
STRUCTURE
AND PROPERTIES

Behavior of Organosilicon Surfactants in Langmuir Films on the Surface of Water

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Abstract—The behavior of organosilicon surfactants of different structure in model systems—Langmuir films—at the water/air interface is studied. It is shown that, under the compression of Langmuir films, the conformational states of surfactants of different structure are different. The obtained data make it possible to explain a high stability of polymer suspensions synthesized in the presence of organosilicon surfactants.

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The study of colloid-chemical properties of organosilicon surfactants showed that the surface activity and thickness of the interfacial adsorption layer considerably depend on the structure of the main organosilicon chain, specifically on the concentration of functional groups and their arrangement in the main chain [1].

These effects are especially distinct from comparison of the colloid-chemical properties of dimeric and comb-shaped organosilicon surfactants. For example, the surface activity of dimeric surfactants containing aminopropyl groups at the ends of the PDMS(NH₂) organosilicon chain is 3.7 mN m²/mol, while for the comb-shaped surfactant containing main-chain aminopropyl groups PMADMS₆₀ this value is 14.2 mN m²/mol; the layer thickness is 13.1 and 33.5 nm, respectively. The concentrations of surfactants at which the minimum interfacial tension is attained are appreciably different: 2.5–3.0 wt % for PDMS(NH₂) and 0.05–0.10 wt % for PMADMS₆₀ [2].

The hypothesis concerning formation of interfacial layers on the surface of monomer droplets and polymer-monomer particles (PMPs) in the presence of surfactants insoluble in water was advanced in [3]. According to this hypothesis, a surfactant adsorbed from the monomer phase at the monomer droplet/water interface does not ensure a high stability of monomer emulsion in water; after cessation of mixing, the emulsion delaminates. The stability of emulsion

grows considerably if polystyrene taken in an amount of 1 wt % in terms of the monomer is dissolved in the monomer. It is known that the polymer is incompatible with organosilicon surfactants; therefore, the rate of surfactant diffusion from the volume to the interfacial adsorption layer increases and the development of core-shell particles is promoted [4]. Thus, the monomer emulsion becomes stable if an organosilicon surfactant and polystyrene are involved in formation of the interfacial layer [5–9].

Formation of the interfacial layer on the surface of polymer-monomer particles produced during polymerization initiation occurs in a similar manner. The effect of the polymer is more pronounced in this case, because it is formed in interfacial layers at the boundary with water, which functions as a polymer precipitator, and gives rise to a peculiar carcass of the surface of PMPs, thereby increasing the strength of the interfacial layer. In the volume of PMPs, the surfactant is displaced to the interfacial layer during polymer formation [8]. Knowing the conformational state of organosilicon surfactants in model systems—Langmuir films—is of importance for describing the structuring of organosilicon compounds at the interface and the mechanism governing formation of interfacial adsorption layers of these compounds on polymer-monomer particles in the heterophase polymerization of vinyl monomers.

Table 1. Characteristics of the initial organosilicon compounds

Name	Structure	M_w , g/mol	D	ρ , g/cm ³
2-(Carboxyethyl)- ω -(trimethylsiloxy)polydimethylsiloxane; (PDS), $n = 8$	$\text{HOOC}-(\text{CH}_2)_2-\text{Si}(\text{CH}_3)_2-\text{O}-\left[\text{Si}(\text{CH}_3)_2\right]_n-\text{Si}(\text{CH}_3)_2-\text{CH}_3$	812	1.40	1.0
α,ω -Bis(10-carboxydecyl)oligodimethylsiloxane; PDMS(COOH), $n = 30$	$\text{HOOC}-(\text{CH}_2)_{10}-\text{Si}(\text{CH}_3)_2-\text{O}-\left[\text{Si}(\text{CH}_3)_2\right]_n-\text{Si}(\text{CH}_3)_2-(\text{CH}_2)_{10}-\text{COOH}$	2 750	1.88	0.97
α,ω -Bis(3-aminopropyl)oligodimethylsiloxane; PDMS(NH ₂), $n = 30$ (Aldrich)	$\text{H}_2\text{N}-(\text{CH}_2)_3-\text{Si}(\text{CH}_3)_2-\text{O}-\left[\text{Si}(\text{CH}_3)_2\right]_n-\text{Si}(\text{CH}_3)_2-(\text{CH}_2)_3-\text{NH}_2$	2 480	1.85	0.99
α,ω -Bis(trimethylsiloxy-oligodimethylmethyl-(10-carboxydecyl)siloxane; PDMMCDs, $m = 14$ and $n = 32$	$\text{CH}_3-\text{Si}(\text{CH}_3)_2-\text{O}-\left[\text{Si}(\text{CH}_3)_2-\text{O}-\left[\text{Si}(\text{CH}_3)_2\right]_m-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-\text{CH}_3\right]_n-\text{Si}(\text{CH}_3)_2-\text{COOH}$	4 750	1.75	0.98
α,ω -Bis(trimethylsiloxy-oligodimethylmethyl(3-aminopropyl)siloxane: I—PMADMS ₆₀ ($n = 300$, $m = 60$) II—PMADMS ₅₀ ($n = 50$, $m = 50$) III—PMADMS ₁₂ ($n = 50$, $m = 12$) IV—PMADMS ₁ ($n = 82$, $m = 1$)	$\text{CH}_3-\text{Si}(\text{CH}_3)_2-\text{O}-\left[\text{Si}(\text{CH}_3)_2-\text{O}-\left[\text{Si}(\text{CH}_3)_2\right]_m-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-\text{CH}_3\right]_n-\text{Si}(\text{CH}_3)_2-\text{NH}_2$	29 400 9 596 5 230 6 199	1.80 1.83 1.85 1.87	1.01 1.01 0.98 0.96

The goal of this study was to explore the conformational rearrangements of organosilicon chains of surfactants under their compression in Langmuir films at the water/air interface.

EXPERIMENTAL

The objects of research were water-insoluble carboxyl and amino functional dimeric and comb-shaped organosilicon oligomers with different arrangements and concentrations of carboxyl functional substituents in the siloxane chain (Table 1). The average molecular mass of organosilicon compounds was determined by gel permeation chromatography relative to polystyrene standards; the density of the compounds was determined by pycnometry (GOST (State standard) R 53654.1-2009).

The properties of Langmuir films were investigated using a Minitrough Extended Langmuir trough (KSV, Finland) under compression and expansion between movable barriers; the surface area was varied at a rate of 15 cm²/min⁻¹. The surface pressure was measured with an accuracy of 0.1 mN/m⁻¹ according to the Wil-

helmy method with the use of a rough platinum plate. The surface area per molecule was estimated with an accuracy of 3%. The surface potential was measured by the vibrating electrode method using a SPOT sensor (KSV, Finland). The accuracy of measurements was 1 mV. The morphology of Langmuir films directly on the surface of water was visualized using a BAM 300 Brewster angle microscope (KSV, Finland). Micrographs presented in this study were geometrically corrected with allowance for observation under a Brewster angle of 53.1° and corresponded to an interfacial surface area of 200 × 200 μm. To protect the subphase surface from external effects leading to its oscillations, the Langmuir trough with sensors and the Brewster angle microscope were installed under a protective cover on a base with active vibration protection (Accurion, Germany). Demineralized water, which was purified with a Milli-Q Integral Water Purification System (Millipore, United States), was used as a subphase. The subphase was thermostatted at 20°C. Analytical-grade toluene (Khimmed, Russia) was used as a solvent for organosilicon surfactants.

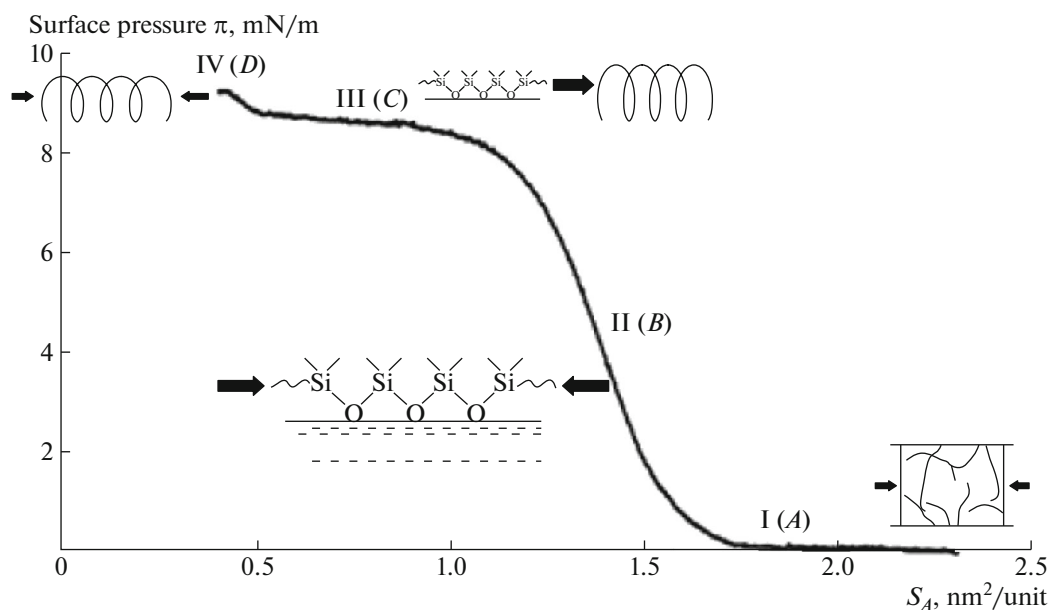


Fig. 1. Model of conformational changes of PDMS at the water/air interface: (A) Si and O atoms are adsorbed at the interface, randomly rotating chains; (B) the Si atom is displaced to the air phase; (C) the plateau corresponds to transition from the extended chain to the formation of helices; and (D) the densely packed layer of helices [10].

RESULTS AND DISCUSSION

The structuring of dimeric and comb-shaped organosilicon surfactants at the interface is determined by a high conformational mobility of the siloxane chain and the nature of functional groups. Learning of their conformational state in Langmuir films is of importance for describing the mechanism governing formation of interfacial adsorption layers of these compounds on polymer-monomer particles in the heterophase polymerization of vinyl monomers.

To estimate conformational changes of the organosilicon chain during displacement of the surfactant in the interfacial absorption layer by the polymer formed during polymerization, the behavior of organosilicon surfactants during their compression on the surface of water in Langmuir monolayers was investigated.

The authors of [10–12] developed a model that describes the behavior of organosilicon surfactants in Langmuir layer under compression, in particular, as a function of a change in the surface pressure (Fig. 1).

According to these models, in the initial region of the isotherm, the organosilicon chain is flat with methyl groups being oriented toward the air phase (Fig. 1, step A). Upon further compression, the isotherm demonstrates growth of the surface pressure related to coming together of polymer chains, ordering of methyl groups, and displacement of silicon atom to the air phase (step B). Upon further compression (step C), the conformation of the siloxane chain changes and forms, in accordance with some authors, helical structures or a bilayer at the interface (Fig. 2). At step D, deformation of the formed surfactant layer takes place;

according to one hypothesis, helices undergo deformation, while according to the other one folded layers are formed [10–12].

Figure 3 shows surface pressure and surface potential isotherms for the studied dimeric organosilicon compounds with end carboxyl and amino groups (PDMS(COOH) and PDMS(NH₂)). Regions A, B, C, and D may be distinguished on the surface pressure isotherms by analogy with the published data [10].

On the initial section of the isotherm, the organosilicon chain is flat, and the area per surfactant molecule is 8 nm². It may be assumed that in this state the density of the PDMS monolayer is $\rho_a = 1.0 \text{ g/cm}^3$ [13]. Upon further compression, an increase in the surface pressure is observed on the isotherm, organosilicon chains change their conformational state, and the area per surfactant molecule shortens to 6 nm² (Fig. 3, step B). Thereupon, at step C, as in the case of polydimethylsiloxane without functional groups for which isotherm was described in [10], there is a plateau, on which the area per surfactant molecule at a constant pressure decreases. On this isotherm region, the formation of helical structures or bilayer of the organosilicon chain occurs. The ability of organosilicon chains to form helical structures was confirmed by von G. Damschun using X-ray diffraction analysis [14, 15].

Further compression leads to a rise in pressure and causes collapse of the monolayer at a surface pressure of 40 and 22 mN/m for PDMS(NH₂) and PDMS(COOH), respectively. Thus, the presence of side functional groups does not reflect on the conformational transitions of organosilicon chains.

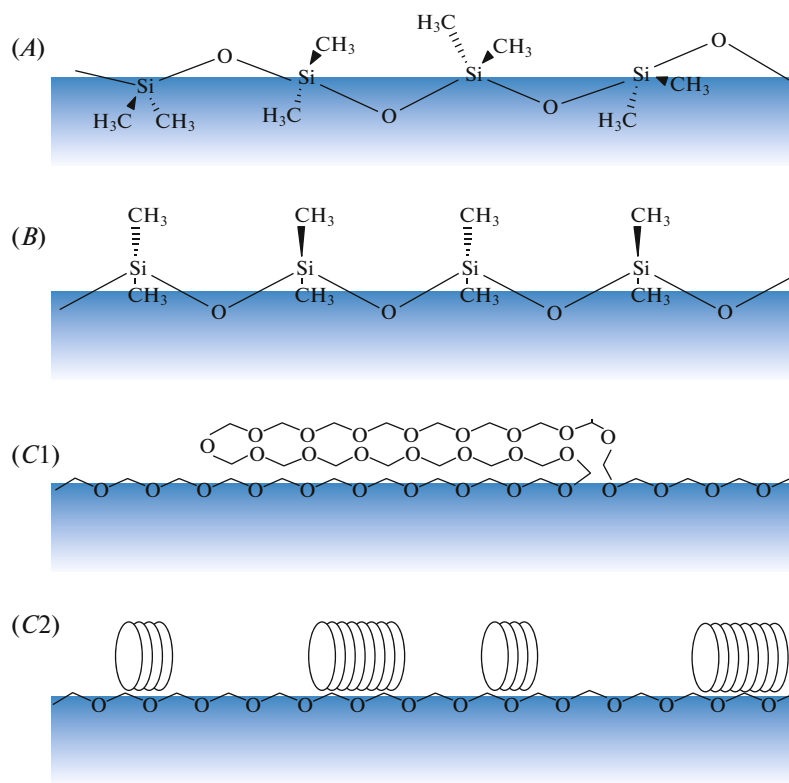


Fig. 2. (Color online) Model of conformational chains of PDMS at the water/air interface: (A) freely rotating chains, (B) monolayers with orderly oriented methyl groups, (C1) PDMS folded chains, and (C2) vertical layers of PDMS helices [11].

The behavior of comb-shaped organosilicon surfactants is different from that of the above-described dimeric surfactants. Figure 4 presents surface pressure and surface potential isotherms for compression of the surfactant Langmuir layer. On the surface pressure and surface potential isotherms obtained for the comb-shaped organosilicon surfactants, there are two regions with different compressibility coefficients of the monolayer; their boundaries are determined by the values of areas A_0 , A_1 , and A_2 . Conformational changes of organosilicon chains are estimated from change in the surface pressure and surface potential, because the surface pressure is a characteristic of monolayer; specifically, it reflects the difference in surface tensions of a pure substrate and a substrate with the monolayer, and the surface potential is connected with the dipole moment of individual polar groups of a surfactant molecule and their concentration on the subphase surface and orientation relative to the interface.

First point A_0 is determined by extrapolation of the linear region of surface potential curve 2 (Fig. 4) and amounts to 16, 68, and 7.5 nm² for PMADMS₁, PMADMS₆₀, and PDMMCDS, respectively (step A). At constant surface potentials of 250, 250, and 80 mV for PMADMS₁, PMADMS₆₀, and PDMMCDS, the surface pressure grows. This process ends by attaining the plateau at areas A_1 (step B) equal to 13, 53, and

4 nm² for PMADMS₁, PMADMS₆₀, and PDMMCDS, respectively (step C). Point A_2 corresponds to collapse of the monolayer and amounts to 26 and 2.3 nm² for PMADMS₆₀ and PDMMCDS (step D). For PMADMS₁ the third step observed on the compression isotherm begins after the stationary region of the surface pressure isotherm (point A_2 , 7 nm²) and ends by inflection at $A_3 = 6.3$ nm². This section is probably related to the presence of functional amino groups [16].

On the compression isotherms of the comb-shaped surfactant, behavior different from that of dimeric surfactants is seen on region C. At areas A_0 , the surface potentials for PMADMS₁ and PMADMS₆₀ are 250 mV. These values are higher than the corresponding data for the dimeric organosilicon surfactants (170 mV, Fig. 3a) [17]. On section C, the isotherm obtained for the dimeric surfactant shows a plateau which is also typical of the isotherm of PMADMS₁, as opposed to PMADMS₆₀ and PDMMCDS, for which there is no plateau on the isotherm. Possibly, this may be explained by the fact that, in the case of the dimeric surfactant, the helical structure is formed in a manner similar to that in polydimethylsiloxane without amino groups: the helical structure appears owing to pulling of a part of oxygen atoms from under the phase of water. As regards PMADMS₁, the presence of a small amount (~1 mol %) of methyl(3-aminopropyl)siloxane units does not hin-

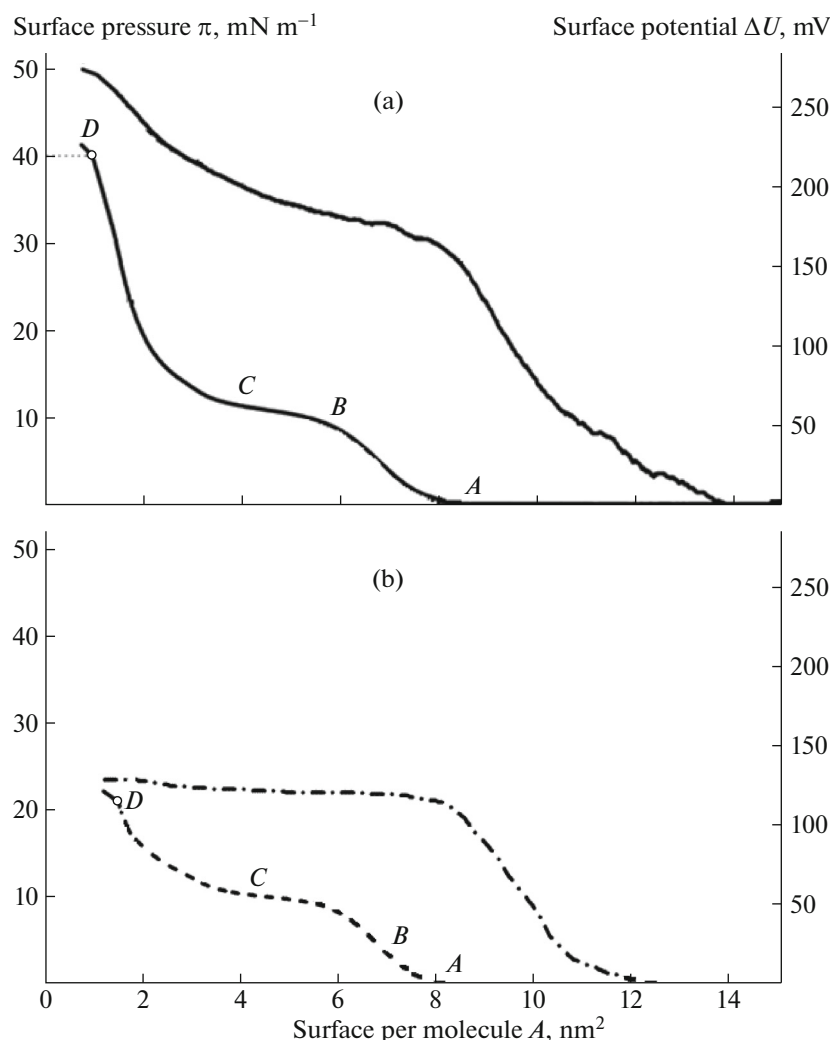


Fig. 3. Isotherms of surface pressure and surface potential under compression of the Langmuir layer: (a) PDMS(NH₂) and (b) PDMS(COOH) on the surface of water; $T = 20^\circ\text{C}$. See text for explanations.

der helix formation. It may be assumed that the siloxane chain itself easily coils and its ability to form helices is limited only on chain segments containing hydrated amino groups.

In the case of PMADMS₆₀ hindrance is created by hydrated nitrogen atoms. When dimeric PDMS is used, this interaction does not reflect very much on helix formation, because amino groups occur at both ends of the polymer chain.

It is probable that, in a comb-shaped organosilicon surfactant molecule, formation of the helical structure proceeds according to the mechanism different from that operative in the case of a dimeric organosilicon surfactant molecule. This difference is associated with a high concentration of amino groups and the presence of a C3 spacer between an amino group and a polydimethylsiloxane chain. Because the polydimethylsiloxane chain contains one aminopropyl group per five repeating units, it may be suggested that hydro-

philic groups are oriented toward the aqueous phase. On the isotherm obtained for the comb-shaped organosilicon, region C is characterized by an increased surface pressure. This finding may apparently be attributed to the specifics of helical structure formation in the organosilicon polymer chain; namely, the area per surfactant molecule decreases, while a monotonic increase in the surface concentration of amino groups persists.

Owing to the complexity of this process, polydimethylsiloxane containing amino groups is not subject to the ideal phase transition (the region of constant pressure on the isotherm), which is observed for polydimethylsiloxane without functional groups. As for the formation of helical structures in amino-containing polydimethylsiloxanes, siloxane chains form either helices or polylayers, in accordance with [18, 19].

Upon further compression (step D), the structure of the surfactant alters: according to [11], this is the ordering of helices to vertical layers [11], while accord-

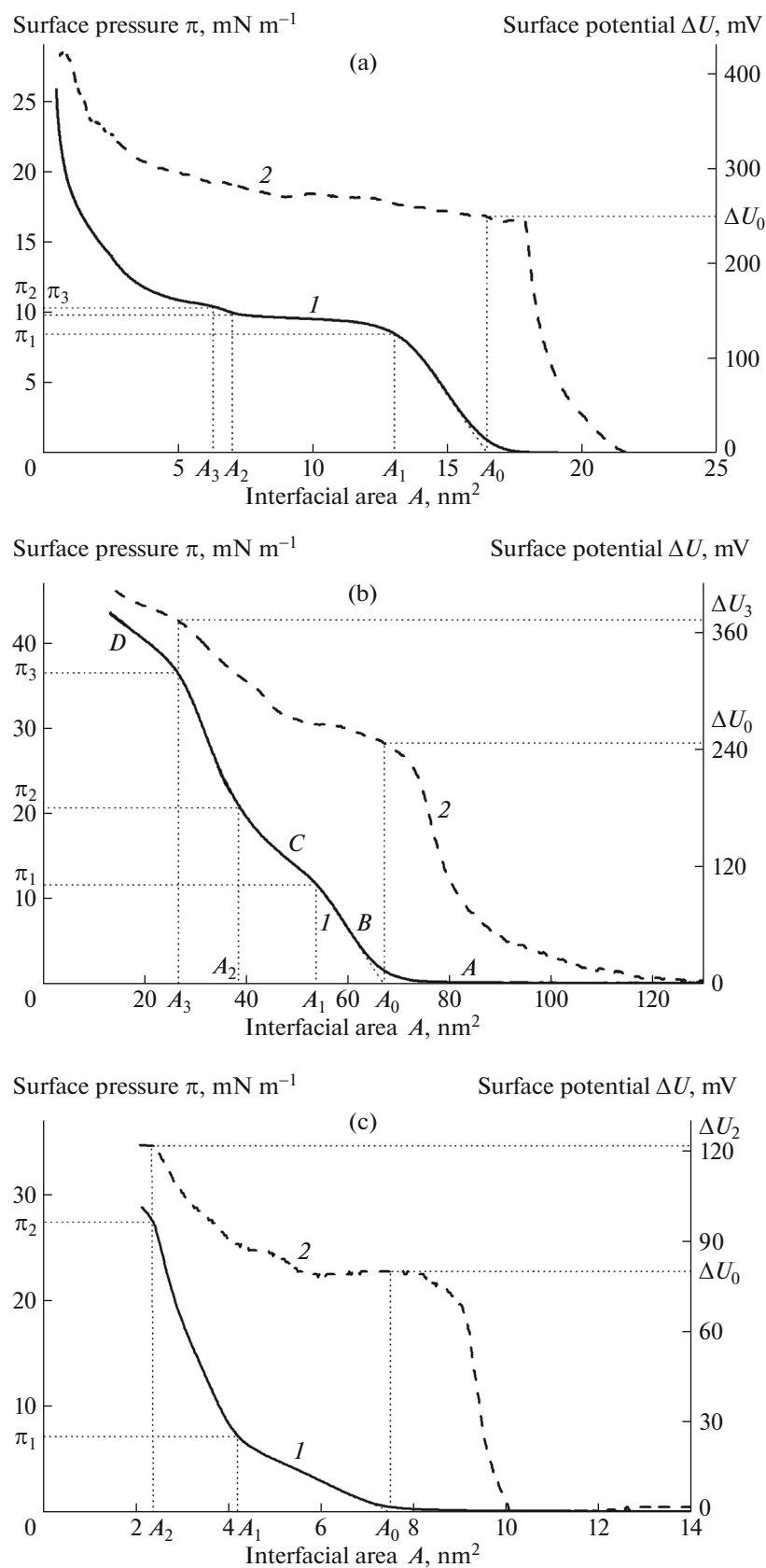


Fig. 4. Isotherms of surface pressure and surface potential under compression of the Langmuir layer: (a) PMADMS1, (b) PMADMS₆₀, and (c) PDMMCDS on the surface of water; $T = 20^\circ\text{C}$. See text for explanations.

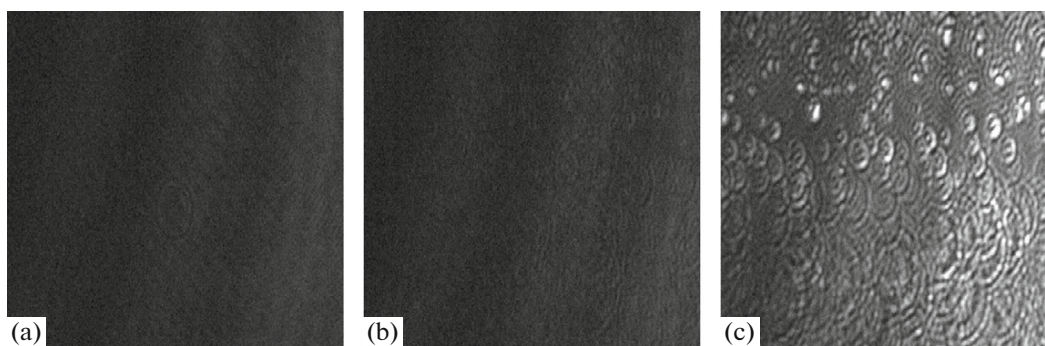


Fig. 5. Optical micrographs taken under the Brewster angle for the surface of PMADMS₁ Langmuir layer on the surface of water under compression to π : (a) 7.6, (b) 10.5, and (c) 15 mN/m.

ing to [12], folded layers composed of the helices of polymer chains are formed [12]. The area per surfactant molecule in the compressed state attains its minimum and amounts to 13 and 6.3 nm² for PMADMS₆₀ and PMADMS₁, respectively (Fig. 4, point *D*).

At the time of collapse (point *D*) of the monolayer of organosilicon surfactant PMADMS₁, transition to the disordered three-dimensional state occurs. At this point, micrographs were taken under the Brewster angle on which bright domains of the three-dimensional phase are seen (Fig. 5).

Analogous data are obtained for organosilicon surfactants with end functional carboxyl groups (PDMCDS). Under compression of the monolayer on the region from A₀ to A₁ (Fig. 4c, curve *I*), presumably the conformation of the main siloxane chain and the mutual arrangement of side functional groups change, while their degree of hydration remains unchanged. On the corresponding region of the surface potential isotherm, a horizontal plateau is observed at 80 mV. Possibly, the reorientation of molecular segments does not cause a change in intramolecular dipoles. A rise in the surface potential to 90 mV under compression to A₁ is possibly associated with onset of the process of reorientation of the main chain and side groups at the interface; this process is accompanied by an increase in the polarization of a molecule. On this region, in much the same way as the comb-shaped surfactant with terminal amino groups (PMADMS₆₀), the helical structure is formed; that is, carboxyl groups are immersed in the aqueous phase and siloxane chains are oriented toward the air phase.

The detailed study of surface pressure and surface potential isotherms for linear and comb-shaped organosilicon surfactants made it possible to reveal a difference in the mechanisms governing formation of helical structures in organosilicon surfactant molecules. On going from dimeric to comb-shaped surfactant molecules, the conformational behavior at the

interface alters; specifically, the surface potential and surface pressure grow during formation of helical structures or bilayers of organosilicon surfactant chains. Change in the behavior of organosilicon chains is probably associated with the presence of a large amount of hydrated functional groups that hinder the ideal phase transition of surfactant molecules. Development of three-dimensional ordered structures at large areas of surfactant molecules may be responsible for a high stability of polymer suspensions synthesized in their presence.

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