Spectral Studies of Hydrogen Bonding and Interaction in the Absorption Processes of Sulfur Dioxide in Poly(ethylene glycol) 400 + Water Binary System

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Spectral Studies of Hydrogen Bonding and Interaction in the Absorption Processes of Sulfur Dioxide in Poly(ethylene glycol) 400 + Water Binary System

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In previous work, poly(ethylene glycol) 400 (PEG) (1) + water (2) solutions (PEGWs) were used as a promising medium for the absorption processes of SO_2. When conventional UV, Fourier transform infrared (FTIR), and ^{1}H NMR spectroscopic techniques were used for inspection of spectral changes of PEGWs with increasing SO_2 concentration, the spectral results suggest that H_2O can interact with PEG by hydrogen bonds in PEGW; furthermore, SO_2 can interact with PEG in various PEGWs by hydrogen-bonding interactions in the absorption processes of SO_2. The results of this work can be used to provide important absorption mechanism for the design and operation of the absorption and desorption process in flue gas desulfurization (FGD) with potential industrial application of PEG aqueous solutions.

1. Introduction

Sulfur dioxide (SO_2) is a significant atmospheric pollutant, and therefore it is severe in environmental protection. Emissions of SO_2 into the atmosphere have steadily increased with industrial development. The combustion of coal, due to its high sulfur content,[1] means it is necessary to dedicate particular attention to eliminating the resulting emission of SO_2. Among the many procedures employed to desulfurize exhaust gases, organic solvents used as absorbents have been identified as an option among the regenerative processes[2−4] 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;[5] therefore, in this work and in a number of other studies, great attention has been paid to alcohol/water systems for SO_2 removal.[6−10]

Fourier transform infrared (FTIR) spectroscopy and UV spectroscopy are very useful methods to probe molecular associations among molecules, since FTIR spectroscopy gives precise information about water-sensitive bonds;[11,12] furthermore, FTIR spectroscopy 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 addition, UV spectroscopy gives important information about various electronic transitions. Generally, FTIR[13,14] and UV spectroscopic techniques offer the advantages to measure the association properties and hydrogen-bonding capability and to assess interaction among PEG, SO_2, and water as function of concentration of the involved species.

Poly(ethylene glycol) 400 (PEG) is an important industrial solvent, which has been used in the absorption processes of SO_2[15] because of its favorable properties, such as low toxicity, low vapor pressure, and low melting point. Previous results[15] show that the addition of H_2O into PEG decreased the solubility of SO_2 in PEG; meanwhile, $w_1 = 0.80$ PEGW (mass fraction)

exhibits an extreme maximum value of 778 mg/L to dissolve SO_2 when SO_2 concentration is designed at $\Phi_1 = 5 \times 10^{-4}$ (volume fraction) in the gas phase. In the entire composition range, pure PEG shows the strongest capabilities to dissolve SO_2 and the solubility is 1330 mg/L at the same gas composition. The above results may be related to the excess properties of aqueous PEG solutions[16] because minimum excess volume value (V_m^E) presents at around $x_1 = 0.15$ (molar fraction) ($w_1 = 0.79$) PEGW, which exhibited an extreme minimum value and may be related to the hydrogen-bonding interactions among PEG, H_2O, and SO_2, and similar hydrogen-bonding interactions among ethylene glycol (EG), H_2O, and SO_2 had been published in our previous work.[17] The study of absorption processes of SO_2 in PEGW includes the following three steps: (1) gas−liquid equilibrium data for a gaseous mixture of SO_2 + N_2 with PEG aqueous solutions; (2) density, viscosity, and excess properties for PEG aqueous solutions; and (3) spectral properties of PEG + SO_2 + H_2O interactions. Previous articles cover the first two steps of this study.[15,16] The present work was mainly focused on investigating the possible interaction mechanism among PEG, H_2O, and SO_2 in the absorption processes of SO_2 by FTIR, UV, and ^{1}H NMR spectroscopic techniques.

2. Experimental Section

Pure SO_2 gas (99.9%) and pure N_2 gas (>99.9%) were purchased from the Beijing Gas Center, Peking University (China). Analytical-grade PEG 400 with a number-average molecular weight of 400 (380−420) was purchased from Beijing Reagent Company. It was used after drying over molecular sieves (type 4A) and decompression filtration before measurements. The purity of the sample was checked by density determination at 298.15 K. The density of PEG at 298.15 K was found to be 1.1218 g·cm^{-3},[16] in good agreement with the published literature.[18] Double-distilled water was used.

UV spectra were recorded on a Varian Cary 1E UV−vis spectrometer. ^{1}H NMR spectra were acquired on a Bruker ARX-400 nuclear magnetic resonance spectrometer and $(CH_3)_2SO$ (dimethyl sulfoxide, DMSO) was used as NMR solvent. 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 to 400 cm^{-1}. The spectrometer possesses autoalign energy opti-

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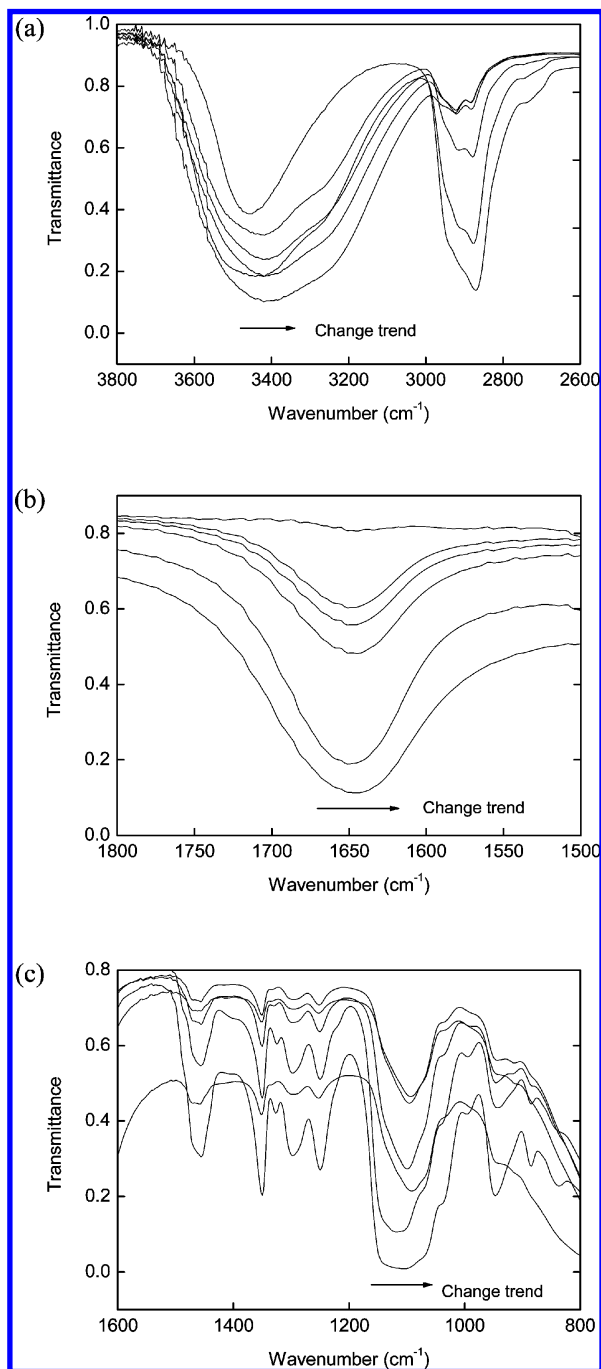
Figure 1. FTIR spectra of PEG + H_2O: (a) 2600−3800 cm^{-1}, (b) 1500−1800 cm^{-1}, and (c) 800−1600 cm^{-1}. The change trend was found with increasing H_2O concentration.

mization and a dynamically aligned interferometer and is fitted with a constringent $BaSO_4$ 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; and then 15 μL of solution was used on the FTIR spectrometer in every one of measurements, and the thin layer of samples are less than typically 2 μm thickness. All spectral experiments of PEG + SO_2 + H_2O were performed at room temperature and atmospheric pressure.

3. Results and Discussion

3.1. Spectral Properties of PEG + H_2O. The recorded IR spectra of PEG + H_2O are shown in Figure 1. In Figure 1a the stretching vibrational band of hydroxyl in PEGW is found to
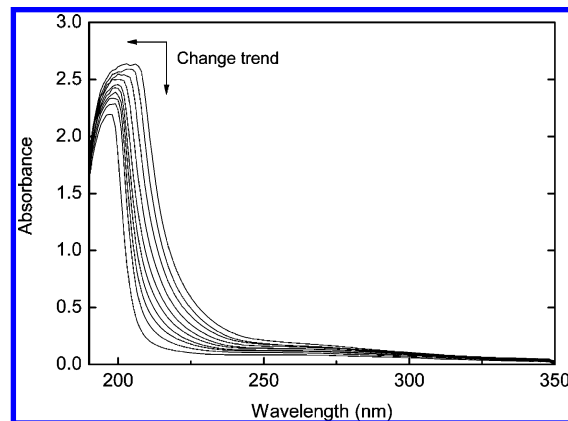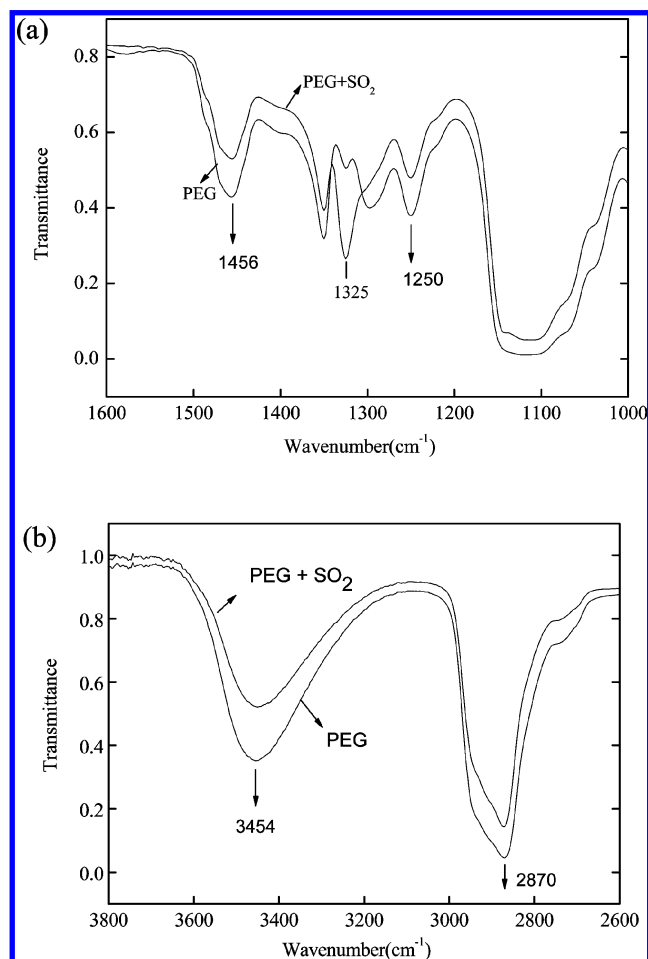

Figure 2. Absorption spectral changes of PEG + H_2O. The change trend was found with increasing H_2O concentration.

shift toward lower frequency, from 3451 to 3417 cm^{-1}, with increasing H_2O concentration. The fact that the stretching vibrational band of hydroxyl in PEGW shifts toward lower frequency indicates that the interactions are due to the variational property of hydroxyl oxygen in PEG. In Figure 1b the bending vibrational frequency of water changes from 1651 to 1645 cm^{-1}, which has been reported to appear at 1645 cm^{-1} in water-saturated low-density polyethylene.[1] The fact that H−O−H bending vibrational band shifts toward lower frequency indicates that the interactions result from the variational property of hydrogen atom in H_2O. Meanwhile, from Figure 1c the stretching vibrational band of C−O−C in PEG shifts toward lower frequency from 1119 to 1091 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 may occur in two ways: (1) hydrogen-bonding interaction of the hydrogen atom in H_2O with the hydroxyl oxygen atom in PEG by cross-linking, forming −$CH_2CH_2O(H)\cdots HOH\cdots$, and (2) hydrogen-bonding interaction of the hydrogen atom in H_2O with the ether oxygen atom in PEG, forming −CH_2−CH_2−$O(CH_2$−CH_2-)$\cdots HOH\cdots$.

Figure 2 shows that the electronic transitions blue-shift from 197 to 203 nm with increasing H_2O concentration in PEGW. The absorption band can be due to the n → σ^* electronic transition of unshared electronic pair of hydroxyl oxygen in PEG because the n → σ^* electronic transitions of H_2O and of ether oxygen in PEG are often found at the vacuum ultraviolet region. With increasing H_2O concentration, hydrogen-bonding interaction of the hydroxyl oxygen of PEG with the hydrogen of H_2O happened easily, so that the n → σ^* electronic transition of hydroxyl oxygen in PEG become more difficult. The present results show that the hydrogen bonds in PEGW form −$CH_2CH_2O(H)\cdots HOH\cdots$.

3.2. Spectral Properties of PEG + SO_2. The recorded IR spectra of PEG and PEG + SO_2 are shown in Figure 3. In Figure 3a, a asymmetry stretching band of SO_2 at 1325 cm^{-1} was observed, and the C−O−C asymmetry stretching band at 1101 cm^{-1} grows wider, which may be related the symmetry stretching band of SO_2. In Figure 3b an interesting phenomenon is displayed. In the absence of SO_2, the stretching vibrational band of hydroxyl in PEG was observed at 3451 cm^{-1}. In the presence of SO_2, the band was changed into a peakier band. The phenomenon could be because the addition of SO_2 destroys the original hydrogen-bonding interaction among PEG molecules and forms new hydrogen-bonding interactions of hydroxyl hydrogen atoms in PEG with oxygen atoms in SO_2.

Figure 3. FTIR spectra of PEG and PEG + SO$_2$ in the range (a) 1600−1000 cm^{-1} and (b) 3800−2600 cm^{-1}.
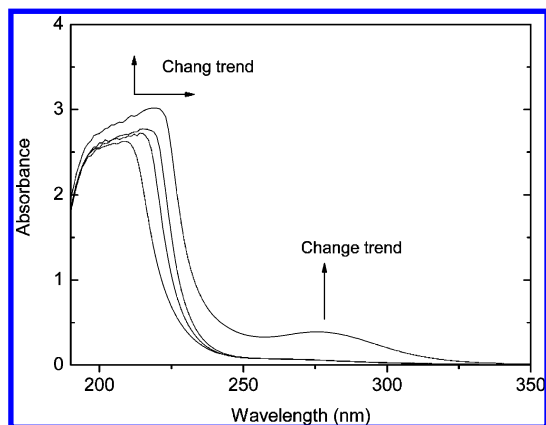
Figure 4. Absorption spectral changes of PEG + SO$_2$. The change trend was found with increasing SO$_2$ concentration.

In Figure 4, the characteristic bands of PEG and SO$_2$ were respectively identified, but no information on a complexing reaction could be obtained. From the figure the absorption band of n $\rightarrow$ π* electron transition of oxygen atom in SO$_2$ (Π_3^4) is observed at 277 nm, and the absorption intensity increases with increasing SO$_2$ concentration. Another absorption band shifts from 209 to 220 nm and the absorption intensity increases, which was mainly due to π $\rightarrow$ π* electron transition of sulfur atom in SO$_2$ (Π_3^4) and n $\rightarrow$ σ* electron transition of hydroxyl oxygen atom in PEG. The shift results from the hydrogen-bonding interaction of oxygen atoms in SO$_2$ with hydroxyl hydrogen atoms in PEG. Oxygen atoms in SO$_2$ bonding with

hydroxyl hydrogen atoms in PEG results in the following two results: (1) the decreasing effects of oxygen atoms on sulfur atom in SO$_2$ make the π $\rightarrow$ π* 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 $\rightarrow$ σ* electron transition of hydroxyl oxygen atom in PEG change easier also.

The ^{1}H NMR spectral results of PEG in the presence and absence of SO$_2$ are shown in Figure 5. Figure 5a shows that the chemical shifts of hydrogen in −CH$_2$− appear at δ = 3.510, 3.475, 3.423, 3.410, and 3.398 ppm (34 H), and the chemical shift of hydroxyl hydrogen appears at δ = 4.545 ppm (2 H) in the ^{1}H NMR spectrum of pure PEG. However, with increasing SO$_2$ concentration in PEG, the chemical shift of hydrogen atoms in −OH groups shifts from δ = 4.545 to 4.444 ppm (Figure 5b−e). The shift is because 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 of chemical shift of hydroxyl hydrogen in PEG moves toward higher magnetic field.

According to the above IR, UV, and ^{1}H NMR spectral results, it is expected that hydrogen-bonding interaction of PEG with SO$_2$ forms −CH$_2$CH$_2$OH$\cdots$OSO$\cdots$.

3.3. Spectral Properties of PEGW + SO$_2$. The recorded IR spectra of H$_2$O and H$_2$O + SO$_2$ are shown in previous work.[17] In the spectra, two special stretching bands are observed at 1333 and 1152 cm^{-1}, which can be attribute to the asymmetry stretching vibration (V_{as}) and stretching vibration (V_s) of SO$_2$.[19]

The recorded IR spectra of w_1 = 0.80 PEGW and w_1 = 0.80 PEGW + SO$_2$ are shown in Figure 6. In Figure 6a the stretching band at 1327 cm^{-1} was observed. In Figure 6b, in the absence of SO$_2$, the stretching vibrational band of hydroxyl in PEG was observed at 3443 cm^{-1} and the band was broad; in the presence of SO$_2$, the band was changed into a peakier band. The phenomenon can be due to the new hydrogen-bonding interaction of the hydroxyl hydrogen in PEG with the oxygen in SO$_2$.

In Figure 7, with increasing SO$_2$ concentration, the absorption band of n $\rightarrow$ π* electron transition of oxygen atom in SO$_2$ is observed at 277 nm and the absorption intensity of the band increases. Meanwhile, the special absorption band red-shifts from 200 to 223 nm and the absorption intensity of the band increases also. The results show that π $\rightarrow$ π* electron transition of SO$_2$ and n $\rightarrow$ σ* electron transition of oxygen atom of PEG in w_1 = 0.80 PEGW change with increasing SO$_2$ concentration.

The above results suggest the hydrogen-bonding interaction between hydrogen atoms in PEG molecules and oxygen atoms in SO$_2$ molecules occurred. When such hydrogen-bonding interactions are formed, hydroxyl hydrogen atoms in PEG molecules are attracted by oxygen atoms in SO$_2$ and the bond length between hydrogen atom and oxygen atom in PEG molecules is elongated. In this situation, the π $\rightarrow$ π* electron transition of SO$_2$ and the n $\rightarrow$ σ* electron transition of oxygen atom in PEG occur more easily, so red-shift phenomena occurred.

The SO$_2$ molecule is known to be polar and the sulfur atom to be electropositive; thus, the sulfur atom behaves as an electron acceptor, and its interaction with PEG 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 suppose that the PEG−SO$_2$ complex is less stable, as suggested by its lower downshifted frequency and its stronger desorption capacity. Such a shift observed in FTIR spectra was attributed to the interactions
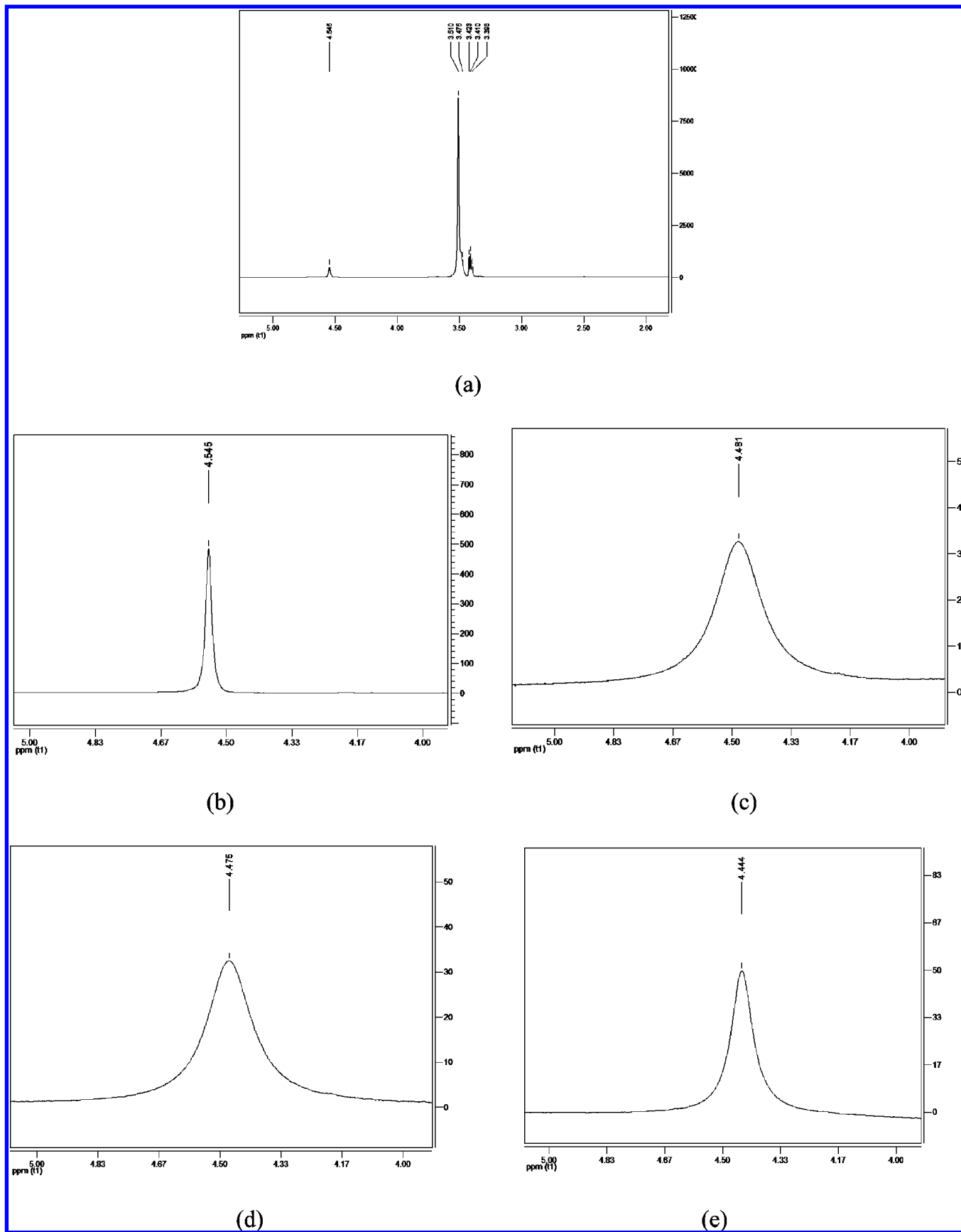
Figure 5. ^{1}H NMR spectra of PEG in the presence and absence of SO$_2$. (a) Full ^{1}H NMR spectrum of PEG. (b−e) Partial spectra: (b) PEG, (c) PEG after 1 min ventilation of SO$_2$, (d) PEG after 5 min ventilation of SO$_2$, and (e) PEG after 10 min ventilation of SO$_2$.

of PEG with SO$_2$. Comparing the spectra of $w_1 = 0.80$ PEGW + SO$_2$ and $w_1 = 0.80$ PEGW, it is observed that the H−O−H

bending band and the characteristic bands of PEG are not obviously shifted in the mixture under the influence of SO$_2$

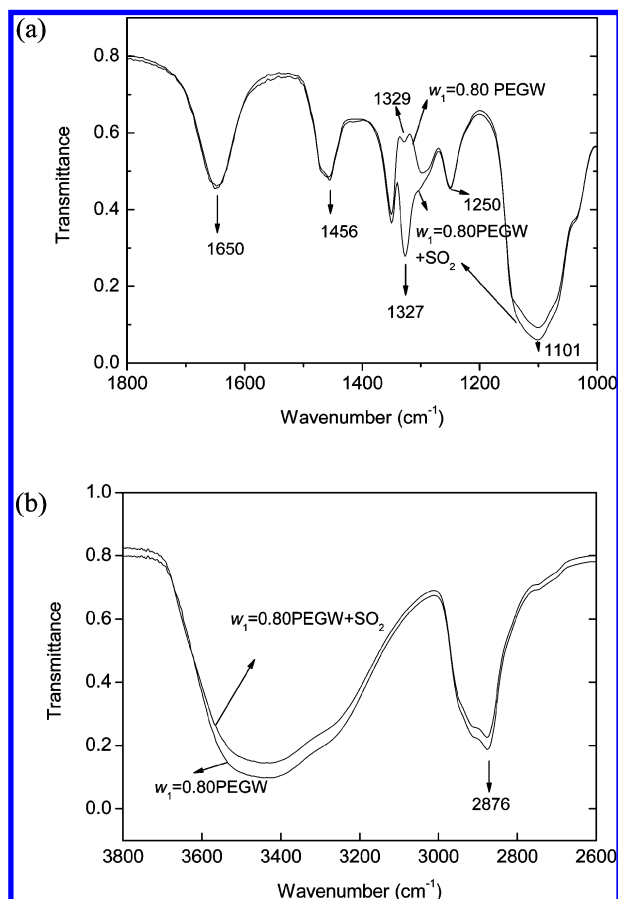**Figure 6.** FTIR spectra of $w_1 = 0.80$ PEGW and $w_1 = 0.80$ PEGW + SO$_2$ in the range (a) $1800-1000$ cm^{-1} and (b) $4000-2400$ cm^{-1}.
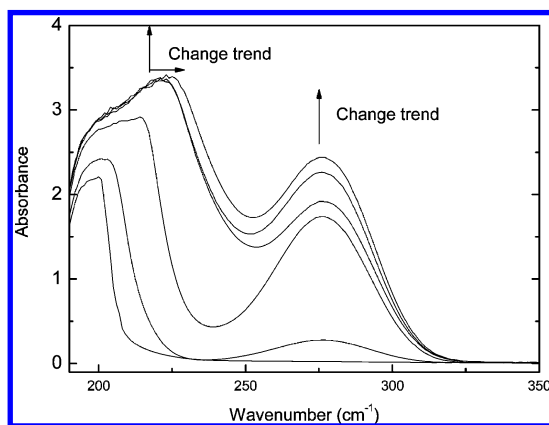

Figure 7. Absorption spectral changes of $w_1 = 0.80$ PEGW + SO$_2$. The change trend was found with increasing SO$_2$ concentration.

(Figure 6). The constant H−O−H bending band in the absorption processes of SO$_2$ is mainly due to the hydrogen-bonding interaction of PEG and SO$_2$ rather than the reaction of water and SO$_2$.

According to overall results, it is expected that the hydrogen-bonding interactions[20,21] among molecules forms $\cdots$H−O−(CH$_2$$\cdots$CH$_2$)O−H$\cdots$OSO$\cdots$. The hydrogen-bonding interaction of SO$_2$ with PEG is very useful to desorb SO$_2$ from PEGWs by pressure reduction, by temperature rise, and by use of a carrier gas in following work. But the above results give us only the present information; the exact molecular mechanism of interactions requires further investigation.

4. Conclusion

PEGW presents native hydrogen-bonding sites for the absorption of SO$_2$ so that the absorption and desorption properties of SO$_2$ can be related to hydrogen-bonding interactions among molecules. Present results show that the possible interactions in PEGW may occur in the following two ways: (1) hydrogen-bonding interaction of the hydrogen atom in H$_2$O with the hydroxyl oxygen atom in PEG by cross-linking, forming −CH$_2$CH$_2$O(H)$\cdots$HOH$\cdots$; and (2) hydrogen-bonding interaction of the hydrogen atom in H$_2$O with the ether oxygen atom in PEG, forming −CH$_2$−CH$_2$−O(CH$_2$−CH$_2$-)$\cdots$HOH$\cdots$. In addition, in the absorption processes of SO$_2$ in pure PEG or w_1 = 0.80 PEGW, the spectral analyses suggest that SO$_2$ can interact with PEG by hydrogen bonds, forming −O−CH$_2$-CH$_2$O−H$\cdots$OSO$\cdots$.

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