

Capillary viscometry of corn and wheat starches gelatinized by NaOH solutions at room temperatures

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ABSTRACT

Inspired by the previous studies on the viscosity growth behavior of rice starch during NaOH gelatinization, we performed continuous capillary viscometry of the dilute dispersions of corn and wheat starches gelatinized in NaOH solutions at room temperatures. We confirmed that the viscosity-time data series of both starches formed sigmoid curves, just like the case of rice starch. The results clearly contrasted to those obtained for the normal gelatinization in hot distilled water, which formed convex curves during the whole process. The growth process of viscosity for cold NaOH gelatinization was described by the kinetic model, composed of the first-order reaction hypothesis for the degree of gelatinization and the fluidity-type mixing rule of viscosity for ungelatinized and gelatinized parts. The present results suggested that cold NaOH gelatinization of starches generally produced viscosity growth curves of a sigmoid type, and were consistent with our concept that the sigmoidal kinetic behavior has a physicochemical origin based on complex formation caused by alkali-starch interactions.

KEYWORDS: viscosity, corn starch, wheat starch, gelatinization, NaOH

INTRODUCTION

Gelatinization is a reaction phenomenon, characteristic of all kinds of starches, and plays a

central role in food processing and industrial manufacturing of starch-based products. Although various approaches have appeared for studying gelatinization, involving rheological and enzymatic methods, DSC and SEM observations, we still have poor knowledge especially in a wide range of dispersion media and the relationship with microscopic structure [1].

From an applied viewpoint, attention has mainly focused on the "results" of gelatinization. However, as a subject of soft matter science, the core of interest for starch gelatinization should lie in its "reaction process". From such a viewpoint, the old proposals by Marchant and Blanshard [2] and French [3] should attract much attention. They provided in their literature an important insight that gelatinization is a semi-cooperative process, i.e., during gelatinization the swelling of amorphous phase (gelatinized part) promotes the disruption of crystallites (ungelatinized part).

Although a well-known gelatinization phenomenon is that which occurs for starches heated in water, starches even gelatinize at room temperatures in some special media, such as the solutions of alkali, urea, DMSO and some neutral salts. These facts verify that heating is not a necessary condition for gelatinization, but suggest that it might only occur from the chemical effect on the destruction of hydrogen bonds between starch chains and/or water molecules. However, past studies have hardly addressed the issues of such "cold chemical gelatinization" [4–7], especially the reaction processes. We believe that such

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chemical phenomena of non-heated starches should attract more interest to advance and broaden our understanding of gelatinization.

In view of this background, we have recently studied the flow characteristics of nonglutinous rice starch gelatinized in 0.146 M NaOH solutions at room temperatures [8, 9]. In the first work [8], we carried out batch-type rotational viscometry to examine the storage-time dependence of viscosity for the samples gelatinized in NaOH solution at 20°C, and found that viscosity increased exponentially with time in the early stage of gelatinization. Such kinetic behavior showing a concave curve has never been reported.

To confirm this finding, we performed a second study involving continuous capillary viscometry [9], and demonstrated that the whole viscosity-time data series of cold NaOH gelatinization formed sigmoid curves, in clear contrast to those obtained for normal gelatinization in hot water, all providing convex curves [10].

For these experimental results, we have then proposed the kinetic model to theoretically describe and distinguish both types of viscosity growth process, on a common basis of the first-order reaction equation for gelatinization degree [8]. It was shown that the sigmoidal growth of viscosity observed in cold NaOH gelatinization could be theoretically derived from the mixing rule of a fluidity (η^{-1}) type, which is distinct to that of a viscosity (η) type normally employed for describing convex growth in hot water gelatinization [10].

Furthermore, for the origin of this novel kinetic behavior, we have proposed the physicochemical hypothesis based on the concept of starch complex formation [8]. If such a general mechanism truly works in real phenomena, NaOH gelatinization of other starches should also produce sigmoidal growth of viscosity.

Corn and wheat starches possess almost the same general composition as rice starch, and are widely used as an ingredient of food, pharmaceutical and other industrial products. Alkali gelatinization of corn starch is, in practice, utilized in the production of corrugating adhesives [11–13]. This type of chemical treatment of these starches might produce new biodegradable materials. However, to our

knowledge, reports about rheological property and kinetic behavior during alkali gelatinization of these starches do not exist.

Hence, the purpose of the present article was to report the growth process of viscosity for the dilute dispersions of nonglutinous corn and wheat starches gelatinized in NaOH solutions at room temperatures, and to compare the results with those obtained for gelatinization in hot water. We employed here the method of continuous capillary viscometry to obtain smooth viscosity-time data series during the whole process of gelatinization [9].

To confirm the validity of the physicochemical concept stated to explain the new kinetic behavior, it is important to clarify whether the phenomenon observed in cold NaOH gelatinization is specific to a particular plant origin (rice).

EXPERIMENTAL

Materials

A nonglutinous type of corn and wheat starch powders (USA) were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Using isothermal (120°C) thermo-gravimetric analysis (DTA 7000/TG 7000; Ulvac Sinku Riko, Inc., Yokohama, Japan), the water contents in corn and wheat starches were evaluated as 12.5% and 12.4% respectively. The contents of water, protein, fat, ash, and carbohydrate in the corn starch were estimated by the Japan Food Research Laboratories (Osaka Branch, Japan) to be 12.6%, 0.3%, 0.6%, less than 0.1% and 86.5%, respectively. Those in the wheat starch were estimated as well to be 12.6%, 0.3%, 0.6%, 0.2% and 86.3% respectively. The amylose ratios of corn and wheat starches were also determined by the Japan Food Research Laboratories to be 24% and 25% respectively, using amylose/amylopectin assay kit (Biocon Ltd., Japan).

Sample preparation

For the viscometry of gelatinization in hot water, dispersions of 5.0% corn starch and those of 3.0% wheat starch were prepared, following a previously described method [9]. For the study of cold NaOH gelatinization, 1.0% starch dispersions were prepared according to the previous procedure [9], except for the NaOH concentration, where 0.146 M

for rice starch was changed to 0.170 and 0.133 M for the present corn and wheat starches respectively.

In the preparation procedure, when hot distilled water (65–90°C) or cold NaOH solution (5–30°C) was added to starch (slurry), the measurement of gelatinization time t [min] was initiated ($t = 0$). All the sample dispersions were sufficiently dilute to show small scales of viscosity ($\leq 20 \text{ mPa}\cdot\text{s}$) with high Newtonian property, particularly in the early stage of gelatinization process in which we are most interested. Use of glass capillary viscometers was then justified as an appropriate method of viscometry.

Capillary viscometry

Using ubbelohde-type glass capillary viscometers (Kinematic Viscosimeter, Sogo Laboratory Glass Works Co. Ltd, Kyoto, Japan), capillary viscometry was performed continuously until $t = 200$ or longer for gelatinization in hot water, and until $t = 40$ or longer for cold NaOH gelatinization, according to previously described procedures [9].

The real flow measurement was carried out iteratively with short intervals depending on each efflux time of the flow. For each flow measurement at a gelatinization time t [min], the viscosity η [mPa·s] of the sample was calculated from an efflux time through the conventional formula [9].

RESULTS AND DISCUSSION

Viscosity growth curves

Figure 1 shows the viscosity-time data obtained for corn (a) and wheat (b) starch samples gelatinized in hot water (only the data at $t < 200$ are presented in the figure). Although quantitative differences existed between corn and wheat starches and also among different temperatures, all of the data series formed convex curves during the whole gelatinization processes. They could be described by the first-order kinetic model based on the normal type of mixing rule for viscosity [10].

For corn starch (Figure 1 (a)), viscosity measured within 400 min was larger at higher temperatures. Within 400 min, the data series at 78 and 75°C seemed to reach the equilibrium, but those at 70 and 65°C were still slightly increasing. Much difference was observed in the size of viscosity

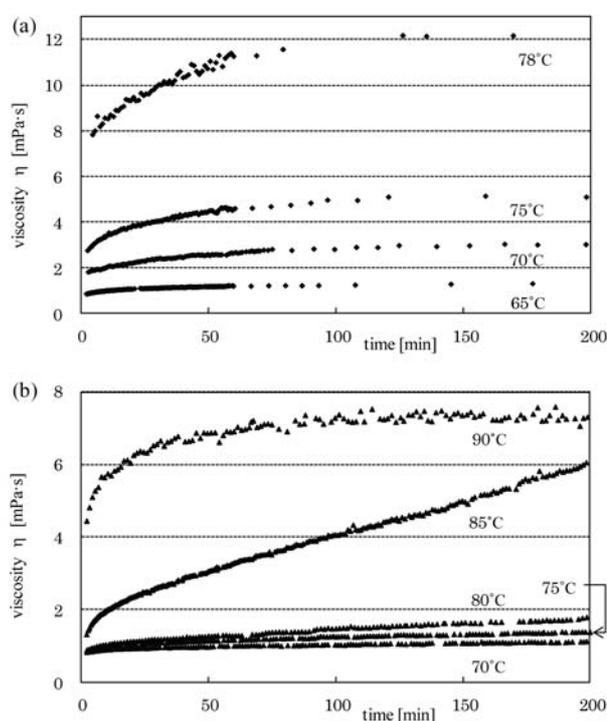


Figure 1. The viscosity-time data series ($t < 200$) for 5.0% corn starch (a) and 3.0% wheat starch (b) gelatinized by hot water.

between 78 and 75°C. At 78°C, viscosity reached $12 \text{ mPa}\cdot\text{s}$ at the equilibrium.

For wheat starch (Figure 1 (b)), only the data at 90°C reached the equilibrium ($\approx 7.5 \text{ mPa}\cdot\text{s}$) within $t < 300$, and the rest were still growing. A large difference in viscosity was observed between 85 and 80°C.

Figure 2 shows the viscosity-time data series for the samples gelatinized in NaOH solutions at different room temperatures. In contrast to those for the gelatinization in hot water, almost all of them formed clear sigmoid curves. The concavity property in the first half of growth curve seems more obvious at lower temperatures, and obscure at 30°C. All of the data series reached the equilibrium within much shorter times than those in hot water. Furthermore, the samples gelatinized at lower temperatures required longer times to reach the equilibrium and provided larger viscosity values at the equilibrium.

For example, clear sigmoid curves are observed for corn starch gelatinized at 10, 15 and 20°C

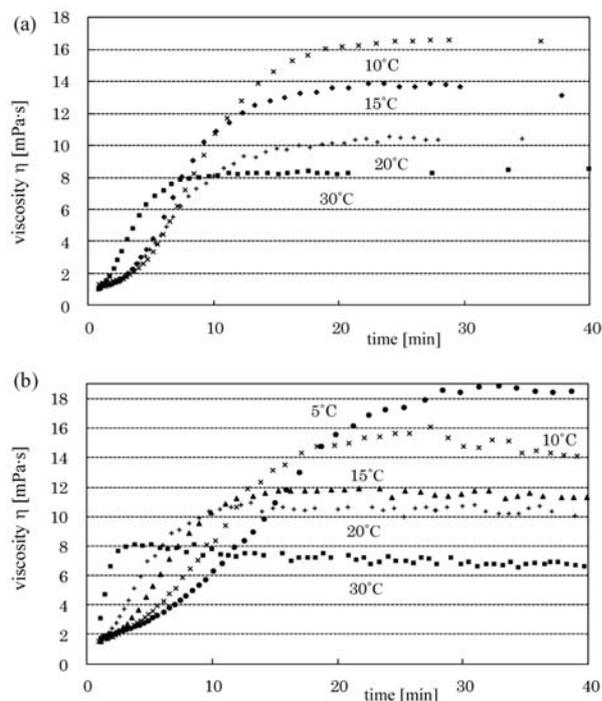


Figure 2. The viscosity-time data series ($t < 40$) for 1.0% corn starch gelatinized in 0.170 M NaOH solutions (a) and wheat starch gelatinized in 0.133 M NaOH solutions (b).

(Figure 2 (a)). As a typical case, comparable with the previous case of rice starch, the viscosity at 15°C reached the maximum (14mPa·s) at $t = 22$, which was a bit larger than that (12mPa·s) for rice starch of the same concentration at the same temperature [9].

In the case of wheat starch samples as well (Figure 2 (b)), the data series at 5, 10 and 15°C showed clear sigmoid curves. The samples gelatinized at lower temperatures reached larger equilibrium values with longer times. The viscosity at 5°C attained 18mPa·s, and that at 15°C reached at $t = 24$ the maximum value (12mPa·s) of the same scale as rice starch gelatinized at the same temperature.

Thus, at least qualitatively, the kinetic behavior of the growth of viscosity and its temperature dependence in cold NaOH gelatinization of corn and wheat starches were the same as those observed for rice starch [9]. Each viscosity-time data series could be quantitatively analyzed with the kinetic method described below.

Kinetic analysis of viscosity growth in NaOH gelatinization

The growth curves of viscosity observed for the gelatinization in hot water and in cold NaOH solutions could be described and distinguished with the kinetic models proposed in the previous articles [8, 9]. The models consist of the first-order reaction rate equation $dx/dt = K(1-x)$ for the degree of gelatinization $x \equiv [G]/([UG] + [G])$, defined as the ratio of the gelatinized part (G) to the sum of ungelatinized (UG) and gelatinized parts of starch [1], and the mixing rules of viscosity. The former dictates the time evolution $x(t)$ for the degree of gelatinization, with K denoting a rate constant. This basic equation is commonly assumed for the two kinds of gelatinization. The latter is a law of blending viscosity for ungelatinized and gelatinized parts, and determines the dependence of viscosity $\eta(x)$ on the degree of gelatinization.

The normal and simplest type of mixing rule is expressed as the additive law of viscosity itself: $\eta(x) = (1-x)\eta_{UG} + x\eta_G$ where η_{UG} and η_G denote the viscosities which are proper to ungelatinized and gelatinized parts, respectively. In the actual experiment, η_G is identified with the equilibrium (practically the maximum) value of measured viscosity. The above normal type of mixing rule, combined with the reaction rate equation, provides the time evolution of viscosity:

$$\eta(t) = \eta_G - (\eta_G - \eta_{UG})e^{-Kt}, \quad (1)$$

which evolves in time with a convex property ($d^2\eta/dt^2 < 0$) in the whole gelatinization process ($0 \leq t < \infty$). This property coincides with real gelatinization process observed in hot water [9, 10], including the present case (Figure 3), and the kinetic analysis could be performed by linearizing Eq. (1):

$$\ln(\eta_G - \eta) = \ln(\eta_G - \eta_{UG}) - Kt. \quad (2)$$

In contrast, sigmoid curves of viscosity growth observed in cold NaOH gelatinization of rice, corn and wheat starches cannot be described by the above model, and hence other possibilities must be explored. Then, in the previous articles [8, 9], keeping the rate equation for the degree

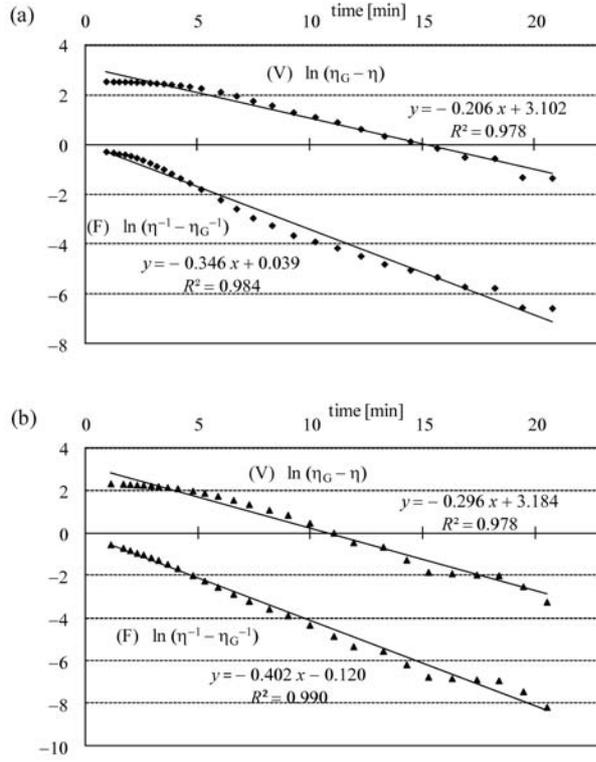


Figure 3. The linearization of viscosity-time data series for the corn (a) and wheat (b) starches gelatinized respectively in 0.170 and 0.133 M NaOH solutions at 15°C.

of gelatinization unchanged, we selected another type of a simple mixing rule, i.e. the additive law of fluidity:

$$\eta^{-1}(x) = (1-x)\eta_{UG}^{-1} + x\eta_G^{-1}.$$

This mixing rule, combined with the first-order reaction rate equation, provides the following time evolution of viscosity:

$$\eta^{-1}(t) = \eta_G^{-1} + (\eta_{UG}^{-1} - \eta_G^{-1})e^{-Kt}. \quad (3)$$

Then, some calculations deduce that the time-dependence of viscosity $\eta(t)$ is a sigmoid function. The first half of the viscosity-time curve is concave: $d^2\eta/dt^2 > 0$, ending with an inflection point located at $\eta = \eta_G/2$. Furthermore, under the condition: $\eta_{UG} \ll \eta_G$, Eq. (3) predicts that viscosity increases exponentially in the initial stage ($Kt \ll 1$) of gelatinization: $\eta(t) \approx \eta_{UG} e^{Kt}$. This approximation could be utilized in the case that the measured data were scattered at a later stage of gelatinization

and that the equilibrium value was η_G unclear. This is actually the case that occurred for batch-type measurement [8].

The linearization of Eq. (3) gives:

$$\ln(\eta^{-1} - \eta_G^{-1}) = \ln(\eta_{UG}^{-1} - \eta_G^{-1}) - Kt, \quad (4)$$

which is used to analyze the measured viscosity-time data of cold NaOH gelatinization. The linear regression analysis was applied to check the validity of the present analysis, and to determine the value of rate constant.

For example, Figure 3 presents the linearized data series for corn (a) and wheat (b) starches gelatinized in NaOH solutions at 15°C, ranging to the maximum viscosity. For each starch sample, the linearization was done with both the two models, i.e., with the left-hand side of Eq. (2), indicated in figures by the symbol (V), and with that of Eq. (4) indicated by (F). To each data series, the regression line, equation and R^2 value were added in figures. For both corn (a) and wheat (b) starches, the obtained R^2 values ensured that the (F) model provided higher linearity than the (V) model. The (V) model generated deviations between the linearized data series and the regression lines in very early stages of gelatinization ($t < 3$). We note that this feature was commonly observed at all temperatures (the rest of the data not shown).

In Figure 3, the coefficients 0.346 (a) and 0.402 (b) appearing in the regression equations for the (F) model represent the values of rate constant $K[\text{min}^{-1}]$ for the present corn and wheat starches respectively. These might be regarded as the rate constant values averaged over the whole reaction processes ranging to the maximum viscosity. They could be compared with that (0.134) obtained previously for rice starch at the same temperature [9], although the concentrations [M] of added NaOH were different among three samples: 0.133 (wheat), 0.146 (rice) and 0.170 (corn).

From the (V) model, we obtained the rate constant values which were different from the above. Then, using Eqs. (1) and (3) with rate constant values thus obtained, we added to the viscosity-time data series for each starch sample measured at 15°C the

theoretical curves derived from the (V) and (F) models respectively (Figure 4). For both starches (corn (a) and wheat (b)), it was indicated that the kinetic model with the mixing rule of fluidity type gives better description of NaOH gelatinization at 15°C; the theoretical curves from the (F) model fitted better with the whole measured data series than those from the (V) model. The (V) model does not produce sigmoid curves, and in addition, generates forbidden deviations (negative viscosity) in the very early stages of gelatinization.

In the above analysis, rate constants were determined by applying the kinetic model uniformly to the whole data series, in which it was assumed that the reaction evolved in a whole process with a single value of rate constant. However, as suggested by Figures 3 and 4, this assumption is not completely validated even for the (F) model. Therefore, to give a detailed argument for the reaction rate, for instance, to discuss the temperature dependence, we should develop more careful kinetic

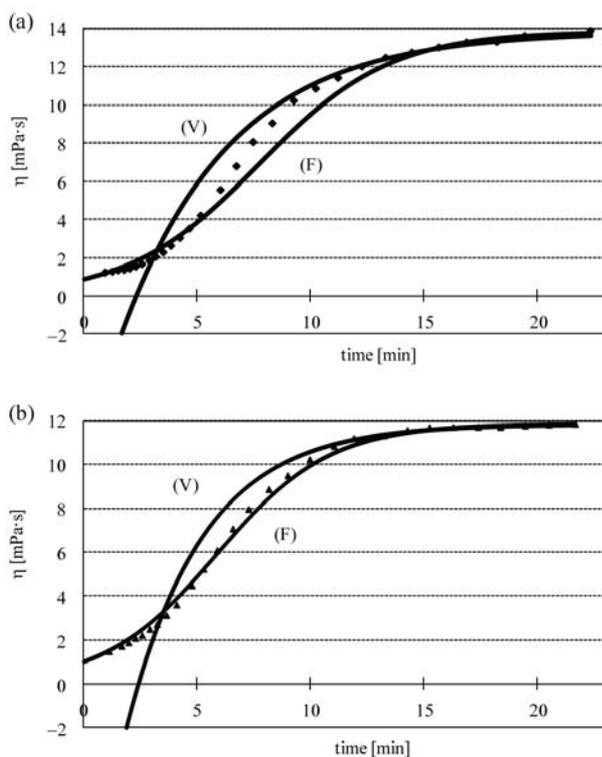


Figure 4. The viscosity-time data series added with two theoretical (solid) curves constructed from the kinetic models (V) and (F), for the corn (a) and wheat (b) starches gelatinized at 15°C.

method allowing a non-uniform value of rate constant. We hope to address this issue in the future.

Hypothetical discussion based on complex formation

The present experiment confirmed that the novel kinetic behavior firstly discovered for rice starch is not specific to a particular plant origin, and suggested that it might rather appear in cold NaOH gelatinization of general starches and have physicochemical origins such as those caused by alkali-starch interactions. It is quite interesting if such general mechanisms really work in this phenomenon.

For such candidates, we have already proposed the following hypothesis based on two types of complex formation arising from general alkali-starch interaction [8]. Before describing this concept, we should first clarify the meaning of the kinetic results we obtained. In our standpoint based on the first-order reaction, the change in the shape of viscosity growth curve from a convex type to a sigmoid type means the alteration of the mixing rule from a viscosity type (V) to a fluidity type (F). Mathematically, this alteration of mixing rule can be interpreted as an enhancement of the rheological independency of a gelatinized part [8]. Then, we hypothesized that such an enhancement effect could be induced by that of structural independency generated from some complex formation. The complexes formed inside the starch granules could work as structurally isolated objects, reducing the semi-cooperative property of gelatinization process in hot water, suggested by Marchant and Blanshard [2] and French [3]. The structural independency carried by complexes was hypothesized to induce rheological independency, resulting in the alteration of viscosity mixing rule, i.e., the change of viscosity dependence $\eta(x)$ on the degree of gelatinization.

In the present case of cold NaOH gelatinization, the following types of complex formation would be possible. One is a type of complex formed by direct NaOH-starch interaction, through the cation exchange: $\text{St. - OH} + \text{NaOH} \rightarrow \text{St. - ONa} + \text{H}_2\text{O}$. The importance of this interaction was actively discussed by Oosten [14–16]. This exchange reaction could occur at the hydroxyl groups of starch chains, i.e., both amylose and amylopectine.

This type of complex formation was first discussed a hundred years ago as an alkali metal-adsorption phenomenon of starch [17–19].

Another type of complex could be formed through the following indirect chemical process. The amylose of seed-originated starches generally includes a certain amount of lipids, some of which are free higher fatty acids, like palmitic acid. NaOH penetrating into starch granules neutralizes the fatty acids to generate sodium salts of fatty acids. Even without heating, this neutralization should evolve much faster than the normal saponification of triglyceride. These “micro soaps” generated inside the starch granules possess both large hydrophobic and hydrophilic groups, and should work as strong surfactants. They could then form strong complexes mainly with amylose, being stable at the room temperatures (5–30°C). This type of alkali-induced complex formation might only occur for starches with sufficient amounts of amylose including lipids, and hence is predicted to decline, in part, for glutinous type of starches or for defatted starches. This prediction requires verification by future studies.

In addition to the above two kinds of NaOH-starch interactions, it may be that we should consider the hydration state of starch chains. In the case that gelatinized starch is fully hydrated in cold NaOH solution compared with that in heated water, as the third candidate of complex, the starch-water complex might enhance the structural independency of gelatinized part. For this issue, we can only point out the presence of two opposite effects on the stability of hydration state.

One effect would come from thermodynamical condition. In NaOH solution, hydroxyl ion as an anion with strong ability to destroy the hydrogen bond increases the number of monomolecular water, which should contribute to the disruption of the structural integrity of starch granules and the hydration of starch chains. At the present room temperatures, the molecular motion of water is less active, and hence hydration state of starch chains is thermodynamically more stable, than in heated water. This could make the starch chains in the amorphous phase less mobile and depress the cooperativity in gelatinization process.

However, anion should also destroy the hydrogen bond between starch chains and water molecules,

thereby destabilizing the hydration state. This chemical instability would more or less cancel the above thermodynamical stability. We thus inferred that starch-water complex in cold NaOH gelatinization cannot be a strong candidate of depressing the cooperativity.

CONCLUSIONS

Continuous capillary viscometry revealed that the viscosity-time data series of nonglutinous corn and wheat starches gelatinized in NaOH solutions at room temperatures formed sigmoid curves, in contrast to those of the same starches gelatinized in hot water. This difference in the kinetic behavior is qualitatively the same as that previously observed for rice starch. The results then demonstrated that a sigmoidal behavior in the growth process of viscosity in cold NaOH gelatinization is not specific to a particular plant origin, and were consistent with our concept that the origin is physicochemical. The present hypothesis proposed to explain the sigmoidal behavior is based on two kinds of starch complexes, formed inside the starch granule.

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