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Intermolecular interaction between the pendant chain of perfluorinated ionomer and methanol

Shingo Urata [a,*], Jun Irisawa [a], Akira Takada [a], Seiji Tsuzuki [b],
Wataru Shinoda [b], Masuhiro Mikami [b]

[a] *Research Center, Asahi Glass Co., Ltd. (AGC), 1150 Hazawa-cho,*
Kanagawa-ku, Yokohama, Kanagawa 221-8755, Japan
[b] *National Institute of Advanced Industrial Science and Technology (AIST),*
1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

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Abstract

A comparison between water and methanol on the interaction with a pendant chain model for perfluorosulfonic ionomers (PFI), $CF_3OCF_2CF_2SO_3^-$, was made by using molecular orbital calculation. Intermolecular interaction energy (E_{int}) of the most stable complex for $CF_3OCF_2CF_2SO_3^- + CH_3OH$, where methanol associates with sulfonic acid group, is −10.38 kcal/mol at the MP2/aug-cc-pVDZ//B3LYP/6-31 + G* level, and it is almost the same with that of $CF_3OCF_2CF_2SO_3^- + H_2O$ complex (−10.58 kcal/mol). Since an association of methanol to the sulfonic acid group is quite advantageous in energy, it is expected that, similarly to water, methanol would likely populate around the acidic site. On the contrary, according to a systematic E_{int} analysis for 500 random configurations, dissimilar distribution of E_{int} was observed for methanol compared with water. This is because methyl group substitution reduces oxygen surface area and causes more attractive dispersion energy with $CF_3OCF_2CF_2SO_3^-$ by about 1.0 kcal/mol on average compared with water. To see how the difference in the interaction energy affects the solvation structure of methanol and water to the PFI, molecular dynamics simulations of a $CF_3OCF_2CF_2SO_3^-$ molecule in methanol solutions have also been carried out at the methanol concentration of 10–90 mol%. Consequently, water probably associates with the sulfonic acid group-pushing methanol close to hydrophobic sites. It was also observed that methanol molecule tends to point its methyl group toward the solute at hydrophobic sites. These results demonstrated that methanol should locate in the vicinity of hydrophobic site compared with water due to methyl group substitution.

Keywords: Molecular orbital calculation; Molecular dynamics simulation; Ionomer; Intermolecular interaction

1. Introduction

Direct methanol fuel cell (DMFC) has been developed for portable power sources and electric vehicle due to several advantages, such as high efficiency, low emissions and convenient refueling [1]. Solid electrolyte membranes composed of perfluorosulfonic acid polymers, such as Flemion® and Nafion®, are commonly used for the fuel cell membranes because of high proton conductivity. A number of efforts have been made to improve cell performance, and recently high power densities are achieved [2–6]. Contrarily, several problems have not yet been solved for practical applications: one is slow oxidation of methanol at the anode compared with hydrogen cell [1] and another is the methanol transport through the membrane to the cathode, known as methanol-crossover [6–9]. The latter phenomenon causes fuel loss and the cell potential reduction due to mixed potential at the cathode, and thus less than about 2 M concentration of methanol has to be utilized [7]. Small angle X-ray and neutron scatterings (SAXS, SANS) suggest that water swollen membranes of perfluorinated ionomers form meso-scale separation of hydrophilic and hydrophobic regions [10–17], and both of proton and methanol are

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* Corresponding author. Tel.: +81 45 374 7074; fax: +81 45 374 8730.
E-mail address: shingo-urata@agc.co.jp (S. Urata).

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thought to conduct through the hydrophilic region composed of sulfonic acids and water. It is thus important to optimize the size of hydrophilic cluster in order to satisfy two capabilities that is, high proton conductivity and sufficient methanol transport inhibition, at the same time. For this purpose, several new membranes have been suggested [18–22].

Intermolecular interaction between solvents and the pendant side chain of ionomers should be one of the key factors to determine the size and geometry of the hydrophilic cluster. In this article, we therefore try to analyze the intermolecular interaction energies between the pendant chain model of Flemion® ($CF_3OCF_2CF_2SO_3^-$) and a methanol. To understand overall characteristics of the interactions, we investigate not only the stable configurations but also a variety of orientations, in which a methanol molecule locates at the various positions with random orientation around $CF_3OCF_2CF_2SO_3^-$. The intermolecular interactions of the random configurations are estimated by Hartree–Fock (HF) level of ab inito calculation combined with empirical dispersion energy in the same manner with our previous work [23]. Molecular dynamics (MD) simulations of a solute, $CF_3OCF_2CF_2SO_3^-$, in 10, 25, 50, 75 and 90 mol% methanol concentrations of solution are also performed to elucidate the difference between water and methanol on coordination probability around the pendant side chain model.

2. Results and discussion

2.1. Interaction energies of geometrically optimized complexes

In order to discuss detailed difference of the interaction energies of the two systems, $CF_3OCF_2CF_2SO_3^- + CH_3OH$ (SA–Me) and $CF_3OCF_2CF_2SO_3^- + H_2O$ (SA–W), we calculated the energies for several geometrically optimized complexes at the MP2/aug-cc-pVDZ//B3LYP/6-31 + G* level. Four types of configurations were selected as initial ones from the 500 random orientations to compare the interaction energies at various positions along the side chain. The optimized geometries were displayed in Figs. 1 and 2 for methanol and water, respectively, and calculated interaction energies were summarized in Table 1. The complexes, where water and methanol interact with sulfonic acid in terms of hydrogen bonding O–H . . . O (M-a in Fig. 1 and W-a in Fig. 2), are the most stable. The interaction energies are almost the same (−10.38 and −10.58 kcal/mol for methanol and water, respectively). Contrarily, the contribution of each energy component in the methanol complex is different from that in the water complex: in the case of W-a, electrostatic interaction (E_{es}) is dominant and large repulsion energy (E_{rep}) is noticeable [23], while smaller electrostatic and larger correlation energies (E_{corr}) and consequently smaller repulsion energy were observed for M-a as shown in Table 1. Induction energy (E_{ind}) is about 1.5 kcal/mol more attractive in W-a complex in comparison with M-a.

The configuration W-b, in which water associates with sulfonic oxygen and the second CF_2 group from the acidic site, shows sufficiently attractive interaction, however, the interaction energy is less than that of W-a complex by about 1.0 kcal/mol. Less attractive electrostatic interaction and induction energy account for their difference. On the other hand the configuration M-b, in which methanol contacts with SO_3^- and two CF_2 groups, has almost the same size of interaction with the most stable configuration M-a. And also, the energy components, such as E_{corr}, E_{es}, E_{ind} and E_{rep}, are also analogous to those of M-a. It is thus expected that methanol would more widely disperse along the pendant side chain in comparison with water.

The configurations M-c and M-d, where methanol contacts CF_3 or CF_2 groups with hydrogen bonding, O–H . . . F, show weak binding energies. It was difficult to

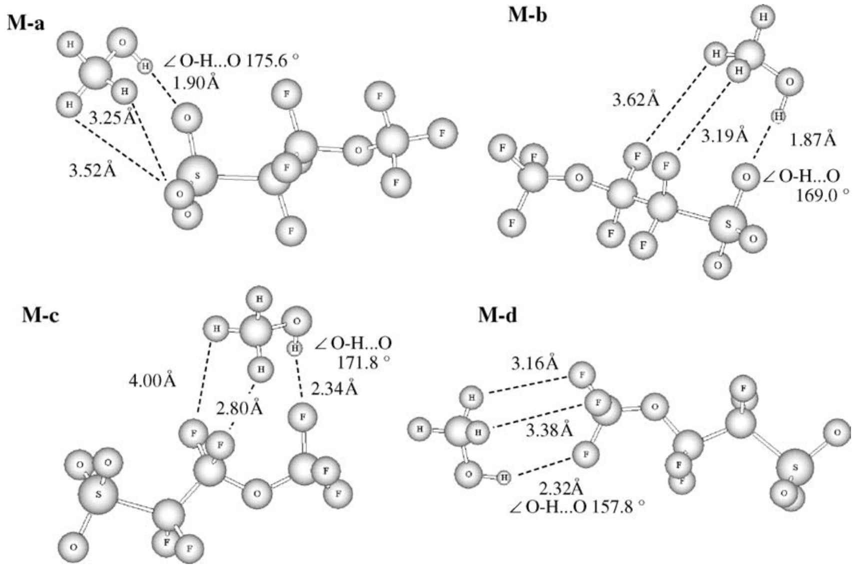

Fig. 1. Optimized geometries of $CF_3OCF_2CF_2SO_3^- + CH_3OH$ at the B3LYP/6-31 + G* level.