Molecular Dynamics Simulation of Nafion Oligomer Solvation in Equimolar Methanol−Water Mixture

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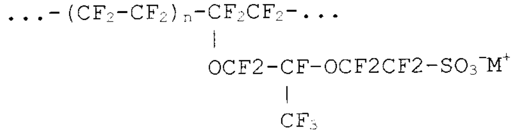
The solvation of Nafion oligomer in equimolar water−methanol solution was studied by means of molecular dynamics simulations. The skeleton in water−methanol system was found to be substantially folded; its geometry was close to that in pure water. Pronounced flexibility of the skeleton was observed. At the same time, the side chains turned out to be very stiff. No conformation transitions in the side chains were monitored. The skeleton was mostly solvated by methanol. A minor preference for water in the vicinity of the sulfate group was observed. The lifetime of the hydrogen bonds of water and methanol were estimated. The lifetimes for the two components were very close to each other and several times longer than rotational correlation times of individual solute molecules in the bulk.

1. Introduction

Solid ionomer membranes are widely used in liquid and gas separations,[1,2] water electrolysis, electroorganic synthesis[3], catalysis,[3,4] sensors,[5−7] electrode modification,[8] electrochemical synthesis of chlorine and alkali,[9] and particularly, in polymer electrolyte fuel cells, which are seen as the most promising renewable energy source for emission free vehicles.[10,11] The prospective use of ionomer membranes includes also nanoparticle synthesis[12] and protective closing and packaging. Ionomers are polymers, which consist of a hydropohobic organic backbone and hydrophilic side chains, typically terminated by sulfonate or carboxylate groups. The contrast between the hydropobic skeleton and ionic side chains determines the unique sieving properties of the ionomer membranes. When exposed to water or other hydrophilic solvents, such as low alchohols, ionomer membranes tend to segregate into two subphases. The hydrophilic subphase is formed by water and the ionic side chains which tend to dissociate as water content increases; the hydrophobic subphase is formed by the organic backbone. The best known ionomer is Nafion (DuPont), which is the most promising membrane material for the hydrogen−oxygen fuel cells. The structural formula of Nafion monomer is the following:



$$\begin{array}{l} \ldots-(CF_2-CF_2)_n-CF_2CF_2-\ldots \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad OCF2-CF-OCF2CF2-SO_3^-M^+ \\ \qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad\quad CF_3 \end{array} \quad (1)$$

The side chain is shown in Figure 1.

Significant experimental and theoretical efforts were put into characterization of the microstructure of dry and swollen Nafion membranes (e.g., refs 13−19). Most of the work was done with water as a solvent. However, the incorporation of nonaqueous solvents, such as low alcohols, is known to affect the morphology of swollen membranes. Alchohols soften or even partly solubilize the polymer.[20,21] Rivin et al.[22,23] recently found that the uptake of water−ethanol mixture by Nafion membranes is much higher than the uptake of pure components. The solubility depends strongly on the composition of the solvent mixture and reaches a maximum at, approximately, 1:1 molar ratio. It was assumed that ethanol tends to surround the hydrophobic skeleton, while water interacts more strongly with the ionic side chains and counterions. The elevated uptake of water−methanol mixture by Nafion membranes was observed by Nandan et al.[24] Pilar et al. performed electron spin resonance studies of Nafion microstructure and found that the aggregation of Nafion backbone in alcohol is less pronounced than in water. Pellegrino and Kang[2] found that incorporation of alcohols affects the solubility and diffusivity of methane and carbon dioxide in Nafion membranes and demonstrated its applicability to gas separation. Preferential removal of alcohols from aqueous solutions by Nafion membranes was studied by Pasternak and Dorawala.[1]

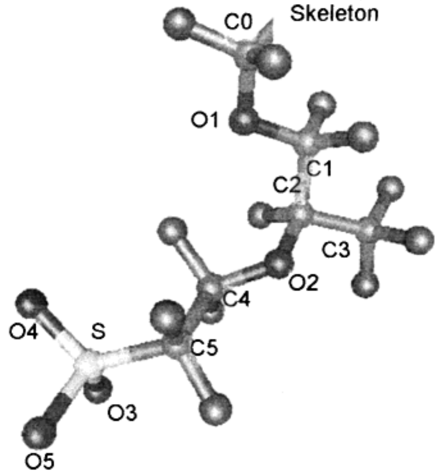


Figure 1. Nafion side chain optimized in a vacuum.[47]

It is worth noting that the water−methanol binary system, similarly to other mixtures of associating liquids, exhibits a prominent nonideal behavior. The mixture properties deviate significantly from those of the pure components. The nonideal behavior of the water−methanol binary system is revealed in many physical properties such as the strongly negative volume and enthalpy of mixing, a substantial depression in the freezing

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TABLE 1: Lennard-Jones Parameters for Nafion[a]

atom	σ, Å	ϵ, kJ/mol	
	Lennard-Jones parameters		
	Nafion		
C	3.473	0.3981	
F	3.093	0.3035	
S	3.550	1.0465	
O2, O4	3.07	0.7117	
O3, O4, O5	3.15	0.8372	
	Covalent Bond, Å		
C−C	1.602	C−S	1.80
C−F	1.370	S−O	1.49
C−O	1.380		
	Covalent Angles, deg		
CCC	109.6	CCS	112.6
CCF	109.7	FCS	110.7
CCO	109.5	CSO	106.75
COC	109.5	OSO	115.0
	Partial Atomic Charges, amu[a]		
S	1.4124	F(C2)	−0.1913
O3,O4,O5	−0.632	C3	0.4947
C5	0.3216	F(C3)	−0.1649
F(C5)	−0.3278	C1	0.3228
C4	0.3218	F(C1)	−0.1637
F(C4)	−0.1662	O1	−0.2742
O2	−0.2604	C0	0.3218
C2	0.401	F(C0)	−0.1641
C(skel)	0.3846	F(skel)	−0.1923

[a] Total charge of the side chain is −1.

temperature, an azeotropic type of the vapor−liquid phase diagram. It is well-known that many substances are dissolved easily in solvent mixtures, while they are hardly soluble in the pure components and vice versa.[25] The methanol−water system forms a complex network of hydrogen bonds. Both components are able to donate hydrogen bonds to SO_3^- groups of Nafion, that is, water and methanol molecules may “compete” as hydrogen bond donors. At the same time, the binary system contains CH_3 groups that are able to interact strongly with the perfluorohydrocarbon skeleton via van der Waals interactions.

The peculiar behavior of Nafion solvated in water-alcohol mixtures can be better understood from a comparison of the skeleton conformation and the structure of solvation shells, which are formed around the skeleton and the side chain, in the pure component solvents and the mixture. Thus, it is of theoretical and practical interest to investigate the specifics of interactions of different fragments of Nafion polymer with water-alcohol binary solvents on a molecular level. The molecular dynamics (MD) simulations of Nafion oligomers in pure water and pure methanol were reported earlier. [26] That study revealed the preferential conformation of the side chain of Nafion oligomers, characterized the flexibility of the perfluorohydrocarbon skeleton and the side chains, and demonstrated the solvation shell of the side chain in pure solvents by means of radial distribution functions and three-dimensional spatial distribution functions. In this paper, we perform MD simulation of the solvation of a relatively short Nafion oligomer in a water−methonol mixture and compare the observed structural properties with those characteristic to the pure component solvents.

2. Simulation Details

We consider the sodium salt of Nafion with 16 CF_2 groups ($n = 7$ in formula 1), resulting in an equivalent molecular weight of 1164 in the acid form. The force field employed was based on the classical DREIDING force field.[27] All covalent bonds were supposed to be rigid. For this simulation, we modified the equilibrium bond distances and angles according to experimental and ab initio data on perfluoroalkanes, perfluoroethers, sulfonic acid, and dimethylsulfoxide.[28−33] The values of equilibrium bond distances and angles are shown in Table 1. The torsional potential of the fluorocarbon backbone was calculated by the density functional theory in ref 32 and applied to the CCCC dihedral angles of the skeleton. The FCCF and FCCC dihedrals were disregarded. To the side chain dihedrals, the DREIDING torsional potential[27] was applied.

The Lennard-Jones (LJ) parameters were taken from successful simulations of smaller compounds, which contain the same groups as Nafion,[30,33,34] in particular, of low perfluoroalkanes and Na_2SO_4 in aqueous solutions. The OPLS parameters were assigned to the ester oxygens.[35] The LJ parameters are given in Table 1. The partial charges were introduced through the Gasteiger procedure[36] and equilibrated to yield the total charge of $-e$ per monomer unit. The partial charges for the skeleton carbons and fluorines determined by this procedure turned out to be close to those used in ref 34, taking in account that the hydrogen atoms of difluoromethane are positively charged. The charges on sulfone oxygens turned out to be substantially lower in absolute value than $-e$, used for SO_4^{2-},[30] yet close to those used by Ennari et al.[37] The charges are given in Table 1. The perfluoroalkane skeleton was terminated by two dummy carbon atoms, which had zero charge and a negligible Lennard-Jones energy constant. For an extensive discussion of the force field, see ref 26.

The molecule of water was presented by the SPC/E potential of Berendsen et al..[38] This three-center model gives good agreement with experimental data on density, potential energy, and molecular mobility in the bulk water at ambient conditions. The molecule of methanol was described by the three-center potential of van Leewen and Smit,[39] which provides the best fit to the experimental vapor−liquid-phase diagram of the pure methanol. Natrium ion was considered as a charged LJ particle.[40]

The model Nafion oligomer was composed of four monomer units. The MD simulations were carried out at $T = 298$ K, both in water and methanol. The LJ and electrostatic potentials were cut off at 14 Å. To account for the long-range electrostatic interactions, the Ewald summation was employed. All covalent bonds were kept rigid using the SHAKE algorithm.[41] The temperature and pressure were maintained by the Nose−Hoover thermostat.[42,43] The equations of motion were solved by the Verlet scheme[44] with the time step of 1 fs. The MD simulations were performed using the MDynaMix software package[45] on a Silicon Graphics Octane 300 workstation. The Gopenmol program[46] was used for visualization of the results.

In the initial configuration of the MD simulation, one four-unit oligomer molecule was placed in a cavity, surrounded by 1024 solvent molecules, which were arranged at the sites of a face-centered cubic lattice at a low density of 0.2 g/cm^3. During the first 10 ps of the simulation trajectory, the cubic simulation box was gradually squeezed to the density of 0.7 g/cm^3. To establish a preliminary equilibrium in the solvent, squeezing was followed by 40 ps NVT simulation with the oligomer molecule kept rigid. After this preliminary equilibration, we performed a 200 ps simulation in NPT ensemble simulation at $P = 1.0$ atm. The density and different contributions to the potential energy of the system were constant after the first 100 ps of the simulation. After the equilibration, statistics were collected over ca. 500 ps.The equilibrium density was 0.946 g/cm^3, which is ca. 10% higher than that of the bulk equimolar mixture of water and methanol mixture. Every 40 fs, the configuration of the whole system was saved to disk for

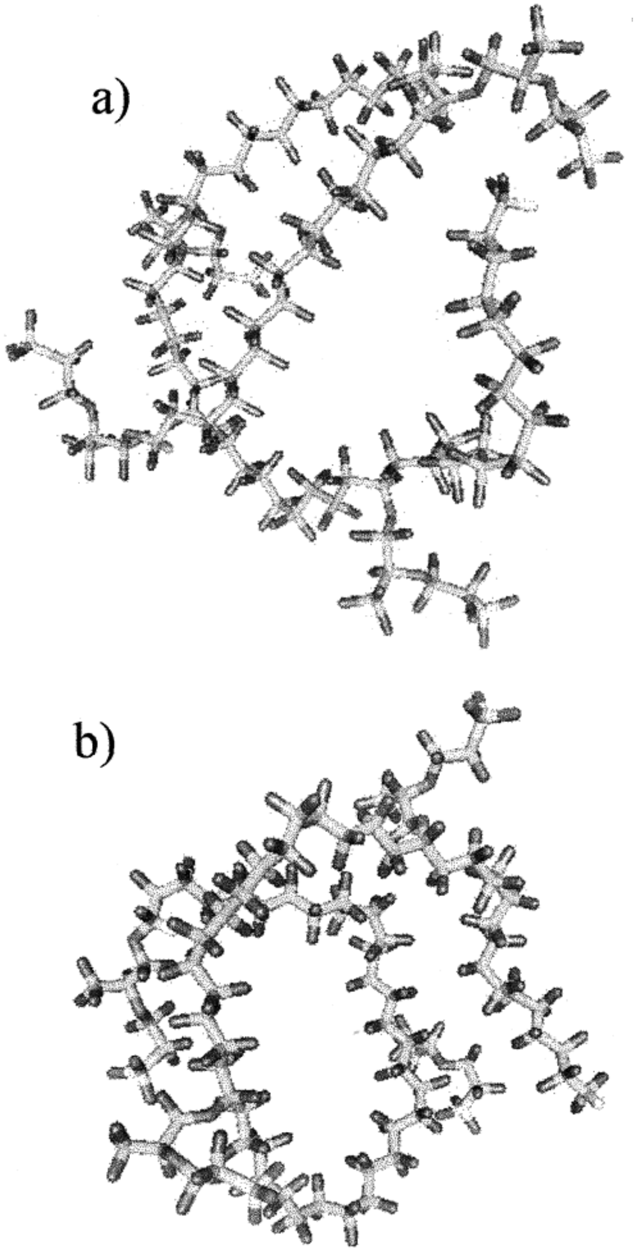

Figure 2. Snapshot of the molecular configuration of the four-unit oligomer in equimolar water−methanol mixture (a) and in pure water (b).[26]

statistical analysis, which was performed with the TRANAL program of the M.DynaMix package.[45]

3. Results and Discussion

Geometry of the Fluorocarbon Skeleton. In the initial configuration, the oligomer had a spiral-like conformation, which is shown in ref 26. The configurations, observed after the 200 ps equilibration period, were substantially different from the initial one. A snapshot of the Nafion oligomer is presented in Figure 2. In general, the geometry of the perfluorohydrocarbon skeleton of the Nafion oligomer in the mixed solvent was similar to that in pure water. The CCCC dihedrals showed preference to *trans* conformations. On average, every fifth CCCC dihedral was found in the *gauche* conformation. The geometry of the skeleton was substantially more folded compared to that in pure methanol (Figure 2), where the ratio of the number of *gauche* and *trans* CCCC torsions was roughly 1 to 6.

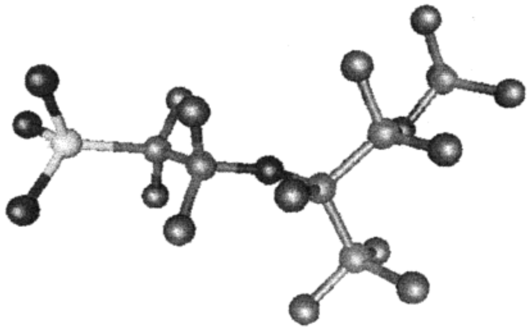

Figure 3. Preferential conformation of the side chain of the four-unit Nafion oligomer in equimolar water−methanol solution.

The skeleton showed a notable mobility; 12 conformational transitions over CCCC dihedral angles were observed between the side chains, against four conformational transitions in pure water and seven in pure methanol. Unfortunately, we were unable to collect reliable statistics on the conformation transitions in the skeleton due to a limited simulation time (ca. 500 ps). Also, the equilibration time in the present study was limited to 200 ps. In the case of insufficient equilibration, intensive exchange between water and methanol molecules in the first solvation shell may lead to an artificially high mobility of the skeleton and side chains. The contribution of the solvent−solute interactions for each component to the potential energy of the system experiences some fluctuations, which are probably associated with the conformation transitions in the oligomer. However, no consistent trend that may have appeared due to a continuous substitution of one component by the other in the first solvation shell was noted. Also, contrary to the skeleton, the side chains showed low mobility, as discussed below.

Geometry of the Side Chain. The side chains of oligomer molecules in the methanol−water solvent appeared to be very stiff. Within the 500 ps averaging period, no conformational transitions were observed in any of four side chains of the oligomer molecule. In general, the conformation of the side chains in the binary solvent agrees well with the results of Hartree−Fock and quantum density functional theory potential energy optimization of the side chain in a vacuum, performed by Paddison and Zawodzinsky.[47] The only significant difference was found for the O2−C4−C5−S angle: we observed *trans* conformation of this dihedral while *gauche* conformation was obtained in ref 47. The preferential conformation of the side chain is presented in Figure 3.

Solvation of the Skeleton. The polymer−solvent correlation functions show that the skeleton is mostly surrounded by methanol. Thus, our results confirm the assumptions made in refs 21−23, 40, and 48 on the basis ofexperimental observations. The preference for methanol is due to the van der Waals interactions between the CH_3 groups of methanol and the skeleton, which are stronger than those between the skeleton and water. The comparison of CF_2−O(CH_3OH) and CF_2−C(CH_3OH) correlation functions shows that methanol molecules are arranged in such a way that their CH_3 groups point toward the skeleton. The preference concentration of methanol is visible only in the first solvation shell.

Solvation of the Side Chain. Similar to the picture observed for the Nafion oligomer in the pure solvents, the SO_3^- group, which terminates the side chain, is strongly hydrophilic and demonstrates substantial hydrogen bonding to the solvent, while the ether-like oxygen atoms of the side chain show a very weak tendency to hydrogen bonding. This is demonstrated by the oxygen−oxygen radial distribution functions (RDF) shown in

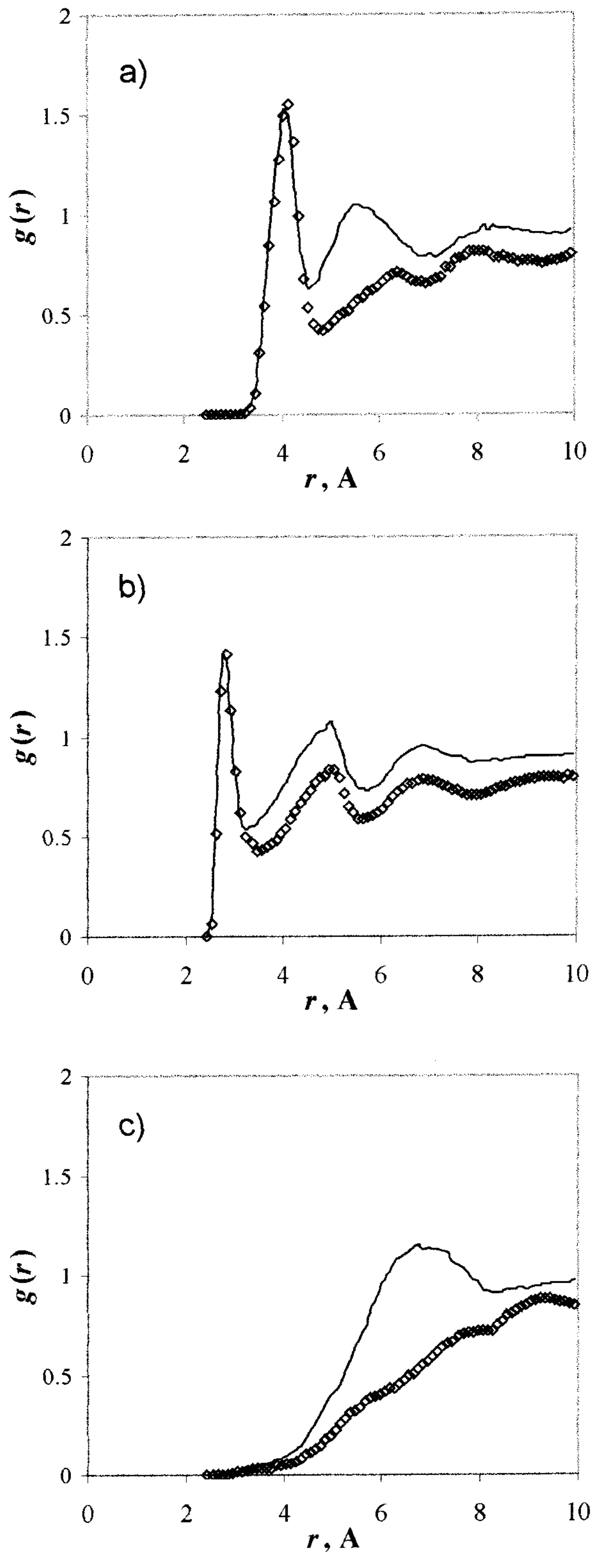

Figure 4. Radial distribution functions for pairs formed by atoms of the side chain and oxygen atoms of water (lines) and methanol (points). (a) S$-$O$_{solvent}$; (b) O$_{SO3}-$O$_{solvent}$; (c) O1$-$O$_{solvent}$.

Figure 4. We found no preference for either of the components in the first solvation shell of the side chain, for the RDFs of the oxygen atoms of the two components practically coincide. The O1$-$O$_{solvent}$ RDFs differ substantially for the two components. The RDF of methanol has a notable peak at ca. 6.5 Å, which is not observed on the RDF of water. This difference reflects a substantial preference for methanol to be located in the close vicinity of the perfluorohydrocarbon skeleton, due to the strong van der Waals interactions between the skeleton and the CH_3 groups of methanol molecules. O1 atom is located in the base of the side chain very close to the skeleton. The solvent access to the side chain is spatially hindered, so that one should not expect visible first peaks corresponding to the solvent molecules, which form the hydrogen bonds to O1. That is why the O1$-$O$_{solvent}$ RDFs reflect a preference for methanol to be located around the base of the side chain in general, rather than the intensity of hydrogen bonding between O1 and the solvent.

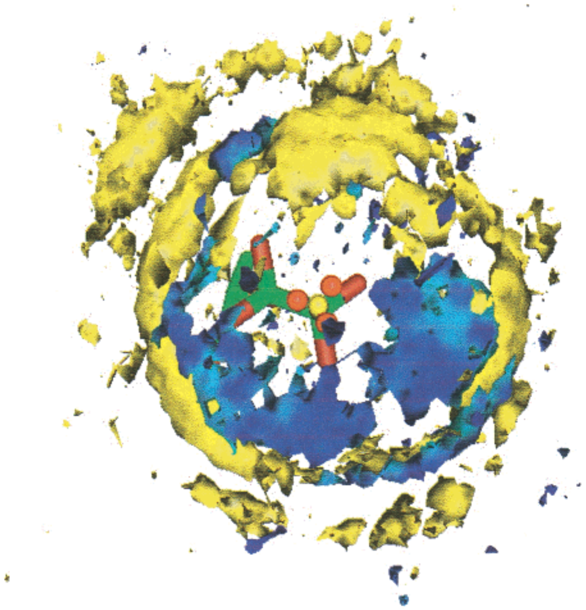

Figure 5. Average coordinates of the atoms of the side chain in a reference coordinate system attached to S$-$O5 and S$-$C5 vectors and spatial distribution functions of the solvent oxygens around the side chain. The average local density of oxygens in gray regions is at least 2.2 times as large as the average number density of the solvent. Water in blue, methanol in yellow.

To characterize quantitatively the number of hydrogen bonds between the solvent and the oligomer side chain, we applied the same geometry criteria that had been used previously.[26] Two oxygen atoms were considered to form a hydrogen bond via a hydrogen atom if the distance between the oxygens did not exceed 3.4 Å, while the OHO angle exceeded 120°. With the criteria employed, each of the oxygens of a SO_3^- group was found to form, on average, 0.45 and 0.41 hydrogen bonds to water and for methanol, correspondingly. The group as a whole forms 1.35 hydrogen bonds to water and 1.2 to methanol. Thus, we did not find a predominance of one of the components in the first solvation shell of the SO_3^- group.

We analyzed the hydrogen-bond lifetime in terms of the residence time of oxygen atoms, using the same algorithm as in the previous work.[26] We assumed a hydrogen bond between a molecule of the solvent and a SO_3^- group of Nafion to be established, when the distance between the oxygen atoms belonging to the solvent molecule and the SO_3^- group remained shorter than 3.4 Å within 2 ps. The hydrogen bond was considered to be broken when this distance exceeded 3.55 Å or when it remained larger than 3.4 Å within 1 ps. The estimation of the residence time was based on the assumption that the probability of a hydrogen bond to be destroyed within time interval t can be presented as $1 - a\exp(-bt)$.

Using these criteria, we obtained the solute$-$solvent hydrogen-bond lifetimes of 9.13 ps for water and 9.17 ps for methanol. Thus, the lifetime of hydrogen bonds between the SO_3^- groups and solvent is equal to several rotational correlation times of water and methanol. The hydrogen-bond lifetimes for the two components are very close to each other and somewhat shorter compared to those for the pure components.

The structure formation caused by the interactions of the side chain with the solvent can be demonstrated with three-dimensional spatial distribution functions (SDF).[49] SDF is a three-dimensional density profile, calculated in a reference coordinate system rigidly attached to the side chain. We built the reference coordinate system on S−O5 and S−C5 vectors. The SFDs obtained for four side chains of the oligomer were averaged out. Figure 5 shows the coordinates of the atoms of the side chain in the reference system averaged over the trajectories and the regions where the average local density of the solvent oxygens is 2.2 times as large as the average number density of the solvent. As in pure methanol and pure water, only the first solvation shell can be clearly identified from the SDFs. The first shell is formed by the molecules of the solvent that form hydrogen bonds to SO_3^- groups. In general, the structure of the solvation shell is similar to those obtained in the pure solvents. Water and methanol tend to occupy the same regions of space in the vicinity of SO_3^- group; practically no difference between the structure of the shells is seen.

4. Conclusions

The MD simulation of the solvation of Nafion oligomers in the water−methanol binary mixture has revealed several specific features of the polymer conformation and the solvent distribution as compared to the solvation in the pure component solvent. Although the CCCC torsion angles of the skeleton showed a preference to *trans* conformation, the overall structure of the skeleton was substantially folded, similar to that observed in pure water and less folded than that observed in pure methanol. However, the skeleton in the binary solvent showed a notable mobility: The number of conformational transitions in the skeleton was three times as large as than in pure water. At the same time, the side chains of the oligomer turned out to be very stiff. Within the 500 ps simulation, no single conformation transitions in the side chains were observed. The difference in flexibility of the skeleton and the side chain in the binary system may be related to the anomalous solubility of the binary system.

The solvation of the skeleton and the side chain was explored by means of the radial distribution functions, spatial distribution functions, and hydrogen-bond lifetimes. We have shown that the solvent forms a pronounced first anisotropic solvation shell around the SO_3^- group of the side chain. No clear second shell was found. The average numbers of water and methanol molecules in the first solvation shell are almost equal, a minor preference for water was found. The lifetimes of the hydrogen bonds between the SO_3^- group and either of the solvent components are about 9 ps, that is, they are much longer than the rotation correlation times in the pure solvent. At the same time, the skeleton and the side chain base are mostly surrounded by methanol due to stronger van der Waals interactions with the CH_3 group of methanol. These observations agree with conclusions made earlier in experimental studies [21−23,40,48] on a preferential solvation of the membrane backbone by methanol. The molecular simulation methods and force fields developed in this work are suitable for studies of solvation and transport in perfluorinated polyelectrolytes.

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