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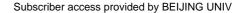
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Hydrogen Bonding and Interaction in the Absorption Processes of Sulfur Dioxide in Ethylene Glycol + Water Binary Desulfurization System

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In this work, ethylene glycol (EG) (1) + water (2) solutions (EGWs) were used as the promising medium for the absorption and desorption processes of SO_2 . Desorption data showed that SO_2 can be desorbed easily from EGWs + SO_2 at 333 K. $\Phi_1 = 70-90\%$ (volume fraction of EG in EGWs) were considered as reasonable compositions of desulfurization solution. Considering the industrial flue gas desulfurization (FGD) processes, $\Phi_1 = 80\%$ EGW (approximately 0.5 molar fraction of EG) was confirmed as the optimum composition of desulfurization solution. When conventional UV, FTIR, and 1H NMR spectroscopic techniques were used for inspection of spectral changes of SO_2 in EGWs, the spectral results suggest that SO_2 can interact with EG by hydrogen bonds.

1. Introduction

Sulfur dioxide (SO₂) is an important atmospheric pollutant, and therefore it is severe in environmental protection. The main source is flue gas from the burning of fuels with high sulfur content from 0.03 mg·m⁻³ in the air up to several g·m⁻³ in a typical flue gas. The removal of SO₂ from flue gas is an increasingly important environmental challenge. The reasons are the governmentally controlled lowering of the admissible emission limit and the numerous desulfurization processes which produce large volumes of solid waste, like the limestone scrubbing process. In recent years, there has been a growing interest in the use of organic solvents for SO₂ removal, and organic solvents used as absorbents have been identified as an option among the regenerative process²⁻⁶ because regeneration can be done by pressure reduction, by temperature increase, and by use of a carrier gas. Of the numerous organic solvents, alcohols show favorable absorption and desorption capabilities for acid gases in industrial processes;⁷ therefore, our research group has paid great attention to the alcohol + water system for SO_2 removal for several years. $^{8-11}$

Ethylene glycol (EG) is an important industrial solvent, which has been used in the absorption experiments in our previous works $^{10-12}$ because of its favorable properties, such as low vapor pressure, low toxicity, low viscosity, and low melting point. EG presents native hydrogen bonding sites that the potential desorption characters present in the regenerative processes of solutions dissolving SO_2 .

FTIR spectroscopy and UV-vis spectroscopy are very successful methods to probe the molecular structure of association effects among molecules, since the FTIR spectroscopy gives precise information about water sensitive bonds ^{13,14} and the UV spectroscopy gives important information about various electronic transitions. Generally, FTIR spectral technique ^{15,16} and UV spectroscopic technique offer the advantages to measure the association properties and hydrogen bonding capability and to assess interaction of alcohol with water by analyzing band

shifts and changes of band shape. Furthermore, FTIR is also advantageous to evaluate the vibrational properties of bonds through very thin solution films, which are usually difficult to handle for the floating properties of solution.

In a recent work, 12 $\Phi_1 = 70-90\%$ EGWs showed the strongest solubility for SO₂. The present work was mainly focused on showing the desorption results of SO₂ in various EGWs + SO₂ and investigating the hydrogen bonding and interaction of EG with SO₂ by conventional UV, FTIR, and 1 H NMR spectroscopic techniques.

2. Experimental Section

The certified standard mixture ($SO_2 + N_2$, $\Phi_{SO_2} = 1.97 \times 10^{-3}$) was purchased from the Standard Things Center (Beijing, China). EG ($\geq 99.4\%$) was purified from Beijing Chemical Plant (EG, A.R. $\geq 98.0\%$, Beijing, China) dehydrated by Na_2SO_4 and refined by rectification. Bi-distilled water was used. The apparatus used in this work was based on a dynamic analytic method and shown in our pervious work. ¹¹

FTIR spectra were recorded on a Bruker VECTOR22 FTIR spectrometer with a resolution of 1 cm⁻¹ at 298 K in the range from 4000 cm⁻¹ to 400 cm⁻¹. The spectrometer possesses autoalign energy optimization and a dynamically aligned interferometer and was fitted with a constringent BaSO₄ pellet for the measurement of aqueous solution, an OPUS/IR operator, and IR source. A baseline correction was made for the spectra that were recorded in air; then 20 μ L solution was used on the FTIR spectrometer in every one of the measurements, and the thin layer of samples was less than typically 2 μ m thickness. UV spectra were recorded using a Varian CARY 1E UV-vis spectrometer with a resolution of 0.2 nm at room temperature in the region of 190-900 nm. A baseline correction was made for the spectra recorded in deionized water. The ¹H NMR spectrum was recorded using a Bruker ARX-400 nuclear magnetic resonance instrument, and (CH₃)₂SO (DMSO) was used as an NMR solvent. All spectral experiments of EG + SO₂ + water were performed at normal temperature and pressure.

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3. Results and Discussion

3.1. Desorption Data of EGWs + SO_2 . The desorption runs were carried out using EGWs dissolving SO_2 , preheated to 333.15 K, and stirred by an agitator at atmospheric pressure for 20 min (Table 1). The table presents the $\Phi_1 = 80\%$ and $\Phi_1 = 70\%$ EGWs exhibit stronger capability to release SO_2 .

Our previous work¹² showed that $\Phi_1 = 70-90\%$ EGWs exhibit stronger capabilities to dissolve SO2. The result gave us important information to optimize the composition of EGWs for the SO₂ absorption and desorption processes. In industrial operations, flue gas has a large quantity of energy as well as high relative humidity. If $\Phi_1 = 80\%$ is used in the industrial processes, the high energy in the flue gas will vaporize part of the water from EGW so that the Φ_1 moves toward 90%. The process does not affect the EGW's absorption and desorption properties toward SO_2 because the Φ_1 of 90% has a strong capacity to absorb and release SO2. On the contrary, the high relative humidity of the flue gas will make the Φ_1 move toward 70%, which still has a high capacity to absorb and release SO₂. Meanwhile, we find that there exists a correlation between those two important macroscopic properties and surface activity behavior and viscosity properties of EGWs. For supporting the above results, the viscosities and surface tension of EGWs were determined at various temperatures and atmospheric pressure (see Supporting Information). Experimental results show that $\Phi_1 = 80\%$ EGW owns more reasonable surface tension and lower viscosity than pure EG.

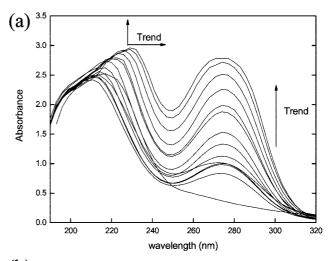
The result analyses of the absorption processes, the desorption processes, the viscosity and surface tension data, and the industrial operational analyses show that the $\Phi_1=80\%$ EGW (approximately 0.5 molar fraction of EG) can be used as the optimum composition of solution for the SO_2 absorption and desorption processes. The strong absorption and desorption capacity of EGWs toward SO_2 can be due to the hydrogen bonding and interaction between EG and SO_2 , so conventional UV, FTIR, and 1H NMR spectroscopic techniques were used to explore the interaction among molecules in the this work.

3.2. UV Spectral Properties of EGW and EGW + SO₂. The previous results 12 show that $\Phi_1 = 80\%$ EGW exhibits stronger capacity to absorb SO₂ than pure EG and pure water. If dissolved SO₂ molecules are hydrolyzed to form HSO₃ and polythionic acids, they will display higher absorption rate and lower desorption rate for SO₂, but $\Phi_1 = 80\%$ EGW dissolving SO₂ shows high desorption rate at 333 K (Table 1). The interaction between EGW and SO₂, which is related with the hydrogen bonding and interactions among molecules, plays a more important role in the absorption and desorption processes. Therefore, UV spectral properties of absorption processes of SO₂ in EG (Figure 1a) and $\Phi_1 = 80\%$ EGW (Figure 1b) were determined to discuss the interaction among EG, water, and SO₂. $\Phi_1 = 80\%$ EGW + SO₂ and EG + SO₂ was prepared in the previous gas liquid equilibrium (GLE) study. 12

In Figure 1, the characteristic bands of EG and SO_2 were respectively identified in UV spectra, but no information on a complexing reaction could be obtained. In Figure 1a, with increasing SO_2 concentration, the absorption band of $n \to \pi^*$ electron transition of oxygen atom in SO_2 (Π_3^4) is observed at 274 nm, and the absorption intensity of the band increases. The special absorption band shifts from 211 to 229 nm, and the absorption intensity increases. The special band was mainly

Table 1. Desorption Data of EGWs Dissolving SO_2 at 333.15 K for 20 min

volume percent of EG, %	100	90	80	70	60	50	40	20	0
desorption rate in 20 min. %	95	83	91	91	85	86	82	80	82



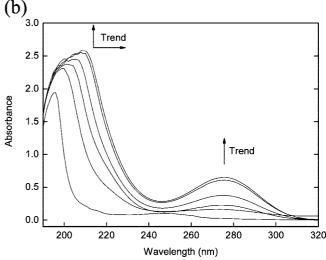


Figure 1. Absorption spectral changes of EG + SO₂ (a) and Φ_1 =80% EGW + SO₂ (b).

related to the $\pi \to \pi^*$ electron transition of SO₂ (Π_3^4) and n $\to \sigma^*$ electron transition of the oxygen atom in EG. The shift can be due to the addition of SO₂, which destroys the original hydrogen bonding and interaction among EG molecules and forms the new hydrogen bonding and interaction of hydroxyl hydrogen atoms in EG with oxygen atoms in SO₂.

In Figure 1b, with increasing SO₂ concentration, the absorption band of $n \to \pi^*$ electron transition of oxygen atom in SO₂ is observed at 275 nm and the absorption intensity of the band increases. Meanwhile, the special absorption band red shifts from 196 to 208 nm, and the absorption intensity of electron transition increases also. The absorption wavelength, which is lower than EG + SO₂ system, is due to the hydrogen bonding and interaction of EG with water.¹⁷ The red shift in the wavelength ranging from 196 to 208 nm is due to the addition of SO₂, which affects the hydrogen bonding and interaction of EG and water in EGW and forms the new hydrogen bonds of hydroxyl hydrogen atoms in EG with oxygen atoms in SO₂. The results show that $\pi \to \pi^*$ electron transition of SO₂ and n $\rightarrow \sigma^*$ electron transition of oxygen atom in EG become more difficult in $\Phi_1 = 80\%$ EGW than in pure EG. In the other words, there was stronger interaction between EG and SO₂ so that higher absorption capacity of SO_2 in $\Phi_1 = 80\%$ EGW was observed.

The above results suggest the hydrogen bonding and interaction between hydrogen atoms in EG molecules and oxygen atoms in SO₂ molecules occurred. When such hydrogen bonds

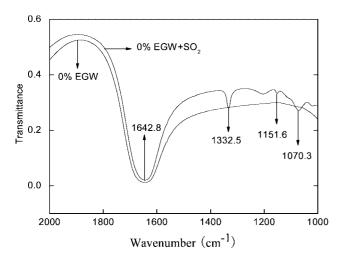


Figure 2. FTIR spectra of water $+ SO_2$ and water.

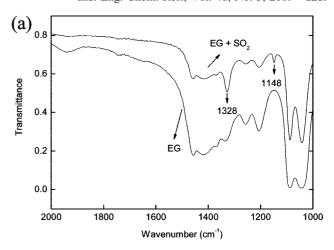
are formed, hydroxyl hydrogen atoms in the EG molecules are attracted by the oxygen atoms in SO₂ and the bond length between hydrogen atom and oxygen atom in EG molecules is elongated. In this situation, the $\pi \to \pi^*$ electron transition of SO₂ and n $\to \sigma^*$ electron transition of the oxygen atom in EG occur more easily, so red shift phenomena occurred.

3.3. FTIR Spectral Properties of EG and EGW + SO₂. The recorded IR spectra of water + SO₂ and water are shown in Figure 2. From the spectra three stretching bands are observed at 1332 cm⁻¹, 1151 cm⁻¹, and 1070 cm⁻¹. The two absorption peaks at 1332 cm⁻¹ and 1151 cm⁻¹, which are reported at 1344 cm⁻¹ and 1145 cm⁻¹ for SO₂ in noncomplexing CCl₄, ¹⁸ can be attributed to the V_{as} and V_{s} of SO₂ because the IR and Raman spectra indicate the following values for the fundamental frequencies: $V_{s} = 1151.38$ cm⁻¹, $\delta = 517.69$ cm⁻¹, and $V_{as} = 1361.76$ cm⁻¹. The band at 1070 cm⁻¹ can be attributed to the stretching band of S=O in sulfite. The spectra suggested that sulfurous acid was formed when water was used to absorb SO₂.

The recorded IR spectra of $EG + SO_2$ and EG are shown in Figure 3. From Figure 3a two stretching bands at 1328 cm⁻¹ and 1148 cm⁻¹ were observed. From Figure 3b an interesting phenomenon was displayed. In the absence of SO_2 , the stretching vibrational band of hydroxyl in EG was observed at the range of 3600-3000 cm⁻¹,and the band was broad. In the presence of SO_2 , the band was changed into the peaky band. The phenomenon could be due to the addition of SO_2 which destroys the original hydrogen bonding and interaction among EG molecules and forms the new hydrogen bonding and interaction of hydroxyl hydrogen atoms in EG with oxygen atoms in SO_2 .

The recorded IR spectra of $\Phi_1 = 80\%$ EGW + SO₂ and $\Phi_1 = 80\%$ EGW are shown in Figure 4. From Figure 4a two stretching bands at 1330 cm⁻¹ and 1149 cm⁻¹ were observed. No the stretching band of S=O was observed in the spectrum. From Figure 4b, in the absence of SO₂, the stretching vibrational band of hydroxyl in EG was observed in the range of 3600-3000 cm⁻¹ and the band was broad; in the presence of SO₂, the band was changed into the peaky band. The phenomenon can be due to the new hydrogen bonding and interaction of hydroxyl hydrogen atoms in EG with oxygen atoms in SO₂.

The SO_2 molecule is known to be polar and the sulfur atom to be electropositive; thus, SO_2 behaves as an electron acceptor by the sulfur atom, and its interaction with EG should occur with the hydrogen of the hydroxyl group. Such an interaction should decrease the double bond character of SO_2 and so induce a lower absorption frequency, as is observed. From the FTIR spectral results recorded on the aqueous solution, one can



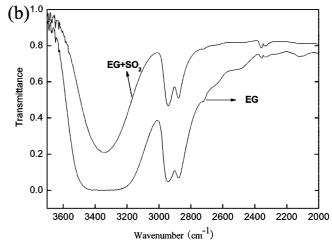
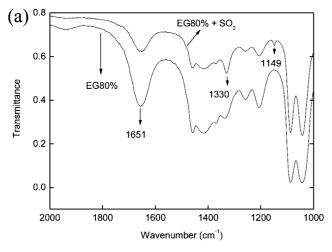


Figure 3. FTIR spectra of EG + SO₂ and EG in the range of 1600-650 cm⁻¹ (a) and the range of 3700-2000 cm⁻¹ (b).

suppose that the EG–SO $_2$ complex is the less stable one, as suggested by its lower downshifted frequency and its stronger desorption capacity. Such a shift observed in FTIR spectra was attributed to the interactions of EG with SO $_2$. Comparing the spectra of $\Phi_1=80\%$ EGW + SO $_2$ and $\Phi_1=80\%$ EGW, it is observed that the H–O–H bending band and the characteristic bands of EG are not obviously shifted in the mixture under the influence of SO $_2$ (Figure 4a). The constant H–O–H bending band in the absorption processes of SO $_2$ is mainly due to the hydrogen interaction of EG and SO $_2$ rather than the reaction of water and SO $_2$.

3.4. ¹H NMR Spectral Properties of EG and EG + SO₂. The ¹H NMR spectral results of EG in the presence and absence of SO₂ are showed in Figure 5a,b.

Figure 5a shows that the chemical shifts of hydrogen in $-\text{CH}_2-$ appear at $\delta=3.390$ ppm, 3.396 ppm, 3.397 ppm, and 3.403 ppm (4H), and the chemical shift of hydrogen in -OH appears at $\delta=4.461$ ppm, 4.466 ppm, 4.470 ppm, 4.475 ppm, 4.480 ppm, 4.483 ppm, and 4.489 ppm (2H) in the ^1H NMR spectrum of pure EG. In the presence of SO₂, however, this appears at $\delta=3.406$ ppm (4H) and 4.500 ppm (2H) in Figure 5b. Meanwhile, the coupling ways of two kind of hydrogen disappeared, and only two chemical shift peaks were displayed. Because the bond length of O-H in EG molecules becomes longer and the electron cloud of hydrogen atoms in EG molecules becomes thinner, the chemical shift of hydrogen atoms in -OH group shifts from $\delta=4.461-4.489$ ppm to 4.500 ppm and the chemical shift of hydrogen atoms in $-\text{CH}_2$ — shifts from $\delta=3.390-3.403$ ppm to 3.406 ppm in DMSO. The results



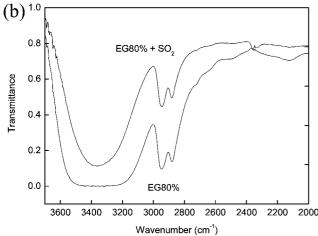


Figure 4. FTIR spectra of $\Phi_1 = 80\%$ EGW + SO₂ and $\Phi_1 = 80\%$ EGW in the range of 1800-1000 cm⁻¹ (a) and 3700-2000 cm⁻¹ (b).

show that there is hydrogen bonding and interaction between EG and SO_2 so that the shielding effect from oxygen atoms of SO_2 makes the signal move to a lower magnetic field.

According to overall results, it is expected that hydrogen bonding and interaction among molecules is formed as \cdots HO-CH₂CH₂O-H \cdots OSO \cdots . The hydrogen bonding and interaction makes the desorption of SO₂ from EGW occur easier. The hydrogen bonding and interaction of SO₂ with EG is very useful to desorb SO₂ from EGWs by pressure reduction, by temperature rise, and by use of a carrier gas.

4. Conclusion

In this work, the $\Phi_1=80\%$ EGW was confirmed as the optimum composition of desulfurization solution, and the corresponding desorption efficiency of SO₂ in $\Phi_1=80\%$ EGW + SO₂ arrived at 91%. EGW presents native hydrogen bonding sites for the absorption of SO₂ so that the absorption and desorption properties of SO₂ in EGWs^{18,19} can be related to hydrogen bonding and interaction^{20,21} among molecules. The spectral analyses suggest that SO₂ can interact with EG by hydrogen bonds as ···HO-CH₂CH₂O-H···OSO··· and SO₂ can be desorbed easily from EGW.

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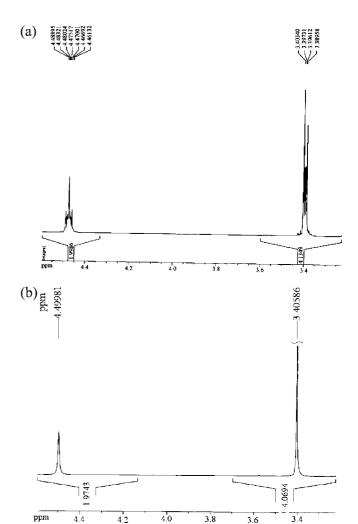


Figure 5. ¹H NMR spectra of EG in the presence and absence of SO₂ (a) presents ¹H NMR spectra of EG + SO₂ and (b) presents ¹H NMR spectra of EG.

China) for their suggestions on the hydrogen bonding mechanism of EG with SO₂.

Supporting Information Available: Surface tension properties of EGWs and viscosity properties of EGWs. This material is available free of charge via the Internet at http://pubs.acs.org.

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