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Spectroscopic study on the intermolecular interaction of SO_2 absorption in poly-ethylene glycol+H_2O systems

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Abstract−Poly-Ethylene Glycol (PEG) 300+H_2O solutions (PEGWs) has been used as a promising medium for the absorption of SO_2. We investigated the UV, FTIR, ^{1}H-NMR, and fluorescence spectra in the absorption processes of SO_2 in PEGWs to present an important absorption mechanism. Based on the spectral results, the possibility of intermolecular hydrogen bond formation by hydroxyl oxygen atom in the PEG molecule with hydrogen atom in H_2O and S···O interaction formation by the oxygen atoms in PEG with the sulfur atom in SO_2 are discussed. This shows that the spectral changes may be due to the formation of -CH_2CH_2O(H)···HOH··· and -CH_2-CH_2-O(CH_2-CH_2-)···HOH··· in PEGWs and the formation of -CH_2CH_2OH···OSO···, and intermolecular S···O interaction between PEG and SO_2 as the formation of -$CH_2CH_2OCH_2CH_2O$(H)···(O)S(O)··· and -CH_2-CH_2-O(CH_2-CH_2-)···(O)S(O)···. The existence of these bonds benefits the absorption and desorption processes of SO_2 in PEGWs.

Keywords: Poly-ethylene Glycol (PEG) 300, Sulfur Dioxide, Absorption, Hydrogen Bonding, S···O Interaction

INTRODUCTION

Sulfur dioxide (SO_2), which is emitted from power plants and industrial plants, is a significant source gas of atmospheric pollution that threatens the environment and human health [1]. It needs to be removed from flue gases before it is released. Many technologies for removing SO_2 have been proposed, of which the conventional procedures, such as limestone scrubbing [2-4] and ammonia scrubbing, have some inherent disadvantages, including high capital and operating costs, a larger water requirement, poor quality of byproduct, and secondary pollution [5,6]. Because of the favorable absorption and desorption properties for acid gases in industrial processes, organic solvents have become the subject of increasing interest in recent years [7-9]. Wei, Zhang and their co-workers have paid great attention to the alcohol system to remove SO_2 for several years [10-18].

Poly-ethylene glycol (PEG) 300, an important industrial solvent, has been used in the absorption study of SO_2 for its low toxicity, low vapor pressure, and low melting point. Both PEG and its aqueous solutions (PEGWs) indicate that the strong solubility of SO_2 may be related to hydrogen bonding and interaction between PEG and SO_2. This work is a continuous study based on the previous investigations, such as density, viscosities, excess molar volumes [19] and solubility of SO_2 in PEGWs [20], and the spectroscopic study can provide an important absorption mechanism for the design and operation of PEGWs in further industrial desulfurization application.

For the researches of the SO_2 absorption mechanism in PEGW, FTIR, UV, and fluorescence spectroscopy are used to probe the intermolecular hydrogen bonding [21,22] and interaction among molecules, since FTIR spectroscopy presents precise information about water-sensitive bonds [23,24] and the PEG characteristic vibrational properties. Furthermore, FTIR is also advantageous for evaluating vibrational properties of bonds through very thin solution films, which are usually difficult to handle for the floating properties of solution. UV and fluorescence spectroscopy give important information about various electronic transitions. Generally, FTIR [25,26], UV, and fluorescence spectroscopy offer the advantages of measuring the association properties and hydrogen bonding capability, and assessing the interaction of alcohol with water by analyzing band shifts and changes.

The present work mainly focuses on spectral investigation, which is part of the continuation of this ongoing study on the solubility properties, because knowledge about the absorption mechanism is another important feature in industrial natural gas treating processes except for the basic physicochemical properties published before

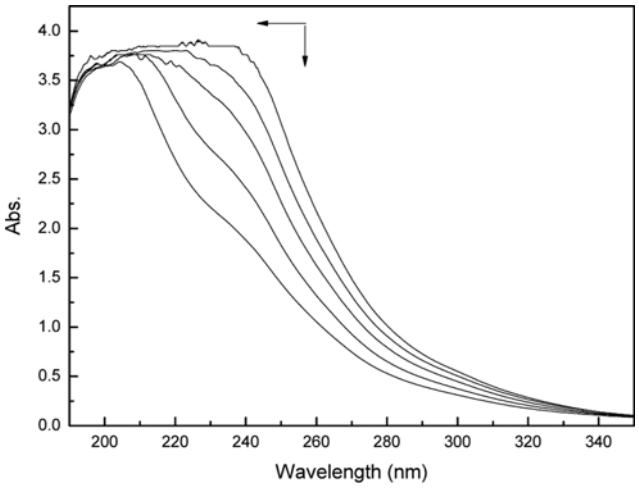

Fig. 1. UV spectral changes of PEGW at various mass fractions with increasing H_2O concentration.

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[19,20]. Our results provide an important molecular mechanism for the design and operation of the absorption and desorption process in flue gas desulfurization (FGD) with potential industrial application of various PEGWs.

EXPERIMENTAL

The analytical grade PEG with a purity of 99% (mass fraction) was purchased from Beijing Reagent Company (China), which was used after drying over molecular sieves (type 4A) and oscillation degassing. The purity of PEG was checked in the previous work [19]. The SO_2 gas (99.9%) and the certified standard mixture (SO_2+N_2, $y_{SO_2}=5\cdot10^{-4}$) were purchased from the Beijing Oxygen Plant Specialty Gases Institute Company. All the gases were decompressed and filtered before measurements. Double-distilled water was used, and the mixture solutions were prepared by mass using an analytical balance (Sartorius BS224S) with a precision of ±0.0001 g.

UV-vis spectra were recorded on a Varian CARY 1E UV-vis spectrometer in the range of (190 to 900) nm. Fluorescence spectra were acquired using an F-4500 fluorescence spectrophotometer employing a 500 W Hg-Xe high pressure lamp. FTIR spectra were recorded on a Bruker VECTOR22 FTIR spectrometer with a resolution of 1 cm^{-1} at 298 K in the range from 4,000 cm^{-1} to 400 cm^{-1}. The spectrometer possesses auto-align energy optimization and a dynami-

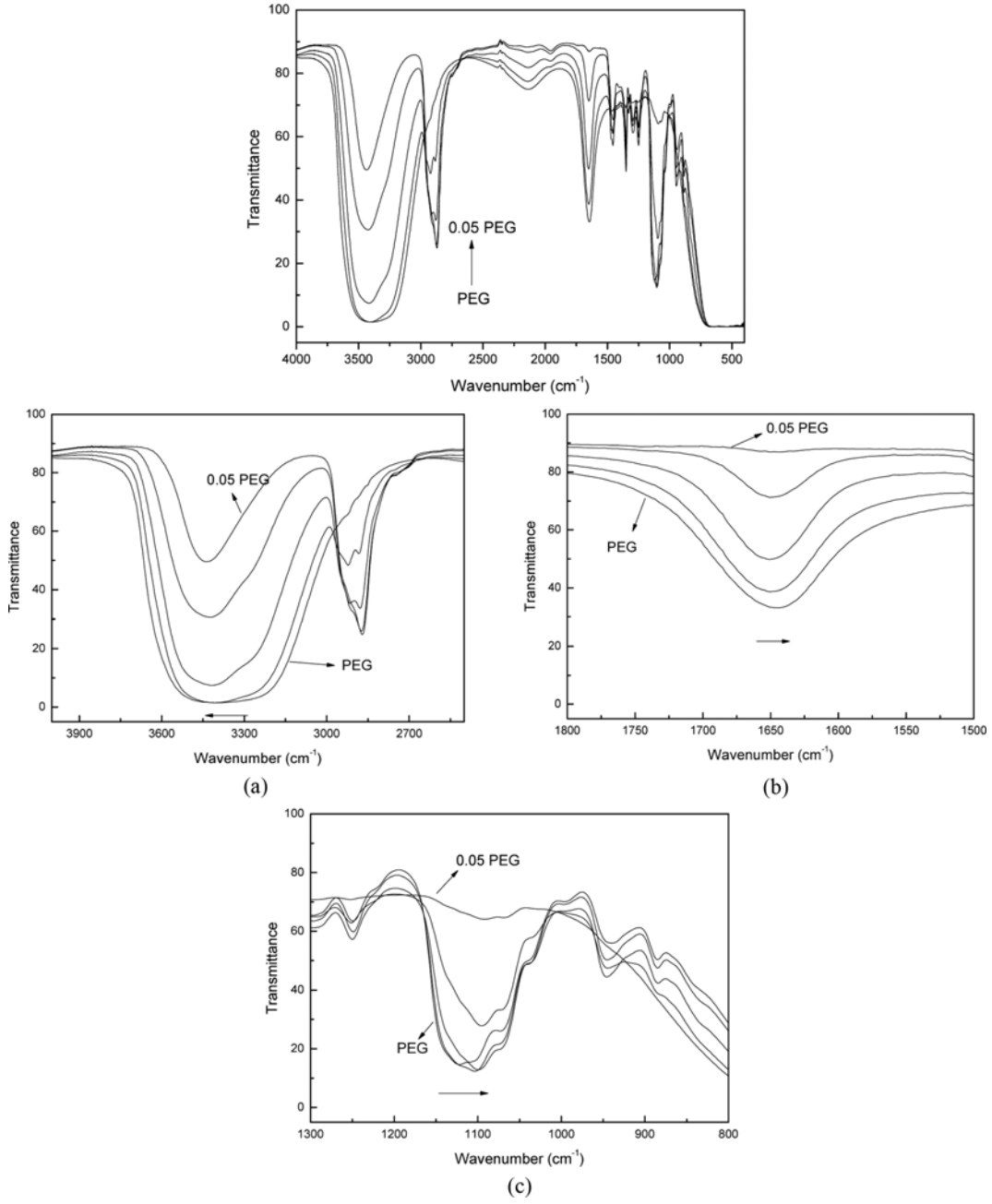

Fig. 2. FTIR spectral changes of PEGW at various mass fractions with increasing H_2O concentration: (a) 4,000-2,500 cm^{-1}, (b) 1,800-1,500 cm^{-1}, and (c) 1,300-800 cm^{-1}. The changing trend was found with increasing H_2O concentration.

cally aligned interferometer, and is fitted with constringent BaF_2 pellets 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; and then 15 mL solution was used on the FTIR spectrometer in every one of the measurements; the thin layer of samples are typically less than 2 μm thickness. ^{1}H-NMR spectra were acquired using a Bruker ARX-400 nuclear magnetic resonance spectrometer and DMSO-d6 was used as an NMR solvent.

RESULTS AND DISCUSSION

1. Spectral Properties of PEG+H_2O

UV spectral changes of PEG+H_2O are shown in Fig. 1.

Fig. 1 shows that the electronic transition band blue-shifts in the range of (190 to 250) nm with the increasing H_2O concentration in PEGWs. The absorption band is assigned to the n→* electronic transition of unshared electronic pair of hydroxyl oxygen atoms and ether oxygen atoms in PEG because the n→* electronic transition of H_2O is often found at the vacuum ultraviolet region. With the increasing H_2O concentration, intermolecular hydrogen bonding of hydroxyl oxygen atoms and the ether oxygen atoms in PEG with hydrogen atoms in H_2O happened easily. The results showed that PEG and H_2O incurred intermolecular interaction and formed hydrogen-bonding as the formation of -$CH_2CH_2OCH_2CH_2O$(H)···HOH··· and -CH_2-CH_2-O(CH_2-CH_2-)···HOH···.

The FTIR spectral changes of PEG+H_2O are shown in Fig. 2.

From Fig. 2, the fundamental stretching and deformation vibrations of water were present in the region of (3,700 to 3,000) cm^{-1} and (1,700 to 1,600) cm^{-1}, and the C-O-C asymmetry stretching vibrational band (Vas) of PEG was from 1,150 cm^{-1} to 1,000 cm^{-1}, so information about the interaction of PEG and H_2O was obtained by detailed analysis of four parameters, such as peak position, intensity, bandwidth, and shape. From Fig. 2(a) the stretching vibrational band of hydroxyl in PEGW is found to shift toward higher frequency from 3,406 cm^{-1} to 3,438 cm^{-1} with increasing H_2O concentration. The fact that the stretching vibrational band of hydroxyl in PEGW shifts toward higher frequency indicates that the interactions are due to the variational property of hydroxyl oxygen and ether oxygen in PEG. From Fig. 1(b) the bending vibrational frequency of water changes from 1,651 cm^{-1} to 1,643 cm^{-1}, which has been reported to appear at 1,645 cm^{-1} in water saturated low density polyethylene [27]. The fact that H-O-H bending vibrational band shifts towards lower frequency indicates that the interactions result from the variational property of hydrogen atom in H_2O. Meanwhile, from Fig. 1(c) the stretching vibrational band of C-O-C in PEG shifts toward lower frequency from 1,106 cm^{-1} to 1,092 cm^{-1}, which indicates that interactions can be related to the variational property of oxygen atom in C-O-C in PEG. According to the above results, we present that the possible interactions between PEG and water result from the following two ways: (1) hydrogen bonding and interaction of hydrogen atom in H_2O with hydroxyl oxygen atom in PEG by cross-linking as the formation of -CH_2CH_2O(H)···HOH···; and (2) hydrogen bonding and interaction of hydrogen atom in H_2O with ether oxygen atom in PEG as the formation of -CH_2-CH_2-O(CH_2-CH_2-)···HOH···.

The present results show that the intermolecular hydrogen-bonding interaction in PEGW form as -$CH_2CH_2OCH_2CH_2O$(H)···HOH···

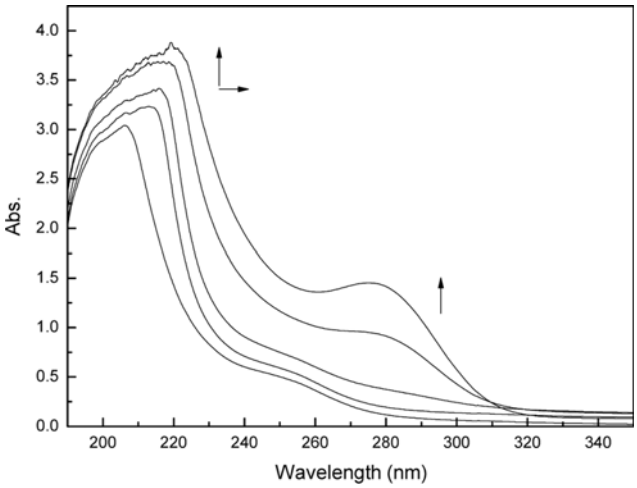

Fig. 3. UV absorption spectral changes of PEG with the increasing SO_2 concentration.

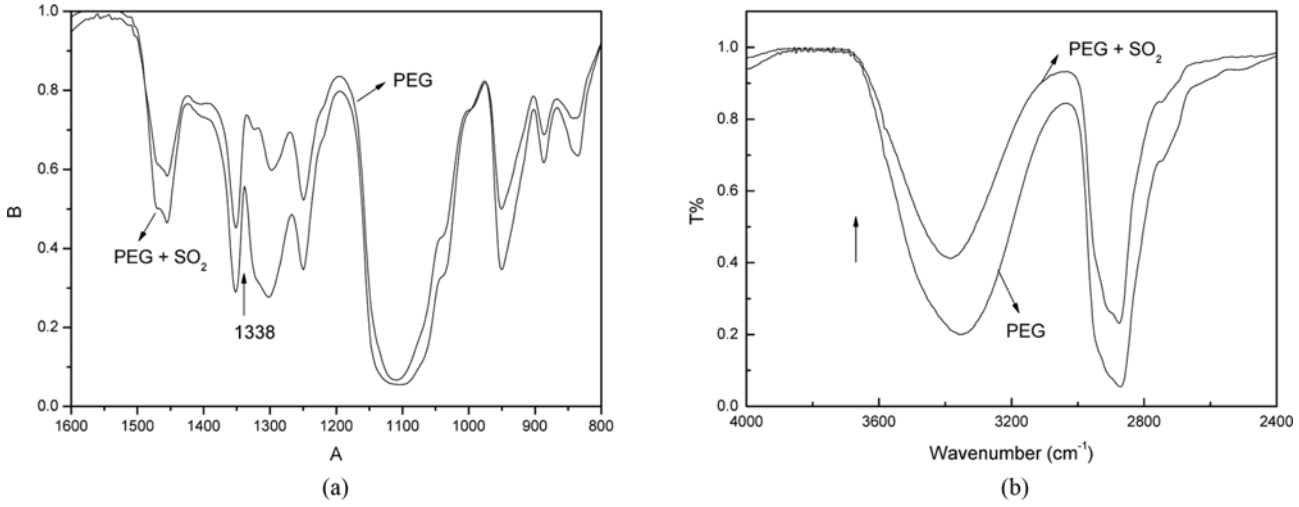

Fig. 4. FTIR absorption spectra of PEG and PEG+SO_2: (a) 1,600-800 cm^{-1}, (b) 4,000-2,400 cm^{-1}.

and -CH_2-CH_2-O(CH_2-CH_2-)···HOH···.

2. Spectral Properties of PEG+SO_2

In Fig. 3, the characteristic bands of PEG and SO_2 are respectively identified, but no information on a complexing reaction could be obtained. From the figure, the absorption band of n→π* electron transition of oxygen atom in SO_2 (Π_3^4) was observed at 278 nm and the absorption intensity of the band increases with increasing SO_2 concentration. Another absorption band, which was mainly due to $\pi \rightarrow \pi^*$ electron transition of sulfur atom in SO_2 (Π_3^4) and n→σ* electron transition of hydroxyl oxygen atom in PEG, shifts from 206 nm to 219 nm and the absorption intensity of the band increases. The shift results from the intermolecular hydrogen bond

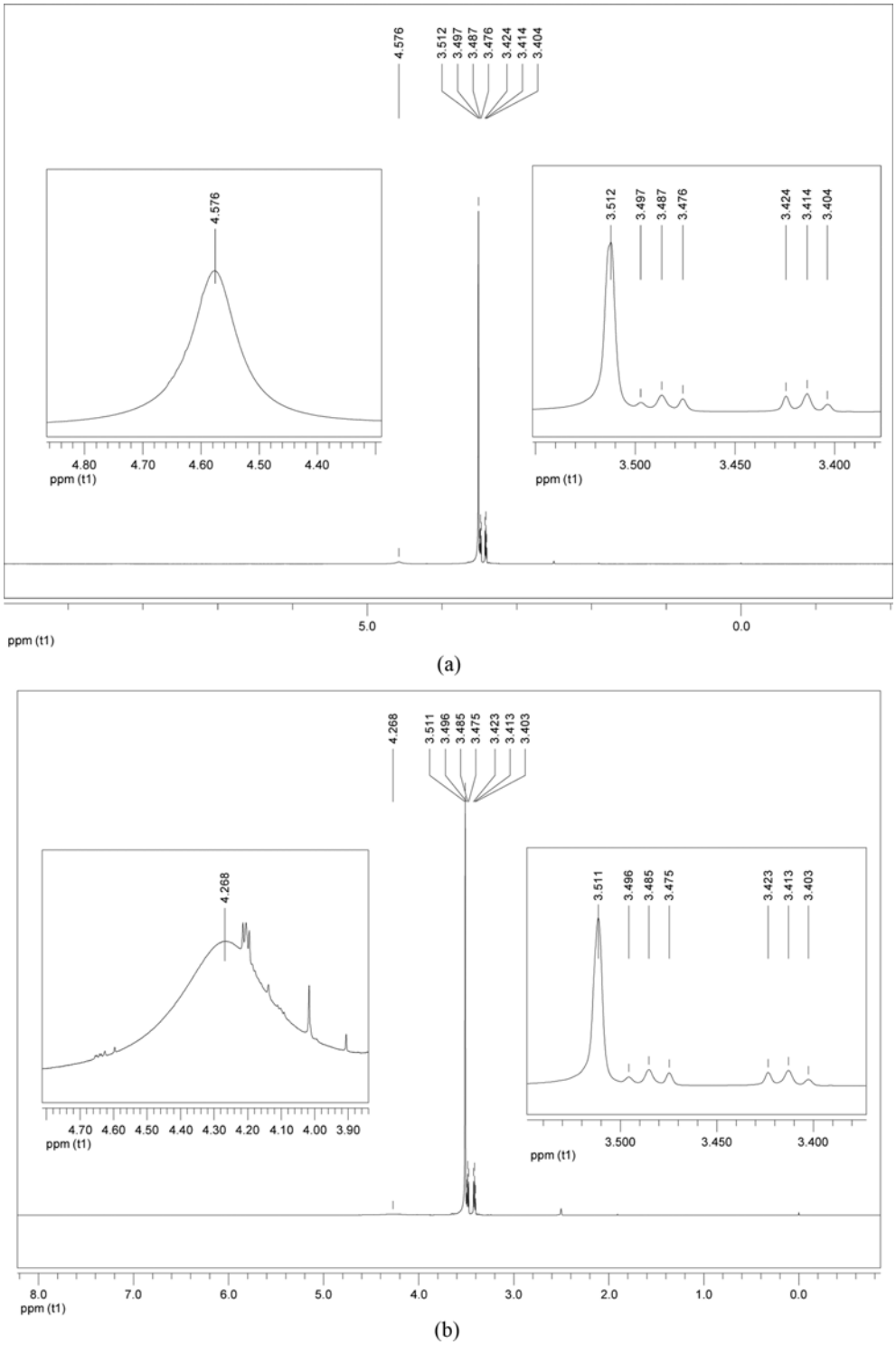

Fig. 5. ^{1}H-NMR spectral changes of PEG300 in the presence and absence of SO_2. (a) ^{1}H-NMR spectrum of PEG, (b) ^{1}H-NMR spectrum of PEG300+SO_2.

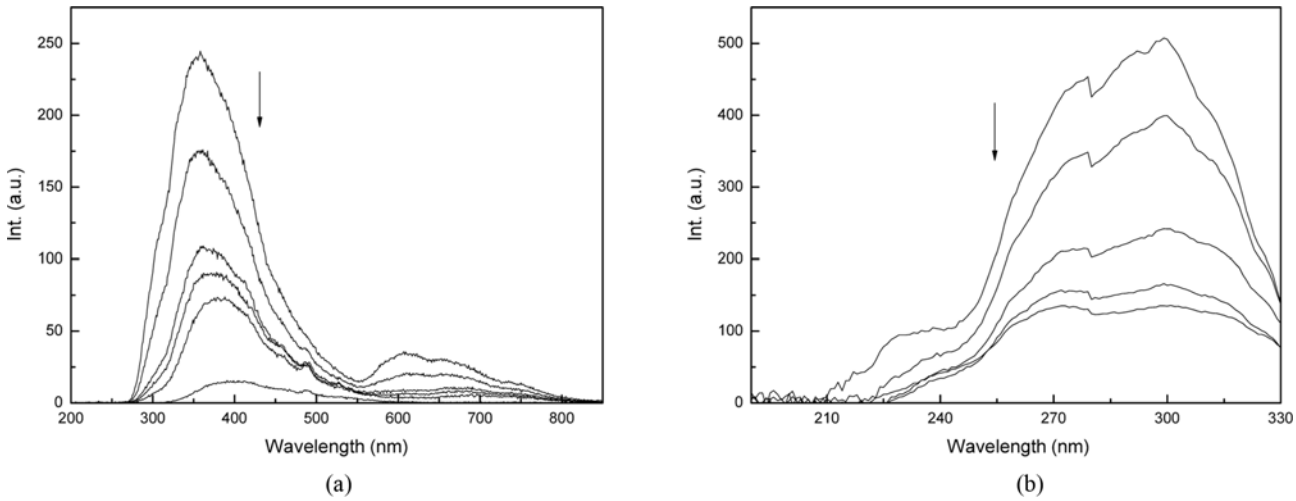

Fig. 6. Fluorescence spectral change of PEG with the increasing SO_2, concentration (a) excitation spectra and (b) emission spectra.

of oxygen atoms in SO_2 with hydroxyl hydrogen atoms in PEG and intermolecular S···O interaction. The bonding of oxygen atoms of SO_2 with hydroxyl hydrogen atoms of PEG results in the following results: (1) the decreasing effects of oxygen atoms on sulfur atom of SO_2 make the $\pi \rightarrow \pi^*$ electron transition of sulfur atom in SO_2 change easier; and (2) the decreasing effects of hydroxyl hydrogen atoms on hydroxyl oxygen atoms in PEG make the $n \rightarrow \sigma^*$ electron transition of hydroxyl oxygen atom in PEG also change easier.

The recorded FTIR spectra of PEG and PEG+SO_2 are shown in Fig. 4.

In Fig. 4(a), an asymmetry stretching band (Vas) of SO_2 is observed at 1,327 cm^{-1}, and the C-O-C asymmetry stretching band at 1,061 cm^{-1} change is stronger, which shows that the C-O-C asymmetry stretching band of PEG is affected by SO_2. The absorption peak at 1,327 cm^{-1}, which is reported at 1,344 cm^{-1} for SO_2 in non-complexing CCl_4 [23], can be attributed to the *V*as of SO_2 because the IR and Raman spectra indicate the following values for the fundamental frequencies: symmetry stretching band (Vs)=1,151.38 cm^{-1}, δ=517.69 cm^{-1}, and Vas=1,361.76 cm^{-1}. Meanwhile, the phenomenon that the Vas of SO_2 shifts towards lower wavenumber than Vas=1,361.76 cm^{-1} can be due to the interaction of the sulfur atoms in SO_2 with other atoms. 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 hydroxyl oxygen atom (electronegative) in PEG should occur by the way of intermolecular S···O interaction, which could not be discussed in the previous EGW+SO_2 system [25] and PEGW+SO_2 system [26].

However, the symmetry stretching band (Vas) of SO_2 at 1,151 cm^{-1} is strongly masked by the vibrations of PEG. In Fig. 4(b) a phenomenon is displayed. In the absence of SO_2, the stretching vibrational band of hydroxyl in PEG is observed at 3,355 cm^{-1}. In the presence of SO_2, the band is changed into a more peaked band at 3,384 cm^{-1}. The phenomenon could be due to the fact that the addition of SO_2 affects the original hydrogen-bonding interaction among PEG molecules and forms new intermolecular hydrogen bonding of hydroxyl hydrogen atoms in PEG with oxygen atoms in SO_2 and intermolecular S···O interaction.

The ^{1}H-NMR spectral results of PEG in the presence and absence of SO_2 are shown in Fig. 5.

Fig. 5(a) shows that the chemical shifts of hydrogen in -CH_2- appear at δ=(3.404-3.512) ppm, and the chemical shift of hydroxyl hydrogen appears at δ=4.576 ppm (2H) in the ^{1}H-NMR spectrum of pure PEG. However, with increasing SO_2 concentration in PEG, the bond length of O-H in EG molecules becomes longer and the electron cloud of hydroxyl hydrogen atoms in PEG molecules becomes thinner, so the signal changes into single peak and the chemical shift of hydrogen atoms in -OH groups shifts from δ=4.576 ppm to 4.268 ppm in DMSO (Fig. 5(a) and (b)). The phenomena can be due to the fact that the interaction of oxygen atoms in SO_2 bonding with hydroxyl hydrogen atoms in PEG increases the shielding effect of hydroxyl hydrogen atoms in PEG, so that the signal changes into single peak and the signal of chemical shift of hydroxyl hydrogen in PEG moves towards a higher magnetic field.

Stable state fluorescence spectra with selective excitation of PEG with the increasing SO_2 concentration were recorded and are shown in Fig. 6. Upon excitation at 230 nm, where the $n \rightarrow \sigma^*$ electron transition of oxygen atom of PEG absorbs, strong fluorescence with emission positions at 300-450 nm and 580-620 nm are observed. The fluorescence intensity of the $\sigma^* \rightarrow n$ electron transition of oxygen atom of PEG decreases with the increasing SO_2 concentration. The phenomena can be due to the intermolecular interaction of the oxygen atom in PEG with SO_2 as the formation of S···O interaction.

According to the above IR, UV, ^{1}H-NMR, and fluorescence spectral results, it is expected that PEG bonds with SO_2 by the intermolecular hydrogen bonds of -CH_2CH_2OH···OSO··· and intermolecular S···O interaction.

3. Spectral Properties of PEGW+SO_2

Fig. 7 shows the UV spectra of PEGW+SO_2, and the concentration of PEG was 0.10, 0.20, and 0.30 in mass fraction, respectively. All the three figures show a common phenomena that the absorption intensity of the band increases with the increasing SO_2 concentration and the special absorption band red shifts. The absorption band observed around 280 nm was $n \rightarrow \sigma^*$ electron transition of oxygen atom in SO_2 and the band intensity increases with the increasing SO_2 concentration. Meanwhile, the special absorption band present around 200 nm was found to red shift together with the in-

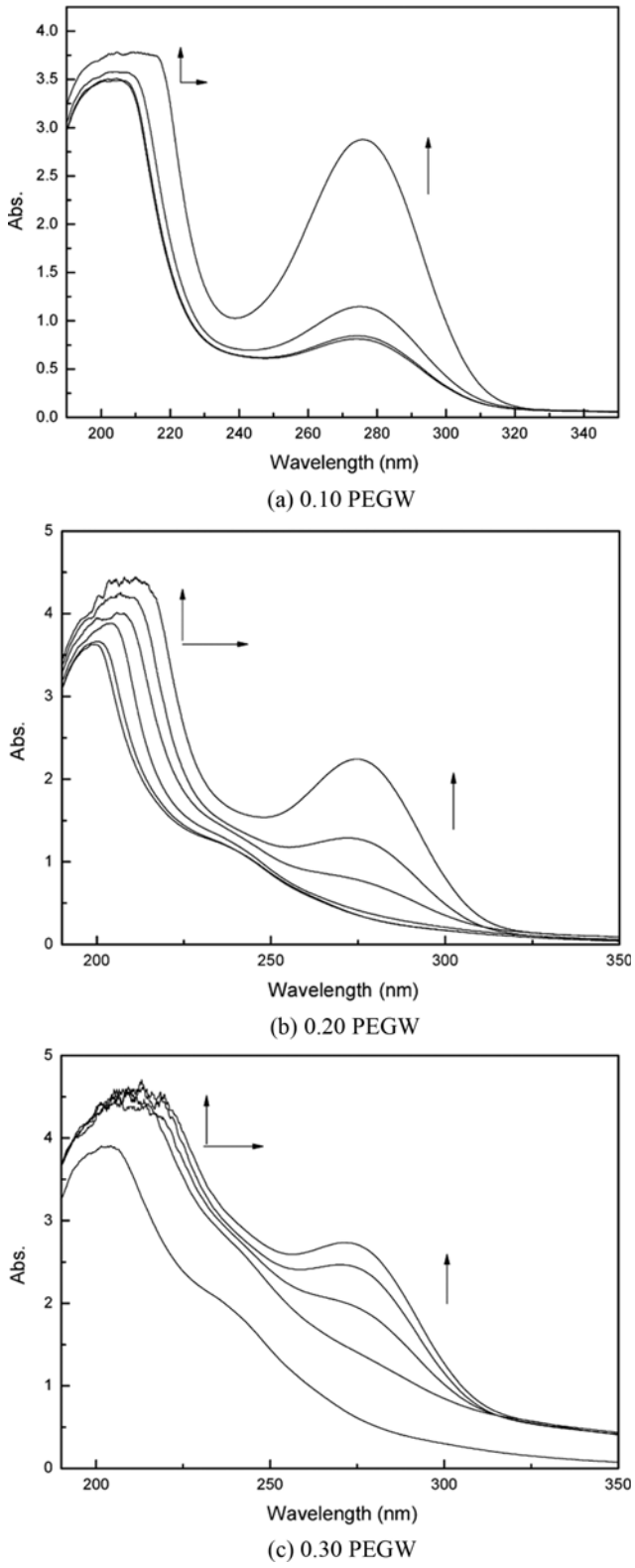

Fig. 7. UV spectral changes of PEG in PEGW with the increasing SO_2 concentration.

creasing absorption intensity. The results suggest the $\pi \rightarrow \pi^*$ electron transition of SO_2 and $n \rightarrow \sigma^*$ electron transition of oxygen atom of PEG in PEGW with the increasing SO_2 concentration.

The recorded FTIR spectra of H_2O and H_2O+SO_2 are shown in

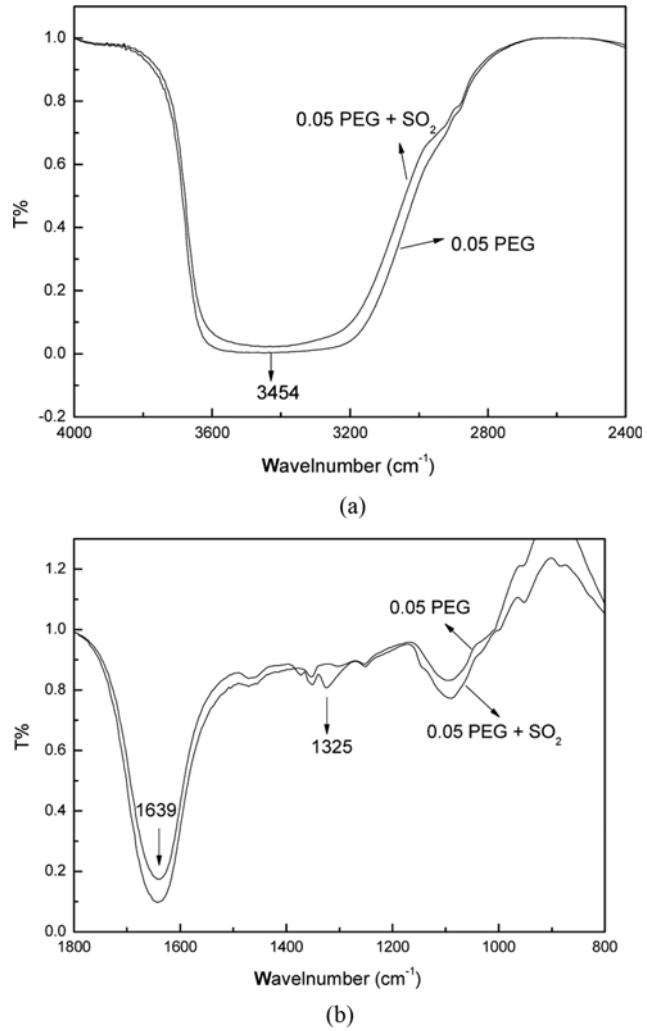

Fig. 8. FTIR spectral changes of 0.05 PEG in mass fraction with the increasing SO_2 concentration. (a) 4,000-2,400 cm^{-1}, and (b) 1,800-800 cm^{-1}.

the previous work [20]. From the spectra two special stretching bands are observed at 1,332 cm^{-1} and 1,151 cm^{-1}, which can be attributed to the Vas and Vs of SO_2 [21]. Fig. 8 is the FTIR spectra of PEGW+ SO_2 with the concentration of PEG was 0.05 in mass fraction. In Fig. 8(a), the stretching vibrational band of hydroxyl in PEGW when w_1=0.05 was observed at 3,444 cm^{-1} and changed into a more peaked band and shifted toward lower frequency observed at 3,384 cm^{-1} in the presence of SO_2. This phenomenon can be explained by forming the new intermolecular hydrogen bonding. Together with Fig. 8(b), in which the stretching band was observed at 1,325 cm^{-1}, and both the Vas and Vs of SO_2 shifts toward a lower wavenumber. This phenomenon was attributed to the interactions of PEG with SO_2 as the way of S···O.

Fluorescence spectra with selective excitation wavelength of PEGW with the increasing SO_2 concentration is shown in Fig. 9. Strong fluorescence emission peak are observed at the positions of 330-350 nm and 590-610 nm upon excitation wavelength at 205 nm. The fluorescence intensity of the $\sigma^* \rightarrow n$ electron transition of oxygen atom of PEG in PEGW decreases with the increasing SO_2 concentration. The phenomena can be due to the intermolecular interaction

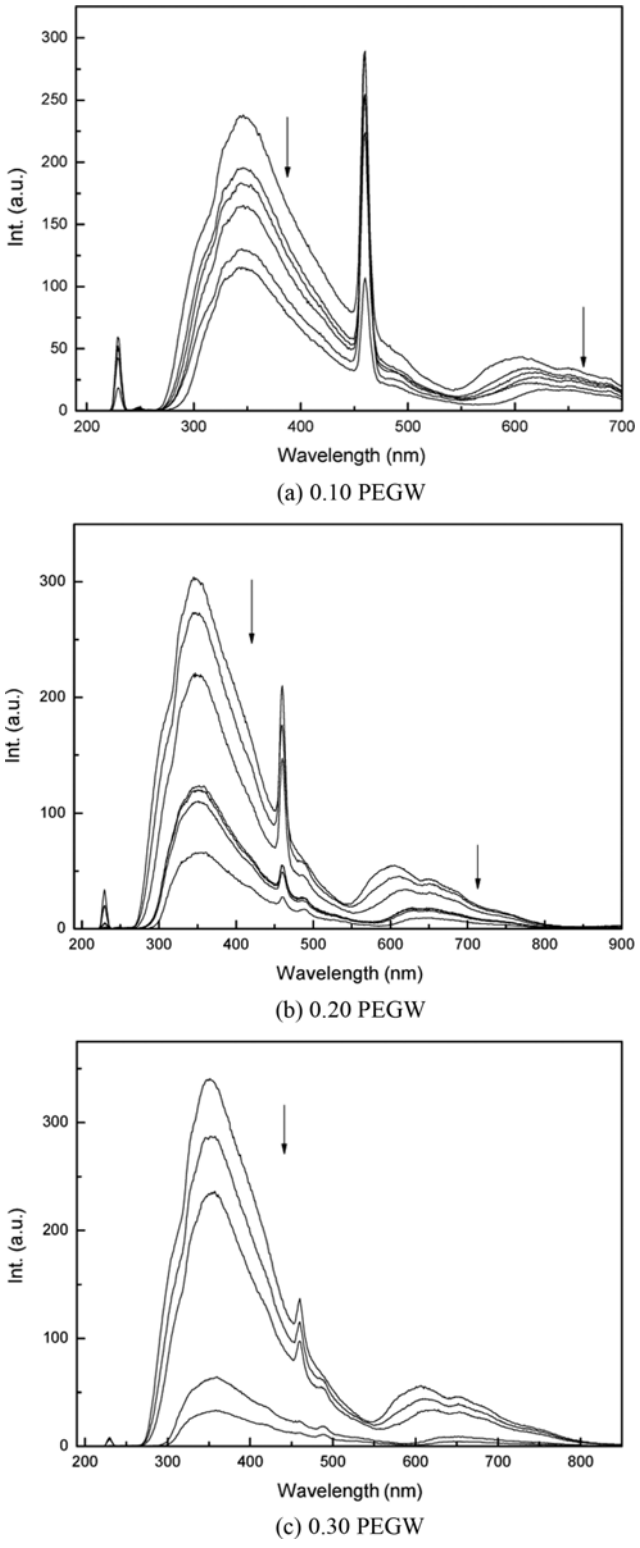

Fig. 9. Fluorescence spectral changes of PEG in PEGW with the increasing SO_2 concentration.

of the oxygen atom in PEG with SO_2 as the formation of S···O interaction.

From the above discussion, conclusions can be drawn that the addition of SO_2 affects the original hydrogen-bonding interaction among PEG molecules and forms the new intermolecular hydrogen bonding of hydroxyl hydrogen atom in PEG with oxygen atom in SO_2 as the formation of -$CH_2CH_2OCH_2CH_2OH$···OSO···. Meanwhile, comparing the spectra of w_1=0.05 PEGW+SO_2 and PEG+SO_2, the constant H-O-H bending band in the absorption processes of SO_2 is mainly due to the hydrogen interaction of PEG and SO_2 rather than the reaction of water and SO_2.

CONCLUSION

The pure PEG and its binary aqueous solutions (PEGW) present an optimized property for the absorption of SO_2 because of its native hydrogen bonding sites for SO_2, so the absorption properties of SO_2 can be related to hydrogen bonding and intermolecular S···O interaction among molecules. The present results show that the possible interactions in PEGW result from the following two ways: (1) hydrogen bonding and interaction of hydrogen atom in H_2O with hydroxyl oxygen atom in PEG by cross-linking as the formation of -CH_2CH_2-O-CH_2CH_2O(H)···HOH···; and (2) hydrogen bonding and interaction of hydrogen atom in H_2O with ether oxygen atom in PEG as the formation of -CH_2CH_2-O(CH_2CH_2-)···HOH···. In addition, the spectral analyses of added SO_2 in pure PEG or w_1=0.05 PEGW suggest that SO_2 can interact with PEG by hydrogen bonds as the formation of -$OCH_2CH_2OCH_2CH_2OH$···OSO···, and intermolecular S···O interaction of hydroxyl oxygen atom of PEG or ether oxygen atom in PEG with sulfur atom of SO_2 as the formation of -CH_2CH_2-O-CH_2CH_2O(H)···(O)SO··· and -CH_2CH_2-O-(CH_2CH_2OH)···(O)SO···.

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