



Thermal properties of frozen water in the native and amorphous starches with various hydration degrees



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ARTICLE INFO

Article history:

Received 23 December 2014
Received in revised form 5 May 2015
Accepted 14 May 2015
Available online 23 June 2015

Keywords:

Starches
Water clusters
Size effect
DSC

ABSTRACT

The melting process of frozen water (FW) in various starches (rice, wheat, potato) that have crystal lattices of A- and B-type has been studied by means of differential scanning calorimetry (DSC). The dependences of the melting temperature (T_m) and heat (Q_m) of FW on the size of the water clusters forming in starches with various humidity (the so-called size effect) and on conformational changes of starch molecules upon the destruction of native starch crystals (starch amorphization) have been considered. It has been found that in the native starches with low humidity (<35%) the T_m of FW lies below 0 °C and decreases with the decrease of their humidity. The sizes of the water clusters formed under these conditions have been estimated. In contrast, such a size effect in amorphous starches has not been observed and possible reasons for its masking have been discussed. Still, all the values of T_m for FW obtained in the amorphous starches are also negative thereby indicating the dispersed state of water in these systems. Conversely, the size effect for Q_m of FW in starches with low humidity, very pronounced in the amorphous state and barely visible in the native one, has been found. It has been established that the starch amorphization leads to a redistribution of the relative amounts of FW and unfrozen water (UFW) resulting in the decrease of Q_m for FW in both A- and B- starch types. Finally, it has been concluded that in all the investigated starches there exist water clusters with T_m and Q_m lower than that of bulk water.

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1. Introduction

During the last decades research on starch structure has made substantial progress. Nonetheless the knowledge concerning the details of the architecture of polymer chains in granules still remains rather limited. Even more limited is the reliable information concerning the particular placement of water molecules within the complicated hierarchical structure of starch granules. Investigations of a hydration shell in starches are based on the same principle as in the other biopolymers. Water, being strongly bounded to the polymer, demonstrates unique properties which are different from that of bulk water, in all biopolymer systems. The particular organization of water nearby a biomolecule surface has been investigated for a long time using various techniques (Deodhar & Luner, 1980; Eliasson & Gudmundsson, 1996; Mrevlishvili, 1984; Roos, 1995; Slade & Levine, 1991). Still, from time to time new effects are observed (Chai & Pollack, 2010; Chai, Yoo, & Pollack, 2009) and this problem regains attention (Lobyshev & Solovey, 2011).

From the standpoint of calorimetry, investigations of the phase transition in water that freezes at cooling below 0 °C (frozen water, FW) are of non-vanishing interest. The unfrozen water (UFW) that is most strongly bounded to a biopolymer is an intrinsic part of its native structure and thus does not melt. Note that the water–biopolymer interaction energy is generally assumed to be larger than the water–water one. The UFW reveals itself in calorimetric experiments exclusively in the dependence of heat capacity of the biopolymer–water system on the hydration degree. The classification of water as being either frozen (free) or unfrozen (bound) in a biopolymer–water system seems to be a bit oversimplified (Franks, 1986). Nevertheless it is widely used up to now (Park, Venditti, Jameel, & Pawlak, 2006; Suzuki & Kitamura, 2008; Tananuwong & Reid, 2004a, 2004b; Tran, Thitipraphunkul, Piyachomkwan, & Siroth, 2008). It is worth mentioning that the quantitative separation between these water states depends on the experimental technique used as well as on the time-scale of the experiment and on the model of the biopolymer structure employed.

The complicated hierarchical supermolecular structure of starch leads to a strongly heterogenic distribution of water in native granules (Blenow, 2004; Donald, 2004; Eliasson & Gudmundsson, 1996; Preiss, 2004). Several different types of water can be specified

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with respect to the localization within the granule. Mainly they are the hydration water incorporated into the crystalline starch structure, the amount of which in crystals of A- and B-types differs by 5–6 times (French, 1984; Hizukuri, 1996), and the water in the amorphous phase of the native starch. It is worth mentioning that the amorphous phase constitutes about 70% of the total granule mass (Eliasson & Gudmundsson, 1996). Besides, one can distinguish “micro-capillar” water (Gabuda & Rzhavin, 1978) that resides in the so-called granule growth-rings of different density. The content of such water is apparently different in amorphous growth-rings and in the ones containing nano-crystalline structures. In general, different distribution of water molecules within the granule and, hence, different strength of their interaction with the polymer chains of a starch leads to distinct thermal properties of various water types from each other as well as from that of bulk (pure) water.

Numerous calorimetric studies, including ours, of the water state in various biopolymers with small water content have shown that the melting temperature (T_m) of FW differs from that of bulk water and depends on the water concentration in the system studied. This effect has been observed in humid proteins (Tseretely & Smirnova, 1992) and DNA (Mrevlishvili, 1984) as well as in concentrated solutions of carbohydrates of both natural and artificial origin (Slade & Levine, 1991) and starches (Belopolskaya, Tsereteli, Grunina, Smirnova, & Rodriguez, 2010; Belopolskaya, Tsereteli, Grunina, & Smirnova, 2011; Grunina, Tsereteli, Belopolskaya, Smirnova, & Rodriguez Castillo, 2013). The natural assumption arose that the observed effect is caused by the change of the size of small particles, usually referred to as clusters, that are formed in the water surrounding of a biopolymer with low humidity (the so-called size effect). The influence of the surface energy on the energy balance of small particles has been actively discussed during the last decades, see, e.g. (Berry & Smirnov, 2009; Bershtein & Egorov, 1994; Godovsky, 1976; Hill, 2001; Makarov, 2010; Park et al., 2006; Wunderlich, 1980; Yuryev, Wasserman, Andreev, & Tostoguzov, 2002). The dependence of thermodynamic properties of clusters on sizes have been considered both in three dimensions (Berry & Smirnov, 2009; Hill, 2001; Makarov, 2010; Park et al., 2006) and in one dimension. Interestingly, the latter case has been applied to lamellar crystals of synthetic polymers (Bershtein & Egorov, 1994; Godovsky, 1976; Wunderlich, 1980) and lamellas of starch crystallites (Yuryev et al., 2002).

It is worth mentioning that the dependences of T_m of FW on the biopolymer hydration degree obtained in different studies have similar character. At least, the minimum T_m is observed at the minimum content of FW in all the studies (Mrevlishvili, 1984; Park et al., 2006; Slade & Levine, 1991; Suzuki & Kitamura, 2008; Tananuwong & Reid, 2004a, 2004b; Tran et al., 2008). However, in the case when the amounts of UFW and FW are comparable, the absolute values of T_m for FW reported in the vast majority of studies exceed, sometimes substantially, the well-known value for the bulk water (Nakamura, Minagawa, Hatakeyama, & Hatakeyama, 2004; Park et al., 2006; Suzuki & Kitamura, 2008; Tananuwong & Reid, 2004a, 2004b; Tran et al., 2008). This issue will be particularly addressed here.

The picture concerning the dependence of the melting heat, Q_m , of FW on the biopolymer hydration degree is not so unambiguous. Here, we focus on the data for starches only. Naturally, the Q_m of FW in the starch–water system with an excess of water is almost equal to that of pure water. When the hydration degree of a starch decreases, so does the melting heat of water. This is also natural, since the quantity of FW decreases with respect to the total sample mass. Our first results on thermal properties of FW in the starches of A- and B-types in dependence on humidity were analogous (Belopolskaya et al., 2010, 2011; Grunina et al., 2013). Simultaneously, it has been shown that the thermal destruction of

starch crystals leads to a decrease of the obtained Q_m of FW, with the total amount of water in the sample being fixed (Belopolskaya et al., 2010, 2011; Grunina et al., 2013).

The differences in the existing experimental results arise substantially, if one normalizes the values of the Q_m for FW on its mass, i.e. if the values of Q_m are compared for the water clusters themselves. Then from some works it follows that Q_m of water clusters in starches is smaller than that of bulk water (Tananuwong & Reid, 2004a, 2004b), whereas the opposite relation results from the other works (Suzuki & Kitamura, 2008; Tran et al., 2008). In other words, whether the melting heat of water clusters changes with starch hydration degree at all, and if it does then what is the dependence, remains not fully clarified.

Thus, the main goal of this work is to elucidate the size effect for T_m and Q_m of water clusters that are formed in the starches with various hydration degrees by means of DSC. Another, equally important goal is to clarify the changes of T_m and Q_m of FW due to conformational changes of starch molecules upon the thermal destruction of starch native crystals. Further, particular attention is devoted to the influence of A- and B-type crystalline lattices of the starches studied on thermal properties of FW. Last but not least, the method that allows one to determine genuine melting temperatures from the experimental data obtained in the regime of continuous scanning in the DSC is developed.

2. Methods and materials

Investigations of thermal properties of water in starch–water systems were performed with the Differential Scanning Microcalorimeter (Setaram DSC-111, France) with sensitivity of $3 \times 10^{-6} \text{ J s}^{-1}$. The temperature was controlled with a precision not less than $\pm 0.2^\circ\text{C}$ over the whole measured interval -60 to 120°C . This precision was evaluated by the comparison of the onset temperatures for melting of the calibration substances, obtained by the DSC-111 for different masses and heating rates, with their known reference data (Bershtein & Egorov, 1994). Here, high purity indium, $T_m = 156.4^\circ\text{C}$, and distilled water, $T_m = 0^\circ\text{C}$ (273.2 K) (Rabinovich & Havin, 1978), were chosen as the reference substances. For the studies of the thermal properties of water in starches with various hydration degrees the peak temperatures of its melting curves, T_{max} , were employed. However, it is firmly established that the T_{max} of an observable DSC curve is the higher the larger is the mass of a sample, the melting heat of the transition, Q_m , and the heating rate, V_{heat} . Moreover, the shape of the melting curve depends on the thermal conductivity of the used DSC and the calorimetric vial. In order to eliminate these “defects” the special correction procedure was proposed, see Section 3.1 for details. The accuracy of the peak temperatures was determined, taking the sample mass dependence into account, to be not lower than $\pm 0.5^\circ\text{C}$.

The power calibration was performed with respect to the known values of the melting enthalpies for the same reference substances. The corresponding values coincided within 1% with the sensitivity curve of the DSC-111, measured with the help of the standard Joule-effect device. The melting heats of the FW in starches were determined with the uncertainty of about 5% for the heating rate $V_{\text{heat}} = 5^\circ\text{C min}^{-1}$. Various regimes of heat treatment including different heating rates (1 ; 5°C min^{-1}) and annealing of samples at different temperatures during various time intervals were used depending on the particular task.

In this work, the wheat starch (“Fluka”) was studied in addition to the starches of potato (“Aldrich”) and rice (“Sigma”), for which the investigations of their thermal properties had been started by us earlier (Belopolskaya et al., 2010, 2011; Grunina et al., 2013). Granules of the wheat starch contain mainly crystallites of A-type (Cornell, 2004). Nano-crystallites of A-type (rice and wheat) and B-type (potato) have various amount of crystallite water

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