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Multifunctional membranes based on photosensitive crown-ether derivatives with advanced properties

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ABSTRACT

This review discusses recent works on monolayer, multilayer and polymer films of various crown-ether derivatives. Preparation and investigation of such membrane nanostructures based on photosensitive and surface-active crown-ethers is a rapidly growing field at the "junction" of colloids and polymers, materials sciences and nanotechnology. These membranes can serve as convenient models for studying the self-organization and molecular recognition processes at interfaces that are typical for biomembranes. The results obtained for such structures by absorption and fluorescence spectroscopy, atomic force and Brewster-angle microscopy, surface pressure and surface potential isotherm measurements have been described. The possibility of developing multifunctional materials possessing advanced properties has been demonstrated.

Contents

Acronyms

ΔV	surface potential values
16-MHPC	poly(16-di(metacryloyloxyhexadecanoyl)glicero-3-phosphoryl choline
AFM	atomic force microscopy
BAM	Brewster-angle microscopy
BDCE	butadienyl crown ether
C18	stearic acid
LB	Langmuir–Blodgett
OMS	optical molecular sensor
PCEDs	photosensitive crown-ether derivatives
PVC	poly(vinyl chloride)
PVS	poly(vinyl stearate)
SAMs	surface active monomers
SERS	surface-enhanced Raman scattering
S-PCED	S-containing PCED monolayers

1. Introduction

Preparation and investigation of the ultrathin films based on photosensitive crown-ether derivatives (PCEDs) are currently one of the fascinating and rapidly growing fields of research at the "junction" of polymers and colloids, physical–organic and biological chemistry, bio- and nanotechnology [1–12]. Such membrane nanostructures can be

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considered as important model systems and materials widely used to simulate the structure and functions of biological membranes [2,10–12]: monomolecular layers (monolayers) and Langmuir–Blodgett (LB) films [4–7,12–16], planar bilayer lipid membranes [2,11–13], and spherical bi- and multilayer membranes (vesicles, liposomes, and their analogs) [5,6,11–14,16]. The principal shortcoming of such systems is their low stability, making them distinct from natural membranes stabilized by the electrostatic and hydrophobic interactions between integral and peripheral proteins, peptides, and glycolipids [5–9,12,16]. One of the first and most successful approaches to solve the problem of producing membrane nanosystems was achieved by the manufacture of polymer monolayers and liposomes on the basis of surface active monomers (SAMs) described by Fendler [5], Bader and coworkers [6]. The following points are the most important for developing the theory and practice of producing function oriented membranes and nanostructures possessing a set of specified properties as follows: (1) selecting the optimal ways to synthesize the SAMs of a specified structure, (2) optimizing the methods for obtaining the ultrathin organized films of these SAMs and establishing the self-association mechanism of mixed SAM and PCED mono and multilayers, (3) studying the reactions occurring in these layers in order to form certain nanostructures and developing physicochemical methods for investigating various types of ultrathin organized SAM and PCED base films, and (4) determining systems that are promising for subsequent use in the capacity of functional membranes and other types of nanomaterials.

2. Monolayers based on O-containing PCEDs

A modern class of photochromic materials such as crown-containing styryl dyes (type I PCED, Fig. 1a), have been synthesized at the Photochemistry Center of the Russian Academy of Sciences [17] and recently become the subject of intense studies [17–21]. The presence of a crown-ether fragment in these dyes facilitates their selective bonding to metal cations. Spectral measurements taken in organic and water–organic media have shown that cation influences the physicochemical properties of the sensor molecule [17]. The photochromic properties of PCEDs are the reasons why they can transform during two photoinduced reversible reactions (Fig. 1b): *trans–cis* C═C double-bond isomerization or [2 + 2] photocycloaddition to form substituted cyclobutanes [17].

Studies of PCED types Ia–Ic [18–21] showed their capability of forming stable monolayers at the air–water and water–alkali metal salt solution (Fig. 2, the isotherms presented refer to PCED type Ib). Their main parameters (surface area (A) per PCED molecule, surface pressure (π) and potential (ΔV); the collapse pressure and potential of the monolayer) are at their minimum at the water surface and grow higher in the presence of salts in the water subphase (Fig. 2a and b), which points to an interaction between PCEDs and alkaline or alkaline earth metal cations. The authors [18–21] believe that the inclusion of a cation in a PCED monolayer increases the mutual repulsion of the positively charged molecules and the surface area (A) per type-Ib PCED molecule in the monolayer (Fig. 2a).

The area occupied by a type-Ic PCED molecule on the surface of water and 1 mM salt solutions was found to be half that for type-Ia and type-Ib PCED molecules points to a pronounced change in the molecular organization of the monolayer as a result of the translocation of the hydrophobic aliphatic substitute from position 3 to position 5 in the benzothiazole ring structure [19]. Based on the data obtained by the methods of the surface-enhanced Raman scattering (SERS) and Brewster-angle microscopy (BAM) [19,20], it was concluded that the structures of PCED monolayers formed on the surface of water by various salt solutions differed substantially. To study the structure of PCED monolayers in more detail, atomic force microscopy (AFM) was used. The analysis of AFM data showed that a type-Ib PCED monolayer transferred by the Langmuir–Blodgett method from the water surface onto mica is an accumulation of a large number of aggregates differing in size (light areas in Fig. 3a). It is important that the height of the aggregates is 1.8 nm on average, which corresponds to the length of the aliphatic substitute in type-Ib PCEDs. In the presence of salts (for example, NaCl), a "practically homogeneous" type-Ib PCED monolayer forms (Fig. 3b). Such changes in the structure of monolayers are also characteristic of other PCEDs, which is an additional evidence of the interaction between the dye in the monolayer and cations in the water subphase.

Valuable information on the packing of PCEDs in monolayers directly at interfaces was obtained from absorption and fluorescence spectroscopy data [19–22]. For example, an intense absorption band is present in the electronic spectra of types Ia–Ic PCED monolayers (recorded directly on the surface of distilled water and 10 mM salt solutions) in the region of 450±5 nm (Fig. 4). As the surface pressure π is increased from 5 to 30 mN/m, the absorption maximum in the spectrum of type-Ib PCED monolayers is shifted from 446 to 438 nm, which is due to the formation of the aggregates detected earlier by the AFM method. The increase in absorption is associated with the surface density of chromophores growing higher upon the contraction of the PCED monolayer. The maximum absorption intensity in the spectra of type-Ib monolayers in the presence of NaCl substantially exceeds the absorption intensity of similar monolayers in the presence of $CaCl_2$, $MgCl_2$, or KCl (Fig. 4), which is due to the selectivity of cations bonding to the PCED in the monolayer [19–21].

It is important that the exposure of types Ia–Ic PCED monolayers formed on the surface of salt subphases to light at constant π is observed to cause reversible changes in their absorption intensity (Fig. 5a, b). The absorption intensity (at 446 nm) of type Ia PCED monolayers is, in this case, observed to decrease sharply a few seconds after their photoactivation with light 438 nm in wavelength, which is close to the absorption maximum of the PCED. Once the absorption intensity becomes constant, irradiation is stopped and the absorption intensity (at 446 nm) starts increasing until it almost reaches its original values (Fig. 5a, b).

These reversible changes in the absorption intensity are associated with the *trans–cis* and *cis–trans* C═C double-bond isomerization processes in the crown ether molecule (Fig. 1b). These effects are characteristic of other amphiphilic dyes as well [17,19]. The nature of the metal cation and the character of molecule organization in the monolayer influence the photoisomerization process. At low surface pressures (around 3 mN/m), the reversible changes in the absorption intensity of type-Ib monolayers formed on the surface of a 10-mM KCl solution (Fig. 5a, curve 1) are somewhat greater than those of similar monolayers obtained on the surface of a 10-mM NaCl solution (Fig. 5b, curve (1)) under similar conditions. However, at higher surface pressure values (about 9 mN/m), these changes for type-Ib PCED monolayers on the surface of a 10 mM KCl solution (Fig. 5a, curve (2)) are substantially smaller than those for similar monolayers on the surface of a 10 mM NaCl solution (Fig. 5b, curve 2); this is so even at still higher surface pressures (around 14 mN/m). Thus, optimal conditions for forming stable monolayers and their interaction with alkaline and alkaline-earth metal cations were found for types Ia–Ic PCEDs differing in cycle size, as well as in the length and position of the alkyl substitute in the molecule.

3. Monolayers based on S-containing PCEDs

Researchers [23,24] synthesized a new amphiphilic butadienyl crown ether (BDCE) (Fig. 1c) with two sulfur atoms in the crown-ether ring structure of the molecule. BDCE was found to be capable of forming relatively stable monolayers on the surface of water (with a collapse pressure around 42 mN/m), as well as solutions of alkaline salts (π = 40–45 mN/m) and heavy metal salts (π = 23–40 mN/m), which in most cases is substantially higher than the collapse pressure for the monolayers of other dithio- derivatives of the PCEDs (π = 25.5–34.5 mN/m) were studied earlier [19–21]. The material difference between the isotherms of BCED monolayers on the surface of 1 mM $Hg(ClO_4)_2$ solution and those of similar monolayers on the surface of other salt solutions, as well as water (Fig. 6a), proves to a specific

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