

Fall 11-11-2015

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## Recommended Citation

[1] Prickett, R. C., Elliott, J. A. W., McGann, L. E., *Cryobiology* (2010) 60, 30-42. [2] Zielinski, M. W., Elliott, J. A. W., et al., *Cryobiology* (2014) 69, 305-317. [3] Prickett, R. C., Elliott, J. A. W., et al., *The Journal of Physical Chemistry B* (2011) 115, 14531-14543. [4] Elliott, J. A. W., McGann, L. E., et al., *The Journal of Physical Chemistry B* (2007) 111, 1775-1785.

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## ICE FORMATION IN ION CONTAINING HYDROGEL FILMS

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The states of water in polymers, including ice formation, is of increasing interest for a broad range of science and engineering, including the application and the longevity of water-borne polymeric coatings, cryogenic preservation of cells and organs, ice mediated porous structure formation, freeze-drying process in food preservation, low temperature operation of batteries and supercapacitors, and the tailing pond sedimentation in oil sands production. The freezing point of water is heavily influenced by the polymer-water interaction and the concentration of ionic species in the water and in the polymer backbones. Various species of salt ions are abundant in the operating conditions for the polymeric materials, but their effect on the water in polymers has not been studied exhaustively. Polyampholytes, which contains both cationic and anionic groups in their backbones, are an interesting class of material with its hygroscopic nature with intrinsic self-healing ability. By tuning the salt concentration, the water freezing point in the polyampholytes is expected to be widely tunable, rendering the material as a promising lubrication layer at low temperatures. The overall scope of our work is to understand, in depth, (i) the phenomenon of freezing point depression of water in ion containing polyampholyte hydrogels and (ii) the effect of the restricted ice formation on the surface lubrication of the hydrogel coatings. In the current presentation, I will talk about the scope (i).

Here, we hypothesize a simplified model for the water in polyampholyte films to predict the freezing point depression in aqueous solution with multiple solutes that mimics true environmental conditions. Specifically, we aim to predict the freezing point depression of water in polyampholytic hydrogels that contains multiple salt components. First of all, it is important to note that the water molecules can exist in the hydrogel in various forms, ranging from tightly bound molecules adsorbed on polymer network, to weakly bound molecules, to free, bulk-like molecules. The amount of bound water can be determined with the parameters for the synthesis of the polymer network. The fraction of bound and free waters can be quantified by the degree of swelling. Free water can be described as the mixture of water and ions that are not bound to the polymer networks. Its freezing point depression can be precisely predicted with a multisolute osmotic virial equation by Elliott et al [1-4]:

$$\Delta T_m = \frac{RT_m^\circ \pi (M_{water} / \Delta S_{fus,water}^\circ)}{1 + R\pi (M_{water} / \Delta S_{fus,water}^\circ)} \quad (1)$$

where  $R$  is the universal gas constant,  $T$  is the temperature,  $M_{water}$  is the molar mass of water,  $T_m^\circ$  is the absolute freezing point of pure water, and  $\Delta S_{fus,water}^\circ$  is the standard molar entropy change of fusion of water. The osmolality,  $\pi$ , can be deduced from multi-solute osmotic virial equation, which designates fitting parameters for each ionic components in water. The behavior of water is studied with various experimental methods, such as differential scanning calorimetry (DSC) for determining the phase transitions of free and bound water, nuclear magnetic resonance spectroscopy (NMR) for the molecular structure around the water molecules and around the infused ions, and fourier transform infrared spectroscopy (FT-IR) for detecting specific polymer-water interactions, as well as microscopic techniques to directly observe ice formation events. In short, the effect of multicomponent salt on water freezing point depression in polyampholytes can be systematically predicted by (i) decoupling the relative amount of bound and free water as a function of polymer synthesis parameters, (ii) elucidating the nature of bound water and their role in ice formation, and (iii) predicting the freezing point depression of free water component by the multisolute osmotic virial equation.

### REFERENCES:

- [1] Prickett, R. C., Elliott, J. A. W., McGann, L. E., *Cryobiology* (2010) 60, 30-42.
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