

# Hydrogen Bonding and Intermolecular S···O Interaction in the Absorption Processes of SO<sub>2</sub>

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**Abstract:** In previous work, isothermal gas-liquid equilibrium (GLE) data show that diethylene glycol (DEG) (1) + water (2) solutions (DEGWs) can be used as the promising medium for the absorption processes of SO<sub>2</sub>, which showed that  $w_1 = 0.60$  DEG (mass fraction) presents the extreme minimum solubility of 110 mg·L<sup>-1</sup> to SO<sub>2</sub> when the SO<sub>2</sub> concentration in the gas phase was set at  $\Phi_{\text{SO}_2} = 5 \times 10^{-4}$  and the solubility of SO<sub>2</sub> in pure DEG is 259 mg/L at the same gas phase composition. The UV, FTIR, <sup>1</sup>H-NMR, and fluorescence spectra in the SO<sub>2</sub> absorption processes in DEGWs were investigated to present important absorption mechanism for the design and operation of the absorption and desorption processes in flue gas desulfurization (FGD) processes. Based on the spectral results, the possibility of intermolecular hydrogen bonding formation by the DEG hydroxyl oxygen atom with the H<sub>2</sub>O hydrogen atom and S···O interaction formation by the the DEG molecule hydroxyl oxygen atom with the SO<sub>2</sub> molecule sulfur atom are discussed. The existence of these bonds benefits the absorption and desorption of SO<sub>2</sub> in DEGWs.

**Keywords:** Hydrogen Bond; S···O Interaction; Diethylene Glycol; Sulfur Dioxide; Flue Gas Desulfurization

Sulfur dioxide (SO<sub>2</sub>) is an important atmospheric pollutant in the environmental protection, and therefore it is severe in environmental protection. Removal of SO<sub>2</sub> from flue gas is an increasingly important environmental challenge, on one hand, because of the lowering of the admissible emission limit, and, on the other hand, due to the fact that numerous desulfurization processes, such as limestone scrubbing that produces a large volume of solid waste. This letter is a continuation of the systematic program on the absorption processes of SO<sub>2</sub> in the binary mixtures of diethylene glycol (DEG) + water (DEGW) <sup>[1]</sup>. DEG presents native hydrogen bonding sites that the potential desorption characters are presented in the regenerative processes of solutions dissolving SO<sub>2</sub>; therefore, it has in this work and its similar complexes in other studies been paid great attention to alcohol + water system for SO<sub>2</sub> removal <sup>[2-6]</sup>.

In the previous work <sup>[1]</sup>,  $w_1 = 0.60$  DEG (mass fraction of DEG in DEGW) presents the extreme minimum solubility of 110 mg·L<sup>-1</sup> to SO<sub>2</sub> when the SO<sub>2</sub> con-

centration in the gas phase was set at  $\Phi_{\text{SO}_2} = 5 \times 10^{-4}$ , and the solubility of SO<sub>2</sub> in pure DEG is 259 mg/L at the same composition. The present work was mainly focused on investigating absorption mechanism for the design and operation of the absorption and desorption process in flue gas desulfurization (FGD) with potential industrial application of DEG aqueous solutions.

**In various DEGWs**, the interactions of DEG with H<sub>2</sub>O are due to the variational property of hydroxyl group in DEG because the band is found to shift toward higher frequency from 3356 cm<sup>-1</sup> to 3422 cm<sup>-1</sup> with increasing H<sub>2</sub>O concentration. The bending vibrational frequency of H<sub>2</sub>O changes from 1652 cm<sup>-1</sup> to 1645 cm<sup>-1</sup>, which indicates that the interactions of DEG with H<sub>2</sub>O result from the property of hydrogen atom in H<sub>2</sub>O. Meanwhile, the stretching vibrational band of C-O-C in DEG is found to shift toward lower frequency from 1061 cm<sup>-1</sup> to 1057 cm<sup>-1</sup>, which indicates that interactions can be related to the property of ether oxygen atom of DEG. Based on above results, the interactions between DEG and H<sub>2</sub>O can be due to the following two ways: (1) intermolecular hydrogen bonding and interaction of hy-

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drogen atom in H<sub>2</sub>O with hydroxyl oxygen in DEG as the formations of -CH<sub>2</sub>CH<sub>2</sub>O(H)⋯HOH⋯; and (2) weak intermolecular hydrogen bonding and interaction of hydrogen in H<sub>2</sub>O with ether oxygen in DEG as the formation of -CH<sub>2</sub>-CH<sub>2</sub>-O(CH<sub>2</sub>-CH<sub>2</sub>-)⋯HOH⋯.

The electronic transitions blue shift from 208 nm to 195 nm with increasing H<sub>2</sub>O concentration in DEGWs. The absorption band is assigned to the n→σ\* electronic transition of unshared electronic pair of hydroxyl oxygen atom in DEG because the n→σ\* electronic transition of H<sub>2</sub>O and the n→σ\* electronic transition of ether oxygen atom in DEG are often found at the vacuum ultraviolet region. With increasing H<sub>2</sub>O concentration, intermolecular hydrogen bonding and interaction of hydroxyl oxygen atom in DEG with hydrogen atom of H<sub>2</sub>O easily happened; however, the hydrogen bonding and interaction makes the n→σ\* electronic transition of hydroxyl oxygen in DEG become more difficulty. Above results show that the intermolecular hydrogen bonding and interaction in the DEGW be formed as -CH<sub>2</sub>CH<sub>2</sub>O(H)⋯HOH⋯.

**In the DEG + SO<sub>2</sub> system**, with increasing SO<sub>2</sub> concentration, the new absorption peak at 1327 cm<sup>-1</sup>, which are reported at 1344 cm<sup>-1</sup> for SO<sub>2</sub> in non-complexing CCl<sub>4</sub> [7, 8], can be attribute to the *V*<sub>as</sub> of SO<sub>2</sub> because the IR and Raman spectra indicate the following values for the fundamental frequencies: symmetry stretching band (*V*<sub>s</sub>)=1151.38cm<sup>-1</sup>, δ=517.69 cm<sup>-1</sup>, and *V*<sub>as</sub>=1361.76 cm<sup>-1</sup>. Meanwhile, the phenomenon that the *V*<sub>as</sub> of SO<sub>2</sub> shifts towards lower wavenumber than *V*<sub>as</sub>=1361.76 cm<sup>-1</sup> can be due to the interaction of the sulfur atom in SO<sub>2</sub> with other atom. SO<sub>2</sub> molecule is known to be polar and the sulfur atom to be electropositive; thus, SO<sub>2</sub> behaves as an electron acceptor by the sulfur atom, and its interaction with hydroxyl oxygen atom (electronegative) in DEG should occur by the way of intermolecular S⋯O interaction, which can not be discussed in the previous EGW + SO<sub>2</sub> system [9]. Unfortunately, the symmetry stretching band (*V*<sub>s</sub>) of SO<sub>2</sub> at 1151 cm<sup>-1</sup> is strongly masked by the vibrations of DEG. An interesting phenomenon was displayed. In the absence of SO<sub>2</sub>, the stretching vibrational band of hydroxyl in DEG was observed at 3375 cm<sup>-1</sup>. In the presence of

SO<sub>2</sub>, the band was changed into a peakier band. The phenomenon could be due to that the addition of SO<sub>2</sub> affects the original hydrogen bonding and interaction among DEG molecules and forms the new intermolecular hydrogen bonding of hydroxyl hydrogen atoms in DEG with oxygen atoms in SO<sub>2</sub> and intermolecular S⋯O interaction.

The characteristic bands of DEG and SO<sub>2</sub> were respectively identified, but no information on a complexing reaction could be obtained. The absorption band of n→π\* electron transition of oxygen atom in SO<sub>2</sub> (π<sub>3</sub><sup>4</sup>) is observed at 276 nm and the absorption intensity of the band increases with increasing SO<sub>2</sub> concentration. Another absorption band, which was mainly due to π→π\* electron transition of sulfur atom in SO<sub>2</sub> (π<sub>3</sub><sup>4</sup>) and n→σ\* electron transition of hydroxyl oxygen atom in DEG, shifts from 208 nm to 219 nm and the absorption intensity of the band increases. The shift results from the intermolecular hydrogen bonding of oxygen atoms in SO<sub>2</sub> with hydroxyl hydrogen atoms in DEG and intermolecular S⋯O interaction. The bonding of oxygen atoms of SO<sub>2</sub> with hydroxyl hydrogen atoms of DEG results in the following two results: (1) the decreasing effects of oxygen atoms on sulfur atom of SO<sub>2</sub> make the π→π\* electron transition of sulfur atom in SO<sub>2</sub> change easier; (2) the decreasing effects of hydroxyl hydrogen atoms on hydroxyl oxygen atoms in DEG make the n→σ\* electron transition of hydroxyl oxygen atom in DEG change easier also.

The chemical shifts of hydrogen in -CH<sub>2</sub>- appear at δ = 3.420~3.604 ppm (8 H), and the chemical shift of hydroxyl hydrogen appears at δ = 4.640, 4.626, and 4.612 ppm (2H) in the <sup>1</sup>H-NMR spectrum of pure DEG. However, with increasing SO<sub>2</sub> concentration, the signal changes into single peak and the chemical shift of hydrogen atoms in -OH groups shifts from δ = (4.640 to 4.612) ppm to 4.507 ppm in DMSO. The phenomena can be due that the interaction of oxygen atoms in SO<sub>2</sub> bonding with hydroxyl hydrogen atoms in DEG increases shielding effect of hydroxyl hydrogen atoms in DEG, so that the signal changes into single peak and the signal of chemical shift of hydroxyl hydrogen in DEG move to-

wards higher magnetic field.

Stable state fluorescence spectra with selective excitation of DEG with increasing SO<sub>2</sub> concentration were recorded. Upon excitation at 205 nm, where the n→σ\* electron transition of oxygen atom of DEG absorbs, strong fluorescence with emission positions at 290-320 nm and 580-620 nm were observed. The fluorescence intensity of the σ\*→n electron transition of oxygen atom of DEG decreases with increasing SO<sub>2</sub> concentration. The phenomena can be due to the intermolecular interaction of the oxygen atom in DEG with SO<sub>2</sub> as the formation of S···O interaction.

**In H<sub>2</sub>O + SO<sub>2</sub> system,** the recorded IR spectra of H<sub>2</sub>O and H<sub>2</sub>O + SO<sub>2</sub> are shown in the previous work [9]. From the spectra two special stretching bands are observed at 1332 cm<sup>-1</sup> and 1151 cm<sup>-1</sup>, which can be attribute to the *V*<sub>as</sub> and *V*<sub>s</sub> of SO<sub>2</sub> [8].

According to above spectral results, it is expected that DEG bonds with SO<sub>2</sub> by the intermolecular hydrogen bonds of -CH<sub>2</sub>CH<sub>2</sub>OH···OSO··· and S···O interaction.

**In DEGW + SO<sub>2</sub> system,** In the recorded IR spectra of *w*<sub>1</sub> = 0.60 DEGW and *w*<sub>1</sub> = 0.60 DEGW + SO<sub>2</sub>, the stretching band at 1329 cm<sup>-1</sup> was observed. Meanwhile, the phenomenon that the *V*<sub>as</sub> of SO<sub>2</sub> shifts lower wavenumber than *V*<sub>as</sub> = 1361.76 cm<sup>-1</sup> can be due to the interaction of the sulfur in SO<sub>2</sub> with hydroxyl oxygen in DEG by the way of S···O interaction. In the absence of SO<sub>2</sub>, the stretching vibrational band of hydroxyl in DEG was observed at 3385 cm<sup>-1</sup> and the band was broad; in the presence of SO<sub>2</sub>, the band was changed into a peakier band. The phenomenon can be due to the new hydrogen bonding of hydroxyl hydrogen in DEG with oxygen in SO<sub>2</sub> and intermolecular S···O interaction.

With increasing SO<sub>2</sub> concentration, the absorption band of n→σ\* electron transition of oxygen atom in SO<sub>2</sub> is observed at 276 nm and the absorption intensity of the band increases. Meanwhile, the special absorption band red shifts from 197 nm to 211 nm and the absorption intensity of band increases also. The results show that π→π\* electron transition of SO<sub>2</sub> and n→σ\* electron transition of oxygen atom of DEG in *w*<sub>1</sub> = 0.60 DEGW

with increasing SO<sub>2</sub> concentration.

The above results suggest the hydrogen bonding and interaction between hydrogen atoms in DEG and oxygen atoms in SO<sub>2</sub> occurred. When such hydrogen bonds are formed, hydroxyl hydrogen atoms in the DEG molecules are attracted by the oxygen atoms in SO<sub>2</sub> and the bond length between hydrogen atom and oxygen atom in EG molecules are elongated. Such an interaction decreases the double bond character of SO<sub>2</sub> 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 DEG-SO<sub>2</sub> complex is the 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 of DEG with SO<sub>2</sub>. Comparing the spectra of *w*<sub>1</sub> = 0.60 DEGW + SO<sub>2</sub> and *w*<sub>1</sub> = 0.60 DEGW, it is observed that the H-O-H bending band and the characteristic bands of DEG are not obviously shifted in the mixture under the influence of SO<sub>2</sub>. The constant H-O-H bending band in the absorption processes of SO<sub>2</sub> is mainly due to the hydrogen interaction of DEG and SO<sub>2</sub> rather than the reaction of water and SO<sub>2</sub>. Meanwhile, FTIR results support that there are S···O interaction of the sulfur atom in SO<sub>2</sub> with hydroxyl oxygen atom in DEG. The hydrogen bonding and interaction of SO<sub>2</sub> with DEG is very useful to desorb SO<sub>2</sub> from DEGWS by pressure reduction, by temperature rise, and by use of a carrier gas in following work. But above results only give us the present information, the exact molecular mechanism of interactions requires further investigation. But in *w*<sub>1</sub> = 0.06 DEGW, which shows lower solubility to SO<sub>2</sub> [1], the hydrogen bonding and S···O interaction among molecules present passive effects on the absorption of SO<sub>2</sub> in DEGW. Stable state fluorescence spectra with selective excitation of DEGW with increasing SO<sub>2</sub> concentration were recorded. Upon excitation at 205 nm strong fluorescence with emission positions at 290-320 nm and 580-620 nm were observed. The fluorescence intensity of the σ\*→n electron transition of oxygen atom of DEG in DEGW decreases with increasing SO<sub>2</sub> concentration, which was due to the interaction of the oxygen atom in DEG with SO<sub>2</sub> as the formation of

S...O interaction.

DEGW presents native hydrogen bonding sites for the absorption of SO<sub>2</sub> so that the absorption and desorption properties of SO<sub>2</sub> can be related to hydrogen bonding and interaction<sup>[10, 11]</sup> among molecules. Present results show that the possible interactions in DEGW result from the following two ways: (1) hydrogen bonding and interaction of hydrogen atom in H<sub>2</sub>O with hydroxyl oxygen atom in DEG by cross-linking as the formation of -CH<sub>2</sub>CH<sub>2</sub>O(H)...HOH...; (2) hydrogen bonding and interaction of hydrogen atom in H<sub>2</sub>O with ether oxygen atom in DEG as the formation of -CH<sub>2</sub>-CH<sub>2</sub>-O(CH<sub>2</sub>-CH<sub>2</sub>-)...HOH... In addition, in the absorption processes of SO<sub>2</sub> in pure DEG or w<sub>1</sub> = 0.60 DEGW, the spectral analyses suggest that SO<sub>2</sub> can interact with DEG by hydrogen bonds as ...OSO...-OCH<sub>2</sub>CH<sub>2</sub>O-H...OSO..., and intermolecular S...O interaction of hydroxyl oxygen atom of DEG with sulfur atom of SO<sub>2</sub>.

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