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MONOMOLECULAR FILMS OF DIPEROXIDES ON THE WATER–AIR INTERFACE

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The monomolecular films of diacylic diperoxides on the water/air interface studied. The behavior of monomolecular films of diperoxides affected by the structure of their molecule. The numerical values of the areas of molecules that extrapolated to zero pressure are different. This indicates a different conformation of the molecules in the monolayer. The optimal geometric structures of the diperoxides molecules and their electronic properties were calculated by the quantum-chemical method. Calculations of conformational states of the molecule of diperoxides carried out. Experimental data and quantum-chemical calculations consistent with each other.

Keywords: diperoxides, monomolecular layers, quantum-chemical calculation, conformation.

1. Introduction

Polyfunctional peroxide compounds are successfully used for obtaining polymer–mineral composites, polymers with special properties, nanomaterials, and processing of various surfaces [1, 2]. Peroxide initiators are widely used in the processes of emulsion and suspension polymerization [3–5]. Therefore, for the successful use of polyfunctional peroxides, the information about their behavior at the interface surface is required.
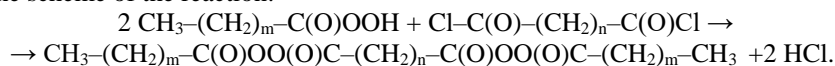
The preparation of monomolecular films is one of the widely used methods of studying the behavior of the substances on the air-water interface [6]. This method opens up the ability to control the structure of materials, to organize and orientate the molecules in monolayers, providing the maximum efficiency of the chemical reactions [7].

The preparation of Langmuir films is associated with the formation of monolayers of surfactants on the liquid-air interface – when spreading droplets of a solution on the water surface. Many insoluble in the water amphiphilic substances represent polar molecules of organic substances containing the hydrophilic part – "head" and a hydrophobic part – "tail" capable of spreading on the water surface as a monomolecular layer. While investigating the dependence of the surface pressure from the monolayer area Langmuir found the existence of various phase states in such films. Monomolecular films of insoluble amphiphilic substances on the surface of the liquid were called Langmuir films [6]. The classic method for obtaining Langmuir films is the use of a special cuvette with a barrier, which serves to regulate surface pressure by changing the area covered by the surfactant. At low pressure, the molecules are in a state of "two–dimensional gas". The increase of the pressure through the barrier leads to the formation of ordered monolayers of condensed liquid.

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The present work studies the monomolecular films of diacylic diperoxide initiators formed on the aqueous surface due to the presence of hydrophilic and hydrophobic components in the molecule. The surface pressure of diperoxide compound monolayers was determined. The heterogeneous processes occur with the participation of these compounds and the results of this study may be useful for predicting the behavior of diperoxide on the phase boundary. The results of the study of monolayers at the phase boundary were compared with the quantum chemical calculations of diacyl diperoxide compounds.

2. Materials and experimental procedures

The diperoxides (DP) were synthesized by the interaction of corresponding peroxycarboxylic acids and the dichloride of dicarboxylic acids in the presence of pyridine [5]. The scheme of the reaction:

$$2\ CH_3–(CH_2)_m–C(O)OOH + Cl–C(O)–(CH_2)_n–C(O)Cl \rightarrow$$
$$\rightarrow CH_3–(CH_2)_m–C(O)OO(O)C–(CH_2)_n–C(O)OO(O)C–(CH_2)_m–CH_3\ +2\ HCl.$$

The diperoxides were washed with water and recrystallized. The purity of synthesized peroxides determined by iodometric analysis [8] was at least 98.5–99.5 %.

The investigated diperoxide compounds had different carboxylic (R_1) and dicarboxylic (R_2) radicals of various sizes and flexibility. Their general formula and numeration of DP are:

$$CH_3–(CH_2)_m–C(O)–O–O–C(O)–(CH_2)_n–C(O)–O–O–C(O)–(CH_2)_m–CH_3\ ,$$

were n=2, m=8 (**I**); n=3, m=8 (**II**); n=4, m=0 (**III**); n=4, m=3 (**IV**); n=4, m=8 (**V**); n=8, m=0 (**VI**); n=8; m=1 (**VII**); n=8, m=8 (**VIII**); C_6H_5, n=4 (**IX**); m=8, $n–C_6H_4$ (**X**). ; n=4: m=5 (**XI**).

The monomolecular films of DP of different types were formed. We used the vertical Langmuir surface scales to measure the surface pressure of monomolecular films [6]. The solvent effects on the area of the peroxide molecules in their monolayer were studied. The surface pressure (π, mN/m) of the monolayers of the peroxides was measured using a vertical installation. Solutions of peroxides in a certain solvent were applied to the aqueous surface of the cuvette measuring from 60 to 16.5 cm. The monolayer was compressed on the surface of the water by a Teflon barrier. All measurements were made at a compression speed of 1 mm/s and constant temperature 293±0.5 K. To obtain a monomolecular layer a drop of peroxide solution from a micropipette was applied on a clean aqueous surface. The monolayer was compressed in 10 minutes. Before applying the monolayer the water surface was updated by moving the Teflon barrier on it. In all cases, the error did not exceed ± 5 %.

Surface pressure isotherms were obtained as the dependence of the pressure π on the area occupied by one molecule of the test substance S. The number of monomer units x of the substance in the monolayer was determined by the formula:

$$x=Ng/M, \tag{1}$$

where M is the molecular weight of the monomer unit; N – Avogadro number; g – the amount of substance on the substrate surface, grams.

Knowing the number of monomer units that are contained on the surface, the area S was determined by the formula:

$$S=a/x, \tag{2}$$

where a is the surface area of the monolayer; x is the number of monomer units (mole of a substance in a monolayer).

Surface pressure was determined by the formula:

$$\pi = g \Delta P / b, \tag{3}$$

where g – gravitational constant, m/s^2; ΔP – change of load, g; b – perimeter of the plate, m.

Quantum–chemical calculations for diacylic diperoxides were carried out using the semiempirical program MOPAC2016 [9] with the graphical interface Winmostar [10]. We used different semiempirical methods to optimize the geometric structure and calculate the heat of formation ($\Delta_f H^{298}$) and energies of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals, as well as charges on atoms by Mulliken.

3. Results and discussion

The surface pressure of DP compound monolayers was studied for didecanoyldiperphthalate (**X**), diacetyldiperadipinate (**III**), dienanthioyldiperadipinate (**XI**) and didekanoyldiperadipinate (**V**) in different organic solvents. For diperoxides **III**, **XI** and **V** the radical between the peroxide groups R_2 is the adipic acid residue –$(CH_2)_4$–, and peroxide **X** has the flat radical –C_6H_4–residue of phthalic acid. The end radicals R_1 of peroxide **III** are small. The end radicals R_1 in peroxides **V** and **X** are the same and equal CH_3–$(CH_2)_8$–, diperoxide **XI** end radical is smaller: CH_3–$(CH_2)_5$–. The isotherms for the surface pressure of the studied diperoxides were obtained by applying films from chloroform (Fig. 1). The behavior of the investigated diperoxides on the water-air interface is different. Diperoxides **X** and **III** form monomolecular layers of the condensed type [6] on the surface of the water. In fact, the residues of adipic acid in the molecule **III** and phthalic acid in **X** are practically no–flexible.
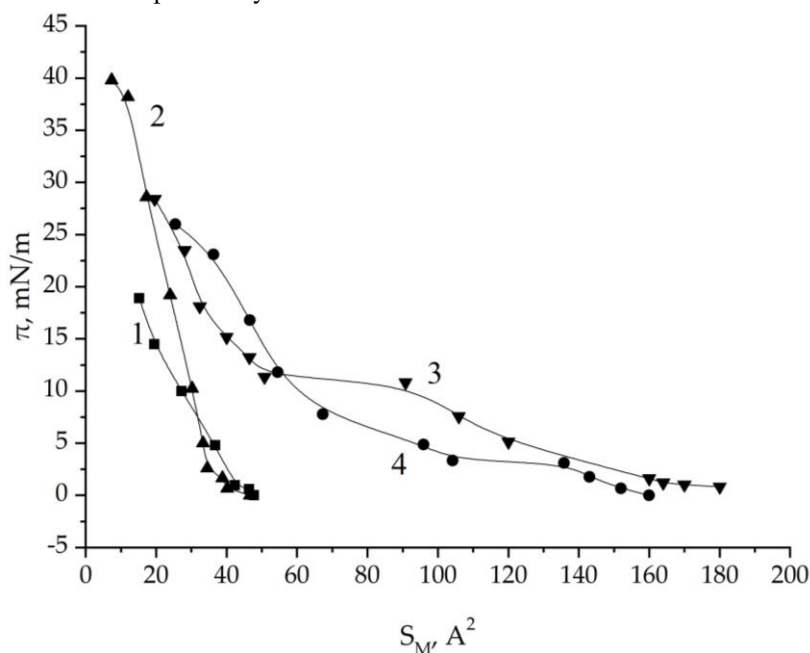

Fig. 1. Isotherms of surface pressure for peroxide monolayers: *1* – **X**; *2* – **III**; *3* – **V**; *4* – **XI**. Diperoxide was applied to the interface using chloroform

For diperoxide **V** (Fig. 1, curve 3) at small surface pressures the film exists in the two–dimensional gaseous state (G), and further compression converts the film to the stretched liquid state (L_1). The compression of the film in the state (L_1) converts it to the condensed state (L_2). The change in the area of the diperoxide molecule from ~90 $Å^2$ to ~50 $Å^2$ occurs at virtually unchanged surface pressure. On this site, $CH_3–(CH_2)_8–$ end radicals of peroxide **V** are squeezed out of the aqueous surface. The behavior of diperoxide **XI** is similar to that of the behavior of **V** (Fig. 1, curve 4).

The isotherms have a different nature (Fig. 1). Diperoxides containing the radical R_2, between the O–O bonds, the remainder of adipic acid, in the monolayer behave differently. It indicates the low flexibility of the group $–(CH_2)_4–$ in the peroxide molecule. The isotherms are changing with increase the end radical R_1. The conformation state of the molecule in the monolayer is changed for peroxide. It indicates the displacement of the radicals $CH_3–(CH_2)_8–$ from the surface of the water. The monolayers of diperoxide **X** are rigid. The radical located in the middle of the molecule, the remainder of phthalic acid is flat and stiff.

The various solvents were used when the film applied to the interface of the water-air. It influenced the nature of the isotherms and the extrapolated values of the areas corresponding to the molecule in the monolayer (Fig. 2).
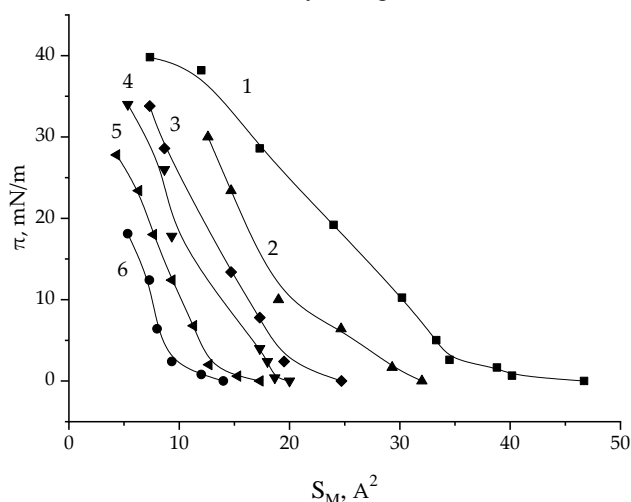

Fig. 2. The isotherms of surface pressure of monolayers of diacetyldiperadipinate (**III**) when applied from a solvent: *1* – chloroform; *2* – tetrachloromethane; *3* – toluene; *4* – cyclohexane and butylacetate; *5* – benzene and ethylbenzene; *6* – xylene and ethyl acetate

The isotherms of surface pressure of monolayers of diperoxide **III**, obtained from various organic solvents on the water-air interface are shown in Figure 2. It should be noted that the isotherms for films of DP **III**, obtained on the surface from solution in xylene and ethyl acetate, are practically identical (curve 6). Similarly, monolayers formed from cyclohexane and butylacetate (curve 4) and benzene and ethylbenzene (curve 5) are the same.

The numerical values of the areas (S_0) occupied by the molecules of the studied diperoxides in the monolayer formed from various solvents are given in Table 1.

The smallest areas in the monolayer have **III** molecules. The area of the **XI** diperoxide in the monolayer is slightly smaller than the corresponding values for the **V**. The numerical values of the extrapolated areas for all investigated diperoxides depend on the solvent from which the monolayer was formed. Numerical values of the areas of diperoxide in monolayer, which were formed from the different solvents, indicate the possible different packaging of the molecules in the monolayer. The hydrophilic peroxide groups are on the boundary of the phase separation. The hydrophobic terminal hydrocarbon radicals can be located both in the plane of the section and oriented toward the air phase at high pressures in the monolayer. Since the size of the aliphatic radical between the peroxide groups is small, its effect on the change in the area of the molecule in the monolayer when compressed will below.

Table 1

The extrapolated values of the areas corresponding to the molecule diperoxide in a monolayer

Solvent	Area per molecule (S_0), Å^2		
	Diperoxide		
	III	**XI**	**V**
Acetone	12.0	–	31.0
Dioxane	13.0	–	26.0
Benzene	31.5	35.6	40.0
Toluene	30.5	36.6	43.0
Chloroform	42.0	80.0	95.0
Ethylacetate	46.5	10.3	37.0
Tetrachloromethane	50.0	56.3	68.0

Thus, the results of the study of monolayers of diacylic peroxide surface pressure give information about their behavior on the water-air interface and predict their reactivity in these conditions.

Quantum–chemical calculations can give important information about the structure and electronic properties of the studied diperoxides. The conformational analysis will allow you to find the areas of the molecules and the degree of packing of the diperoxides at the interface.

We carried out quantum-chemical calculations using some of the semiempirical methods: AM1, PM3, PM5, PM6, MNDO and RM1 for the diperoxide **IV** molecule. The values of the heat of formation ($\Delta_f H^{298}$) of diacylic diperoxide **IV** calculated by semiempirical methods (Table 2) and were obtained based on thermochemical experiments [11]. The numerical values of $\Delta_f H^{298}$ calculated by the PM3 and RM1 almost coincide with the experimental data. The semiempirical method RM1 has more opportunities compared to others (Table 3).

Table 2

The results of calculations of physical-chemical parameters for diperoxide **IV** by semiempirical quantum-chemical methods

Method	$\Delta_f H^{298}$, kJ/mol	μ, D	HOMO, eV	LUMO, eV	η, eV	S, Å^2	V, Å^3
AM1	−1038.1	5.089	−11.089	0.348	5.719	395.2	426.64
PM3	−1106.9	3.914	−11.440	−0.760	5.600	398.26	440.37
PM5	−1044.7	1.992	−10.717	−1.133	4.792	393.32	432.86
PM6	−1044.7	1.993	−10.717	−1.133	4.792	393.32	432.87
MNDO	−986.9	3.419	−11.041	0.358	5.699	413.54	446.11
RM1	−1079.1	6.073	−11.018	0.453	5.736	393.79	426.75

The experimental value $\Delta_f H^{298}$ is thermochemical determined −1206.9 kJ/mol [11].

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Table 3

The results of the calculation of physical and chemical parameters of investigated
diperoxides by semiempirical method RM1

Diperoxide	$-\Delta_f H^{298}$, kJ/mol	$-\Delta_f H^{298*}$, kJ/mol	I_x, eV	HOMO, eV	LUMO, eV	η, eV	S, Å²	V, Å³
I	1214.7	1365.0	10.833	−10.833	0.250	5.542	542.3	590.7
II	1246.1	1347.6	10.915	−10.915	0.194	5.555	544.4	632.1
III	977.9	1080.1	11.151	−11.151	0.441	5.796	287.1	294.9
IV	1079.1	1206.9	11.018	−11.018	0.454	5.736	393.8	426.8
V	1240.4	1406.9	10.663	−10.663	0.387	5.525	554.2	635.5
VI	1046.3	1161.3	11.212	−11.212	0.508	5.860	356.0	381.7
VII	1063.0	1206.1	10.975	−10.975	0.540	5.758	358.9	429.3
VIII	1364.7	1488.1	11.061	−11.061	0.499	5.780	673.1	748.2
IX	693.2	–	9.913	−9.913	−0.633	4.640	395.1	435.4
X	1076.7	–	10.340	−10.340	−0.936	4.702	536.5	662.9
XI	1214.7	–	11.179	−11.179	0.818	5.999	487.7	510.0

*Thermochemical data [11].

The diperoxide compound **IV** is polar according to the obtained calculations. The dipole moments (μ) for it were calculated by different methods (1.993–6.073 D). The numerical values of the ionization potential (I_x) of diperoxide **IV** and the associated energy parameter HOMO are close (–11.089 to –10.717 eV). The numerical values of the energy of LUMO vary in the wider range from –1.133 to 0.453 eV. The numerical values of the total squares of molecules (S) and the volume of molecules (V) are close and depend on the calculation method. The total areas of the diperoxide molecules calculated by quantum-chemical methods are more than 10 times different from the corresponding values at the phase boundary (Tables 1, 3). This fact is explained by the fact that only 1/6 or 1/10 of the total area of the molecule can be placed at the interface. Also, the numerical value of the area in the monolayer is affected by the conformational state of the diperoxide molecule.

The structure of the investigated diperoxides in the basic state of the molecule is rod-shaped (Fig. 3). All DP's have many conformations at the expense of the flexibility of hydrocarbon radicals. Different conformational states of the DP molecules are characterized by practically the same energy and can substantially change the dipole moment.
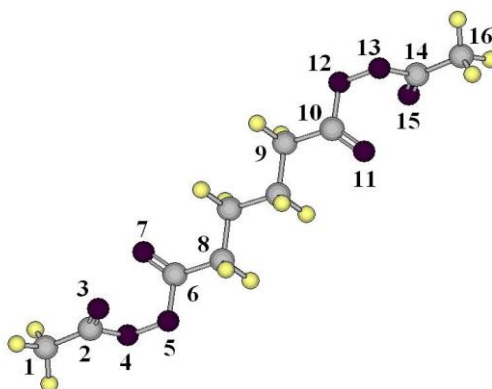

Fig. 3. The optimal geometrical structure of diperoxide **III**

The physicochemical parameters for the atoms that are part of the O–O groups and are located near them were calculated. The reactivity of the diperoxide molecules is due to the presence of peroxide groups in their composition. The numbers of heavy atoms (C and O) are shown in Figure 3. The parameters of carbon atoms, which are in positions away from peroxide groups, are practically the same. For diperoxides (**III, VI, IX**), at the ends of which the CH$_3$ group or the phenyl group C$_6$H$_5$ are located, the constant of the thermal decay rate is lower than for all other compounds, where the terminal radical is large [9]. The calculation of charges on heavy atoms (C and O) in the molecules of diperoxides indicates this. Thus, for the DP with terminal CH$_3$ group (**III, VI**) the numerical value of the charge on atoms 1 and 16 is –0.224 and –0.253. For all other compounds at the ends of which the molecules contain longer hydrocarbon radicals, the value is slightly lower and lies within –0.153 – –0.183 (Table 4). In the case of compound **IX,** the stabilizing effect of the phenyl radical is explained by the coupling effect of the electrons of the peroxide group and the substituent. The length of the peroxide bonds in the molecules of the studied DPs are close (1.3640–1.4139 Å). The length of the O–O bond in crystalline benzoyl peroxide is 1.46 Å according to the literary data [12]. The length of the connection of C–O in the carbonyl group of DP containing aliphatic radicals is the same and equal to 1.2093–1.2205 Å.

Table 4

The charges on atoms by Mulliken for the studied diperoxides

Atom	Diperoxide							
	I	II	III	VI	VIII	IX	X	XI
C(1)	–0.183	–0.179	–0.227	–0.253	–0.175	–0.163	0.153	–0.157
C(2)	0.330	0.328	0.334	0.342	0.327	0.367	0.330	0.334
O(3)	–0.280	–0.288	–0.313	–0.288	–0.291	–0.318	–0.313	–0.321
O(4)	–0.119	–0.122	–0.154	–0.117	–0.116	–0.152	–0.157	–0.139
O(5)	–0.150	–0.152	–0.118	–0.155	–0.156	–0.115	–0.111	–0.136
C(6)	0.316	0.325	0.330	0.324	0.322	0.337	0.361	0.334
O(7)	–0.297	–0.310	–0.285	–0.313	–0.310	–0.295	–0.275	–0.322
C(8)	–0.152	–0.162	–0.183	–0.158	–0.159	–0.163	–0.114	–0.158
C(9)	–0.144	–0.103	–0.155	–0.154	–0.176	–0.153	–0.097	–0.158
C(10)	0.324	0.324	0.334	0.331	0.328	0.334	0.361	0.334
O(11)	–0.289	–0.310	–0.320	–0.320	–0.288	–0.315	–0.274	–0.322
O(12)	–0.158	–0.151	–0.138	–0.135	–0.117	–0.137	–0.130	–0.136
O(13)	–0.115	–0.120	–0.137	–0.138	–0.152	–0.129	–0.135	–0.139
C(14)	0.324	0.334	0.345	0.346	0.321	0.377	0.337	0.334
O(15)	–0.280	–0.287	–0.317	–0.321	–0.309	–0.335	–0.321	–0.321
C(16)	–0.183	–0.174	–0.224	–0.224	–0.154	–0.153	–0.151	–0.157

All four carbonyl groups in the compound **IX** have the largest length of 1.2550 Å. The length between carbon and oxygen atoms in carbonyl groups is 1.2255 Å for a DP containing a phenyl nucleus between the peroxide groups (**X**).

Both peroxide groups in the molecule of DP have the same reactivity. The rigidity (η) of the studied DP's is low (Tables 2, 3). This indicates the possibility of reactions of these compounds with both electrophilic and nucleophilic reagents.

The solvent affects the nature of the isotherms and the extrapolated values of the areas corresponding to the molecule in the monolayer. The data obtained show that the nature of most isotherms belongs to the condensed type.

The conformational analysis of the DP **XI** was performed by changing the placement of the terminal radicals R_1 rotating around the O–O axis of the peroxide groups. In the main state, the diperoxide molecule is placed planarly on the water-air interface and is in a two–dimensional gaseous state (Fig. 4, *a*). Peroxide groups –C(O)–O–O–C(O)– are located on the surface of the water. The energy of the molecule at the same time is minimal (Fig. 4, *d*).
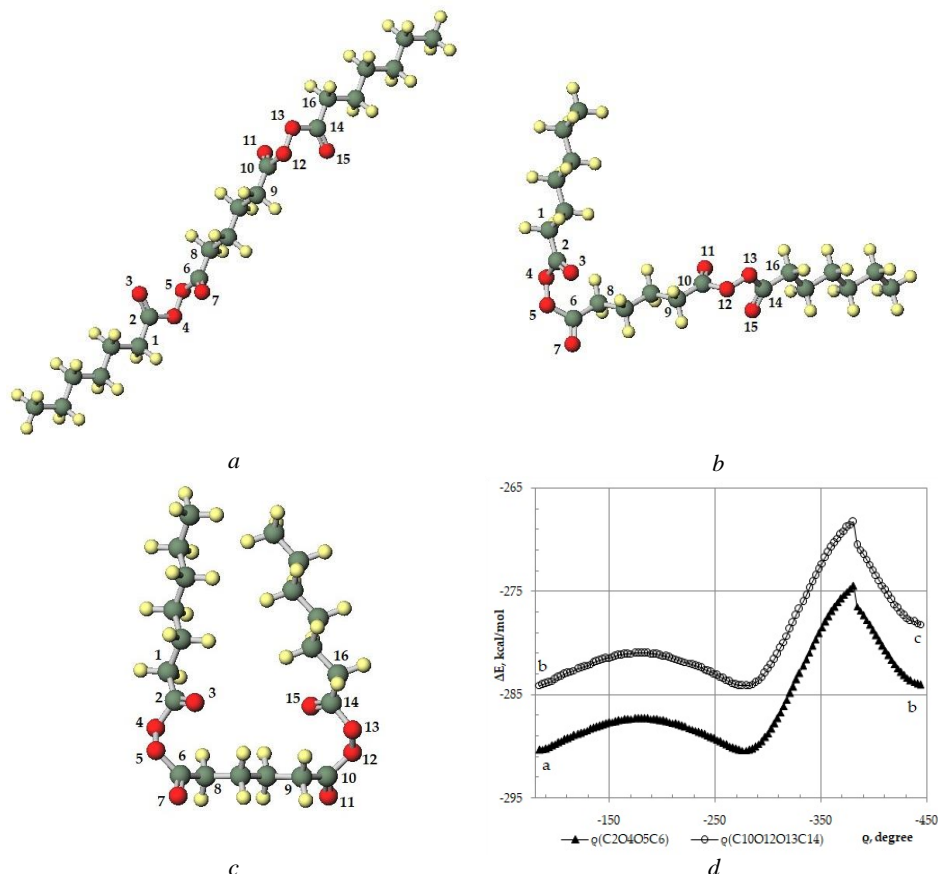

Fig. 4. Conformational states of the DP **XI** molecule: the two–dimensional gaseous state (*a*);
film in the expanded liquid state (*b*); film in a condensed state (*c*).
The paths of conformational transitions when the torsion angles (ρ)
of the groups C(2)O(4)O(5)C(6) and C(10)O(12)O(13)C(14) are changed (*d*)

When increasing surface pressure one of the terminal radicals displaces from the phase separation. Due to the change in the torsion angle C(2)O(4)O(5)C(6) from (–84 °) to (–444 °) the position of the carbonyl groups C(2)=O(3) and C(6)=O(7) changed, while the energy of the molecule increases. Figure 4, *b* depicts a peroxide molecule for this case, and Figure 4, *d* shows the transition path from the state (*a*) to the state (*b*). With further increasing surface pressure, the second radical R_1 is superseded by changing the torsion angle C(10)O(12)O(13)C(14) from (–84 °) to (–444 °), as well the position of the carbonyl groups C(10)=O(11) and C(14)=O(15) changes (Fig. 4, *c*). The energy of the DP **XI** molecule increases even more and the path of this change is shown in Figure 4, *d*.

4. Conclusions

The monolayers of 11 diperoxides of the different structures were formed on the water-air interface using the Langmuir method. The solvent affects both the nature of the isotherms and the extrapolated values of the areas corresponding to the molecule in the monolayer. The nature of most isotherms belongs to the condensed type.

From the investigation of the behavior of diperoxide monomolecular films on the water-air interface, the different conformations of the molecules in the monolayer were found. Diperoxides with small radicals $CH_3–(CH_2)_m–$ form on the surface condensed monolayers. The radical located between peroxide groups $–(CH_2)_n–$ is stiff. Hydrophilic peroxide groups are located on the surface of the water, and hydrophobic hydrocarbon radicals can squeeze from surface to air.

The conformational analysis of the studied peroxides indicates that the area of the molecule at the interface takes different values. The correspondence of theoretically calculated and experimental data indicates the correctness of the used semiempirical quantum–chemical methods. The numerical values of the calculated areas are correlated with the corresponding values found for the molecules of the diperoxides in the monolayer. The results of this study may be useful for predicting the behavior of diperoxide on the phase boundary in heterogeneous processes with the participation of these compounds.

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МОНОМОЛЕКУЛЯРНІ ПЛІВКИ ДИПЕРОКСИДІВ НА МЕЖІ РОЗДІЛУ ФАЗ ВОДА–ПОВІТРЯ

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Вивчено мономолекулярні плівки діацильних дипероксидів (ДП) на основі аліфатичних сполук на межі розділу фаз вода–повітря. Пероксиди мають формулу:

R_1–C(O)–O–O–C(O)–R_2–C(O)–O–O–C(O)–R_1.
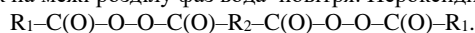
Наявність у молекулі гідрофільних та гідрофобних функціональних груп дає можливість формувати мономолекулярні плівки на межі розділу фаз вода–повітря. Показано, що досліджувані дипероксиди утворюють мономолекулярні плівки конденсованого типу. Пероксидні групи молекул ДП лежать на межі розділу фаз вода–повітря, а кінцеві радикали R_1 можуть розташовуватись як на межі розділу фаз, так й орієнтуватися в сторону газової фази. На поведінку мономолекулярних плівок дипероксидів впливає структура їхніх молекул. Розчинник, який використовували для нанесення пероксидів на межу розділу фаз, впливає на форму ізотерм поверхневого тиску та на числові значення площ пероксиду в моношарі. Показано, що радикал, який знаходиться між пероксидними групами, практично не піддається деформації. При зростанні поверхневого тиску бічні гідрофобні радикали в молекулі ДП можуть витіснятися з межі розділу фаз. Числові значення площ молекул, які екстраполювались до нульового тиску, різні, що свідчить про різну конформацію молекул у моношарі. На конформаційний стан молекул ДП впливає розчинник, який застосовували для нанесення ДП на межу розділу фаз. Різні конформації молекул ДП можуть впливати на швидкість термічного розкладу пероксидних груп. Оптимальні геометричні структури молекул дипероксидів та їх електронні властивості обчислено квантово-хімічним методом. Проведено розрахунки конформаційних станів молекули дипероксидів. Експериментальні дані та квантово-хімічні розрахунки узгоджуються між собою. Результати дослідження поверхневого тиску дипероксидів та їхні квантово-хімічні розрахунки можуть бути корисними для прогнозування поведінки цих ініціаторів на межі розділу фаз вода–повітря.

Ключові слова: дипероксиди, мономолекулярні шари, квантово-хімічний розрахунок, конформація.