

Oxidation of monoglyceride, diglyceride, and triglyceride monolayers by aqueous potassium permanganate solution¹

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Abstract

Studies were carried out on the oxidative degradation of monoolein, monolinolein, diolein, dilinolein, triolein and trilinolein monolayers by injecting KMnO_4 solution under the monolayers. The effect of the initial surface pressure on oxidative degradation was also studied by measuring changes in the surface pressure and surface potential with time. The surface shear viscosities of these six lipids were measured in order to predict their molecular interactions at the air/water interface. The rates of oxidation for these lipids were found to be in the following order: dilinolein > monolinolein > monoolein > trilinolein > diolein > triolein. Interestingly, the surface shear viscosities of these six lipids were found to decrease in the same order. In the present study, an attempt has been made to correlate the effect of the initial surface pressure, the number of double bonds and the number of hydroxyl groups with the oxidation of these lipids by potassium permanganate solution.

Keywords: Lipid; monolayer; potassium permanganate; surface potential; surface pressure.

Introduction

The oxidation of insoluble monolayers by aqueous potassium permanganate solution has been studied by many investigators [1–8] by measuring simultaneously the time t dependences of the apparent molecular area (\AA^2) and the surface pressure. As one spreads a monolayer on the aqueous potassium permanganate solution, the oxidation of the monolayer and evaporation/solubilization of the solvent occur simultaneously; this affects the area/surface pressure at the very beginning of the oxidation process. Therefore, in the present study, the KMnO_4 solution was injected under the

monolayer after compressing it to the desired surface pressure.

It has been reported [7] that the intermediate products formed during the cleavage of the double bonds contain *cis*-epoxy groups. As some of the products after oxidation are insoluble in water, the surface potential of the monolayer is considered to be a more reliable parameter to predict the rate of the oxidation reaction.

The oxidation of the unsaturated monoglycerides, diglycerides or triglycerides is responsible for rancidity in oil-containing products. The effects of various monoglycerides and diglycerides on the oxidative stability of soybean oil has been investigated by measuring the rates of disappearance of headspace oxygen in purified oils containing 0, 0.25, and 0.5% monostearin, distearin, monolinolein or dilinolein [9]. The monoglycerides and

¹Dedicated to the memory of K. Meguro.

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diglycerides act as pro-oxidants in soybean oil but the mechanism of this effect was not delineated. In this paper, we present the effect of the number of double bonds and the initial surface pressure on the oxidation of monoglycerides (monoolein, monolinolein), diglycerides (diolein, dilinolein) and triglycerides (triolein, trilinolein).

Experimental

Materials

All lipids (99% pure) were supplied by Kraft Inc. Chloroform, methanol and hexane were purchased from Fisher. Lipid solutions were prepared in a mixed solvent system containing chloroform-methanol-*n*-hexane (1:1:3) of spectroscopic grade. Inorganic chemicals of reagent grade, and twice-distilled water were used.

Methods

The surface pressure π and the surface potential ΔV of the lipid monolayers were measured on a 0.02 M NaCl subsolution at 25°C and pH 6–7 as described in a previous work [10]. At various initial surface pressures, 5 ml of KMnO_4 solution (1 mg ml^{-1}) in 0.02 M NaCl were injected under the monolayers, resulting in a final concentration of $12.5 \mu\text{g}$ of KMnO_4 per milliliter of subsolution (total volume of subsolution, 400 ml). Fresh subsolution (5 ml) was removed after injecting the KMnO_4 solution in order to maintain the same air gap for surface potential measurements. For thorough mixing of the KMnO_4 in the subsolution, magnetic bars were rotated at slow speed. The surface tension and surface potential with respect to time were measured after carrying out the initial stirring.

The surface shear viscosities of these lipids were measured using a deep-channel surface viscometer for the monolayers at a surface pressure of 10 dyn cm^{-1} [11–14]. In the deep-channel surface viscometer, the channel walls are stationary, concentric cylinders; the floor of the viscometer moves

with a constant angular velocity. A small Teflon particle was placed at the interface in order to determine the center-line velocity and the time for the particle to complete a rotation was recorded. Each experiment was repeated five times and the average velocity of the particle was used for calculating the surface shear viscosity. The surface pressure was measured in the surface viscometer at the beginning as well as at the end of the experiment to establish that the monolayer did not dissolve in the subsolution.

Results and discussion

Oxidation of monoolein and monolinolein monolayers

Figure 1 shows the π -area and ΔV -area curves for monoolein and monolinolein. The area per molecule of monoolein (26 \AA^2) is greater than that of monolinolein (24 \AA^2), which is consistent with their molecular structure and the literature values [15]. Monoolein has a double bond at the C_9 position whereas monolinolein has two double bonds at the C_9 and C_{12} positions. The second kink at the C_{12} position in monolinolein allows the molecule to cover less area compared with monoolein, as shown in Fig. 2. Both the surface pressure and the surface potential decreased with

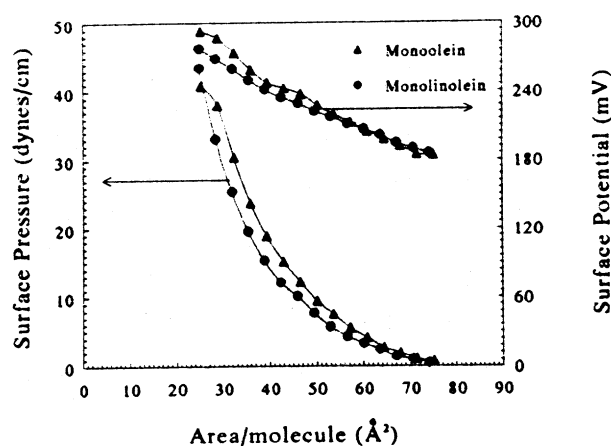


Fig. 1. π -Area and ΔV -area curves of monoolein and monolinolein monolayers.

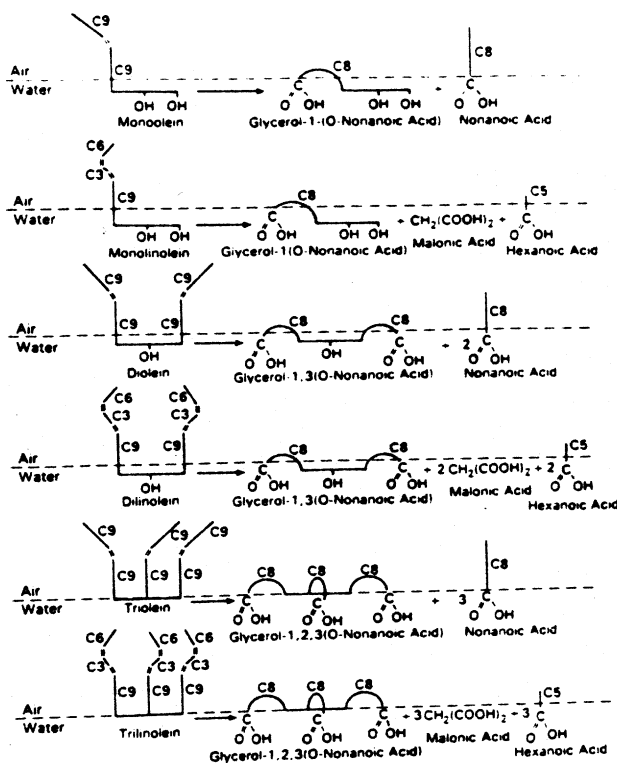


Fig. 2. A schematic diagram of lipid molecules after oxidation at the air/water interface.

time in the case of monoolein and monolinolein after the addition of KMnO_4 (Figs. 3 and 4). This is due to the solubility of glycerol-1-*o*-nonanoic acid and short-chain fatty acids formed in the monoolein and monolinolein. Both parameters decreased more sharply for monolinolein compared with monoolein at the same initial surface pressure. This may be due to the solubility of short-chain acids produced by oxidation (malonic acid and hexanoic acid) in the monolinolein monolayer whereas the nonanoic acid formed in the monoolein monolayer is less soluble than malonic acid and hexanoic acid. At higher initial surface pressure, the surface pressure and the surface potential decreased more rapidly (Figs. 3 and 4). This is presumably due to the increased desorption rate of the short-chain acids from the air/water interface. These results show that monoolein and monolinolein react even at high surface pressure (35 dyn cm^{-1}). This may be due to the presence of

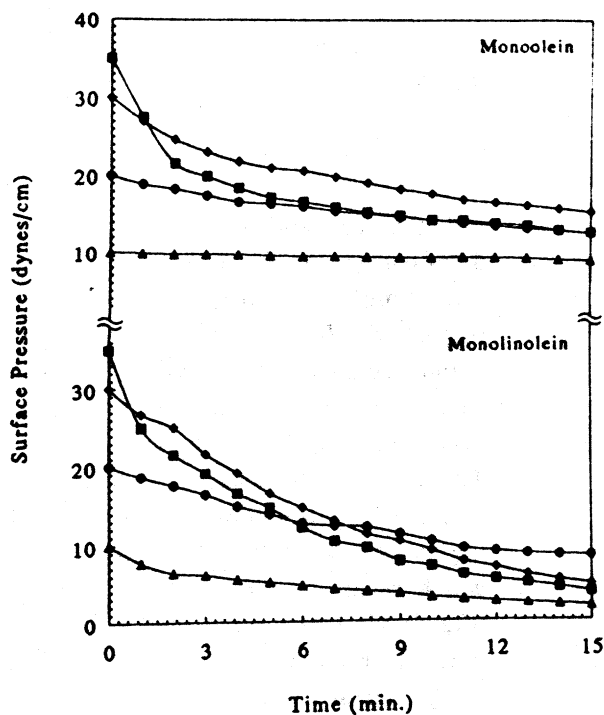


Fig. 3. Effect of KMnO_4 solution on the surface pressure of monoolein and monolinolein monolayers.

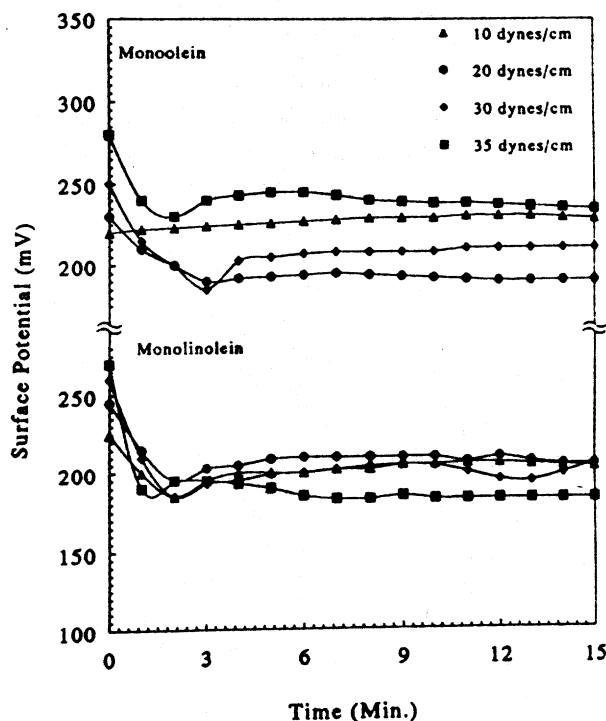


Fig. 4. Effect of KMnO_4 solution on the surface potential of monoolein and monolinolein monolayers.

two hydroxyl groups per molecule and the cis double bond which give a high anchoring effect to the interface.

Oxidation of diolein and dilinolein monolayers

The π -area and ΔV -area curves for diolein and dilinolein are shown in Fig. 5. The areas per molecule of diolein and dilinolein are 53 \AA^2 and 49 \AA^2 , respectively. In the case of dilinolein, when KMnO_4 is injected under the monolayer, the surface pressure increases (Fig. 6) but its surface potential decreases (Fig. 7) at low initial surface pressure. This means that oxidation is taking place but the glycerol-1,3-*o*-nonanoic acid product is not dissolving in the subsolution due to its two alkyl chains, which results in an increase in surface pressure (Fig. 2). However, the surface pressure and surface potential remain constant when KMnO_4 solution is injected at a surface pressure of 20 dyn cm^{-1} , indicating that there is no oxidation taking place at this surface pressure. This also suggests that the dilinolein molecules are tightly packed at this surface pressure and the double bond is not accessible to KMnO_4 in water. If indeed this is the case, diolein should not react at a lower surface pressure than dilinolein because diolein has only two double bonds per molecule. It is evident from Fig. 6 that at 10 dyn cm^{-1} there is a slight increase in surface

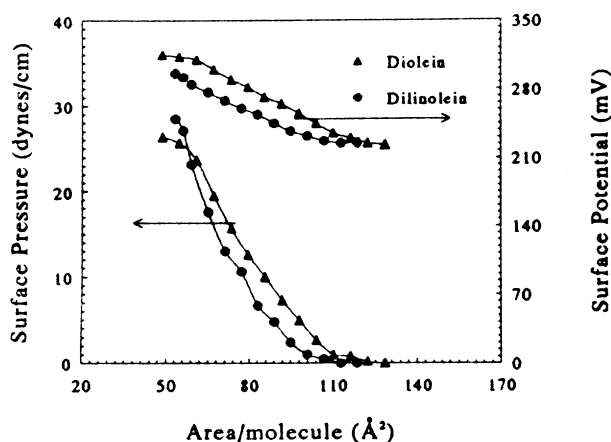


Fig. 5. π -Area and ΔV -area curves of diolein and dilinolein monolayers.

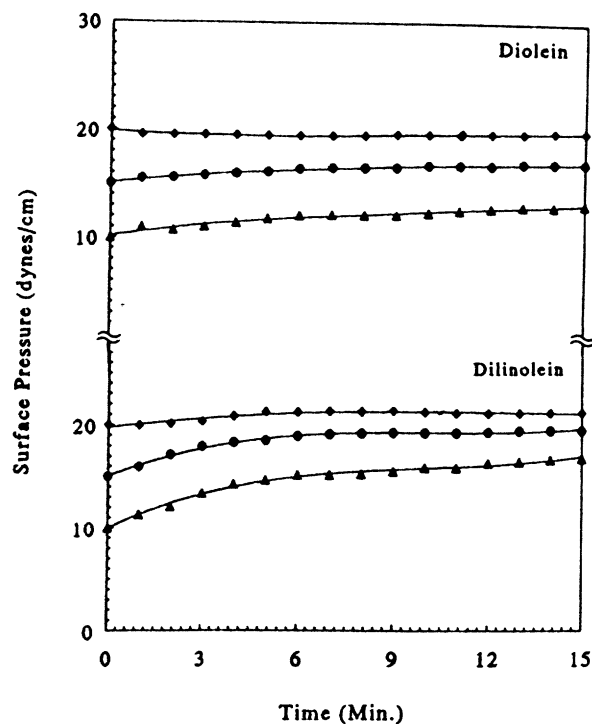


Fig. 6. Effect of KMnO_4 solution on the surface pressure of diolein and dilinolein monolayers.

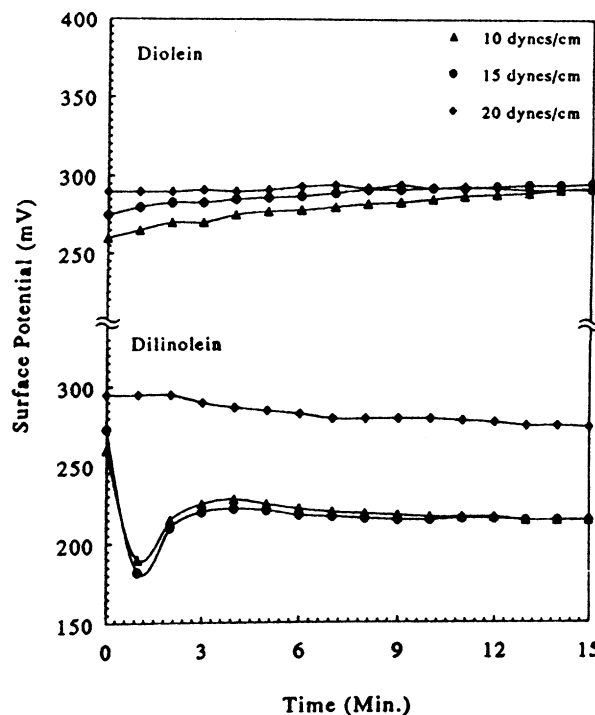


Fig. 7. Effect of KMnO_4 solution on the surface potential of diolein and dilinolein monolayers.

pressure. The surface potential for diolein at an initial surface pressure of 20 dyn cm^{-1} is constant and the surface potential at initial surface pressures of 10 and 15 dyn cm^{-1} increases and reaches the same surface potential as is obtained when the film is at a surface pressure of 20 dyn cm^{-1} after 15 min. This means that the number of electric dipoles is the same for all diolein films regardless of their initial surface pressures. The results also suggest that formation of *cis*-epoxy groups in diolein molecules at low surface pressures is taking place, which increases both the surface pressure as well as the surface potential of the monolayers (Figs. 6 and 7) [7].

Oxidation of triolein and trilinolein monolayers

The areas per molecule of triolein and trilinolein are 80 \AA^2 and 76 \AA^2 , respectively (Fig. 8) [16]. For trilinolein, when KMnO_4 solution is injected under the monolayer at $\pi = 5 \text{ dyn cm}^{-1}$, the surface pressure increased but the surface potential decreased slowly. At high surface pressure ($\pi = 10 \text{ dyn cm}^{-1}$), a similar trend was observed (Figs. 9 and 10). Trilinolein oxidized and glycerol-1,2,3-*o*-nonanoic acid remained at the surface; this requires more area than for the trilinolein molecule due to the formation of three carboxylic groups, as shown in Fig. 2. At high initial surface pressure, trilinolein

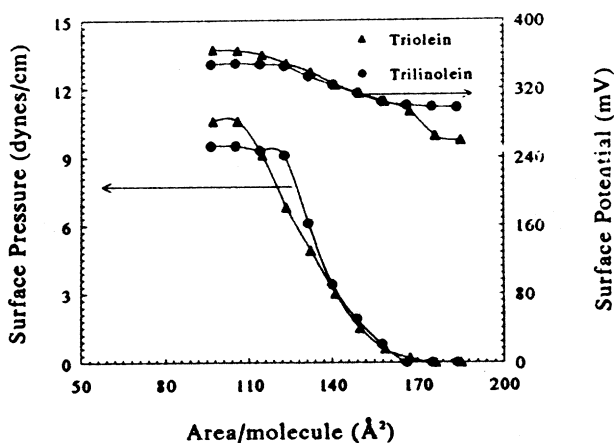


Fig. 8. π -Area and ΔV -area curves of triolein and trilinolein monolayers.

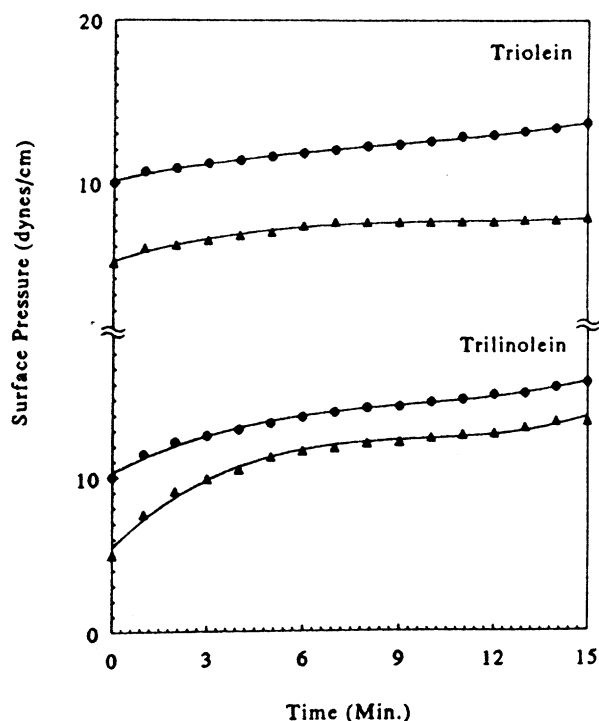


Fig. 9. Effect of KMnO_4 solution on the surface pressure of triolein and trilinolein monolayers.

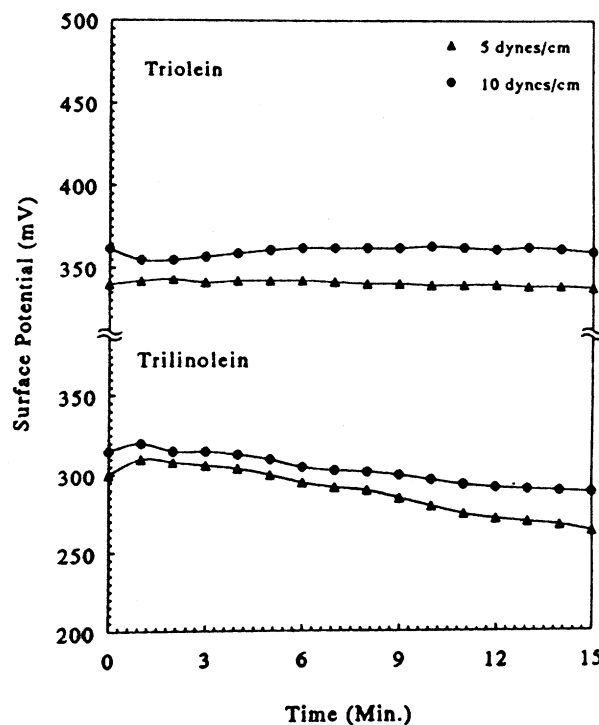


Fig. 10. Effect of KMnO_4 solution on the surface potential of triolein and trilinolein monolayers.

molecules are squeezed out of the water due to the lack of polar groups to provide anchoring on the water surface. Similar results are shown by triolein, but changes are less pronounced because triolein has only three double bonds per molecule as compared with six in trilinolein.

Effect of surface shear viscosity of lipid monolayers on the oxidation

The surface shear viscosity of lipid monolayers provides useful information about the interaction of the polar groups with the subsolution as well as molecular interactions in the monolayer. The surface shear viscosity of the monolayer increases as the interaction (or anchoring) of the polar group with the subsolution increases (e.g. the surface shear viscosity of monoolein is higher than that of diolein (Table 1)). The surface shear viscosity also increases as the chain-chain interactions increase (e.g. dilinolein has a higher surface shear viscosity than diolein (Table 1)). If we compare the surface shear viscosity (Table 1) with the KMnO_4 -induced oxidation rate of monoglycerides (Fig. 4), diglycerides (Fig. 7) or triglycerides (Fig. 10), it is evident that the presence of linoleic acid chains increases the surface shear viscosity as well as the oxidation rate of the glycerides, compared with the oleic acid chains. This supports our explanation that both the surface shear viscosity and the oxidation rate of the monolayers are a function of lipid structure and of their interaction with each other as well as with the subsolution.

Conclusions

The results of these studies on monoglycerides, diglycerides and triglycerides indicate that the rates of oxidation of dilinolein and monolinolein monolayers are significantly high compared with those of the other lipid monolayers. Monoolein and monolinolein monolayers even react at high surface pressure (35 dyn cm^{-1}). Both the rate of the oxidation reaction in the monolayer and the surface

TABLE I

Surface shear viscosity of lipid monolayers at a surface pressure of 10 dyn cm^{-1}

Lipid	10^{-4} Surface shear viscosity ^a (P)
Dilinolein	9.614
Monolinolein	7.447
Monoolein	6.149
Trilinolein	4.697
Diolein	3.405
Triolein	2.760

^aAt 25°C .

shear viscosity of the monolayer are functions of lipid structure and of their interaction with each other as well as with the subsolution.

Acknowledgments

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