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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: II. Structure and Transport Properties of Water, Hydronium Ions, and Methanol"

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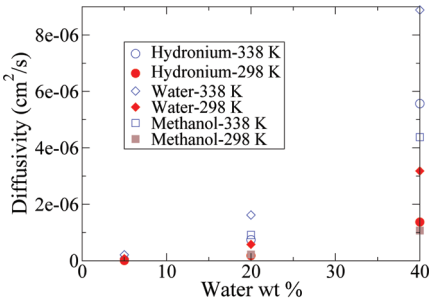
The simulations effected and the results reported had an unfortunate, inadvertent error. Specifically, the Lennard-Jones (LJ) potential size parameter for the F3C forcefield that was used for water and hydronium ions, σ_{F3C}, is equivalent to the Vander Waals's radius of the corresponding species. However, 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 $\sigma_{F3C} = 1.122\sigma_{LAMPPS}$. 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, the diffusivities 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) Diffusivities of different species (section III.C of ref 1): Figure 1 displays corrected values for the diffusivities as a function of water content (replaces the Figures 6 and Figure 7a of ref 1). The diffusivity of hydronium ions are close to our earlier-reported values of 2.33×10^{-8} and 3.03×10^{-6} cm^2/s for 5 and 40 water wt %, respectively; however, the diffusivities for water and methanol are lower by an approximately order of magnitude compared to the resulted reported. Despite the fact that there are no literature reports on the water diffusivity values in Nafion at 40 wt % water content, extrapolation of the values reported for Nafion[2,3,5−9] to 40 wt % water does indicate that the corrected values for the water diffusivities in SPEEK are comparable to those in Nafion (on an order of magnitude basis). The latter is consistent with the conclusions of our original article (page 8371 of ref 1).



(a)

Figure 1. Diffusivities of water, hydronium and methanol in SPEEK with change in water wt % and temperature.

(ii) Hydronium ion distribution around sulfur (section III.A of ref 1): Figure 2 shows the changes in radial distribution functions (RDFs) of S(sulfonic acid)-O-(hydronium) with varying water content. Although there is more pronounced change in the RDFs with varying water content as compared to our earlier work, it is still less pronounced as compared to the case for Nafion.[4] This is consistent with the corresponding result in earlier work (page 8368 of ref 1). This is also reflected in coordination number analysis. Coordination number of O(hydronium) around sulfur from the dissociated sulfonic acid groups are obtained as 0.9 and 0.54 for 20 and 40 water wt %, respectively (old values were 1.19 and 0.87 respectively). By comparing these values to those in Nafion (page 8369 of ref 1), we deduce that hydronium ions are more tightly bound to the sulfur atoms in SPEEK. The preceding conclusion is consistent with the results reported in our earlier paper (page 8369 of ref 1). We also note here that the reference numbers in Figure 2 of section III.C of ref 1 (refs 10 and 12 should read as refs 11 and 13, respectively).

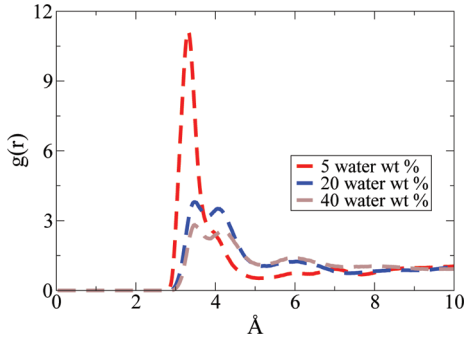


Figure 2. RDFs plotted at different water weight percent for S(sulfonic acid)-O(hydronium ion).

(iii) Methanol distribution around sulfur (section III.B of ref 1): An increase of methanol concentration from 3.33 to

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40 wt % increases the methanol coordination number around sulfur from a value of 0.42 to 5.7 (against 0.38 to 4.5 as noted on page 8369 of ref 1). Concomitantly, the water coordination number around sulfur decreases from 7.93 to 5.3 when the structure is considered to a distance of up to 5.3 Å (corresponding to the first valley in the radial distribution functions of water around sulfur) and changes from 19.21 to 12.83 when the structure is considered up to a distance of 7 Å (corresponding to the first valley in the radial distribution function of methanol around sulfur). The arguments we advanced and the overall conclusion (page 8369 of ref 1) that the methanol molecules are bound to sulfonic group more strongly in SPEEK membranes than Nafion remain equally applicable with our new results.

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