Elucidating the relationship between the states of water and transport properties of ions in swollen polymer networks

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Abstract

The transport of ions through polymer matrix is essential in a wide variety of technologies such as microfluidic, batteries, fuel cells, and desalination/water purification. Conventionally, the transport properties of ions are often correlated with the water content in the swollen polymers. However, water in the polymer exists in three states: non-freezable, intermediate water, and free water. While it is intuitive to expect that water molecules at different states would contribute to the ion sorption and diffusion differently, there lacks systematic studies of the relationship between the state of water and ion transport properties. In this study, we prepare three polymer networks: non-charged cross-linked poly(ethylene oxide) from poly(ethylene glycol) diacrylate (PEGDA) and poly(ethylene glycol) methyl ether acrylate (PEGMEA), zwitterionic polymers from sulfobetaine methacrylate (SBMA) and PEGDA, and polyelectrolytes from 2-acrylamido-2-methyl-1-propanesulfonate sodium (AMPS) or [2-(acryloyloxy)ethyl] trimethyl ammonium chloride (AETMAC) and PEGDA. The effect of polymer composition on the state of water was systematically investigated using the Differential Scanning Calorimetry (DSC). The number of non-freezable water molecules was 1.8 per ethylene oxide unit, 8.1 per SBMA, 15.1 per AMPS, and 8.7 per AETMAC, which is consistent with the simulation results from the literature. Increasing the PEGDA content increases the cross-linking density, which is related to the decrease in the amount of the free water. Interestingly, the cross-linking density has a negligible effect on the amount of non-freezable water in copolymers of AETMAC-co-PEGDA and PEGMEA-co-PEGDA, while decreasing the PEGDA content from 80% to 50% increases the amount of non-freezable water by 26% for AMPS-co-PEGDA and 44% for SBMA-co-PEGDA. Most importantly, we have successfully applied the Gordon-Taylor model to correlate the glass transition temperature of the swollen polymers with the non-freezable water, instead of the total water. For the first time, the diffusivity of sodium chloride in these swollen polymers was satisfactorily described using the free volume model and the free water content, instead of the total water.