# Hydrogen bonding interactions between ethylene glycol and water: density, excess molar volume, and spectral study

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**Studies of the density and the excess molar volume of ethylene glycol (EG)-water mixtures were carried out to illustrate the hydrogen bonding interactions of EG with water at different temperatures. The results suggest that a likely complex of 3 ethylene glycol molecules bonding with 4 water molecules in an ethylene glycol-water mixture (EGW) is formed at the maximal excess molar volume, which displays stronger absorption capabilities for $SO_2$ when the concentration of $SO_2$ reaches $400\times10^6$ (volume ratio) in the gas phase. Meanwhile, FTIR and UV spectra of EGWs were recorded at various EG concentrations to display the hydrogen bonding interactions of EG with water. The FTIR spectra show that the stretching vibrational band of hydroxyl in the EGWs shifts to a lower frequency and the bending vibrational band of water shifts to a higher frequency with increasing the EG concentration, respectively. Furthermore, the UV spectra show that the electron transferring band of the hydroxyl oxygen in EG shows red shift with increasing the EG concentration. The frequency shifts in FTIR spectra and the shifts of absorption bands in UV absorption spectra of EGWs are interpreted as the strong hydrogen bonding interactions of the hydrogen atoms in water with the hydroxyl oxygen atoms of EG.**

hydrogen bond, ethylene glycol, water, density, excess molar volume

## 1 Introduction

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[1,2] and the UV spectroscopy gives information about various electronic transitions. Generally, FTIR spectral techniques[3,4] and UV spectral techniques offer the advantages to measure the association properties and hydrogen bonding capability to assess interactions of alcohol with water by analyzing band shifts and changes in 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 addition, alcohol-water systems show favorable scrubbing and desorption properties in factual industrial processes[5], so the scrubbing mechanism and molecular existent forms of the system attract our eyes; and then our research group has been paying great attention to scrubbing techniques by alcohol-water systems for several years[6,7]. In the recent work, EGWs of 70% (volume concentration of EG) show stronger solubility (Figure 1) for $SO_2$ (168.84 mg/L) detected by gas-liquid equilibrium (GLE) measurements when the concentration of $SO_2$ in the gas phase reaches $400\times10^6$ (volume ratio) and the GLE measurements and data will be reported in the near future. EGWs present native hydrogen
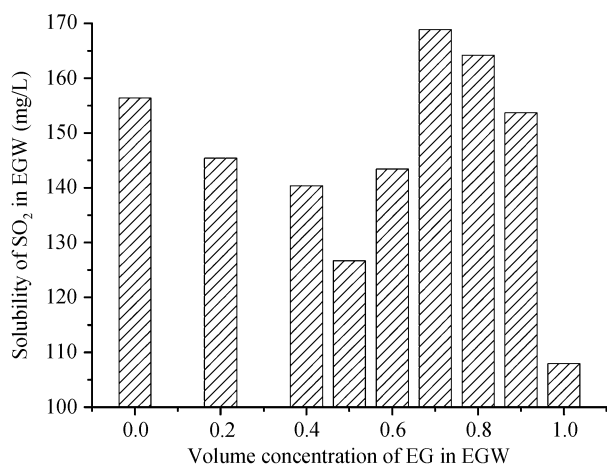
**Figure 1** Solubility of $SO_2$ at various volume concentrations of EGWs when the concentration of $SO_2$ in the gas phase reaches $400\times10^{-6}$ (volume ratio).

bonding sites for the absorption of $SO_2$ so that the scrubbing and desorption properties[8,9] may be related to strong hydrogen bonding interactions[10,11] between the hydrogen in water and the hydroxyl oxygen in EG.

In this report, the analytical results of density show that the maximal excess molar volume of EGWs appears at above 0.4 (molar fraction of EG) or 67% (volume concentration of EG). The finding suggests that the likely complex of 3 ethylene glycol molecules bonding with 4 water molecules is formed at the maximal excess molar volume. The frequency shifts in FTIR spectra and the shifts of absorption bands in UV absorption spectra of EGWs are interpreted as the formation of hydrogen bonds of water molecules with the surrounding hydroxyl groups of EG molecules. In addition, the works of other groups[4,12−15] showed that the likely complex of one ethanol molecule linking with two water molecules can be formed by hydrogen bonding interactions, which was determined by the FTIR and UV spectra in our work as a comparison.

## 2 Experimental section

High pure EG ($\geqslant$99.8%) was purified from commercial EG (A.R, $\geqslant$98.0%, made in China) through dehydration by anhydrous $Na_2SO_4$ and refined by a rectification process. Ethanol (HPLC grade, $\geqslant$99.8%) was made in China.

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 auto-align energy optimization and a dynamically aligned interferometer, and fitted with a constringent $BaSO_4$ pellet for the measurement of aqueous solutions, an OPUS/IR operator, and an IR source. A base line correction was made for the spectra that were recorded in air; and then 20 μL solution was used to perform on the FTIR spectrometer in each of the measurements and the thickness of the thin layer of samples was less than a typical thickness of 2 μm.

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 to 900 nm. A base line correction was made for the spectra recorded in deionized water.

The densities[16,17] of the pure liquids and the mixtures were measured with a capillary pycnometer that gave an accuracy of 2 parts in $10^5$. Degassed pure water was used as the calibrating substance. A thermostatically controlled, well-stirred water bath whose temperature accuracy was controlled to ± 0.02 K was used for all the density measurements. Binary mixtures were prepared by mass, using an analytical balance with a precision of ±0.0001 g (TG328B, Shanghai, China). The uncertainty of the density measurements was estimated to be ±0.1%.

Then the excess molar volume ($V^E$)[18] of each EGW was calculated by the following formula:

$$V^{\mathrm{E}} = V_m - \sum_{i=1}^{2} V_i x_i, \qquad (1)$$

where $V_i$ is the molecular volume of EG; $x_i$ is the molar fraction of EG; $V_m$ is the molar volume of an EGW.

For a binary system, $V_m$ is calculated by the following formula:

$$V_m = \left( x_1 M_1 + x_2 M_2 \right) / \rho_m, \qquad (2)$$

where $\rho_m$ represents the density of an EGW; $M_1$ and $M_2$ are the molecular weights of EG and water; $x_1$ is the molar fraction of EG; $x_2$ is the molar fraction of water.

## 3 Results and discussion

Various EGWs display different solubility for $SO_2$ from $SO_2/N_2$ mixtures. The solubility may be related to the special molecular structure between EG and water, which may result from the hydrogen bonding interactions of EG with water. Considering the possible interactions, firstly, the densities of EGWs were determined at various temperatures and the data are shown in Table 1 and Figure 2.

**Table 1**  Experimental densities ($\rho$) of EG (1) + water (2)

| Molar fraction of EG in EGW, $x_1$ | $\rho$ (g $\cdot$ cm$^{-3}$) at the following temperatures of $T$/K | | | |
| | 308.15 | 313.15 | 318.15 | 323.15 |
|---|---|---|---|---|
| 0.0000 | 0.9941 | 0.9922 | 0.9900 | 0.9880 |
| 0.0145 | 1.0007 | 0.9984 | 0.9967 | 0.9943 |
| 0.0312 | 1.0080 | 1.0047 | 1.0025 | 1.0007 |
| 0.0484 | 1.0139 | 1.0115 | 1.0090 | 1.0052 |
| 0.0686 | 1.0220 | 1.0180 | 1.0152 | 1.0122 |
| 0.0883 | 1.0280 | 1.0244 | 1.0213 | 1.0181 |
| 0.1107 | 1.0335 | 1.0305 | 1.0280 | 1.0233 |
| 0.1621 | 1.0466 | 1.0426 | 1.0399 | 1.0350 |
| 0.2247 | 1.0583 | 1.0547 | 1.0513 | 1.0464 |
| 0.3032 | 1.0690 | 1.0660 | 1.0628 | 1.0569 |
| 0.4035 | 1.0793 | 1.0762 | 1.0733 | 1.0677 |
| 0.5366 | 1.0887 | 1.0855 | 1.0829 | 1.0770 |
| 1.0000 | 1.1030 | 1.0999 | 1.0978 | 1.0910 |
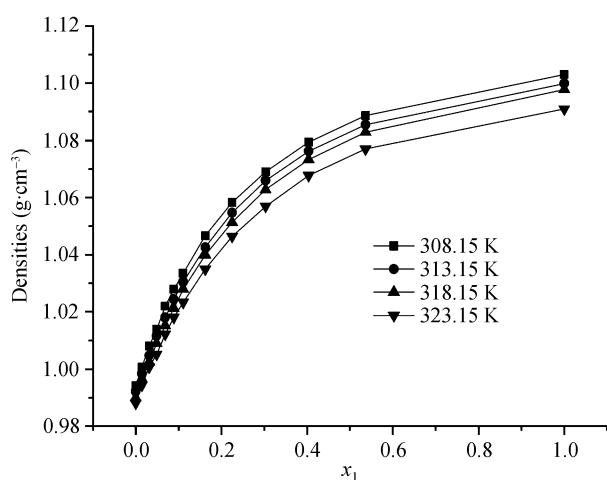


**Figure 2**  Experimental densities of EGWs at different concentrations and different temperatures. $x_1$: EG molar fraction for EG (1) + water (2) mixtures.

Figure 2 shows that densities increase rapidly with increasing EG concentrations, and then increase lentamente from 0.4 to 1.0 (molar fraction). Meanwhile, densities of EGWs decrease obviously with increasing temperatures.

So, $V^E$ of each EGW was calculated by formula (1), and the values of $V^E$ are shown in Table 2, and the curves of $V^E$ are shown in Figure 3.
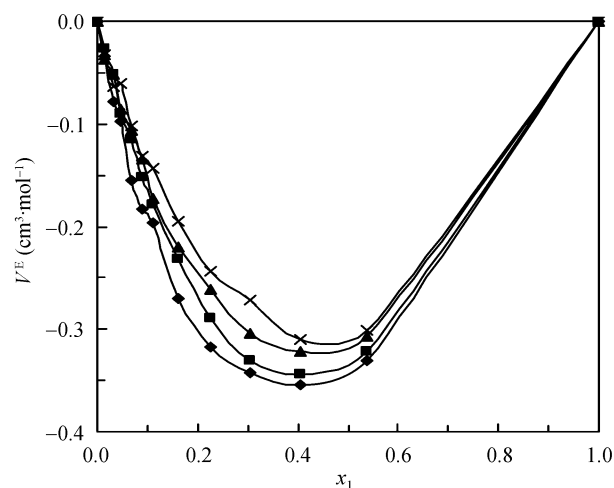


**Figure 3**  Changes of the excess molar volumes of EGW with increasing molar fraction of EG in ethylene glycol (1) + water (2) mixtures at different temperatures. ◆ 308.15 K; ■ 313.15 K; ▲ 318.15 K; × 323.15 K.

**Table 2**  Excess molar volumes, $V^E$, for EG (1) + water (2)

| Molar fraction of EG in EGW, $x_1$ | $V^E$ (cm$^3 \cdot$ mol$^{-1}$) at the following temperatures of $T$/K | | | |
| | 308.15 | 313.15 | 318.15 | 323.15 |
|---|---|---|---|---|
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.0145 | −0.0342 | −0.0270 | −0.0375 | −0.0326 |
| 0.0312 | −0.0777 | −0.0510 | −0.0516 | −0.0632 |
| 0.0484 | −0.0976 | −0.0907 | −0.0856 | −0.0609 |
| 0.0686 | −0.1552 | −0.1157 | −0.1057 | −0.1023 |
| 0.0883 | −0.1825 | −0.1527 | −0.1349 | −0.1317 |
| 0.1107 | −0.1956 | −0.1792 | −0.1733 | −0.1433 |
| 0.1621 | −0.2698 | −0.2323 | −0.2206 | −0.1943 |
| 0.2247 | −0.3173 | −0.2892 | −0.2605 | −0.2434 |
| 0.3032 | −0.3419 | −0.3304 | −0.3036 | −0.2718 |
| 0.4035 | −0.3549 | −0.3437 | −0.3216 | −0.3097 |
| 0.5366 | −0.3311 | −0.3214 | −0.3063 | −0.3015 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Figure 3 shows that all the $V^E$ values in different EGWs are negative and the extremum of $V^E$ appears near 0.4 (molar fraction) and it keeps increasing with increasing temperatures at the same EG molar fraction. On the basis of these findings, we consider that hydrogen bonds were formed between hydroxyl of EG and water over the whole concentration range of EGWs. At the maximal excess molar volume, there presents the closest aggregates.

FTIR spectra of OH stretching vibration and bending vibration of water in EGWs and ethanol water system (EW) were determined respectively and the spectral data are shown in Table 3.

Table 3, Figures 4 and 5 show that the bending vibrational frequency of water changes from 1645 to 1659 cm$^{-1}$, where it is assumed there is a maximum of hydro-

**Table 3** FTIR spectral data of OH stretching vibration of alcohol-water and bending vibration of water

| ① Volume fraction of EG in EGW (%) | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| ① OH stretching vibration (cm$^{-1}$) | 3349 | 3355 | 3370 | 3370 | 3372 | 3374 | 3391 | 3392 | 3396 |
| ① $K$ (N·cm$^{-1}$) | 6.217 | 6.240 | 6.296 | 6.296 | 6.303 | 6.311 | 6.373 | 6.378 | 6.393 |
| ① Bending vibration of H$_2$O (cm$^{-1}$) | 1657 | 1656 | 1655 | 1653 | 1651 | 1651 | 1650 | 1648 | 1647 |
| ② Volume fraction of ethanol in EW (%) | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |
| ② OH stretching vibration (cm$^{-1}$) | 3364 | 3386 | 3384 | 3385 | 3389 | 3398 | 3394 | 3394 | 3401 |
| ② $K$ (N·cm$^{-1}$) | 6.273 | 6.356 | 6.348 | 6.352 | 6.367 | 6.401 | 6.386 | 6.386 | 6.412 |
| ② Bending vibration of H$_2$O (cm$^{-1}$) | 1659 | 1653 | 1653 | 1652 | 1653 | 1653 | 1651 | 1649 | 1645 |

$K$ represents the bond force constant of OH stretching vibration in alcohol-water systems. OH stretching vibration of pure water is displayed at 3424 cm$^{-1}$ (average $K$ = 6.499 N/cm) and bending vibration of pure water is displayed at 1645 cm$^{-1}$. Meanwhile, OH stretching vibration of EG is observed at 3343 cm$^{-1}$ (average $K$ = 6.196 N/cm) and OH stretching vibration of ethanol is detected at 3335 cm$^{-1}$ (average $K$ = 6.166 N/cm).
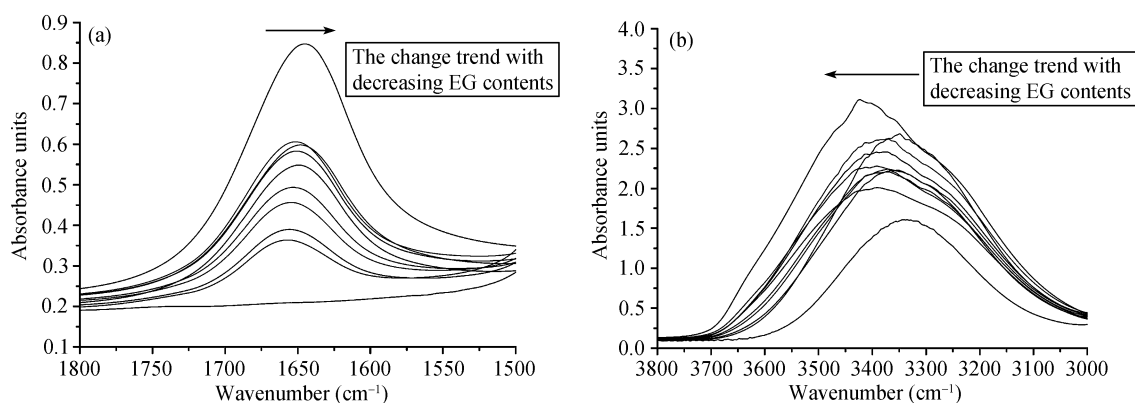


**Figure 4** FTIR spectra of various volume concentrations of EGWs. (a) represents the spectra of the bending vibration of H$_2$O in various volume concentrations of EGWs; (b) represents the spectra of the OH stretching vibration of EGWs in various volume concentrations of EGWs.
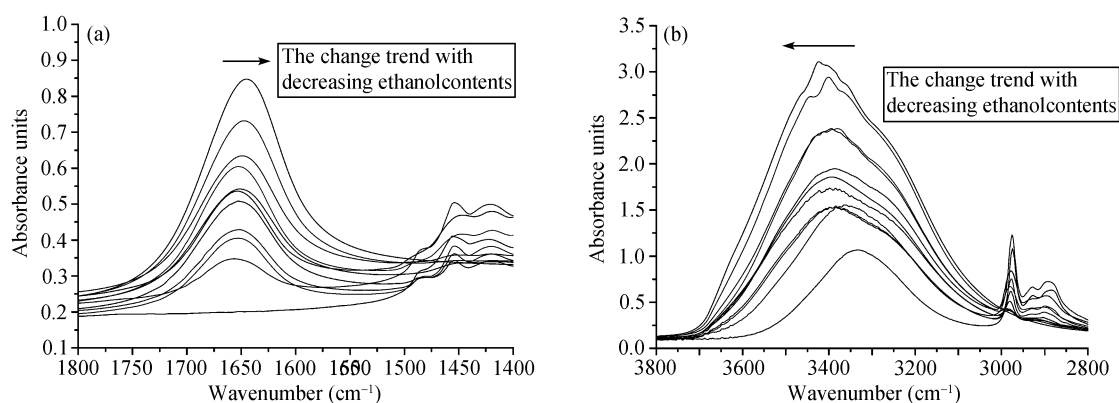


**Figure 5** FTIR spectra of various volume concentrations of EWs. (a) represents the spectra of the bending vibration of H$_2$O in various volume concentrations of EW; (b) represents the spectra of the OH stretching vibration of EW systems in various volume concentrations of EWs.

gen bonding association in alcohol-water systems. This band has been reported to appear at 1645 cm$^{-1}$ in water saturated low density polyethylene[1]. The fact that OH bending vibrational band shifts towards a higher frequency in EGWs indicates that there are possible hydrogen bonding interactions of hydrogen atoms in water with hydroxyl oxygen atoms in EG by cross-linking in the form of $\cdots$HOH$\cdots$. Meanwhile, the stretching vibrational band of OH groups in EGWs is found to shift to a low frequency from 3401 to 3349 cm$^{-1}$ with increasing the EG concentration; the average $K$ increases with decreasing alcohol concentrations. These results indicate that there are hydrogen bonding interactions between the oxygen atoms of water and the hydrogen atoms of OH in alcohol and may form the structure of R′CH$_2$OH$\cdots$OH(H) $\cdots$ (R′ represents —CH$_3$ or —CH$_2$OH). Figure 6 shows that there may form congeries among EG mole-

cules compared with Figures 4 and 5. When water is added into EG, it may affect the existence of congeries and present new existent form in EGWs.

Figure 7 shows that blue shift phenomena happening with increasing concentrations of alcohol-water mixtures may be attributed to the electronic transitions of the unshared electronic pair of hydroxyl oxygen. The electronic transitions from 190 to 200 nm may be due to $n \rightarrow \sigma^*$ electronic transitions of alcohol in alcohol-water mixtures because the $n \rightarrow \sigma^*$ electronic transitions of water are often found at the vacuum ultraviolet region. With increasing water contents in the alcohol-water system, hydrogen bonding interactions of hydroxyl oxygen of alcohol with hydrogen of water happen more easily; however, the interactions make the electronic transition of hydroxyl oxygen in alcohol become more difficult under the effect of hydrogen bonds. Above results show that the hydrogen bonds in the alcohol-water system may be formed as R′CH$_2$O(H)$\cdots$HOH (R′ represents —CH$_3$ and —CH$_2$OH).

FTIR and UV spectra indicate that there may form a hexatomic ring between one hydroxyl group of the alcohol molecule and two H$_2$O molecules in an alcohol-water system. Meanwhile, there may be two surplus hydrogen bonding sites from two hydrogen atoms of two H$_2$O molecules in the hexatomic ring, and then the two hydrogen atoms may interact with other hydroxyl groups of alcohol. The most likely complex (Figure 8(a)) may be related to 2 water molecules and 1 hydroxyl group of the ethanol molecule resulting in a molar ratio of 2:1[12−15] (molar fraction of ethanol in an EW system is displayed at 0.333). The experimental data on densities, excess
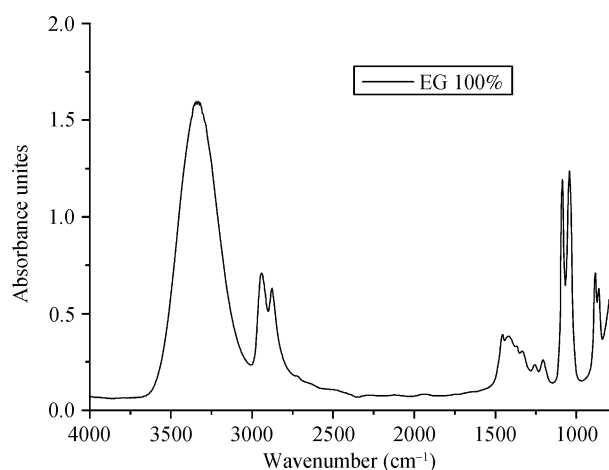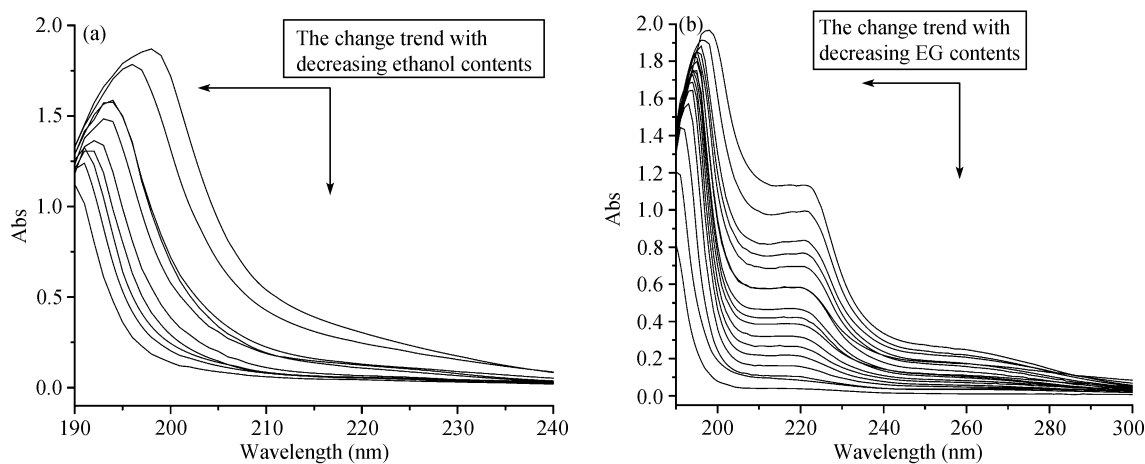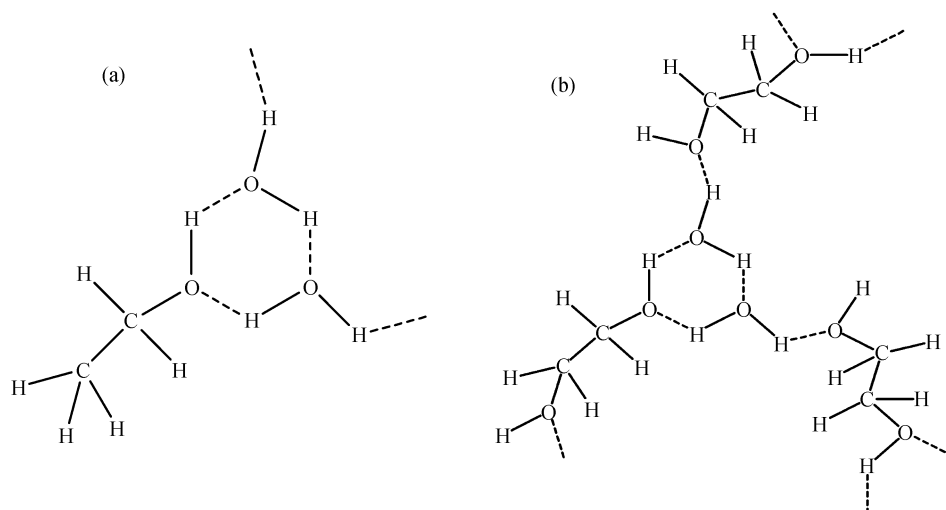


**Figure 6**  FTIR spectrum of pure EG.



**Figure 7**  Absorption spectra at various concentrations of ethanol and ethylene glycol. (a) represents EWs and (b) represents EGWs.

**Figure 8** Possible hydrogen bonding interaction forms of water with alcohol in alcohol-water systems. (a) represents the reference form in EWs and (b) represents the presumptive existent form in EGWs.

molar volume analyses, and spectral properties of EGWs show that the most likely complex between ethylene glycol and water in EGWs has a molar ratio of 4:3 (the molar fraction of EG in EGW is presented at 0.428) and the presumptive form by hydrogen bonding interactions of ethylene glycol with water is shown in Figure 8(b). However, the interaction forms are not fixed and every OH group of alcohol may interact with one $H_2O$ molecule or two $H_2O$ molecules in EGWs (Figure 8(b)). The interaction of EG with water may be strengthened in the presumptive molecular structure and there is a lower site-blocking effect in EGWs. In the molecular structure, the hexatomic ring may strengthen the hydrogen bonding interactions of ethanol with water and minimize the total energy of an alcohol-water system.

## 4  Conclusion

In this work, the density analyses of EGWs showed that the maximal excess molar volume of an EGW was displayed at above 0.4 (molar fraction). This result suggests that the likely complex of 3 ethylene glycol molecules bonding with 4 water molecules is formed at the maximal excess molar volume in an EGW. The frequency shifts in FTIR spectra and the shifts of absorption bands in UV absorption spectra of EGWs at the maximal excess molar volume are interpreted as result of strong hydrogen bonding interactions of the water hydrogen atoms with the hydroxyl oxygen atoms in EG.

1  Lasgabaster A, Abad M J, Barral L, Ares A. FTIR study on the nature of water sorbed in polypropylene (PP)/ethylene alcohol vinyl (EVOH) films. Eur Polym J, 2006, 42: 3121－3132

2  Dharmalingam K, Ramachandran K P. FTIR and dielectric studies of molecular interaction between alkyl methacrylates and primary alcohols. Physica B, 2006, 4: 1－5

3  Palombo F, Paolantoni M, Sassi P, Morresi A, Cataliotti R S. Spectroscopic studies of the "free" OH stretching bands in liquid alcohols. J Mol Liq, 2006, 125: 139－146

4  Yuan B, Dou X M. Near-infrared spectral studies of hydrogen-bond in water-methanol mixtures. Spectrosc Spect Anal (in Chinese), 2004, 11: 1319－1322

5  Desulphurization in coal combustion systems. The Institution of Chemical Engineering. 1989

6  Li X X, Liu Y X, Wei X H. Hydrolysis of carbonyl sulfide in binary mixture of diethylene glycol diethyl ether and water. Chinese J Chem Eng, 2005, 13(2): 234－238

7  Wei X H. Desulfurication & decarburization solution activities. CN. 02130605. 2. 2002

8  Potteau E, Levillain E, Lelieur J P. Mechanism of the electrochemical reduction of sulfur dioxide in non-aqueous solvents. J Electroanal Chem, 1999, 476: 15－25

9  van Dam M H H, Lamine A S, Roizard D, Lochon P, Roizard. Selective sulfur dioxide removal using organic solvents. Ind Eng Chem Res, 1997, 36: 4628－4637

10  Ivopoulos P, Sotiropoulou M, Bokias G, Staikos G. Water-soluble hydrogen-bonding interpolymer complex formation between poly (ethylene glycol) and poly(acrylic acid) grafted with poly(2-acryla-

mido-2-methylpropanesulfonic acid). Langmuir, 2006, 22: 9181－9186

11  Schofield D P, Lane J R, Kjaergaard H G. Hydrogen bonded OH-stretching vibration in the water dimer. J Phys Chem A, 2007, 111: 567－572

12  Errington J R, Boulougouris G C, Economou I G, Panagiotopoulos A Z, Theodorou D N. Molecular simulation of phase equilibria for water-methane and water-ethane mixtures. J Phys Chem B, 1998, 102: 8865－8873

13  Dashnau J L, Nucci N V, Sharp K A. Hydrogen bonding and the cryoprotective properties of glycerol/water mixtures. J Phys Chem B, 2006, 110: 13670－13677

14  Nose A, Hamsaki T, Hojo M, Kato R, Uetara K, Ueda T. Hydrogen bonding in alcoholic beverages (distilled spirits) and water-ethanol mixtures. J Agric Food Chem, 2005, 53: 7074－7081

15  Tong J B, Liu S L, Li M P, Zhang S W. Study on the spectrum of ethanol-water association system. Liq Sci Tech (in Chinese), 2003, 3: 83－84

16  Tsierkezos N G, Molinou I E. Densities and viscosities of ethylene glycol binary mixtures at 293.15 K. J Chem Eng Data, 1999, 44: 955－958

17  Naidu B V K, Rao K C, Subha M C S. Densities and viscosities of mixtures of some glycols and polyglycols in dimethyl sulfoxide at 308.15 K. J Chem Eng Data, 2002, 47: 379－382

18  Pal A, Sharma S. Excess molar volumes and viscosities of binary liquid mixtures of ethylene glycol diethyl ether + ethylene glycol monomethyl, + diethylene glycol monomethyl, + triethylene glycol monomethyl ethers at 298.15 and 308.15 K. J Chem Eng Data, 1999, 44: 1067－1070