



The nature of nonfreezing water in carbohydrate polymers



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ABSTRACT

In an aqueous environment, carbohydrate polymers are surrounded by hydration shells consisting of water molecules that are sometimes called “bound”. When polymer solutions are subjected to low temperatures, a part of water turns into ice, another part remains in the biopolymer phase and is called “nonfreezing water”. Thermodynamic analysis of water freezing shows that the amount of non-freezing water does not reflect the amount of bound water, neither can it be used as a measure of strength of polymer–water interactions. Upon deep cooling, crystallization of water should desiccate polymers more than is observed in experiment. The reason for existence of non-freezing water is an interplay between the crystallization of water and the glass transition in biopolymers that prevents dehydration.

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1. Introduction

Interactions of biomolecules, including carbohydrate polymers, with their hydration shells and with bulk water define their dynamics and therefore strongly affect their functions. When a biopolymer dissolves in water, some water molecules come into direct contact with various molecular groups of the polymer. The properties of such water molecules can change compared to those that are in contact only with other water molecules. These two groups of water molecules are often called “bound” and “free” respectively. There is however, no universally accepted and theoretically justified criterion to distinguish between the two groups of water molecules. In general, two groups of methods are used: dynamic methods that probe relaxation of different populations of water molecules (Modig, Liepinsh, Otting & Halle, 2004; Nandi & Bagchi, 1997) and thermodynamic methods that are based on monitoring the thermodynamics of dehydration of the polymers. According to the latter way of thinking, the part of water that can be withdrawn under standard desiccating conditions is free, the remainder is bound (Robinson, 1931). Perhaps surprisingly, the desiccating force commonly used to distinguish between types of water is not the controlled relative humidity, but the freezing of water. In practice, such experiments are performed using the differential scanning

calorimetry (DSC) at subzero temperatures. In calorimetric experiments, the enthalpy of ice melting is monitored and recalculated to the mass of water that undergoes the melting transition. If this mass is lower than the total mass of water in the system, the difference in the masses constitutes the amount of nonfreezing (or nonfreezable) water.

It is sometimes implied that the freezable and nonfreezable water corresponds to free and bound water respectively. There is however no experimental or theoretical evidence to support the idea that the amount of nonfreezable water is the same as the amount of water in direct contact with polymer molecules. Still, based on the shape of the DSC melting peaks, many authors further divide the freezable water into two contributions: freezable free and freezable bound (Hodge, Edward & Simon, 1996). Indeed, often a DSC trace contains two peaks: one close to 0 °C and another at lower temperature. Assuming that the lower temperature peak corresponds to the transition involving bound water, the total amount of bound water is calculated as the sum of nonfreezable and freezable bound water (Hatakeyama & Hatakeyama, 1998). Alternatively, it was suggested that nonfreezing behavior of water in polymers is due to kinetic factors (Bouwstra, Salomonsdevries & Vanmiltenburg, 1995; Roorda, Bouwstra, Devries & Junginger, 1988). Furthermore, Belton (Belton, 1997) proposed an explanation of the nonfreezing water phenomenon based on the temperature dependence of the vapor pressure of supercooled water.

In this article, based on thermodynamics of water freezing, a relation between the strength of polymer–water interactions and the amount of nonfreezing water is derived. The effect of the

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polymer glass transition on the amount of nonfreezing water is revealed.

2. Methods

Calculations presented in this paper were performed using MATLAB (The Math Works Inc). For calculations of phase diagrams and other plots, arrays of volume fractions were generated, then mass and mole fractions corresponding to these volume fractions were calculated. Then temperatures, activities and heat capacities were calculated. For calculation of heat capacity, numerical differentiation was used.

3. Thermodynamics of water freezing

When the temperature of an aqueous solution is decreased below 0 °C, water may not crystallize due to presence of other substances that lower the freezing/melting temperature of water. This happens due to the fact that the presence of other substances decreases the chemical potential of water in the liquid solution μ_w^{liq} , while the chemical potential of water in ice $\mu_w^{0,ice}$ is not affected. From equality of chemical potential of water in the two phases it follows:

$$\mu_w^{0,ice}(T) = \mu_w^{0,liq}(T) + RT \ln a_w \quad (1)$$

where a_w is the activity of water in the liquid phase, T is the temperature. Considering the change of chemical potential of pure water during the crystallization or melting, one can see that

$$\Delta\mu_w^{0,cr}(T) = -\Delta\mu_w^{0,melt}(T) = RT \ln a_w \quad (2)$$

where $\Delta\mu_w^{0,cr}(T)$ and $\Delta\mu_w^{0,melt}(T)$ are the changes of chemical potential of pure water during water crystallization and ice melting respectively at temperature T . The change observed at crystallization $\Delta\mu_w^{0,cr}(T)$ is equal to zero at T^0 – the pure water melting temperature and it is negative below this temperature. Assuming constant enthalpy ΔH and entropy ΔS of melting of ice and the fact that $\Delta H = T^0 \Delta S$ at T^0 , one arrives at the following equation:

$$\Delta\mu_w^{0,cr}(T) = \Delta H \left(\frac{T}{T^0} - 1 \right) \quad (3)$$

Here the chemical potential change represents the driving force of the crystallization phase transition (Kocherbitov, 2013) and can be considered as the desiccating force mentioned above. The value of the driving force calculated from Eq. (3) is valid only for the case of pure water. In case of polymer solution in equilibrium with ice, the force is balanced by the water activity term (Eq. (2)). One can say that the desiccating force defined by Eq. (3) is able to remove from the solution water molecules with activities higher than those defined by Eq. (2). Combining these equations one arrives at:

$$\left(\frac{1}{T^0} - \frac{1}{T} \right) \Delta H = R \ln a_w \quad (4)$$

Eq. (4) is an extension of the Schröder equation (Schröder, 1893) for non-ideal systems and applicable to all systems interacting with water, including biopolymers. This equation shows how temperature can be used to control water activity in the system. For example, at temperature of –20 °C (in equilibrium with ice) the water activity is lowered to about 0.81.

The practical use of this equation is limited by the need to relate the water activity to water content. The relation between these two parameters is often called the sorption isotherm and it has different forms depending on the nature of the substance. Typically, hydrophilic polymers and oligomers show negative deviations from the ideal behavior i.e. the water activity coefficients $\gamma_w = a_w/x_w$ are lower than one. This might be interpreted as an evidence of stronger interactions between the polymers and water

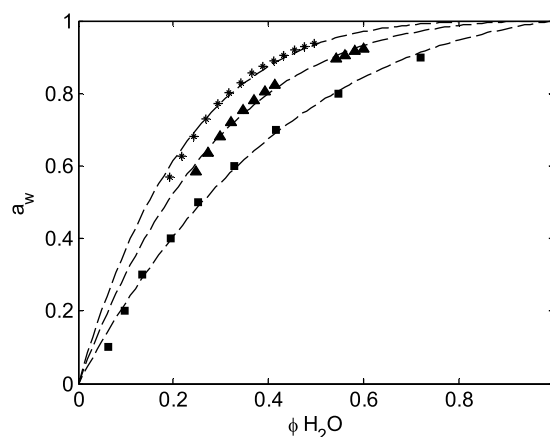


Fig. 1. Activity of water in mixtures with glycerol (squares), hyaluronic acid (triangles) and xanthan gum (stars) as function of volume fraction of water. The dashed lines show fitting using Flory-Huggins equation.

compared to water-water interactions. This is however not necessarily true. The main interaction that defines the water activity in aqueous systems is formation of hydrogen bonds, which lowers the water vapor pressure and is the main reason why such a low molecular weight substance as water has a relatively high boiling point. A hydrophilic polymer is able to form more hydrogen bonds than a single water molecule and by that lower the vapor pressure of water p_w and as a consequence, the water activity:

$$a_w = \frac{p_w}{p_w^0} \quad (5)$$

where p_w^0 is the vapor pressure of pure water. Thus, negative deviations from the ideal behavior of hydrophilic polymers can be simply a size effect.

The dependence of water activity on water content (or vice versa) can be approximated by several different models, for example BET (Brunauer, Emmet & Teller, 1938) or GAB (de Boer, 1968) models. The drawback of the two models is in the assumption of adsorption at the solid-air interface, which is not the case for interactions of water with biopolymers in the bulk (Kocherbitov & Arnebrant, 2010). Another model that can be used to describe dependence of water activity on composition of the biopolymer-water mixture is the Flory-Huggins model:

$$\ln a_w = \ln(1 - \phi_p) + \phi_p - \frac{\phi_p}{N} + \chi \phi_p^2 \quad (6)$$

$$\chi = \frac{w}{RT} \quad (7)$$

where ϕ_p is the volume fraction of polymer and w is the regular solution interaction parameter. When the polymer chains are long ($N \gg 1$), the third term in the right hand side of the Eq. (6) can be neglected. By using the volume fraction instead of the mole fraction (and taking into account the polymerization degree N), the Flory-Huggins model eliminates the effect of size and shows deviations from the ideal behavior on the level of intermolecular interactions. Hence, despite the use of only one parameter χ (in some cases the degree of polymerization N can also be used as fitting parameter), the Flory-Huggins model describes water activity in hydrophilic polymers or oligomers rather well. It is however not able to describe the glassy part of water sorption isotherms of polymers (this is probably the reason why it is not routinely used to fit water sorption isotherms of biopolymers).

Fig. 1 demonstrates application of the Flory-Huggins equation for description of experimental data on water activity in glycerol, hyaluronic acid and xanthan gum. The fitting parameters are presented in Table 1. In all cases χ has positive values, indicat-

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