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EFFECT OF SURFACTANTS ON ASCORBIC ACID AND NICOTINIC ACID ATMOSPHERIC OXIDATION KINETICS

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The kinetics of atmospheric oxidation of ascorbic acid and nicotinic acid in aqueous solutions of surfactants has been studied. It has been shown that the kinetics of vitamins' oxidation process was described by first-order reaction equation. The conditions in which oxidation occurs have great importance: in the pre-micellar region the rate of vitamins' oxidation increases, while in the post-micellar region it decreases.

***Keywords*:** ascorbic acid, nicotinic acid, surfactant, atmospheric oxidation.

Introduction. In the last decade the study of antioxidant properties of ascorbic acid (AscA) and nicotinic acid (NicA) in the presence of surfactants has great interest [1–4]. The activity of AscA and NicA strongly depends on the nature of environment, in which the oxidation process occurs. Micellar solutions and microemulsions have the most significant interest as microenvironment. These systems are representative for many pharmaceutic, cosmetic and food products, and due to this fact, the behavior of AscA and NicA in micellar solutions and microemulsion systems has scientific and practical importance [5, 6]. Micelles and microemulsions are detected as models for studying the effect of heterogeneous environment on dynamics and mechanism of reaction [7, 8]. The molecular associates-micelles can also be detected as models of microenvironment of biological systems and help to understand natural processes [8, 9].

Environmental pollution increases due to human activity, which in its turn has been the reason of formation of active forms of oxygen. Formation of active forms of oxygen occurs in different biological systems. In the absence of control that process can lead to membrane dysfunction, inactivation of protein and destruction of DNA [10]. For preventing oxidation processes and for mitigation of oxidative stress many biologically active agents, including vitamins, are used as antioxidants. In those conditions vitamins can be oxidized and the study of vitamins oxidation process has both theoretical and practical significance.

In this paper the atmospheric oxidation of AscA and NicA in the presence of surfactants is studied by UV-spectroscopy.

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Experimental Part. Anionic surfactant sodium dodecylsulfate (SDS, “Aldrich”, >98.0%), cationic surfactant dodecyltrimethylammonium chloride (DTAC, “Aldrich”, >98.0%), non ionic surfactant hexadecylpoly[oxyethylene(20)] alcohol ($C_{16}A_{20,}$ Shostkinsk, Russia, >98.0%), AscA (bioXtra crystalline, “Sigma”, >99.0%) and NicA (“Aldrich”, >99.0%) were used without further purification. The samples were prepared by direct mixing of the components immediately before experiments. Twice-distilled water was used as solvent. All experiments were carried out at 22±0.5°*C*. The pH of solutions is 4.8 at concentration of vitamins 10^{-4} *mol*/*L* and was not controlled by using buffer solutions.

UV-spectra of aqueous-micellar solutions of surfactants in the absence and presence of vitamins are recorded on spectrophotometer PGI UV T60 with emission slit of 2 *nm* and wavelength range 190–1100 *nm*.

Results and Discussion. The adsorption spectra of aqueous solutions of AscA and NicA at different times after preparing their solutions are presented in Fig. 1. It follows from Fig. 1,a, that the maximum intensity of adsorption is observed at λ=265 *nm*, which is in good agreement with literature data [7, 8] and represents absorption of hydrogenated form of AcsA. For NicA the characteristic adsorptions are observed at λ_1=211 *nm* and λ_2=262 *nm* (Fig. 1,b). AscA and NicA were exposed to atmospheric oxidation in solution, and this process was monitored by changes in the intensity of characteristic absorption for AscA at λ=265 *nm* and for NicA at λ=262 *nm*. The experiments were performed for pre-micellar and micellar solutions of surfactants: the critical micelle concentration (cmc) for studied surfactants in the presence of AscA and NicA were taken from [11, 12].

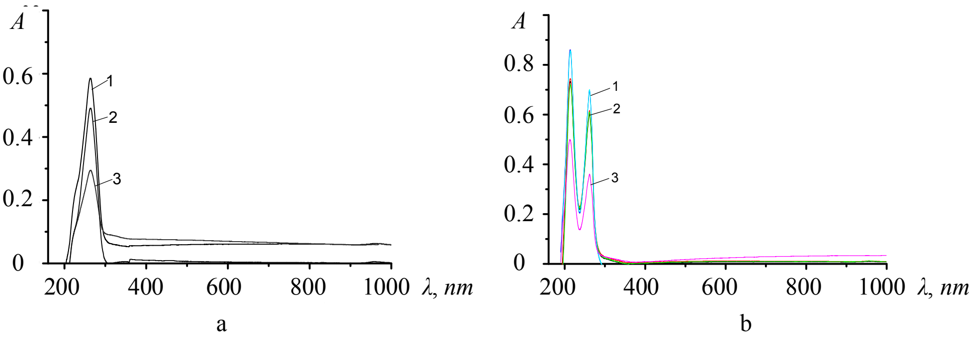


Fig. 1. Adsorption spectra of AscA (a) and NicA (b) at different times after preparing solution: $C_{\text{AscA}} = 0.12 \cdot 10^{-4}$ *mol*/*L*; $C_{\text{NicA}} = 1.2 \cdot 10^{-4}$ *mol*/*L*; $t = 0$ (1) , 20 (2), 60 (3) *min*.

The kinetic plots of $A = f(t)$ at atmospheric oxidation of AscA in the presence of different surfactants are presented in Fig. 2, and the $A = f(C_{\text{surf}})$ concentration dependences are presented in Fig. 3. The analogous plots are also observed for atmospheric oxidation of NicA.

Analysis of kinetic data revealed that the kinetic plots of adsorption satisfy the first-order reaction equation, and the oxidized reactions of AscA and NicA were expressed by the following [13]: $\lg\frac{a}{a-x}=\frac{Kt}{2.3}$, where a is initial concentration of reacting compounds, x is amount of the reacted substance at moment t.

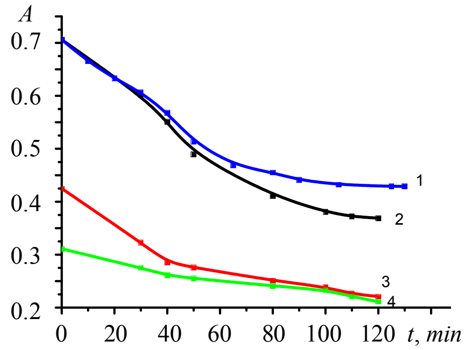


Fig. 2. Kinetic plots of atmospheric oxidation of AscA in the pre-micellar region:
$C_{\text{AscA}} = 0.13 \cdot 10^{-4}$ *mol/L*; $C_{\text{SDS}} = 2.0 \cdot 10^{-3}$ *mol/L*;
$C_{\text{DTAC}} = 1.0 \cdot 10^{-2}$ *mol/L*; $C_{\text{C}_{16}\text{A}_{20}} = 1.1 \cdot 10^{-4}$ *mol/L*,
$\lambda = 265$ *nm*.

1) AcsA–H_2O; 2) AscA–SDS–H_2O;
3) AscA–DTAC–H_2O; 4) AscA–$C_{16}A_{20}$–H_2O.

The values of *x* were obtained by calibration plot of adsorption spectra data (for each system). From the linear dependence $\lg\frac{a}{a-x} = f(t)$, the values of rate constants were obtained and given in Tab. 1 and 2. The values of rate constant do not change in the presence of surfactants practically as expected theoretically.

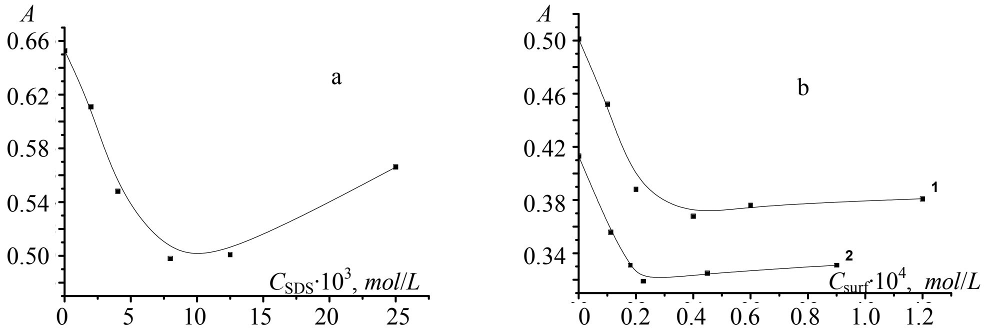


Fig. 3. Plots of adsorption of AscA–surfactant–water solutions vs. surfactant concentration:
a) SDS; b) DTAC (1) and $C_{16}A_{20}$ (2). $C_{\text{AscA}}=0.12 \cdot 10^{-4}$ *mol/l*, $\lambda=265$ *nm*.

Based on the data of *x* the plots of consumption of vitamins vs. reaction time are presented in Fig. 4. From those plots the values of initial rate of oxidation $[W_0]$ were obtained and given in Tab. 3. From $W_0 = f(C_{\text{surf}})$ dependences it follows (Fig. 5) that the rate of atmospheric oxidation of vitamins depends on their concentration by first-order.

From Fig. 2, 3 and Tab. 1, 3 it follows that: 1) the rate of oxidation of vitamins increases in the order SDS > DTAC > $C_{16}A_{20}$; 2) the rate of oxidation of vitamins increases in the pre-micellar region, while micelles inhibit the oxidation. According to literature data [14], when the surfactants of pre-micellar concentrations are added into water, system becomes more “hydrophobic” due to structural changes of water. This leads to decrease insolubility of oxygen in surfactant aqueous system in the pre-micellar region, and as a result the rate of oxidation increases.

Table 1

Amount of reacted vitamin (x), atmospheric oxidation rate constant (K) and atmospheric oxidation time (t) of AscA (1) and NicA (2) in the presence of surfactants.
$[AscA] = 0.13\cdot10^{-4}$ mol/L, $[NicA] = 1.20\cdot10^{-4}$ mol/L

$[SDS]\cdot10^3$, *mol/L*	*t*, *min*	$x\cdot10^5$, *mol/L*	$K\cdot10^4$, s^{-1}	$[DTAC]\cdot10^2$, *mol/L*	*t*, *min*	$x\cdot10^5$, *mol/L*	$K\cdot10^4$, s^{-1}	$[C_{16}A_{20}]\cdot10^3$, *mol/L*	*t*, *min*	$x\cdot10^5$, *mol/L*	$K\cdot10^4$, s^{-1}
1											
2	12	0.15	1.95	1	12	0.075	0.87	0.112	20	0.015	0.09
	25	0.30			25	0.15			40	0.028	
	50	0.55			55	0.33			80	0.056	
	75	0.80			75	0.40			120	0.064	
4	20	0.55	5.55	2	23	0.30	2.03	0.180	20	0.024	0.14
	30	0.85			45	0.52			55	0.057	
	50	1.30			60	0.70			100	0.090	
	60	1.50			80	0.85			120	0.104	
8	23	1.20	10.10	4	17	0.44	5.42	0.225	20	0.030	0.18
	45	2.10			35	0.85			45	0.060	
	70	3.00			45	1.10			70	0.090	
	80	3.45			60	1.39			100	0.110	
2											
$[SDS]\cdot10^3$, *mol/L*	*t*, *min*	$x\cdot10^5$, *mol/L*	$K\cdot10^5$, s^{-1}	$[DTAC]\cdot10^2$, *mol/L*	*t*, *min*	$x\cdot10^5$, *mol/L*	$K\cdot10^6$, s^{-1}	$[C_{16}A_{20}]\cdot10^3$, *mol/L*	*t*, *min*	$x\cdot10^5$, *mol/L*	$K\cdot10^7$, s^{-1}
2	23	0.25	1.45	1	18	0.11	7.78	0.112	15	0.010	9.05
	33	0.35			45	0.25			30	0.0215	
	48	0.50			55	0.29			60	0.0375	
	80	0.75			70	0.37			80	0.0480	
4	10	0.30	3.45	2	28	0.36	16.69	0.180	10	0.010	18.68
	33	0.80			50	0.61			35	0.040	
	70	1.50			70	0.78			65	0.065	
	90	1.75			85	0.90			85	0.080	
8	20	1.00	7.17	4	15	0.40	34.57	0.225	10	0.015	
	30	1.50			25	0.65			35	0.050	
	64	2.90			55	1.20			70	0.090	
	90	3.70			70	1.50			95	0.110	

Table 2

Amount of reacted vitamin, atmospheric oxidation rate constant and atmospheric oxidation time of AscA and NicA in the absence of surfactants

$[AscA]\cdot10^4$, *mol/L*	*t, min*	$x\cdot10^5$, *mol/L*	$K\cdot10^4$, s^{-1}	$[NicA]\cdot10^4$, *mol/L*	*t, min*	$x\cdot10^4$, *mol/L*	$K\cdot10^4$, s^{-1}
0.13	10	0.0075	1.10	1.25	9	0.007	1.15
	28	0.022			11	0.100	
	55	0.040			21	0.190	
	85	0.049			52	0.500	
0.60	10	0.036	1.10	2.40	7	0.090	1.15
	30	0.040			18	0.290	
	55	0.168			32	0.500	
	135	0.373			41	0.600	
3.00	20	0.043	1.10	-	-	-	-
	55	0.980					
	105	1.590					
	120	1.620					

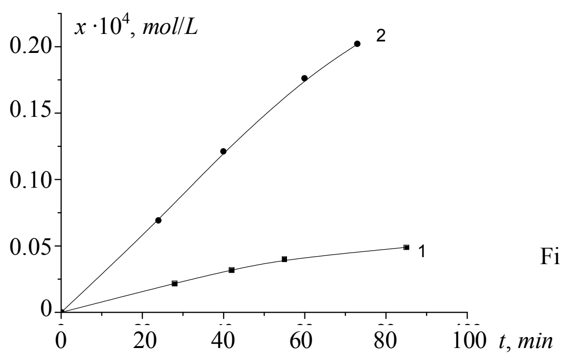


Fig. 4. Plots of reacted vitamins amount *x* vs. time of reaction: $C_{AscA} = 0.13\cdot10^{-4}$ *mol/L* (1); $C_{NicA} = 3.00\cdot10^{-4}$ *mol/L* (2).

Table 3

Initial rate of atmospheric oxidation of AscA and NicA in the absence and presence of surfactants

$[AscA]\cdot10^4$, *mol/L*	$W_0\cdot10^7$, *mol/L · min*	$[NicA]\cdot10^4$, *mol/L*	$W_0\cdot10^7$, *mol/L · min*	$[SDS]\cdot10^3$, *mol/L*	$W_0\cdot10^7$, *mol/L · min*		$[DTAC]\cdot10^2$, *mol/L*	$W_0\cdot10^7$, *mol/L · min*		$[C_{16}A_{20}]\cdot10^3$, *mol/L*	$W_0\cdot10^8$, *mol/L · min*	
					AscA	NicA		AscA	NicA		AscA	NicA
0.13	0.8	1.2	0.1	2.0	12	10	1.0	6	6	0.11	0.7	0.6
0.60	3.4	2.4	1.6	4.0	28	26	2.0	13	13	0.18	1.2	1.1
3.00	18.0	3.0	3.3	8.0	5	5	4.0	24	25	0.23	1.5	1.4

Another picture can be observed in the micellar system. Oxygen is concentrated mainly in hydrophobic zone of micelle, while AscA is concentrated in the aqueous phase [15, 16]. The same is in the case of NicA. Thus, meeting of reagents with one another is difficult and the rate of oxidation decreases. It must be noted that due to oxidation of hydrated form of AscA the intensity of adsorption increases.

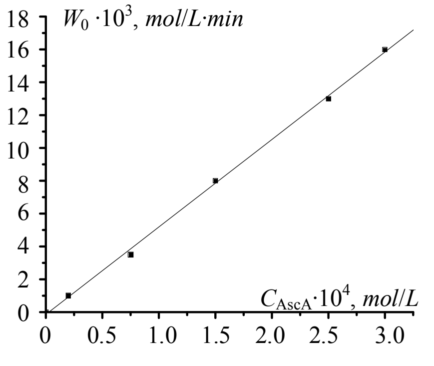
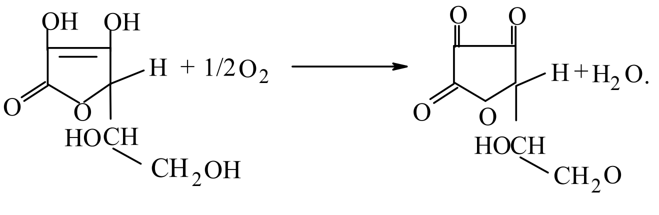
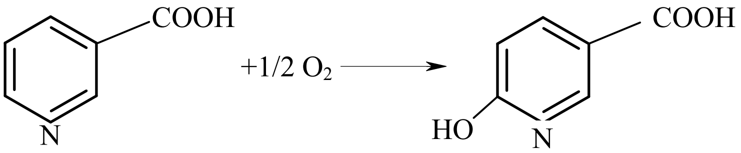


Fig. 5. Plot of atmospheric oxidation of AscA vs. concentration of AscA.

Mechanism of reaction of AscA with oxygen has complex nature [17]. Based on the obtained kinetic data the first step of AscA reaction with oxygen can be presented by the following relation:



The scheme of NicA oxidation mechanism in the organism is given in [18]. On the first step of oxidation 6-hydroxynicotinic acid is formed. Further oxidation in the absence and presence of microbes occurs in different ways. As the value of reaction order by NicA is 1, taking into account the literature data, the first step of NicA atmospheric oxidation can be presented by the following relation:



Thus, the use of surfactant at pre-micelle concentrations promotes oxidation of studied vitamins, while in the organized systems (micelles) the process of oxidation inhibits. The analogous conclusion can be made for organized biological systems-cells. But it must be noted that the slow rate of vitamins oxidation in the cells is associated not only with low concentration of available oxygen, but apparently, with the specific properties of the cell membrane.

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