightarrow \pi^*$ absorption band to $\pi \rightarrow \pi^*$ absorption band increases significantly as the polarity of solvent increases, which obeys the Ham effect.[34] Meanwhile, the position of $n \rightarrow \pi^*$ absorption band moves to a shorter wavelength in ethylene glycol derivatives, and the wavelengths of EG, EGME, EGDME, n-C_6H_{14} are 275 nm, 276.5 nm, 277 nm and 288.5 nm, respectively, which is consistence with the $E_T(30)$ values measured by Reichardt's dye (56.3, 52.0, 38.2, and 31.0 kcal/mol).[35] For $n \rightarrow \pi^*$ absorption band, the interaction between sulfur atoms in SO_2 and oxygen atoms in derivatives promotes to the stabilization of n nonbonding orbital rather than π^* antibonding orbital. In addition, hydroxyl group are capable of the hydrogen bond formation, lowing the energy of n orbital.[36] Both of the effects cause the hypochromatic shift. As a result, charge-transfer interaction and hydrogen bonding exist in the solutions of SO_2 in ethylene glycol derivatives.

3.5 IR Analysis

IR spectra of SO_2 in ethylene glycol derivatives were recorded to investigate the interactions, and typical spectra are shown in Fig. 4. As in literature,[37] liquid SO_2 has three fundamental vibrational frequencies: 1361.76 cm^{-1}, 1151.38 cm^{-1} and 517.69 cm^{-1}, which is attribute to asymmetrical stretching vibration ($\bar{\nu}_{as}$), symmetrical stretching vibration($\bar{\nu}_s$) and bending vibration(γ), respectively.[37] As shown in figures, the asymmetrical stretching vibrations and bending vibrations of SO_2 in each solvent can be seen obviously, while symmetrical stretching vibrations in some solvents are covered by the stretching vibrations of C-O-C. According to the results, bending vibration wavenumbers of SO_2 in ethylene glycol derivations increase with the solvent polarity increasing (from 527 cm^{-1} in ethers to 528.5 cm^{-1} in diols), in contrast, asymmetrical stretching vibration wavenumbers decreases (from 1327 cm^{-1} in ethers to 1323 cm^{-1} in diols), as a result of the charge-transfer interaction and hydrogen bond between SO_2 and the derivatives, conforming to the vibration shift rule in polar solvents.[38]





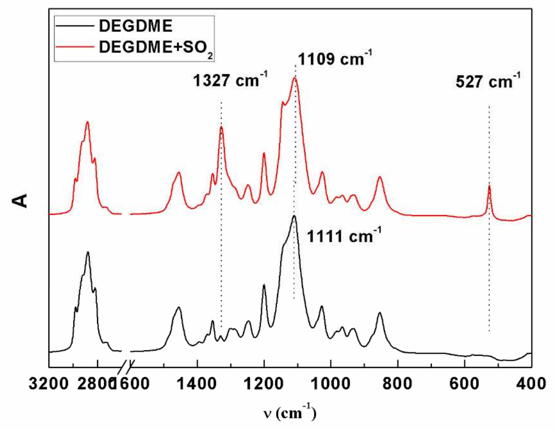


Fig. 4 IR spectra of DEG, DEGME and DEGDME before and after SO_2 absorption.

In addition, stretching vibration wavenumbers of C-O and O-H are constant in diols or monomethyl ethers before and after SO_2 absorption, which demonstrates that the absorption process of SO_2 absorbed in these solvents is the deformation of hydrogen bond in solvents, and the formation of intermolecular hydrogen bond between SO_2 and alcohols. However, the stretching vibration of C-O in ethylene glycol dimethyl ethers moves to lower wavenumbers after SO_2 absorption, which is in agreement with the mechanism of charge-transfer interaction between SO_2 and ethers.

3.6. NMR Analysis

NMR experiments were conducted to investigate the absorption mechanism of SO_2 in ethylene glycol derivatives, with deuterate regents as both internal and external references. The ^{1}H-NMR spectra of TriEGDME before and after SO_2 absorption are shown in Fig. 5. Compared the internal reference method before and after SO_2 absorption, no significant chemical shift is observed, indicating that the absorption is a physical process without the formation of new compounds. For pure TriEGDME, the chemical shifts of ^{1}H-NMR signals move upfield with an external reference. Meanwhile, the chemical shift for each hydrogen atom moves to a noticeable lower field after SO_2 absorption with an external reference. Buckingham[39] have suggested that apart from the electronic distribution in the molecule, the chemical shift δ of H atoms is still influenced by several factors:

$$\Delta\delta = \delta_{\mathrm{obsd}} - \delta_0 = \delta_{\mathrm{b}} + \delta_{\mathrm{a}} + \delta_{\mathrm{w}} + \delta_{\mathrm{e}} + \delta_{\mathrm{s}}$$

where δ_{b} is caused by the bulk magnetic susceptibility differences between the sample and reference; δ_{a} is derived from anisotropy of the molecular magnetic susceptibility of the solvent molecules; δ_{w} is based on the dispersion interaction between solutes and solvents; δ_{e} represents the polar effect caused by dipolar solute molecule; and δ_{s} is the specific interaction like hydrogen bonding and charge transfer between solutes and solvents.

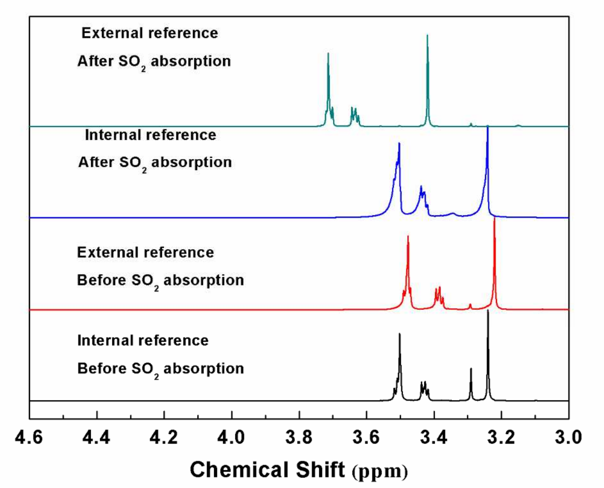
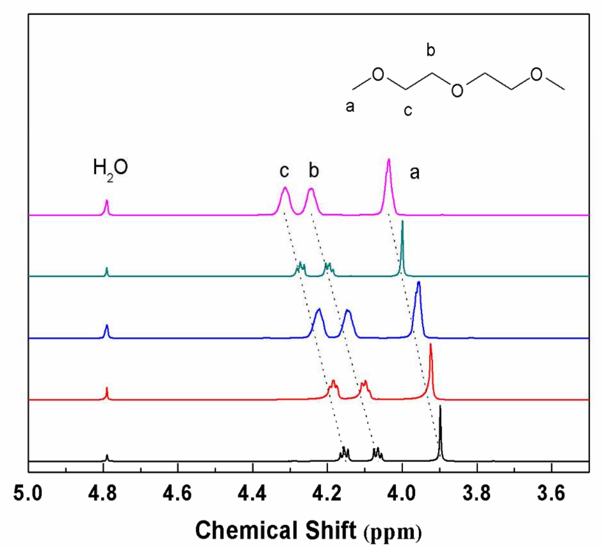


Fig. 5 The ^{1}H-NMR spectra of TriEGDME with internal and external references before and after SO_2 absorption. (d^6-DMSO as references)

According to the equation, the differences of pure TriEGDME chemical shifts between internal and external references methods are based on both of the shape of the sample and dipole-dipole interaction between TriEGDME and d^6-DMSO. For TriEGDME with the external reference method before and after SO_2 absorption, the charge-transfer interaction between SO_2 and TriEGDME induces the chemical shift moving highfield, theoretically. However, SO_2 molecule with a Π_3^4 bond induces a significant downfield movement by the aromatic ring current effect, just like the aromatic solvent-induced shift (ASIS) of benzene, which is the mean factor of the results here. [40]



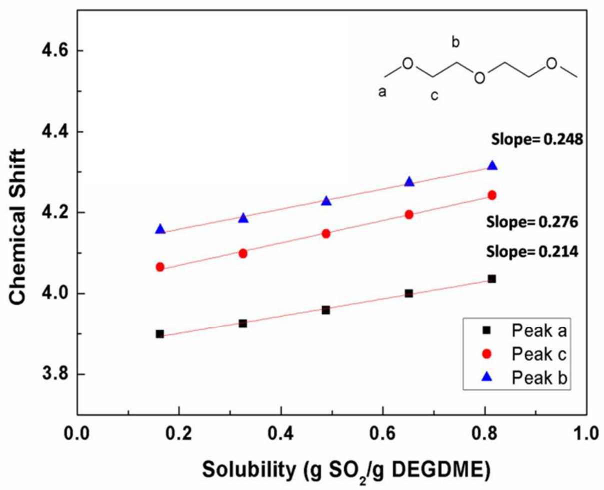


Fig. 6 The ^{1}H-NMR spectra and chemical shifts changes of DEGDME with different concentrations of SO_2 absorbed. (D_2O as an external reference)

^{1}H-NMR spectroscopy experiments of DEGDME with different concentrations of SO_2 were also conducted with D_2O as a reference, and the spectra were shown in Fig. 6. When the concentration of SO_2 increases, the NMR signals of all hydrogen atoms shift downfield with respect to the position of pure DEGDME. What's more, the chemical shifts is proportional to the SO_2 concentration as shown in Fig. 6, so ^{1}H-NMR is a promising method to the determination of SO_2 concentrations in solvents.

The charge-transfer interaction between n-butyl ether and SO_2 was also studied by ^{1}H-NMR spectroscopy with external references. The SO_2-induced chemical shift changes of all hydrogen atoms in n-butyl ether (NBE) were calculated, and it demonstrates that the changes of chemical shifts are consistent with the distance between the hydrogen atoms and the oxygen atom, which interacts with the sulfur atom in SO_2. Above all, the effect of charge-transfer interaction between sulfur dioxide and ethylene glycol diethers has been proven, and the chemical shift changes of hydrogen atoms in carbon atomic chains can be used as an indicator to investigate the binding sites of SO_2 in ethylene glycol derivatives.

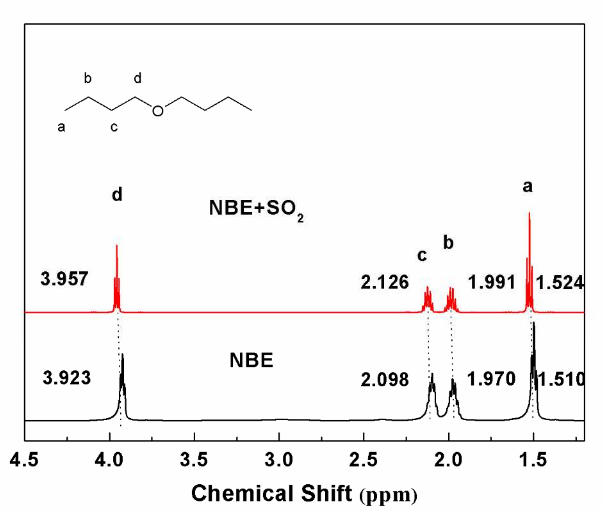


Fig. 7 ^{1}H-NMR spectra of n-butyl ether before and after SO_2 absorption. (D_2O as an external reference)

According to the ^{1}H-NMR spectra of DEGDME absorbed SO_2, the chemical shift changes per unit SO_2 concentration (g SO_2/ g solvent) of three hydrogen atoms are 0.214, 0.248 and 0.276, as the positions from the end to the center. It demonstrates that the interaction between sulfur atom in SO_2 and the oxygen atom in the center oxygen atom in DEGDME. Another illustrative example is the interaction between SO_2 and DEG, and the spectra were shown in Figure 8. The chemical shift changes ($\Delta\delta$) of hydrogen atoms are 0.099 (hydroxyl), 0.188 and 0.183. It means sulfur atoms in SO_2 prefer to interact with the central oxygen atom, which is consistent with DEGDME.

The applications of ^{13}C-NMR with external references were also taken into consideration. Compared the chemical shifts of DEGDME before and after SO_2 absorption, the positions have a slight shift to a higher field due to the decrease of electron-withdrawing ability for ether groups, caused by the charge-transfer interaction. (see Fig. S6 in ESI†)Considering that the chemical shifts in ^{13}C-NMR cover a larger range, the influence of ASIS in ^{13}C-NMR is not a significant factor as in ^{1}H-NMR.

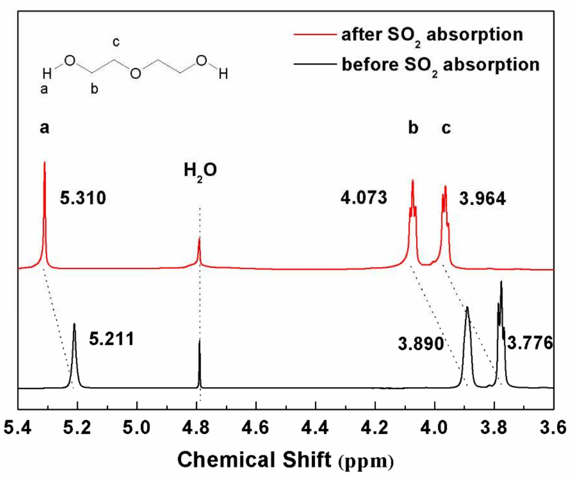


Fig. 8 ^{1}H-NMR spectra of DEG before and after SO_2 absorption. (D_2O as an external reference)

4. Conclusions

Solubilities of SO_2 in ethylene glycol derivatives were determined by a dynamic isothermal gas-liquid equilibrium (GLE) experiment at the temperatures ranging from 293.15 K to 313.15 K and a constant pressure of 122.7 kPa. Thermodynamic parameters of the absorption process were calculated based on the GLE data. The GLE results indicate that the absorption properties of ethylene glycol derivatives increase in the order: diol < monomethyl ether < dimethyl ether, with the enthalpy values of the absorption process ranging from –23.2 to –43.3 kJ/mol. The regeneration experiments found that the absorption of SO_2 is reversible, and the solvents can be reused without a significant loss of absorption capacity for at least 5 recycles.

The interactions between SO_2 and derivatives were investigated by spectroscopy experiments including UV, IR and NMR techniques. Particularly, a novel ^{1}H-NMR method with external references was employed in this work. Spectroscopic investigation showed that the interaction between SO_2 and ethylene glycol derivatives is based on charge-transfer interaction between sulfur atoms (SO_2) and oxygen atoms (–O–), and the hydrogen bond formed between sulfur dioxide and hydroxyl. Thus, the ethylene glycol derivatives with desirable absorption capacities and excellent regeneration abilities are promising alternatives to conventional sorbents in SO_2 separation. More importantly, the ^{1}H-NMR spectroscopy with external references has a potential application in the investigation of physical interactions between acid gases and solvents.

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Notes and references

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Table of Contents

Solubility Properties and Spectral Characterization of Sulfur Dioxide in Ethylene Glycol Derivatives

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NMR with external references is applied in the mechanism study of sulfur dioxide absorption