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CHANGES IN ENTHALPY AND HEAT CAPACITY ASSOCIATED WITH THE GELATINIZATION OF POTATO STARCH, AS EVALUATED FROM ISOTHERMAL CALORIMETRY

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ABSTRACT

Enthalpy changes during the interaction between potato-starch granules and water at various temperatures ranging from 25 to 77° were studied by isothermal calorimetry. From the temperature variation of the observed enthalpy changes, the enthalpy levels of ungelatinized and gelatinized starches in water were evaluated, and the heat of gelatinization was found to be $\Delta h_{\text{cal}} = 17.6 \pm 1.7$ J.g^{-1} at 61°, in good agreement with the value found by differential scanning calorimetry. The heat-capacity change associated with gelatinization was $\Delta c_p = -0.06 \pm 0.13$ J.K^{-1}.g^{-1}.

INTRODUCTION

When dry starch is immersed in water or equilibrated with water vapor at room temperature, heat is evolved by the formation of hydrogen bonds between the two components. The process is accompanied by swelling of granules due to water molecules penetrating the accessible portion and coating the surface of the micellar network.

At more elevated temperatures, a disruption of the hydrogen bonds constituting the micellar network in the granules occurs and promotes further hydration on new sites which arise from deformation of the micelles. In this case, the process is macroscopically irreversible and is characterized by heat absorption. The starch granule is gelatinized, and thus the process is technically termed "gelatinization".

Although the macroscopic changes of the granules involved in the two cases just mentioned differ from each other depending on the temperature, they are attributed to a cooperative combination of the two essential processes, hydration and disruption of micellar structure.

One of the potential tools for studying this process is differential scanning

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calorimetry (DSC), in which the endothermic-heat effect during the gelatinization is measured quantitatively. In fact, various authors have reported DSC studies on starch–water interaction[1–5]. In preceding papers[6–8], we reported that the extent of starch gelatinization is limited at a given temperature. It was found that the process is at all times in a state of equilibrium when the starch–water suspension is heated at a scan rate lower than 0.5 $K.min^{-1}$. On this basis, the DSC endothermic curves observed were analyzed in terms of equilibrium thermodynamics, and the size of a cooperative unit for the gelatinization process was determined to be 290 D-glucosyl residues[8].

We now further consider the thermodynamic properties for the interaction between starch granules and water. The enthalpy change upon mixing starch granules with water was measured by isothermal calorimetry at various temperatures. The results are compared with those derived from DSC[8,*].

EXPERIMENTAL

Potato starch. — The sample of starch was the same as that used previously[6–8]. The potato starch (lot EPE 7693, reagent grade) was purchased from Wako Chemical Co. Ltd., Tokyo. This specimen had been purified without any chemical and enzymic treatments and, at the final stage of preparation, it had been dried at a temperature below 50° so that its physicochemical characteristics were minimally affected. The sample was used after sieving, and washing with water. The sieved sample had a granular size of 63 to 73 μm. Prior to use, it was dried *in vacuo* at room temperature. The water content of the sample was 13.6%, as measured by the weight loss after oven-drying *in vacuo* for 10 h at 105°. The X-ray diffraction pattern and the photo-micrograph of the potato starch sample used have been shown previously[6,7].

Calorimeter. — The calorimetric measurements were performed in a Microcalorimeter Model TCC-204-D1 (Rhesca Co., Ltd., Tokyo) with a Break-Ampoule Attachment. This calorimeter is of the heat-conduction type, and has sample and reference calorimetric units which are arranged in an aluminum heat-sink with dimensions[10] of 310 × 200 × 300 cm. The temperature of the heat-sink can be controlled over the range of -10 to $+90$°. The starch sample was sealed in a glass ampoule which, after thermal equilibration, was broken in distilled water (30 mL). Starch (400–700 mg) was placed in a weighed ampoule, which was then reweighed and sealed. As a blank experiment, the empty ampoule was broken in distilled water (30 mL) in the reference unit.

In order to obtain a homogeneous mixture, the starch–water suspension was stirred for 120 s after an ampoule had been broken. The heat change associated

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[*] In our previous paper[8], we used the term "DTA" instead of "DSC", in accordance with a recommendation by the International Confederation for Thermal Analysis[9], as the instrument used had no power-compensation circuit. However, the interpretation of the results is essentially the same as for that of those obtained by the so-called DSC study. Because of the recent common usage, we use the term "DSC" herein.

with the swelling, or gelatinization, of starch in water was recorded for at least 240 min (until the calorimeter signal returned to its base-line), and the enthalpy for reaction was determined from the area under the recorded curve of heat evolution, or absorption, as a function of time. The calorimeter was electrically calibrated at each temperature of measurement by means of a manganine heater mounted in the reaction vessel in the calorimeter. The electrical calibration value was standardized at 25° by the heat of dissolution of KCl using a value[11] of $\Delta H = 17.55$ kJ mol^{-1}. The amount of heat experimentally measured was in the range of −800 to +800 mJ.

RESULTS AND DISCUSSION

Typical recordings of the calorimeter signal observed for the starch–water system at various temperatures are shown in Fig. 1. It was found that, whereas the process is exothermic at temperatures below 55°, it is endothermic at temperatures higher than 60°, above which the potato-starch granules undergo gelatinization. The observed enthalpy changes in the reaction are plotted against the temperature of measurement in Fig. 2. The plot shows the enthalpy level of the potato starch–water system at each temperature, relative to that of a hypothetical state where the raw starch granules (unswollen and ungelatinized) coexist with water. It is evident that, in both the low and the high temperature ranges, the plots are straight lines within experimental error; thus, the heat capacities of raw and gelatinized starches were found independent of temperature over the narrow temperature range studied.

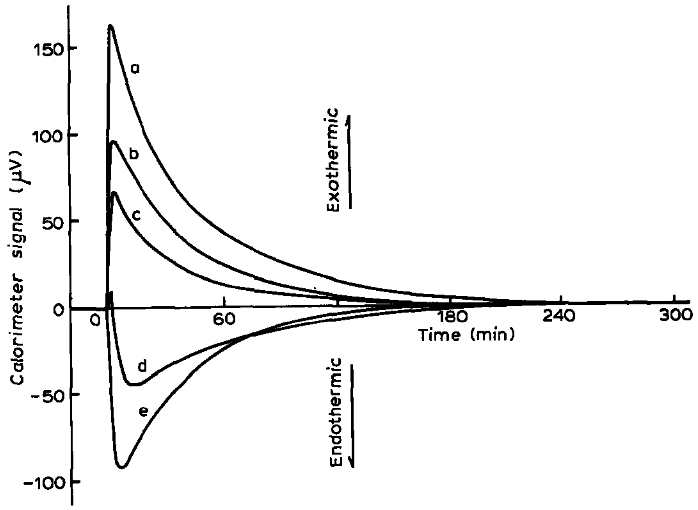

Fig. 1. Recordings of calorimeter signal observed upon mixing of starch with water at various temperatures. [Conditions were: (a) starch (0.6464 g) + H_2O (30 mL) at 30.0°; (b) starch (0.5867 g) + H_2O (30 mL) at 49.7°; (c) starch (0.4155 g) + H_2O (30 mL) at 55.3°; (d) starch (0.6761 g) + H_2O (30 mL) at 60.2°; and (e) starch (0.5303 g) + H_2O (30 mL) at 73.2°. The calorimeter sensitivity under the steady heat effect was $A = 23.62$ μW.μV^{-1} at 30.0°.]

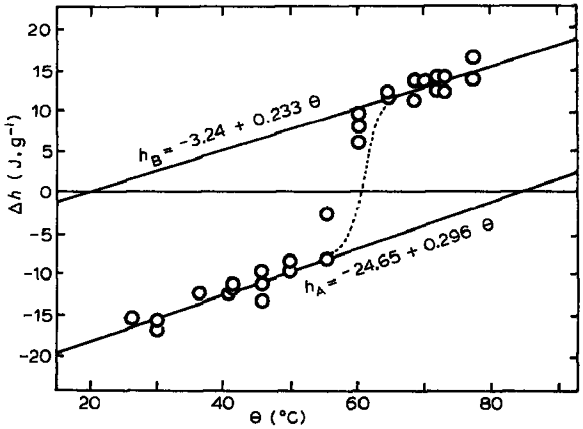

Fig. 2. The observed enthalpy changes, Δh, as a function of temperature of measurements, θ. [The solid lines were drawn by linear least squaring. The dotted line shows the enthalpy level of the starch–water suspension during transition calculated by Eqs. *4* and *5*.]

The linear least-squares line for the low-temperature range gives

$$h_{\mathrm{A}} = (-24.65 \pm 2.04) + (0.296 \pm 0.050)\,\theta, \tag{1}$$

and, for the high-temperature range,

$$h_{\mathrm{B}} = (-3.24 \pm 8.38) + (0.233 \pm 0.118)\,\theta, \tag{2}$$

where h_{A} and h_{B} are the enthalpies of raw and gelatinized starches, respectively, and are expressed in $\mathrm{J.g^{-1}}$, and θ is the temperature in degrees Celsius. On the basis that the difference between the low- and high-temperature processes is gelatinization, we obtain the enthalpy of gelatinization by the relation

$$\Delta h = h_{\mathrm{B}} - h_{\mathrm{A}}. \tag{3}$$

At the gelatinization temperature, $\theta = 61.44°$, which was obtained for the same sample in the previous DSC experiment[8], the heat of gelatinization is $\Delta h = 17.6 \pm 1.7\ \mathrm{J.g^{-1}}$. This value is in good agreement with the value of $17.07 \pm 0.92\ \mathrm{J.g^{-1}}$ determined by the previous scanning calorimetry[8]. Also from the aforementioned data, the heat-capacity change associated with starch gelatinization was found to be $\Delta c_p = -0.06 \pm 0.13\ \mathrm{J.K^{-1}.g^{-1}}$.

In our previous study, we determined[8] the cooperative unit size of potato starch during its gelatinization to be $\beta = 48{,}000$. Using this value, the enthalpy level of the transition step was calculated by the relation

$$h = (1 - \alpha)\,h_{\mathrm{A}} + \alpha h_{\mathrm{B}}, \tag{4}$$

where α is the fraction of gelatinized species. The values of α at each temperature were computed by using the van't Hoff relation

$$\frac{\mathrm{d}\ln\alpha/(1-\alpha)}{\mathrm{d}T}=\frac{\beta\,(h_B-h_A)}{RT^2} \tag{5}$$

The dotted line in Fig. 2 is the calculated result. Considering the technical difficulty in measuring the heat of reaction at a temperature in the transition range, the isothermal data seem to fall in a reasonable level within the experimental uncertainty.

Differentiation of the enthalpy change during the reaction gives the excess heat-capacity curve which would be observed by DSC measurement[12,13]. This relation is shown in Fig. 3. The curve obtained by differentiating the enthalpy function and by assuming the value of β to be 48,000 is given by the solid line, and the excess heat-capacity values during the gelatinization process, obtained in the previous DSC study[8], are shown by the open circles. The theoretical DSC curves calculated on the basis of processes having the cooperative unit size of β = 24,000 (curve b, Fig. 3) and β = 96,000 (curve c, Fig. 3) are also shown, for comparison. It is evident that the excess heat-capacity values actually observed well fit the curve drawn with the value of β = 48,000.

Although many investigators have reported the enthalpy change of starch gelatinization as evaluated by the DSC technique[1-5,8], no-one has ever mentioned the heat-capacity change associated with the gelatinization process. In principle, by DSC measurement, the heat-capacity change may be estimated from the change in

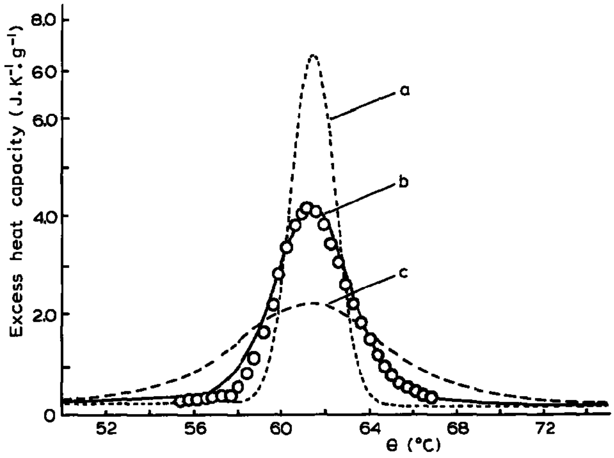

Fig. 3. Excess heat-capacity curves for the starch gelatinization, drawn on the basis of the van't Hoff relation by differentiating the enthalpy function which was obtained in the present isothermal calorimetry. [The cooperative unit sizes used for the calculation of curves are; (a) β = 96,000, (b) β = 48,000, and (c) β = 24,000. The open circles are the excess heat capacity values experimentally observed for the starch–water suspension in the previous DSC study[8].]

base line before and after the endothermic-heat effect to be studied[12–15]. However, the difference in heat capacity between ungelatinized and gelatinized starch is so small that it cannot be quantitatively evaluated by the DSC instruments sold commercially, because of their uncertainly limitations. In this study, using isothermal calorimetry, the heat capacity difference was found to be $\Delta c_p = -0.06$ $J.K^{-1}.g^{-1}$. Although this value has a large uncertainty (± 0.13 $J.K^{-1}.g^{-1}$), its absolute magnitude is very much smaller than those reported for the thermal unfolding of many globular proteins[14,15]. The unfolding of globular proteins is known to be accompanied by a positive change in the heat capacity, 0.4–0.7 $J.K^{-1}.g^{-1}$. The positive value is considered to be a reflection of the involvement of the change in hydrophobic interactions; hydrophobic groups originally buried in the interior of protein molecules will be exposed to the surface upon unfolding. However, the gelatinization of starch is obviously of a different nature and causes no remarkable change in the hydrophobic effects. Thus, it is most likely that, unlike the unfolding of proteins, the small change in the heat capacity found for the gelatinization of starch in water is mainly attributable to displacement of the hydrogen bonds between starch micelles and water molecules.

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