MOLECULAR SIMULATION OF NANOSCALE DISTRIBUTION AND MOBILITY OF WATER AND DIMETHYLMETHYLPHOSPHONATE IN NAFION AND SULFONATED POLYSTYRENE

Aleksey Vishnyakov* and Alexander V. Neimark
Department of Chemical & Biochemical engineering, Rutgers, The State University of NJ
* presenting author; email avishnja@rci.rutgers.edu

ABSTRACT

Polyelectrolyte membranes (PEM) such as Nafion (DuPont TM) and sulfonated polystyrene based block copolymers used as compartment separators in fuel cells and other electrochemical applications, are also of interest as permselective diffusion barriers in protective fabrics. By means of molecular dynamics (MD) simulations, we explore the molecular mechanisms of sorption and mobility of water and nerve agent simulant dimethylmethylphosphonate (DMMP) in Nafion and sulfonated PS. It is shown that the composition of the solvent strongly affects the membrane permeability, which cannot be predicted purely from the data for pure compounds. This effect is related to complex microphase segregation in the membranes swollen in aqueous solutions of polar solvents. The results obtained demonstrate possible mechanisms of the diffusion of alcohols and alkylphosphonates in hydrated ionomer membranes and reveal properties controlling the utilization of PEM for protective fabrics.

INTRODUCTION

Two prospective groups of polyelectrolyte membranes (PEM) for protective application include perfluorinated membranes such as Nafion and triblock copolymers, where central polyolefin hydrophobic block is confined between smaller hydrophilic blocks made of sulfonated polystyrene. Permselective properties of both materials are based on their complex nanostructure: upon hydration, they segregate onto hydrophilic and hydrophobic subphases. Water and air supposedly diffuse through the mobile hydrophilic subphase, while organic agents get trapped in a immobile hydrophobic subphase. Because the hydrophilic sidechains of Nafion polymer are relatively small and attached directly to the hydrophobic backbone, the scale of the segregation is very limited: depending on hydration and equivalent weight, the size of hydrophilic aggregates varies between ca 20 to 60Å [1]. Hydrophobic and hydrophilic domains form bi-continuous irregular network. Triblock copolymers form regular hexagonal and lamella structures with segregation scale determined by block length. Conflicting reports were published on the possible nanoscale inhomogeneity of the hydrophilic subphase itself [2,3]. In this work, we will discuss the connection between its nanostructure and solvent mobility.

SOLVATION AND MOBILITY OF WATER AND DMMP IN NAFION

In Nafion simulations, we modeled a thin film of the polymer formed by six four-unit Nafion fragments in a contact with the mixture of solvents composed of 60 DMMP molecules and 420 water molecules, which roughly corresponds to 1:1 vol solvent composition. K+ was chasen as counterion. The system was equilibrated in NPT ensemble at 303K and 1atm and proceeded for 1ns for mobility evaluation. Molecular models were developed by us previously [4]. During equilibration period, the hydrophilic sidechains protruded into the solvent. The sulfonate groups were mostly surrounded by water, as radial distribution functions clearly showed. Counterions dissociated from the sidechains and were diffusing in water.

The resulting picture effectively represents an interface between the hydrophobic subphase presented by a film of polymer backbone and the hydrophilic subphase presented by solvents, counterions and sidechains (Figure 1). Surprisingly, we did not find any substantial dissolution of DMMP in the polymer phase. Rather, DMMP molecules were located at the interface between the hydrophilic and hydrophobic subphases, despite water and DMMP being well miscible. In order to demonstrate this observation quantitatively, we calculated a number of simultaneous contacts of DMMP molecules with water molecules and the backbone. It was found that only about 1% (average) of DMMP molecules belonged exclusively to the hydrophobic subphase. About 4% of DMMP molecules belonged neither to the hydrophilic nor to the hydrophobic subphase. That is, they were surrounded by other DMMP molecules, or located in the centers of DMMP mini-clusters, that were observed in that system. Finally, 72% of the DMMP molecules belonged to both hydrophilic and hydrophobic subphases (had at least one hydrogen), and 23% were "dissolved" in water, i. e. had a hydrogen bond to a water molecule, but no neighbors among fluorocarbon groups of the backbone. This means that DMMP tended to be located at the interface between water and Nafion

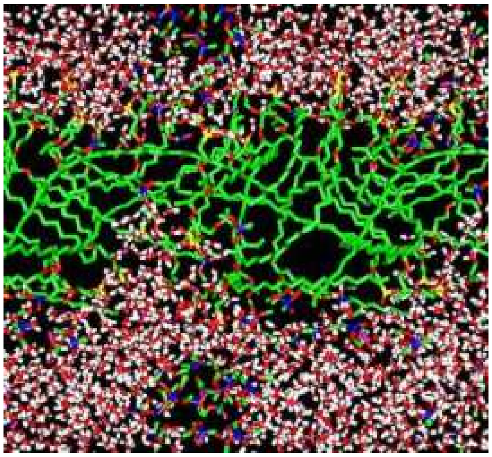

FIGURE 1. Shapshot of Nafion polymer layer solvated in water-DMMP mixture. The presence of Nafion reduces the solubility of DMMP in water. DMMP concentrates on the surface of polymer rather than is dissolved in water. C in green O in red H in white P in blue S in orange K in pink

NANOSTRUCTURE AND SOLVENT DIFFUSION IN SULFONATED POLYSTYRENE

In polystryrene simulations, we considered ca 50 Å fragments of PEM, which were modeled for 4-6 ns after equilibration. We considered 40% and 100% PS sulfonation levels, as well as random 1:1 copolymers of PS and PE at 100% PS sulfonation. The counterion was Ca^{2+} (molecular models are described in ref [5]). The systems are shown in Table 1.

TABLE 1. The list of polymer systems and their properties Solvent content shown in wt % to dry polymer weight. n_{HB} denotes the number of hydrogen bonds per water molecule

Polymer, % sulfonat.	H2O, wt %	DMMP, wt%	ρ, g/cm^3	D_W 10^{-9} m/s^2	D_{DMMP} 10^{-9} m/s^2	n_{HB} ‡ $_{H2O-H2O}$	n_{HB} ‡ W_{-DMMP}	n_{HB} ‡ $_{W--O3S}$	n_{HB} ‡ total
sPS, 40	15		1.180	0.030		0.74		0.91	1.65
sPS, 40	30		1.177	0.21		1.17		0.66	1.83
sPS, 40	54	0	1.165	0.91		1.47		0.49	1.96
sPS, 40	54	10	1.168	0.58	0.035	0.96	0.03	0.50	1.49
sPS, 40	54	50	1.178	0.36	0.041	1.40	0.13	0.45	1.98
sPS, 40	54	100	1.188	0.19	0.052	1.30	0.25	0.45	1.95
sPS, 100	15		1.251	0.012		0.28		1.16	1.44
sPS, 100	50		1.242	0.067		0.86		0.94	1.8
sPS-PE, 100	39		1.208	0.109		0.95		0.56	1.51

In all hydrated sPS samples, we observed prominent nanoscale segregation onto hydrophilic and hydrophobic subphases, somewhat similar to that in hydrated Nafion, but at a smaller scale. Similarly to Nafion, the hydrophilic subphase is discontinuous at small level of hydration and becomes continuous at higher hydrations (>15%wt). The segregation is shown in Fig. 2, which shows the areas occupied by water molecules. The lower the sulfonation level, the stronger the segregation: at 100% sulfonation every hydrophobic benzene ring has a sulfonate group attached to it, which reduces the possible spatial scale of segregation to the polymer chain diameter. Because the small segregation length and large interface are, most counterions are still bound to at least one sulfonate group, even at highest water content. Naturally, water diffusion increases radically with the increase of the water content.

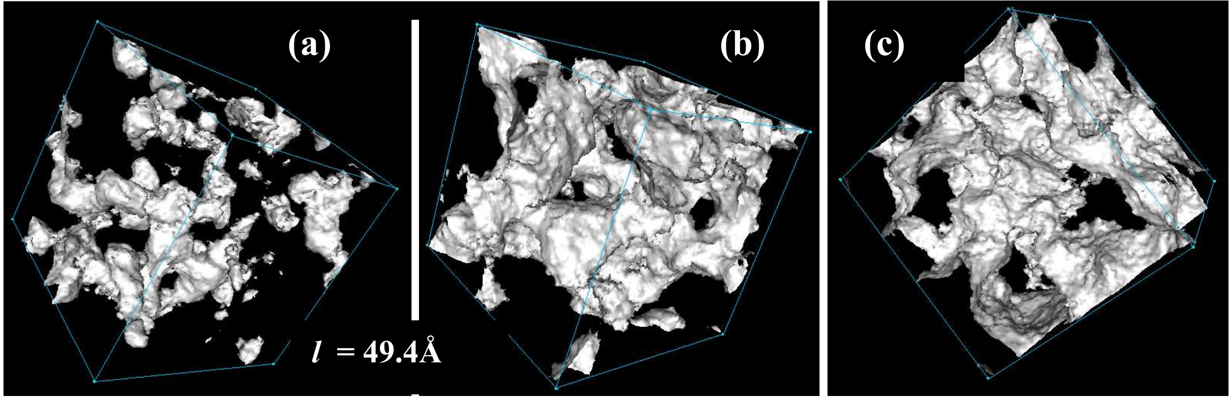

FIGURE 2. Snapshots of the hydrophilic subphase (water and counterions) in hydrated sulfonated polystyrene at 40% sulfonation level. Water content (to dry polymer weight) (a) 15% (b) 30% (c) 54%.

A cluster analysis of the sPS-water-DMMP samples shows that in all systems, the mobile species (water, DMMP, and counterions) form a single continuous subphase. However, at higher DMMP concentrations (50 and 100 wt %), DMMP may be considered as creating a continuous subphase of its own. Therewith, the water diffusion coefficient steadily reduces with the increase of the DMMP content (and, respectively, the increase of the DMMP diffusion coefficient), despite the apparent increase of the cumulative volume occupied by the mobile species, which mix perfectly in the bulk (Table 1). These unforeseen observations indicate that water and DMMP have separate pathways through the system. Within the solvated sPS, DMMP molecules accept only 0.75 hydrogen bonds in average at the DMMP content of 50% and 100% wt compared to 1.3-1.4 bonds accepted by water. This is in contrast to the bulk solution, where DMMP molecules accept 1.5-2 hydrogen bonds from water molecules in average, which is on a par with water molecules

CONCLUSION

The main conclusion of this simulation work is that the nanostructure of PEM in mixture of water and hydrophilic phosphor-organic compounds is very complex and cannot be reasonably predicated from single-component data. Despite DMMP is hydrophilic and water-soluble, its pathways through the membrane are quite different from those of water. Because DMMP does not readily mix with the hydrophobic phase either, the application of PEM for protection will remain problematic as soon as the absorption of DMMP by the polymer remains comparable to the polymer weight [6]. Our current efforts are directed onto the predictions of self organization of triblock copolymers using mesoscale simulation methods

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