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# The role of the electrostatic energy of molecular dipoles in the formation of polar LB films

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## Abstract

In the paper a thesis is developed about the destructive function of free energy of the electrical double layer field from oriented molecular dipoles in monomolecular layers of surface-active substances during the formation of polar LB films. The change of the electrostatic energy of monomolecular layer of dipoles during the transfer of the monolayer from the water surface to the substrate is considered. A comparison is made between the electrostatic energy of the transferring monolayer and the energy of monolayer adhesion between hydrophobic radicals in the LB film structure. A model is proposed for estimating the maximal polarization, obtained without any special measures preventing the disintegration of the polar state. Some physical–chemical approaches for fixing the LB film polar state are discussed. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Polar LB films; Energy of dipole layer; Adhesion between layers

## 1. Introduction

The LB film formation method is a very effective technological approach to the construction of and experimental research into new polar materials. The latter can find practical application in pyroelectric and piezoelectric transducers and in nonlinear optics [1,2]. Polar LB films have spontaneous polarization because of noncentrosymmetry of their structure. Therefore, X- and Z-type deposition [3,4] and Langmuir–Schaefer method [5] are used to obtain polar LB films. According to a number of studies [6–8], X-, Z- and Y-type LB films have the same bimolecular period in the normal direction. It was Langmuir, who first supposed that in the meniscus zone considerable variation of a monolayer structure could occur, accompanied by overturn of molecules [9]. There is no evidence in literature that a stable X- or Z-type film can be obtained, which has noncentrosymmetry and monomolecular period simultaneously. This also concerns films deposited by Langmuir–Schaefer method [6]. However, full compensation is not achieved at the monolayer reconstruction in the meniscus zone. The noncompensated part reaches 1–10% and determines polar characteristics of such LB films [10].

The above mentioned reasons defined the use of the alternate layers method [11–14] for the forma-

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tion of LB films for the purposes of this study. The method implies consequential transfer of two different monomolecular layers of surfactants, formed simultaneously on separate parts of the water surface in one trough. Thus, the substrate is immersed in water through one monolayer, for example A, and is withdrawn through another, B. However, It was found that during the realization of this, the most reliable, method some unexpected difficulties may arise, when forming LB films with the bimolecular layer period roughly equal to the sum of A and B molecules length.

Pyroelectricity in LB films was reported by Blinov [15]. Since that the pyroelectrical coefficient has been increased 3–5 times. Richardson et al. [14] obtained the value of 1.5 nC $cm^{-2}$ $K^{-1}$ using acid and amine substituted *t*-butylcalix(8)arene.

In the present paper, an attempt is made to explain slow progress of research into new polar materials based on LB films. A thesis is developed about the destructive function of free energy $W_e$ of the electrical double layer field associated with oriented molecular dipoles in monolayers of surfactants during the formation of polar LB films.

There are many factors that could influence the deposition process. A number of studies consider the thermodynamics of the process of a monolayer transfer from the water surface to a substrate [8,16–19]. In these works the energy of the interaction between polar groups of surfactants and water as well as adhesion between monolayers by hydrophobic and hydrophilic radicals in the LB film structure is taken into account. However all these works concern the traditional formation of LB films from one compound. In the case of the formation of polar alternate layer films from two different monolayers the electrostatic energy of molecular dipoles in the LB film has the dominant influence. This is explained by the use of monolayers of surfactants having the same direction of polarization in the LB film. At least it is important that during one immerse–withdrawal cycle, the total polarization of the deposited layer is not equal to zero.

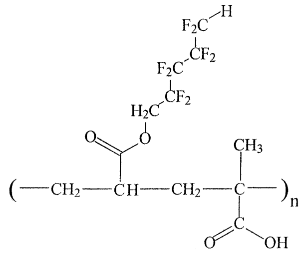
In the experimental part of the paper we give the description of the results of the formation of polar LB films from two different surfactants, having the opposite surface potential in monomolecular layers on the water surface.

In the discussion of the results an estimation is made of the change of the electrostatic energy of molecular dipoles during the transfer of the monolayer from the water surface to the substrate. The structure of the LB film becomes unstable when the free electrostatic energy of oriented molecular dipoles in the LB film starts exceeding the adhesion energy of the neighboring monomolecular layers at hydrophobic radicals. It is assumed that in this case at the exit of the substrate from the water subphase in the meniscus zone the reorganization of the depositing monomolecular layer, and perhaps the monolayer already deposited, could occur, accompanied by the decrease of the value of polarization. Such an approach allows an estimation of the maximum LB film polarization.

## 2. Experimental details

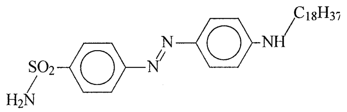
Two compounds were used for the formation of the alternate LB films: stereoregular copolymer of fluorinated alkylmethacrylate and methacrylic acid (A) and *p*-(*p*-octadecyl-aminophenylazo)benzenesulfamide (B). Compound B was chromatographically pure.

(A)



A

(B)



B

Compound A was synthesized in the Institute of Macromolecular Compounds (St. Petersburg, Russia). Compound B was synthesized in the

Research Institute for Organic Semiproducts and Dyes (Moscow, Russia).

Solutions of the compounds were prepared in the following solvents: the mixture of chloroform – methanol – benzene – dimethylformamide (volume proportion 1:1:2:2) for compound A and the mixture of methanol–chloroform–benzene (1:1:6) for compound B. In both cases the concentration was 1 mg $ml^{-1}$.

Distilled water was used as a subphase. The temperature of the water and air was 18–20 °C. The study of the monolayers on the water surface and the formation of the alternate LB films were made on NT-MDT LB5 trough. The trough area is $45 \times 11$ $cm^2$. The surface pressure was measured by Wilhelmy plate made of filtering paper. The trough was separated on two parts by a polytetrafluoroethylene barrier with a rotating cassette for substrates.

The monolayer of compound A was formed in the left side of the trough, the monolayer of compound B in the right side. The compression of both monolayers was performed simultaneously in the same conditions (except for the feedback pressure). When the surface pressure was less than 2 mN $m^{-1}$ the speed of the barrier motion was 30 mm $min^{-1}$, then 20 mm $min^{-1}$. The formation of the alternative structure was made at the surface pressure of 18 mN $m^{-1}$ (compound A) and 33 mN $m^{-1}$ (compound B). The maximum speed of the immerse and the withdrawal of the substrate was 20 mm $min^{-1}$.

For the purpose of atomic-force microscopy and X-ray studies rectangular silicon plates with the thickness of 0.35 mm were used as a substrate. Before the deposition they were processed in 10% solution of hydrofluoric acid. After this the substrates became hydrophobic. To obtain capacitor structures glass plates with the thickness of 0.4 mm were used as a substrate. After the first electrode had been deposited the substrate surface was made hydrophobic by the solution of dimethyldichlorsilane.

In the course of study LB films with various sequence of monomolecular layer deposition and the different number of layers *n* were formed: $(AA)_n$, $(BB)_n$, $(AB)_n$ and $(BA)_n$. The samples were investigated in a small-angle X-ray diffractometer, as well as an atomic-force microscope. In order to define the pyrocoefficient and to estimate the polarization of the LB films capacitor structures were built on glass substrate with the area of aluminum electrodes of 1 $mm^2$. The electrodes were formed by vacuum evaporation. The pyrocoefficient was measured by quasistatic method in the temperature range 20–150 °C using PAR-124 electrometer in the charge-measuring mode.

## 3. Results and discussion

Monomolecular layers of compounds A and B on the water surface were studied by measuring compression isotherms and surface potential curves (Figs. 1 and 2). Both monolayers were stable up to collapse state. The behavior of the suspension thread during anisotropic compression of monolayer A suggests that it was in the liquid crystal state. The phase state of monolayer B was liquid crystal at the surface pressure below 6 mN $m^{-1}$ while at pressure above it was close to the solid state, having characteristic relaxation time about 1 min. On distillated water the surface potential reaches $-450$ mV for compound A and $+1200$ mV for compound B. The monolayers were not ionized. The main results of the study of the samples are presented in Table 1.

The transfer coefficient is the ratio of the surface area of a monolayer, transferred from the water surface to a substrate, to the total area of the substrate surface covered by this monolayer. Usually, it ranges from 0 to 1 [6–8]. In the case of $(AB)_n$ formation the transfer coefficient for compound B varied from 2 to 10 (see Table 1).

Moreover, this took place at the surface pressure of 33 mN $m^{-1}$ which is 5–7 mN $m^{-1}$ less than collapse pressure (Fig. 1). When the surface pressure of deposition was decreased to 25 mN $m^{-1}$ the transfer coefficient decreased up to 2. At low values of the surface pressure the earlier deposited on the substrate monolayer began to ‘slip’ down to the water surface. The decrease of the withdrawal speed had no effect on the transfer coefficient of monolayer B. At a speed exceeding 25 mm $min^{-1}$ the substrate came off water wet. If the substrate was stopped during the withdrawal through monolayer B the monolayer area stayed exactly constant. This indicates that in the process of the formation of monolayer in the meniscus zone a regular transfer of the monolayer from the water surface to that of the substrate, preserving the initial structure, did not occur [20].

The pyroelectric coefficient was defined as the ratio of the variation in polarization (or, roughly, the variation of a charge on the plates of capacitor samples) to the variation of temperature. Typical pyrocoefficients as a function of temperature for three different samples of $(AB)_{10}$ are shown in Fig. 3. For $(BA)_{10}$ samples, the temperature curve of the pyrocoefficient was similar to that in Fig. 3. However, the polarization of the samples was opposite. When the samples were cooled from 140 °C to the room temperature the polarization was restored. The samples heated above 145 °C, the electrical charge on the capacitor plates did not change up to 190 °C. It might be supposed that at these temperatures the polarization is zero. Under this assumption the estimation of polarization of the samples at the room temperature would give the values of $(0.5–0.7) \times 10^{-6}$ C cm$^{-2}$. The dipole moment of molecule A is equal to 12 D at the volume of 1000 Å$^3$ and that of molecule B being 4 D at 300 Å$^3$. A theoretical estimation of the polarization of molecules used in the case of favorable packing gives the value of $4 \times 10^{-6}$ C cm$^{-2}$.

The study of surface topography of samples AB and BA made by means of an atomic-force microscope (NT-MDT, Russia) revealed that LB films of BA type have a more homogeneous and smoother surface [20].

The samples of $(AB)_{16}$ type did not show layered structure when measured in a small-angle diffractometer. The corresponding X-ray scattering curves do not have Bragg's and Kiessig's peaks, which would indicate that the obtained sample is smooth and has a layered structure. The films of $(BA)_{16}$ type at the room temperature had

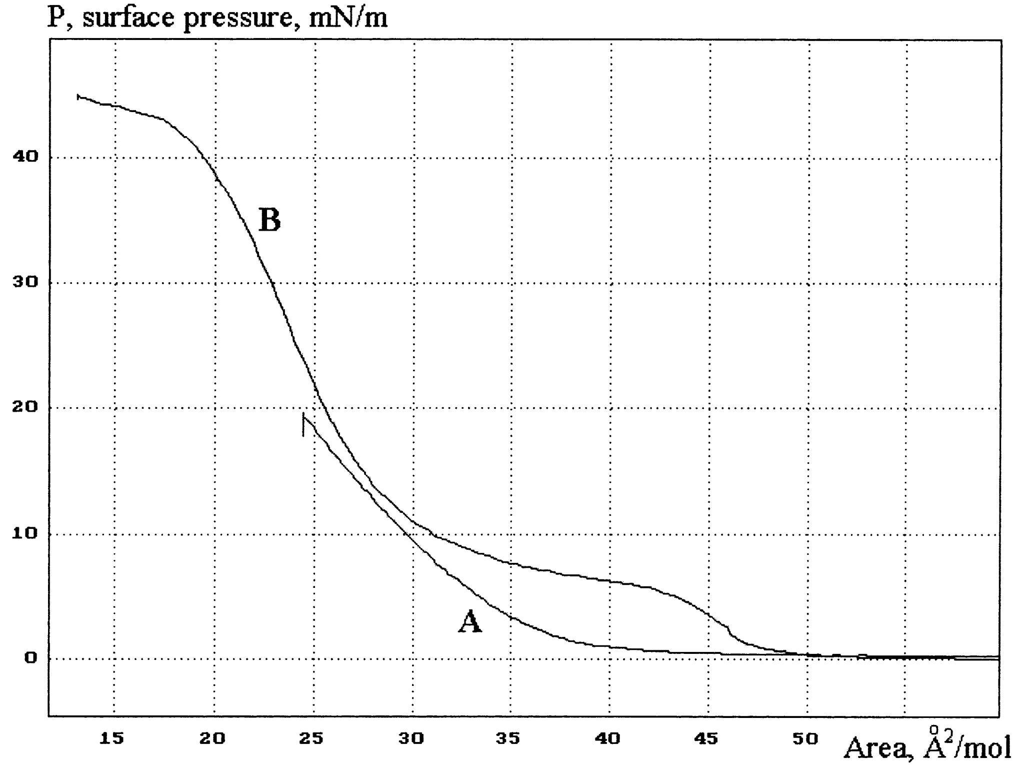


Fig. 1. Compression isotherms of monomolecular layers of the compounds A and B.

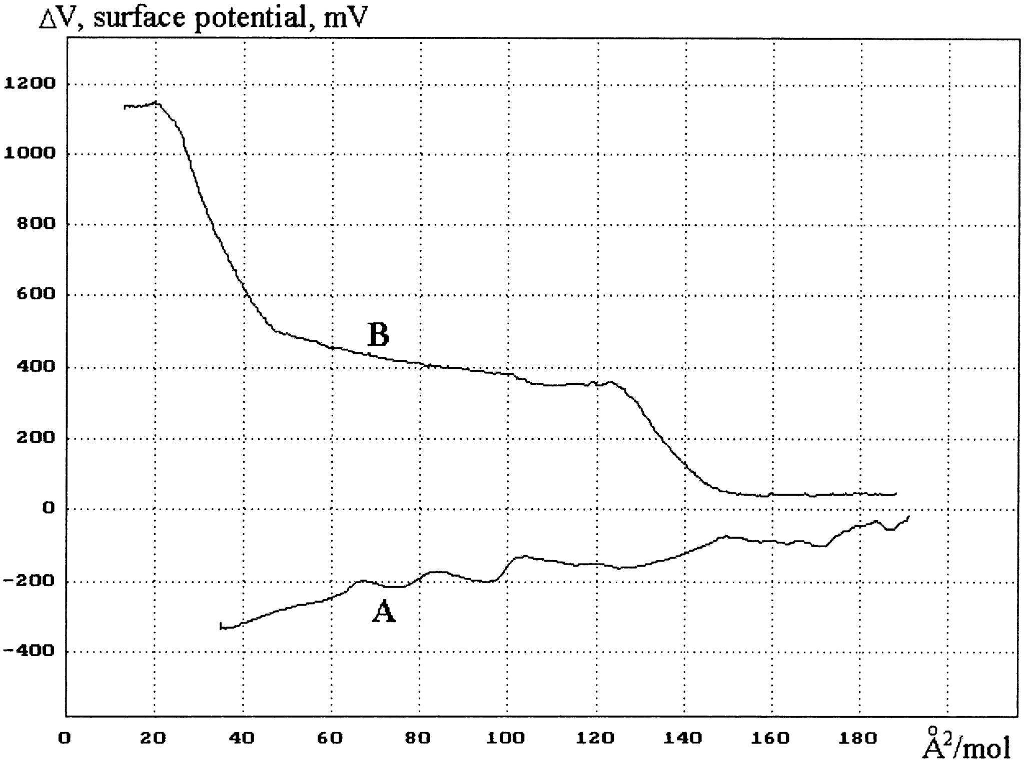


Fig. 2. Surface potential as a function of area per copolymer chain (compound A) or per molecule (compound B).

Table 1
Main results of the study of the samples

| The sequence of layer deposition | $(AA)_n$ | $(BB)_n$ | $(AB)_n$ | $(BA)_n$ |
|---|---|---|---|---|
| Transfer coefficient for monolayer A | 0.95–1.10 | – | ~1 | ~1 |
| Transfer coefficient for monolayer B | – | 0.95–1.05 | 2–10 | ~1 |
| Maximum pyrocoefficient, $\beta$ ($10^{-9}$ C cm$^{-2}$ × K) | <0.02 | <0.02 | 2.6 | 2.6 |
| Polarization at 20 °C, $P$ ($10^{-6}$ C cm$^{-2}$) | ~0 | ~0 | 0.7 | 0.5 |
| Root-mean-square deviation of height (Å) | 20 | 20 | 80 | 20 |
| Layer period (Å) | 22 | 47.9 and 40.1 | Absent | 47.5 |

a weak Bragg's peak, corresponding to a period of 47.5 Å, and Kiessig's peaks, corresponding to the total film thickness of 617 Å. From the results of molecule modeling it follows that the length of a compound B molecule is about 37 Å. The samples, formed from component B only, i.e. $(BB)_{10}$, revealed a layered structure with Bragg's peaks, corresponding to the periods of structure of 47.9 and 40.1 Å. The presence of the two periods seems to indicate the existence of two phases in the LB film structure, which is rarely observed. Kiessig's peaks were also present on the diffractogram, corresponding to the total film thickness of 518 Å.

Thus, the samples of AB type have a far less organized structure than that of BA type. Moreover, The samples formed by Y-type deposition from singular compounds have a layered structure, the transfer coefficient being close to 1.

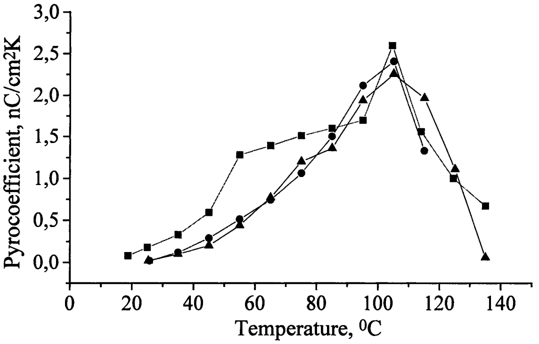


Fig. 3. Temperature dependence of pyrocoefficient for different $(AB)_{10}$ samples.

In order to explain the unusually high transfer coefficient for monolayer B during the formation of AB structures a following model was proposed. In the meniscus zone at the line of contact between monomolecular layer B and the substrate the free electrostatic energy of a monolayer increases several times due to the decrease of the effective dielectric permittivity. At the LB film surface the effective dielectric permittivity is roughly equal to half a sum of the dielectric constant of the LB film material (2–3) and the dielectric constant of air, which is equal to 1, that is 1.5–2.0. However the process of the decrease of the effective dielectric constant starts earlier, when the thickness of the water interlayer between monolayer B and deposited on the substrate monolayer A decreases to 10–20 Å. The rise of the free energy of molecules in this area of monolayer B locally reduced the surface pressure of collapse. The monolayer loses stability to surface pressure fluctuations caused by thermal molecular motion, which initializes an uncontrolled reconstruction of the monolayer in this zone, i.e. local collapse occurs (see Fig. 4).

Consider in detail the variation of electrostatic energy of a monolayer of surfactant molecule dipoles during the transfer from the water surface to that of the LB film. Usually the electrostatic field energy in a dielectric environment is expressed through its density [21]:

$$W_{\mathrm{e}} = \int_{o}^{v} \frac{\varepsilon_0 \varepsilon E^2}{2} \mathrm{d}v \tag{1}$$

where $\varepsilon_o = 8.85 \times 10^{-12}$ F m$^{-1}$ dielectric permittivity of vacuum; $\varepsilon$, relative dielectric permittivity; $E$, electric field strength; $v$, volume of considered part of dielectric.

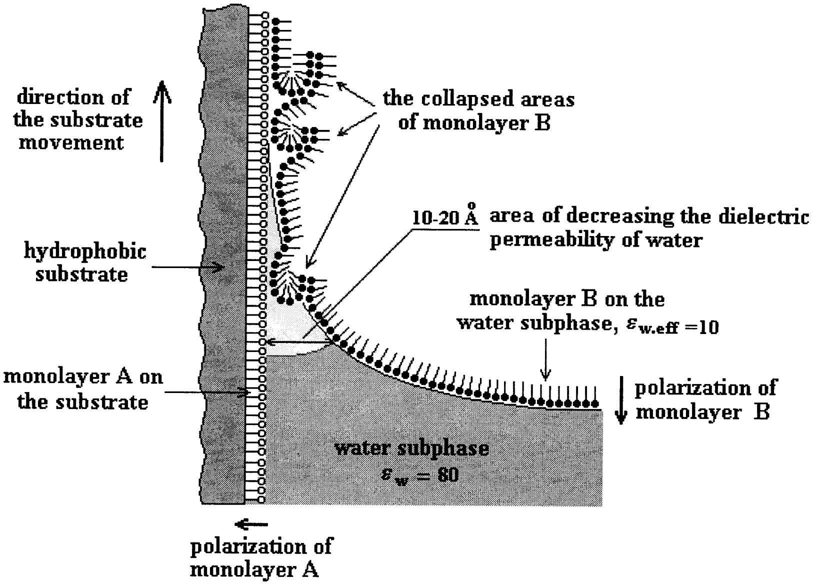


Fig. 4. Schematic diagram of the induced collapse of the monolayer B at the drawing substrate from the water subphase.

It is convenient to use the equivalent expression:

$$W_e = \frac{C\varphi^2}{2} \tag{2}$$

where $C$ is electrical capacity of the considered LB film layer or its part, and $\varphi$ electrical potential across the dipole layer.

The capacity can be written as:

$$C = \frac{\varepsilon_0 \varepsilon S}{d} \tag{3}$$

where $\varepsilon$ is average dielectric permittivity of the considered volume of monolayer or LB film, $S$ is the area of considered film part, $d$ its thickness.

Consider the case when the structure of nonionic surfactant monolayer on the water and on the LB-film surface is equivalent. Such an assumption is true and is usually satisfied during the deposition of Y-type LB-films as suggested first in the work [9]. Using Eqs. (2) and (3), the electrostatic energy of dipole monolayer on the water $W_{e.w}$ and on the LB film surface $W_{e.LB}$ can be written as:

$$W_{e.w} = \frac{\varepsilon_0 \varepsilon_{w.eff} \varphi_w^2}{2d} \tag{4}$$

and

$$W_{e.LB} = \frac{\varepsilon_0 \varepsilon_{lb} \varphi_{LB}^2}{2d} = \frac{\varepsilon_0 \varepsilon_{lb} \varphi_w^2}{2d} \frac{\varepsilon_{w.eff}^2}{\varepsilon_{lb}^2} \tag{5}$$

where $\varepsilon_{lb}$ is dielectric permittivity of monolayer or LB film, having the value 2.2–3.0, $\varphi_w$ is electrical potential jump on nonionic surfactant monolayer on the water surface, experimentally measured value, $\varphi_{LB}$ is electrical potential jump on the oriented dipole layer of surfactant molecules on the LB film surface, $\varepsilon_{w.eff}$ is the effective value of dielectric permittivity in the area of polar group location, when monolayer is located on the water surface, usually ranges from 6 to 11 [22,23].

The difference of the electrostatic energy in the considered cases is equal to

$$\Delta W_e = W_{e.LB} - W_{e.w} = \frac{\varepsilon_0 \varepsilon_{w.eff} \varphi_w^2}{2d}\left(\frac{\varepsilon_{w.eff}}{\varepsilon_{lb}} - 1\right) \tag{6}$$

If we assume that $d$ is equal to the typical monolayer thickness of 25 Å, and $\varphi_w = 1.0$ V, we will obtain the possible range of electrostatic energy variation: 30–90 mJ m$^{-2}$.

According to Clint and Walker [19] the adhesion energy $\gamma$ (of Van der Waals nature) of two neighboring layers in the LB film structure at hydrophobic interfaces ranges from 18 mJ m$^{-2}$ for perfluorinated radicals to 39 mJ m$^{-2}$ for aliphatic radicals. In the case of the interaction between aliphatic and perfluorinated radical combinations $\gamma = 29$ mJ m$^{-2}$. This energy determines the tensile strength of the LB film structure normal to the film. It is clear that the increase of the monolayer electrostatic energy can be commensurate and even exceed several times the adhesion energy at deposition from the water subphase to the substrate. Obviously, if in the LB film formation process some areas appear locally in the meniscus zone, where

$$\Delta W_e > \gamma \tag{7}$$

then the structure of these areas will be thermodynamically unstable and it will change in such a way that the polarization energy will not exceed $\gamma$. The process of reconstruction of the upper monolayers of the LB film to a more stable thermodynamic state seems to start at conditions less strict than those defined by relation Eq. (7). Possible hypothetical variants of such reorganization are shown schematically in Figs. 5 and 6.

At the withdrawal of the substrate from the water subphase, the water removal process occurs in the meniscus zone. This process goes quickly enough. That is, it goes several orders quicker than the structure depolarization process due to redistribution of external free charges from gas environment. It is important to note the difference between the dipole structure of the LB film obtained by the traditional method from one monolayer and the dipole structure of polar alternate layer films from two different monolayers of surfactants. In the first case the dipoles of polar groups of two neighboring layers have the opposite direction, and the bilayer formed during the withdrawal of the substrate does not have macroscopic polarization. In the second case the situation is different. The dipoles of the neighboring

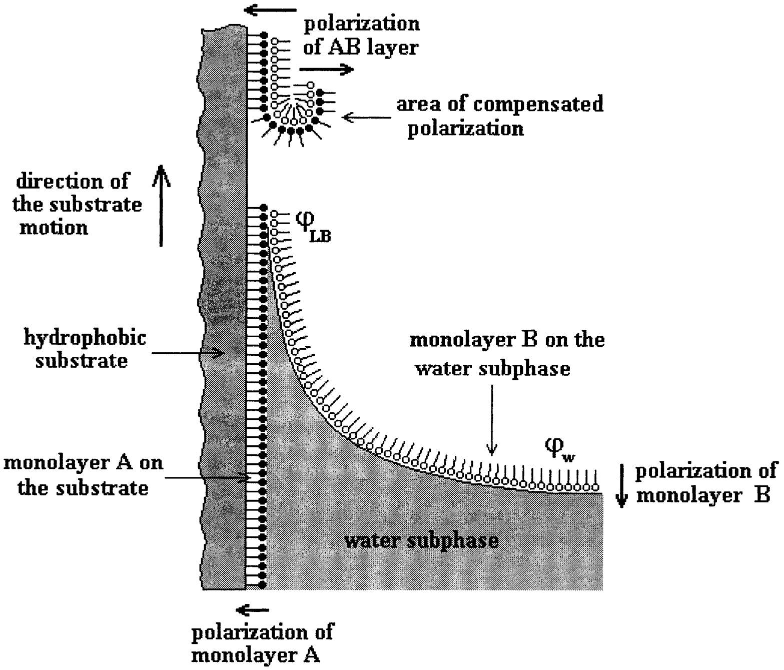


Fig. 5. Schematic diagram of formation process of the structure with the compensated polarization. The exchange of component A and B occurs in the zone of contact of the monolayer A and B by the polar groups. The case of liquid-crystal phase monolayers.

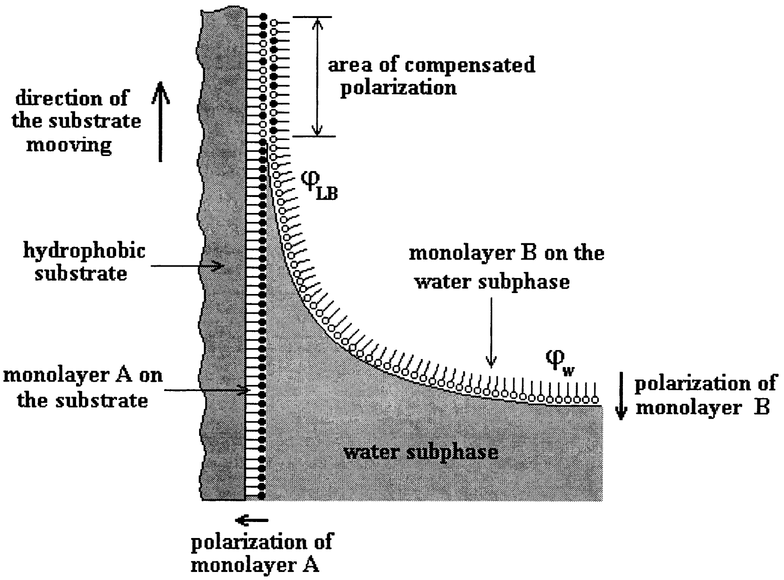


Fig. 6. Schematic diagram of formation process of the structure with the compensated polarization. The polar bilayers exfoliate from the LB film surface and form the areas with the compensated polarization. The case of solid state monolayers.

layers do not compensate each other, and the resulting macroscopic polarization of the formed bilayer is not equal to zero. It is because of this reason that the increase of electrostatic energy can cause structural reconfiguration in the bilayer with the decay of the polar state in the meniscus zone while water is being removed (Figs. 5 and 6).

Assuming in (Eq. (6)) $W_{e.LB} \gg W_{e.w}$ and using the well-known electrostatic relation

$$\varphi = \frac{\sigma S}{C} \tag{8}$$

where $\sigma$ is the surface density of charge on the face of the electrical double layer, one can evaluate the maximum value of

$$\sigma_{\max} = \sqrt{\frac{2\gamma\varepsilon_0\varepsilon_{\mathrm{lb}}}{d}} \tag{9}$$

before reorganization takes place. Putting $\gamma = 30$ mJ $\mathrm{m}^{-2}$ and $d = 25$ Å, one will have $\sigma_{\max} = 2 \times 10^{-6}$ C $\mathrm{cm}^{-2}$. This is approximately 5–15 times less than the value obtained from theoretical estimations for ideally packed molecules, used in the polar LB film formation. Thus, Eq. (9) represents a very strong restriction. Obviously, this consideration is applicable to all LB films.

Eq. (9) can be useful for analyzing measures which may prevent the decay of the polar state. The following physical–chemical methods can be proposed, that are aimed at increasing $\sigma_{\max}$ or, correspondingly, at increasing of the dielectric polarization (when $\varepsilon_{\mathrm{lb}} \gg 1$ the surface density of charge is close to dielectric polarization):

1. Increasing $\varepsilon_{\mathrm{lb}}$ during LB film formation. One of the possibilities in the realization of this approach includes the following. At the A and B monolayers formation a third component can be added which microheterogenically mixes with them and has high dielectric permittivity, for example [24]. In this paper it was shown, that the molecules of the chloranil and bromanil type could be suitable. They can be included into the LB film composition as molecular associates incorporating water so that the dielectric permittivity reaches 20. After the LB film is formed and heated above 60 °C, water and then chloranil (or bromanil) are removed from the LB film structure leaving the skeleton of A and B molecules and decreasing the dielectric permittivity by almost an order of magnitude. However, the polarization can be increased by a maximum of four times by such a method.
2. The best way to increase the polarization consists of increasing the adhesion to hydrophobic terminal groups. It can be realized, for example by including several percent of a third component C in the A and B layers (Fig. 7).

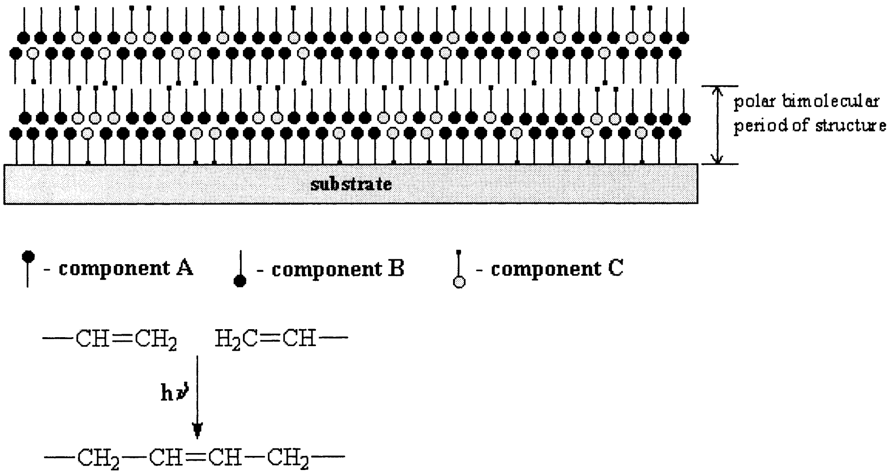


Fig. 7. The increase of adhesion energy at the interface of hydrophobic radicals due to polymerization of terminal groups of component C under the action of ultraviolet rays.

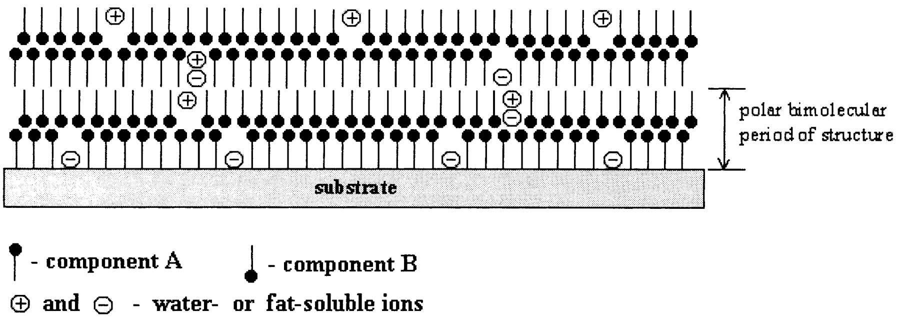


Fig. 8. Fixing of polar state by introduction of water- and fat-soluble ions in the LB film polar structure.

The component C must have an active group in the terminal part of the hydrophobic radical able to polymerize under an external influence, for example, ultraviolet rays. For instance, this terminal group may include a carbon–carbon double bond, e.g. $-CH=CH_2$. In this case after exposure to UV-radiation a number of terminal groups in neighboring layers may lock and the LB tensile strength on hydrophobic surfaces can increase 100 times and more. This is equivalent to an increase in $\gamma$ in Eq. (9).

3. Another important approach is the introduction of special ions both into the water subphase and into the hydrophobic matrix of monomolecular layers used for polar LB film formation (Fig. 8). Such artificially introduced ions may accelerate the process of polarization compensation caused by surfactant molecular dipole orientation in the LB film structure. However, it is difficult to evaluate the effectiveness of such a method.

Obviously, the use of polymer components will increase the activation barrier for the decay process of the LB film polar state after its formation. The use of polymer components also improves the mechanical characteristics of LB films as well as their thermostability.

## 4. Conclusion

When investigating LB films of new polar materials not only the high dipole moment of the molecules used should be considered but also special measures should be taken to prevent the decay of the polar structure during the formation process. Such reconfiguration in the meniscus zone may occur as the result of an increase in the electrostatic repulsion between molecular dipoles caused by the local reduction of dielectric permittivity when water is removed.

The proposed mechanism for structural irregularities in the LB structure film is universal. Apparently, it should be taken into consideration when any attempts are made to form LB films with a complex molecular architecture.

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