Oxidation of Lipid in Bulk and Dispersion Systems

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The oxidation kinetics of unsaturated lipids was examined in bulk, emulsion and micelle systems, and the related literature was also summarized. A kinetic equation of the autocatalytic type was applicable for the lipid oxidation in all these systems. The oxidation of a lipid is affected by many factors. In a dispersion system, such as an emulsion and micelle, the size of the dispersion phase is one of these factors. In spite of a higher specific surface area, the lipid was more slowly oxidized in both the emulsion and micelle systems containing smaller particles in the dispersion phase. This fact could be explained by dilution of the substrate by the hydrophobic moiety of a surfactant for both systems.

Key words: oxidation, kinetics, dispersion system, emulsion, micelle

1. Introduction

A lipid is one of major ingredients of foods and plays important roles in nutrition and taste. However, a lipid containing unsaturated fatty acids is prone to oxidation. Lipid oxidation is one of the major causes of the deterioration of foods containing lipids, and is affected by many factors. The state and structure of lipids in foods are also considered to be important factors as well as the conditions of how the foods are stored. An emulsion and solubilization in micelles, which is a dispersion system, are common structures in lipid-containing foods for both home cooking and industry.

Rapid developments in nanotechnology have allowed us to focus on its application to foods. A decrease in the particle size of an emulsion produces an increase in the specific surface area of the particles. The high surface area would elicit an effect at the interface between the oil and aqueous phases on the reactions occurring in the emulsion or micelle. Because the lipid in the emulsion and micelle is oxidized by oxygen which is supplied through the interface, an increase in the specific surface area could possibly facilitate the oxidation.

In this context, the lipid oxidation in different systems was measured in order to examine the effect of the droplet size in the system on the oxidation kinetics. The kinetics of the lipid oxidation in a bulk system is also described because it provides basic information for analysis of the kinetics in dispersion systems.

2. Oxidation in bulk system

Lipid oxidation is a complicated process that proceeds through initiation, propagation, and termination steps. Labuza [1] reviewed the kinetics of the lipid oxidation in foods. Brimberg [2] discussed the oxidation mechanism based on kinetics. We also reported the autoxidation...
kinetics of polyunsaturated fatty acids (PUFAs) in single and two-component bulk systems.

Figure 1 shows the oxidation processes of ethyl γ-linolenate and ethyl arachidonate [3]. The oxidation processes for ethyl esters of other n-6 and n-3 PUFAs were also measured. Fatty acids with a higher degree of unsaturation more rapidly proceeded. This tendency was also observed by Miyashita et al. [4], Cho et al. [5], Nawar [7], and Shahidi and Wanasundara [8]. Based on the rate expression proposed by Bolland [8], the following equation could be derived for the oxidation of the n-6 PUFAs [3]:

\[ \frac{dY}{dt} = -kY(1-Y) \]  

(1)

where \( Y \) is the fraction of the unoxidized substrate, \( t \) is the time and \( k \) is the rate constant. The autocatalytic type equation was also applied to the lipid oxidation by Özilgen and Özilgen [9]. The integration of Eq. (1) under the condition of \( Y=Y_0 \) at \( t=0 \) gives:

\[ \ln \left( \frac{(1-Y)/Y}{(1-Y_0)/Y_0} \right) = -kt \ln \left( \frac{(1-Y)/Y}{(1-Y_0)/Y_0} \right) \]  

(2)

The parameter \( Y_0 \) was conveniently introduced to solve Eq. (1), and reflects the initial state of the used PUFA. The insert of Fig. 1 illustrates the applicability of Eq. (2) to the oxidation processes of ethyl γ-linolenate and ethyl arachidonate. Equation (1) could describe the entire oxidation process of the n-6 PUFA. The first half of the n-3 PUFA oxidation process could be described by Eq. (1), but the latter half could not. The latter half was expressed by first-order kinetics.

The stoichiometric coefficient between n-6 PUFA and oxygen was estimated through the thermogravimetric measurement during its oxidation [10]. Figure 2 shows the relationship between the relative weight gain, \( \Delta w/w_0 \), and fraction of the unoxidized substrate, \( Y \), for the oxidation of ethyl arachidonate at 50°C (\( \Delta w \) and \( w_0 \) are the increment in weight and the initial weight of the substrate, respectively). The following equation can be derived if oxygen is added to only PUFA and no degradation of the PUFA and its oxidized product occurs:

\[ \frac{d(\Delta w/w_0)}{dY} = \frac{M_X}{M_F} \frac{dn_X}{dn_F} \]  

(3)

where \( M \) and \( n \) are the molecular mass and number of moles, respectively. The subscripts F and X indicate the fatty acid (substrate) and oxygen, respectively. The number 2 on the right-hand side was ascribed to the addition of a saturated fatty acid to the substrate of the same weight as an internal standard for the gas chromatographic determination of an unoxidized substrate. The line in the figure represents the relationship when the stoichiometric coefficient, \( \gamma = dn_X/dn_F \), is 1. The plots are scattered along this line indicating that the coefficient is 1 throughout the entire oxidation process.

An actual food lipid is a mixture of acylglycerols consisting of a variety of saturated and unsaturated fatty acids. As a very simple model system of a lipid, the oxidation processes of linoleic acid or methyl linoleate in the presence of a saturated fatty acid or its methyl ester were measured [11]. Linoleic acid was oxidized more slowly at the lower weight ratios of linoleic acid to lauric acid (Fig. 3). The rate constant for the kinetic expression of the autocatalytic type was proportional to the weight fraction of linoleic acid in the mixture (Insert of Fig. 3). This dependency is reasonable because the rate expression of the autocatalytic type is derived based on the
assumption that the oxidation rate of a PUFA is proportional to both the concentrations of the unoxidized and oxidized substrates. Similar results were obtained for other combinations of linoleic acid or methyl linoleate with lauric acid or methyl laurate.

Two PUFAs or their esters were mixed, and their oxidation processes were observed [12]. The oxidation of the less-oxidative PUFA was promoted as its content in the mixture decreased, while the oxidation of the more-oxidative PUFA was delayed with a decrease in its content. A kinetic model was proposed whereby the PUFA acts as the diluent for another PUFA, and the oxidation rate of the PUFA was proportional to the product of the unoxidized PUFA concentration and the sum of the concentrations of the oxidized PUFA and the other oxidized PUFA.

### 3. Oxidation in dispersion system

Many foods are a combination of water and lipids in emulsified forms, such as oil-in-water (O/W) or water-in-oil (W/O) emulsions. This combination makes the foods sensitive to deterioration like lipid oxidation. The oxidation mechanism depends on the reactive species present in the system and their physicochemical environments [13-15]. In the O/W emulsions, the common cause of the oxidative instability is the interaction between the lipid hydroperoxides at the droplet surface and transition metals originating from the aqueous phase [16-18]. Transition metals can break down hydroperoxides of unsaturated lipids into alkoxy radical radicals. However, because this process slowly occurs, it is assumed to be less important for the oxidative stability in O/W emulsions [19]. The oxygen concentration also influences the lipid oxidation. Because oxygen is more soluble in food oils than in water [20], the lipid oxidation is promoted in the lipid phase unless oxygen is removed from the system.

An analytical technique is important to follow the progress of the lipid oxidation. Many analytical techniques have been developed to measure the oxidation of bulk fats and oils [7]. These techniques are also applicable to monitoring the lipid oxidation in emulsions or micelles, although the oil often needs to be extracted prior to the analysis. Since lipid oxidation is chemically complicated, it is advisable to use at least two or more different analytical techniques to obtain an adequate description of the process [21]. The selection of more appropriate and sensitive analytical techniques to follow the oxidation will allow a more detailed understanding of its process.

The surface charge of the dispersion phase also plays an important role in the lipid oxidation [17, 22]. Ambrosone et al. [23] studied the effect of edible surfactants on the lipid oxidation of W/O emulsions having the droplet size of less than 1 μm, and found that the oxidative stability was affected by the nature of the interface; the lower the polarity, the higher the antioxidant effect.

The interfacial layer between the oil and aqueous phases is also suggested to act as a physical barrier that separates the lipid substrates from pro-oxidants in the aqueous phase. Silvestre et al. [24] reported that the long polar head-group of a surfactant forms a thick interfacial layer which is a physical barrier to lipid oxidation.

Radical scavengers like certain sugars and amino acids in an aqueous solution can retard lipid oxidation. McClements and Decker [21] described the radical scavenging properties of various sugar and amino acid moieties of emulsifiers. Roozen et al. [25, 26] found that the oxidation rate decreased as the concentration of the oil droplets increased in a colloidal dispersed system in which linoleic acid was solubilized by a non-ionic surfactant (Tween 20). McClements and Decker [21] explained this finding by the movement of the lipids from the micelle to the interior of the emulsion droplets, and concluded that the incorporation of lipids into the emulsion droplets is more effective for protecting them against oxidation than solubilizing them in micelles. Therefore, when explaining the protection against oxidation by micelles, an approach relative to other influencing factors should always be considered. Oxidation is a complex reaction and so far no research has produced clear evi-
dence of the exact contribution of these influences although many suggestions have been made [27, 28].

Particle size is also an important factor affecting the lipid oxidation in dispersion systems. Gohtani et al. [29] reported that a decrease in the oil-droplet size of an emulsion increased the oxidation rate. Osborn and Akoh [30] reported for structured lipid based O/W emulsions that a difference in particle size between 0.1 μm and 100 μm had no effect on the lipid oxidation.

Imai et al. [31] measured the oxidation of methyl linoleate in O/W emulsions having droplet sizes from 17 nm to 8.0 μm, which were prepared using polyglyceryl monolaurate as a surfactant, at 40°C and analyzed its process based on the kinetic equation of the autocatalytic type (Fig. 4). The oxidation rate constant was lower for emulsions with smaller oil droplets. Nakaya et al. [32] also observed similar results and explained them by the wedge effect of the hydrophobic acyl residues of a surfactant. We proposed another model for describing the dependence of the rate constant on the oil-droplet size of the emulsion [31]. Under some assumptions, the rate constant $k$ for an oil–droplet covered with a surfactant is given by Eq. (4):

$$
\frac{k}{k_m} = 1 - \frac{6V_i}{a(D_o - 2D_H)}
$$

where $k_m$ is the rate constant for methyl linoleate which is not covered by the surfactant, $D_o$ is the diameter of an oil droplet fully covered with the surfactant molecules, $D_H$ is the thickness of the hydrophilic layer which covers the oil droplet, $V_i$ is the volume of a hydrophilic moiety of the surfactant, and $a$ is the residual area per surfactant molecule. Equation (4) could well explain the dependence of the $k$ value on the size of the dispersion phase as shown in the insert of Fig. 4.

Miyashita et al. [33] found that, in a colloidal dispersion system, the position of the double bond on an unsaturated fatty acid influences its oxidative stability. The closer the double bond to the methyl end, the greater its stability. In a microscale droplet in an O/W emulsion the lipid is also very susceptible to oxidation when situated at the surface [14, 34]. The position of the lipid molecule is determined by its polarity, and might indirectly influence its oxidative susceptibility. Kobayashi et al. [35] observed an increase in the oxidation products with an increase in the number of bis-allylic positions in organic solvents, but found the opposite results in an aqueous emulsion and liposomes. Chaiyasit et al. [36] concluded that the surfactant hydrophobic tail group size plays a minor role in the lipid oxidation in O/W emulsions having the oil–droplet size of around 0.4 μm.

Compounds, such as sugars and surfactants, could influence the lipid oxidation. The addition of sucrose and various other sugar alcohols to an O/W emulsion stabilized by non-ionic surfactants was found to decrease the lipid oxidation rate [37]. However, in aqueous colloidal dispersion systems, reducing sugars were shown to promote the lipid oxidation [38]. An excess of anionic surfactant in an O/W emulsion was found to increase the oxidative stability of the oil droplets [37]. This could be explained by the repulsion or attraction of transition metals to the negatively charged surface or by a tighter packing of the surfactant molecules on the droplet interface, which acted as an efficient physical barrier. The role of non-ionic surfactants, alone or in combination with other compounds, on lipid oxidation is still unclear and needs further investigation [21].

The oxidation of lipids in foods is often retarded by antioxidants. There are many kinds of synthetic or natural antioxidants with different antioxidative mechanisms. Many research studies have been done and reviewed [6, 19, 39, 40].

The fatty acids having a higher degree of unsaturation were more stable against their oxidation in aqueous colloidal dispersion systems [41–45]. A review of the peroxidation of liposomal lipids exhibited the physicochemical properties of liposomes that determined their peroxidation. These properties can help to understand or analyze the lipid oxidation behavior of the hydrophobic moiety of esters present as micelles in an aqueous solution. Ponginebbi et al. [27] found that an emulsifier protected

![Fig. 4](image-url) Oxidation processes of methyl linoleate in O/W emulsions having different initial oil droplet diameters [31]. The initial median diameters of oil droplets were (□) 43 nm, (△) 79 nm, (○) 0.92 μm and (◇) 5.9 μm. Insert: Dependence of the rate constant $k$ on the initial oil-droplet size.
the fatty acid against oxidation at concentrations higher than its Critical micelle concentration (CMC). This fact was explained by the formation of micelles and mixed micelles that diluted the substrate or replaced it at the interface thereby making it less accessible to radical attack. However, the results are not conclusive; they could also be explained by the induced oxidation competition between the emulsifier and the fatty acids. Xie et al. [46] showed a greater oxidation rate in anionic micelles than in non–ionic micelles. Din et al. [47] found that cationic and non–ionic surfactant micelles catalyze the oxidation of oxalic acid by chromium (VI), but that an anionic surfactant had no effect on the oxidation.

Chen et al. [28] enzymatically synthesized monolinoeoyl trehalose and measured the oxidation process of its linoleoyl residue at various concentrations. The process could be expressed by a rate equation of the autocatalytic type (Fig. 5). The rate constant was higher for the higher substrate concentration, but it was not in proportion to the concentration at substrate concentrations higher than its CMC as shown in the insert of Fig. 5. The migration of oxygen into the hydrophobic core of the linoleyl residues through the hydrophilic trehalose layer of the substrate micelles was suggested to affect the overall oxidation of the linoleoyl residue.

4. Oxidation in encapsulated system

Microencapsulation of a lipid as a core material with a wall material is a promising technology in the food and other industries [48]. One of the functions is the suppression or retardation of oxidation of an encapsulated PUFA [49, 50]. The oxidation of encapsulated PUFA is affected by many factors, such as temperature, relative humidity, weight ratio of the core material to wall one and drying method. Microencapsulation of a lipid consists of two steps: one is the emulsification of a core material with a dense solution of a wall material, and another is the drying of the emulsion. The oil–droplet size in the emulsion also affects the oxidation process of the encapsulated lipid. Minemoto et al. [51] reported that encapsulated linoleic acid of a small oil–droplet size oxidized more slowly than that with a large droplet size. The effects of the oil–droplet size, the weight ratio of the oil to wall material and the storage temperature on the oxidation of methyl linoleate microencapsulated with maltodextrin by spray–drying were also examined [52], and the oxidation of methyl linoleate was more retarded for the microcapsules prepared from the emulsion having smaller oil droplets (Fig. 6).

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Fig. 5 Oxidation processes of linoleoyl residue of its trehalose ester at 35°C in an aqueous solution [28]. The concentrations of the ester were (○) 0.12 mmol/L, (△) 0.17 mmol/L, (□) 0.76 mmol/L, and (●) 2.00 mmol/L. Insert: Dependence of the rate constant $k$ on the concentration of linoleoyl trehalose. The dotted line was drawn based on the assumption that the rate constant is in proportion to the substrate concentration.

Fig. 6 Oxidation process of methyl linoleate in the microcapsules at 50°C [52]. The oil–droplet sizes in the original emulsion were (○) 0.02 μm and (△) 1.0 μm.
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バルク系および分散系における脂質の酸化

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脂質は栄養面のみならず嗜好性の点でも重要な食品成分の一つである。しかし、不飽和脂肪酸を含む脂質は酸化されやすく、酸化されると臭覚を生じるのみならず、人体に好ましくない影響を及ぼす場合もある。一方、食品分野でナノテクノロジーに対する関心が高まっており、固形や液体粒子の微細化による新たな機能性をもつ食品素材の開発が期待されている。エマルションのような脂質を分散相とする系で、分散相の粒子径を小さくすると、比表面積が増大するため、脂質の酸化が促進されることが知られている。しかし、系統的な検討は十分に行われていない。そこで著者らは、水中油滴 (O/W) 型エマルションの油相ミセルに可溶化された脂質の酸化速度に及ぼす分散相の粒子径の影響について検討した。その結果を概観するとともに、関連する論文を総括する。また、分散系における脂質酸化の基礎となるバルク系での脂質の酸化反応速度についても著者の既往の研究の概要を紹介する。さらに、粉末化した脂質の酸化速度に及ぼす分散粒子径の影響についても簡単に紹介する。

バルク系での n-6 系不飽和脂肪酸 (PUFA) の酸化過程は自己触媒の反応速度形式で表現できる。また、熱重量分析装置および定温で加熱した示差走査熱量計による測定から、n-6 系 PUFA の酸化過程における酸素との化学量論法は全期間を通じて 1 であった。さらに、n-3 系 PUFA の酸化過程の前半も自己触媒型の反応速度式で表現できた。しかし、n-3 系 PUFA の酸化過程の後半は同式で表現できず、1 次反応速度を適用した。食用脂質の複数の脂肪酸の相違に基づくトリオシルグリセロールである。その後、酸化過程に対する基礎的知見を得るために、PUFA に飽和脂肪酸またはそのエステルを混合した系における PUFA の酸化過程を測定した。飽和脂肪酸は PUFA に対する抑制剤として作用し、酸化速度定数が低下した。一方、ある PUFA に別の PUFA を混合すると、各 PUFA の残存量と酸化により消失した割合 PUFA 量の和の積に比例すると考える一種の自己触媒型の反応速度式で表現できた。

次に、不飽和脂肪酸を油相とする O/W 型エマルション系での脂質の酸化に関与する多くの因子について概観した。さらに同系で、分散粒子径が脂質の酸化速度定数に及ぼす影響を検討したところ、油滴を微細化すると、100 nm 以下で分散粒子径になると、比表面積が飛躍的に増大するにもかかわらず、分散粒子径が小さいほど酸化速度定数が低下した。また、液相活性剤ミセル中に不飽和脂肪酸を可溶化させた場合でも、分散粒子径が小さいほど酸化速度定数が低下した。これらの現象を、液相活性剤の界面張力が脂質を希釈することによる効果に起因するとみなし、モデルにより定量的に表現できることを示した。

脂質の粉末化は、液状脂質と包括剤の厚木水溶液から調製した O/W 型エマルションを凍結乾燥などにより急速に脱水することにより得られる。この第一段階で O/W 型エマルション中の油滴径が粉末化したのちの脂質の酸化過程に及ぼす影響を検討したところ、乳化時の油滴径が小さいほど脂質の酸化が遅延されることが見出された。