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Phase transitions in frozen water containing sugars and other solutes

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Most materials, including dissolved sugars in water, do not crystallise during freezing at their eutectic temperature, Te. Therefore, freeze-concentration of solutes increases with decreasing temperature, and at temperatures below the Te the viscosity of the unfrozen solute phase increases, as, in addition to the lowering temperature, water is removed from the supersaturated solution as ice. At low temperatures the high viscosity delays ice formation and the unfrozen phase may solidify into a glassy state before all water is removed from the solution as ice. Ice formation ceases due to glass formation and, therefore, frozen materials at low temperatures often contain maximally freeze-concentrated, amorphous solutes. Differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and dielectric analysis (DEA) have been used to show that maximally freeze-concentrated sugar solutions, when properly frozen, show during heating a glass transition, Tg′, which is followed by ice melting endotherm with onset at Tm′. Low molecular weight sugars have low Tg′ and Tm′ slightly above Tg′ (Table 1). High molecular weight materials, such as carbohydrate polymers, have Tg′ and Tm′ at about the same temperature close to the melting point of pure water. Most maximally freeze-concentrated carbohydrate matrices contain about 80% w/w solids and 20% w/w unfrozen water and have Tg′ well above the Tg of pure water of 135°C.

State diagrams are used to characterize the physical state of amorphous, biological materials as a function of temperature and water content. State diagrams can be based on experimental measurements of the Tg, solubility, and equilibrium melting temperature at various water contents. At freezing temperatures, ice formation occurs according to the equilibrium melting temperature curve until the freezing temperature is sufficiently low to allow maximum ice formation. Time-dependent ice formation is often observed in DSC scans of rapidly cooled solutions. Heating scans of rapidly cooled sugar solutions exhibit a glass transition at a relatively low temperature and a devitrification exotherm at a higher temperature which is followed by the ice melting endotherm.

Table 1. Glass transition temperatures of maximally freeze-concentrated sugars.

Material	Tg′(°C)	Tm′(°C)
Fructose	57	46
Glucose	57	46
Lactose	41	30
Maltose	42	32
Sucrose	46	34
Trehalose	40	30
Xylose	65	53

In practical applications the solids composition may be modified according to available processing and storage conditions to improve material stability and the state diagrams are used to derive proper freezing, frozen storage and freeze-drying conditions for various materials.

Roos, Y.H. (1993) Melting and glass transitions of low molecular weight carbohydrates. Carbohydr. Res. 238: 39–48.

Roos, Y.H. (1995) Phase Transitions in Foods, Academic Press, San Diego, CA.