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OXIDATION KINETICS OF PRIMARY ALCOHOLS AND METHYLINOOLEATE IN SODIUM DODECYL SULPHATE MICELLES

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The study concerns with the oxidation kinetics of primary alcohols and methylinooleate in sodium dodecyl sulphate micelles. The authors realise the effect of pH on the speed of the process and the structure of the alcohol, determining its location in the micellar system, affects the process.

Introduction

Lipid peroxidation plays an important role in the vital functions of the organism, as cellular tissues are composed mainly of lipid membranes [1]. However, study of these processes directly at the lipid membrane is not simple. Biological membranes contain a variety of unsaturated compounds [2, 3]. The simplest analogue of such compounds is methylinooleate (LH). Therefore, aqueous micellar methylinoleate systems are models for studying oxidative processes in biological systems as well as for testing natural antioxidants and their analogues [4, 5]. The environment pH affects on the speed and mechanism of biological processes. Therefore, the oxidation of methylinooleate requires different pH's to be studied.

The surfactants (SAA) used in these models are ionogenic or non-ionogenic. Some of them undergo chain oxidation through the free-radical mechanism [6], i.e., they are not inert components of the system. Obviously, the total mechanism of the process will be much more complicated. Therefore, sodium dodecyl sulphate (SDS) was chosen as the surfactant, which is practically not subject to chain oxidation under experimental conditions [7].

One of the reasons for the oxidisability of non-ionic surfactants is the presence of primary alcoholic groups in the hydrophilic part of the molecule.

In addition, alcohols can influence the diffusion processes taking place between the aqueous and organic phase in some model systems [8]. Therefore, the aim of this work was to study the oxidation of primary alcohols and methylinooleate in sodium dodecyl sulphate micelles at different pH values.

Experimental part

We use methylinooleate (LH), 2,2′-azobis(2-methylpropionamidine)dihydrochloride (AAPH), ethanol (C_2H_5OH) and octanol ($C_8H_{18}O$). We study the kinetics of the chain oxidation of methylinooleate in aqueous micelles under the following conditions: temperature

(37.0±0.1) °C, pH of aqueous phosphate buffer 7.4±0.02. The surfactant used was SDS. Oxygen absorption kinetics was studied by YSI 5300A oxygen biological monitor (Yellow Spring Instruments Co., USA). For initiating we used a water-soluble AAPH initiator. Its solutions have a slightly acidic medium. Therefore, in experiments with deionised water the pH of the system was 5.5±0.02. Computer simulation was carried out using software Kinetica-2012 [9].

Results and Discussion

Fig. 1 shows typical time dependences of the oxygen absorption rate {$W(O_2)$} during oxidation of methylinooleate and ethanol in SDS micelles in buffer solution.

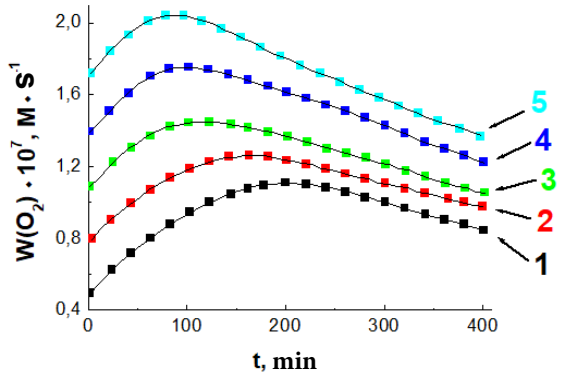

Fig. 1. Time dependence of the oxidation rate of LH and C_2H_5OH. [LH] = $5 \cdot 10^{-3}$ mol/l, [C_2H_5OH] = 0.1 mol/l, [SDS] = 0.1 mol/l, $W_i \cdot 10^9$ mol/(l·s): 1 - 2; 2 - 3; 3 - 4; 4 - 6; 5 - 8, where W_i is an initiation rate

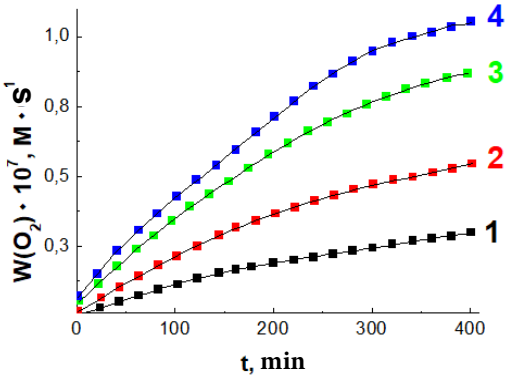

Fig. 2. Time dependence of the oxidation rate of C_2H_5OH and LH. [LH] = $5 \cdot 10^{-3}$ mol/l, [C_2H_5OH] = 0.1 mol/l, [SDS] = 0.1 mol/l, $W_i \cdot 10^9$ mol/(l·s): 1 - 2; 2 - 4; 3 - 6; 4 - 8

The figure shows that after a certain time the maximum value of $W(O_2)$ is reached, which depends on W_i. The nature of the "oxygen absorption rate - time" relationships during oxidation of LH and octanol in buffer solution is similar to that shown in Fig. 1.

Fig. 2 shows the time dependence of the oxidation rate of C_2H_5OH and LH when oxidised in deionised water. In contrast to oxidation in buffer solution, $W(O_2)$ did not reach maximum. The same is for LH and octanol oxidising in deionised water.

$W(O_2)$ is a function of W_i^n, n – per initiator [5]. In contrast to micellar, in homogeneous systems the oxygen absorption rate during LH oxidation is constant, the chains are broken by a bimolecular reaction and $n = 0.5$.

Table 1 shows the time-order dependencies of the initiator order calculated from the experimental data obtained.

Table 1. Dependence of initiator order on time during oxidation of the studied alcohols and LH

		Initiator order				
		50 minutes	100 minutes	200 minutes	300 minutes	400 minutes
C_2H_5OH	Buffer solution	0.70	0.57	0.36	0.34	0.34
	Deionised water	1.01	0.98	0.98	1.00	0.93
$C_8H_{18}O$	Buffer solution	0.58	0.59	0.61	0.54	0.48
	Deionised water	1.03	1.01	0.77	0.73	0.72

[LH] = $5 \cdot 10^{-3}$ mol/L, [C_2H_5OH] = 0.1 mol/L, [$C_8H_{18}O$] = 0.05 mol/L, [SDS] = 0.1 mol/L. n was calculated using the formula $\ln(W(O_2)) = n \cdot \ln(W_i)$.

By Table 1, the initiator order during oxidation in buffer solution is less than in deionised water. During the process, a decrease of n is observed in the buffer solution.

If $n = 0.5$, the chains are broken in a bimolecular reaction; if $n = 1$, the chains are broken in a monomolecular reaction; in the range from 0.5 to 1, the mechanism is mixed.

The initiator is calculated using the methodology developed for homogeneous systems in a quasi-stationary regime. The change in oxygen absorption rate in micellar systems (see Fig. 1, 2) can be explained by the non-stationary nature of the process [10, 11]. A computer simulation was carried out for this purpose. The diagram [12-15] shows the general oxidation mechanism:

(i) AAPH → $r^{\bullet} + N_2$	$k_i = 10^{-6}$ s^{-1}
(1) $r^{\bullet} + O_2 \rightarrow rO_2^{\bullet}$	$k_1 = 10^8$ l· mol^{-1}·s^{-1}
(2) $rO_2^{\bullet} + rO_2^{\bullet} \rightarrow O_2$	$k_2 = 5 \cdot 10^4$ l·mol $^{-1}$·s^{-1}
(3) $rO_2^{\bullet} + LH \rightarrow L^{\bullet} + rOOH$	$k_3 = 50$ l·mol^{-1}·s^{-1}
(4) $L^{\bullet} + O_2 \rightarrow LO_2^{\bullet}$	$k_4 = 10^8$ l·mol $^{-1}$·s^{-1}
(5) $LO_2^{\bullet} + LH \rightarrow L^{\bullet} + LOOH$	$k_5 = 70$ l·mol $^{-1}$·s^{-1}
(6) $LO_2^{\bullet} + LO_2^{\bullet} \rightarrow O_2$ + products	

[LH] = 0,005 mol/l, $[O_2] = 2 \cdot 10^{-4}$ mol/l

As $W(O_2)$ is proportional to the peroxyradical concentration, the kinetics of $LO_2^{\bullet}$ accumulation was calculated (Fig. 3).

$$W(O_2) = k_5 \cdot [LO_2^{\bullet}] \cdot [LH] \quad (1)$$

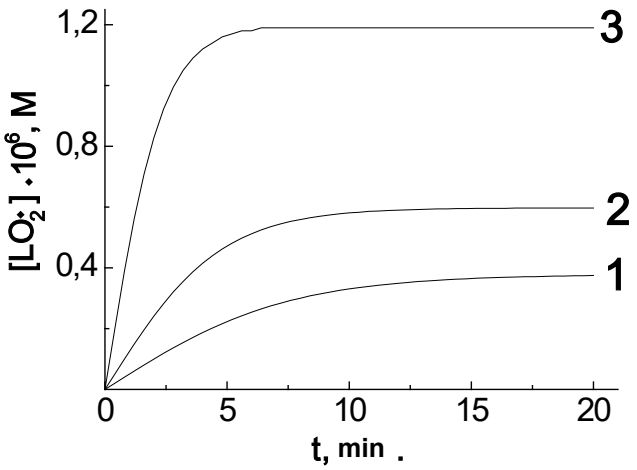

Fig. 3. Modelling of $LO_2^{\bullet}$concentration versus time for LH oxidation. $[O_2] = 2 \cdot 10^{-4}$ M, [LH] = 0.01 M. $W_i \cdot 10^9$, M: 1 – 0,4; 2 – 1; 3 – 4. The modelling was carried out according to the above scheme. $2k_6 = 10^4$ l·mol $^{-1}$·s^{-1}

By Fig. 3, the higher W_i, the quicker stationary concentration of $LO_2^{\bullet}$ is reached. It is corresponding to the maximum rate of the process. After reaching the maximum $W(O_2)$, a decrease was observed (see Fig. 1). The modelling suggests it is due to the consumption of the main oxidising component, methylinooleate. Depending on W_i, 10–30% of LH can be consumed during the experiment. Thus the initiator order should be calculated at the maximum rates {W(max)} when the concentration of $LO_2^{\bullet}$ has reached a constant value. The initiator order will be 0.5, i.e. $W(O_2)$ is directly proportional to $W_i^{0.5}$. Fig. 4. The resulting dependence.

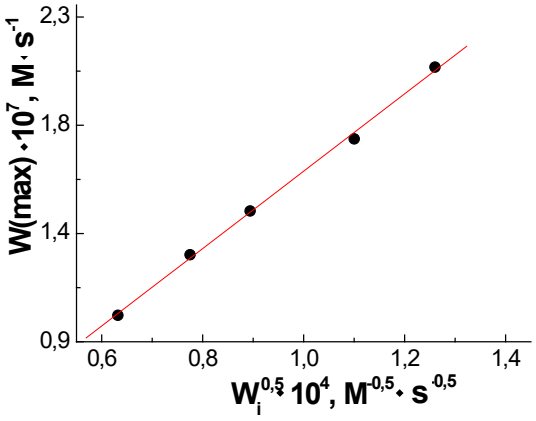

Fig. 4. Dependence of maximum oxygen absorption rate on $W_i^{0.5}$. [LH] = 5·10^{-3} mol/l, [SDS] = 0.1 mol/l, [C_2H_5OH] = 0.1 mol/l. The dependence is based on the data of Fig. 1.

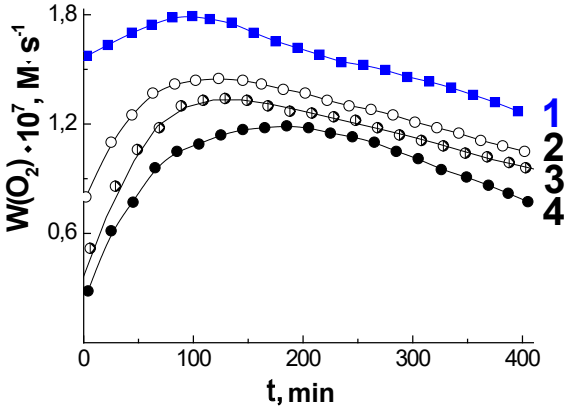

Fig. 5. Time dependence of the oxidation rate of C_2H_5OH and LH. [LH] = 5·10^{-3} mol/l, [SDS] = 0.1 mol/l, [C_2H_5OH], mol/l: 1 - 0; 2 - 0.1; 3 - 0.2; 4 - 0.5. W_i = 4·10^{-9} mol/(l·s)

As the maximum $W(O_2)$ is directly proportional to $W_i^{0.5}$. It corresponds to bimolecular chain breaking by reaction (6) in the scheme above. During oxidation in deionised water, maximum oxygen absorption rates were not achieved due to the lower efficiency of the initiator in a weakly acidic environment, which corresponds to a reduction in W_i.

Fig. 5. There is a graph of the time dependence of the oxygen absorption rate during oxidation of C_2H_5OH and LH in buffer solution at different concentrations of alcohol.

The oxidation rate decreases with increasing alcohol concentration. It can be explained by the presence of initiator and ethyl alcohol in the aqueous phase, so C_2H_5OH is able to intercept part of the radicals formed during the breakdown of the initiator (see diagram above) in the reaction (rO_2 + $^{\bullet}C_2H_5OH$), which leads to a decrease in the overall rate of the process. The similar effect is during the oxidation of C_2H_5OH and LH in deionised water.

The oxidation of $C_8H_{18}O$ and LH in both buffer solution and deionised water decreases with increasing alcohol concentration $W(O_2)$. In contrast to ethanol, octanol is predominantly distributed in the organic phase of the system, i.e. in micelles. Micelles are microreactors [3] with an organic oxidation substrate, i.e. LH, inside them. Increasing the octanol concentration dilutes the LH in the micelle core and consequently reduces the oxidation rate. Fig. 6. The comparison of the oxidation rates of methylinooleate and ethanol versus time as the pH of the medium changes.

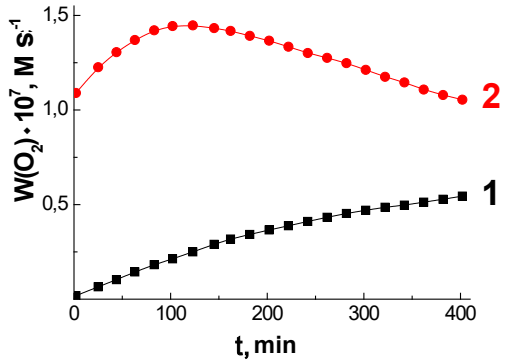

Fig. 6 Time dependence of C_2H_5OH and LH oxidation rate: 1 - in deionized water, 2 - in buffer solution. [LH] = 5·10^{-3} mol/L, [SDS] = 0.1 mol/L, [C_2H_5OH] = 0.1 mol/L, W_i = 4·10^{-9} mol/(l·s)

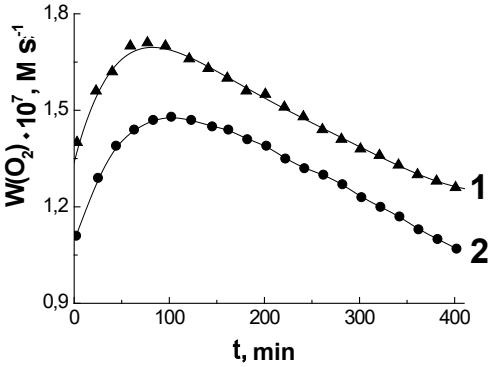

Fig. 7. Time dependence of the oxidation rate in buffer solution: [LH] = 5·10^{-3} mol/l, [SDS] = 0.1 mol/l, W_i = 4·10^{-9} mol/(l·s), 1 - [$C_8H_{18}OH$] = 0.05 mol/l, 2 - [C_2H_5OH] = 0.05 mol/l

By Figure, the oxidation involving ethanol proceeds faster in buffer solution than in water. The reason is the initiators of this type are less effective in acidic environments [3]. The similar effect is for octanol. Fig. 7. The comparison of the time dependence of the oxidation rate in a micellar SDS - LH system in the presence of different alcohols.

According to the figures, oxidation process is faster in the presence of octanol than in the presence of ethanol. This can be explained by the fact that ethanol, being in the aqueous phase with the initiator, is able to interact with the radicals formed there during its decomposition by the reaction ($rO_2^{\bullet}$ + ROH). As a result, the initiation speed is decreases, reducing the speed of the overall process.

Conclusions

Thus, the oxidation mechanism of methylinooleate and the alcohols examined is determined by the pH of the medium. Also there is alcohol in the aqueous or micellar phases.

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