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A concavity property of the viscosity growth curve during alkali gelatinization of rice starch

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Abstract

A qualitative difference between the viscosity–time curves for thermal and strong alkali gelatinization of rice starch was demonstrated using continuous capillary viscometry. During the thermal (60, 70, 75, 80 °C) gelatinization with distilled water, the viscosity growth curves kept a convexity property, in accordance with the past known results. In contrast, the viscosity growth curves for the cold (15, 20 °C) gelatinization with a 0.146 N NaOH solution showed a concavity property in the first half of whole gelatinization process. This result confirmed our previous result having been obtained from batch-type measurement with use of a cone-plate viscometer. On the basis of the first-order reaction hypothesis for gelatinization degree, this novel viscosity growth behavior in cold alkali gelatinization could be described in terms of the mixing rule of viscosity distinct from that had been applied to thermal gelatinization.

Keywords: Alkali; Capillary viscometry; Concavity; Gelatinization; Kinetics; Rice starch; Viscosity

1. Introduction

In the studies of starch gelatinization, a kinetic approach has been vigorously employed. From an academic standpoint, it would partly be because a gelatinization phenomenon is a nonequilibrium process and a kinetic model has been considered to be characteristic of an underlying reaction mechanism. On the other hand, from the viewpoint of the applications to food processing and general starch industry, kinetic information on starch gelatinization is essential to consider a process design with a good reaction control.

So far, many authors have treated starch dispersions heated in excess water, and studied, usually on the basis of the first-order reaction model, rate constants for samples in given gelatinization conditions (Bakshi & Singh, 1980; Kubota, Hosokawa, Suzuki, & Hosaka, 1979; Lund, 1984; Okechukwu, Rao, Ngoddy, & Mcwatters, 1991; Slade & Levine, 1991). As a means of the experimental technique, recent kinetic studies have concentrated on differential scanning calorimetry (Lund & Wirakartakusumah, 1984; Ojeda, Tolaba, & Suárez, 2000; Wirakartakusumah, 1981; Yeh & Li, 1996; Zanoni, Schiraldi, & Simonetta, 1995) and other modern methods such as those based on changes in granule size measured by means of laser diffraction (Okechukwu & Rao, 1996a,b) and in electrical conductance (Karapantsios, Sakonidou, & Raphaelides, 2000; 2002).

Among the above past researches, Kubota et al. (1979) and Okechukwu et al. (1991) studied the time evolution of rheological quantities such as consistency coefficient with constant flow behavior index and apparent viscosity, which we would henceforth call 'viscosity η' for short. With different experimental techniques, they obtained viscosity–time curves for rice, potato, and cowpea starches gelatinized under isothermal conditions at various heating temperatures. In both cases, with growth of gelatinization time, viscosity was shown to grow up to some equilibrium value η_G with a convexity property $d^2\eta/dt^2 < 0$.

In contrast, one of the present authors (H.Y.) and his collaborators have very recently observed that the viscosity growth curve of rice starch gelatinized at 20 °C in the 0.146 N NaOH solution indicated a concavity property $d^2\eta/dt^2 > 0$ in the early stage of gelatinization process (Yamamoto, Makita, Oki, & Otani, 2006). This novel characteristic in the kinetic behavior of viscosity in (cold) alkali gelatinization was argued to be described in terms of the mixing rule of viscosity $\eta(x)$ which is different from that having been so far applied to the usual thermal gelatinization. Here, the mixing rule of viscosity means the relation between viscosity η and gelatinization

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degree x (a gelatinized fraction of starch). In that work, gelatinization degree was assumed in both types of gelatinization to grow with time obeying the standard first-order reaction hypothesis $dx/dt = K_1(1-x)$ with K_1 a rate constant.

Starch gelatinization due to strong alkali is considered to occur due to the destruction of hydrogen bonds between starch molecules, driven by hydroxide ions penetrating into the starch granule. Academically, this phenomenon would be an interesting research object because it does not require any heating process as for thermal gelatinization; it occurs at room temperatures and, therefore, has sometimes been called as cold gelatinization. In that sense, for some purposes such as rheological measurement, alkali gelatinization is technically advantageous in carrying out the observation of reaction process, particularly under an isothermal condition. As an industrial application, the paste obtained through the alkali gelatinization of corn starch is actually utilized in manufacturing the corrugated paper. However, much less is known for this gelatinization phenomenon than for usual thermal gelatinization. Although some works have been done (Suzuki & Juliano, 1975; Oosten, 1982; 1983; 1990; Otsuka, Moritaka, Fukuba, Kimura, & Ishihara, 2001; Moritaka, Ishihara, Matsumoto, Iino, & Kimura, 2003), no kinetic approach had appeared before our previous work.

From the experimental aspect, our previous work was based upon batch-type measurement with use of a cone-plate type rotational viscometer, for which the obtained viscosity–time data became dispersed after long gelatinization time. In the early stage of gelatinization process, however, measured data were sufficiently regular and viscosity was found to grow exponentially, i.e. with a concavity property as gelatinization proceeded in time.

In the conventional viscometry including that using a cone-plate type viscometer, ungelatinized starch particles sediment easily during the measurement. This phenomenon usually tends to lower the viscosity measured in the early stage of gelatinization, although it is difficult to evaluate the real magnitude of such effect that should depend on each instrument used for the measurement. Anyhow, the sedimentation effect is normally unavoidable and could influence the viscosity growth behavior in the early stage of gelatinization. For such a reason, in order to confirm the above qualitative difference between the viscosity growth behavior for alkali and thermal gelatinization, it is especially desirable to *demonstrate the difference directly* by means of the *same* experimental method applied to both types of gelatinization.

A batch-type cone-plate viscometry employed in our previous work would generally be inadequate for a hot water–starch system since the sample is more or less exposed to air and it is thus difficult to prevent from evaporation at high experimental temperatures, which might significantly influence the measured viscosity. Further, kinetic data taken from batch samples are affected by fluctuations, which could unavoidably be generated in the preparation process.

From these reasons, we carried out in the present work the continuous measurement of viscosity using a glass capillary viscometer settled in an isothermal water bath. The sample is dilute rice starch dispersions gelatinized by NaOH with a fixed normality at several room temperatures. In comparison with the use of a rotational viscometer, this method can be more reliably applied to the samples during both types of gelatinization. Actually, as a reference standard phenomenon, this viscometry method was employed also for the thermal gelatinization of rice starch in hot distilled water. Then, the observed viscosity–time data for both types of gelatinization could be directly compared.

2. Materials and methods

2.1. Sample preparation

In this work, powders of nonglutinous rice starches ‘Better Friend’, gifted from Shimada Chemical Co. Ltd (Niigata, Japan), were used without any purification. Table 1 shows the composition of the starch powder taken from supplier information.

For the measurement of thermal (60, 70, 75, 80 °C) gelatinization, 800 g of 5 wt% starch dispersions with large heat capacity were prepared in the following way. Distilled water (110 g) was added to the starch powders (40 g) weighed into a 1000-ml beaker. This mixture was stirred in 1 min using a glass rod of 7-mm diameter to obtain a starch slurry. Fifteen seconds after starting the stirring, approximately 700 g of hot distilled water was weighed into another 1000-ml beaker in which a 5-ml pipette and a standard thermometer had been settled. Forty-five seconds after that, 650 g of the above hot distilled water was added to the starch slurry at which the measurement of gelatinization time (min) was to start ($t=0$). Using the same glass rod as above, the sample was stirred again 30 times with the beaker kept to be in a hot water bath to prevent from cooling. The temperatures of the added hot water were 65, 87, 92 and 98 °C, respectively, for the samples measured (gelatinized) at 60, 70, 75 and 80 °C.

For the study of alkali gelatinization (measured at 15, 20, 30 °C), 1 wt% starch dispersions were prepared in the following way: 99.0 g of the 0.146 N NaOH solution (15, 20, 30 °C) was added to the starch powders (1.00 g) weighed into a 200-ml beaker. The NaOH–starch mixture in the beaker was stirred 100 times in about 25 s with use of a glass rod of 7-mm diameter to obtain a homogeneous dispersion. The gelatinization time (min) was to start ($t=0$) at which the NaOH solution was added to the starch.

Table 1
The composition of rice starch powder, informed from the manufacturer, Shimada Chemical Co. (Niigata, Japan)

Ingredients	Wt%
Carbohydrate	85.3
Moisture	13.5
Lipid	0.7
Protein	0.3
Ash	0.2
Ca	0.029
Na	0.011

The normality of NaOH was determined from the previous result of Yamamoto et al. (2006) to be 0.146 N for which the 4 wt% rice starch dispersion had shown at $t=10$ the flow behavior being approximately the Newtonian flow. In that work, we further examined the time dependence of Newtonian property by applying the linear regression analysis with an intercept fixed to be zero to the obtained shear stress (0–2.0 Pa)—shear rate data. We observed that the validity of this approximation was kept quite high ($R^2 \geq 0.96$) in the time range $7 \leq t$ (min) ≤ 35 in which sample showed the concave viscosity–time curve with the viscosity (Pa s) scale of O(10^{-3})–O(10^{-1}). The deviation ($R^2 < 0.9$) from the Newtonian flow appeared after long gelatinization time ($t > 40$) in the viscosity (Pa s) scale of O(10^{0})–O(10^{1}).

Compared with that case, the present sample (1 wt%) was much more dilute, and we will in fact see in the next section that the viscosity (Pa s) scale observed in the present alkali gelatinization is only of O(10^{-3})–O(10^{-2}). Therefore, during all the period of measurement, the present sample for alkali gelatinization should keep the flow behavior, which is very close to the Newtonian flow.

The starch concentration of the sample for thermal gelatinization was different from that for alkali gelatinization. This value (5 wt%) of concentration was so determined that the prepared sample provided, owing to thermal gelatinization, almost the same scale O(10^{-2}) of the largest viscosity (Pa s) within the period of measurement, as that for alkali gelatinization. However, we did not treat thermal gelatinization in the previous work, and hence there had existed no data, which are of value for reference to check the Newtonian property of this sample.

Therefore, as the supplementary experiment to the present work, we carried out cone-plate flow measurement at various high temperatures (75, 78, 80 °C) and gelatinization time to judge the Newtonian property of this 5% sample. It turned out that the Newtonian property was sufficiently high and that its degree depended on the magnitude of viscosity. For example, in the low viscosity region up to 3.0 ($\times 10^{-2}$ Pa s) the validity of the linear regression was extremely high ($R^2 \geq 0.99$), and was kept still quite high ($R^2 \geq 0.95$) up to 6.0 ($\times 10^{-2}$ Pa s) which corresponds to the largest value of viscosity measured with the present capillary viscometry (Section 3).

Thus, all the sample starch dispersions were dilute and showed sufficiently small scale of viscosity to keep the high Newtonian property, particularly in the early stage of gelatinization process, which we are most interested in. The use of glass capillary viscometers was hence justified as an appropriate method of viscometry.

2.2. Capillary viscometry

Ubbelohde-type glass capillary viscometers KINEMATIC VISCOSIMETER (Sogo Laboratory Glass Works Co. Ltd, Kyoto, Japan, U-0596, U-07115, U-08119, U-1077) were used for the present viscometry. Using a pipette, approximately 15 ml of the sample fluid was injected into the viscometer settled in a water bath (Yamato Scientific Co. Ltd, Tokyo, Japan, UNI-THERMO BATH VISCOSITY MODEL BR-61) which with a standard thermometer was thermostated accurately. After confirming that the sample temperature coincided with the temperature fixed for measurement, the sample fluid was sucked up to the upper part of the viscometer. The time (s) taken for the liquid meniscus to pass from the upper mark to the lower mark was measured by two persons with stopwatches. The measured values were averaged to provide an efflux time τ (s) at the measurement (gelatinization) time t (min) defined below.

Just before each measurement, the sample fluid was sucked up to the upper part of the viscometer and was made to flow down. This preliminary flow test was done once before each real measurement to prevent the flow path from drying. Gelatinization (measurement) time t (min) was defined as the sum of the half of an efflux time τ (s)/120 and the time (min) at which the liquid meniscus passed through the upper mark. The measurement was carried out continuously within the time range t (min) ≤ 90 with very short intervals depending on each efflux time τ.

From the measured efflux time τ (s), the viscosity η (Pa s) of the sample was calculated by using the formula

$$\frac{10^3\eta}{\rho} = \nu = C_1\tau - \frac{C_2}{\tau} \tag{1}$$

where ρ (g/cm^3) is the density of the sample fluid and ν(10^{-2} cm^2/s$\equiv$cSt) is the kinematic viscosity. The viscometer constants C_1(cSt/s$=10^{-2}$ cm^2/s^2) and C_2(cSt s$=10^{-2}$ cm^2) were determined by means of calibration with the standard liquids with known values of kinematic viscosity (Nippon Grease Co., Ltd, Osaka, Japan, Standard Liquid for Calibrating Viscometers, JS2.5, JS10, JS50, JS100, JS200, JS500). For each viscometer and for each measurement temperature, two kinds of standard liquids with adequate values of kinematic viscosity were selected.

For each sample condition, the preparation and the continuous viscometry were duplicated at least once to check the reproducibility of the result. In the next section we will show for each temperature the viscosity–time data which indicated more smooth curve than another.

3. Results

3.1. Thermal gelatinization

In Fig. 1(a) are plotted the viscosity–time data obtained from the measurement at four different temperatures (60, 70, 75, 80 °C) for the thermal gelatinization of 5 wt% rice starch dispersions. Among these samples, the one gelatinized at 80 °C indicated O(10^{-2}) scale of viscosity (Pa s) during all the period of viscometry, which was much larger than those observed at other temperatures. The three curves obtained at 60, 70 and 75 °C are enlarged in Fig. 1(b) with the viscosity (Pa s) axis of a smaller scale O(10^{-3}) to show their behavior more clearly than those in Fig. 1(a).

For all the samples, the values of viscosity continued to grow within the present time range ($t \leq 90$) of measurement.

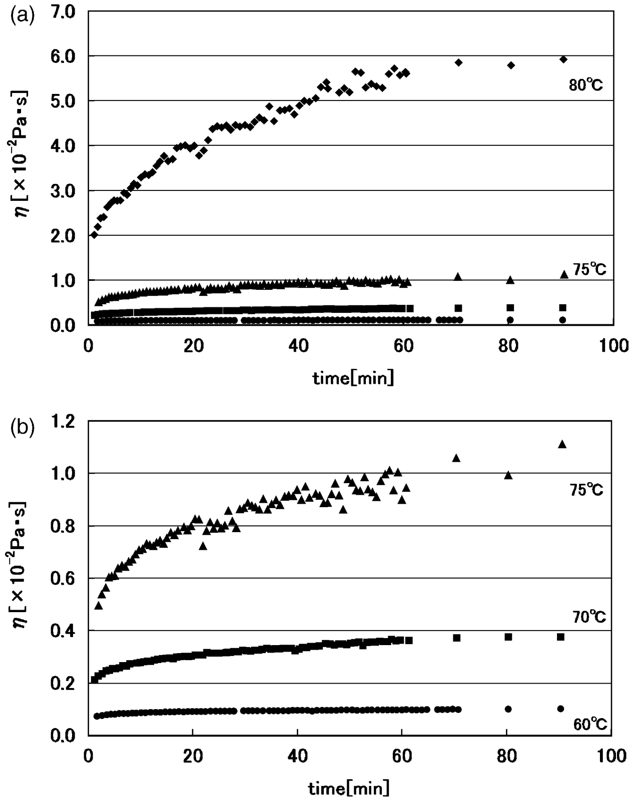

Fig. 1. (a) The viscosity–time data obtained for thermal gelatinization of 5 wt% rice starch dispersion heated at four different temperatures. The data series represented in terms of circle, square, triangle, and diamond were obtained, respectively, for the gelatinization at 60, 70, 75 and 80 °C. (b) Only the data series measured at 60, 70 and 75 °C are shown in a smaller scale.

The maximum values of viscosity ($\times 10^{-2}$ Pa s) at 60, 70, 75 and 80 °C were obtained at the end ($t=90$) of measurement as 0.10, 0.38, 1.1, and 5.9, respectively. Anyhow, from these two figures we find that the shapes of all the viscosity growth curves for the present thermal gelatinization are *convex* during the whole period of measurement. This result is consistent with that previously observed by other workers (Kubota et al., 1979; Okechukwu et al., 1991).

3.2. Alkali gelatinization

In Fig. 2(a) are plotted the viscosity–time data taken for the alkali gelatinization of 1 wt% samples (15, 20, 30 °C). The viscosity of the sample gelatinized at higher temperature showed a faster increase at the initial stage of gelatinization and reached the maximum at earlier gelatinization time; 45, 29 and 14 min at 15, 20 and 30 °C, respectively. However, the maximum values of measured viscosity ($\times 10^{-2}$ Pa s) were higher for the sample gelatinized at lower temperatures; 1.2, 1.1, 0.80 for the samples gelatinized at 15, 20, and 30 °C, respectively.

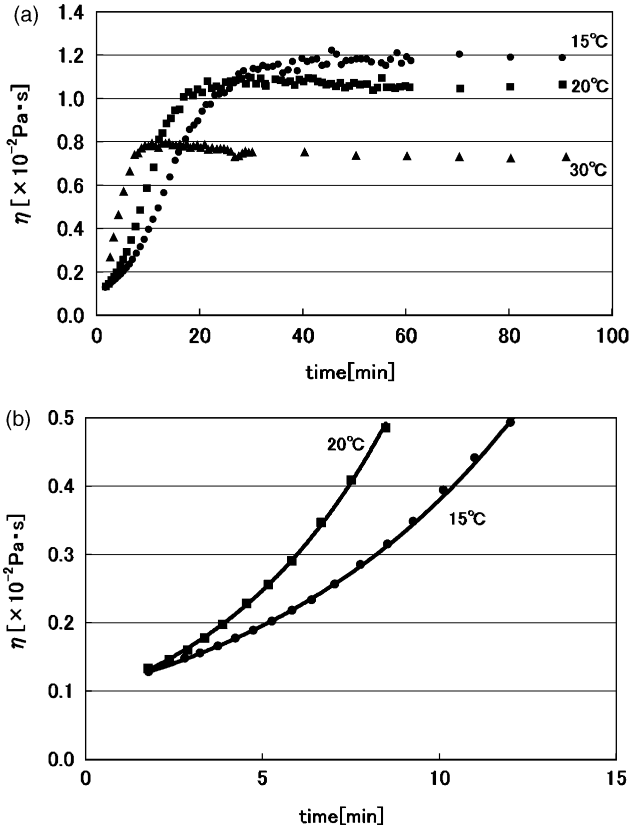

Fig. 2. (a) The viscosity–time data of 1 wt% rice starch dispersion gelatinized by 0.146 N NaOH at three different temperatures. The data series represented in terms of circle, square, and triangle were obtained, respectively, for the gelatinization at 15, 20 and 30 °C. (b) The parts of the viscosity growth data obtained at 15 and 20 °C which provide the best fittings with exponential functions of time.

The shapes of these viscosity growth curves are convex in the second halves of the whole gelatinization process, as those in the thermal gelatinization (Fig. 1). From Fig. 2(a), however, one finds the first halves of these curves to be *concave*, although the curve at 30 °C did not have enough data point and the concavity property was not clearly recognized. The concavity property of the curves at 15 and 20 °C can be more obviously demonstrated in Fig. 2(b) where the early stages of these data are enlarged. These parts of the viscosity–time data can be fitted with exponential curves

$$\eta = 0.101\exp(0.132t), \quad 1.79 \le t \le 13.13, \quad \text{at} \quad 15\ {}^{\circ}\text{C} \qquad (2)$$

$$\eta = 0.092\exp(0.197t), \quad 1.76 \le t \le 8.48, \quad \text{at} \quad 20{}^{\circ}\text{C} \qquad (3)$$

where viscosity η and time t are defined in terms of the units 10^{-2} Pa s and min, respectively. Both of the fittings are attained with markedly high accuracy ($R^2 > 0.999$). A quantitative difference between these two curves is mainly characterized in terms of an exponent.

This notable property of the viscosity growth data during the alkali gelatinization of rice starch, is qualitatively identical with that observed in our previous work where the data had been collected through the batch-type measurement with use of a cone-plate viscometer. With the present method of a continuous capillary viscometry, much smooth curves were obtained during the whole gelatinization process compared with that in the previous work, and a direct comparison between thermal and alkali gelatinization was made possible. Caused by the both types of gelatinization, viscosity (Pa s) of the samples prepared from the same starch materials evolved in time up to almost the same scale $O(10^{-3})$–$O(10^{-2})$, but along qualitatively different paths during the reaction process. This fact demonstrates that the concavity property of the viscosity growth curve in the early stage of alkali gelatinization is intrinsic to gelatinization mechanisim but *not* due to the sedimentation effect of ungelatinized starch particles.

4. Theoretical analysis and discussions

4.1. Gelatinization kinetics with mixing rule

As had been argued in the previous work, the above qualitative difference between the shapes of viscosity growth curves in the early stage of thermal and alkali gelatinization can be described by choosing different types of viscosity mixing rule for ungelatinized and gelatinized fractions of starch, even on the common basis of the first-order reaction hypothesis for gelatinization degree.

Similarly to a standard kinetic treatment (e.g. Lund, 1984), the basic scheme of our theory is to consider a starch gelatinization phenomenon as a kind of chemical reaction process, in which an ungelatinized part UG of starch is changed to a gelatinized part G. During the reaction, the sum of their amounts [UG] and [G] should hence equal to the amount of an ungelatinized part UG at the initial time (denoted by the symbol 0) of gelatinization, i.e.

$$[\mathrm{UG}] + [\mathrm{G}] = [\mathrm{UG}]_0 \tag{4}$$

The first-order reaction hypothesis for gelatinization kinetics is that gelatinization degree x defined as the ratio of [G] to $[\mathrm{UG}]_0$ obeys the following equation

$$\frac{dx}{dt} = K_1(1-x) \tag{5}$$

with K_1 being a reaction rate constant of $(\text{time})^{-1}$ dimension. Under the initial condition $x(t=0)=0$, Eq. (5) possesses the solution

$$x = 1 - e^{-K_1 t} \tag{6}$$

In the past works on starch gelatinization kinetics, gelatinization degree has been related with various observable quantities (Lund, 1984). For example, one may consider the following simple relation between gelatinization degree and viscosity η of the sample

$$\eta = \eta_{\mathrm{UG}}(1-x) + \eta_{\mathrm{G}}x \tag{7}$$

where η_{UG} and η_{G} ($>\eta_{\mathrm{UG}}$) denote, respectively, the proper viscosity of ungelatinized (UG) and gelatinized (G) parts of the sample.

Equation (7) is a standard type of viscosity mixing rule where viscosity η itself obeys a linear additive law. Substituting of the solution (6) for x into this mixing rule (7) leads to the time evolution of viscosity. One finds its second derivative with respect to time to be negative at finite t

$$\frac{d^2\eta}{dt^2} = -(\eta_{\mathrm{G}} - \eta_{\mathrm{UG}})K_1^2 e^{-K_1 t} < 0 \tag{8}$$

This implies that the viscosity–time curve is convex during the whole gelatinization process. This consequence is consistent with the results of thermal starch gelatinization including the present case. Such a kinetic treatment is essentially identical with that taken by Kubota et al. (1979) who considered as a rheological observable the consistency coefficient with a constant flow behavior index.

The above kinetic treatment, however, cannot describe the viscosity growth curves observed for the present alkali gelatinization which indicated a concavity property $d^2\eta/dt^2 > 0$ up to some gelatinization time. Therefore, if one wishes to maintain the fundamental hypothesis of first-order reaction (5), he must adopt other types of mixing rule than Eq. (7).

In the previous work, we thus considered that fluidity, i.e. the inverse of viscosity η^{-1} should obey a linear additive law

$$\phi = \phi_{\mathrm{UG}}(1-x) + \phi_{\mathrm{G}}x \tag{9}$$

where $\phi(\equiv \eta^{-1})$ is the fluidity of the sample, and $\phi_{\mathrm{UG}}(\equiv \eta_{\mathrm{UG}}^{-1})$ and $\phi_{\mathrm{G}}(\equiv \eta_{\mathrm{G}}^{-1})$ satisfies the inequality $\phi_{\mathrm{UG}} > \phi_{\mathrm{G}}$. Inserting Eq. (6) into the mixing rule (9), we get the time evolution of fluidity

$$\phi(t) = \eta^{-1}(t) = \phi_{\mathrm{G}} + e^{-K_1 t}(\phi_{\mathrm{UG}} - \phi_{\mathrm{G}}) \tag{10}$$

From this follows the second derivative of viscosity with the result

$$\frac{d^2\eta}{dt^2} = \frac{K_1^2(\phi_{\mathrm{UG}} - \phi_{\mathrm{G}})e^{-K_1 t}}{(\phi_{\mathrm{G}} + (\phi_{\mathrm{UG}} - \phi_{\mathrm{G}})e^{-K_1 t})^3}((\phi_{\mathrm{UG}} - \phi_{\mathrm{G}})e^{-K_1 t} - \phi_{\mathrm{G}}) \tag{11}$$

where the first fractional factor in the right-hand side is always positive. The sign of the second derivative is hence determined by the second factor $D(t) \overset{\mathrm{def}}{=} (\phi_{\mathrm{UG}} - \phi_{\mathrm{G}})e^{-K_1 t} - \phi_{\mathrm{G}}$. This factor $D(t)$ decreases monotonically with time and takes at the equilibrium a negative value $D(\infty) = -\phi_{\mathrm{G}}$. Therefore, if $D(0) = \phi_{\mathrm{UG}} - 2\phi_{\mathrm{G}}$ is positive, i.e. $\eta_{\mathrm{G}} > 2\eta_{\mathrm{UG}}$, the sign of second derivative can be positive $d^2\eta/dt^2 > 0$ up to some finite time t^* at which the viscosity growth curve indicates an inflection point with the viscosity $\eta^* = \eta_{\mathrm{G}}/2$.

The condition $\eta_{\mathrm{G}} > 2\eta_{\mathrm{UG}}$ could reasonably be satisfied for real starch samples including the present case. The above theoretical consequence implies that a shape of the viscosity–time curve is *concave* in the first half ($t < t^*$) of gelatinization process, which is consistent with the present experimetal result for cold alkali gelatinization (Fig. 2).

4.2. Analysis of viscosity–time curves for alkali gelatinization

Under the condition $\eta_{\mathrm{UG}} \ll \eta_{\mathrm{G}}$, Eq. (10) can legitimately be reduced to the relation $\phi(t) = \phi_{\mathrm{UG}}e^{-K_1 t}$ unless $K_1 t \gg 1$. This expresses that viscosity grows exponentially $\eta(t) = \eta_{\mathrm{UG}}e^{K_1 t}$ in a certain initial stage of gelatinization in agreement with the present observation (Fig. 2(b)). Using such an exponential truncation, we could estimate from Eqs. (2) and (3) the reaction rate constants $K_1(\mathrm{min}^{-1})$ in the early stage of gelatinization to be 0.132 (15 °C) and 0.197 (20 °C), respectively. The estimated values of η_{UG} ($\times 10^{-2}$ Pa s) for them were close to each other (0.09–0.10). For reference, we would mention that, in the previous work for the 4.4 wt% rice starch dispersion gelatinized by 0.146 N NaOH at 20 °C, K_1(min^{-1}) and η_{UG} ($\times 10^{-2}$ Pa s) estimated with such an exponential approximation were about 0.165–0.168 and 0.12, respectively.

After the exponential growth period, the measured viscosity increased almost linearly with time, i.e. with the maximum growth rate, approximately at the half of the maximum viscosity η_G (Fig. 2(a)). This fact accords with the prediction from the above kinetic argument based on fluidity mixing rule. The precise determination of the position of an inflection point, however, would require more data points in each linear region.

At each temperature, the scale of η_{UG} estimated with the exponential truncation was smaller only by O(10^{-1}) than that of η_G, and the largest value of K_1t in the fitted region was 1.6. These facts suggest that the use of an exponential truncation is not valid in the present case compared with the previous case where η_G/η_{UG} was much larger due to the larger starch concentration (4.4 wt%). The precise determination of a rate constant thus necessitates an analysis based on the full content (10) of the theory.

Equation (10) is exactly transformed to

$$\ln(\phi - \phi_G) = -K_1 t + \ln(\phi_{UG} - \phi_G) \tag{12}$$

which states that a quantity $\ln(\phi - \phi_G)$ converted from the experimental η–t data should be linear in t with a coefficient K_1. The estimation of K_1 only requires the value of $\eta_G(=\phi_G^{-1})$. This value was determined rather clearly as the stable maximum value of viscosity at the equilibrium in a smooth viscosity–time curve, and this is an advantageous point of the present continuous viscometry. Note that knowledge of the value of η_{UG} is not necessary.

As has already been seen in Fig. 2(a), the magnitude of η_G depends greatly on gelatinization temperature. For example, η_G ($\times 10^{-2}$ Pa s) at 15 °C was estimated to be about 1.2. With this value, the quantity $\ln(\phi - \phi_G)$ was plotted in Fig. 3 for time ranges with three different upper limits. In Fig. 3(a) are plotted the data ($t \leq 44.7$) up to $t = 45.7$ at which the sample showed the maximum viscosity. Even in this long time period, the linearity was kept high ($R^2 = 0.947$), and the coefficient 0.134 might give the rate constant K_1(min^{-1}) averaged over the whole gelatinization period at 15 °C. The R^2 value becomes higher in the time range with a smaller upper limit, and was kept to be 0.99 up to $t \leq 35.3$ (Fig. 3(b)). The data within the very early time range $t \leq 6.4$ showed the highest linearity ($R^2 = 0.999$) with a rate constant 0.150 (Fig. 3(c)). In the time range $t \leq 13.1$ where the best exponential fitting was obtained in the above analysis, K_1 was estimated here to be 0.174 with $R^2 = 0.996$ (not shown in Fig. 3).

A similar analysis can also be applied to the data measured at 20 °C (Fig. 4). Anyhow, as seen above, the value of a rate constant estimated from a gradient of the regression line of $\ln(\phi - \phi_G)$ data fairly depends on the time range one chooses. As was suggested also in our previous work, this might be linked with the fact that the whole gelatinization process consists of multiple reaction stages characterized with different values of a rate constant. This fact was naturally expected from the past speculations (e.g. French, 1984).

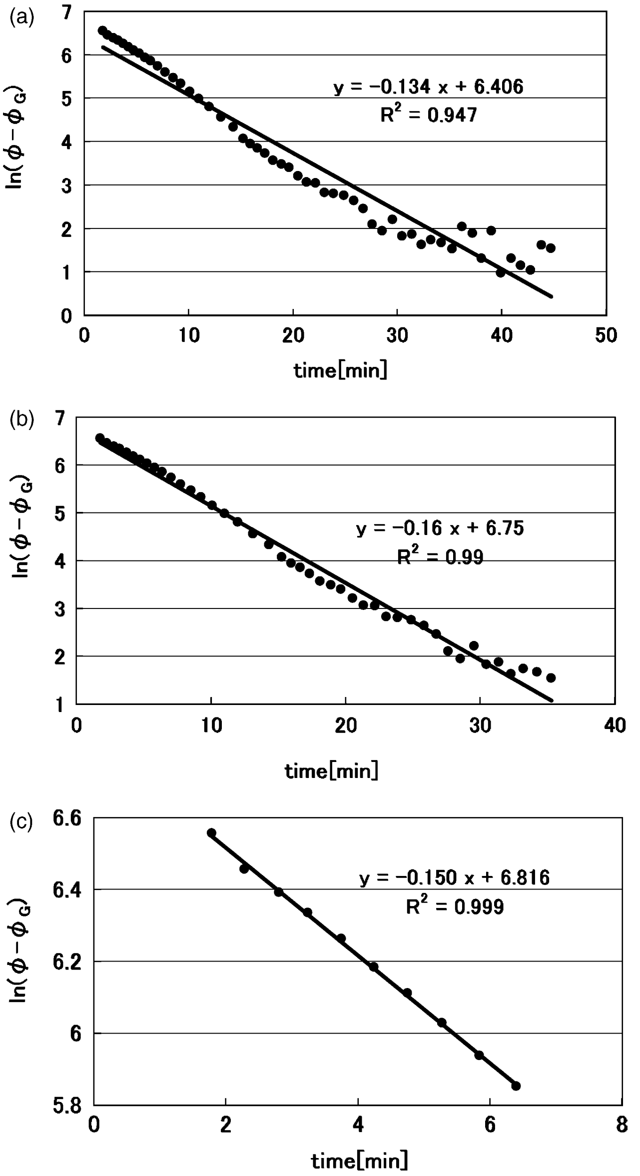

Fig. 3. $\ln(\phi - \phi_G)$ vs. time data of 1 wt% rice starch dispersion gelatinized by 0.146 N NaOH at 15 °C. The data were plotted in the time ranges: (a) t (min) ≤ 44.7, (b) t (min) ≤ 35.3, and (c) t (min) ≤ 6.4.

5. Discussions

We have observed the value of η_G to be larger at lower gelatinization temperatures (Fig. 2(a)). This would partially be originated from the fact that a cluster property of the disperse medium (a water–NaOH solution) significantly depends on temperature. At lower temperatures the mean cluster size of water molecules becomes larger and the viscosity of water solution should generally increase. Such an effect possibly enhances the viscosity of hydrocolloid dispersions, although it is difficult to actually evaluate the magnitude of this enhancement effect. Another possibility might be that the

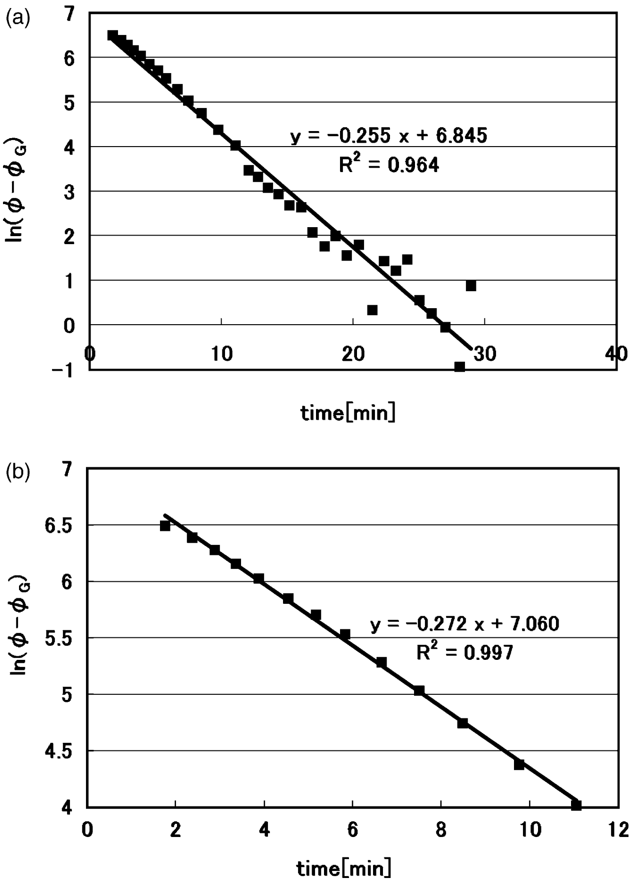

Fig. 4. $\ln(\phi-\phi_G)$ vs. time data of 1 wt% rice starch dispersion gelatinized by 0.146 N NaOH at 20 °C. The data were plotted in the time ranges: (a) t (min) ≤ 29.0 and (b) t (min) ≤ 11.1.

extent of gelatinization of starch particles depends on temperature, as was in the case of usual thermal gelatinization (Fig. 1). If this is the case, the determination of the activation energy by employing the Arrhenius model, would anyhow not be reliable (Lund, 1984).

Finally, we should comment on a possible origin of the concavity property of the viscosity growth curve for alkali gelatinization and its temperature dependence. On the first point, we already proposed in the previous work, a fundamental hypothesis based on amylose complex formation induced by strong alkali (NaOH). For the details one should refer to our previous article (Yamamoto et al., 2006), and below we present only some essential points.

In the strong alkali gelatinization of rice starch, NaOH, after penetrating into starch granule, could react with lipids originally included in amylose to generate the sodium salts of higher fatty acids. As strong surfactants these sodium salts of higher fatty acids could form strong and stable complexes with amylose (Tomasik & Schilling, 1998). As a result, the initial stage of alkali gelatinization would become unable to cooperatively induce strain in the crystallites of amylopectin. Recall here that such a semi-cooperative phenomenon has been proposed to play an important role in gelatinization process (Evans, 1986; French, 1984; Gray & Schoch, 1962; Marchant & Blanshard, 1978). The structural change described above could lead to rheologically high independency of gelatinized part and the reduction of the influence on ungelatinized part. We argued in the previous article that this enhancement of rheological independency is mathematically consistent with the fluidity mixing rule given by Eq. (9), leading to the concavity property of the viscosity growth curve.

At lower temperatures, the new complexes formed by strong alkali should be thermodynamically more stable, so that a concave region of curve might be elongated. In order to examine this quantitative prediction in real samples, the precise experimental determination of the position of an inflection point in the measured curve is necessitated. Namely, more data points must be taken over a short time range. The present work suggests that the continuous capillary viscometry could be a promising means for such an investigation. Also, the theoretical framework to allow the variety of the positions of an inflection point should be constructed. These problems both in experimental and theoretical aspects remain to be solved and shall be addressed in the future.

6. Conclusions

Using the method of continuous capillary viscometry, viscosity–time curves were obtained for rice starch dispersions gelatinized by strong alkali (0.146 N NaOH) solutions at room temperartures (15, 20, 30 °C), and by usual hot (60, 70, 75, 80 °C) distilled water. The observed curves for alkali gelatinization were more smooth during whole gelatinization than that had been obtained previously from batch-type measurement with use of a cone-plate type viscometer.

The present experiments clearly demonstrated that viscosity evolves in time with a concavity property in the first half of the cold (15, 20 °C) alkali gelatinization process. An exponential curve provided a good approximation to the time dependence of viscosity in the early stage of gelatinization. These kinetic characteristics were not observed for usual thermal gelatinization which proceeded in a full period with a convexity property.

The samples gelatinized by NaOH solutions at lower temperatures reached larger viscosity at the equilibrium and seemed to show a concavity property more clearly.

Such a novel kinetic process with a concavity property for the cold alkali gelatinization was argued to be described theoretically in terms of the first-order reaction hypothesis for gelatinization degree, combined with the mixing rule of viscosity which is different from that has been applied to thermal gelatinization.

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