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INVESTIGATION OF INTERACTION OF SODIUM LAURYL ETHOXY SULFATE AND $\dot{O}H$ RADICALS OBTAINED FROM INSOLUBLE PEROXO SOLVATES

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Reaction ability of sodium lauryl ethoxy sulfate and $\dot{O}H$ radicals obtained from UV radiation of water solutions of $ZnO \cdot 0.8H_2O_2$, $MgO \cdot 0.42H_2O_2$ and $CaCO_3 \cdot 0.21H_2O_2$ peroxo solvates has been investigated. Substance oxidation by $\dot{O}H$ radicals was carried out by concurrent oxidation reaction method. To determine the hydrogen peroxides amount in peroxo solvates, permanganatometric method has been employed. Electron spectroscopy method has been carried out for determination of optical density. The results show, that obtained peroxo solvates accelerate the reaction between 4,4-dimethyl-4-nitrosoaniline (PNDMA) and $\dot{O}H$ radicals. The rate of constants of the reaction was obtained.

Keywords**:** peroxo solvates, discoloration reaction, UV radiation, $\dot{O}H$ radicals, PNDMA.

Introduction. Surface active agents that are called Surfactants (SAS) are widely used in household and industrial products. After using surfactants as well as their products are mainly discharged onto sewage treatment plants and then dispersed into environment through effluent discharge onto surface waters and sludge disposal on lands. SAS have different behavior and fate in environment. Due to their chemical features, surfactant molecules may be absorbed directly onto organic, mineral particles and sediments. Once SAS enter the environment they undergo many processes such as sorption and degradation or may interact with other pollutants (carcinogens, pesticides, oil products, heavy metals, etc.) increasing their toxicity. One of negative impact of the presence of SAS in aquatic ecosystem is the ability to form foam on water surfaces even in low concentrations. The foam hinders the heat exchange transfer between atmosphere and water, as well as dissolving of atmospheric oxygen in water and causes oxygen consumption to exceed resupply, thus, inhibiting the sedimentation and degradation of particles, mineralization of organic compounds, thereby water self-purification [1–3].

It is well known that innate H_2O_2 has significant role in transformation of natural water reservoir contaminations [3]. The concentration of H_2O_2 in natural

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waters has been determined equal from 10^{-6} to 10^{-5} M [4]. In this case water is in, so called, oxidant state. These features of peroxides are also of importance for their use in chemical reactions and in our daily life.

H_2O_2 is powerful oxidant, which can directly generate different intermediate particles ($\dot{O}H$, O_2^-, $R\dot{O}_2$) in water, degrading organic pollutants, which accounts the role of H_2O_2 as purifiers in natural waters [5]. The natural and human made pollutant conversions in water are of great importance. Hydroxyl radicals are highly reactive and have high oxidizing ability. SAS are characterized by low ability of biodegradation. It was interesting to study their interaction with active agents formed by hydrogen peroxide coordinated to salts, i.e. of peroxo solvates. Peroxo solvates as solid forms of hydrogen peroxide are promising oxidants, oxygen sources in portable respiration apparatus and whiteners. The high decontaminating activity, found recently for some compounds of this class, made it possible to develop on their basis environmentally friendly disinfectants with broad-spectrum antimicrobial action. Therefore, from the point of view of environmental safety it's interesting to study their interaction with active agents derived from the created peroxo solvates.

The peroxo solvates are specific forms of oxygen compounds. The peroxo solvates of inorganic compounds gain a wide application year by year, which is explained not only by the active oxygen, which is easily separated from it, but also by a range of certain features of peroxide solvates [6–8].

Materials and Methods. Peroxo solvates have been synthesized by the known method characterized by IR and *X*-ray spectroscopy and obtained data were reported [9–13]. Obtained insoluble peroxo solvates, differ from soluble peroxo solvates in ability to regulate the rate of hydrogen peroxide transformation into liquid phase in time, whereas to dissolve all content at once, because of solubility of former peroxo solvates.

Thus, four titration phases endpoints have been observed for $ZnO \cdot 0.8H_2O_2$ and $MgO \cdot 0.42H_2O_2$, and three – for $CaCO_3 \cdot 0.21H_2O_2$ [9–11]. For determination of hydrogen peroxides amount in peroxo solvates, permanganatometric method has been employed. Sodium lauryl ethoxy sulfate (SLES) has been chosen as SAS. This compound is widely used.

Pollutant oxidation by radicals was carried out by concurrent oxidation reaction method, based on determination of relative change in optical density as the result of the reaction of the dyestuff (4,4-dimethyl-4-nitrosoaniline (PNDMA)) and $\dot{O}H$ radicals in the presence of pollutant and without it [10, 11]. The UV radiation source was a photolytic equipment with mercury lamp as a radiation source. Electronic absorption method has been carried out for appropriate measurements.

Results and Discussions. The reaction ability of the pollutant with OH radicals obtained from the figures of UV radiation of water solutions has been investigated. For this purpose, firstly, the influence of solid reagents (ZnO, MgO, $CaCO_3$) and then of the different concentrations of SLES on the reaction has been examined. Solid reagents do not influence on the reaction rate. Second factor has been found to influence the reaction kinetics on the rate of discoloration reaction in the presence and absence of peroxo solvates (Fig. 1–3).

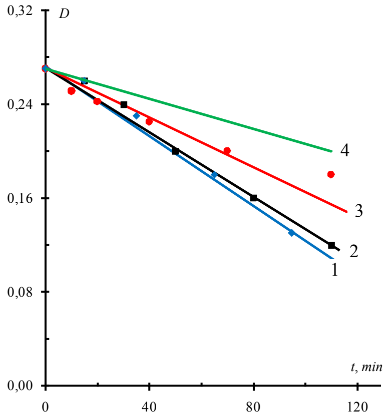

Fig. 1. The dependence of PNDMA optical density (*D*) from UV radiation (λ=313 *nm*) time in the presence of $ZnO \cdot 0.8H_2O_2$, in the case of different concentrations of SLES, where 1. [SLES] = 0; 2. [SLES] = $9 \cdot 10^{-6}$ *M*; 3. [SLES] = $9 \cdot 10^{-5}$ *M*; 4. [SLES] =$1{,}8 \cdot 10^{-4}$ *M*.

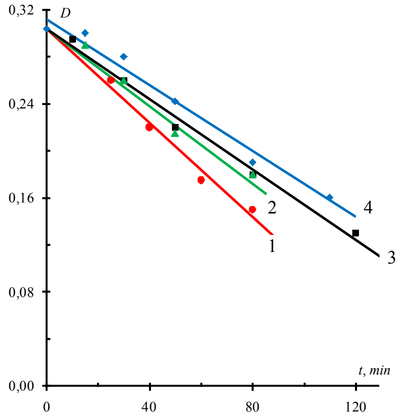

Fig. 2. The dependence of PNDMA optical density (*D*) from UV radiation (λ=313 *nm*) time in the presence of $MgO \cdot 0.42H_2O_2$, in the case of different concentrations of SLES, where 1. [SLES] = 0; 2. [SLES] = $9 \cdot 10^{-6}$ *M*; 3. [SLES] = $9 \cdot 10^{-5}$ *M*; 4. [SLES] =$1{,}8 \cdot 10^{-4}$ *M*.

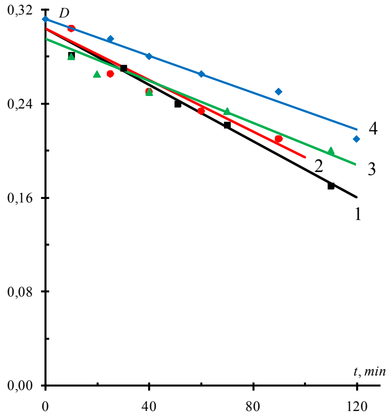

Fig. 3. The dependence of PNDMA optical density (*D*) from UV radiation (λ=313 *nm*) time in the presence of $CaCO_3 \cdot 0.21H_2O_2$, in the case of different concentrations of SLES, where 1. [SLES] = 0; 2. [SLES] = $9 \cdot 10^{-6}$ *M*; 3. [SLES] = $9 \cdot 10^{-5}$ *M*; 4. [SLES] =$1{,}8 \cdot 10^{-4}$ *M*.

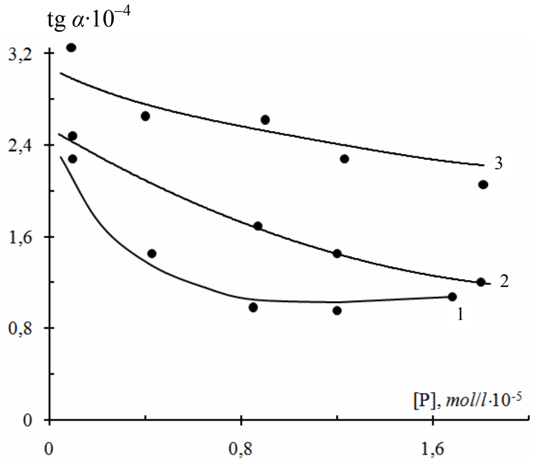

Fig. 4. The dependence of tgα from SLES concentration for:
1 – $ZnO\cdot0.8H_2O_2$; 2 – $MgO\cdot0.42H_2O_2$; 3 – $CaCO_3\cdot0.21H_2O_2$.

Derived from the liner dependences, values of tgα have been calculated for each concentration of SLES and used peroxo solvates. The plot of reaction rate *vs* SLES concentrations were performed. We calculated tgα values for each concentration of pollutant and used retrieved straights dependences of each peroxo solvate. Then we built the SLES concentration– tgα dependence of the reaction (Fig. 4).

To determine the reactions' rate constants of SLES and $\dot{O}H$ radicals obtained from radiation of peroxo solvates we used the following formula [14, 15]:

$$K_{OH+P}=1.25\cdot10^{10}\ ([PNDMA]\ /\ [P])\ [(W_1/W_2)-1],\ mol^{-1}\cdot l\cdot s^{-1},$$

where [P] is the SLES concentration; $1.25\cdot10^{10}$ is the constant of the reaction PNDMA+ $\dot{O}H$; W_1, W_2 are the reaction's speed in the presence and absence of SLES.

The table presents the results of rate constants of SLES and $\dot{O}H$ radicals interaction in the presence of peroxo solvates.

Used peroxo solvates	K_{OH+P}: rate constants of the reaction of radicals SLES and $\dot{O}H$, $mol^{-1}\cdot l\cdot s^{-1}$	
	in presence of peroxo solvates	in presence of hydrogen peroxide
$ZnO\cdot0.8\ H_2O_2$	$9.0\cdot10^8$	$1.4\cdot10^9$
$MgO\cdot0.42\ H_2O_2$	$1.3\cdot10^7$	
$CaCO_3\cdot0.21H_2O_2$	$3.25\cdot10^8$	

Thus, we established that peroxo solvates accelerate the reaction that is caused by the presence of solvated peroxide. Under the influence of obtained peroxide compounds the photochemical destruction of SAS was processed rapidly. The rate constants of SLES and $\dot{O}H$ radicals speed reaction in the presence of the peroxo solvates of ZnO, MgO and $CaCO_3$ were obtained.

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