

Monolayers of Benzodithia-Crown-Ether Derivative: Surface Active and Photosensitive Properties

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Abstract Monolayers based on the novel multifunctional compound K29 (the amphiphilic and photosensitive derivative of dithiacrown-ethers) were obtained and investigated. The studied ion-selective and photosensitive properties of K29 in monolayers demonstrated its ability to form complexes with mercury cations which were detected by significant changes in the K29 monolayer isotherms and absorption spectra. Such obtained supramolecular systems are promising as models of the molecular organization and recognition processes at the interfaces.

Keywords: monolayers, membranes, crown-ethers, ion selectivity, photosensitivity, mercury

1. Introduction

Design and study of supramolecular systems as future nanomaterials for various applications is one of the most interesting and rapidly developing area of science, located "at the interface" of bioorganic, colloid and polymer chemistry [1,2]. Remarkable examples of such supramolecular systems are monomolecular layers (monolayers) of multifunctional surface-active compounds (surfactants). For example, addition of surface active substitutions in the crown ether molecules leads to the unique amphiphilic compounds, which have both fundamental and practical importance [3]. Supramolecular systems including monolayers and Langmuir-Blodgett films aggregates and complexes based on amphiphilic photosensitive crown-ethers can be considered as unique models for investigating of biological and synthetic membranes [3,4]. Monolayers of crown ethers can serve as a convenient model for investigation of self-assembly and molecular recognition processes at the interface. Such processes are the most general for biological membrane function. On the other hand these supramolecular systems are promising as nanomaterials for various applications, in particular as sensitive membranes for ion-selective electrodes [2,5].

It is known that the replacement of one or more oxygen atoms in the crown ether to other donor atoms can significantly change the ability of the ligand to bind metal cations [3]. For example, the 1,10-dithia-18-crown-6-ether has very low affinity for the alkali metal cations as compared to 18-crown-6-ether, but at the same time it forms much more stable complexes with cations of heavy metals in organic solvents [3]. The great interest attaches to compounds capable of forming "guest-host" complexes with organic molecules, such as "complexants" for biogenic diamines, catecholamines, amino acids and other

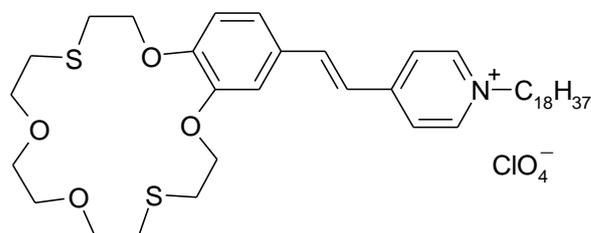
nitrogen-containing biologically active compounds [2,3]. Recently synthesized bicyclic ligand ("bis-crown ether"), consisting of two cyclopolyether fragments and protonated polyamine. This bicyclic ligand can form complexes with amino acids [6]. In this case, the positively charged polyamine interacts with the carboxyl groups of amino acids and cyclopolyether fragments interact with protonated amino groups [6]. Crown ethers with ethylene bonds are capable of reversible cis-trans photoisomerization reaction by photoactivation in the visible range. This phenomenon is widely used to create photoswitchable crown ether molecules that are promising for the development of optical chemosensor materials [7,8,9,10].

The aim of this work was to develop and study of monolayers based on amphiphilic and photosensitive dithia-crown-ether derivative (K29) capable of forming complexes with mercury cations.

2. Experimental Part

2.1. Materials

Synthesis of amphiphilic and photosensitive derivative dithia-crown-ether (code of synthesis - K29) has been developed by Gromov S.P. and coworkers in Center of Photochemistry Russian Academy of Sciences and described previously [3]. General formula ($C_{45}H_{68}ClNO_8S_2$) and K29 molecular structure described below.



2.2. Methods

The measurements of the surface pressure isotherms (π) and surface potential (ΔV) vs. area (A) per molecule K29 in the monolayer is the main research methods [11]. Obtained π - A isotherms of K29 monolayer showed phase separation and the packing density of the K29 molecules at the interface. The value of the surface pressure was determined by the equation [8,9,10,11]:

$$\pi = \gamma_0 - \gamma,$$

γ_0 and γ , - surface tension of pure water surface subphase and the surface coated with surfactants (in mN/m). The measurements of the surface pressure (Langmuir trough by company «NIMA-NFT», England-Germany) by Wilhelmy method [11] are based on the position change of a thin paper plate (15x15 mm) that is half-submerged in the water subphase before and after spreading the K29 solution (1,074 mM in chloroform). To improve the accuracy of π - A isotherm measurements (up to 0.01 mN/m) of K29 monolayers, all parameters were kept constant in the experiment, only the salt concentration in the aqueous subphase was changing.

The ΔV values of K29 monolayer at the water/air was calculated from the Helmholtz equation [8,9,10,11]:

$$\Delta V = n \mu (1/e_0),$$

n - the number of molecules in the monolayer, μ - the average value of the effective dipole moment of the molecule in the plane normal to the interface, e_0 - permittivity of vacuum. ΔV - A isotherms of K29 monolayer are obtained by the vibrating electrode method which is based on measurement of the potential between the metal electrode disk vibrating at an ultrasonic frequency above the water subphase (several millimeters) and Pt-electrode immersed in an aqueous subphase [11].

Spectral characteristics of the obtained monolayers were studied using spectrophotometric system based on spectrophotometer Hitachi 330 [8,9,10,11]. The K29 monolayers were formed on bidistilled water or mercury (II) perchlorate aqueous solutions. The salt concentrations were used from 10^{-8} to 10^{-3} M. The monolayers were transferred to quartz or glass substrates for measuring the absorption spectra of K29 monolayers in the 350-600nm wavelength area (the increase of intensity at wavelengths less than 350nm is due to the light absorption of the glass plate). The measurement error of the wavelength of maximum absorption is 1nm and the measurement error of the absorption intensity - 0.00001 relative units.

3. Results and Discussions

Firstly, we investigated the K29 monolayers that were obtained by spreading the K29 solution on bidistilled water. The unexpected effect in the study of this novel photosensitive ionophore monolayer was the presence of a small but reproducible pressure (about 0.5mN/m) while spreading the individual K29 solution (5 μ l) on the bidistilled water (Figure 1, curve 1). It was found that the K29 compound forms unstable liquid-expanded monolayers on water in spreading the K29 solution at 25 and 40 μ l (Figure 1, curves 2, 3). However, the collapse pressure of liquid-expanded state (I) of monolayer of the individual K29 was quite high and in the range of 27-28mN/m at $A = 0.40$ - $0.5\text{nm}^2/\text{molecule}$ (Figure 1, curve 3).

This indicates a nearly horizontal position of complicated K29 molecules regarding the interface at the initial time of the experiment (5 min after spreading the solution on the bidistilled water). A gradual increase in the value of the surface potential of -300 to -100mV in a wide range of $A = 10\text{nm}^2$ to $A = 2\text{nm}^2$ (Figure 1 b, curve 1), from -50 to +100mV in a wide range of $A = 2.0\text{nm}^2$ to $A = 0,5\text{nm}^2$ (Figure 1 b, curve 2), from 150 to 250 mV in a wide range of $A = 1.2 \text{nm}^2$ to $A = 0.4 \text{nm}^2$ (Figure 1 b, curve 3) for increased amounts of K29 solution deposited on the water subphase. Further decline of the potential values at a small area is due to the technical conditions of measurement monolayer is small areas in the vicinity of the vibrating electrode (in this region potential values do not change at the large amounts of K29 solution from 65 to 100 μ l). A small increase of the surface pressure values in this range (at small areas) associated with the transition of the individual K29 monolayer to the liquid-condensed state (II).

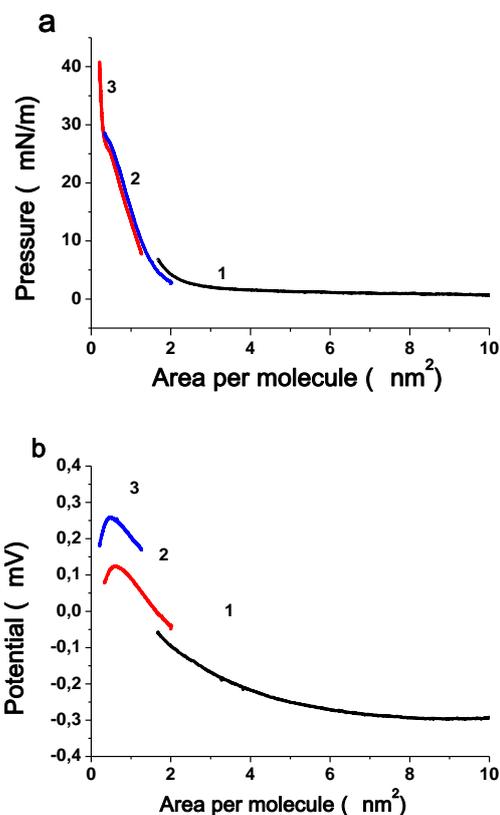


Figure 1. Surface pressure (a) and surface potential (b) isotherms vs. area per molecule in the monolayer of the dithia-crown-ether derivative (K29) on the bidistilled water surface at the different spreading volume: 5 μ l (1), 25 μ l (2), 40 μ l (3).

The initial pressure of the monolayer is about 12mN/m at $A = 0.78\text{nm}^2/\text{molecule}$ after spreading 65 μ l of K29 solution. Collapse pressure in the liquid-condensed state (II) of the K29 monolayer was about 50-51mN/m at $A = 0.30$ - $0.35\text{nm}^2/\text{molecule}$ (Figure 2 a, curve 1). The investigation of K29 interaction in a monolayer with heavy metal cations from the aqueous subphase has both fundamental and practical interest. Isotherms of K29 monolayers on salts solutions of heavy metals (in particular - mercury perchlorate) have a qualitative similarity with the K29 isotherms on water with some quantitative differences (Figure 1). The starting point of

monolayer compression is 7.6-12.0mN/m at $A = 0.78$ - $0.80\text{nm}^2/\text{molecule}$ and almost the same for all concentrations of mercury cations (from 10^{-8} to 10^{-4} M) in the same K29 spreading volume (65 μl) of the (Figure 2, curves 2-4), that is almost the same as the starting point of monolayer compression on the water (Figure 2, curve 1). By further compression of K29 monolayers to the pressure 30mN/m areas per molecule are following: 0.45nm^2 on the water, 0.54nm^2 at a concentration of 10^{-6} M mercury perchlorate, 0.50nm^2 - at 10^{-5} M, 0.43nm^2 - at 10^{-4} M (Figure 2, curves 2-4). Collapse pressure for K29 monolayers at the surface of mercury solutions is from 53mN/m to 62mN/m at the concentrations of 10^{-6} M - 10^{-4} M respectively $\text{Hg}(\text{ClO}_4)_2$ (Figure 2a).

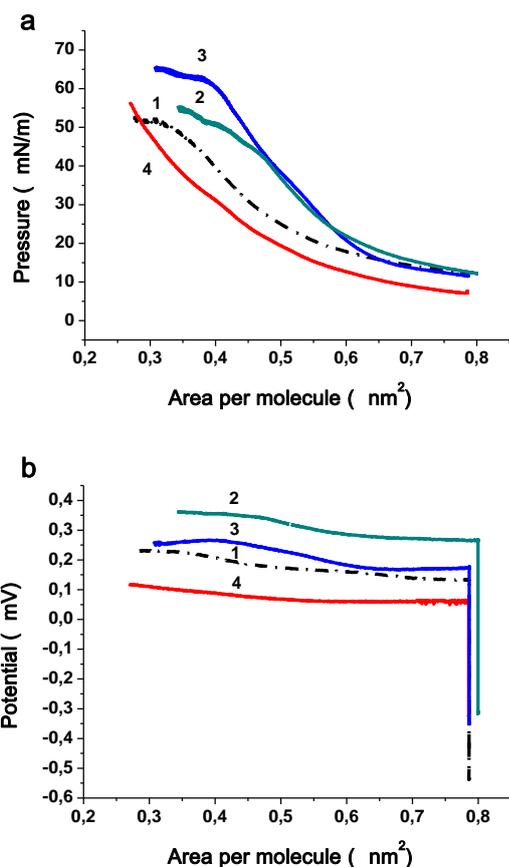


Figure 2. Surface pressure (a) and surface potential (b) isotherms vs. area per molecule in the monolayer of the dithia-crown-ether derivative (K29) on the bidistilled water (1) and $\text{Hg}(\text{ClO}_4)_2$ aqueous solutions surface at the different salt concentrations: 10^{-6} M (2), 10^{-5} M (3) и 10^{-4} M (4)

Significant differences in the parameters of the π -A isotherms of K29 monolayers in case $\text{Hg}(\text{ClO}_4)_2$ and water were found. The differences are due to the formation of specific complexes between macrocyclic fragment K29 and Hg^{2+} cation. A significant increase in the area of the monolayer in the case of 10^{-6} - 10^{-5} M $\text{Hg}(\text{ClO}_4)_2$ concentrations can be explained by intermolecular repulsion between complexes (K29-Hg^{2+}) which have an uncompensated positive charge. On the other hand the monolayer area decrease in the case 10^{-4} M concentration of the $\text{Hg}(\text{ClO}_4)_2$ is likely due to the “release” part of some complexes from the interface to the aqueous subphase as supramolecular aggregates.

For K29 monolayers obtained onto solutions of different $\text{Hg}(\text{ClO}_4)_2$ concentrations (from 10^{-8} to 10^{-3} M) in the aqueous subphase observed a qualitative change of the surface potential isotherms (Figure 2 b, Figure 3 b). The gradual increase in the values of the surface potential (500-600mV) over a broad range of areas per K29 molecule (from $A = 1.9\text{nm}^2$ to $A = 0.3\text{nm}^2$) (Figure 2 b, curves 2-4) at a concentration of $\text{Hg}(\text{ClO}_4)_2$ from 10^{-8} to 10^{-5} M in the aqueous subphase is observed. This is also characteristic of K29 monolayers on bidistilled water (Figure 2 b, curve 1). In contrast, there is a sharp jump of the surface potential (300 mV) in a very narrow range of the area per K29 molecule (from $A = 1.2\text{nm}^2$ to $A = 1.1\text{nm}^2$) (Figure 3 b) at a concentration of $\text{Hg}(\text{ClO}_4)_2$ from 10^{-4} to 10^{-3} M in the aqueous subphase. This is a further important indicator of the formation complexes between K29 and mercury cations. Different absolute values of changes of the surface potential for all the cases (Figure 3) can be reduced to the total relative range of ΔV values (about 300-600mV) whether gradually or abruptly these parameters increase.

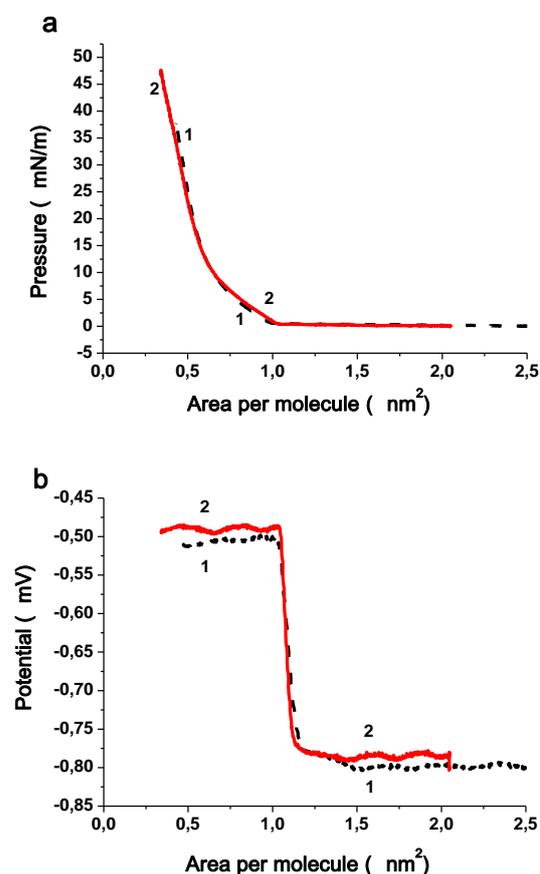


Figure 3. Surface pressure (a) and surface potential (b) isotherms vs. area per molecule in the monolayer of the dithia-crown-ether derivative (K29) in the monolayer on $\text{Hg}(\text{ClO}_4)_2$ aqueous solution (10^{-3} M) surface at the different spreading volume: 20 μl (1), 25 μl (2)

Two isotherms of surface pressure and surface potential of the area per K29 molecule in the monolayer on the surface of aqueous solutions of $\text{Hg}(\text{ClO}_4)_2$ with the same concentration of 10^{-3} M (Figure 3 a and b, curves 1 and 2), as shown in this case as an indicator of a sharp rise in ΔV and visual proof K29 monolayer stability in the presence of high concentrations of mercury, as well as the reproducibility of the measurements.

A comparative study of the absorption spectra of monolayers K29 compound transferred from distilled water and aqueous solutions of $\text{Hg}(\text{ClO}_4)_2$ at constant surface pressure (about 10 mN/m) were fulfilled (Figure 4). The obtained results confirmed the above data. In all cases a broad maximum absorption in the range 350-450nm, as shown in Figure 4. Specifically, for a monolayer of K29 compound transferred from double distilled water, this maximum is "poorly defined" (most "effective") and is 0.00214 relative units at 429 nm and $\text{Hg}(\text{ClO}_4)_2$ aqueous solutions (Figure 4, curve 1). At the same wavelength the absorption intensity for a K29 monolayer transferred from 10^{-5} M $\text{Hg}(\text{ClO}_4)_2$ aqueous solution is 0.00335 relative units, i.e. 57% higher than for the monolayer transferred from the water. The absorption maximum for K29 monolayer transferred from $\text{Hg}(\text{ClO}_4)_2$ is 0.00575 relative units at 406 nm, which is 209% higher than for the monolayer transferred from water (Figure 4). The shift the absorption maximum of the K29 monolayer in the presence of mercury salts is 23nm to shorter wavelengths. This is an additional and direct evidence of the complex formation between K29 and mercury cations.

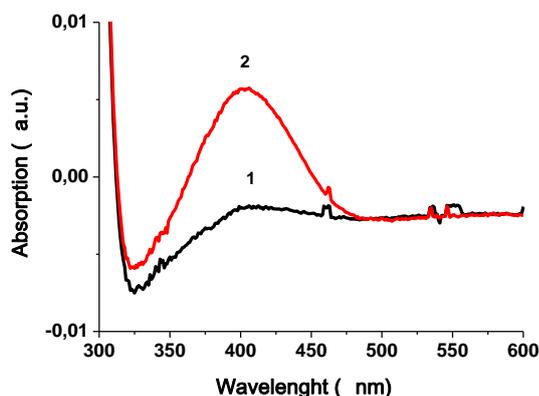


Figure 4. Absorption spectra of K29 monolayer on the water surface (1) and $\text{Hg}(\text{ClO}_4)_2$ aqueous solution (10^{-5} M) (2) at the 10mN/m surface pressure.

Thus, the obtained systems based on benzodithia-crown-ether derivative are promising as nanomaterials for mercury cation detection.

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