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Intermolecular Hydrogen Bond Interactions in *N*-Carboxymethyl Chitosan and $n\text{H}_2\text{O}$: DFT and NBO Studies

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Abstract: Membrane is the most important component in Proton Exchange Membrane Fuel Cell (PEMFC) which is widely developed in recent years. One of the membranes used in the PEMFCs is *N*-carboxymethyl chitosan. The aim of this research is to identify the possibility of intermolecular hydrogen bond interactions in *N*-carboxymethyl chitosan and $n\text{H}_2\text{O}$ ($n=1-5$) by using density functional theory to perform all the calculations. In this letter, we report all the possibility of hydrogen bond interactions by analyzing natural bond orbital to measure the relative strength of the hydrogen bonding interactions and the charge transfer of $n-\sigma^*$ from O-H. Interaction of *N*-carboxymethyl chitosan and $5\text{H}_2\text{O}$ was found to be the strongest hydrogen bond among others with a stabilization energy of 56.93 kcal/mol. The value of stabilization energy was confirmed using molecular orbital calculation. Hydrogen bond interaction was predicted influenced by existing of the carboxylic group.

INTRODUCTION

The fuel cell has been considered as promising alternative energy sources for future energy that is combined with a cleaner environment due to the limitation of fossil energy resources such as petroleum, coal and gases [1]. The fuel cell is capable of continuous energy conversion as long as they were fed a sufficient supply of natural gas, hydrocarbons, or alcohol [2]. Proton Exchange Membrane Fuel Cell (PEMFC) is one of many kinds of fuel cells that has been developed because it is very efficient and environmentally friendly [3].

The membrane used in PEMFC has a negative fixed charge which is usually called a proton exchange membrane. The membrane has a role to transport cation which is hydrogen ions (proton) in an electrolyte membrane from anode to cathode without transport any electron [4].

In most current literature, PEMFC used a perfluorocarbon based electrolyte membrane called Nafion[®]. Nafion[®] has many advantageous properties such as mechanical robustness, stable at the operating temperature of fuel cells (approximately 80 °C), and stable in the proximity of chemicals with high proton conductivity (0.08 S/cm) [2]. On the other hand, Nafion[®] could not be reused, leads to a high environmental and production cost of the PEMFC. Prices in the range of 600-700 \$/m² for these membranes set a strong impediment. In addition, Nafion[®] is susceptible to dehydrate, leads to a decrease in proton conductivity at high temperatures [2, 5, 6].

These shortcomings have led to the search for alternatives materials to substitute Nafion[®] as a membrane electrolyte in fuel cells, membrane with the ability to operate at a higher temperature, higher mechanical robustness and lower production cost, but with a proton conductivity level near Nafion[®]. One of the proposed materials which have the potential to be used in PEMFC is carboxymethyl chitosan. *N*-carboxymethyl chitosan as a polymer has a long chain with hydroxyl, amine, and carboxylic groups that are the potential to be developed to find other alternative sources membrane electrolyte. *N*-carboxymethyl chitosan has hydrophilic and hydrophobic domains that allow proton transfer. Its carboxylic domain could form hydrophilic pathways through its hydrogen bonds. Proton transfer can be indicated by the existence of hydrogen bonds between *N*-carboxymethyl chitosan and water

molecules by seeing ² charge transfer inter-lone pairs from proton's acceptor to the anti-bonding orbitals from proton donor [7].

This particular study was about proton transfer associated ³ with occurrence to form a hydrogen bond that can be studied using NBO analysis. NBO analysis on the ratio of acceptor orbitals in both intra- and intermolecular OHO hydrogen bonds which tell us the ³ major difference from both of them. When in intramolecular OHO hydrogen bonds, ⁴ protons are moved to an orbital which determines the direction hydrogen bonds [8]. The most significant thing in NBO analysis for the hydrogen bond system is the charge transfer among the lone pairs of proton acceptor and the antibonds of proton donor. The $E^{(2)}$ between the LP of atom Y and σ^* of the Z-H bond relates to the intensity of the Z...HY interaction and probably gives qualitative descriptions of the contribution to the total interaction energy of *N*-carboxymethyl chitosan and $n\text{H}_2\text{O}$ [9]. Moreover, the hydrogen bonds formed can be shown through the existence of donor and acceptor of electron lone pairs [10].

This research investigation represents our contribution to *N*-carboxymethyl chitosan and $n\text{H}_2\text{O}$ that can give a new perspective in the comprehension of the probability proton transfer. We proposed to optimize the molecular association and tried to analyze the detail types of hydrogen bond through the DFT and NBO techniques [9, 11–14].

EXPERIMENTAL

⁶ DFT method was calculated at the B3LYP level theory and 6-31G** basis set by using NWChem 6.6 software. This research has applied the full counterpoise procedure to eliminate BSSE and ZPE error [9,15]. In the beginning, the geometry of dimer *N*-carboxymethyl chitosan molecules is calculated. Furthermore, the *N*-carboxymethyl chitosan membrane matrix interacted with n water molecules ($n=1-5$) on H_{50} atom bound to O_{49} of the carboxylic group. The probability of interaction on *N*-carboxymethyl chitosan on H_{50} is higher than others because H_{50} has a more positive partial charge by about 0.49858 and there are no steric obstacles around it. In the optimized geometry, there were ¹⁴ no imaginary frequencies and that means the molecules were stable [9].

The natural bond orbital analysis provides an efficient technique for studying ¹¹ the probability of hydrogen bond interactions in *N*-carboxymethyl chitosan and $n\text{H}_2\text{O}$. NBO analysis was considering all possible interactions between donor and acceptor and determines their stabilizing energy based on second-order perturbation theory [9, 16].

$$E^2 = \Delta E_{i,j} = q_i = \frac{F_{i,j}^2}{E_i - E_j} \quad (1)$$

¹ $E^{(2)}$ is second-order perturbation stabilization energy, q_i is occupancy of donating orbital, E_i and E_j are the energy of NBO donor and acceptor, and $F_{i,j}$ is Fock matrix element between NBO i orbital and j orbital [10,17].

RESULTS AND DISCUSSION

Optimized Structures of *N*-Carboxymethyl Chitosan and $n\text{H}_2\text{O}$

The geometries of all proposed *N*-carboxymethyl chitosan and $n\text{H}_2\text{O}$ ($n=1-5$) were ⁹ optimized at the B3LYP/6-31G** level theory. Changes in the interaction energy of *N*-carboxymethyl chitosan was determined by added n -water molecules to its dimer. Dimer *N*-carboxymethyl chitosan was chosen to represent the *N*-carboxymethyl chitosan polymer because of the interaction energy and enthalpies between dimer, trimer, and oligomer with water are almost similar [18].

In this model, the *N*-carboxymethyl chitosan molecule is linked by $\text{OH} \cdots \text{O}$ ¹⁷ hydrogen bond to a water molecule in Fig 1. Oxygen atom from water ($n=5$) interacts with the *N*-carboxymethyl chitosan hydrogen atom through hydrogen bonding ($\text{O}_{49}-\text{H}_{50} \cdots \text{O}_{54}$, $r_{\text{OH}} = 1.502 \text{ \AA}$). While at the other hydrogen bond $\text{O}_{49}-\text{H}_{50} \cdots \text{O}_{54}$ was longer ($r_{\text{OH}} = 1.776 \text{ \AA}$) when $n=1$. The hydrogen bonds in complex of *N*-carboxymethyl chitosan and $n\text{H}_2\text{O}$ could be classified into low, medium and strong hydrogen bonding. That character was divided by several parameters i.e bend, energy, and bond length. In this study we found that by added water to interact with *N*-carboxymethyl chitosan, there was a fluctuated type of hydrogen bond. The most stable hydrogen bond according to its bend was the interaction of *N*-carboxymethyl chitosan and $1\text{H}_2\text{O}$ where $\text{O}_{54} \cdots \text{O}_{49}-\text{H}_{50}$, bend = 173.46° and the lowest was 155.14° for *N*-carboxymethyl chitosan and $3\text{H}_2\text{O}$. Hydrogen bonding will be strong if the bend of $\text{OH} \cdots \text{O}$ approach

to 180°. On the other hand hydrogen bonds are strong if it's bond length of $r_{OH} = 1.2-1.5 \text{ \AA}$, medium if bond length of $r_{OH} = 1.5-2.2 \text{ \AA}$, and low if $r_{OH} = 2.2-2.3 \text{ \AA}$. We can notice that hydrogen bonds in complex *N*-carboxymethyl chitosan and nH_2O were classified to medium hydrogen bonding since we found all of the bond lengths are between 1.502 Å until 1.776 Å.

In *N*-carboxymethyl chitosan and $1H_2O$ until *N*-carboxymethyl chitosan and $5H_2O$ complexes, it was found that by added water molecules will make hydrogen bond stronger from its bond length because the more we added water, the shorter bond length of $OH \cdots O$. But, it could not be generalized from its bend because there was increasing and decreasing bend of $OH \cdots O$. Hence, further approaching was needed to investigate the hydrogen bonding. So, this particular investigation could give more explanation of hydrogen bond type in order to study proton transfer.

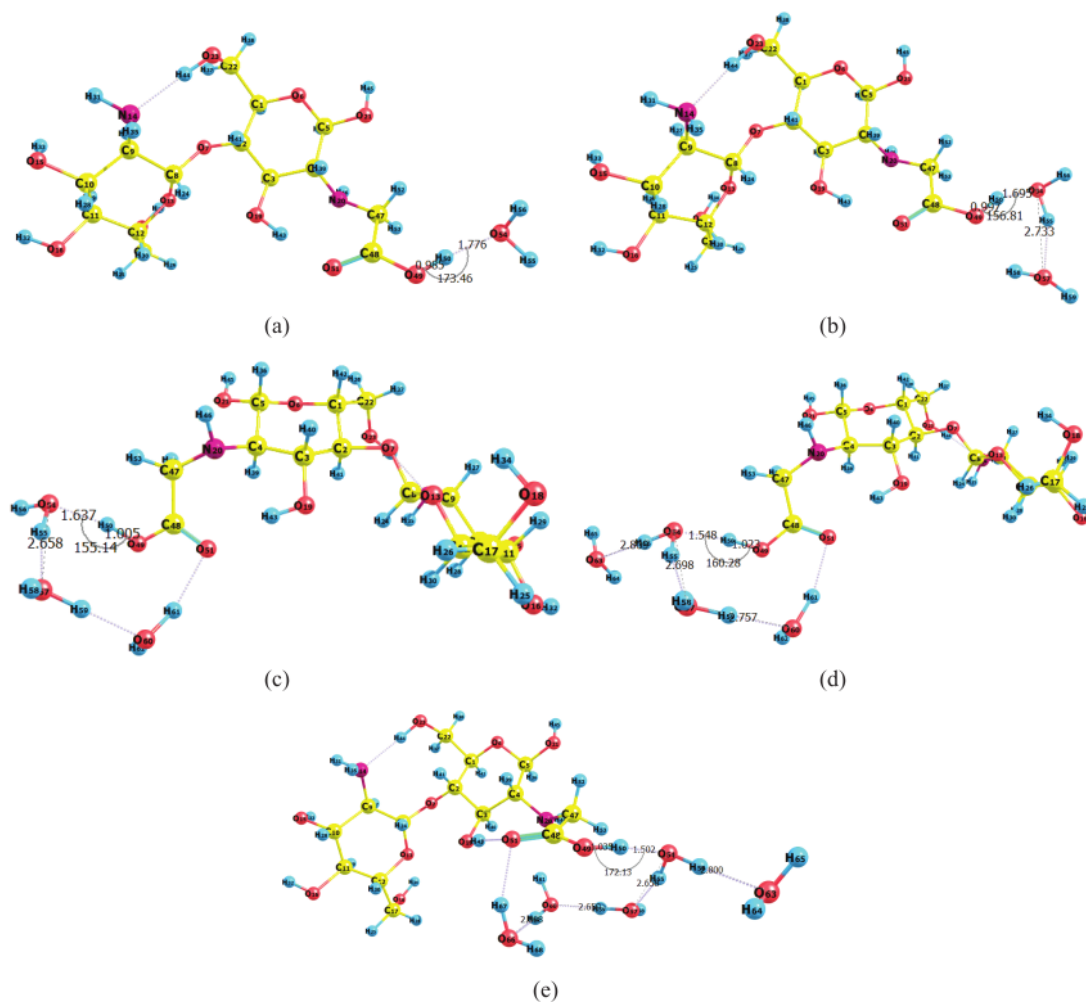


FIGURE 1. Optimized geometry for *N*-carboxymethyl chitosan and nH_2O ; (a) $n=1$; (b) $n=2$; (c) $n=3$; (d) $n=4$; (e) $n=5$.

Natural Bond Orbital (NBO) Analysis

The natural bond orbital was used to explore the charge transfer and conjugative interaction in molecular systems for studying intra and intermolecular bonding and interaction among bonds [19]. The NBO calculation of all interactions of *N*-carboxymethyl chitosan dimer and *n* water molecules has been done using NBO 07 program. The stabilizing energy of interaction involved in hydrogen bonds shows in Table 1. In NBO analysis, second-order stabilization energy ($E^{(2)}$) was used to characterize the types of interaction between occupied and unoccupied NBO typed Lewis orbitals which contribute to the electron delocalization from bonding (BD) or lone pair orbitals (LP) to anti-bonding orbitals (BD*) [10,20]. The stabilization energy ($E^{(2)}$) was also used to characterize the interaction of hydrogen bonds between lone pair (LP (Z)) from a Z-atom and anti-bonding orbital (BD* (Z-H)) [10]. The NBO analysis on the interaction of *N*-carboxymethyl chitosan dimer and *n* water molecules shows that there were interactions intermolecular electron lone pairs.

TABLE 1. Second-order perturbation stabilization energies of H-bonded in *N*-carboxymethyl chitosan and *n*H₂O

N-CMC + nH ₂ O	Donor (i)	Akseptor (j)	E ⁽²⁾ (kcal/mol)	Distance, r (Angstrom)
1	LP (2) O54	BD* (1) O49-H50	22.79	O54---H50 1.776
2	LP (2) O54	BD* (1) O49-H50	29.22	O54---H50 1.695
	LP (2) O57	BD* (1) O54-H55	18.33	O57---H55 1.824
3	LP (2) O51	BD* (1) O60-H61	7.19	O51---H61 1.886
	LP (2) O54	BD* (1) O49-H50	34.56	O54---H50 1.637
	LP (2) O57	BD* (1) O54-H55	31.33	O57---H55 1.637
	LP (2) O60	BD* (1) O57-H59	26.05	O60---H59 2.168
4	LP (2) O51	BD* (1) O60-H61	6.72	O51---H61 1.891
	LP (2) O54	BD* (1) O49-H50	47.29	O54---H50 1.548
	LP (2) O57	BD* (1) O54-H55	26.18	O57---H55 1.728
	LP (2) O60	BD* (1) O57-H59	24.1	O60---H59 1.767
	LP (2) O63	BD* (1) O54-H56	18.26	O63---H56 1.834
5	LP (2) O51	BD* (1) O19-H43	7.37	O51---H43 1.895
	LP (2) N20	BD* (1) O60-H61	10.29	N20---H61 2.076
	LP (2) O54	BD* (1) O49-H50	56.93	O54---H50 1.502
	LP (2) O57	BD* (1) O54-H55	30.11	O57---H55 1.683
	LP (2) O60	BD* (1) O57-H59	33.14	O60---H59 1.66
	LP (2) O63	BD* (1) O54-H56	18.77	O63---H56 1.828
	LP (2) O66	BD* (1) O60-H62	18.07	O66---H62 1.849

The O-H...O hydrogen bonds largely contribute to the stability of *N*-carboxymethyl chitosan and *n*H₂O molecular arrangement was the intermolecular interaction of LP (2) O₅₄ → BD* (1) O₅₀-H₄₉ which about 56.93 kcal/mol. The strongest interaction between *N*-carboxymethyl chitosan dimer with (H₂O)₅ was found in the bonds of *N*-carboxymethyl chitosan dimer and water with consideration to the intermolecular relationship and the greatest energy among all interactions in *N*-carboxymethyl chitosan and *n*H₂O. The amount of energy indicated the easiness of electron lone pair donation. If there was electron-lone pair donation, it indicated there were existences of hydrogen bonds of inter- hydroxyl groups with water molecules which mean it was able to transfer proton. The stronger the intermolecular hydrogen bonding, the easier the intermolecular transfer of proton [10, 21]. Compared to the intramolecular hydrogen bond which has the second-order stabilization energy of 7.37 kcal/mol from the contribution of LP (2) O₅₁ as a donor and BD* (1) O₁₉-H₄₃ as an acceptor, the stabilization energy for intermolecular hydrogen bond was higher than its intramolecular hydrogen bond. It indicated that intermolecular hydrogen bond interaction which built from interaction of carboxylic group and water molecules has a stronger contribution to make proton transfer worked.

Molecular Orbital

The quantum parameter related to the electronic structure is electron affinity (A) and ionization potential (I) of corresponding molecules with energies of HOMO and LUMO [10].

$$I = - \text{HOMO}$$

$$A = -\text{LUMO}$$

From those values, the electronegativity (X) can be obtained from the equation:

$$X = \frac{(I+A)}{2} \quad (2)$$

TABLE 2. The molecular orbital parameter in interaction *N*-carboxymethyl chitosan and *n*H₂O

<i>N</i> -CMC- <i>n</i> H ₂ O	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE (E _{LUMO} -E _{HOMO}) (eV)	A (eV)	I (eV)	X (eV)
1	-6.0230	0.3608	6.3838	-0.3608	6.0230	2.8310
2	-6.0948	0.2533	6.3481	-0.2533	6.0948	2.9207
3	-6.1688	-0.0351	6.1337	0.0351	6.1688	3.1019
4	-0.2217	0.0074	0.2291	-0.0074	0.2217	0.1071
5	-0.2355	0.0024	0.2379	-0.0024	0.2355	0.11653

HOMO energy showed the ability to donate electron while E_{LUMO} showed the molecular ability to receive electron. If molecules have a low value of E_{LUMO} it means the ability to receive more electrons [10]. The energy gaps reflect the chemical activities of molecules and the ability to make an electron transfer process while *N*-carboxymethyl chitosan and 4H₂O are the lowest one of energy gaps according to Table 2 [10, 22].

CONCLUSIONS

The hydrogen bond interactions between *N*-carboxymethyl chitosan and *n*H₂O (*n*=1-5) have been investigated using DFT/B3LYP level theory and 6-31G** basis set. NBO was used to investigate quantitatively the intermolecular hydrogen bonds. The interaction of *N*-carboxymethyl chitosan and 5H₂O was found as the strongest one with stabilizing the energy of 56.93 kcal/mol. The existence of electron lone-pairs donation shows the existence of hydrogen bonds between carboxylic groups and water molecules which can be predicted as the ability to proton transfer towards other carboxylic groups but this study still needs a further experimental approach to support the idea of proton transfer in carboxymethyl chitosan.

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