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Note

Oxidation Process of Linoleic Acid Encapsulated with a Polysaccharide by Spray-Drying

Eiichiro ISHIDO,[1] Koichi HAKAMATA,[1] Yasumasa MINEMOTO,[2] Shuji ADACHI[1,*] and Ryuichi MATSUNO[1]

[1]*Division of Food Science and Biotechnology, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan*
[2]*Department of Chemical and Biochemical Engineering, Toyama National College of Technology, Hongo 13, Toyama 939-8630, Japan*

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The oxidation processes of linoleic acid encapsulated with gum arabic or maltodextrin at various weight ratios by spray-drying were analyzed using the model in which the free energy of activation for the rate constant of the autocatalytic type kinetics was assumed to obey a Gaussian distribution. The model could well express the oxidation processes, and the rate constant corresponding to the mean value of the free energy of activation, $\bar{k}$, was greater for linoleic acid encapsulated at the higher weight ratio. Emulsions of linoleic acid and maltodextrin solution with different diameters were spray-dried to prepare the microcapsules. The oxidation processes of linoleic acid within the microcapsules were also calculated using the model. The $\bar{k}$ value was smaller for the emulsion with a smaller diameter.

Keywords: oxidation, encapsulation, linoleic acid, spray-drying, free energy of activation

A polyunsaturated fatty acid (PUFA) is prone to oxidation. The encapsulation of PUFA into a powdery matrix of a wall material is achieved by two operations: one is an emulsification of the PUFA with a dense solution of the wall material, and the other is a rapid dehydration of the emulsion. The encapsulated PUFA is oxidized much more slowly than the bulk one (Maloney *et al*., 1966; Imagi *et al*., 1990; Minemoto *et al*., 1997; Minemoto *et al*., 2002). The oxidation process of PUFA encapsulated by hot-air-drying using a single-droplet method possessed two characteristic features. One is a relatively rapid oxidation during the early stage of storage; the other is a very slow progress or leveling off of the oxidation during prolonged storage. We postulated that these features were ascribable to a heterogeneity in the interaction of the PUFA molecules with the wall material, and that the PUFA molecule strongly interacting with the material was hardly oxidized and vice versa. Based on this supposition, we proposed a kinetic model for describing the oxidation process (Adachi *et al*., 2000). In the model, a free energy of activation for the rate constant of the autocatalytic-type rate equation was assumed to obey a Gaussian distribution. The model could well express the oxidation process of linoleic acid encapsulated with a polysaccharide by hot-air-drying using the single-droplet method.

In this study, the applicability of the model to the oxidation processes of linoleic acid encapsulated with gum arabic or maltodextrin at various weight ratios by spray-drying was examined for the results previously reported by Minemoto *et al*. (2002). Furthermore, the emulsions of linoleic acid and maltodextrin solution with different median diameters were spray-dried to produce microcapsules. The oxidation processes of linoleic acid within the microcapsules were observed and analyzed based on the model.

*To whom correspondence should be addressed.
E-mail: adachi@kais.kyoto-u.ac.jp

Materials and Methods

Materials Linoleic acid (purity: > 90%) and methyl palmitate (> 95%), which was used as an internal standard for the gas chromatographic determination of unoxidized linoleic acid, were purchased from Tokyo Kasei Kogyo, Tokyo. Maltodextrin with a dextrose equivalent of 2–5 was purchased from Matsutani Chemical Industries, Osaka. Tween 85 (polyoxyethylene sorbitan trioleate, HLB=11.0) was purchased from Wako Pure Chemical Industries, Osaka. All other chemicals were purchased from either Wako Pure Chemical Industries or Nacalai Tesque, Kyoto.

Encapsulation of linoleic acid with maltodextrin Maltodextrin (45 g) and Tween 85 (0.9 g) were dissolved in distilled water (300 g) with slight heating. Linoleic acid (9 g) was added to the maltodextrin solution and then emulsified with a rotor/stator homogenizer (Polytron PT20SK, Kinematica, Switzerland). The median diameter of the emulsions was 2.13 μm, which was measured using a laser diffraction particle size analyzer (SALD-2100, Shimadzu, Kyoto). The coarse emulsions were further emulsified with a high-pressure homogenizer (PEL-20, Nanomizer, Tokyo) at 500, 1000 or 1500 kg-f/cm^2 to prepare the fine emulsions. The median diameters of the emulsions were 0.604, 1.04 and 1.44 μm.

An emulsion was fed into a spray-drier using a centrifugal atomizer (LB-8, Ogawara, Kanagawa) to prepare the microcapsules. The operating conditions of the drier were the same as in our previous study (Minemoto *et al*., 2002).

Oxidation of encapsulated linoleic acid Ten milligrams of microcapsules were weighed in a flat-bottom glass cup (1.5 cm i.d. and 3 cm height). Ten to fifteen cups were prepared for each sample. The cups were placed in a desiccator where the relative humidity was regulated at 12% with a saturated solution of lithium chloride. The desiccator was stored in the dark at 37°C. At appropriate intervals, a cup was removed from the desiccator, and the amount of unoxidized linoleic acid was determined by gas chromatography according to our previous procedures (Minemoto *et al*., 2002).

A kinetic model We proposed a model by which the oxidation process of PUFA encapsulated with a wall material by hot-air-drying using the single-droplet method could be well expressed (Adachi *et al.*, 2000). The model is briefly described here.

The oxidation kinetics of the bulk n-6 PUFA could be expressed by the equation of the autocatalytic type in terms of the fraction of unoxidized PUFA, Y (Özilgen and Özilgen, 1990; Adachi *et al.*, 1995).

$$\frac{dY}{dt} = -kY(1-Y), \qquad (1)$$

where t is the time. The rate constant k is related to the free energy of activation, $\Delta G^{\neq}$, by Eq. (2) based on Eyring's theory of the absolute reaction rate.

$$k = \left(\frac{\kappa_B T}{h}\right)\exp\left(-\frac{\Delta G^{\neq}}{RT}\right), \qquad (2)$$

where h is Planck's constant, κ_B is Boltzmann's constant, R is the gas constant, and T is the absolute temperature. The difference in the susceptibility to the oxidation of the encapsulated PUFA molecules was believed to be reflected in the $\Delta G^{\neq}$, and the distribution of $\Delta G^{\neq}$ was assumed to follow the Gaussian one with the standard deviation of σ and mean value $\Delta \overline{G}^{\neq}$:

$$f(\Delta G^{\neq}) = \frac{1}{\sqrt{2\pi}\sigma}\exp\left[-\frac{(\Delta G^{\neq} - \Delta \overline{G}^{\neq})^2}{2\sigma^2}\right]. \qquad (3)$$

From these equations, the overall fraction of unoxidized PUFA at any time t, $\overline{Y}(t)$, can be expressed by Eq. (4).

$$\overline{Y}(t) = \frac{RT}{\sqrt{2\pi}\sigma}\int_{-\infty}^{\infty}\exp\left[-\frac{(RT/\sigma)^2(\ln k - \ln \overline{k})^2}{2}\right] \times \frac{e^{-kt}}{(1-Y_0)/Y_0 + e^{-kt}} d(\ln k), \qquad (4)$$

where $\overline{k}$ is the rate constant corresponding to $\Delta \overline{G}^{\neq}$, and Y_0 is the initial value of Y and reflects the initial state of the PUFA (Adachi *et al.*, 1995).

Results and Discussion

Equation (4) has two unknown parameters, $\overline{k}$ and σ. A set of $\overline{k}$ and σ values that fit the experimental $\overline{Y}(t)$ values was determined by the trial-and-error method to minimize the sum of the residual squares between the calculated and experimental results. The equation also includes another parameter Y_0. The Y_0 value for each microcapsule was not measured. Therefore, the value of 0.993 was used throughout this study as a representative one based on our previous experiences.

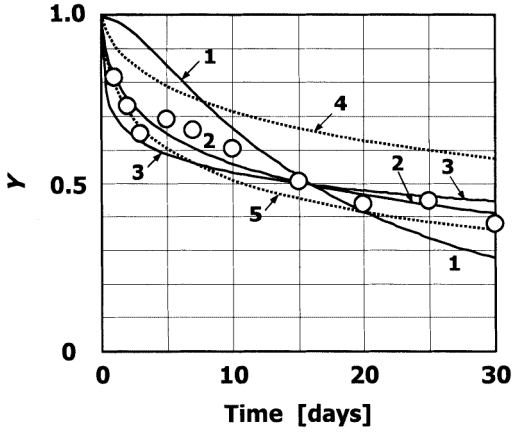

Fig. 1. Estimation of the $\overline{k}$ and σ/RT values that fit the experimentally-observed fractions of unoxidized linoleic acid encapsulated with gum arabic at a weight ratio of 0.2. The storage conditions were 37°C and 12% relative humidity. The data were cited from our previous study (Minemoto *et al.*, 2002). The solid curves, 1, 2 and 3, were calculated for σ/RT=1.0, 2.9 and 5.0 at a fixed $\overline{k}$ value of 3.4×10^{-6} s^{-1}, and the dotted curves, 4 and 5, were for $\overline{k}=1.0\times10^{-6}$ and 5.0×10^{-6} s^{-1} at a fixed σ/RT value of 2.9.

The symbols in Fig. 1, which are cited from our previous paper (Minemoto *et al.*, 2002), show the experimentally-observed oxidation process at 37°C and at nearly 12% relative humidity for linoleic acid encapsulated with gum arabic at a weight ratio of 0.2 (linoleic acid to gum arabic). The median diameter of the emulsions was 0.68 μm (Minemoto *et al.*, 2002). The solid and dotted curves were calculated for some σ/RT values at a fixed $\overline{k}$ value and for some $\overline{k}$ values at a fixed σ/RT value, respectively, using the model. The set of values of $\overline{k}=3.4\times10^{-6}$ s^{-1} and σ/RT=2.9 minimized the sum of the residual squares between the calculated and experimental $\overline{Y}$ values. The model could

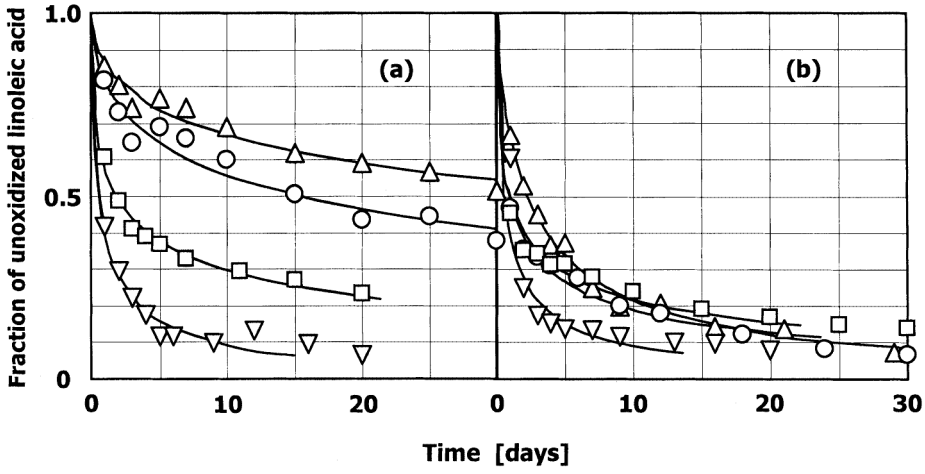

Fig. 2. Comparison of the fractions of unoxidized linoleic acid calculated using the model with those for linoleic acid encapsulated with (a) gum arabic or (b) maltodextrin at a weight ratio of (△) 0.1, (○) 0.2, (□) 0.5 or (▽) 1.0. The microcapsules were stored under the same conditions as in Fig. 1. The experimental points were cited from our previous study (Minemoto *et al.*, 2002).

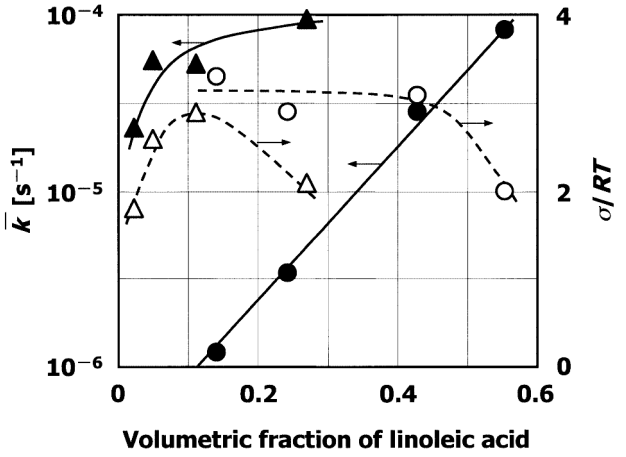

Fig. 3. Relationship between the $\bar{k}$ or σ/*RT* value and the volumetric fraction of linoleic acid in the microcapsules prepared with (●, ○) gum arabic and (▲, △) maltodextrin. The closed and open symbols represent the $\bar{k}$ and σ/*RT* values, respectively.

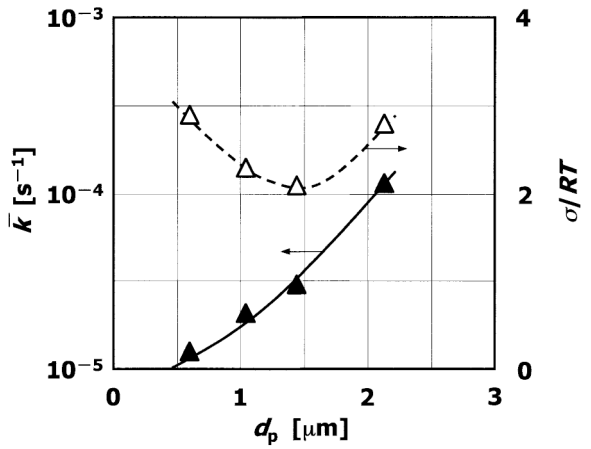

Fig. 5. Dependences of the $\bar{k}$ and σ/*RT* values on the median diameter of the emulsions prepared with linoleic acid and maltodextrin solution. The symbols ▲ and △ represent the $\bar{k}$ and σ/*RT* values, respectively.

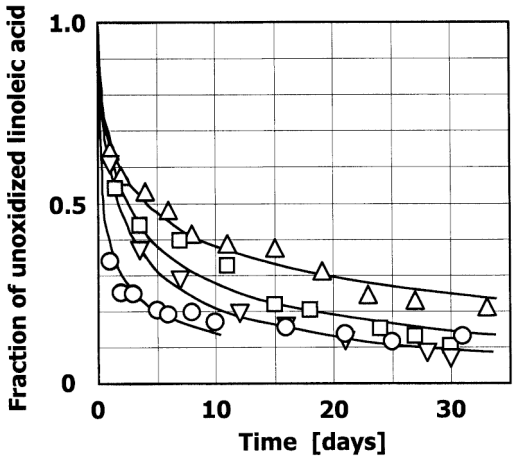

Fig. 4. The oxidation processes of linoleic acid encapsulated with maltodextrin at a weight ratio of 0.2. The storage conditions were the same as in Fig. 1. The symbols △, □, ▽ and ○ indicate the median diameters of the emulsions, which were measured prior to spray-drying: 0.604, 1.04, 1.44 and 2.13 μm, respectively. The curves were calculated using the $\bar{k}$ and σ/*RT* values that were estimated to fit the experimental points.

well express the rapid and gradual decreases in the $\bar{Y}$ value during the early and later stages of storage, respectively.

The oxidation processes of linoleic acid encapsulated with gum arabic and maltodextrin at different weight ratios (Minemoto *et al*., 2002) were also calculated using the model as shown by the solid curves in Fig. 2. Linoleic acid encapsulated with gum arabic at the smaller ratio was more resistant to oxidation. Maltodextrin was a less effective wall material for the suppression of linoleic acid through microencapsulation by spray-drying at any weight ratio. In any case, the model could well express the oxidation process of the encapsulated linoleic acid.

The volumetric fraction of linoleic acid within the microcapsule would affect its state, that is, the strength of its interaction with the wall material. The $\bar{k}$ and σ/*RT* values, which were determined to fit the experimental results in Fig. 2, are plotted versus the volumetric fraction of linoleic acid in the microcapsule (Fig. 3). The fraction was estimated under the assumptions that the weight of linoleic acid in the microcapsule was given by multiplying the weight of linoleic acid in the emulsion and its encapsulation efficiency (Minemoto *et al*., 2002), and that the densities of the linoleic acid and the wall material were 910 and 1500 kg/m^3, respectively. The encapsulation efficiency was defined as the ratio of the actual amount of linoleic acid in the microcapsules to that calculated from the composition of emulsion used to prepare the microcapsules. Because the encapsulation efficiencies of linoleic acid with maltodextrin were low, the volumetric fractions of linoleic acid in the maltodextrin-based microcapsules were low. For both wall materials, the $\bar{k}$ value was larger at the higher volumetric fraction, and reached the k value for the non-encapsulated linoleic acid (4.7×10^{-5} s^{-1}) (Adachi *et al*., 1995; Ishido *et al*., 2001). This would indicate that linoleic acid more strongly interacts with the wall material at the smaller volumetric fraction. The σ/*RT* values were about 2 to 3 irrespective of the volumetric fraction.

Figure 4 shows the oxidation processes of linoleic acid encapsulated with maltodextrin by spray-drying the emulsions with different median diameters. Although maltodextrin was a less effective wall material for suppressing the oxidation of the encapsulated linoleic acid as shown in Fig. 2, it was used because the emulsions with different median diameters could be easily prepared with the high-pressure homogenizer. Linoleic acid within the microcapsule prepared from the emulsion with smaller diameter was more resistant to oxidation. The oxidation processes were calculated using the model as shown by the solid curves; the model could well express these processes. The $\bar{k}$ and σ/*RT* values, which were estimated to fit the experimental results, are plotted versus the median diameter of the emulsions, d_p, used for preparation of the microcapsules (Fig. 5). The $\bar{k}$ value was smaller for the microcapsule prepared from the emulsion with smaller diameter. This would indicate that the fraction of linoleic acid molecules interacting strongly with maltodextrin was higher for the acid droplets of smaller diameter. The nature of the interaction, unfortunately, remains unclear. The σ/*RT* values were about 2 to 3 irrespective to the diameter of the linoleic acid droplets in the emulsion.

As mentioned above, the model could well express the oxidation of linoleic acid encapsulated with a wall material by spray-drying. This would imply there is heterogeneity in the interaction of the fatty acid with the wall material within the microcapsule.

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Nomenclatures

d_p median diameter of oil droplet in emulsion, m
h Planck's constant, Js
k rate constant, s^{-1}
$\overline{k}$ rate constant corresponding to $\Delta\overline{G}^{\neq}$, s^{-1}
R gas constant, J/mol•K
T absolute temperature, K
t time, s
Y fraction of unoxidized linoleic acid, –
$\overline{Y}$ overall fraction of unoxidized linoleic acid, –
$\Delta G^{\neq}$ free energy of activation, J/mol
$\Delta\overline{G}^{\neq}$ mean value of $\Delta G^{\neq}$, J/mol
κ_B Boltzmann's constant, J/K
σ standard deviation of $\Delta G^{\neq}$, J/mol
⟨subscript⟩
0 initial

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