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Dynamic surface properties of C_{60}-arginine and C_{60}-L-lysine aqueous solutions

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ABSTRACT

The surface properties of the solutions of two derivatives of C_{60} fullerene with lysine and arginine were investigated by measurements of surface tension, dilational surface rheological properties, characteristics of capillary waves, and by Brewster angle microscopy. It is shown that the adsorption of the derivatives is irreversible and they can form a dynamic network at the interface with almost zero surface pressure and high dynamic surface elasticity, up to ~100 mN/m. The adsorption layers of C_{60}-Lys and C_{60}-Arg are characterized by strongly different surface rheological properties and distinct morphologies after an external mechanical perturbation due to different numbers of amino acid residues per C_{60} fullerene.

1. Introduction

Water soluble derivatives of fullerenes have a great potential in medicine due to their membranotrophic, cytoprotective, radioprotective, antioxidant, antimicrobial and antiviral properties [1–7]. It was found that the derivatives of C_{60} with some aminoacids can display cytotoxicity to cancer cell lines [3], neuroprotective action [4] and antioxidant activity [5]. These substances can penetrate cellular membranes to perform activated transmembrane transport of bivalent metal ions [6] and to reduce the damage caused by hydrogen peroxide [7]. Although it is well known that spread and adsorbed layers of amphiphile molecules at the liquid − gas interface allow modeling of some processes in biomembranes [8], information on surface properties of the solutions of fullerene derivatives is quite scarce.

At the same time, significant efforts were directed to the investigation of spread layers of insoluble fullerene derivatives at the water surface with the aim of formation of regular surface films of fullerenes [9–12]. The use of unique chemical and physical properties of fullerenes in nanoscale systems requires preparation of well-organized thin films of these substances. The Langmuir − Blodgett method based on the layer transfer from the surface of water onto a solid support has been most widely used for the preparation of such ordered thin films. However, the preparation of a stable and uniform monolayer of pure fullerenes is a difficult task because of their aggregation at the air/water interface, making the monolayer heterogeneous and very fragile [13,14]. To overcome this problem the chemical modification of fullerenes leading to water insoluble derivatives has been frequently used [9–12,15]. Although one can also use the adsorption layers of soluble fullerene derivatives to obtain stable Langmuir − Blodgett films, to the best of our knowledge only Liu et al. used this possibility and studied the surface properties of the solutions of dodecahydroxylated-fullerene with the aim to produce a homogeneous layer onto a solid support [15].

The main aim of this work is the investigation of surface properties of the solutions of amino acid derivatives of C_{60} fullerene and the kinetics of the adsorption layer formation in these systems. The bulk properties of aqueous solutions of C_{60}-arginine and C_{60}-L-lysine have been recently studied and a significant difference has been discovered in the self-aggregation of these two derivatives in bulk solutions [16,17]. While the diameter of C_{60}-L-lysine aggregates was always less than 1000 nm, the aggregation in C_{60}-arginine solutions depended strongly on concentration and resulted in visible macroscopic aggregates at concentrations higher than 1 g/l. Therefore, it is also possible to expect some distinctions in the interactions between the adsorbed molecules at the liquid − gas interface for these two fullerene derivatives.

From the point of view of fundamental colloid science the amino acid derivatives of C_{60} fullerene belong to the group of nanoparticles

with a rigid core and a soft corona. A lot of studies are devoted to the bulk properties of the dispersions of these particles [18,19]. At the same time, information of the adsorption layers of the particles with a corona is scarce probably because of the difficulties to characterize the size and properties of the corona in the surface layer. Although the fullerene derivatives are a rare example of rigid particles with well-characterized corona, the properties of their surface films at the liquid-gas interface have been studied until now by a limited number of experimental methods, mainly by the measurements of surface pressure [9–14].

It has been shown recently that one can obtain important information on the mechanism of the adsorption layer formation in complex liquids by measuring the kinetic dependencies of the dynamic surface elasticity [20–23]. These dependencies can be non-monotonical if the adsorption of amphiphilic substances is accompanied by the formation of aggregates at the interface and/or by the increase of the adsorption layer thickness. On the other hand, the fast matter exchange between the aggregates and the surrounding adsorption layer can result in the generation of higher harmonics in the course of the induced surface tension oscillations. In this work this approach together with the investigation of the morphology of the adsorption layer is applied to the solutions of amino acid derivatives of C_{60} fullerene.

2. Experimental

C_{60} fullerene and amino acid derivatives of this fullerene with L-lysine $C_{60}(C_6H_{14}N_2O_2)_2H_2$ (C_{60}-Lys, Fig. 1) and arginine $C_{60}(C_6H_{13}N_4O_2)_8H_8$ (C_{60}-Arg, Fig. 1) were obtained from ZAO "ILIP" Ltd. (St. Petersburg, Russia) and used as received. The mass fraction purity of the samples was 99.9% (C_{60} fullerene) and 99.8% (amino acid derivatives of C_{60} fullerene), respectively.

All solutions of fullerene derivatives were prepared in triply distilled water. An apparatus made from glass was used during the last two steps of distillation. The physico-chemical properties of aqueous solutions of C_{60}-Lys and C_{60}-Arg are described in detail in [16,17].

The C_{60} fullerene was dissolved in toluene and the solution was spread dropwise onto the water surface by a Hamilton microsyringe.

The surface tension was measured by the Wilhelmy plate method using a roughened glass plate attached to an electronic balance. The complex dynamic surface elasticity was measured by the oscillating barrier method at a fixed frequency of 0.1 Hz. The corresponding experimental equipment and procedures were described in detail elsewhere [21]. The oscillations of the solution surface area in a polytetrafluoroethylene (PTFE) Langmuir trough were produced by a movable PTFE barrier sliding along polished brims of the trough. A mechanical generator transformed the rotation of an electric motor into the translational motion with reversion and allowed control of the

oscillation amplitude and frequency. The moving part of the generator was connected to the barrier by a steel rod. The barrier glided back and forth along the Langmuir trough and produced oscillations of the liquid surface area A with a relative amplitude of 5%. The induced oscillations of the surface tension γ were measured by the Wilhelmy plate method. The complex dynamic surface elasticity ε was calculated according to the following relation

$$\varepsilon(\omega) = \delta\gamma/\delta\ln A$$

where δγ and δA are the increments of the surface tension and surface area, respectively.

If the phase shift between the oscillations of the surface area and surface tension is known, it is possible to determine the real and imaginary parts of the dynamic surface elasticity, which is in general a complex quantity. The imaginary part of the complex dynamic surface elasticity of the solutions under investigation proved to be much less than the real part. Therefore, only the results for the real part are discussed below.

The experimental set-up to measure the damping coefficient and length of capillary waves was described in details elsewhere [24]. Capillary waves were excited by applying a sinusoidal voltage from an electric generator to a thin metallic blade placed above the surface of the investigated solution. The distance between the blade and the surface determines the initial amplitude of the waves and was less than a millimeter. The laser beam reflected from the liquid surface oscillated due to the propagation of capillary waves and was directed to a position-sensitive photo detector. The measurements of the amplitude and phase of the electric signal from the detector as a function of the distance between the blade and the beam spot on the liquid surface allowed determination of the damping coefficient and the wavelength.

All measurements of the dynamic surface properties were started after purification of the surface using a movable barrier on the surface of the Langmuir trough and a Pasteur pipette connected with a pump. All measurements were performed at a temperature of 20 ± 1 ˚C.

The morphology of the adsorption layers of fullerene derivatives was investigated in situ by the Brewster angle microscope BAM1 (NFT, Göttingen, Germany) equipped with a 10 mW He-Ne laser. The solution under investigation was placed in the Langmuir through and equilibrated at room temperature for 20 h before images were obtained.

The measurements of the size distribution of C_{60}-Lys and C_{60}-Arg aggregates in aqueous solutions and of the electrokinetic potential were carried out by dynamic light scattering using the Malvern Zetasizer device (Malvern Instruments, United Kingdom). The relative uncertainty of the zeta-potential determination was about 5%.

3. Results and discussion

The analysis of the results on the dynamic light scattering discovered aggregates with characteristic sizes of 20 and 300 nm in solutions of C_{60}-Lys and of 80 and 500 in solutions of C_{60}-Arg apart from monomers with the mean diameter of 2 nm. The size distribution of C_{60}-Lys aggregates did not change for a few hours after the solution preparation but the size of C_{60}-Arg aggregates increased noticeably during this time. The electrokinetic potential in the systems under investigation was in the range − 35 to − 45 mV.

The derivative of the C_{60} fullerene with L-lysine did not display any surface activity for one day if the concentration c is less than 0.3 g/l. At c = 0.3 g/l the surface tension coincided with the value for pure water within error limits (± 0.5 mN/m) during 25 h after the surface formation but started to decrease slowly after that reaching a plateau value of about 71 mN/m in about 29 h (Fig. 2). At the same time, the real part of the dynamic surface elasticity started to deviate earlier from the value of pure water, was about 20 mN/m in 25 h after the surface formation and reached ∼ 33 mN/m in 29 h. The increase of concentration to 0.5 g/l accelerated the adsorption kinetics (Fig. 3). The surface
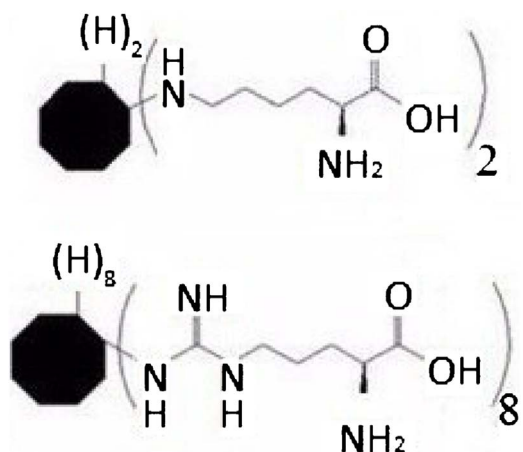

Fig. 1. A schematic illustration of amino acid derivatives of the C_{60} fullerene with lysine − a) and with arginine − b).