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Dilational surface elasticity of monolayers of charged polystyrene nano- and microparticles at liquid/fluid interfaces

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HIGHLIGHTS

- Dynamic elasticity of monolayers of PS particles depends strongly on surface pressure.
- Long range interactions between charged particles operate through the oil phase.
- At high surface coverage, the dilational surface elasticity reaches 200 mN/m.
- The elasticity of monolayers of PS particles is much higher than for soft particles.

GRAPHICAL ABSTRACT
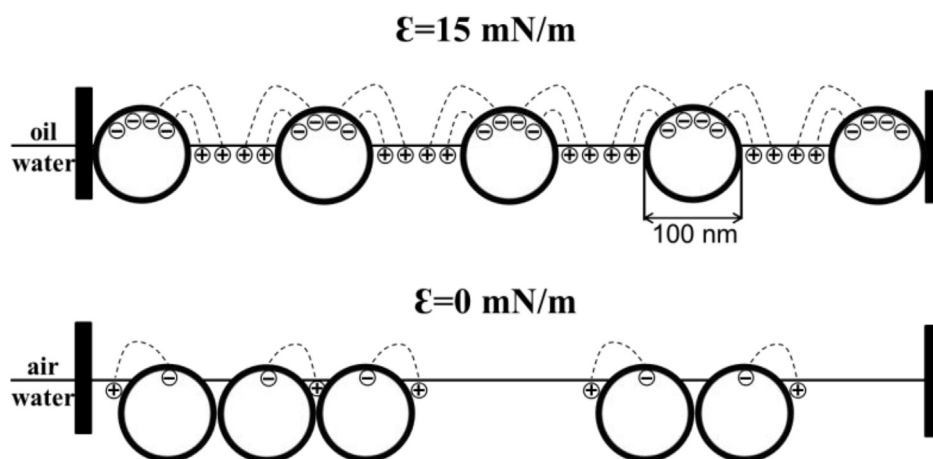
ABSTRACT

Measurements of the dilational dynamic surface elasticity allow determination of some distinctions between the properties of monolayers of charged polystyrene nano- and microparticles at the water/air and water/oil interfaces. For example, the surface elasticity at the water/oil interface is lower and does not depend on the solution's ionic strength unlike the case of water/air interface. The obtained results at relatively low surface pressures (<15 mN/m) and homogeneous surface compression agree with a recent theory taking into account the residual charges at the particle/oil interfaces. At higher surface pressures, the behavior has some similarities with the properties of the monolayers of silica nanoparticles but differs strongly from the behavior of monolayers of soft microgel particles.

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1. Background

Recent interest in the properties of monolayers of micro- and nanoparticles at liquid/fluid interfaces is mainly connected with the strong stabilizing influence of solid particles on foams and emulsions [1–8]. In spite of intensive studies, the mechanism of

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stabilization has not been understood to a sufficient extent yet [3,4,6,8]. Most of the authors consider that the particles form a rigid skin around the drops or bubbles creating a strong steric hindrance to coalescence, but a stabilization due to bridging of thin films is also possible [1,4,9–11]. There is a general agreement that among macroscopic parameters of particle monolayers their rheological properties, especially the dilational ones, are the most relevant for estimating the stability of the corresponding liquid/fluid dispersions [3,6,7,9,12–16]. Some authors discovered good correlations between the interfacial dilational modulus and the stability of emulsions and foams [12,13,17]. In particular, it was shown that one can obtain stable foams if the system meets the Gibbs criterion, i.e., the surface elasticity is higher than half of the surface tension [3,13]. On the other hand, measurements of the surface rheological properties give important information on the interactions between micro- and nanoparticles in the surface layer [6–8,18–22].

Substantial attention has been paid until now to the rheological properties of monolayers of silica nanoparticles and their complexes with surfactants [3,7,12,13,18,23,24]. The dilational dynamic surface elasticity of the adsorbed layers of the complexes of nanoparticles with a cationic surfactant proved to be extremely high at the approach to equilibrium (up to ~1000 mN/m) and depended on the deformation amplitude [18]. These properties are a result of the collapse of the brittle monolayers under the action of periodical surface compressions/expansions and the formation of a heterogeneous multilayer structure.

Recently, the dynamic elasticity of soft microgel particles has been measured by the oscillating drop method [8,25]. The surface rheological properties of the microgel monolayers of poorly cross-linked poly(N-isopropylacrylamide) (PNIPAM) chains proved to be intermediate between those of flexible macromolecules and solid particles [6]. The kinetic dependencies of the dynamic surface elasticity displayed a local maximum like in the case of adsorption of linear amphiphilic polymers and non-globular proteins [26–28]. This feature is connected with the interaction of peripheral chains of microgel shells leading to the formation of a distal region of loops and tails at relatively high surface pressures. Kobayashi and Kawaguchi have recently observed a similar local maximum of the dynamic surface elasticity of monolayers of polystyrene (PS) microparticles grafted with diacetone acrylamide chains and a transition from solid-like to liquid-like viscoelastic behavior with the increase of the oscillation frequency [29].

Although the properties of the monolayers of non-grafted PS microparticles were discussed by numerous authors [1,6,11,30–34], only few of them studied the dynamic properties and applied methods of dilational surface rheology. To the best of our knowledge, apart from our recent paper on the dilational properties of monolayers of PS microparticles at the water/air interface [19], only Hilles et al. reported the dynamic surface elasticity of a monolayer of PS particles at a single frequency and at the water/n-octane interface and found non-linear effects in surface rheology [33]. Much more attention in studies on layers of PS particles was paid to the origin of long-range repulsive interactions between the particles at liquid/fluid interfaces. The interpretation of the contribution of the electric double layer at the particle/water interface in these interactions remains controversial to date [10,30,32,35]. According to Aveyard et al., the repulsive forces originate mainly from the residual charges at the particle/nonpolar fluid interface and can lead to dipolar interactions between the particles [30]. The theoretical model of these authors predicts an asymptotic dependence of the surface pressure π on the characteristic interparticle distance L in the monolayer at large L as a power law $\pi \sim L^{-5}$. Very recently, Petkov et al. [35] have taken into account the particle finite size and obtained another asymptotic law $\pi \sim L^{-3}$. This result agrees excellently with their experimental data for silica microparticles

at the water/air interface and a little worse with some literature data on PS particles at the water/oil interface.

In our previous study, methods of the dilational surface elasticity were applied to spread monolayers of PS microparticles at the water/air interface [19]. The dynamic surface elasticity at surface pressures close to 30 mN/m proved to be extremely high (~500 mN/m) and similar to the results for adsorption layers of the complexes between silica particles and surfactant molecules probably due to strong hydrophobic attractions between the particles [18]. At the same time, other characteristic features of the viscoelasticity of the monolayers of PS microparticles differed strongly from the properties of previously studied systems.

The main aim of this work is to compare the dilational surface viscoelasticty of monolayers of PS particles of different size (micro- and nanoparticles) at water/oil interfaces with the properties of layers of the same particles at the water/air interface and of particles of different chemical nature. Another aim is to examine the theory by Petkov et al. for a larger number of systems including monolayers of PS nanoparticles at the two interfaces.

2. Materials and methods

The two kinds of dispersions of PS particles with sulfate groups at their surface were supplied by Molecular Probes (USA) as surfactant free aqueous dispersions and contained monodisperse microparticles with the diameter of 1 μm (8% w/v, 1.6×10^{11} particles/ml) and nanoparticles with the diameter of 100 nm (8% w/v, 1.5×10^{14} particles/ml). The surface charge density of microparticles was 2.0 μC/cm^2, which corresponds to an area per charged sulfate group of 8.2 nm^2, as reported by the supplier. The surface charge density of the nanoparticles was 0.2 μC/cm^2, which corresponds to an area per sulfate group of 64 nm^2, as reported by the supplier.

Octane (99% pure) was passed through a chromatographic alumina oxide column four times before use. The interfacial tension at the oil/water interface was 51.1 mN/m. Isopropanol (Sigma–Aldrich) was purified by distillation. Sodium chloride (Merck) was preliminarily heated in a muffle furnace at about 750 °C for the elimination of possible organic impurities. Fresh triple-distilled water was used in all experiments.

The dynamic dilational elasticity was measured by a KSV NIMA system (KSV Instrument Ltd., Finland) based on the oscillating barrier method. A filter paper plate with the width of 1 cm was used as Wilhelmy plate. It was positioned in the middle of the Langmuir through parallel to the moving barrier. The Langmuir trough from Teflon was designed according to Aveyard et al. and consisted of a lower and upper part [30]. The lower part for the oil phase had additional stainless steel brims and an area of $42 \times 7 \text{ cm}^2$. It was equipped with two stainless steel barriers moving symmetrically in opposite directions to compress or expand the water/oil interface at a given speed (frequency) and amplitude. The surface tension oscillations in the oscillating barrier method are the result of the harmonic changes of the surface area of a flat liquid/fluid interface in a Langmuir trough at a given amplitude. All the measurements in this work were performed at relative amplitudes of area oscillations of 2–8% and at a frequency of 0.01 Hz.

The aqueous dispersions of microparticles (as supplied) and diluted 20 times in the case of nanoparticles were mixed with isopropanol at a volume ratio of 1:2, subjected to ultrasonification and used for spreading at the water/oil interface. The spreading volume of the mixture was less than 500 μL. The drops of a volume less than 2 μL were placed successfully onto the water/oil interface by a Hamilton syringe with needle tip close to the interface.

The morphology of the nanoparticle monolayers was investigated by the Brewster angle microscope BAM1 (NanoFilm