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Ab initio calculation of hydration and proton transfer on sulfonated *nata de coco*

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ABSTRACT

The repeating unit of sulfonated "*nata de coco*" is D-glucose sulfonate. This research aims to determine the most stable structures of sulfonated *nata de coco* polymer membrane, the energy and hydrogen bonds, in order to understand the characteristics, local hydration, and proton transfer on the membrane on the ab initio electronic structure calculation. The minimum energy structure for its monomer (two, three, four and five) are calculated by B3LYP/6-311G (d) method. The calculations show that there is no significant energy change on the structure interaction of two, three, four and five monomer of sulfonated *nata de coco* with one water molecule, which is about -18.82 kcal/mole. Those calculations that two monomers form of sulfonated *nata de coco* might be used to further calculation and research, because it can be considered as the representative for their polymer. The optimization and B3LYP/6-311G (d) calculation shows the amount of water molecule used for proton transfer is closely related to the formation of hydrogen bonding with sulfonic group. By the addition of one or two water molecule, the dissociated proton is stabilized by formation of hydronium ion. For further addition of water molecule (three to ten water molecules), the proton dissociation is also stabilized by the formation of Zundel ion and Eigen ion. The calculation of interaction energy with n water molecule (n = 1-10) shows that both energy change (ΔE), and enthalpy change (ΔH) are more negative. This implies that the interaction with water molecule is stronger. The bonding energy is about 14.0-16.5 kcal/mole per water molecule. On the addition of four and eight water molecules, proton dissociation forms two Zundel ion and two Eigen ions and causes lower bonding energy about 2 kcal/mole. Those optimization and energy calculations conclude that the formation of hydrogen bonding among water molecule and sulfonic group affects proton transfer on sulfonated *nata de coco* membrane.

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1. Introduction

Energy is the main component needed for all activities of organism in the earth. At present, fossil-based energy is the main energy source for human but it cannot be renewed and the emission can contaminate the environment. One of the updated energy which is very potential to replace fossil fuel is fuel cell. It turns chemical energy to electric energy through reaction between fuel (hydrogen) and oxygen [1-6]. There are three major components in fuel cell, namely anode, cathode, and polymer membrane as electrolyte.

Polymer Electrolyte Membrane Fuel Cell (PEMFC) is a very efficient fuel cell, eco-friendly which uses solid polymer membrane as electrolyte [7-10]. Nowadays, Nafion is commonly used as the electrolyte membrane. It is a sulfonated polytetraflouro ethylene which has good mechanical and thermal stability, also high proton conductivity (0.08 S/cm). But, it is very expensive (600-1000 \$/m^2), has a high methanol permeability tends to dehydrate at high temperature [11-13] and reduces its proton conductivity at high temperature [14-16].

To solve the weakness, many researches have been developedto replace or to modify Nafion. A previous research indicated that the proton conductivity of sulfonated *nata de coco* membrane is almost similar to its of Nafion® 117. Even though the chemical structure of sulfonated *nata de coco* is different with Nafion, but sulfonated *nata de coco* has hydrophobic and hydrophilic domains which allow proton transfers through cluster network. Due to the presence of water molecules in the media, the equilibrium among proton and hydroxyl ion is achieved. The formation of ester cellulose can make the proton transfer in membrane matrix easier, since the $H^{\delta+}$ from $-O^{\delta-}H^{\delta+}$ in sulfonic group is very easy to lose and then it interacts with water, producing protonated water. Besides that, $O^{\delta-}$ will also interact with other protonated water, and this interaction causes proton transfer and it increases the proton conductivity of sulfonated *nata de coco* membrane. In addition, the hydrophilic and sulfonic group can form intramolecular and intermolecular hydrogen bonding. The ability of electrolyte membrane to take water will determine its ability to conduct proton [17].

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Table 1. Structural data from optimized sulfonated *nata de coco*.

n Monomer + n H_2O	**- $SO_2O\cdots H$, (Å)**					**Hydrogen bonds, (Å)**		**Figure**
	$r_{O\text{-}H}$ ($r_{52\text{-}53}$)	**$r_{O\text{-}H}$ ($r_{48\text{-}49}$)**	**$r_{O\text{-}H}$ ($r_{72\text{-}73}$)**	**$r_{O\text{-}H}$ ($r_{97\text{-}98}$)**	**$r_{O\text{-}H}$ ($r_{121\text{-}122}$)**	**O···O**	**O···H**	
2 + 0	0.97	0.97	-	-	-	2.85	1.98	1a
2 + 1	0.97	1.00	-	-	-	2.63	1.67	2a
3 + 0	0.97	0.97	0.97	-	-	-	-	1b
3 + 1	0.97	0.97	1.01	-	-	2.58	1.59	2b
4 + 0	0.97	0.97	0.97	0.99	-	2.68	1.68	1c
4 + 1	0.97	0.97	0.99	1.02	-	2.68; 2.56; 2.80	1.73; 1.54; 1.83	2c
5 + 0	0.97	0.97	0.97	0.96	0.99	2.65; 2.76	1.74; 1.87	1d
5 + 1	0.97	0.97	0.97	0.97	1.01	2.57; 2.73; 2.78	1.57; 1.77; 1.87	2d

$$\Delta E = E_{\text{two monomers of sulfonated nata de coco - n water}} - E_{\text{two monomers of sulfonated nata de coco}} - E_{\text{water}} \qquad (1)$$

$$\Delta H = H_{\text{two monomers of sulfonated nata de coco - n water}} - H_{\text{two monomers of sulfonated nata de coco}} - H_{\text{water}} \qquad (2)$$

$$\Delta G = G_{\text{two monomers of sulfonated nata de coco - n water}} - G_{\text{two monomers of sulfonated nata de coco}} - G_{\text{water}} \qquad (3)$$

$$\Delta E = E_{\text{dimersf-air}} - E_{\text{dimerss}} - E_{air} \qquad (4)$$

High proton conductivity is expected from the maximum movement of protons which enable proton transfer from anode to cathode. To know completely the cause of proton transfer in various membrane molecular structures, it needs a computational model. Many researches have been done in developing the proton transfer in conductive membrane. One of the examples is the study of flexibility of side chain position (SSC) and main chain toward proton transfer in perflouro sulfonic acid polymer membrane (PFSA/PTFE). It explains that the formation of hydrogen bonding among water molecule is based on the connectivity of acid group (it is the degree of separation or aggregation of side chain group). This research also shows that Zundel ion ($H_5O_2^+$) plays an important role in facilitating proton transfer in minimum hydration condition. Proton dissociation starts to occur in addition of five water molecules. Besides that, the change in main chain conformation of PTFE also influences hydration process and proton transfer, where pleated main chain is favorable than straight chain, hydrogen bonding is stronger and reduce the need of water to dissociate proton and can increase the PEMs conductivity for fuel cell [18,19]. Other research about ab initio computation of hydration and proton transfer in sulfonated poly(phenylene) sulfone ionomer shows that in meta-meta-sSPO$_2$ dimer, the amount of water molecule needed for proton transfer to the first hydration shell is closely related to the existence of hydrogen bonding near sulfonic acid group: three water molecules for meta conformation and four water molecules for *orto* conformation. sSPO$_2$ ionomer is more effective to result proton which moves in low water content [20]. Classical molecule dynamics method (MD) and ab initio molecule dynamics (AIMD) have been used to determine mobility of proton as a function of hydration condition and effect of sulfonated functional group [21-28]. So, this research will study electronic structure, geometry optimization, the proton transfer in sulfonated *nata de coco* polymer membrane, the effects of its intermolecular hydrogen bonding and the addition of n water molecule in various sulfonated *nata de coco*.

2. Computational method

Geometric optimization of the polymer membrane molecule (monomers, dimers, trimers, etc.) is conducted using the density functional theory (DFT) and Becke's three-parameter functional (B3LYP) method with the 6-311G (d) basis set. A polarizing effect on the structure of minimum energy used when the hydrogen atoms act as a bridge to proton transfer. Previous studies indicated of the minimum energy structure, potential energy profiles, the associated energetic penalties for proton transfer in the cluster phosphate and the electronic structure, geometry optimization in pyridine compounds are determined at the DFT / B3LYP 6-31G (d,p) from chemically rational initial configurations and the predicted structural properties with B3LYP method were agreed well with the experimental X-ray data [29,30].

Intra- and inter-molecular interaction in addition of *n* water molecules gradually (it is + *n*H_2O, where *n* = 1-10) into sulfonated *nata de coco* polymer membrane (represented by its two monomers), conducted by using DFT/B3LYP with basis set 6-311G (d), as Rahmawati, Radiman, and Martoprawiro have done in phosphorylated *nata de coco*. The addition of *n* water molecules is aimed to identify the proton transfer/ dissociation and hydrogen bonding around sulfonic group in low hydration degree. Optimization result is expected to get interaction energy among water molecule and sulfonic group. Calculation is performed using DFT method with Becke's three parameter functional (B3LYP) and 6-311G** basis set, and subsequently corrected for zero point energy (ZPE) and basis set superposition error (BSSE), as Wang and Paddison have done in sulfonated poly phenylenesulfone system [20]. All calculations of electronic structure interaction among sulfonated *nata de coco* molecules are conducted using Gaussian09 program. Calculations of energy change (*ΔE*), enthalpy change (*ΔH*), free Gibbs energy change (*ΔG*), use equations (1-3).

3. Result and discussion

Sulfonated *nata de coco* is a polymer that contain of β-1,4 bonds D-glucose sulfonate units (monomer). The minimum energy structures of sulfonated *nata de coco* (two monomer, three monomer, four monomer, and five monomer) are determined by B3LYP/6-311G (d) method (Figure 1), with bond length and bond angle parameters. Hydrogen bonds between sulfonic acid groups (-SO_3H), sulfonic acid group and hydroxyl group (-OH), and between hydroxyl groups are observed. The result that showed the length of O···O and O···H are shown in Table 1. These results is similar with previous research which observed modeling and short side chain (SSC) flexibility of perfluoro sulfonic acid (PFSA) membrane [18,19]. The type of hydrogen bonds formed is medium hydrogen bond [31].

Interaction energy changes of sulfonated *nata de coco* are determined by added one water molecule to its monomer (two, three, four and five) on the same position. The results of various structure optimizations are shown in Figure 2 and Table 1 for its energy.

Those results gave energy data for each structure, so the energy changes can be calculated using the equation (4).

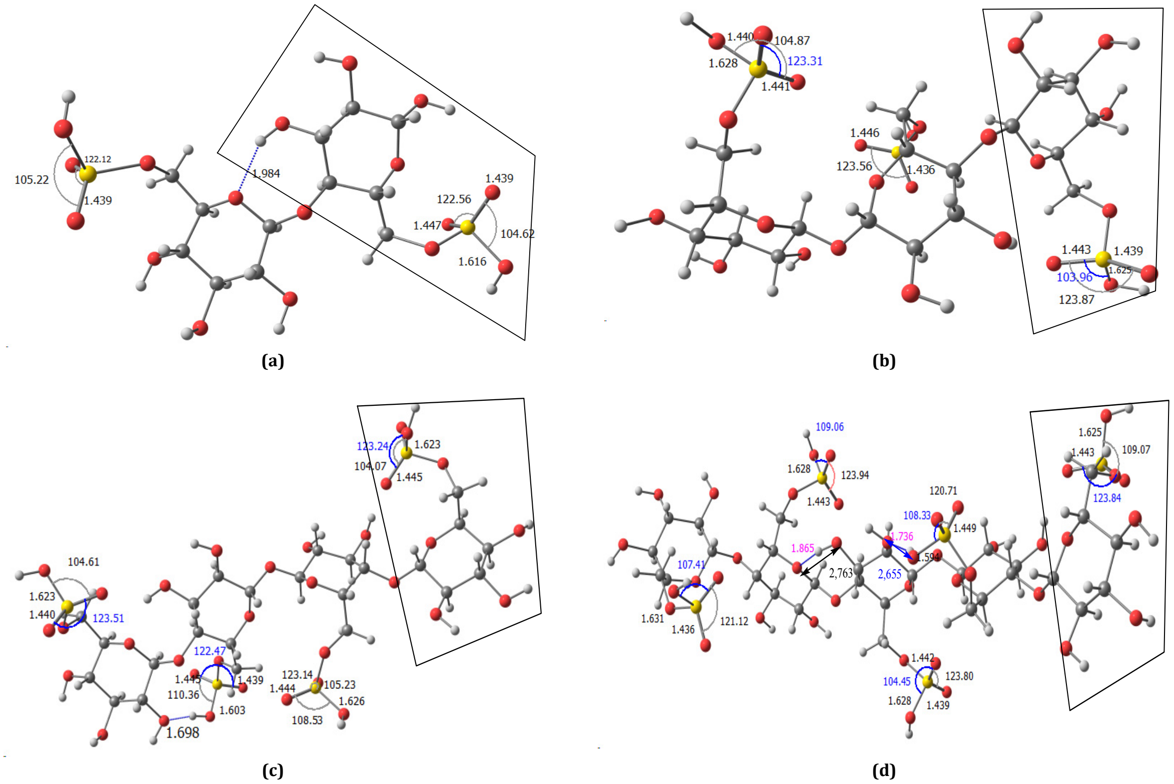

Figure 1. Fully-optimized (B3LYP/6-311G (d)) structure of (a) two, (b) three, (c) four and (d) five monomer of sulfonated *nata de coco*.

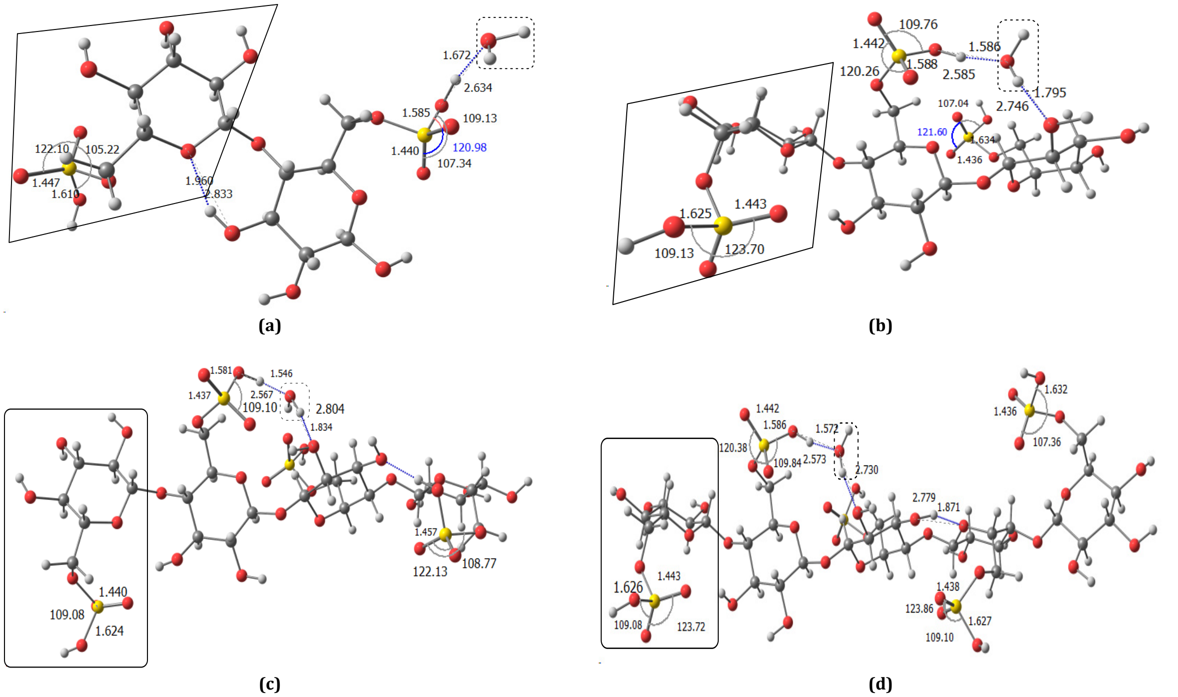

Figure 2. Fully-optimized (B3LYP/6-311G (d)) structure of (a) two, (b) three, (c) four and (d) five monomer of sulfonated *nata de coco* interacted with one H_2O molecule.

The energy calculation (Table 2) showed the longer the chain the more minimum energy given. It does prove that the molecule become more stable with more hydrogen bond formed. Interaction energy changes of the monomers and water showed no significant changes, about -18.82 kcal/mol. These results tell that two monomer structures can represent longer *nata de coco* polymer in the interaction energy calculation with water molecule.

Table 2. Binding energies of (two, three, four and five) monomer of sulfonated *nata de coco.*

Sulfonated *nata de coco*	**E_{ZPE} (Hartree/Particle)**	**Thermal correction to energy**	**E_{elec} (Au)**	**E (Hartree)**	**ΔE (kcal/mole)**
Two monomer	0.399902	0.431827	-2545.9802	-2545.55	-18.8253
Two monomer water	0.425543	0.460023	-2622.4405	-2621.98	
Three monomer	0.588128	0.635654	-3780.7416	-3780.11	-18.8253
Three monomer water	0.614288	0.663921	-3857.2130	-3856.55	
Four monomer	0.777482	0.839830	-5015.5241	-5014.70	-18.8253
Four monomer water	0.803515	0.867512	-5092.0090	-5091.14	
Lima monomer	0.965577	1.043494	-6250.2953	-6249.25	-18.8253
Five monomer water	0.990616	1.071376	-6326.7516	-6325.68	
Water	0.021315	0.024150	-76.433932	-76.40	

Table 3. Structural data from optimized sulfonated *nata de coco* + n water molecules.

Two monomer of sulfonated *nata de coco* + *n* H_2O	**$-S_1$ (O-H)**	**$-S_2$ (O-H)**	**Hydrogen bonds**	
	r_{O-H} (r_{52-53}), Å	**r_{O-H} (r_{48-49}), Å**	**r_{H-O} (r_{49-54}), Å**	**r_{H-O} (r_{53-57}), Å**
0	0.97533	0.96915		
1	0.96963	1.00204	1.67190	
2	1.00573	1.00171	1.67450	1.64164
3	1.00581	1.02665	1.53212	1.64073
4	1.02786	1.02856	1.52457	1.51951
5	1.02632	1.10992	1.34897	1.51651
6	1.64879	1.07917	1.40929	1.00809
7	1.52527	1.57090	1.02360	1.02104
8	1.58032	1.03652	1.50390	1.00937
9	1.73056	1.03620	1.50502	0.98902
10	1.76031	1.72179	0.99477	0.98931

Table 4. Binding energies for the optimized two monomer of sulfonated *nata de coco* + *n* water molecules.

Two monomer of sulfonated *nata de coco* + *n* H_2O	**$E_{tot} = E_{elec}$ (Hartree)**	**E_{BSSE} (Hartree)**	**ΔE_{ZPE} (kcal/mol)**	**ΔE (kcal/mole)**	**ΔG (kcal/mole)**	**ΔH (kcal/mole)**
1	-2622.44054	-2622.43358	-13.858031	-14.033734	-5.2291412	-14.626103
2	-2698.90188	-2698.88829	-28.449383	-28.749961	-11.075514	-29.934699
3	-2775.36509	-2775.34404	-44.172882	-44.746427	-18.273662	-46.523535
4	-2851.83655	-2851.80311	-64.476947	-65.784678	-27.716784	-68.154156
5	-2928.28834	-2928.24725	-74.362376	-75.497542	-29.371792	-78.458761
6	-3004.74953	-3004.70277	-87.382066	-89.098306	-34.182396	-92.652523
7	-3081.21100	-3081.14829	-101.30370	-103.8583	-37.539901	-108.00488
8	-3157.69204	-3157.62826	-127.57458	-130.19506	-55.530155	-134.93401
9	-3234.14725	-3234.07289	-138.12142	-141.02554	-56.205638	-146.35686
10	-3310.62616	-3310.52831	-160.84009	-165.53449	-64.827920	-171.45818

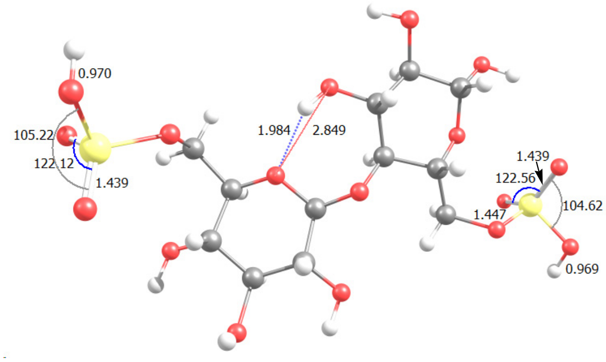

Figure 3. Fully-optimized (B3LYP/6-311G (d)) structure two monomer of sulfonated *nata de coco*.

The structure of sulfonated *nata de coco* polymer is different with the backbone of PTFE from PFSA polymer and the backbone of aromatic phenylene from $SpSO_2$. The sulfonated *nata de coco* polymer connected with ether group, has pyranose ring backbone contained many hydroxyl ions and sulfonic group ($-SO_3H$). This is potential to influence its proton transfer. The minimum energy of two monomers of sulfonated *nata de coco* structure is determined by using B3LYP/6-311G (d) method and performed in Figure 3, with bond length and bond angle parameters.

For conformation showed in Figure 3, the hydrogen bond length (O⋯H) formed is 1.984 Å and the O⋯O in that hydrogen bond is 2.849 Å. The length of O-H in sulfonic group ($-SO_3H$) 0.97 Å is similar with the length of O-H observed in the model and flexibility of short side chain (SSC) of perfluorosulfonic acids (PFSA) [18,19].

In addition to intra- and inter-molecular interactions, to identify proton transfer near the sulfonic group ($-SO_3H$) in low hydration degree, the *n* water molecules (*n* = 1-10) is added gradually in two monomers of sulfonated *nata de coco*. Each of the structure is optimized using B3LYP/6-311G (d) method. The conformation is showed in Figure 4. The optimum results, it is known that the length O-H bond and the hydrogen bonds between molecules *nata de coco* with *n* water molecules (Table 3). From the Table 3, the type of hydrogen bonds formed is medium hydrogen bond [31].

From the optimization result, it is known that the bonding energy of sulfonated *nata de coco* (two monomers) and *n* water molecules can be seen in Table 4.

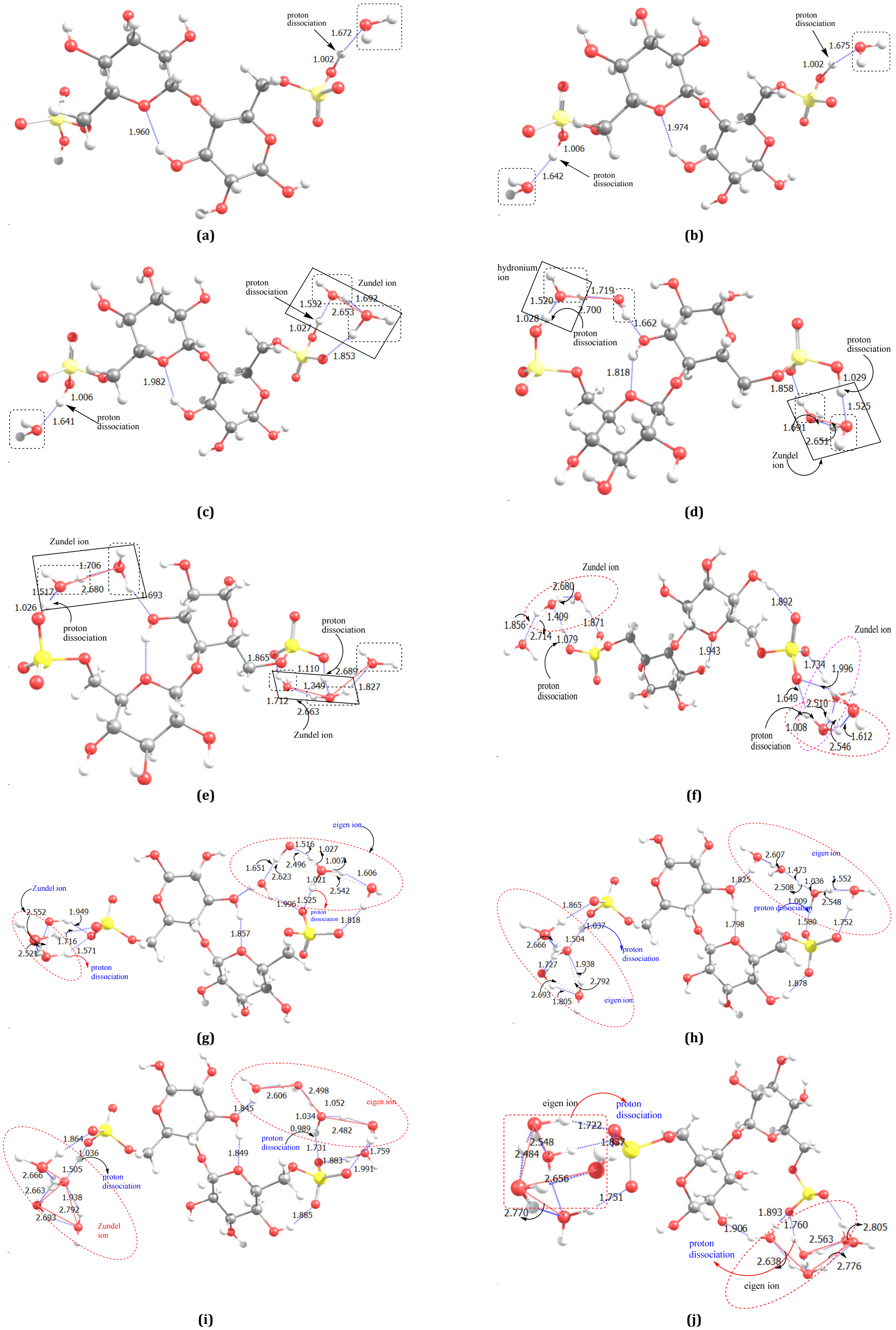

Figure 4. Fully-optimized (B3LYP/6-311G (d)) energy structure of two monomer of sulfonated *nata de coco* with n water molecules: (a) n = 1; (b) n = 2; (c) n = 3; (d) n = 4; (e) n = 5; (f) n = 6; (g) n = 7; (h) n = 8; (i) n = 9; (j) n = 10. The proton dissociation occurs when one water molecules were added.

From Table 4, the energy change (*ΔE*), enthalpy change (*ΔH*) is more negative, this implies that the interaction with water molecules is stronger. This interaction can simplify the proton transfer in membrane matrix, because $H^{\delta+}$ from $-O^{\delta-}H^{\delta+}$ in sulfonic group can easily lose and interact with water to produce protonated water. $O^{\delta-}$ will also interact with other protonated water molecules, and this interaction causes proton transfer and increase proton conductivity of sulfonated *nata de coco* membrane. The interaction among sulfonic group and water will rise up [17].

This is consistent with the previous research, reveals that the ability of membrane in transferring proton is affected by the acid group, and water content [13]. The sulfonated *nata de coco* membrane has similar property with Nafion, where they have hydrophobic carbon backbone and hydrophilic sulfonic side chain. High hydrophylicity of sulfonic group can enhance the ability of water adsorption in membrane [32]. Those hydrophobic and hydrophilic domain enable proton transfer via cluster network. The existence of water in media allows the equilibrium among proton and hydroxyl ion [17].

Table 4 displays the BSSE computational data that corrects the bonding energy among molecules. It shows that the bonding energy trend (ΔE, ΔE_{ZPE}, and ΔH) per water molecule has similar trend, it is about 14.0-16.5 kcal/mole. In addition of four and eight water molecules, the bonding energy per water molecule is around 2 kcal/mole more negative. This is caused by the addition of four water molecules in which the dissociated proton is stabilized by the formation of two Zundel ions while the addition of eight water molecules is stabilized by the formation of two Eigen ions.

Dissociation of proton in sulfonated *nata de coco* is quite different with the dissociation of proton in the model and flexibility of short side chain (SSC) of perfluorosulfonic acid (PFSA) [18,19] and $SPSO_2$ dimer from sulfonated poly (phenylene sulfone) ($sPSO_2$) ionomers [20]. In $SPSO_2$ dimer, proton dissociation starts to occur in the addition of three water molecules, the PFSA for at least five are required to observe dissociation of protons [18-20]. In sulfonated *nata de coco* proton dissociation starts to occur in the addition of one water molecule, where the sulfonated proton is stabilized by the formation of hydronium ion (Figure 4a). In the addition of four to six water molecules, dissociated proton forms Zundel ion and hydronium ion (Figure 4c-f). The presence of Zundel ion reduce the bonding energy, so that the proton transfer is easier. Zundel ion acts as mediator for proton transfer. In addition of seven to ten water molecules, dissociated proton forms two Zundel ions; hydronium ion and Eigen ion (Figure 4g-j). The hydrogen bonds in Eigen ion through hydrogen attached on three water molecules with bonding length of O-O is approximately 2.56 Å. The formation of Eigen ion indicates that the proton moves to the second hydration shell. Proton can move from anode to cathode in fuel cell membrane through Grotthuss mechanism or hydrogen bonding chain mechanism by involving Zundel ion and Eigen ion [33]. Thus, the amount of water molecule in membrane supports the proton conductivity of fuel cell electrolyte membrane.

4. Conclusions

Optimization and energy calculation results using B3LYP/6-311G (d) show that no significant energy changes in (two, three, four, five) sulfonated *nata de coco* monomer (about -18.82 kcal/mole). The amount of water molecule needed for proton transfer in closely related to the formation of hydrogen bonding and sulfonic group. By the addition of one and two water molecules, the dissociated proton is stabilized by the formation of hydronium ion. For further water addition (three to ten water molecules) other than hydronium ion, proton dissociation is also stabilized by the formation of Zundel ion and Eigen ion. The calculation of interaction energy for *n* water molecules (*n* = 1-10) shows the energy change (Δ*E*), enthalpy change (Δ*H*) is more negative, this indicates that the interaction with water molecule becomes stronger. Bonding energy is about 14.0-16.5 kcal/mole per water molecule. The formation of two Zundel ions and two Eigen ions causes the lower bonding energy 2 kcal/mole; it is in addition of four to eight water molecules. Those optimization and calculation results give a basis that the formation of hydrogen bonding among water molecule and sulfonic group affects the proton transfer in sulfonated *nata de coco* membrane.

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