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ADSORPTION OF OLIGOMERIC PEROXIDES ON AEROSIL AND MAGNESIUM OXIDE AND THEIR BEHAVIOR ON THE WATER-AIR PHASES INTERFACE

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Abstract. Oligomeric peroxide adsorption of sebacic acid on aerosil and magnesium oxide was studied. Adsorption process parameters were found. It is shown that the adsorption takes place through the hydrogen bonds formation between OH^- groups of adsorbents surface and peroxide groups. The adsorption process suggests the behavior of peroxide compounds on the water-air phase's interface. Monomolecular film formations on water surface for oligomeric peroxides were studied. It was found that calculated values of the area extrapolated to zero pressure (S_0) depend on the solvent which was used to apply the peroxide in the phases interface. Oligomeric peroxide monolayers considered as condensation-type monolayers. Thermal decomposition of oligomeric peroxide and its di- and monoperoxide analogues was studied. It was shown that total constants of thermal degradation rate k for oligomeric peroxide are higher than those for di- and monoperoxide analogues. There is a correlation between S_0 calculated values and the constants of thermal degradation rate for oligoperoxide. The less is S_0 value the higher is k value. The conformational state of the macromolecule was preserved during transferring the oligomeric peroxide solution in an organic solvent to the phases interface that affects k values.

Keywords: oligomeric peroxides, adsorption, monolayer, reactivity.

1. Introduction

Oligomeric peroxide considered as effective initiators of radical polymerization [1-4]. The initiators of this type compounds can be used to obtain polymer-mineral composites, process the surfaces of different nature or modify polymeric materials. The adsorption of a monomer and initiator on solid surface is affected by the processes involving oligomeric peroxides in the presence of dispersed minerals.

The introduction of dispersed oxides Fe_2O_3, Cr_2O_3 and V_2O_5 into the polymerization mixture affects the thermal decomposition rate of radical polymerization initiators [5]. The destruction of peroxide occurs in both a homogeneous solution and surface of the disperse oxides. Initiator heterolysis might be possible depends on the surface nature. The polymerization rate of the peroxide heterogeneous decomposition on the surface of dispersed mineral decreases in comparison with that of the homogeneous system. The oxidation-reduction interaction of peroxide-surface with dispersed mineral leads to an increase in the polymerization process rate. The nature of the dispersed oxide, apart from the effect on the thermal destruction rate of the peroxide initiator, affects the growth and breakage of the polymer chains. It suggests on the features that will be manifested for aerosil and magnesium oxide. Because of unique properties aerosil and magnesium oxide are often used to produce polymer-mineral composites [6-8]. When the mineral was added to the polymerization system, adsorption of both monomer and peroxide initiator was observed [9]. This feature affects the basic parameters of polymerization and the molecular characteristics of polymers which formed in the filled systems. Aerosil and dispersed oxides Fe_2O_3, Cr_2O_3, V_2O_5, PbO and natural mineral clinoptilolite can affect both the rate of polymerization process and the thermal decomposition of the peroxide initiator [10-13]. Investigated disperse minerals influence on molecular weights of polymers and molecular weights distribution [12-14]. In the presence of disperse minerals, a linear breakage of the growing polymeric radicals with the participation of surface groups of the filler is observed. Surface modification with the dispersed oxide TiO_2 changes the polymerization rate and affects the rate constant of the peroxide thermal decomposition [15]. In the case of polymerization in the presence of disperse minerals, grafting of polymer macromolecules with the filler surface is observed. The degree of macromolecules grafting with the minerals surface depends on the nature

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of the filler and initiator of radical polymerization. Consequently, the nature of disperse minerals surface affects the course of the polymerization process and the properties of polymer-mineral composites, where adsorption of all components plays important role.

So, the aim of this work was to study adsorption of oligomeric peroxide of sebacic acid (OSA) on aerosil and magnesium oxide and their behavior on the water-air phases interface. The peculiarities of the formation of monomolecular layers of oligomeric peroxides of pumelinoic (OPA), azelaic (OAA) and sebacin OSA acids on the water surface were studied.

2. Experimental

Oligomeric peroxides were obtained by the polycondensation reaction on the phases interface of the corresponding dibasic acids chloride and sodium peroxide [16]. The degree of the polycondensation of oligomeric peroxides was within the range of 9–20. The oligomeric peroxides of sebacic (OSA), azelaic (OAA) and pimelic (OPA) acids were studied in this work. To compare the rate constants of the thermal decomposition, the mono- and diperoxide analogues of oligoperoxide were obtained [17, 18]. The adsorption experiments were carried out for a styrene solution, which was released from the inhibitor and fractionated before adsorption experiments. Commercial samples of aerosils (A-175, alumino aerosil (AlA), titanone aerosil (TIA) and methyl aerosil (MeA)) were used in the experiments.

Specific surface area for A-175, AIA, TIA and MeA were determined with a low-temperature adsorption of gaseous nitrogen and their correspondent values were ~190, 170, 120 and 190 m^2/g, respectively. The size of the filler particles was in the range of 10–40 nm with the bulk density of 40–60 g/l. The content of aluminum oxide was 3.5 % and titanium oxide – 40.3 % in AIA and TIA, respectively. Methyl aerosil contained 4.0 % of methoxyl groups. Magnesium oxide (MERCS, 99.5%) with a specific surface area of 40 m^2/g was used in adsorption experiments. OSA adsorption on aerosils and magnesium oxide were carried out in a solution of styrene. Adsorption experiments were carried out in the temperature range of 308–318 K. The OSA solution of known concentration was added to an ampoule containing a certain amount of aerosil, then purged in argon and sealed. During the experiments the ampoules were continuously rotated. After that, the ampoules were removed from thermostat, open and centrifuged. The content of peroxide groups in styrene was determined with the iodometric method [19].

The Langmuir vertical balance was used for the measurement of the monolayers surface pressure of the peroxides. Solutions of peroxides were applied on a water surface of a cuvette in size of 60×16.5 cm. A barrier made of teflon compressed the monolayer on the water surface. All measurements were carried out at a compressive rate of 0.1 cm/s. To obtain a monomolecular layer, a drop of peroxide solution in an organic solvent was applied to a pure aqueous surface. The monolayer was compressed after 10 min. Water surface was renovate using the teflon barrier before every monolayer preparation. Measurement of monolayers surface pressure in different solvents was carried out 3–4 times at 293 K. In all cases, calculation error at the determination of the area value extrapolated to zero pressure did not exceed ±5 rel %.

The thermal decomposition of oligomeric peroxides in organic solvents was investigated in a sealed ampoule. A solution of peroxide of a certain concentration in the solvent was placed in a clean and dry ampoule and was purged with argon before to be sealed. The ampoules were thermostated at temperature value of 353±0.05 K. At certain time intervals, the ampoules were chilled and peroxide concentration was determined by the iodometric method [19]. All organic solvents were thoroughly purified through their fractionation in argon atmosphere [20, 21]. Calculation errors at the determination of the thermal decomposition constants did not exceed 3 %.

3. Results and Discussion

Adsorption of OSA on aerosils and MgO is well described by the well-known equation of Langmuir. The adsorption isotherms of OSA on magnesium oxide at various temperatures are shown in Fig. 1.

The obtained data for the adsorption are linear in the $1/C–1/A$ coordinates (Fig. 2), which allowed to determine the parameters of the adsorption process: the maximum adsorption (A_∞), the adsorption-desorption equilibrium constant (K), and the area of the oligoperoxide link in the adsorption layer (S).

The ΔG, ΔH and ΔS values of the adsorption process were calculated by the temperature dependence of the adsorption constants (Table 1). The thermodynamic parameters of the adsorption processes on the surface of aerosil and magnesium oxide are similar. The area of the peroxide layer is (61–53 $Å^2$) on aerosil surface and (13.7–11.5 $Å^2$) on MgO surface. The different numerical values of S on aerosil and magnesium oxide surface may indicate different orientation of OSA macromolecules in the adsorption layer. Adsorption of OSA occurs due to the formation of hydrogen bonds between peroxide groups and OH^- groups on the surface of the aerosil and MgO. Since number of OH^- groups on the methyl-aerosil surface is very low the OSA adsorption is negligible (Table 1).

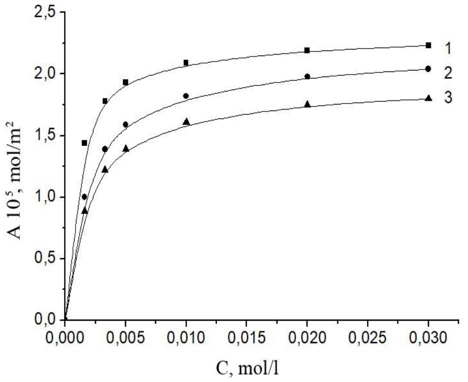

Fig. 1. Isotherms of OSA adsorption on magnesium oxide at 308 K (1); 313 K (2) and 318 K (3). Styrene is a solvent

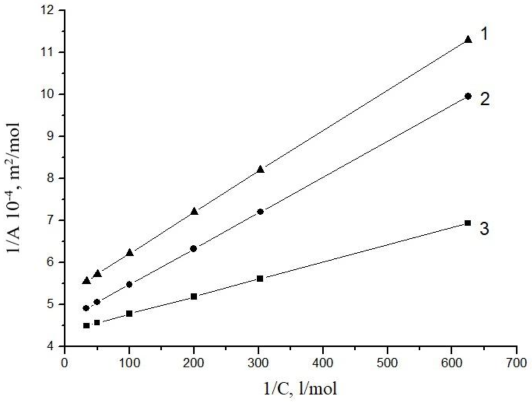

Fig. 2. The dependence of 1/*A* on 1/*C* for the process of OSA adsorption on magnesium oxide at 318 K (1); 313 K (2) and 308 K (3). Styrene is a solvent

Table 1

Physico-chemical parameters of OSA adsorption on the aerosils and magnesium oxide surfaces

Adsorbent	*T*, K	$A_\infty \cdot 10^6$, mol/m^2	$S\ 10^{20}$, m^2	K_p, m^3/kmol	-Δ*G*, kJ/mol	-Δ*H*, kJ/mol	-Δ*S*, J/mol K
Aerosil A175	308	3.10	53	871	17.3	50.2	107
Aerosil A175	313	2.99	56	529	16.3		
Aerosil A175	318	2.74	61	421	16.0		
Aerosil AAl	313	1.99	84	576	16.5	–	–
Aerosil ATi	313	1.14	146	221	14.0	–	–
Aerosil AMe	313	0.29	572	28	8.76	–	–
MgO	308	22.9	13.7	1059	17.8	55.1	121
MgO	313	21.6	13.0	543	17.2		
MgO	318	19.1	11.5	533	17.0		

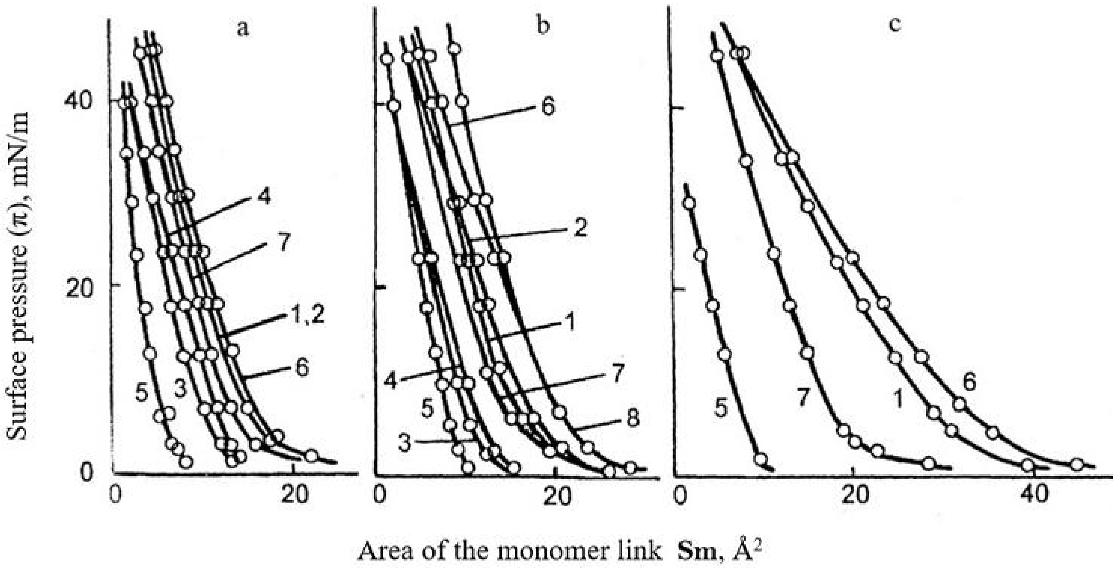

Fig. 3. The isotherms of surface pressure (*π*) of monolayers of OPA (a), OAA (b) and OSA (c) oligomeric peroxides. Solvents are benzene (1); toluene (2); acetone (3); methylethylketone (4); dioxane (5); chloroform (6); chlorobenzene (7); ethylbenzene (8) and ethylacetate (9)

The adsorption processes of peroxide on aerosil and magnesium oxide surface are similar. The adsorption of peroxide groups occurs due to the formation of hydrogen bonds with OH^{-} groups of aerosil or magnesium oxide surface.

The structure of the OPA macromolecules in the adsorption layer may be similar to the behavior of oligoperoxide in the monomolecular layer at the water-air phases interface. The method of studying monomolecular layers has been successfully used to study polymers layers [22, 23]. The nanomaterials were constructed based on monomolecular layers of proteins [24]. Interesting data were obtained in the study of polymeric monomolecular films containing xanthene groups [25]. The value that correspond to the monomeric chain of peroxide in a monolayer (S_m) grows in direction of OPA<OAA<OSA. The isotherms of surface pressure (π) of the studied oligomeric peroxides are shown in Fig. 3. The monolayers of the studied oligomeric peroxides belong to the condensation-type monolayers [26].

Higher size of methylene bridge between peroxide groups leads to the shift of the isotherms towards larger area of the monomer link values (S_m) (Fig. 3). The S_m value is influenced with the nature of the solvent used to form monolayer on the phases interface. The oligomeric peroxides in various solvents are in different conformation states which might be preserved when transferred to a pure water surface. Different conformations of oligomeric peroxide, depending on the solvent, are correlated with the surface pressure isotherms and on the surface area S_m.

The influence of the solution concentration on the surface pressure of oligoperoxides was studied using OPA and OAA. Benzene, styrene and chloroform were used as solvents. The concentration of peroxide varied from 0.04 to 1.0 g per 100 ml. The surface pressure isotherms of OPA monolayers, which were formed on the surface of water from benzene solutions are shown in Fig. 4. The nature of the surface pressure isotherms for OAA is almost the same. The solvent used to apply peroxide to the surface affects the values of area corresponding to the monomer link. It can be concluded that a decrease in the concentration of oligomer peroxide leads to a shift of the surface pressure isotherms towards higher values of the areas corresponding to the monomeric link of OPA. Various types of films from stretched-liquid to condensed-liquid ones can be obtained [20]. The numerical values of the areas that belong to the monomeric peroxide layer (S_m) for the films obtained from the applying solutions of different concentrations are given in Table 2. An increase in the size of the monomer chain on $-CH_2-$ group for OAA leads to the increase in the numerical values of S_m compared to that of OPA. The values of S_m for films formed from chloroform are slightly higher than the corresponding values obtained from benzene or styrene solutions (Table 2). This indicates a higher thermodynamic quality of chloroform in comparison with benzene or styrene. The extrapolated values of the S_m areas that belong to the monomer unit are related to the volume of the oligoperoxide coil in the solution. The transfer of oligomeric peroxide macromolecules to the surface of water largely retains the conformational state of peroxide and affects the reactivity of peroxide groups.

The correlation of S_0 values with the rate constants k of the OSA and thermal degradation in different solvents are given in Table 3. The thermodestruction process in the studied solvents is well described by the kinetic equation of the first order reaction rate (Fig. 5). The effective rate constants k of OSA thermal decomposition were calculated from the inclination of the dependences $\ln(C_0/C_t)$ *vs*. t. The values of k depends on reaction medium. The highest value is observed during the reaction of OSA thermal decomposition in dioxane. The rate constant of the decomposition in ethylbenzene is more than twice as low. It is found that S_0 value is inversely proportional to k value. For example, k values for didecanoildiperoxyadipinate (DP) and lauryl peroxide (PL) of mono- and diperoxide analogues of OSA are given in Table 3.

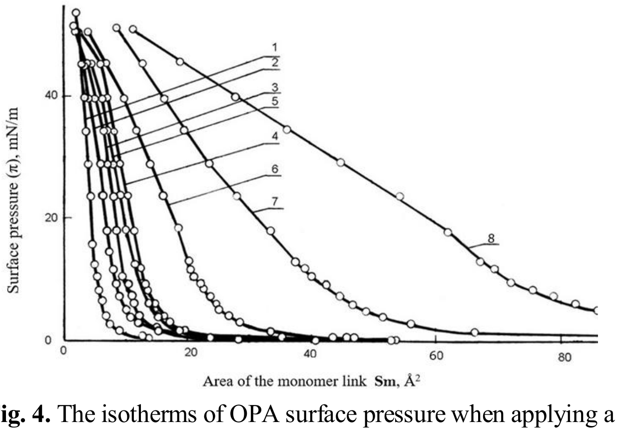

Fig. 4. The isotherms of OPA surface pressure when applying a monolayer from benzene solution of various concentrations (g/dl): 1.0 (1); 0.55 (2); 0.32 (3); 0.25 (4); 0.16 (5); 0.125 (6); 0.08 (7) and 0.04 (8). Temperature is 298 K

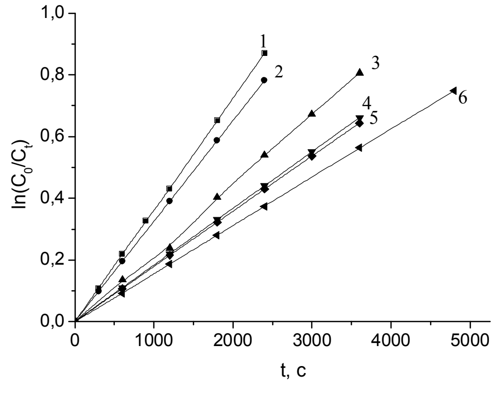

Fig. 5. Kinetetic curves of OSA thermal decomposition at 353 K. Solvents are dioxane (1); ethylacetate (2); chlorbenzene (3); benzene (4); toluene (5) and ethylbenzene (6)

Table 2

The values of the area S_0 (Å^2) corresponding to the monomeric chain of peroxide in the monolayer

Solvent	Oligoperoxide	The values of S_0 at various concentrations of peroxide, g/dl							
		1.0	0.55	0.32	0.25	0.16	0.125	0.08	0.04
Benzene	OPA	5.6	8.6	11.3	14.0	15.0	25.3	42.0	89.5
	OAA	8.6	9.5	12.0	15.0	16.5	26.6	30.6	45.0
Chloroforme	OPA	7.3	14.5	15.3	16.3	17.3	28.6	49.0	95.0
	OAA	9.0	15.6	17.6	–	22.3	31.0	51.0	54.0
Styrene	OAA	7.3	8.6	11.0	12.6	16.0	23.0	33.0	47.3

Table 3

The limit values of the areas corresponding to the chain of OSA (S_0) and thermolysis rate constant (k) of peroxides in various organic solvents at 353 K

Solvent	S_m, Å^2	k 10^5, s^{-1}		
		OSA	DP	PL
Dioxane	7.6	36.2	37.2	33.4
Acetone	10.6	35.6	31.9	–
Ethylacetate	11.0	32.6	24.7	26.1
Methylethylketone	12.0	–	–	–
Chlorbenzene	15.6	22.4	20.9	21.5
Styrene	16.0	19.9	19.2	-
Benzene	16.0	18.4	19.4	17.3
Toluene	17.0	17.9	17.4	16.1
Ethylbenzene	21.3	15.6	14.1	15.1
Chloroform	22.5	24.6	24.8	24.4

The numerical values of k for DP and PL are lower than the corresponding values for OSA, which can be explained by the presence of thermal degradation of oligoperoxide intra-molecular induced decomposition. Since OSA has a oligomeric nature, this peroxide can have a different conformational state at different solvents. When oligomer peroxide from various organic solvents is transferred to the water-air phases interface, its conformational state can be stored. Thus, the values of S_0 obtained in the observed conditions will be different. The different conformational state of oligomeric peroxide will affect the total rate of the thermal decomposition. A correlation between the total constants of oligoperoxide thermal decomposition and the values of the areas corresponding to the monomer link was found.

The thermodestruction of oligomeric peroxides includes the primary homolytic disintegration and the processes of intermolecular and intra-molecular induced decomposition [27]. The numerical values of k for oligomeric peroxide are more than the corresponding values of mono- or diperoxide analogues. The less is S_0 value of oligomer peroxide in the solution, the more is contribution to the effective k value of the induced decomposition processes.

4. Conclusions

The process of oligoperoxide adsorption on the surface of aerosil and magnesium oxide is well described by the equation of Langmuir's monomolecular adsorption. The areas corresponding to the peroxide link in the adsorption layer are 61–53 and 13.7–11.5 Å^2 for the aerosil and magnesium oxide, respectively. This feature indicates the different orientation of the oligomer peroxide in the monolayer. The thermodynamic parameters of the adsorption process for aerosil and magnesium oxide are almost the same indicating its similarity. The ΔG, ΔH and ΔS thermodynamic parameters of the adsorption process are calculated according to the temperature dependence of adsorption-desorption equilibrium constants. Adsorption of oligomeric peroxides on aerosil and magnesium oxide occurs due to the formation of hydrogen bonds between the surface OH^- groups of the adsorbent and peroxide groups. At the boundary of the phase separation the behavior of oligomeric peroxides is similar. The monolayers of the studied oligomeric peroxides belong to the condensation-type. The solvent used to apply oligoperoxide film to water-air phases interface affects the area that correspond to peroxide monomeric link. The oligomer nature of the studied peroxides is manifested when applied peroxide monolayer to water-air phase interface in various organic solvents. The best thermodynamic quality of the solvent results in the increase in the area of the peroxide monolayer. Due to the changes in the conformational state, the reactivity of peroxide groups of oligoperoxide is also changes.

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АДСОРБЦІЯ ОЛІГОМЕРНИХ ПЕРОКСИДІВ НА АЕРОСИЛІ І ОКСИДІ МАГНІЮ ТА ЇХНЯ ПОВЕДІНКА НА МЕЖІ РОЗДІЛУ ФАЗ ВОДА - ПОВІТРЯ

Анотація. *Вивчено адсорбцію олігомерного пероксиду себацинової кислоти на аеросилах та дисперсному оксиді магнію. Знайдено параметри адсорбційного процесу. Показано, що адсорбція здійснюється внаслідок утворення водневих зв'язків поверхневих ОН– груп адсорбентів та пероксидними групами. Процес адсорбції подібний до поведінки пероксидних сполук на межі поділу фаз вода – повітря. Вивчено особливості формування мономолекулярних плівок олігомерних пероксидів на водній поверхні. Встановлено, що числові значення площ, екстрапольовані на нульовий тиск (S_0), залежать від природи розчинника, який застосовували для нанесення пероксиду на межу розділу фаз. Моношари досліджуваних олігомерних пероксидів належать до конденсованого типу. Вивчено термічний розклад олігомерного пероксиду та його дипероксидного та монопероксидного аналогів. Показано, що сумарні константи швидкості термодеструкції k для олігомерного пероксиду вищі, у порівнянні з ди- та монопероксидними аналогами. Між числовими значеннями S_0 та константами термічного розкладу k олігопероксиду існує кореляційна залежність. Чим менше значення S_0, тим вище значення k. При перенесенні розчину олігомерного пероксиду в органічному розчиннику на межу розділу фаз конформаційний стан макромолекули зберігається, що впливає на чисельні значення величин k.*

Ключові слова: *олігомерні пероксиди, адсорбція, моношар, реакційна здатність.*