A computational study of microsolvation effect on ethylene glycol by density functional method

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This study focuses on the conformational analysis of ethylene glycol–(water)_n (n = 1–3) complex by using density functional theory method and the basis set 6-311+G*. Different conformers are reported and the basis set superposition error corrected total energy is $-306.7675171$, $-383.2213135$, and $-459.6941528$ for lowest energy conformer with 1, 2, and 3 water molecules, respectively, with corresponding binding energy $-7.75$, $-15.43$, and $-36.28$ kcal/mol. On applying many-body analysis it has been found that relaxation energy, two-body, three-body energy have significant contribution to the binding energy for ethylene glycol–(water)_3 complex whereas four-body energies are negligible. The most stable conformers of ethylene glycol–(water)_n complex are the cyclic structures in which water molecules bridge between the two hydroxyl group of ethylene glycol.

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I. INTRODUCTION

Ethylene glycol and its oligomers have a wide range of applications including use as pharmaceutical excipients, cosmetic preparations, industrial and biological solvents, food additives, paint formulations chemical intermediates, binders, plasticizers, etc. This molecule has been studied both theoretically and experimentally by methods such as electron diffraction, infrared spectroscopy, microwave spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and variable temperature Raman spectroscopy. Theoretical results of ethylene glycol using ab initio method reported exclusively to the conformers and vibrational frequencies. It has been shown that the most stable conformer is in the gauche form in dilute solution.

Study of aqueous solutions of associating liquids is helpful in understanding molecules associated in clusters. Hydrogen bonding has a considerable effect on the microscopic as well as the macroscopic properties of fluids and plays a fundamental role in the understanding and designing of processes of biological and environmental importance. Though ethylene glycol molecule has been studied both theoretically and experimentally, there are very few studies on the aqueous solutions of ethylene glycol particularly ethylene glycol–water interaction through hydrogen bonding. Because of its significant biological and technological applications, it is important to understand in detail the structural features of this molecule in various environments. Interaction of hydrogen bonded glass forming ethylene glycol with water is very interesting since due to the good solubility of ethylene glycol in water this molecule may form a variety of clusters due to intermolecular and intramolecular geometry of individual molecules. Zahn et al. investigated the dielectric properties of ethylene glycol and water–ethylene glycol mixtures for their use in a pulsed power system designed over a wide range of frequency and temperature. Shinyashiki et al. have carried out dielectric relaxation studies on aqueous solutions of ethylene glycol oligomers and other polymers using time domain reflectometry. The dielectric relaxation study of ethylene glycol–water mixtures was performed over whole concentration range at room temperature to understand the molecular dynamics and interaction of ethylene glycol with water.

The effect of solvation is one of the fundamental issues of chemistry because the structure and reactivity of free molecules are very different from those in the solvent environment. To our knowledge, theoretical studies on microsolvation effect of ethylene glycol, i.e., ethylene glycol–(water)_n complex have not been performed so far. The aim of this work is to study interaction in ethylene glycol–(water)_n (n = 1–3) complex using many-body analysis. We have obtained the most stable conformers for ethylene glycol complex with one, two, and three water molecules, their binding energy and contribution of many-body energies to the binding energy. The paper is structured as follows: Section II gives the computational details. In Sec. III details of many-body energy calculation are given. Results are discussed in Sec. IV. Conclusions are inferred in Sec. V.

II. COMPUTATIONAL DETAILS

All calculations were performed using GAUSSIAN 98 electronic structure package. The geometries of ethylene glycol–(water)_n (n = 1–3) complexes have been optimized using density functional theory (DFT) with, Becke’s three parameter hybrid functional combined with the Lee, Yang, and Parr correlation (B3LYP) and 6-311+G* basis set. It is well known that the inclusion of electron correlation-as well as the use of basis function that includes both, diffuse and polarization functions is necessary for the accurate description of hydrogen-bonding interactions.
Recently it has been shown for ethylene glycol and other molecules that the diffuse functions are important in density functional methods.\(^4\) We have chosen the above basis set that includes diffuse and polarization function for two reasons. First, it is one of the most popular basis sets used in the study of medium and large size hydrogen bonded systems. Second, especially at B3LYP level, this basis set provides small basis set superposition error (BSSE) using counterpoise method.\(^5\) The basis set includes both diffuse and polarization functions has already been used for several hydrogen bonded systems.\(^6\) The energies are corrected for BSSE using counterpoise method and generalized counterpoise method.\(^7\)

**III. MANY-BODY ENERGY CALCULATIONS**

We have used many-body analysis\(^5\) to calculate relaxation energy, two-, three-, and four-body interaction energies. The total energy of the complex is decomposed into relaxation energy and many-body energies as follows:

\[
\Delta E = E(1234) - \{E_A + nE_w\}
\]

\[
= \sum_{i=1}^{n} E(i) - \{E_A + nE_w\} \quad \text{(relaxation energy)}
\]

\[
+ \sum_{i=1}^{n} \sum_{j>i}^{n} \Delta^2 E(ij) \quad \text{(two-body energy)}
\]

\[
+ \sum_{i=1}^{n-2} \sum_{j=1}^{n} \sum_{k>j}^{n} \Delta^3 E(ijk) \quad \text{(three-body energy)}
\]

\[
+ \Delta^4 E(1234) \quad \text{(four-body energy)},
\]

where \(E(i), E(ij), E(ijk), E(1234)\) are the energies of the various monomers, dimers, trimers, and tetramer in the complex and \(E_A, E_w\) are the energies of isolated ethylene glycol and water molecules, respectively. The pairwise two-body interaction energies and higher three-body and four-body interaction energies are defined as the following equations:

\[
\Delta^2 E(ij) = E(ij) - \{E(i) + E(j)\},
\]

\[
\Delta^3 E(ijk) = E(ijk) - \{E(i) + E(j) + E(k)\} - \{\Delta^2 E(ij) + \Delta^2 E(ik) + \Delta^2 E(jk)\},
\]

\[
\Delta^4 E(1234) = E(1234) - \{E(1) + E(2) + E(3) + E(4)\}
\]

\[
- \{\Delta^2 E(12) + \Delta^2 E(13) + \Delta^2 E(14) + \Delta^2 E(23) + \Delta^2 E(24) + \Delta^2 E(34)\}
\]

\[
- \{\Delta^3 E(123) + \Delta^3 E(124) + \Delta^3 E(134) + \Delta^3 E(234)\}.
\]

The BSSE-corrected energy of a subsystem \((ijkl)\) is evaluated in the full basis of a larger system \((1234)\), and denoted by the term \(E(ijkl)\). Accordingly, the \(n\)-body terms are substituted with the BSSE-corrected ones:

\[
\Delta^2 E_c(ij) = E(ij|1234) - \{E(i|1234) + E(j|1234)\},
\]

\[
\Delta^3 E_c(ijk) = E(ijk|1234) - \{E(i|1234) + E(j|1234) + E(k|1234)\}
\]

\[
+ E(k|1234) - \{\Delta^2 E(ij|1234) + \Delta^2 E(ik|1234) + \Delta^2 E(jk|1234)\},
\]

\[
\Delta^4 E_c(1234) = E(1234) - \{E(1|1234) + E(2|1234) + E(3|1234) + E(4|1234)\}
\]

\[
- \{\Delta^2 E(12|1234) + \Delta^2 E(13|1234) + \Delta^2 E(14|1234) + \Delta^2 E(23|1234) + \Delta^2 E(24|1234) + \Delta^2 E(34|1234)\}
\]

\[
- \{\Delta^3 E(123|1234) + \Delta^3 E(124|1234) + \Delta^3 E(134|1234) + \Delta^3 E(234|1234)\}
\]

The binding energy of the complex is the sum of relaxation energy and many-body energies. We have used the method suggested by Valiron and Mayer\(^9\) to correct the total energy for basis set superposition error.

**IV. RESULT AND DISCUSSIONS**

In Figs. 1, 2, and 3, two, five, and three lowest energy conformers for the ethylene glycol complex with one, two, and three water molecules, respectively, are shown. The selected optimized geometries for ethylene glycol–(water)\(_n\) \((n = 1–3)\) complex are represented in Table I along with molecular parameters for ethylene glycol monomer. O–H bond lengths for water monomer are 0.963 Å and the angle H–O–H is 107.04 degrees at B3LYP/6-311++G\(^\ast\) level.

On comparing the geometries of two conformers of ethylene glycol–(water)\(_1\) complex, it can be seen that conformer C11 has a strong hydrogen bond but C12 has two weaker hydrogen bonds. In case of five conformers of ethylene glycol–(water)\(_3\) complex, the longest hydrogen bonded distance is O\(_11\)–H\(_{12}\) (2.22 Å). The two hydrogen bonded distance, the two angles C\(_1\)C\(_2\)O\(_9\) and C\(_2\)C\(_3\)O\(_7\) and another two angles H\(_{12}\)O\(_{11}\)H\(_{13}\) and H\(_{13}\)O\(_{14}\)H\(_{16}\) are exactly similar to each other in both C23 and C24 conformers. In the three conformers of the ethylene glycol–(water)\(_3\) complex, the angles C\(_1\)C\(_2\)O\(_9\), C\(_2\)C\(_3\)O\(_7\), and H\(_{12}\)O\(_{11}\)H\(_{13}\) are slightly changed from the corresponding angles in monomers. The angle H\(_{13}\)O\(_{14}\)H\(_{16}\) is decreased by 2.2 degrees in C31 and is increased by 1.46 and 1.2 degrees in C32 and C33 conformers, respectively, than the corresponding angle in water monomer.

The BSSE corrected total energies for the conformers of ethylene glycol–(water)\(_n\) \((n = 1, 3)\) are tabulated in Table II. Conformers C12, C25, and C33 are the most stable conformers for the ethylene glycol complex with one, two, and three water molecules, respectively, with corresponding BSSE cor-
For ethylene glycol–(water)$_1$ complex, the conformer C12 is only 1 kcal/mol lower in energy than that of the C11 conformer whereas for ethylene glycol–(water)$_2$ complex, C25 conformer is lower in energy than the C21, C22, C23, and C24 by 2.22, 2.37, 2.03, and 1.53 kcal/mol, respectively. For ethylene glycol–(water)$_3$ complex, conformer C33 is 13.63 and 7 kcal/mol lower in energy than C31 and C32 conformers, respectively. The difference in the energy between the most stable conformer and other conformers increases with an increase in number of water molecules.

One similarity can be seen from ethylene glycol–(water)$_1$, ethylene glycol–(water)$_2$, and ethylene glycol–(water)$_3$ complexes that the conformer in which water molecule(s) bridges between the two hydroxyl group of ethylene glycol through hydrogen bonding is the most stable conformer. These are the cyclic structures. It can be said that in ethylene glycol–(water)$_n$ complex, the most stable structures are the cyclic structures in which more number of hydrogen bonds are formed than the open structures. Later through many-body analysis we have shown that these structures have highest binding energy.

Many-body energies for ethylene glycol–(water)$_n$ complex with one, two, and three water molecules are given in
Tables III, IV, and V, respectively. From Table III, it can be seen that for ethylene glycol–(water)$_1$ complex, the contribution of two-body energies to the binding energy (BE) is more than the relaxation energies. In both, C11 and C12 complexes, two-body energy as well as relaxation energy is attractive. The two-body energy is larger for the most stable conformer C12 than C11 whereas for the relaxation energy it is opposite. Similar to the total energy for these two conformers, the difference in binding energies is also less (only 0.19 kcal/mol). The most stable conformer has binding energy −7.75 kcal/mol.

Table IV gives the many-body energies for the five conformers of ethylene glycol–(water)$_2$ complex. It can be seen that most of the two-body energies are attractive except EG–W$_2$ and W$_1$–W$_2$ for conformer C22 and C23, respectively, which are repulsive. For the most stable conformer C25, all the three two-body energies have significant contribution. The highest two-body energy is found for EG–W$_1$ in C22 conformer (−6.18 kcal/mol) among all the five conformers. The highest and lowest total two-body energy is found for the most stable conformer C25 and the most unstable conformer C22, respectively. The relaxation energies here also are attractive and contribute significantly to the binding energy for all the conformers. The three-body energies are repulsive for C21, C22, and C23 conformers whereas these are attractive for C24 and C25 conformers. As compared to two-body energies and relaxation energies, three-body energies are negligible. The contribution of ethylene glycol–water interaction to total two-body energy is more than the water–water interaction except in the C22 conformer in which there is almost equal contribution from these two. The binding energy is highest for the most stable conformer C25 (−15.43 kcal/mol) and lowest for the most unstable conformer C22 (−13.21 kcal/mol).

Many-body energies for the three conformers of ethylene glycol–(water)$_3$ complex are given in Table V. As observed for ethylene glycol–(water)$_1$ and ethylene glycol–(water)$_2$ complexes, here also the two-body energies are attractive except EG–W$_3$ and W$_1$–W$_3$ for the conformers C31 and C32, respectively. The highest two-body energy is observed for EG–W$_1$, for the C32 conformer (−6.02 kcal/mol). In stable conformer C22, respectively.

### TABLE I. Selected geometries for ethylene glycol–(water)$_n$ ($n=1$ to 3) complex optimized using B3LYP/6-311 + +G*.

<table>
<thead>
<tr>
<th></th>
<th>EG</th>
<th>C11</th>
<th>C12</th>
<th>C21</th>
<th>C22</th>
<th>C23</th>
<th>C24</th>
<th>C25</th>
<th>C31</th>
<th>C32</th>
<th>C33</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_1\text{C}_2$</td>
<td>1.529</td>
<td>1.523</td>
<td>1.525</td>
<td>1.529</td>
<td>1.529</td>
<td>1.531</td>
<td>1.519</td>
<td>1.529</td>
<td>1.530</td>
<td>1.529</td>
<td>1.530</td>
</tr>
<tr>
<td>$\text{C}_1\text{O}_7$</td>
<td>1.424</td>
<td>1.417</td>
<td>1.424</td>
<td>1.422</td>
<td>1.434</td>
<td>1.420</td>
<td>1.438</td>
<td>1.428</td>
<td>1.427</td>
<td>1.428</td>
<td>1.409</td>
</tr>
<tr>
<td>$\text{C}_2\text{O}_9$</td>
<td>1.424</td>
<td>1.427</td>
<td>1.424</td>
<td>1.425</td>
<td>1.428</td>
<td>1.420</td>
<td>1.438</td>
<td>1.443</td>
<td>1.447</td>
<td>1.418</td>
<td>1.445</td>
</tr>
<tr>
<td>$\text{H}_8–\text{O}_1$</td>
<td>1.872</td>
<td>1.877</td>
<td>1.933</td>
<td>1.976</td>
<td>1.887</td>
<td>1.875</td>
<td>1.876</td>
<td>1.986</td>
<td>1.745</td>
<td>1.745</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE II. BSSE corrected total energies (in hartrees) for different conformers of ethylene glycol–(water)$_n$ ($n=1$ to 3) complex.

<table>
<thead>
<tr>
<th>$n$</th>
<th>Conformer</th>
<th>Total energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C11</td>
<td>−306.7659302</td>
</tr>
<tr>
<td></td>
<td>C12</td>
<td>−306.7675171</td>
</tr>
<tr>
<td>2</td>
<td>C21</td>
<td>−383.2177734</td>
</tr>
<tr>
<td></td>
<td>C22</td>
<td>−383.2175293</td>
</tr>
<tr>
<td></td>
<td>C23</td>
<td>−383.2180786</td>
</tr>
<tr>
<td></td>
<td>C24</td>
<td>−383.2188211</td>
</tr>
<tr>
<td></td>
<td>C25</td>
<td>−383.2213135</td>
</tr>
<tr>
<td>3</td>
<td>C31</td>
<td>−459.6724243</td>
</tr>
<tr>
<td></td>
<td>C32</td>
<td>−459.6829834</td>
</tr>
<tr>
<td></td>
<td>C33</td>
<td>−459.6941528</td>
</tr>
</tbody>
</table>

### TABLE III. Many-body energies for the two conformers of ethylene glycol–(water)$_1$ complex. All energies are in kcal/mol and BSSE corrected. EG is ethylene glycol and W$_i$ denotes $i$th water molecule in a complex according to Fig. 1.

<table>
<thead>
<tr>
<th>Conformer</th>
<th>Many-body term</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Two body</td>
<td></td>
</tr>
<tr>
<td>EG–W1</td>
<td>−5.98</td>
</tr>
<tr>
<td>$E_{\text{Relax}}$</td>
<td>−1.58</td>
</tr>
</tbody>
</table>

Subtotals and total

Subtotal 2-B | −5.98 |
Total BE      | −7.56 |
TABLE V. Many-body energies for the three conformers of ethylene glycol–water) complex. All energies are in kcal/mol and BSSE corrected. EG is ethylene glycol and W denotes ith water molecule in a complex according to Fig. 2.

<table>
<thead>
<tr>
<th>Many-body term</th>
<th>Conformer</th>
</tr>
</thead>
<tbody>
<tr>
<td>C21</td>
<td>C22</td>
</tr>
<tr>
<td>Two body</td>
<td></td>
</tr>
<tr>
<td>EG–W2</td>
<td>–1.99</td>
</tr>
<tr>
<td>W1–W3</td>
<td>–4.67</td>
</tr>
<tr>
<td>Three body</td>
<td></td>
</tr>
<tr>
<td>EG–W1–W2–W3</td>
<td>0.56</td>
</tr>
<tr>
<td>E_{Relax}</td>
<td>–3.09</td>
</tr>
<tr>
<td>Subtotal 2-B</td>
<td>–11.51</td>
</tr>
<tr>
<td>Subtotal 3-B</td>
<td>0.56</td>
</tr>
</tbody>
</table>


TABLE V. Many-body energies for the three conformers of ethylene glycol–water) complex. All energies are in kcal/mol and BSSE corrected. EG is ethylene glycol and W denotes ith water molecule in a complex according to Fig. 3.

<table>
<thead>
<tr>
<th>Many-body term</th>
<th>Conformer</th>
</tr>
</thead>
<tbody>
<tr>
<td>EGW31</td>
<td>EGW32</td>
</tr>
<tr>
<td>Two body</td>
<td></td>
</tr>
<tr>
<td>EG–W1</td>
<td>–4.98</td>
</tr>
<tr>
<td>EG–W2</td>
<td>–4.08</td>
</tr>
<tr>
<td>EG–W3</td>
<td>1.18</td>
</tr>
<tr>
<td>W1–W2–W3</td>
<td>–1.49</td>
</tr>
<tr>
<td>W1–W2–W3</td>
<td>–4.85</td>
</tr>
<tr>
<td>W2–W3</td>
<td>–4.27</td>
</tr>
<tr>
<td>Three body</td>
<td></td>
</tr>
<tr>
<td>EG–W1–W2–W3</td>
<td>–0.25</td>
</tr>
<tr>
<td>EG–W1–W3</td>
<td>0.69</td>
</tr>
<tr>
<td>EG–W2–W3</td>
<td>0.71</td>
</tr>
<tr>
<td>W1–W2–W3</td>
<td>–0.50</td>
</tr>
<tr>
<td>Four body</td>
<td></td>
</tr>
<tr>
<td>EG–W1–W2–W3</td>
<td>0.16</td>
</tr>
<tr>
<td>E_{Relax}</td>
<td>–4.84</td>
</tr>
<tr>
<td>Subtotal 2-B</td>
<td>–18.49</td>
</tr>
<tr>
<td>Subtotal 3-B</td>
<td>0.65</td>
</tr>
<tr>
<td>Subtotal 4-B</td>
<td>0.16</td>
</tr>
<tr>
<td>Total BE</td>
<td>–22.52</td>
</tr>
</tbody>
</table>

conformer C32 and C33, the contribution from ethylene glycol–water interaction is more than the water–water interaction to the total two-body energies whereas for the conformer C31 the opposite is true. The highest total two-body energy is observed for the most stable conformer C33 (–24.42 kcal/mol) and the lowest is for the most unstable C31 conformer (–18.49 kcal/mol) among the three. The total two-body energies are attractive for all three conformers. The total three-body energy is negligible for the most unstable conformer C31 where as for the remaining two conformers C32 and C33 it has significant contribution to the binding energy. The highest three-body energy is for EG–W1–W2 in conformer C32 (–2.92 kcal/mol). The most stable conformer C33 among the three has all three-body energies being attractive. The contribution from ethylene glycol–water–water interactions is more than water–water–water interactions for all three conformers. The highest total three-body energy is for the C33 conformer (–6.38 kcal/mol). As compared to the two-body and three-body energies, four-body energies are negligible for all three conformers. It is repulsive for C31 and attractive for C32 and C33 conformers. The relaxation energies here also are attractive and have more contribution. The highest relaxation energy is found for C33 conformer (–4.96 kcal/mol).

V. CONCLUSIONS

Many-body interaction is studied in ethylene glycol–water) complex. The two-body energy has more contribution to the binding energy for all the complexes. Relaxation energy also contributes significantly to the binding energy. It has been observed that when water molecule bridges between two hydroxyl groups of ethylene glycol in a conformer, it is more stable than the other conformers and has the highest binding energy.

ACKNOWLEDGMENT

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