Theoretical Study of Intermolecular Hydrogen Bonding and Interaction in Ethylene Glycol-Water Mixtures

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Received: 17 September 2013;

Accepted: 29 October 2013;

Published online: 15 April 2014;

AJC-15046

Aqueous solution of ethylene glycol (EG) were used in the SO₂ absorption processes. Meanwhile, the various spectra suggested that aqueous solution of ethylene glycol can bond with SO₂ by the mean of hydrogen bonding and interaction. It is therefore important to understand the interaction of ethylene glycol with H₂O at the molecular level. In this work, the ground-state structure and energies of ethylene glycol, H₂O, EG₂-H₂O and EG/H₂O₁₋₃ hydrogen bonded clusters were investigated using density functional theory (DFT). Calculated IR spectra, dipole moments and rotational constants for all optimum conformers at the same level are provided for comparison with the experiments. The binding energies ($-D_{e0}$) and the calculated harmonic vibrational frequencies for ethylene glycol and H₂O are in good agreement with previous calculated and experimental results. The $-D_{e0}$ values for ethylene glycol + H₂O shows that the addition of H₂O can disrupt the original hydrogen bonds in ethylene glycol system and ethylene glycol can be easily solved in water.

Keywords: Hydrogen Bonding and Interaction, Ethylene Glycol, Water, Density Functional Theory (DFT).

INTRODUCTION

Sulfur dioxide (SO₂) is an important atmospheric pollutant and therefore it is important in environmental protection. In recent years, there is a growing interest in the use of organic solvents for removal of SO₂ and organic solvents used as absorbents have been identified as an option among the regenerative process¹⁻⁵ 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 processes⁶. Therefore, our research group has paid great attention to alcohol + water system for removal of SO₂ for several years⁷⁻¹⁰.

In the recent work¹¹, Φ_1 = (70 to 90) % (volume fraction of ethylene glycol in aqueous solutions of ethylene glycol) showed stronger capacity to grasp SO₂. Aqueous solutions of ethylene glycol present native hydrogen bonding sites for the absorption of SO₂ so that the absorption and desorption properties of SO₂ in aqueous solutions of ethylene glycol^{12,13} may be related to hydrogen bonding and interaction¹⁴⁻¹⁶ among molecules.

It is therefore important to understand the competition between hydrogen bonding and interactions involving ethylene glycol and H₂O at the molecular level. The purpose of the present computational work is, therefore, to elucidate the hydrogen bonding and interaction between ethylene glycol and H₂O.

EXPERIMENTAL

All quantum chemical calculations were carried out with the Gaussian 03 suite of programs, using reasonable 6-31 + G (3d, 3p) and 6-311 + G (3d, 3p) basis sets and density functional theory (DFT) with the composite B3LYP exchange correlation functional and 6-31 + G (3d, 3p) and 6-311 + G (3d, 3p) basis sets. Frequency calculations were performed following each optimization to obtain the zero point energy (ZPE) and IR spectral data. The binding energies ($-D_{e0}$) of clusters were calculated with respect to the separate molecules at the same level. For a given cluster, the binding energy, $-D_e$ (kcal/mol) and ZPE corrected binding energies, $-D_{e0}$ (kcal/mol), were determined as a difference between the total energies of the clusters and the sum of the total energies of the isolated monomers contained in the clusters as follows:

$$E_{\text{bind}} = -D_e = E_A + E_B - E_{AB} \quad (1)$$

$$E_{\text{bind},0} = -D_{e0} = E_{A,0} + E_{B,0} - E_{AB,0} \quad (2)$$

The $-D_e$ and $-D_{e0}$ values for a trimer or a tetramer are defined similarly.

RESULTS AND DISCUSSION

Various possible structures of ethylene glycol/H₂O₁₋₃ hydrogen bonded clusters are optimized and all optimum geometric structures are presented.

Ethylene glycol monomer and ethylene glycol dimer

Ethylene glycol monomer: The most stable conformer of ethylene glycol is reported as tGg' conformer¹⁷. In this work, the intramolecular H...O bond length in the tGg' is in the range of (2.389 to 2.405) Å under the B3LYP/6-31 and B3LYP/6-311 level, which is reported as 2.362 Å in ref¹⁸. (NLSD/DZVP2 level) and 2.3605 Å in ref¹⁹. (QCISD/6-311++G (2d, 2p) level). In the tGg', the intramolecular HB conformation is comprised of a five-membered quasi-ring and the HB is expected to be weak¹⁶.

In Table-1, the total dipole moments for the geometries optimized with the same basis set are listed for conformers along with the experimentally determined dipole moments. In this work, the dipole moment of tGg' is found in the range of (2.42 to 2.71) D, which were reported in the range of (2.65 to 2.74) D¹⁸⁻²¹. From Table-1, three rotational constants (GHZ) for conformer 1 (Fig. 1, (1)) calculated in this work are higher than the experimental values^{15,18}.

Table-2 showed that the computational stretching and bending vibrational frequencies at the 6-31+G (3d, 3p) and 6-31++G (3d, 3p) levels are in good agreement with previous experimental results^{11,12}.

We present that the values of other bond lengths, bond angles and dihedral angles not given here are available upon request. The intramolecular H...O bond length in the ethylene glycol monomer is 2.3885 Å. The studies of Howard *et al.*²², have primarily focused on the lowest energy conformer; however, the Fig. 1 (1) conformer has been identified in the rotational spectra^{20,23}.

Ethylene glycol dimer: The intramolecular H...O bond lengths of ethylene glycol molecules in the ethylene glycol dimer are determined at 2.8362 Å and 2.8395 Å in this work, which were reported at 2.75 Å and 2.78 Å at the DFT B3LYP/

Fig. 1. Species involved in hydrogen bonding and interaction calculation. Bond lengths are in Å. The dashed lines indicate the possible hydrogen bonding and interaction. Part possible hydrogen bond lengths: (1) 1.8925 Å; (2) 2.2305 Å; (3) 1.8589 Å; (4) 2.86385 Å; (5) 1.9523 Å; (6) 1.8456 Å; (7) 1.7429 Å; (8) 1.8175 Å; (9) 2.8039 Å; (10) 2.2892 Å; (11) 1.9242 Å; (12) 2.0093 Å; (13) 1.7443 Å

6-311g (3df, 3pd) level²⁴. The intermolecular H...O bond lengths of ethylene glycol molecules in the ethylene glycol dimer are determined at 1.8783 Å and 1.8788 Å, which are in agreement with the values of 1.86 Å and 1.89 Å calculated at the DFT B3LYP/6-311g (3df, 3pd) level²⁴.

TABLE-1
ELECTRONIC ENERGIES, DIPOLE MOMENTS, AND ROTATIONAL CONSTANTS OF THE SPECIES.
THE DASHED LINES INDICATE THE POSSIBLE HYDROGEN BONDING AND INTERACTION

No.	Species	E _c (a.u.)	ZPE (kcal/mol)	E ₀ (a.u.)	Dipole (Debye)	Rotational Constants (GHZ)		
1	EG	-230.25985	53.58	-230.17452	2.7055	15.30873	5.54897	4.58297
		-228.59245 ^a	55.21 ^b		2.7396 ^c	15.21460 ^b	5.53833 ^b	4.59503 ^b
		-229.87192 ^b	52.29 ^e		2.65 ^f	15.127	5.311	4.412
		-229.61002 ^c			2.71 ^d	(exptl.) ^f	(exptl.) ^f	(exptl.) ^f
		-229.77942 ^d				14.920 ^f	5.507 ^f	4.524 ^f
		-229.75834 ^e						
2	EG...EG	-460.53248	109.00	-460.35878	1.7182	2.53343	1.05119	0.80422
		-459.23021 ^c			1.625 ^c			
					3.83-4.09 ^g			
3	H ₂ O	-76.42257	13.24	-76.40148	2.2491	820.87618	421.46016	278.48063
		-76.23311 ^d	13.3 ⁱ	-76.43405 ⁱ	2.05 ^d			
		-76.46333 ⁱ			1.856 ^h			
4	H ₂ O...H ₂ O	-152.85541	28.99	-152.80923	2.9007	212.85038	6.55614	6.55275
		-152.93429 ⁱ	29.1 ⁱ	-152.87772 ⁱ				
5	H ₂ O...H ₂ O...H ₂ O	-229.29827	45.93	-229.22512	1.2346	7.01387	6.89139	3.54654
		-229.41364 ⁱ	45.9 ⁱ	-229.33077 ⁱ				
6	(EG) ₂ ...H ₂ O	-536.97384	125.68	-536.77356	5.2739	1.65618	0.87820	0.77308
		-306.69677	69.59	-306.58593	3.9243	4.88867	3.48921	2.20339
7	EG...H ₂ O	-306.08899 ^d			3.72 ^d			
		-306.97240 ^e						
		-383.13587	85.98	-382.99891	1.7273	3.03288	1.93224	1.71296
8	EG...H ₂ O	-459.58199	102.28	-459.41907	2.3963	1.80237	1.48389	1.27787

^aCalculated at the LCAO-SCF/4-31G level (ref. ¹⁷). ^bCalculated at the MP2/6-311 G (d, p) level (ref. ¹⁸). ^cCalculated at the SCF/6-31 + G* (ref. ¹⁹).

^dCalculated at the MP2/6-311 + G (2d, 2p) level (ref. ¹⁹). ^eCalculated at the MP4 (SDTQ) level (ref. ³⁶). ^fCalculated at the MP2/6-31G** level (ref. ²¹).

^gCalculated at the DFT/B3LYP/6-311G (3df, 3pd) level (ref. ²⁴). ^hCalculated at the DFT/B3LYP functional (ref. ²⁶). ⁱCalculated at the DFT/B3LYP/6-31 + G (d, p) level (ref. ²⁷). ^jCalculated at the DFT/B3LPY functional (ref. ³⁷).

TABLE-2
RELATIVE ENERGIES OF THE INTERMEDIATE SPECIES OF ETHYLENE GLYCOL-H₂O SYSTEM

Species	D _c ^a (kcal/mol)	D _{e0} ^b (kcal/mol)	Species	D _c ^a (kcal/mol)	D _{e0} ^b (kcal/mol)
1 (1)	0.0000	0.0000	10 (10)	0.0000	0.0000
2 (1 + 1)	-8.0195	-6.1119	11 (1 + 10)	-5.6726	-4.6247
3 (3)	0.0000	0.0000	12 (1 + 1 + 10)	-17.0493	-13.7737
4 (3 + 3)	-6.4467	-3.9345	13 (3 + 10)	-5.2559	-3.7380
	-6.0 ^b	-4.95 (exptl.) ^c			
		-3.7 ^d			
5 (3 + 3 + 3)	-19.1793	-12.9762	14 (3 + 3 + 10)	-15.8527	-11.2016
6 (1 + 1 + 3)	-19.8103	-14.4577	15 (1 + 1 + 3 + 10)	-29.61191	-23.3871
	-17.9 ^d	-12.1 ^d			
7 (1 + 3)	-9.0047	-6.2311	16 (1 + 3 + 10)	-17.7144	-13.0082
8 (1 + 3 + 3)	-19.3773	-13.4474	17 (1 + 3 + 3 + 10)	-27.7688	-20.2621
9 (1 + 3 + 3 + 3)	-34.1550	-25.1692			

^aRelative electronic energies D_c (kcal/mol) calculated at the B3LYP/6-31G^{*} level. See Table-1 for the species and Fig. 1 for the structures.

^bRelative electronic energies D_{e0} (kcal/mol) calculated at the B3LYP/6-31G + (d) + ZPE level. ^cRef.³¹. ^dCalculated at the DFT/B3LYP/6-31 + G (d, p) level (ref.²⁷)

Calculated binding energy results show that the -D_{e0} value for the most stable ethylene glycol dimer is determined at 6.1119 kcal/mol (Table-2) corrected by ZPE. As one observes in Fig. 1 (2) the most stable dimer configuration consist of two ethylene glycol monomers connected by bifurcated hydrogen bonds and forming a cyclic structure.

In Table-1, the total dipole moments for the geometries optimized with the same basis set are listed for conformers along with the experimentally determined dipole moments. In this work, the dipole moment of ethylene glycol dimer is found at 1.7182 D, which can be due to the dipole-dipole interaction and hydrogen bonds between two ethylene glycol molecules.

From Table-3, we can find that the calculational stretching and bending vibrational frequencies are in good agreement with our previous experimental results^{12,13}.

H₂O monomer, H₂O dimer and H₂O trimer: A schematic representation of the optimized structures and the calculational H...O bond lengths (Å) of H₂O monomer, H₂O dimer and H₂O trimer are shown in Fig. 1 (3, 4 and 5). The intermolecular H...O bond length in the H₂O dimer is calculated as 1.9063 Å in this work, which were reported at 1.903 Å (DFT/MBP functional)²⁵ and 1.970 Å (B3LYP functional)²⁶. The intermolecular H...O bond lengths in the H₂O trimer are calculated at 1.8699, 1.8706 and 1.8985 Å, which are in agreement with reported work²⁷ (1.882 Å, 1.883 Å and 1.909 Å at the B3LYP/6-31 + G (d, p) level) and reported values²⁸ (1.854 Å, 1.858 Å and 1.994 Å at the MP2 functional).

The total energies and the corresponding ZPE corrections for the H₂O monomer, H₂O dimer and H₂O trimer are listed in Table-1. And the corresponding -D_c and -D_{e0} values are listed in Table-2. For the H₂O dimer, the -D_{e0} value of 3.9345 kcal/mol agrees with the calculational result of 3.7 kcal/mol²⁷ and the widely accepted experimental value of 3.59 ± 0.5 kcal/mol²⁹. The calculated -D_{e0} value of 12.9762 kcal/mol for the H₂O trimer is in agreement with the published average value of 12.93 kcal/mol³⁰.

From Table-1, it is worth to point out the DFT values obtained for the dipole moments of these clusters in this work: the moment value of H₂O monomer is 2.2491 D; the moment value of the H₂O dimer is 2.9007 D; and the moment value of the H₂O trimer is 1.2346 D.

The calculated harmonic vibrational frequencies are summarized in Table-3 for the H₂O monomer, the H₂O dimer and the H₂O trimer and compared with the experimental values for H₂O^{13,31,32}. The calculated results are found at 1662 cm⁻¹ in the H₂O monomer, at 1675 cm⁻¹ in the H₂O dimer and at 1679 cm⁻¹ in the H₂O trimer. The theoretical approach predicts also a sizeable blue shift (19-36 cm⁻¹) for H-O-H bending frequencies involving the hydrogen bonds.

(EG)₂-H₂O, EG-H₂O, EG-(H₂O)₂ and EG-(H₂O)₃ clusters: (EG)₂-H₂O, EG-H₂O, EG-(H₂O)₂ and EG-(H₂O)₃ clusters. The optimized molecular geometries and the calculational H...O bond lengths (Å) of (EG)₂-H₂O, EG-H₂O, EG-(H₂O)₂ and EG-(H₂O)₃ clusters are shown in Fig. 1 (6-9). In this work, the intramolecular H...O bond lengths in ethylene glycol molecules are calculated at 2.8639 Å in (EG)₂-H₂O, at 2.8358 Å in EG-H₂O (2.84 Å calculated at the DFT B3LPY/6-311g (3df, 3pd) level)²⁴, at 2.8434 Å in EG-(H₂O)₂ and at 2.8039 Å in EG-(H₂O)₃. Meanwhile, the intermolecular H...O bond lengths between ethylene glycol and H₂O in EG-H₂O are calculated at 1.7429 Å to 2.0096 Å.

The -D_{e0} value for EG-H₂O is of 6.2311 kcal/mol, which is stronger than the -D_{e0} values for the ethylene glycol dimer (6.1119 kcal/mol) and the H₂O dimer (3.9345 kcal/mol). Meanwhile, the -D_{e0} values for (EG)₂-H₂O (about Φ₁ = 87 %) is 14.4577 kcal/mol, for EG-(H₂O)₂ (about Φ₁ = 60 %) is 13.4474 kcal/mol and for EG-(H₂O)₃ (abut Φ₁ = 50 %) is 25.1692 kcal/mol.

The calculated and experimental spectral data for ethylene glycol + H₂O system are summarized in Table-3. The calculated H-O-H bending vibration frequencies are found at 1694 cm⁻¹ in the EG-H₂O, at 1667 cm⁻¹ in the EG-(H₂O)₂ and at 1694 cm⁻¹ in the EG-(H₂O)₃.

Compared with the previous results, the calculational results of the ethylene glycol clusters and H₂O clusters are in agreement with the reportedly calculational and experimental results. From the binding energies, calculated IR spectra, dipole moments and rotational constants, the B3LYP/6-31G + (d) level can be used for the calculation of the ethylene glycol + H₂O + SO₂ system.

For H₂O system, the theoretical approach predicts that it is more difficult to induce H-O-H bending vibration in H₂O when the hydrogen bonds are formed among H₂O molecules.

TABLE-3
CALCULATED VIBRATIONAL FREQUENCIES (IR INTENSITY) AND EXPERIMENTAL FREQUENCIES OF EG + H₂O

C(=O)C(													
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Frequencies are in cm⁻¹, and the intensities are in parentheses in km/mol. Experimental frequencies from references 12 and 13. ^aRef.¹³. ^bReference³¹. ^cRef.³². ^dCalculated at the DFT/B3LYP/6-31 + G (d, p) level (ref.²⁷)

So it needs more energy, *i.e.* the higher frequency to force the H-O-H bending vibration. (2) For the ethylene glycol + H₂O system, the intramolecular H...O bonds lengths of ethylene glycol in (EG)₂-H₂O, EG-H₂O, EG-(H₂O)₂ and EG-(H₂O)₃ clusters are longer than in the ethylene glycol monomer and in the ethylene glycol dimer, maybe, those phenomena result from the hydrogen bonding between ethylene glycol and H₂O molecules. In addition, the previously intramolecular hydrogen bond length of ethylene glycol molecule in the ethylene glycol-H₂O cluster is of 2.8358 Å, value for which we can consider the ethylene glycol intramolecular hydrogen bonds as disrupted.

The -D_{e0} value for ethylene glycol-H₂O is higher than the values for ethylene glycol dimer and for H₂O dimer, which can help to claim that the addition of H₂O can destroy the original intermolecular hydrogen bonds among ethylene glycol molecules and ethylene glycol can be easily solved in water. From above -D_{e0} values, we can see that (EG)₂-H₂O owns higher -D_{e0} value than EG-(H₂O)₂ and the results can help us to explain our previous experimental results¹³ and explore the various volume fraction aqueous solution of ethylene glycol's absorption capacities to SO₂. Although ethylene glycol has a propensity toward internal hydrogen bonds²⁸, water can efficiently bind with ethylene glycol to disrupt the intramolecular hydrogen bond in the ethylene glycol monomer.

Ethylene glycol is a relatively simple molecule, but its condensed phase structures are quite complicated. Previous studies³³ have shown that ethylene glycol has numerous stable

conformations and that can be observed on vibrational spectra. Therefore, the IR spectra of ethylene glycol might have contributions from different conformations and different hydrogen bonding structures as a function of mole fraction in solution. The experimental IR measurements¹² show an increase in the wavenumber (blue shift) with increasing water concentration in the aqueous solution of ethylene glycol. Previous spectroscopic studies³⁴ of methanol-water solutions revealed a similar phenomenon when methanol acts as a hydrogen-bond acceptor. In addition to the comparisons of spectral intensity, a blue shift of the symmetric stretch frequencies is observed in both the calculated and experimental results and hydrogen bonds between ethylene glycol and water within ethylene glycol + H₂O clusters as opposed to intramolecular ethylene glycol-ethylene glycol hydrogen bonds as water is added to the solution³⁵. These results and comparisons suggest that in addition to hydrogen bonding with itself, ethylene glycol can form hydrogen-bonded clusters with water.

Conclusion

The intramolecular H...O bond lengths in ethylene glycol molecules are calculated at 2.8639 Å in (EG)₂-H₂O, at 2.8358 Å in EG-H₂O, at 2.8434 Å in EG-(H₂O)₂ and at 2.8039 Å in EG-(H₂O)₃. Meanwhile, the intermolecular H...O bond lengths between ethylene glycol and H₂O in ethylene glycol + H₂O are calculated at 1.7429 Å to 2.0096 Å. The calculated -D_{e0} value for (EG)₂-H₂O (about 87 % aqueous solution of ethylene

glycol) is 14.4577 kcal/mol, for EG-(H₂O)₂ (about $\Phi_1 = 60\%$) is 13.4474 kcal/mol and for EG-(H₂O)₃ (about $\Phi_1 = 50\%$) is 25.1692 kcal/mol. The addition of H₂O can destroy the original intermolecular hydrogen bonds in ethylene glycol system and ethylene glycol can be easily solved in water.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (21166017), Program for New Century Excellent Talents in University (NCET-12-1017), the Research Fund for the Doctoral Program of Higher Education of China (20111514120002), the Natural Science Foundation of Inner Mongolia Autonomous Region (2011BS0601), the Program for Grassland Excellent Talents of Inner Mongolia Autonomous Region, Inner Mongolia Autonomous Region's Educational Commission (NJZZ11068), Program for Young Talents of Science and Technology in Universities of Inner Mongolia Autonomous Region (NJYT-12-B13), the Inner Mongolia Talented People Development Fund and Yongfeng Boyuan Industry Co., Ltd. (Jiangxi Province, China).

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