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Quantum-chemical modeling of the charge transport properties of the ammonium form of Nafion

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ABSTRACT

Quantum-chemical modeling of structure and cation migration barriers in Nafion-like ammonium substituted ionomers plasticized with dimethyl sulfoxide (DMSO) was investigated by ab initio calculations. We use B3LYP/6-31G* hybrid density functional methods and the PBE/PAW method taking into account the gradient corrections and periodic boundary conditions. It is shown that at a low content of DMSO ($n \leq 4$), NH_4^+ cation removal from the SO_3^--group occurs with a significant energy cost (> 0.4 eV). As the amount of DMSO increases, both the separation energy and the barriers to ammonium ion migration decrease to 0.1–0.2 eV. Ab initio molecular dynamics modeling demonstrated that at a moderate temperature (~350 K), there is a rapid (~15 ps) redistribution of the DMSO molecules between the Nafion chains located at distances ≤2 nm.

1. Introduction

Ion-conducting polymeric membranes are key components of various solid-state electrochemical energy conversion devices (low-temperature fuel cells, electrochemical sensors, metal-ion batteries) [1–5]. The most common and commercially available ion-conducting membranes are perfluorinated sulfonic acid ion-exchange membranes of the Nafion type from the Du Pont company. Polymer electrolytes based on Nafion have a number of advantages such as high ionic conductivity (up to 10^{-1} S/cm) and high chemical and thermal resistance [1]. Recently, Nafion-like membranes in various cationic forms plasticized with organic solvents have attracted considerable interest [6–18]. This interest is due to the search for new materials with high transport properties, high capacitance characteristics and a wide window of electrochemical stability to create more energy-intensive and efficient electrochemical current sources. In this regard, it is of interest to investigate the plasticized Nafion membranes in NH_4^+ form, for which the conductivity is comparable to that of the proton and lithium-ion membrane forms and significantly exceeds the conductivity of the Nafion membrane in other ionic forms of alkali metals [7,14,18]. However, the origins of the high ionic conductivity have not been fully elucidated.

Therefore, this work seeks to carry out a quantum-chemical study of the effect of the amount of the aprotonic plasticizer DMSO [$OS(CH_3)_2$] on the transport properties of the ammonium form of Nafion like electrolyte and on the formation of conducting channels during the thermal motion of the DMSO molecules in Nafion.

2. Modeling details

Quantum-chemical modeling was first carried out for model clusters in the framework of the B3LYP hybrid density functional [19,20] and the 6-31G* basis set using the GAUSSIAN software package [21]. To simulate the studied systems with an infinite polymer chain of Nafion, the approach from [22,23] based on the periodic boundary conditions and PBE functional [24] with a projected plane waves PAW [25] basis set and corresponding pseudopotential was used. The energy cutoff (E_c) was equal to 400 and 800 eV. The MD-VASP approach (15 ps) was used for modeling in the framework of non-empirical molecular dynamics. In this case, the same algorithms that were used for the usual optimization of structure are used but with the energy cutoff E_c = 200 eV. During the calculations, the time step was kept equal to 0.0010–0.0015 ps. Thermalization was performed in a canonic (Nose) ensemble. The external pressure was set to 1 atm throughout the simulations. The temperature was changed during the thermalization process. The initial temperature of the system was T_0 = 0 K, and the system was heated to T_1 = 350 K over 1.5 ps at which point the system was equilibrated for 10–15 ps. The calculations were carried out using the VASP (Vienna ab initio simulation package) program [26–29].

The model used in this work was constructed as 33-143 atom clusters of solvated ammonium salt of perfluorinated sulfonic acid $(CF_3)_2CFO(CF_2)_2SO_3^-NH_4^+ * n((CH_3)_2SO)$, where n = 1–12 (called NH_4Nafion5*nDMSO, Fig. 1) corresponding to the side branches of the Nafion ionomer. For the simulation of the interaction between the

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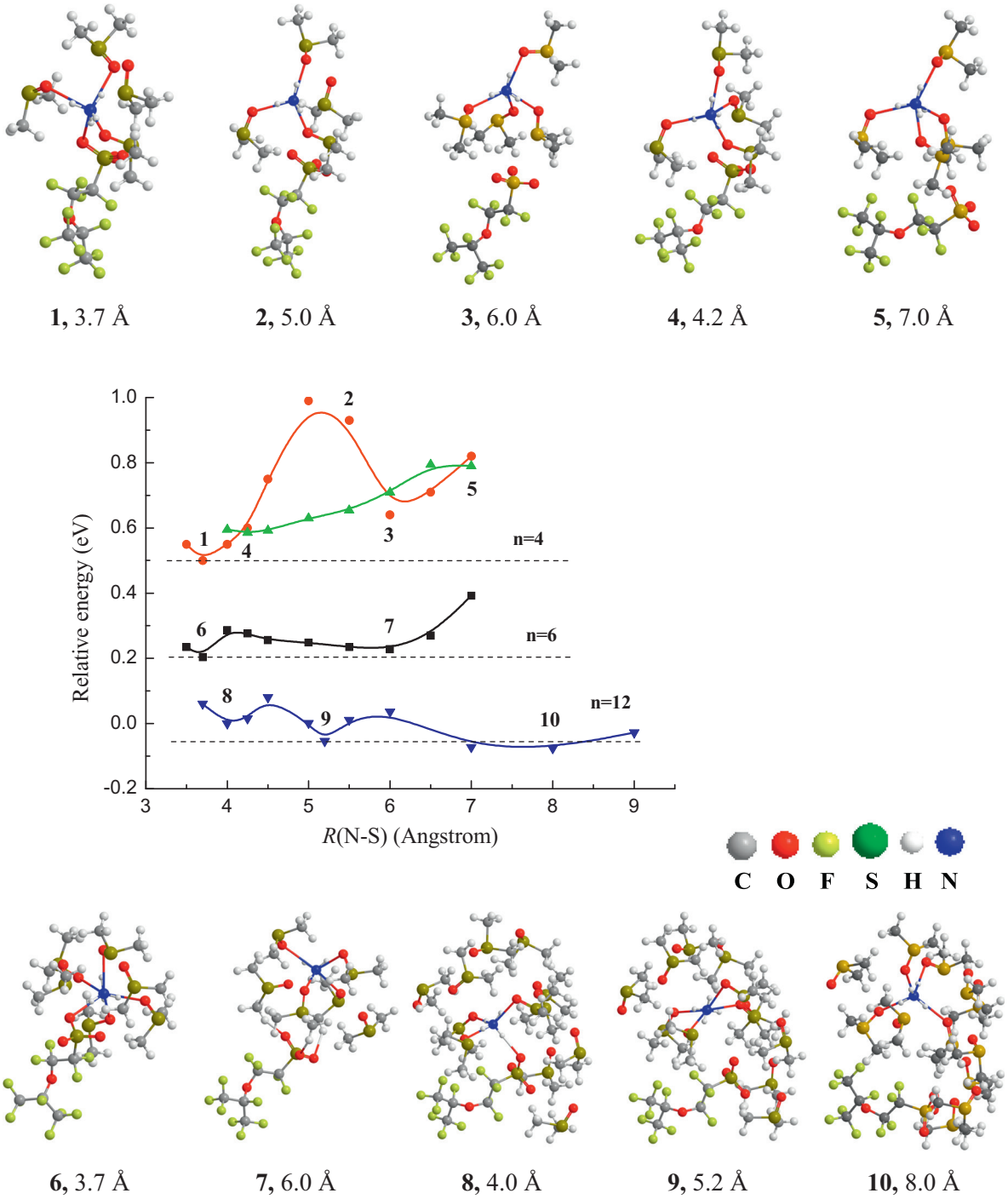

Fig. 1. Structures of NH_4Nafion5*nDMSO clusters and relative energy of NH_4^+ detachment from the sulfo-group with different amounts of DMSO molecules (n). R (N—S) values are given after the comma.

different clusters in space, 177 atom clusters of $CF_3(CF_2)_9OCF_2CF(CF_3)O(CF_2)_2SO_3^-NH_4^+$*12($(CH_3)_2SO$) corresponding to the average repeat unit of the commercial Nafion ionomer were used (Fig. 2). For the construction of the infinite chains translated in the space, a 175-atom fragment —$CF_2(CF_2)_8$(—CF)$OCF_2CF(CF_3)O(CF_2)_2SO_3^-NH_4^+$*12($(CH_3)_2SO$) (called NH_4Nafion15*12DMSO) was used (Fig. 3).

The distance between NH_4^+ cation and SO_3^- group was determined as a distance between N atom and the nearest oxygen atom (R(N—O_s)) and between N atom and S atom (R(N—S)) of the SO_3^- group.

3. Results and discussion

3.1. Dependence of the barrier on DMSO content

Fig. 1 shows the different structures of the NH_4Nafion5*nDMSO clusters and the potential energy for the displacement of the NH_4^+ cation from the sulfo-group. At n = 1–3, the ammonium ion is coupled with SO_3^- - groups. It is coordinated to the oxygen atom (O_S) of the SO_3^- - group and to 1–3 DMSO molecules. When a fourth DMSO molecule is added (Fig. 1, structures **1**–**5**), the coexistence of two isomers