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AN OVERVIEW OF INTERFACIAL TENSION AS A COMPONENT OF FREEZE STRESS IN WINTER CEREAL PLANTS

C.R. OLIEN

USDA, Agricultural Research Service, Department of Crop and Soil Sciences, Michigan State University, East Lansing, MI 48824-1325 (U.S.A.)

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ABSTRACT

Consideration of what might happen at liquid interfaces between ice and hydrophilic plant substances has led to the definition of an adhesive constraint. Equilibration of freezing by a shift in the intensity of melting would result from a shift in activation energy with a corresponding change in latent heat. Measured calorimetrically, the latent heat of freezing water associated with cellulose at − 10 ° C was found to equal the heat of hydration, and these were calculated to be less than the latent heat of freezing of free water. This decrease in latent heat is an energy of adhesion; full development requires absence of solutes. Adhesive interactions predominate as freezing begins in hardy winter cereal plants, and these help to control the initial growth of ice. As the temperature decreases and freezing progresses, hydrolysis of fructan provides periplasmic sugar, which changes freeze stress from adhesive to osmotic.

Winter cereal plants frequently die when the temperature of the frozen crown has been in the range − 10 ° C to − 15 ° C [1]. Kinetic effects of ice initiation or crystal growth, when severe enough to injure, occur at temperatures above − 10 ° C. Injury from freeze dehydration requires temperatures lower than − 15 ° C. Analysis of plant response to temperature versus vapor pressure as independent stress components has indicated that death results from some other effect of ice formation in critical tissues in the − 10 ° C to − 15 ° C temperature range [2]. Consideration of what might be happening at hydrophilic interfaces of freezing plants below − 10 ° C has led to the definition of a plastic adhesive component of interfacial energy [3]. An adhesive constraint that causes fluid dynamics to be plastic vectorizes distortions caused by crystal growth and cell contraction into a disruptive force [4]. A derivation based on imaginary resonance between exchangeable kinetic energy and potential energy, which includes kinetic energy distributed among nontranslational degrees of freedom, has allowed the partitioning of chemical potential into transition components for which alternative means of equilibration can be considered [5].

Development of this concept began with a review of the literature that led to liquid water structure being considered as a continuous system with short-range predictable order having an average coherence of about 60 molecules (several molecular diameters) [6,7], with ice I being the only polymorph that occurs in plants under normal conditions [8,9]. Although other substances, such as certain bacteria, can act as ice nucleators to initiate freezing in supercooled water, only the ice interface is an effective catalyst near the freezing point [10]. The ice interface is very dynamic, with an estimated half-life of 10^{-5} s [9]. Considering the potential energy of a water molecule in liquid to be greater than that of a water molecule in ice, because of bonding attraction and restricted freedom at a lattice site, only hot ice molecules at the interface melt. These acquire potential energy in exchange for kinetic energy and become cold liquid molecules. Conversely, liquid molecules are accelerated and restricted as they approach an available site in the lattice. Only cold liquid molecules arrive at a site with energy less than that needed to escape, and these become hot ice molecules [11].

The Maxwell–Boltzmann distribution of exchangeable kinetic energy has been used to quantify this imaginary resonance [3]. Integration of the moment involved in freezing of liquid when balanced with that of melting of ice and separated by the latent heat permitted definition of the activation energies of freezing and melting. For pure water at 0 °C the activation energies of freezing and melting were estimated to be 375 and 1815 cal mol^{-1}, respectively, with the partial free energies being 50 cal mol^{-1}. The latent heat (1440 cal mol^{-1}) was considered to be the potential energy difference between ice and liquid that equates the total energy of a water molecule in ice at the activation energy of melting with that of a liquid molecule at the activation energy of freezing [3,5]. Therefore, the displacement of total energy of a molecule from the phase equilibrium value equals the displacement of its exchangeable kinetic energy from the activation energy for transition.

When the system is supercooled, free energy of freezing predominates and can result in disruptive work. Gross effects, such as breakage of cell walls in vascular tissues of frozen plants, are readily apparent. More subtle effects can cause crystal growth through membranes and death of protoplasts [1].

Colligative equilibration of freeze energy involves a decrease of water density in the ice interface as a solution concentrates. This requires the presence of small solutes in the liquid which concentrate to the freezing point. The solution forms liquid channels between ice crystals and between other structural substances [4].

Equilibration of freezing by a shift in the intensity of transitional energies with no change in density requires a shift in activation energy which causes a corresponding change in latent heat. Measured calorimetrically, the latent heat of freezing water associated with cellulose at − 10 °C has been found to equal the heat of hydration, and these have been estimated to be approximately 200 cal mol^{-1} less than the latent heat of freezing water from solution [5]. This is close to the estimated difference between nonequilibrium and equilibrium freezing when equilibrium is maintained by decreasing potential energy with decreasing interfacial liquid.

Freezing supercooled water: $\Delta H \simeq T_0 \Delta S$, $\Delta S = 5.2$ cal mol^{-1}
Equilibrium freezing: $\Delta H = \Delta(TS)$, $S_{\text{liq}} = 16.7$ cal mol^{-1}
$\Delta^2 H \simeq S \Delta T = 167$ cal mol^{-1}

This decrease in latent heat is a new latent heat required for transition of water from the interface to a free liquid state, and is an adhesive component of interfacial energy which results in plastic fluid dynamics. Above − 10 °C, adhesion serves a useful purpose in winter cereal plants by controlling early stages of ice crystal growth. Certain arabinoxylan mucilages competitively interact with ice for interfacial liquid and thereby inhibit the growth of ice crystals [11]. The dynamic nature of the ice–liquid interface makes other forms of inhibition difficult [12]. If a substance directly blocked sites of ice crystal growth, but not sites of melting, the temperature would be expected to decrease as the ice melted in an adiabatic system, with the ice melting completely at the normal freezing point in an isothermal system. If a substance totally blocked sites of crystal growth and of melting by direct bonding to ice, the crystal would be expected to be stable to superheating as well as supercooling.

Full development of adhesion through interfacial liquid requires absence of solutes so that freezing equilibrates competitively with hydration. Plants normally contain little periplasmic and intercellular solute. As the temperature decreases after freezing of free water, the energy of adhesion becomes several times greater than the energy of osmotic dehydration.

One mechanism by which cereal plants are protected from injury below −10 °C is through changes in intercellular solutes [13]. Intercellular solute concentration has been evaluated by a perfusion technique. Because the intercellular liquid of cereal plants normally contains little solute, especially substances that could provide nutrients for microorganisms, freezing in crown tissues of winter cereals initially tends toward adhesive interaction. The temperature of plant crowns while freezing in soil is in progress stabilizes in the mild subfreezing range until the free soil moisture has frozen. During this period, called 'freeze incubation', solutes were found to accumulate in the intercellular liquid. Analysis of intercellular liquid showed that most of the additional solute after freeze incubation was fructose and sucrose. Total carbohydrate analysis revealed that these sugars came from the breakdown of fructan [14].

Fructans are the principal storage polysaccharides of winter cereals. They are distributed throughout the vegetative plant and accumulate when photosynthesis exceeds utilization. Their content is especially high during fall and winter. About 30% of the dry weight of winter cereals grown and hardened in a controlled environment for freeze tests is fructan. Fructan of winter cereals is reported to be of the levan type, which consists of a fructofuranose chain linked by 2–6 β bonds and terminating with a glucose. The fructan of 'Rosen' rye consists of 11 fructose plus one glucose.

The periplasmic sugar from fructan breakdown increases the amount of interfacial liquid between hydrophilic polymers as well as between ice and a polymer, increases the latent heat of fusion, changes the stress from adhesive to osmotic, and lowers the freeze injury temperature. We have found that differences in fructan breakdown induced by manipulating the freeze incubation period, and differences between rye and barley cultivars both correlate with kill temperature in freeze tests. Current research involves thermal monitoring of physical and metabolic effects that occur during mild freeze incubation of hardened winter cereal plants.

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