An Inflection Point in the Observable Growth Curve for General-order Reaction Process with Power-law Mixing Rule

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Theoretical treatment of composite or reaction system of food materials requires the mathematical modelling of mixing rule for observables such as thermal, electrical and rheological ones. Typical models are of series, parallel and random type, and are generalized here to a power-law model. In the previous report, the present author developed the kinetics for a general observable $o$ in the first-order reaction process ($R \rightarrow P$) where $o$ increases with reaction order $x \equiv [P]/([R]+[P])$ through a power-law type mixing rule $o = (1-x) o_R + xo_P$ with $o_R < o_P$, and provided a formula for an inflection point (IP) in the observable growth curve. In this article was given a similar argument for IP in the $o$-growth curve for a general $n$-th order reaction process $dx/dt = Kn(1-x)^n$, and the following consequences were obtained. For $\nu \geq 1$, the $o-t$ curve is convex everywhere ($o < o_P$) for any positive $n$. When $n$ is restricted to be a positive integer, the $o-t$ curve can possess IP in the region $-1 < \nu < 1$ with smaller values of $n (=1, 2 \cdots)$, and so for $\nu \leq -1$ only with $n=1$. For $\nu < 1$, the value of observable at IP is given by the formula $o^* = ((1-\nu)/(1-(1-n) \nu))^{1/\nu} o_P$, and the growth rate $do/dt$ depends on $o_R/o_P$ for $n \neq 1$. The results for the power-law rule coincide in the $\nu \rightarrow 0$ limit with those obtained for a logarithmic rule (a random model). An inverse observable $o^{-1}$ decreases with a concavity property for any positive integer $n$.

Key words: Inflection point, Mixing rule, Observable, Power-law, Reaction process

1. Introduction

For the study of reaction phenomena of food materials, such as starch gelatinization and gelation of various hydrocolloids (e.g. protein and polysaccharides), it is a useful approach to concentrate on the time dependence of a certain (rheologically, thermally or electrically) observable quantity of reacting samples with other environmental conditions fixed constant. This type of method called ‘kinetics’ is widely accepted as of importance for studying non-equilibrium phenomena. It is expected that knowledge obtained from kinetic studies could serve to elucidate the underlying reaction mechanisms. For industrial applications, e.g. those to food engineering and processing, such knowledge is essential for a good process design.

The usual basic hypothesis of general reaction kinetics is that some fundamental physicochemical quantities such as molar concentrations of reactants should obey $n$-th order reaction rate equations where a reaction order $n$ is normally considered to take positive integers 1, 2, 3\ldots. For a simple reaction process ($R \rightarrow P$), this rate equation can be expressed in terms of a single reaction degree $x(t) = [R]/([R]+[P])$ (a fraction of product) as a differential equation with respect to reaction time $t$

$$\frac{dx}{dt} = K_n(1-x)^n$$  (1)

where $K_n$ is a rate constant of $(time)^{-1}$ dimension.

For example, several differential scanning calorimetry studies of starch gelatinization have revealed that gelatinization degree $x(t)$ of the ordinary i.e. thermal starch gelatinization follows approximately a simple first-order kinetics $dx/dt = K_1(1-x)$ [1-7]. According to this equation, gelatinization degree $x$ increases from zero to 1 with a convexity property ($d^2x/dt^2 < 0$); a gelatinization rate $dx/dt$ takes the maximum at the initial time $t=0$.

However, a certain, e.g. rheologically, thermally or electrically observable quantity $o$ of the reacting sample should be a certain function $o(x)$ of reaction degree $x$. Therefore, even if reaction degree $x(t)$ undergoes a simple reaction rate equation, the time dependence of observable, being an implicit function $o(x(t))$ of reaction time $t$, becomes generally nontrivial. This generally means that
“kinetics of observable”, i.e. the behavior of an increasing rate $d\alpha/dt$ of some observable quantity could even qualitatively differ from that of reaction degree $x(t)$ itself.

On this issue, there exists an interesting experimental evidence exemplifying that a rheological observable (viscosity) of the same species of sample can show qualitatively different kinetic behaviors. For the usual thermal gelatinization of rice starch dispersed in a neutral water, the viscosity ($\eta$) – time curve shows a convex behavior ($d^2\eta/dt^2 < 0$) during all the gelatinization process [8]. On the basis of the first-order reaction hypothesis, Kubota et al. [8] analyzed the $\eta$–growth curves using the relation

$$\eta(x) = \eta_{UG}(1-x) + \eta_G x \quad (2)$$

where $\eta_{UG}$ and $\eta_G$ denote proper viscosity expressed as that observed at the initial and at the equilibrium states of gelatinization respectively.

However, we have recently discovered for the rice starch dispersion gelatinized at room temperature ($15, 20^\circ$C) by strong alkali (0.146N NaOH) that the $\eta$–t curve exhibits a concavity property ($d^2\eta/dt^2 > 0$) in the early stage ($t < t^*$) of the gelatinization process [9,10]. In the latter the maximum increasing rate of viscosity $d\eta/dt$ was reached at some finite gelatinization time $t^*$ at which the $\eta$–t curve shows an inflection point (IP) at approximately the half of maximum viscosity $\eta_G$. Instead of using Eq. (2) we then analyzed the curves by use of the relation

$$\eta^{-1}(x) = \eta_{UG}^{-1}(1-x) + \eta_G^{-1} x \quad (3)$$

This treatment actually predicts IP to exist at $\eta^{-1} = \eta_{UG}/2$ [10]. The relations (2) and (3) are typical examples of mixing rule for observable, and have the same forms as known as geometry–based (series and parallel) models in the context of thermal conductivity of composite (food) system [11,12]. In the present (food) reaction system, however, the observed position of IP should generally take an arbitraly value ($0 < \eta^*/\eta_G < 1$) depending on experimental conditions.

In view of these backgrounds, the present author developed in the previous report [13] a theoretical analysis for the kinetics of a general observable $\alpha$ which increases with time through a power-law type mixing rule in the first-order reaction process. From dimensional consideration, the power–law model should have the following form

$$\alpha^* = (1-x)\alpha_R + x\alpha_P \quad (4)$$

where $\alpha_R$ and $\alpha_P$ represent the values of an observable being proper to a reactant and a product respectively ($\alpha_R < \alpha_P$).

Physicochemically, a form of the mixing rule should reflect a mixing state of $R$ and $P$ parts of sample materials. The rules (4) at $\nu = \pm 1$ correspond to series and parallel models, and that at the limit $\nu \rightarrow 0$ (a logarithmic rule) has been called a random model [11]. The present power–law model (4) can then be regarded as a generalized version of these composition models having been proposed in the studies of transport phenomena, and can be applied in the reaction phenomena where an observable $\alpha$ of the whole system depends even nonlinearly ($\nu \neq 1$) on reaction degree $x$. Such a case would occur for example in the above mentioned viscosity growth process in alkali starch gelatinization under different conditions of alkali normality and temperature.

In the previous report [13], it was demonstrated for $\nu < 1$ that an observable – time curve could possess IP at $\alpha^* = (1−\nu)^k \alpha_P$ with the maximum growth rate $d\alpha/dt = (1−\nu)^k\alpha_P K_1$. These results coincide in the $\nu \rightarrow 0$ limit with those obtained for a logarithmic ($\ln \alpha$) type mixing rule. For any first–order reaction with IP found in the observable growth curve, we can thus determine through the above formula the mixing parameter $\nu$ from the position of IP ($\alpha^*$) relative to the equilibrium value ($\alpha_G$), observed experimentally.

Certainly, however, not all of the reactions with food materials are of first order. The reaction caused by multiple collisions of molecules could exist for food materials. For example, some process of biopolymer gelation close to the gel point was described as the second-order reaction [14,15]. Lopes da Silva et al. in fact obtained, in the gelation process of high-methoxyl pectins/sucrose system, the storage modulus – time curves showing IP [15]. We therefore believe that, from a generic viewpoint of food engineering and processing, whether IP could exist or not for the reaction (1) with a general order $n = 1, 2, 3 \cdots$ is an interesting problem, and that a general formula of IP, if present, would be useful for the kinetic study of reaction with wide range of food materials.

Another interesting issue to be examined is a possibility for the existence of IP in an inverse observable $\alpha^{-1}$ – time curve. For example, when viscosity (or elastic modulus) grows with the mixing rule (4) in starch gelatinization (or polymer gelation) process, can fluidity (or compliance) – time curve have IP?

In the present work, we address these theoretical issues that remain to be solved in the previous work [13]. Technically, we will adopt an approach being a little bit different from that in the previous work. We shall combine
the mixing rule (4) with the reaction rate equation (1) without using its explicit solution $x(t)$. This approach will enable us to avoid complicated calculations and to make the argument transparent.

2. General $n$-th order kinetics with a general power-law mixing rule

From Eq. (1) follows

\[ \frac{d^2x}{dt^2} = -nK_n^2 (1-x)^{2n-1} \leq 0 \]  

(5)

A reaction degree $x(t)$ evolves in time from 0 to 1 with a convexity property for all positive $n$.

As in the previous work [13], we introduce dimensionless (relative) parameters $O=\rho_o/\rho_p$, $\tilde{O}=\rho_R/\rho_p<1$, and we would call them ‘relative observable’ and ‘relative proper observable’ respectively. The mixing rule (4) then reads as

\[ O' = \tilde{O} + \gamma x \]  

where a constant $\gamma$ is defined by $\gamma = 1 - \tilde{O}'$ and satisfies the relation $\gamma < 0$ for any $v \neq 0$.

Differentiating of the mixing rule (6) with respect to time provides the relation

\[ \frac{dO}{dt} = v^{-1} \gamma O^{1-v} \frac{dx}{dt} \]  

(7)

The second derivative of relative observable is then calculated to be

\[ \frac{d^2O}{dt^2} = v^{-1} \gamma O^{1-v} \left( \frac{dx}{dt} \right)^2 + \frac{d^2x}{dt^2} \]  

\[ = v^{-1} \gamma K_n^2 (1-x)^{2n-1} \left( (v^{-1} - 1) O^{1-v} - n \right) \]  

(8)

where the reaction rate equation (1) and its derivative (5) have been used. A term in the large parentheses in the right-hand side of Eq. (8) can be rewritten with the help of the relation $\gamma = 1 - O'$ being derived from the mixing rule (6) and a definition of $\gamma$. Eq. (8) is then transformed to the following form

\[ \frac{d^2O}{dt^2} = v^{-1} \gamma K_n^2 (1-x)^{2n-1} D(O) \]  

(9)

with a factor

\[ D(O) = (1-v^{-1})(1-O') - n \]  

(10)

In the right-hand side of Eq. (9), a product of factors except $D(O)$ is positive definite during the reaction process ($0 \leq x < 1$). Therefore, the concavity property of an observable - time curve, namely the positivity of Eq. (9) is equivalent to the positivity of $D(O)$.

This factor $D(O)$, as an implicit function of $t$, depends on time through relative observable $O$. One can find $D(O)$ to depend monotonically on time, since $D(O)$ is a monotone function of an observable $O$ and $D(O)$ itself is a monotonically increasing function of time as was checked from Eq. (7). Further, the function $D(O)$ takes at the equilibrium ($O = 1$) a negative constant $D(1) = -n$, implying that the observable growth curve is always convex near the equilibrium. At the initial state ($O = \tilde{O}=\rho_o/\rho_p$), $D(O)$ takes

\[ D(\tilde{O}) = (1-v^{-1})(1-\tilde{O}') - n \]  

(11)

Hence, the possibility that an observable - time curve shows a concave behavior in the early stage of reaction process depends on the positivity of the right-hand side of Eq. (11), being a ‘discriminant’ for the present issue. In other words, the problem that remains is to examine whether the following inequality can hold or not

\[ n < (1-v^{-1})(1-\tilde{O}') \equiv f(v) \]  

(12)

which is reduced at $n=1$ to Eq. (9) in the previous report [13].

We now explicitly search for a solution of the inequality (12) for each value of $v$ ($\neq 0$), noting that relative proper observable $\tilde{O}$ is a small positive constant. If a mixing parameter $v$ is larger than or equal to 1, the first and the second factors of $f(v)$ are restricted to be in the regions $0 \leq 1-v^{-1} < 1$ and $1-\tilde{O}' < 0$ respectively. This means $f(v) \leq 0$, and is left no possibility for the existence of a positive $n$ to satisfy the inequality (12). An observable grows with time keeping a convexity property everywhere ($\rho_o \leq \sigma < \rho_p$).

In the region $v < 1$, there exists a possibility that the inequality (12) holds, and depends on a scale of relative proper observable $\tilde{O}=\rho_R/\rho_p$ (Table 1). In the followings, we will consider for simplicity only the case that a reaction order $n$ takes a positive integer.

Let us consider first the case that a mixing parameter is in the positive region $0 < v < 1$. For example, when $v$ equals to $1/2$, $f(v)$ takes $\tilde{O}' = 1/2$ and Eq. (12) is reduced to $\tilde{O} < 1/(1+n)^2$. Then, if relative proper observable is small enough to satisfy $\tilde{O} < 1/(1+n)^2 = 0.25$, one finds $n=1$ to satisfy the condition. If $\tilde{O} < (1/3)^2 = 0.111\ldots$, both $n=1$ and 2 are solutions. For a smaller value of $\tilde{O}$, the possibility is left for a larger integer $n$, i.e. a higher reaction order.

For the case $v = 1/4$, $f(v)$ takes $3(\tilde{O}' - 1)$ and Eq. (12) is reduced to $\tilde{O} < (3/(3+n))^4$. Then, if $\tilde{O} < (3/4)^4 = 0.3164\ldots$, $n=1$ satisfies the condition, and if $\tilde{O} < (3/5)^4 = 0.1296$, both $n=1$ and 2 are the solutions.

For the case that a mixing parameter is in the negative region $-1 < v < 0$, we have similar possibilities as those for
the case $0 < \nu < 1$. For example, when a mixing parameter $\nu$ is $-1/2$, $f(\nu)$ takes $3(1-\bar{O}^{1/2})$ and Eq. (12) is reduced to $\bar{O} < ((3-n)/3)^{1/2}$. Therefore, if $\bar{O} < (2/3)^{1/2} = 0.4444\ldots$ at least $n=1$ is a solution, and if $\bar{O} < (1/3)^{1/2} = 0.111\ldots$ both $n=1$ and 2 are the solutions. When $\nu = -1/4$, at most $n=1, 2, 3$, and 4 can satisfy the inequality (12) and the upper limit of actual solutions, i.e. the maximum of a possible reaction order $n$ is determined by the magnitude of relative proper observable $\bar{O}$ (Table 1).

In the case that a mixing parameter $\nu$ is equal to or smaller than $-1$, two factors of $f(\nu)$ in Eq. (12) are in the regions $1 < 1 - \nu^{-1} < 2$ and $0 < 1 - \bar{O}^{1} < 1$ respectively. Accordingly, at most $n=1$, i.e. the first-order reaction can be a unique solution, the actual possibility of which depends on the magnitude of $\bar{O}$. For example, when a mixing parameter $\nu$ equals to $-2$, $f(\nu)$ takes $3/(2)(1-\bar{O}^{1})$, and Eq. (12) is reduced to $\bar{O} < ((3-2n)/3)^{1/2}$. If and only if $\bar{O} < (1/3)^{1/2} = 0.5773\ldots$, the condition (12) is realized for $n=1$.

In summary, when a mixing parameter is in the regions $\nu < 0$ and $0 < \nu < 1$, an observable - time curve exhibits a concavity property in the early stage of reaction process if relative proper observable $\bar{O}$ is small enough to satisfy the inequality

$$\bar{O} < \left(\frac{1-\nu}{1-(1-n)\nu}\right)^{1/2}$$

(13)

This condition (13) was directly derived from the inequality (12). In addition, for the case $\nu < 0$, the upper bound for
a possible reaction order exists $n < 1 - \nu^{-1}$. In contrast, for the case $0 < \nu < 1$, the upper bound of $n$ is absent; any natural number can be a solution. The actual solutions are determined by the physical condition (13). In Table 1 are listed some examples ($\nu = 1/2, 1/4, -1/4, -1/2, -1, -2$) of the function $f(\nu)$ and the corresponding possible solutions of $n$ with the condition for relative proper observable $\tilde{O}$.

Under the condition (13), an observable - time curve possesses IP at the relative observable given by

$$O^* = o^*/o_p = \left( \frac{1 - \nu}{1 - (1 - n) \nu} \right)^{1/n}$$  \hspace{1cm} (14)

This formula can be derived as the solution of $D(O) = 0$. From this formula with the mixing rule (6) follows the reaction degree at IP, as given by $\nu' = 1 - n \nu'^{-1} (1 - (1 - n) \nu)^{-1}$. At this IP, the relative observable grows with the maximum rate, calculated as

$$\frac{dO}{dt} \bigg|_{\nu'} = n^n (1 - \nu)^{1+1-n} (1 - (1 - n) \nu)^{-1} \gamma^{1+1-n} (\nu - 1)^{1-n} K_0$$  \hspace{1cm} (15)

The above results for IP are respectively $n$-generalized expressions of $O^*$, $x^*$ and $dO/dt |_{\nu'}$ having been found for the first-order reaction [13]. The time $t^*$ at IP, if desired, can be obtained from $x^*$ by solving the rate equation (1). Eq. (14) indicates that the observable $o^*$ at IP is, for every case, proportional to proper observable $o_p$ with a proportional constant depending only on $n$ and $\nu$. In contrast, as seen in Eq. (15), the maximum growth rate of observable depends on relative proper observable in a nonlinear way (recall that $\gamma = 1 - \tilde{O}^{-1}$), except for the first-order reaction.

For the expression of $O^*$ in Eq. (14) to be a well defined continuous function of $\nu$, the positivity of the term in large parentheses is necessary, i.e. $(1 - \nu)(1 - (1 - n) \nu) > 0$. For the first-order reaction ($n = 1$), this inequality just requires $\nu < 1$ with no lower bound. Whereas for a higher-order reaction ($n > 1$) with $\nu < 1$, it gives the lower bound for $\nu$: $\nu > (1 - n)^{-1}$, which is formally equivalent to that appeared above $(n < 1 - \nu^{-1})$. For example, it gives $\nu > -1$ for the second-order reaction, $\nu > -0.5$ for the third-order reaction, and $\nu > 0$ for $n = \infty$. Fig. 1 displays the $\nu$-dependence of $O^*$ in the region $-1 \leq \nu < 1$ for the reaction order $n = 1, 2, 3$ and 4. $O^*$ has the maximum for a higher-order reaction ($n \geq 2$), which decreases with the increase of $n$ (Fig. 1).

### 3. Continuity at $\nu = 0$: a logarithmic case

As a substitute of an exceptional case ($\nu = 0$) of the power-law type mixing rule (4), we consider the logarithmic mixing rule expressed by

$$\ln o = (1 - \nu) \ln o_R + \nu \ln o_p$$  \hspace{1cm} (16)

or in terms of dimensionless variables,

$$\ln O = (1 - \nu) \ln \tilde{O}$$  \hspace{1cm} (17)

Eq. (16) is equivalent to $o = o_R\nu + o_p$ (a random model) and appears at the limit $\nu \to 0$ of the power-law model (4). Taking time derivatives by use of Eq. (1), we get

$$\frac{dO}{dt} = (\ln \tilde{O}^{-1}) K_0 (1 - \nu)^{1-n} O$$  \hspace{1cm} (18)

and

$$\frac{d^2O}{dt^2} = (\ln \tilde{O}^{-1}) K_0^2 (1 - \nu)^{2-n} O (\ln O^{-1} - n)$$  \hspace{1cm} (19)

Eqs. (18) and (19) indicate that under the condition $\tilde{O} < e^2$, an observable - time curve possesses IP at which $O^* = e^n$, observable - time curve possesses IP at which $O^* = e^n$, $x^* = 1 - n (\ln O^*)^{-1}$ and $dO/dt |_{\nu^*} = n e^n (\ln O^*)^{1-n} K_0$.

![Fig. 1 Ratios ($O^*$) of the observable $o^*$ at IP to that $o_p$ at the equilibrium for the first-order ($n=1$), second-order ($n=2$), third-order ($n=3$) and fourth-order ($n=4$) reactions, and their dependence on a mixing parameter in the range $-1 \leq \nu < 1$.](image)
Noting the elementary mathematical formulas: \( \lim_{v \to 0} (1 - v)^{-1} = e \), \( \lim_{v \to 0} v^{-1} = -d \tilde{O}^1 / dv \bigg|_{v=0} = \ln \tilde{O}^{-1} \), one can confirm that all the results derived in Sec. 2. for the power-law rule coincide in the \( v \to 0 \) limit with those derived for the present logarithmic rule. The \( v \)-dependence of the results including at \( v = 0 \) is thus continuously \( (-\infty < v < \infty) \) realized.

### 4. Kinetics of inverse observable

In this section, we examine whether an inverse \( o^{-1} \) of the variable \( o \) that increases with time under a power-law mixing rule (4), can have IP in its decreasing (\( o^{-1} \)-t) curve.

From Eq. (6) follows \((O^{-1})^{-1} = (\tilde{O}^{-1})^{-1} + \gamma x \). This means that relative inverse observable \( O^{-1} \) obeys the same form of the mixing rule as Eq. (6) for which \( O, v, \tilde{O} \) and \( \gamma \) should be replaced with \( O^{-1}, -v, \tilde{O}^{-1} \) and \( \gamma \) respectively. Then, from the expressions of Eqs. (7) and (9), we obtain

\[
\frac{dO^{-1}}{dt} = -v^{-1} O^{-1} \frac{dx}{dt} \tag{20}
\]

\[
\frac{d^2O^{-1}}{dt^2} = v^{-1} \gamma K_2 (1-x)^{2+n-1} O^{-1} \tag{21}
\]

where a product of factors except for a new factor \( E(O) = (1+\nu^{-1})(O^{-1} - 1) + n \) is positive definite. Eq. (20) shows that an inverse observable \( O^{-1} \) continues to diminish from \( o^{-1} \) to \( o^{-1} \) as reaction evolves in time.

The factor \( E(O) \) in Eq. (21), depending monotonically on time, takes at the equilibrium a positive value \( E(O=1) = n \). IP could then exist in the \( o^{-1} \)-t curve only if \( E(O) = (1+\nu^{-1})(O^{-1} - 1) + n \) is negative. In the region \(-1 < v \), however, one finds after the similar consideration to that having been done for D(\( \tilde{O} \)) that the present discriminant \( E(\tilde{O}) \) turns out to be positive valued with any positive \( n \). If a reaction order \( n \) is further restricted to be a positive integer, \( E(\tilde{O}) \) is found to be positive definite in the region \( v < -1 \) as well.

For the similar argument, we have for the logarithmic mixing rule (17)

\[
\frac{dO^{-1}}{dt} = -(\ln \tilde{O}^{-1}) O^{-1} \frac{dx}{dt} \tag{22}
\]

\[
\frac{d^2O^{-1}}{dt^2} = (\ln \tilde{O}^{-1}) O^{-1} K_2 (1-x)^{2+n-1} (\ln \tilde{O}^{-1} + n) \tag{23}
\]

Eqs. (22) and (23) show that \( dO^{-1}/dt \) is negative definite and that \( d^2O^{-1}/dt^2 \) is positive definite during reaction (0 \( \leq x < 1 \)) for any positive \( n \).

We thus conclude that, an inverse observable – time curve is concave everywhere in the mixing parameter region \(-1 \leq v \) with any positive reaction order \( n \), and is so

for any \( v \) with a positive integer \( n \).

### 5. Conclusions and comments

We have provided a theoretical analysis for the kinetics of an observable \( o \) in a general \( n \)-th order reaction process \( dx/dt = K_n (1-x)^n \) where \( o \) increases with reaction order \( x \) through a power-law type mixing rule \( o' = (1-x) o_R^\nu + x o_P^\nu \) with \( o_R < o_P \).

In the region \( v \geq 1 \), an observable – time curve is convex everywhere (\( t < \infty \)) for any positive \( n \). In the region \( v < 1 \), if \( o_R/o_P < ((1-v)/(1-(1-n) v))^{1/n} \), an inflection point (IP) exists in the observable – time curve at \( o' = ((1-v)/(1-(1-n) v))^{1/n} o_P \) with the growth rate \( do/dt \), depending on \( o_R/o_P \) for \( n \neq 1 \). The results for a power-law rule coincide in the \( v \to 0 \) limit with those obtained for a logarithmic rule. An inverse observable \( o^{-1} \) decreases in time with a concavity property for any positive integer \( n \).

Finally, we add two comments on the actual application of the present results to the kinetic analysis of reaction process with IP.

The above formula for \( o' \) shows that a ratio of the value at IP to that at the equilibrium is related with a reaction order and a mixing parameter, and is free from a rate constant, as was naturally expected from the dimensional consideration. This implies that, if a reaction order could be known or assumed in advance, a mixing parameter can be determined through the formula from \( o' \) and \( o_P \) observed experimentally. This predictive power is not lost even for the multi-stage reaction characterized with multiple values of a rate constant.

We have carried out the present analysis without using the explicit solution \( x(t) \) for each \( n \)-th order reaction rate equation. Such an approach was useful for the systematic investigation of IP in an observable – time curve. In order to complete the kinetic analysis, i.e. to study the rate constant in a given reaction phenomenon, however, one must consider the explicit time dependence of observable \( o(t) \) using \( x(t) \) to compare with the whole experimental data, as was presented for the case of the first-order reaction [13]. The details of this procedure would depend on a reaction order, and a higher-order (\( n \geq 2 \)) case shall be reported elsewhere [16].

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ベキ乗則型混合則をもつ一般 $n$ 次反応過程の観測量増大曲線における変曲点

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食品素材の複合あるいは反応系を理論的に取り扱うためには、熱的、電気的あるいはレオロジー的な観測量の混合則についてのモデル化が必要である。典型的なモデルは直列、並列そして乱雑型であり、それらをここではベキ乗則モデルに拡張する。前回の報告で著者は、一般的な観測量 $o$ がベキ乗則型の混合則 $o^\prime=(1-x)o_R+xo_P$ を通じて反応度 $x=\left[\frac{\left[P\right]}{\left[R\right]+\left[P\right]}\right]$ と共に増大する 1 次反応過程における観測量 $o$ の速度論を展開した。本論文では、同様の議論を、一般的な $n$ 次反応過程 $dx/dt=K_n(1-x)^n$ における観測量増大曲線の変曲点について実行し、以下の結果を得た。$
u \geq 1$ の場合、任意の正整数 $n$ について $o-t$ 曲線は常に $o<o_P$ 凸型である。$n$ が正整数に制限されるとき、$o-t$ 曲線は、$-1<\nu(\neq 0)<1$ の場合には小さい $n(=1, 2\ldots)$ の値について、$
u \leq -1$ の場合には $n=1$ についてのみ、変曲点をもち得る。$
u < 1$ の場合、変曲点での観測量の値は

$$o^\prime = \left[\frac{(1-\nu)}{(1-(1-n)\nu)}\right]^{1/\nu}$$

という公式で与えられる。そのでの増大速度 $do/dt$ は、$n \neq 1$ の場合、$o_R/o_P$ に依存する。ベキ乗則についての上記結果は $\nu \to 0$ の極限で対数則（乱雑モデル）についての結果と一致する。逆数観測量 $	ilde{o}$ は、任意の正整数 $n$ について、急型の性質を保って減少する。