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Monolayers and Langmuir—Blodgett films of crown-substituted phthalocyanines

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Tetra-15-crown-5-phthalocyanine ligand and its ruthenium complex with axial CO and MeOH groups were synthesized. The properties of their monolayers and Langmuir—Blodgett films were studied. In the case of the ligand, monolayer films of molecular associates are formed. The compatibility of the ligand and stearic acid in a mixed binary monolayer was established. Stearic acid improves the ligand distribution over the water surface and results in the formation of monolayer associates immobilized in its matrix. The condensation effect of Na^+ cations on the mixed monolayers was found. The ruthenium complex $(R_4Pc)Ru(MeOH)(CO)$ forms stable true monolayers. The macrocycle planes in stacking are inclined relatively to the normal to the subphase surface by an angle of 25°. The Langmuir—Blodgett films of the complex were established to have redox peaks. A high electrochemical stability of the Langmuir—Blodgett films and a high electroactivity of phthalocyanine rings were demonstrated. It was shown by impedance spectroscopy that the binding of Na^+ and K^+ ions by Langmuir—Blodgett films of the $(R_4Pc)Ru(MeOH)(CO)$ complex results in an increase in the impedance values in a region of medium frequencies by three and five times, respectively.

Key words: tetra-15-crown-5-phthalocyanine, monolayers, Langmuir—Blodgett films, orientation of macrocycles, electronic spectroscopy, cyclic voltammetry, impedance spectroscopy.

Discotic compounds forming columnar structures in block and dispersions attract researchers´ attention due to a possibility of their assembling to form linear transport systems (channels) extended at a supramolecular level. Phthalocyanines are typical representatives of these compounds. Significant interest in these objects is caused by their unique properties important from both theoretical and practical points of view. These are the lability of the electronic structure of a macrocycle, formation of complexes with the most part of metals, easiness in introducing peripheral substituents and axial ligands of different nature, multistability, *etc.*[1,2] A possibility of self-assembling of phthalocyanines to form linear associates favors the creation of related functional supramolecular systems with a uniform orientation. In almost all cases, ultrathin films assembled by the Langmuir—Blodgett method consist of phthalocyanine nanotubes, whose axes are parallel to the support surface. However, for many practical purposes it seems important that axes of discotic columns would be arranged along a direction close to the normal or at a small angle to the normal. In this case, planes of phthalocyanine macrocycles would be parallel to the support. Such a molecular structure of a film should provide a more efficient transport over channels, for instance, when phthalocyanine is used as a mediator of electron transfer to an electrode in various, including enzymatic, reactions, in redox processes for developing chemical sensors, in photoelectric devices, *etc*. However, this orientation has not been accomplished yet in Langmuir—Blodgett films (LBF), because it is difficult to obtain this orientation in LBF precursors (monolayers on the water surface) for several reasons: amphiphility is absent, water affinity is weak, and stacking formation is thermodynamically favorable. Even if a planar (the angle of inclination of the plane is smaller than 30°) structure can be obtained in a monolayer at large surface areas of the molecules, then the monolayer compression to surface pressures, under which the transfer to solid supports occurs, results in approaching molecules to such an extent that stacking formation becomes preferential. Different procedures are used to improve phthalocyanine spreading over the aqueous subphase and create a planar structure of the monolayer. First, this is a modification of molecules by grafting peripheral substituents. These substituents can be eight hydroxyalkyl groups with the C_3—C_{18} length of the hydrocarbon chain,[3—5] four[6—8] and eight[9] alkyl groups, four

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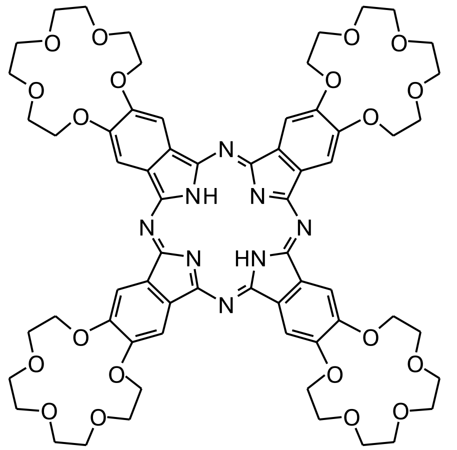
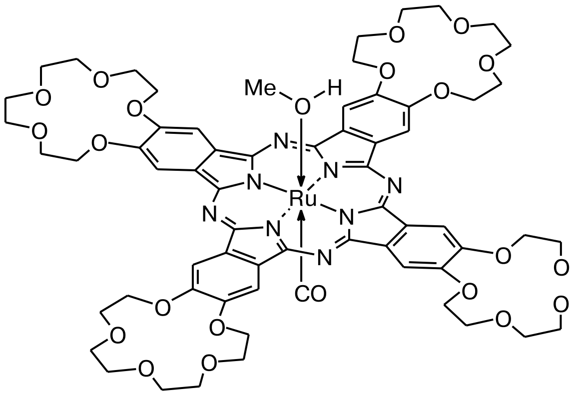
alkoxycarbonyl groups,[10,11] and some other groups.[12–16] It is clear that phthalocyanine modification used in these works is based on amphiphility impacting to the macrocyclic basis. It should be noted that grafting to a hydrophobic water-insoluble macrocycle should not improve the distribution of molecules over the aqueous subphase surface. Nevertheless, rather encouraging results were obtained when the transition to a nonpolar chain occurred through a polar hydroxycarbonyl group.

An alternative direction of the development of a planar packing of molecules is grafting of peripheral polar substituents and, in the case of complexes, introducing polar axial ligands. Note that phthalocyanine complexes with many metals have a high affinity to coordination of water molecules,[12] which can facilitate the formation of a planar organization of molecules.

The authors of the work[17] attempted to create columnar structures perpendicular to the support. They grafted lutetium bisphthalocyaninate molecules to the surface of oxidized silicon. One macrocycle of lutetium bisphthalocyaninate contained four peripheral carboxyl groups to interact with the surface modified by aminosilane, and another macrocycle contained four 15-crown-5 groups. Then this planar matrix was placed in a solution of KSCN and symmetric tetracrown-substituted lutetium bisphthalocyaninate. As a result of the coordination of potassium cations by crown ether moieties, particular columnar structures of length to 25 nm were obtained.





A more simple and reliable method for the creation of these nanoobjects can be a technique of monolayers and Langmuir—Blodgett films. In this work, we synthesized and studied monolayers and LBF of a ligand tetra-15-crown-5-phthalocyanine $H_2(R_4Pc)$ (R_4Pc^{2-} is 4,5,4′,5′,4″,5″,4‴,5‴-tetrakis(1,4,7,10,13-pentaoxatridecamethylene)phthalocyaninate ion) and a ruthenium(II) complex with this ligand also containing axial substituents CO and MeOH.

Experimental

Dicyanobenzo-15-crown-5 was synthesized according to a previously described procedure.[18] Tetra-15-crown-5-phthalocyanine $H_2(R_4Pc)$ was synthesized according to a known procedure[19] by melting of dicyanobenzo-15-crown-5 with hydroquinone in an evacuated tube at 180 °C for 12 h. The subsequent chromatographic purification on a column with neutral alumina (chloroform—methanol (96 : 4, vol/vol) as eluent) gave $H_2(R_4Pc)$ in 60% yield. UV—VIS ($CHCl_3$), λ_{max}/nm (logε): 701 (5.10), 661 (5.01), 644 (4.66), 601 (4.38), 420 (4.48), 348 (4.88). ^1H NMR ($CDCl_3$, 200 MHz), δ: 3.93 (m, 32 H, $C(3)H_2$, $C(4)H_2$); 4.22 (m, 16 H, $C(2)H_2$); 4.77 (m, 16 H, $C(1)H_2$); 8.91 (s, 8 H, H_{Ar}). MALDI-TOF, *m/z*: 1275.3 $[H_2(R_4Pc)]H^+$.

Crown-substituted ruthenium phthalocyaninate with MeOH and CO molecules as axial ligands $(R_4Pc)Ru(MeOH)(CO)$ was synthesized by a known procedure.[20] A mixture of dicyanobenzo-15-crown-5 and $Ru_3(CO)_{12}$ in a molar ratio of 24 : 1 in a sealed tube was heated *in vacuo* at 250 °C for 4 h. The ruthenium complex with tetra-15-crown-5-phthalocyanine and axially coordinated CO and MeOH molecules was isolated in 80% yield by column liquid chromatography on neutral alumina using a $CHCl_3$—MeOH (95 : 5, vol/vol) mixture as eluent. UV—VIS ($CHCl_3$), λ_{max}/nm (logε): 655 (4.97), 593 (4.30), 313 (4.81). IR, ν/cm^{-1}: 1934 (CO). ^1H NMR (DMSO-d_6, 200 MHz), : –0.06 (s, 3 H, MeOH); 3.80 (m, 32 H, $C(3)H_2$, $C(4)H_2$); 4.09 (m, 16 H, $C(2)H_2$); 4.68 (m, 16 H, $C(1)H_2$); 8.81 (s, 8 H, H_{Ar}). MALDI-TOF, *m/z*: 1376.6 $[(R_4Pc)Ru]H^+$, 2750.0 $[(R_4Pc)Ru]_2H^+$, 4125.5 $[(R_4Pc)Ru]_3H^+$, 5496.8 $[(R_4Pc)Ru]_4H^+$. ESI-MS, *m/z*: 1402.5 $[(R_4Pc)Ru(MeOH)]^+$.

Monolayers of $H_2(R_4Pc)$ and $(R_4Pc)Ru(CO)(MeOH)$ were formed from solutions in chloroform (analytical grade). Deionized water (Vodolei) and 0.01 *M* aqueous solutions of KCl or NaCl (reagent grade) were used as subphases. Compression isotherms of monolayers were obtained using an NT-MDT automated Langmuir trough, the trough and barrier being produced from Teflon. The surface pressure was determined by the Wilhelmy method using a glass measuring plate. Solutions of crownphthalocyanines were deposited on the subphase surface from a micropipette (Distriman Gilson) by 5-μL portions. The time of solvent evaporation was 15 min, and the rate of monolayer compression was 0.2 mm s^{-1}.

Monolayers were transferred on quartz plates and gold-plated resonators and electrodes for electrochemical measurements by the Langmuir—Blodgett method under a constant surface pressure of 25 mN m^{-1}. The degree of monolayer transfer and binding of Na^+ ions with LBF were determined by the method of quartz crystal microbalance. Resonators with gold-plated electrodes had a basic frequency of 10 MHz.

Electronic absorption spectra of solutions and LBF in a wavelength interval of 200—900 nm were recorded on a Specord UV-VIS M40 spectrophotometer, whose modification provided spectra recording in the computer memory. For studying solutions, quartz cells with a thickness of 1 and 10 mm (in the case of a dilute solution) were used. To obtain spectra of films, crownphthalocyanine monolayers were transferred onto quartz supports.

Electrochemical studies were carried out on a measuring system developed and produced at the Institute of Physical Chemistry of the Russian Academy of Sciences. The complex includes an IPC-compact electronic potentiostat, an FRA-2 electronic frequency-response analyzer, and the program controlling measuring devices, data transfer to a computer, and primary data processing.

All electrochemical measurements were carried out in an unseparated three-electrode electrochemical cell. A standard $Ag^+/AgCl$ electrode was used as a reference. A platinum network cylindrical electrode served as an auxiliary electrode. The surface area of the auxiliary electrode more than 100-fold exceeded the surface area of the working electrode.

Gold working electrodes on the surface of silicon plates were prepared by a specially developed procedure. At first, holes with specified thickness and shape were created photolithographically on the surface of oxidized silicon plates. An adhesion nickel sublayer 10 nm thick was chemically precipitated into thus prepared (deepened into a silicon plate) area for an electrode. Then a gold layer about 500 nm thick was deposited on this area by the galvanic method. The working surface was a round plate, whose geometric surface area was 0.08 cm^2. The amount of a supported metal was calculated in such a way that after hole filling the electrode surface would be at the same level as the surface of silica surrounding the electrode. This procedure was used to decrease the influence of edge effects caused by a metal layer prominent above the surface. These effects take place for traditional methods for electrode preparation by sputtering. Electrodes obtained by this method possessed a high stability and were appropriate for multiple measurements.

Measurements by cyclic voltammetry (CV) were carried out in the potential range from +1.0 V to –0.6 V against an $Ag^+/AgCl$ reference electrode at a potential sweep of 0.01—1.0 V s^{-1}.

Electrochemical impedance was measured at an equilibrium potential of the redox process in the film $E = (E_{an} + E_{cat})/2$, where E_{an} and E_{cat} are the potentials of the anodic and cathodic peaks of the voltammogram, in the frequency interval from 50 000 to 0.05 Hz. The logarithmic frequency sweep with a density of 9 points per decade was used in measurements. The amplitude of the disturbing signal was 9.8 mV.

Results and Discussion

Discotic symmetric molecules can be organized to form monolayer films on the water surface, *i.e.*, stable Langmuir monolayers can be obtained, due to chemical and structural features of molecules and, first of all, their affinity to linear association (stacking). In addition, the formation of true monolayers depends on several experimental factors: the amount of the deposited solution, its concentration, time between the moments of solution spreading and beginning of measurements (recording of compression isotherms), temperature, and some other factors.

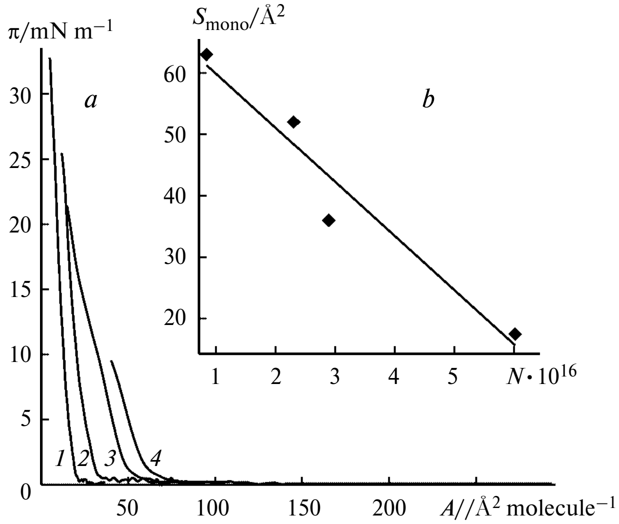


Fig. 1. (*a*) Compression isotherms of monolayers of $H_2(R_4Pc)$. Influence of the amount of a forming solution ($4 \cdot 10^{-4}$ mol L^{-1}) spread on the water surface: 250 (*1*), 120 (*2*), 95 (*3*), and 35 μL (*4*). (*b*) Dependence of the monolayer surface area (S_{mono})on the number of molecules in the monolayer (*N*).

The compression isotherms of the ligand $H_2(R_4Pc)$ obtained for different volumes of solutions forming the monolayer are shown in Fig. 1. The number of molecules in the monolayer, initial surface areas per molecule (A_∞), and limiting surface area (A_o) found by the extrapolation of the first linear region of the isotherm to the surface pressure $\pi = 0$ are given in Table 1 for each volume. Even for the minimum content of molecules on the water surface (see Fig. 1, curve *4*), when the initial surface area per molecule in the monolayer (A_∞ = 294 Å^2) is commensurable with the maximum intrinsic surface area of an $H_2(R_4Pc)$ molecule with an inclined orientation of the macrocycle, the surface pressure does not differ from zero

Table 1. Influence of the volume of a forming solution on the preparation of $H_2(R_4Pc)$ monolayers

V/μL	$N \cdot 10^{-16}$	A_∞/Å^2	A_o/Å^2
35	0.84	294	63
95	2.29	108	52
120	2.89	85	36
250	6.02	36	17.5

Note. V is the volume of a forming solution of $H_2(R_4Pc)$ in chloroform ($4 \cdot 10^{-4}$ *M*), N is the number of molecules in the monolayer, A_∞ is the initial surface area per molecule, and A_o is the limiting surface area per molecule.

and remains unchanged with a decrease in A down to A_o = 63 Å^2. When the initial spreading surface A_∞ increases by 1.5 times, *i.e.*, when the surface area corresponding to the orientation of phthalocyanine macrocycles parallel to the subphase surface is achieved, the position and shape of isotherm *4* (see Fig. 1) remain unchanged. An increase in the number of molecules supported on the water surface (see Table 1) results in a regular decrease in A_o (see Fig. 1, curves *1—3*).

Taking into account these data and the fact that the maximum A_o value obtained for the lowest initial surface concentration of the substance was only 63 Å^2, we can draw the following preliminary conclusions about the organization of the film. Evidently, at any initial concentrations of molecules on the subphase surface they form multilayer aggregates with the orientation of macrocycle planes close to that perpendicular to the water surface. This is indicated by the absence of a signal from the surface pressure sensor at surface areas equal to ~200 Å^2. According to the model calculations, the latter correspond to the formation of contacts between monolayer aggregates of molecules, whose planes are slightly inclined relatively to the normal to the subphase surface. A possibility of forming phthalocyanine bilayers with four *n*-alkoxycarbonyls at the periphery has been mentioned previously.[21] A decrease in the concentration of a forming solution by 2.5 times (from $2 \cdot 10^{-4}$ mol L^{-1} (Fig. 2, curve *2*) to $8 \cdot 10^{-5}$ mol L^{-1} (curve *3*)) and, correspondingly, an increase in the number of deposited droplets do not result in basic changes in the behavior of the $H_2(R_4Pc)$ film: A_o increases by at most 4 Å^2. A twofold increase in the solution concentration (curve *1*) and, correspondingly, a decrease in the number of deposited droplets exert virtually no effect on the behavior of the monolayer.

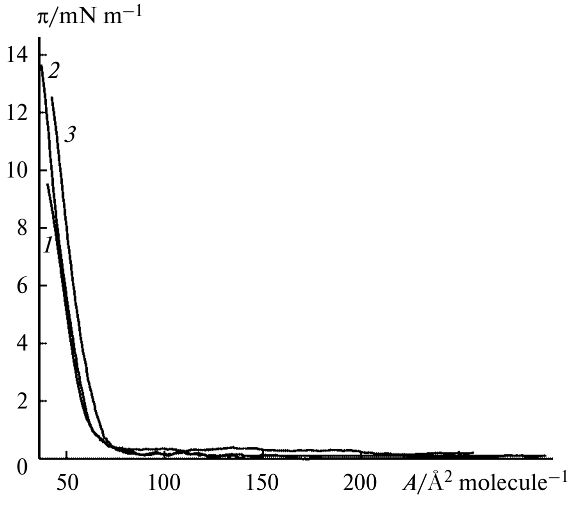


Fig. 2. Compression isotherms of monolayers of $H_2(R_4Pc)$. Influence of the concentration of a forming solution: $4 \cdot 10^{-4}$ (*1*), $2 \cdot 10^{-4}$ (*2*), and $8 \cdot 10^{-5}$ mol L^{-1} (*3*). Water is the subphase, and the number of molecules on the surface is $9 \cdot 10^{15}$.

Evidently, some critical surface concentration determines the distance between molecules. After this concentration was achieved, the molecules began to form associates. Since this occurs in a strongly dilute monolayer, low expenses to monolayer compression (π is close to zero) are compensated by an energy gain accompanying associate formation. When this concentration is exceeded, associates are formed spontaneously, their fraction in the film increases, and the characteristic surface areas per molecule decrease.

Thus, the initial (for monolayer spreading) surface area and, correspondingly, the initial surface concentration of ligand molecules are the most important parameters for the formation of the ligand film on the water surface. The concentration of a supported surface plays the secondary role (Table 2), which indicates, for this system, the identical state of molecules in solutions with different concentrations used for monolayer formation.

It is well known that so-called "spreaders," amphiphilic compounds forming stable monolayers with high fracture pressures, are used to improve the distribution of a substance under study, which cannot form true monolayers by itself, on the water surface. Stearic acid (SA) is one of the most popular spreaders added to a monolayer. This property of SA was used to improve spreading of porphirazines.[22,23]

Note that, when choosing a spreader, one should take into account a possibility of its interaction with the monolayer substance. In particular, the use[24] of SA is caused by its ionic character: carboxylic groups of SA interact electrostatically with the pyridinium groups of the amphiphilic macrocycle. Another mechanism that takes place when stearic acid is chosen as a spreader to decrease the association of crownphthalocyanine molecules on the water surface is the repulsion of charged surfactant molecules and crown ether moieties. For this purpose, we studied mixed monolayers of stearic acid and $H_2(R_4Pc)$ (ratio SA : $H_2(R_4Pc)$ = 2 : 1) on the water surface and an 0.01 *M* aqueous solution of NaCl. The character of the compression isotherms (Fig. 3, curve *3*) and its considerable shift toward larger surface areas relatively to the isotherms of stearic acid (curve *1*) indicate the formation of a mixed

Table 2. Influence of the solution concentration on the preparation of $H_2(R_4Pc)$ monolayers

$N \cdot 10^{-16}$	C/mol L^{-1}	t/min	A_∞/Å^2
0.84	$4 \cdot 10^{-4}$	10	294
0.84	$8 \cdot 10^{-5}$	20	294
0.96	$2 \cdot 10^{-4}$	20	257

Note. N is the number of molecules in the monolayer, C is the concentration of a forming solution, t is the storage time of the monolayer before compression, and A_∞ is the initial surface area per molecule.

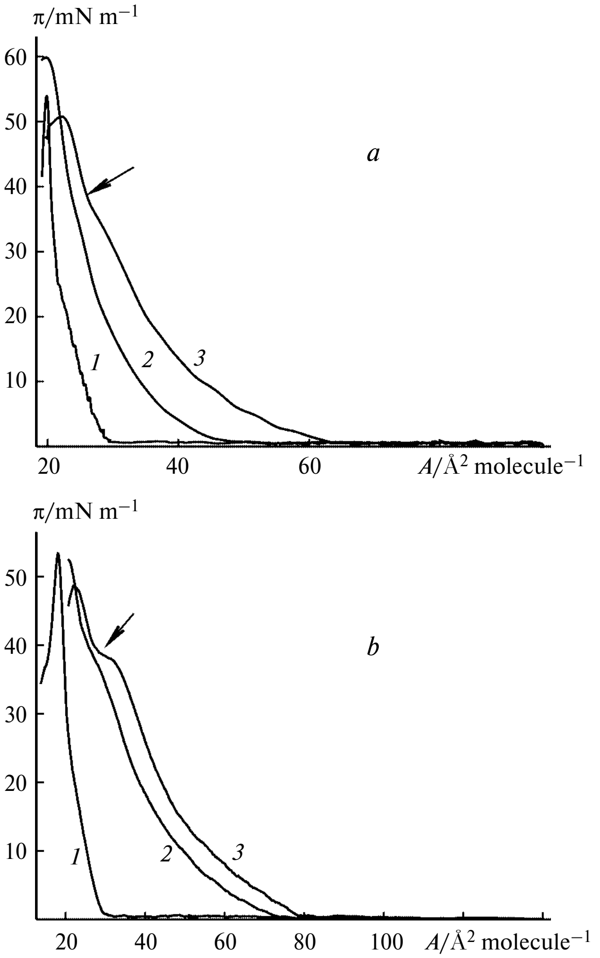


Fig. 3. Compression isotherms of the stearic acid monolayer (*1*) and its mixed monolayers with $H_2(R_4Pc)$ (*2*, *3*) at molar ratios of components of 2 : 1 (*a*) and 1 : 1 (*b*). Subphase composition: water (*1*, *3*) and an 0.01 *M* aqueous solution of NaCl (*2*).

monolayer in which heterogeneous molecules are compatible. This is indicated by the following facts: the shape of the compression isotherm differs from the shape of curves for individual monolayers of stearic acid and $H_2(R_4Pc)$ (see Figs. 1 and 2), has a monotonic character, and contains no pronounced kink points or plateau regions at low π values. Due to compatibility of the components, one can achieve high surface pressures of a mixed binary monolayer and estimate the pressure corresponding to the formation of a multilayer film (shown by arrow in curve *3*). Contributions of the components to the limiting surface area of the mixed monolayer were calculated by the additive scheme and showed that the surface area per ligand molecule increased substantially, *i.e.*, the monolayer (not multilayer as in the case of an individual monolayer) $H_2(R_4Pc)$ film with orientation of molecule planes perpendicular to the subphase surface was formed. The introduction of Na^+ ions into the aqueous subphase results in the considerable condensation of the monolayer (see Fig. 3, curve *2*): the compressibility decreases and the fracture pressure increases. Since the presence of alkaline metal ions induced the extension of stearic acid monolayers, the isotherm parameters indicate the interaction of the Na^+ ions with ligand. Due to this, the crown ether ring gains a planar conformation enhancing stacking interactions.

To reveal more clearly the contribution of phthalocyanine to the behavior of a mixed monolayer, we increased its content (ratio SA : $H_2(R_4Pc)$ = 1 : 1). The results are shown in Fig. 3, *b*. As expected, the characteristic kink point at high surface pressures π transformed into a sufficiently extended region. The pronounced plateau (shown by arrow) indicates the monolayer fracture, which occurs at rather high π exceeding 35 mN m^{-1}. For isotherms of the monolayer formed on a solution of sodium chloride, this region is less pronounced, indicating a higher stability of the monolayer on the same subphase. Evidently, the insertion of Na^+ ions into crown rings (predominantly into those directly contacting with water) increases the degree of ordering in stacking due to the closer arrangement of molecules and their crown ether moieties, which change their conformation due to desolvation and binding of a cation. The stearic acid monolayers are more extended (isotherms are shifted toward larger surface areas) on the surface of aqueous solutions of NaCl than on the water surface. A comparison of the monolayer surface areas for systems of different composition (see Figs. 1—3) indicates that the introduction of stearic acid stabilizes the monolayer and also improves the ligand distribution over the surface.

Based on the data obtained, we can conclude that the tetracrownphthalocyanine ligand does not form a true monolayer with orientation of macrocycles parallel to the surface but form a multilayer film of aggregated molecules with perpendicular orientation of macrocycle planes. Unlike solutions in which crownphthalocyanine molecules can perform free translation movement and rotation in three dimensions, their immobilization on the surface restricts the freedom of molecular motions and thus favors the organization of molecules to form stacking. The formation of mixed ligand monolayers with stearic acid produces a film containing monolayer aggregates in which phthalocyanine planes are perpendicular to the subphase surface.

To elucidate the influence of weakening of interactions between the macrocycles on the behavior of crownphthalocyanine monolayers, we studied films of the ruthenium complex with crownphthalocyanine and axial groups MeOH and CO, *viz.*, $(R_4Pc)Ru(CO)(MeOH)$. This made it possible to enhance the polarity of the central part of tetracrownphthalocyanine and, hence, increase its affinity to surface water molecules, and also decrease the intensity of π—π-interactions between adjacent macrocycles. In fact, the compression isotherms

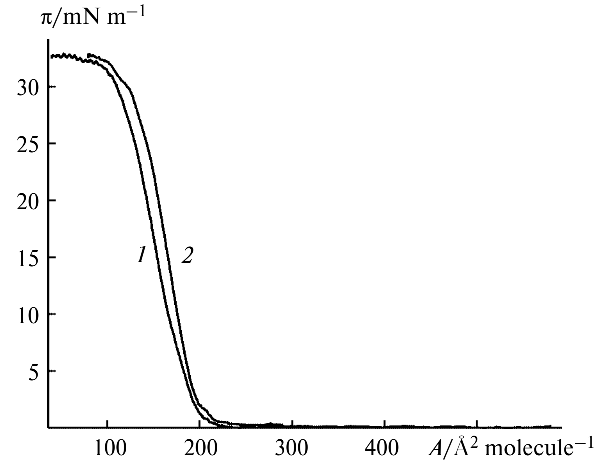


Fig. 4. Compression isotherms of the $(R_4Pc)Ru(CO)(MeOH)$ complex monolayers formed after 200 (*1*) and 100 μL (*2*) of a $7 \cdot 10^{-5}$ *M* solution of the complex were spread on the water surface.

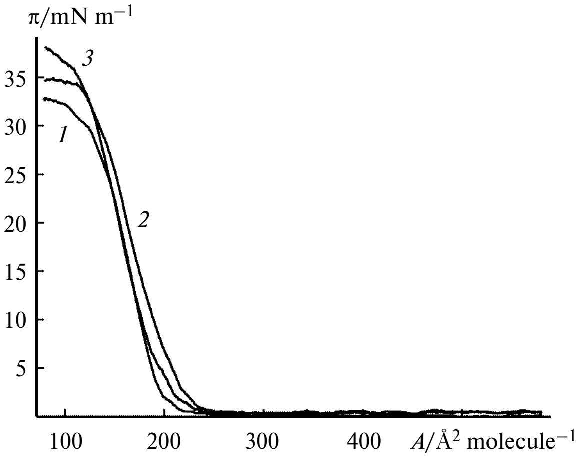


Fig. 5. Compression isotherms of monolayers of the $(R_4Pc)Ru(CO)(MeOH)$ complex obtained on the surface of different subphases: deionized water (*1*), 0.01 *M* aqueous solutionof KCl (*2*), and 0.01 *M* aqueous solution of NaCl (*3*).

reflecting the monolayer structure changed dramatically (Fig. 4) on going from the ligand to its complex $(R_4Pc)Ru(CO)(MeOH)$. The high values of A_0 and fracture pressure and a weak dependence of the position of the compression isotherms on the initial surface area (which twofold changed) indicate the formation of a stable monolayer. The limiting surface areas per molecule (A_0 = 200 Å^2) indicate that the $(R_4Pc)Ru(CO)(MeOH)$ molecules cannot be arranged parallel to the subphase surface. The calculation ignoring the contribution of axial substituents showed that the planes of the molecules were inclined to the normal at an angle of ~25°. Account of the influence of the extraligands at the Ru atom decreases the value of this angle due to an increase in the distance between the molecules that form stacking. It is of interest that, unlike the compression isotherms of the $H_2(R_4Pc)$ monolayers, the introduction of sodium or potassium chlorides into the subphase (Fig. 5) does not significantly change the isotherms. Thus, for the ligand monolayers, the insertion of a sodium cation into the crown ether rings adjacent to water decreases the surface area due to an increase in the order in stacking. On the contrary, for $(R_4Pc)Ru(CO)(MeOH)$, whose molecules are separated by axial substituents at the ruthenium atom, the binding of Na^+ cations, whose size corresponds to the crown ether cavity, does not change the distance between the molecules. An insignificant increase in A_0 for potassium ions is caused by its arrangement between the crown ether planes.

It was necessary to transfer the monolayers to solid supports (quartz and gold films on silicon and glass) for studying the monolayers by optical spectroscopy and electrochemistry. The deposition was performed by the Langmuir—Blodgett method. The transfer coefficient was determined by both the traditional method from the ratio of a decrease in the monolayer surface area to the surface area of the solid support and the method of quartz crystal microbalance. The $(R_4Pc)Ru(CO)(MeOH)$ monolayers were transferred under a surface pressure of 25 mN m^{-1}, the number of layers ranging from 7 to 24. The transfer coefficient determined by two methods was 1.5 for all supports.

We also performed preliminary studies of the binding of sodium ions by LBF of $(R_4Pc)Ru(CO)(MeOH)$ deposited on a quartz resonator. The ratio of the number of $(R_4Pc)Ru(CO)(MeOH)$ molecules in the LBF to the number of bound Na^+ cations was found to be 1 : 1.

The formation of monolayers and LBF is accompanied by the enhancement of the aggregation properties of molecules of crown-substituted phthalocyanines due to the influence of the surface and the effect of the lateral pressure in the monolayers. The bifunctional character of molecules of crown-substituted phthalocyanines can result in both stacking compression along the axis, which takes place in the case of the ligand and its sodium complexes, and stacking extension due to the introduction of axial substituents in the complexes with the central metal atom (Ru) and/or binding of large cations (K^+) with peripheral crown ether moieties of adjacent molecules.

The influence of these factors was studied by a comparison of the electronic absorption spectra of solutions and organized systems (LBF).

The electronic absorption spectrum of the $H_2(R_4Pc)$ ligand dissolved in chloroform ($4 \cdot 10^{-4}$ mol L^{-1}) (Fig. 6, curve *1*) contains two Q bands in the visible region characteristic of solutions of phthalocyanine ligands.[25—28] A decrease in the solution concentration by two orders of magnitude (curve *2*) neither changes the spectrum shape, nor shifts the characteristic bands. The green color of the solution also indicates that the ligand exists in the mono-

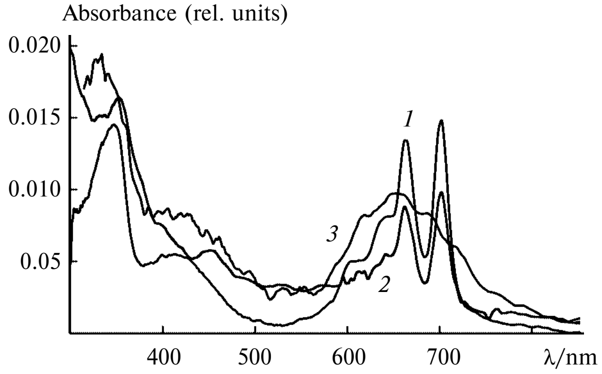


Fig. 6. Electronic spectra of the ligand recorded for its $4 \cdot 10^{-4}$ (*1*) and $5 \cdot 10^{-5}$ *M* (*2*) solutions in chloroform and for the LBF (12 layers) on a quartz plate (*3*).

meric form.[29,30] The electronic spectrum of the LBF of the ligand on the quartz plate (see Fig. 6, curve *3*) contains one broad Q band at 650 nm shifted toward shorter wavelengths compared to both bands of the spectrum of a solution of the ligand. A shift similar to that of the Q band is observed in the region of Soret bands. The presence of two bands in the spectrum of the phthalocyanine ligand is caused[27] by the geometrically induced splitting of the Q band into components Q_x and Q_y. The aggregation accompanying the formation of the Langmuir—Blodgett films eliminates the conditions of the appearance of this effect.

The electronic spectrum of the $(R_4Pc)Ru(CO)(MeOH)$ ruthenium complex in a chloroform solution is characteristic of phthalocyanine complexes[27] (Fig. 7, curve *1*). The absorption bands at 655, 630, and 593 nm are caused by the ground π—π* transitions and assigned to the Q band with two satellites.[31] The Soret band appears at 320 nm. The half-width of the Q band is 500 cm^{-1}. These results indicate that the $(R_4Pc)Ru(CO)(MeOH)$ complex in solution exists in the monomeric form.

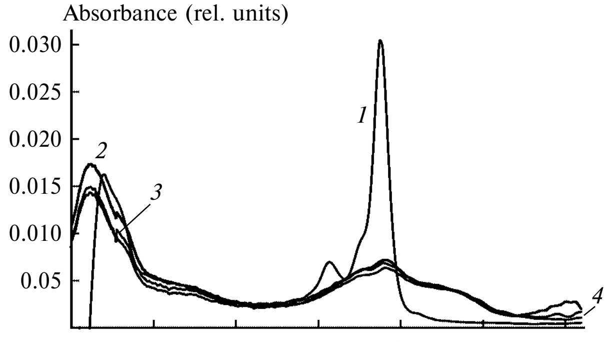


Fig. 7. Electronic spectra of $(R_4Pc)Ru(CO)(MeOH)$ obtained for a $7 \cdot 10^{-5}$ *M* solution in chloroform (*1*), LBF (12 layers) on quartz (*2*), the same LBF after 20-min storage in an 0.001 *M* aqueous solution of NaCl (*3*), and LBF after sodium ions were washed off with water for 60 min (*4*).

The electronic spectrum of the LBF of 12 $(R_4Pc)Ru(CO)(MeOH)$ monolayers differs substantially from the spectrum of a solution of the complex (see Fig. 7, curve *2*). The major Q band broadens and shifts toward the long-wave region. Simultaneously, the Soret band undergoes the hypsochromic shift. Therefore, stacking is formed in the LBF despite the axial substituents in $(R_4Pc)Ru(CO)(MeOH)$. Such spectral changes were multiply observed on going from solutions of phthalocyanines to planar organized systems. The direction of shifts of the spectra depends on many factors: for example, the central complexing cation[32] and length of the hydrocarbon chain of the peripheral substituent.[33] A characteristic feature of the spectrum of the LBF of the ruthenium complex is the appearance of a band in the near-IR region at ~880 nm. This band is absent from the spectra of solutions of both the ligand and $(R_4Pc)Ru(CO)(MeOH)$ complex. The storage of the LBF in a 10^{-4} *M* solution of NaCl for 30 min results in the almost complete disappearance of the new band at 880 nm. This band disappears at least from this region (see Fig. 7, curve *3*) and does not appear again after the LBF is washed with water (curve *4*). Bands in the near-IR region are usually observed for the formation of free-radical structures or charge-transfer complexes.[27,34] In this case, reasons for the appearance and disappearance (shifts) of this band require more detailed studies, which are presently in progress.

Electrochemical studies make it possible to determine the redox characteristics of crownphthalocyanines in LBF, their barrier properties, stability under cyclic treatments, and the influence of complex formation on these parameters of multilayer structures.

The cyclic voltammogram of the heptalayer LBF of $(R_4Pc)Ru(CO)(MeOH)$ on the gold surface for an 0.1 *M* solution of $HClO_4$ and a potential sweep of 100 mV s^{-1} (curve *1*) is shown in Fig. 8. A similar dependence for the initial surface of a gold electrode is also presented in Fig. 8 (curve *2*). Distinct anodic and cathodic peaks related to the reversible oxidation of the phthalocyanine macrocycle are observed at potentials of 0.62 and 0.54 V, respectively. For unsubstituted phthalocyanines RuPc(CO)(py) and $RuPc(py)_2$, the redox transition $[RuPc]^+/[RuPc]^0$ is observed at 0.91 and 0.77 V, respectively.[35] Rather low redox potentials of $(R_4Pc)Ru(CO)(MeOH)$ are caused by the influence of the electron-releasing crown ether substituents. The reproducibility of the voltammograms, at least after 50 scan cycles, indicates the electrochemical stability of the LBF of $(R_4Pc)Ru(CO)(MeOH)$. Based on these data, we calculated the electroactivity of this LBF. The monolayer surface area in the transfer region is 150 Å^2 per molecule. Taking into account the transfer coefficient of the monolayer to a gold support (ρ = 1.5) found by quartz crystal

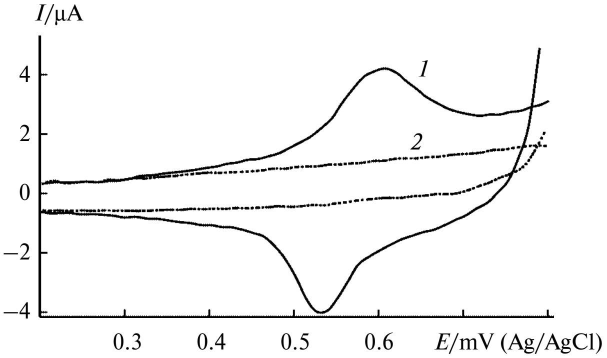


Fig. 8. Cyclic voltammogram of the LB film (7 layers) of $(R_4Pc)Ru(CO)(MeOH)$ on gold in an 0.1 *M* aqueous solution of $HClO_4$ (*1*). Potential sweep is 100 mV s^{-1}. Surface area of the electrode is 0.08 cm^2. Curve *2* was obtained on a pure gold electrode under the same conditions.

microbalance, the surface area per molecule in the LBF is equal to 100 $Å^2$. The oxidation (reduction) of one $(R_4Pc)Ru(CO)(MeOH)$ molecule in the LBF is accompanied by the transfer of one electron carrying a charge of $1.6 \cdot 10^{-13}$ μC. For a number of molecules of 10^{14} per 1 cm^2, the specific transferred charge for one monolayer at 100% efficiency should be 16 μC cm^{-2}. The calculation of the transferred charges of the whole LBF for the anodic and cathodic waves gave close values of 5.6 μC. Taking into account the surface area of the electrode (0.08 cm^2) and the number of monolayers in the LBF, we obtain 10 μC cm^{-2} for one monolayer. Therefore, the electroactivity of phthalocyanine rings in the LBF is 62.5%. A similar calculation[25] for the LBF of copper octakis((2-benzyloxy)ethoxy)phthalocyaninate gave 65%. Among many factors affecting the electroactivity of phthalocyanine films, the authors[25] mentioned the electron transfer rate, transport of counterions, and capacity effects.

To determine the dynamic characteristics of electrode processes, cyclic voltammograms were recorded for different scan rates in a region of 10—1000 mV s^{-1}. A linear dependence of the anodic and cathodic current retained at high scan rates (Fig. 9) due to the fast response of the fine organized system (LBF) is prospective for the use of these films in high-performance sensors.

The barrier properties of the heptalayer LBF of $(R_4Pc)Ru(CO)(MeOH)$ were studied by cyclic voltammetry in an 0.5 *M* solution of KCl in the presence of the redox system (1 mmol L^{-1} $K_3[Fe(CN)_6]$ and 1 mmol L^{-1} $K_4[Fe(CN)_6]$). The cyclic voltammogram exhibited no peaks characteristic of the redox process in this system (without the film). This indicates that the gold electrode was completely blocked by the film of the complex.

The influence of binding of Na^+ and K^+ ions on the electrochemical behavior of the LBF of

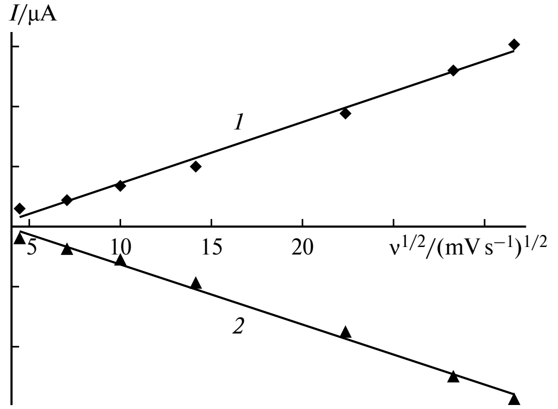


Fig. 9. Current of the anodic (*1*) and cathodic (*2*) peaks of the voltammograms obtained for the LB film (7 layers) of $(R_4Pc)Ru(CO)(MeOH)$ on gold in an 0.1 *M* aqueous solution of $HClO_4$ *vs.* potential sweep.

$(R_4Pc)Ru(CO)(MeOH)$ was studied by cyclic voltammetry and impedance spectroscopy. The measurements were carried out in solutions of 0.1 *M* $HClO_4$ containing additives of 0.01 *M* $NaClO_4$ or 0.01 *M* KCl. The voltammograms obtained in the presence of Na^+ or K^+ ions virtually coincide in shape, current value, and position of peaks with the curves for a solution containing no metal ions. This indicates that the cations either do not enter into the film and bind with peripheral crown ether groups, or their binding weakly affects the redox behavior of the phthalocyanine ring. However, the above results of studying the interaction of the LBF of $(R_4Pc)Ru(CO)(MeOH)$ transferred onto quartz resonators with sodium cations in solution indicate their binding with the films.

The presence of Na^+ and K^+ ions in these films is confirmed by the results of measurements of the electrochemical impedance for the same electrodes and solutions that were used in experiments on voltammetry. As should be expected, cation binding, which does not change the redox properties of the system, exerts a weak effect on the shape of complex impedance diagrams in the coordinates Z_{Re}—Z_{Im} (Fig. 10). We observed only a slight decrease in the impedance values of the system when alkaline metal cations are introduced. These diagrams predominantly reflect the behavior of the system in a low-frequency region that characterizes electrochemical reactions occurring on the electrode surface.

However, a change in the chemical composition of the film, intermolecular interactions in stacking during cation binding, and, in the case of K^+, probably the mutual arrangement of individual molecules as well should affect the dielectric characteristics of the membrane under study. Since these characteristics make the most substantial contribution to the electrochemical response in the region of high and medium frequencies, more detailed diagrams were constructed precisely for this region

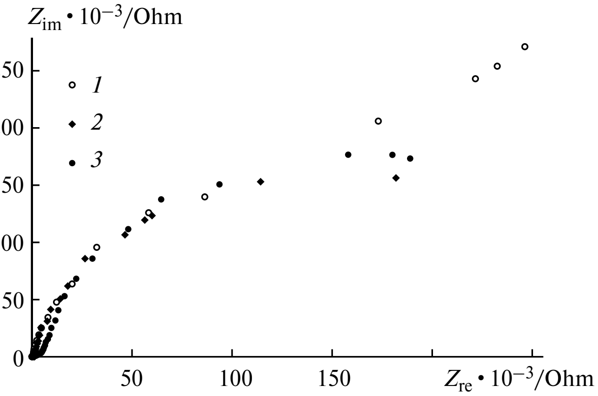


Fig. 10. Complex diagram of the impedance for the LB film (10 layers) of $(R_4Pc)Ru(CO)(MeOH)$ on a gold electrode in the frequency region from 50000 to 0.05 Hz: *1*, 0.1 *M* aqueous solution of $HClO_4$; *2*, aqueous solution of 0.1 *M* $HClO_4$ + 0.01 *M* $NaClO_4$; *3*, aqueous solution of 0.1 *M* $HClO_4$ + 0.01 *M* KCl.

(Fig. 11). The binding of Na^+ and K^+ ions (curves *2* and *3*) substantially changes the shape of the initial diagram (curve *1*) and impedance values. For instance, at a frequency of 107 Hz the impedance of the initial film is 410 Ohm, while for the films containing Na^+ and K^+ ions it is 1250 and 2180 Ohm, respectively. In the case of Na^+ ions, the observed changes in the electrochemical response are completely reversible, and the diagram, obtained after the LBF was washed off to remove sodium cations (1-h storage in 0.1 *M* $HClO_4$), virtually coincides with the initial diagram (see Fig. 11, curve *4*). No complete reversibility is observed for binding of K^+ ions (see Fig. 11, curve *5*), which is likely caused by stronger interactions between the crown ether groups of the phthalocyanine under study and K^+ cations.[36]

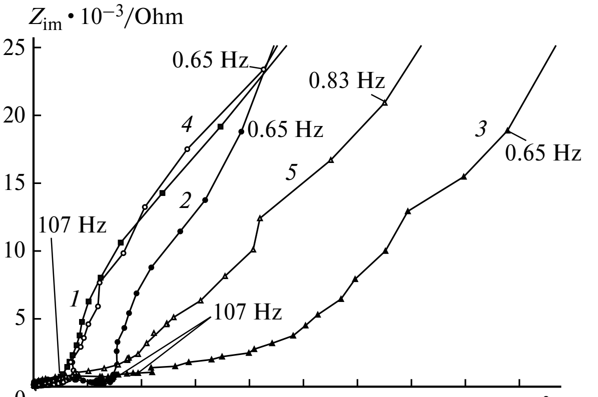


Fig. 11. Complex diagram of the impedance for the LB film (10 layers) of $(R_4Pc)Ru(CO)(MeOH)$ on a gold electrode in different media: *1*, 0.01 *M* aqueous solution of $HClO_4$; *2*, aqueous solution of 0.1 *M* $HClO_4$ + 0.01 *M* $NaClO_4$; *3*, aqueous solution of 0.1 *M* $HClO_4$ + 0.01 *M* KCl; *4* and *5*, storage in an 0.1 *M* aqueous solution of $HClO_4$ for 1 h after tests in solutions containing Na^+ (*4*) or K^+ (*5*) (washing from cations).

Thus, a possibility to form monolayers of tetra-15-crown-5-substituted phthalocyanines on the water surface was studied. In the case of the $H_2(R_4Pc)$ ligand, multilayer films of molecular associates are formed. The ligand is established to be compatible with stearic acid in a mixed binary monolayer. Stearic acid improves the ligand distribution over the water surface and induces the formation of monolayer associates immobilized in its matrix. A condensation effect of Na^+ on the mixed layers was observed. The effect is caused by an increase in stacking ordering due to conformational changes of the crown ring induced by desolvation and cation binding.

The ruthenium complex with tetra-15-crown-5-phthalocyanine and axial ligands $(R_4Pc)Ru(CO)(MeOH)$ forms stable true monolayers. The angle of inclination of the macrocycle planes in stacking relatively to the normal to the subphase surface is 25°.

Based on the electronic absorption spectra of solutions and LBF of the ligand and ruthenium(II) complex with this ligand, we can conclude that the LBF are formed of linear associates of these compounds.

Redox peaks of the LBF of $(R_4Pc)Ru(CO)(MeOH)$ appeared at comparatively low potentials were observed by cyclic voltammetry. A high electrochemical stability of the LBF was demonstrated, and the electroactivity of the phthalocyanine rings was shown to be 62.5%. The LBF of $(R_4Pc)Ru(CO)(MeOH)$ are promising for the use in sensors due to their fast response to electrochemical effects.

It was shown by impedance spectroscopy that the binding of Na^+ and K^+ ions by the Langmuir—Blodgett films of $(R_4Pc)Ru(CO)(MeOH)$ substantially increased the impedance in a region of medium frequencies. Washing of the LBF makes it possible to completely remove Na^+ cations, whereas K^+ cations can be washed off only partially.

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