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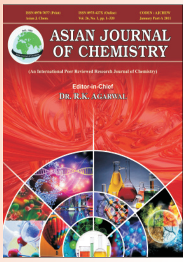

Theoretical Study of Intermolecular Hydrogen Bonding and Interaction in Ethylene Glycol-Water Mixtures

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Aqueous solution of ethylene glycol (EG) were used in the SO_2 absorption processes. Meanwhile, the various spectra suggested that aqueous solution of ethylene glycol can bond with SO_2 by the mean of hydrogen bonding and interaction. It is therefore important to understand the interaction of ethylene glycol with H_2O at the molecular level. In this work, the ground-state structure and energies of ethylene glycol, H_2O, EG_2-H_2O and EG/H_2O_{1-3} 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 H_2O are in good agreement with previous calculated and experimental results. The -D_{e0} values for ethylene glycol + H_2O shows that the addition of H_2O 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 (SO_2) 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 SO_2 and organic solvents used as absorbents have been identified as an option among the regenerative process[1-5] 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 processes[6]. Therefore, our research group has paid great attention to alcohol + water system for removal of SO_2 for several years[7-10].

In the recent work[11], Φ_1 = (70 to 90) % (volume fraction of ethylene glycol in aqueous solutions of ethylene glycol) showed stronger capacity to grasp SO_2. Aqueous solutions of ethylene glycol present native hydrogen bonding sites for the absorption of SO_2 so that the absorption and desorption properties of SO_2 in aqueous solutions of ethylene glycol[12,13] may be related to hydrogen bonding and interaction[14-16] among molecules.

It is therefore important to understand the competition between hydrogen bonding and interactions involving ethylene glycol and H_2O at the molecular level. The purpose of the present computational work is, therefore, to elucidate the hydrogen bonding and interaction between ethylene glycol and H_2O.

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:

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

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

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/H_2O_{1-3} 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' conformer[17]. 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 ref[18]. (NLSD/DZVP2 level) and 2.3605 Å in ref[19]. (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 weak[16].

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) D[18-21]. 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].

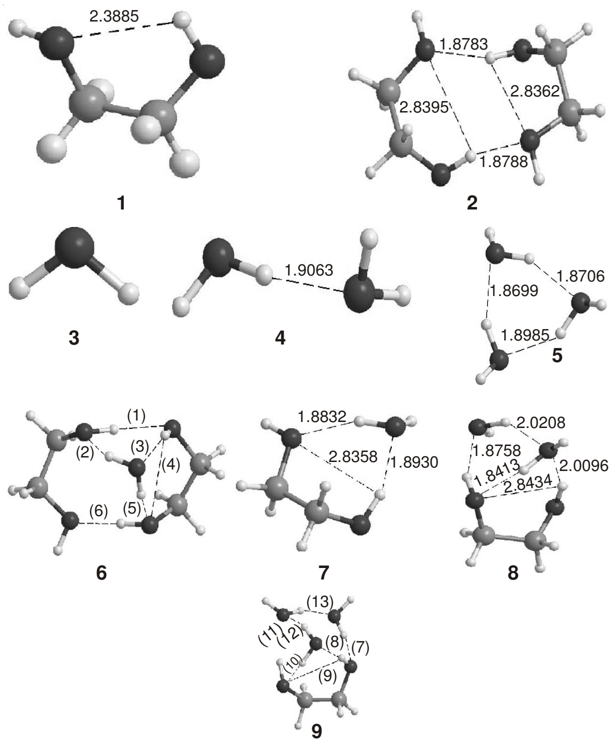

Fig. 1. Species involved in hydrogen bonding and interaction calculation. Bond lengths are in Å. The dashed lines indicate the possible hydrogen bonding and interaction. Part possible hydrogen bond lengths: (1) 1.8925 Å; (2) 2.2305 Å; (3) 1.8589 Å; (4) 2.86385 Å; (5) 1.9523 Å; (6) 1.8456 Å; (7) 1.7429 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

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/6-311g (3df, 3pd) level[24]. 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) level[24].

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

No.	Species	Ee (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 (exptl.)^{f}	5.311 (exptl.)^{f}	4.412 (exptl.)^{f}
		-229.61002^{c}			2.71^{d}			
		-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_2O	-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	$H_2O\cdots H_2O$	-152.85541	28.99	-152.80923	2.9007	212.85038	6.55614	6.55275
		-152.93429^{i}	29.1^{i}	-152.87772^{i}				
5	$H_2O\cdots H_2O\cdots H_2O$	-229.29827	45.93	-229.22512	1.2346	7.01387	6.89139	3.54654
		-229.41364^{i}	45.9^{i}	-229.33077^{i}				
6	$(EG)_2\cdots H_2O$	-536.97384	125.68	-536.77356	5.2739	1.65618	0.87820	0.77308
7	$EG\cdots H_2O$	-306.69677	69.59	-306.58593	3.9243	4.88867	3.48921	2.20339
		-306.08899^{d}			3.72^{d}			
		-306.97240^{e}						
8	$EG\cdots(H_2O)_2$	-383.13587	85.98	-382.99891	1.7273	3.03288	1.93224	1.71296
9	$EG\cdots(H_2O)_3$	-459.58199	102.28	-459.41907	2.3963	1.80237	1.48389	1.27787

[a]Calculated at the LCAO-SCF/4-31G level (ref. [17]). [b]Calculated at the MP2/6-311 G (d, p) level (ref.[18]). [c]Calculated at the SCF/6-31 + G* (ref.[19]). [d]Calculated at the MP2/6-311 + G (2d, 2p) level (ref.[19]). [e]Calculated at the MP4 (SDTQ) level (ref.[36]). [f]Calculated at the MP2/6-31G** level (ref.[21]). [g]Calculated at the DFT/B3LYP/6-311G (3df, 3pd) level (ref.[24]). [h]Calculated at the DFT/B3LYP functional (ref.[26]). [i] Calculated at the DFT/B3LYP/6-31 + G (d, p) level (ref.[27]). [j]Calculated at the DFT/B3LPY functional (ref.[37])

TABLE-2
RELATIVE ENGERIES OF THE INTERMEDIATE SPECIES OF ETHYLENE GLYCOL-H_2O SYSTEM

Species	D_e[a] (kcal/mol)	D_{e0}[b](kcal/mol)	Species	D_e[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 -6.0[b]	-3.9345 -4.95 (exptl.)[c] -3.7[d]	13 (3 + 10)	-5.2559	-3.7380
5 (3 + 3 + 3)	-19.1793	-12.9762	14 (3 + 3 + 10)	-15.8527	-11.2016
6 (1 + 1 + 3)	-19.8103 -17.9[d]	-14.4577 -12.1[d]	15 (1 + 1 + 3 + 10)	-29.61191	-23.3871
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			

[a]Relative electronic energyies De (kcal/mol) caculated at the B3LYP/6-31G* level. See Table-1 for the species and Fig. 1 for the structures. [b]Relative electronic energies D_{e0} (kcal/mol) calculated at the B3LYP/6-31G + (d) + ZPE level. [c]Ref.[31]. [d]Calculated 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].

H_2O monomer, H_2O dimer and H_2O trimer: A schematic representation of the optimized structures and the calculational H···O bond lengths (Å) of H_2O monomer, H_2O dimer and H_2O trimer are shown in Fig. 1 (3, 4 and 5). The intermolecular H···O bond length in the H_2O 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 H_2O trimer are calculated at 1.8699, 1.8706 and 1.8985 Å, which are in agreement with reported work[27] (1.882 Å, 1.883 Å and 1.909 Å at the B3LYP/6-31 + G (d, p) level) and reported values[28] (1.854 Å, 1.858 Å and 1.994 Å at the MP2 functional).

The total energies and the corresponding ZPE corrections for the H_2O monomer, H_2O dimer and H_2O trimer are listed in Table-1. And the corresponding -D_e and -D_{e0} values are listed in Table-2. For the H_2O dimer, the -D_{e0} value of 3.9345 kcal/mol agrees with the calculational result of 3.7 kcal/mol[27] and the widely accepted experimental value of 3.59 ± 0.5 kcal/mol[29]. The calculated -D_{e0} value of 12.9762 kcal/mol for the H_2O trimer is in agreement with the published average value of 12.93 kcal/mol[30].

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 H_2O monomer is 2.2491 D; the moment value of the H_2O dimer is 2.9007 D; and the moment value of the H_2O trimer is 1.2346 D.

The calculated harmonic vibrational frequencies are summarized in Table-3 for the H_2O monomer, the H_2O dimer and the H_2O trimer and compared with the experimental values for H_2O[13,31,32]. The calculated results are found at 1662 cm^{-1} in the H_2O monomer, at 1675 cm^{-1} in the H_2O dimer and at 1679 cm^{-1} in the H_2O trimer. The theoretical approach predicts also a sizeable blue shift (19-36 cm^{-1}) for H-O-H bending frequencies involving the hydrogen bonds.

$(EG)_2$-H_2O, EG-H_2O, EG-$(H_2O)_2$ and EG-$(H_2O)_3$ clusters: $(EG)_2$-H_2O, EG-H_2O, EG-$(H_2O)_2$ and EG-$(H_2O)_3$ clusters. The optimized molecular geometries and the calculational H···O bond lengths (Å) of $(EG)_2$-H_2O, EG-H_2O, EG-$(H_2O)_2$ and EG-$(H_2O)_3$ 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 $(EG)_2$-H_2O, at 2.8358 Å in EG-H_2O (2.84 Å calculated at the DFT B3LPY/6-311g (3df, 3pd) level)[24], at 2.8434 Å in EG-$(H_2O)_2$ and at 2.8039 Å in EG-$(H_2O)_3$. Meanwhile, the intermolecular H···O bond lengths between ethylene glycol and H_2O in EG-H_2O are calculated at 1.7429 Å to 2.0096 Å.

The -D_{e0} value for EG-H_2O 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 H_2O dimer (3.9345 kcal/mol). Meanwhile, the -D_{e0} values for $(EG)_2$-H_2O (about Φ_1 = 87 %) is 14.4577 kcal/mol, for EG-$(H_2O)_2$ (about Φ_1 = 60 %) is 13.4474 kcal/mol and for EG-$(H_2O)_3$ (abut Φ_1 = 50 %) is 25.1692 kcal/mol.

The calculated and experimental spectral data for ethylene glycol + H_2O system are summarized in Table-3. The calculated H-O-H bending vibration frequences are found at 1694 cm^{-1} in the EG-H_2O, at 1667 cm^{-1} in the EG-$(H_2O)_2$ and at 1694 cm^{-1} in the EG-$(H_2O)^3$.

Compared with the previous results, the calculational results of the ethylene glycol clusters and H_2O 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 + H_2O + SO_2 system.

For H_2O system, the theoretical approach predicts that it is more difficult to induce H-O-H bending vibration in H_2O when the hydrogen bonds are formed among H_2O molecules.

TABLE-3
CALCULATED VIBRATIONAL FREQUENCIES (IR INTENSITY) AND EXPERIMENTAL FREQUENCIES OF EG + H_2O

Species	Method	IR(inten.)											
		δ_{OH}	$\nu_{C(H_2)-C(H_2)}$ sym.	$\nu_{C(H_2)-C(H_2)}$ sym.	$\nu_{C(H_2)-O}$	$\nu_{s(SO_2)}$	COH bend	CH_2 twist	$\nu_{as(SO_2)}$	OH bend	--	CH_2 bend	H-O-H bend
EG	Expt.[a]	864	885	1043	1087		1205	1257		1419	1456		
1	Calc.	876	891	1055	1080		1205	1263		1423	1454		
		(36)	(15)	(67)	(91)		(0)	(5)		(36)	(16)		
2	Calc.	865	903	1061	1093		1201	1265		1416	1455		
		(45)	(60)	(66)	(180)		(32)	(30)		(16)	(21)		
H_2O	Expt.												1643[a]
													1658[b]
													1647[c]
3	Calc.												1662
													(97)
													1682[d]
4	Calc.												1675
													(133)
													1693[d]
5	Calc.												1679
													(116)
													1656 [d]
EG80%	Expt.[a]	864	883	1043	1088		1207	1258		1415	1458		1657
6	Calc.	870	889	1062	1089		1205	1257		1410	1444		1657
		(50)	(18)	(14)	(144)		(0)	(19)		(42)	(41)		(0)
7	Calc.	856	901	1059	1088		1215	1266		1412	1450		1694
		(23)	(45)	(45)	(85)		(50)	(15)		(11)	(3)		(75)
8	Calc.	863	887	1066	1093		1205	1238		1408	1442		1667
		(33)	(19)	(86)	(59)		(0)	(9)		(10)	(38)		(98)
9	Calc.	870	889	1073	1100		1205	1250		1406	1455		1694
		(92)	(30)	(68)	(65)		(0)	(3)		(7)	(27)		(57)

Frequencies are in cm^{-1}, and the intensities are in parentheses in km/mol. Experimental frequencies from references 12 and 13. [a]Ref. [13]. [b]Reference[31]. [c]Ref. [32]. [d]Calculated 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 + H_2O system, the intramolecular H···O bonds lengths of ethylene glycol in $(EG)_2$-H_2O, EG-H_2O, EG-$(H_2O)_2$ and EG-$(H_2O)_3$ clusters are longer than in the ethylene glycol monomer and in the ethylene glycol dimmer, maybe, those phenomena result from the hydrogen bonding between ethylene glycol and H_2O molecules. In addition, the previously intramolecular hydrogen bond length of ethylene glycol molecule in the ethylene glycol-H_2O 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-H_2O is higher than the values for ethylene glycol dimer and for H_2O dimer, which can help to claim that the addition of H_2O 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 $(EG)_2$-H_2O owns higher -D_{e0} value than EG-$(H_2O)_2$ and the results can help us to explain our previous experimental results[13] and explore the various volume fraction aqueous solution of ethylene glycol's absorption capacities to SO_2. Although ethylene glycol has a propensity toward internal hydrogen bonds[28], 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 studies[33] 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 measurements[12] show an increase in the wavenumber (blue shift) with increasing water concentration in the aqueous solution of ethylene glycol. Previous spectroscopic studies[34] 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 + H_2O clusteres as opposed to intramolecular ethylene glycol-ethylene glycol hydrogen bonds as water is added to the solution[35]. These results and comparisons suggest that in addition to hydrogen bonding with itself, ethylene glycol can form hydrogen-bonded clusteres with water.

Conclusion

The intramolecular H···O bond lengths in ethylene glycol molecules are calculated at 2.8639 Å in $(EG)_2$-H_2O, at 2.8358 Å in EG-H_2O, at 2.8434 Å in EG-$(H_2O)_2$ and at 2.8039 Å in EG-$(H_2O)_3$. Meanwhile, the intermolecular H···O bond lengths between ethylene glycol and H_2O in ethylene glycol + H_2O are calculated at 1.7429 Å to 2.0096 Å. The calculated -D_{e0} value for $(EG)_2$-H_2O (about 87 % aqueous solution of ethylene glycol) is 14.4577 kcal/mol, for EG-$(H_2O)_2$ (about $\Phi_1 = 60$ %) is 13.4474 kcal/mol and for EG-$(H_2O)_3$ (about $\Phi_1 = 50$ %) is 25.1692 kcal/mol. The addition of H_2O can destroy the original intermolecular hydrogen bonds in ethylene glycol system and ethylene glycol can be easily solved in water.

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