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Addition/Correction

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Correction to "Atomistic Simulations of Structure of Solvated Sulfonated Poly(ether ether ketone) Membranes and Their Comparisons to Nafion: I. Nanophase Segregation and Hydrophilic Domains"

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The simulations effected and the results reported had an unfortunate, inadvertent error. Specifically, the Lennard-Jones (LJ) potential size parameter for the F3C forcefield that was used for water and hydronium ions, σ_{F3C}, is equivalent to the Vander Waals's radius of the corresponding species. However, the LAMMPS simulation software used for obtaining our results specifies the size parameter σ_{LAMMPS} as that corresponding to the first location at which the potential becomes identically zero. Explicitly, this results in the relationship $\sigma_{F3C} = 1.112\ \sigma_{LAMMPS}$. Inadvertantly, we missed this conversion for the water and hydronium molecule force fields (we did use the correct parameters for the other molecules). While much of our conclusions reported in the articles remain correct, some aspects of water behavior and system densities at higher water content do change quantitatively. In the following, we summarize the most significant corrections to our results which arise from rectifying the above error.

(i) Figure 1 displays the corrected radial distribution for the oxygen atoms on water molecules in the SPEEK membrane. It is seen that, depending on the water content, the water molecules in SPEEK does retain some or all of the peaks of bulk F3C water. This conclusion contrasts with our earlier report (page 8361 of ref 1) wherein we claimed that peak at 2.8 Å in bulk F3C water moves to 3.4 Å in SPEEK membrane and the peak at 4.4 Å of bulk F3C water disappears. For the new results, the coordination numbers were seen to vary as 0.51, 2.06, and 3.18 for water contents corresponding to 5, 20, and 40 wt %, respectively (earlier-reported values were 0.09 and 0.84 for water wt % of 5 and 40, respectively[1]). However, comparing our new results to the corresponding values for Nafion membranes, does preserve our earlier conclusion (page 8361 of ref 1) that the water molecules in SPEEK are less structured and therefore less polar and less dielectric compared to the situation in Nafion.

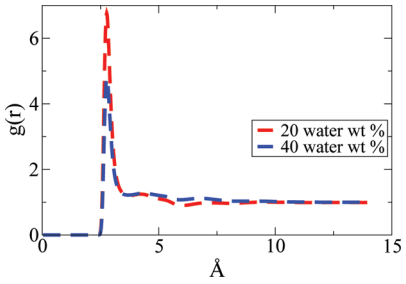

Figure 1. RDFs for O(water)-O(water) at different water wt % 338 K.

(ii) For our corrected interaction potentials, the average distance of the water molecules from the nearest sulfur (which includes both dissociated and undissociated units) atoms 3.6 and 3.54 Å for 20 and 40 water wt %, respectively (earlier-reported values were 5.97 and 7.74 Å for 20 and 40 water wt %). Comparing these new values to the values reported for Nafion,[2] we conclude that water is more tightly bound to sulfonate groups in SPEEK compared to Nafion. This result has been speculated from experiments,[3] but was not observed in our earlier work (page 8364 of ref 1).

Table 1. Density Variations with Change in Water wt %, Methanol wt %, and Temperature[a]

water wt %	density (g/cm^3)	methanol wt %	density (g/cm^3)	temperature (K)	density (g/cm^3)
5	1.14	3.33	1.15	298	1.18
20	1.2	40	1.1	338	1.15
40	1.15				

[a]Water wt % is the wt % of water based on the basis of the weight of all the components of the system (concentration of methanol is kept at 1 M throughout the variations in water wt%). Density in g/cm^3 represents the equilibrated density of the system, whereas methanol wt % denotes the wt% of methanol with respect to total solvent (water +methanol).

(iii) The new system densities are summarized in Table 1. Although at higher water wt % densities are different from old data, most of our conclusions remain intact.

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