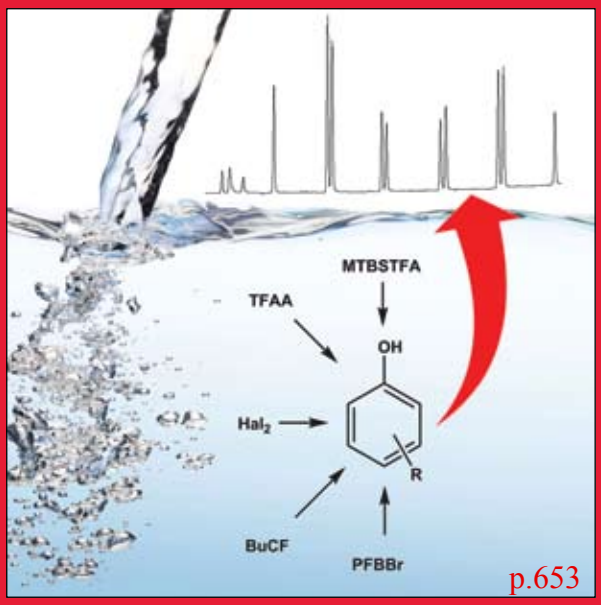
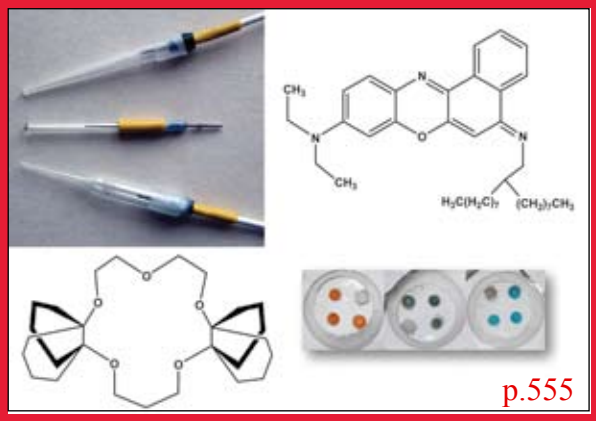
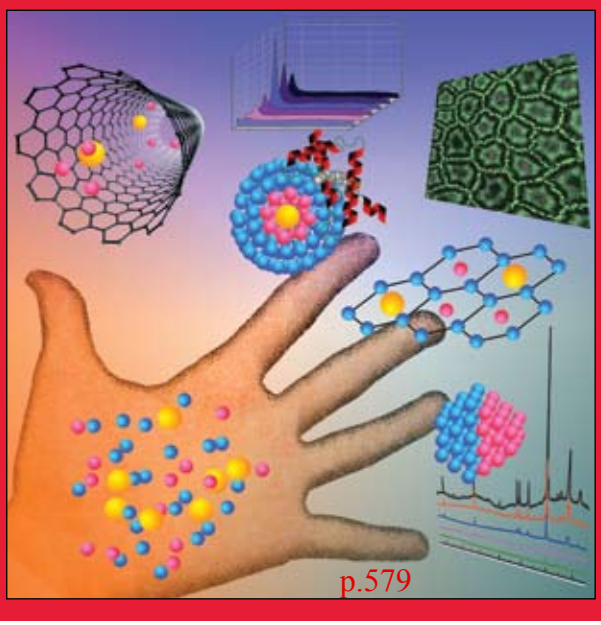
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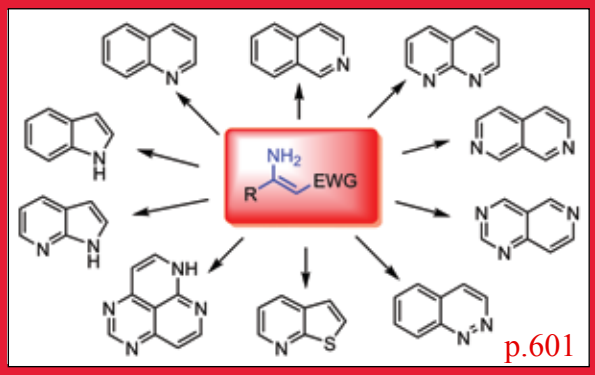
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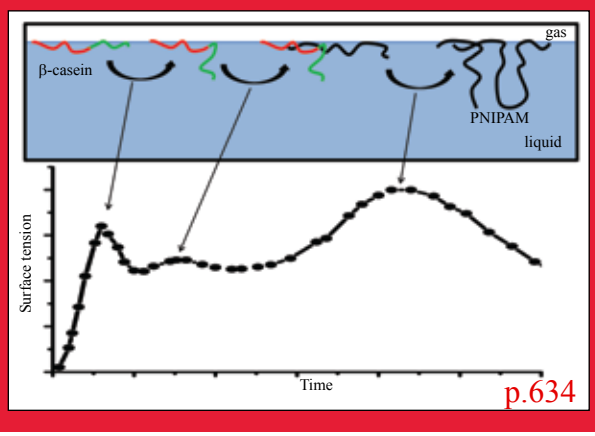
p.653


p.555


p.579



p.601



p.634

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Dilational surface rheology of polymer solutions

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The review concerns main achievements in dilational rheology of polymer adsorption films at the gas/liquid interfaces reported in the last fifteen years. The theoretical foundations of methods of surface rheology and the key results obtained in studies of solutions of amphiphilic nonionic polymers, polyelectrolytes, proteins and their complexes with low-molecular-mass surfactants are discussed. Interest in the surface dilational rheology is mainly caused by a small number of available experimental methods for investigation of the surface of liquids, by the fact that traditional methods of measurement of the surface tension that are widely used in studies of solutions of low-molecular-mass surfactants provide little information when applied to polymer solutions owing to very slow establishment of equilibrium as well as by weak dependence of the surface tension on the polymer concentration. Progress in the surface rheology is driven by the recent studies of the stability of foams and emulsions that demonstrated a key role of the dilational surface rheological properties in the dynamics of liquid-phase disperse systems.
The bibliography includes 191 references.

Contents

I. Introduction 634
II. Theory of dilational surface viscoelasticity: basic concepts 635
III. Experimental methods 638
IV. Dilational surface rheology of solutions of nonionic polymers 639
V. Dilational surface rheology of polyelectrolyte solutions 642
VI. Dilational surface rheology of solutions of polyelectrolyte/low-molecular-mass surfactant complexes 644
VII. Dilational surface rheology of protein solutions 647
VIII. Conclusion 649

I. Introduction

Information on the onset of specific surface forces upon dilation (or compression) of the surface of liquids was for the first time reported in the mid-19th century by Marangoni [1] in a study on the fluid flow under the action of a surface tension gradient and by Plateau [2] in his work on the motion of a compass needle at the gas/liquid interface. Gibbs, who studied foam films, introduced the notion 'surface elasticity' (see his well-known publication 'On the equilibrium of heterogeneous substances' [3] devoted to thermodynamics of heterogeneous systems). In the early 20th century, Boussinesq [4] proposed the first rheological model for a fluid surface by analogy with the Newtonian bulk fluid and introduced two parameters, *viz*., the shear viscosity and the dilational surface viscosity.

Pioneering experimental studies on the shear surface viscosity date back to Plateau;[2] wide use of corresponding methods began in the 1920s.[5,6] The first measurements of the surface dilational properties were reported only in the 1960s; they mainly concerned revision of the theory of damping of capillary waves.[7–9] Then, the method of capillary waves became the main technique in the dilational surface rheology.[10] At that time, research activity was focussed on the adsorption films and spread films of low-molecular-mass surfactants on the liquid surfaces and the method of capillary waves was mainly used in studies on the kinetics of surfactant adsorption.[11,12]

Dilational surface rheology has been intensively developed only about fifteen years, since the time when importance of the rheological surface properties in many technological and natural processes became obvious. It was found that these properties govern the dynamics of emulsion and foam films and, therefore, evaluation of the stability of foams and emulsions should be based on the surface elasticity and surface viscosity data.[13,14] In biological systems, the dynamic surface properties influence, *e.g*., the compression and expansion of pulmonary alveoli,[15]

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the instability of tear film on the eye surface[16] and some processes in cell membranes.[17,18]

Relation between the dilational surface properties (rheology) and the dynamics of free-surface fluids is to a great extent due to the influence of these properties on the propagation of surface waves. In the mid-20th century, it was shown that the dispersion relation for waves on the surface of a complex liquid includes the complex dilational surface elasticity as the key parameter of the interface.[10] This, in particular, provides an explanation for a phenomenon which is known since ancient times and has attracted the attention of many prominent researchers, namely, a strong effect of surfactants on damping of wind-induced waves.[19] Subsequent studies on the propagation of waves in free films and in wetting films disclosed the role of the surface rheological properties in many technological processes, *e.g.*, thin-film coating, extrusion and flotation.[20–22]

In the early stage of development of dilational surface rheology, only one method, dynamic light scattering by capillary waves, was used for measuring the complex dynamic surface elasticity of polymer solutions.[23] At high surface oscillation frequencies (> 10 kHz), the surface elasticities of adsorption films and insoluble monolayers were almost the same. Taking into account this fact, one can assume that main relaxation processes in the polymer adsorption films occur at lower frequencies. Among polymer solutions, only protein solutions were studied in quite detail by the low-frequency methods of dilational surface rheology.[24,25] The results obtained were used to test the proposed mechanism of protein film formation on the liquid surface. They confirmed the formation of 'loops' and 'tails' in the surface layer in the course of adsorption of some proteins.

In the 20th century, studies on the dynamic surface properties of solutions of diphilic polymers were to a great extent reduced to measurements of the dynamic surface tension.[26,27] New experimental methods, such as ellipsometry,[28] X-ray reflection and neutron reflection,[29,30] as well as various kinds of optical spectroscopy of interfaces[31–33] were only applied to equilibrium systems. However, by now we know that the surface tension of polymer solutions is only governed by the local concentration of chain segments in the proximal region of the surface layer (in the surface monolayer), being almost independent of the chain segment distribution outside this region. It follows that the surface tension may not be influenced by changes in the macromolecular conformations in the surface layer. Also, the static surface tension of many polymeric systems is almost independent of polymer concentration in a wide concentration range (in some cases, up to concentrations > 1 mass %).[23,26,34,35] In this case, the use of the Gibbs adsorption equation leads to large errors in the determination of the adsorption value. At the same time, the results of the first measurements of the dynamic surface elasticity of polymer solutions at low frequencies (< 10 Hz) demonstrated high sensitivity of the dilational surface rheological properties to the structure of polymer adsorption films and noticeable changes in the dynamic surface elasticity upon variation of surfactant concentration in a number of systems.[34–36]

Presently, there has been rapid increase in the number of publications on dilational surface rheology. A number of companies produce interfacial tensiometers to measure the surface dilational rheological properties in, *e.g.*, clinical diagnosis.[37,38] The first monograph[39] concerning various aspects of dilational surface rheology was published; also, a number of reviews are available.[18,36,40–49] Some reviews are concerned with solutions of low-molecular-mass surfactants[40,41,49] or insoluble monolayers.[43] Many publications on the surface rheology of protein solutions and solutions of protein/surfactant complexes are focussed on the dynamic surface properties near the equilibrium.[18,44,45,48] The first review on the surface rheology of solutions of synthetic polymers was reported more than a decade ago and is to a great extent out of date.[36] This to some extent concerns yet another study[46] whose authors briefly outlined the main results obtained in the late 2000s.

In this review, we present a detailed consideration of the results obtained in studies on the dilational surface rheology of polymer solutions reported in the last ten to fifteen years. The emphasis is placed on the recent studies reported since 2010 and concerning the kinetics of formation of polymer adsorption films, *i.e.*, measurements of the surface rheological properties far from the equilibrium state of the system. Problems related to the shear surface rheology are left out of consideration. The shear surface rheological properties can be highly sensitive to macromolecular conformations near the interface;[50] however, corresponding experimental results are more difficult to interpret. Owing to the lack of reliable theory most authors restrict themselves to consideration of the shear surface rheological properties on a qualitative level. However, the theory of dilational surface viscoelasticity, which is based on nonequilibrium thermodynamics of surface phenomena,[51] significantly facilitates interpretation of experimental kinetic and concentration dependences of the dilational surface rheological properties.

Basic concepts of the theory of dilational surface viscoelasticity of polymer solutions will be presented in Section II. In Section III, we will briefly outline experimental methods of dilational surface rheology. The main part of the review (Sections IV–VII) concerns specific features of various polymer-containing systems. Namely, we will discuss the surface rheological properties of solutions of one solute (amphiphilic polymer or polyelectrolyte), analyze the properties of solutions of polyelectrolyte/low-molecular-mass surfactant complexes and consider the surface dilational rheology of protein solutions and solutions of protein/surfactant complexes.

II. Theory of dilational surface viscoelasticity: basic concepts

A uniform dilation (compression) of an interface causes the surface (interfacial) tension to change. The response of a system to a surface strain at a given instant depends not only on the surface area at that instant, but also on the prehistory of the system, *i.e.*, the two-phase system under study exhibits a memory effect. In the case of infinitesimal strain, the relation between the system's response (surface tension increment $\Delta\gamma$) and the relative changes in the surface area, $\Delta A/\Delta A_0$, at preceding time instants t is as follows:[52]

$$\Delta\gamma(t) = \int_{-\infty}^{t} G(t-t')\frac{\mathrm{d}\Delta A(t')}{A_0 \mathrm{d}t'}\mathrm{d}t' \qquad (1)$$

where G is the surface relaxation function and t' is the integration variable.

Having applied the Fourier transformation to expression (1), one gets a linear relation [53] between the Fourier transforms of the two functions under consideration

$$\Delta\gamma(\omega) = F\{\Delta\gamma(t)\} \text{ and } \Delta A(\omega) = F\{\Delta A(t)\}$$

in the form

$$\Delta\gamma(\omega) = \varepsilon(\omega)\frac{\Delta A(\omega)}{A_0} \quad (2)$$

Here, the coefficient of proportionality represents the dilational dynamic surface elasticity $\varepsilon(\omega)$ which depends on the angular frequency ω. Generally, this is a complex quantity whose real and imaginary parts are related to the relaxation function as follows:

$$\varepsilon(\omega) = \widetilde{\varepsilon} + \int_0^\infty G(\eta)\sin(\varepsilon\eta)\mathrm{d}\eta + \int_0^\infty G(\eta)\cos(\varepsilon\eta)\mathrm{d}\eta, \quad (3)$$

where $\widetilde{\varepsilon}$ is the static surface elasticity and η is the integration variable.

For small-amplitude harmonic oscillations of the surface area (δA), the dynamic surface elasticity is reduced to the ratio of the complex oscillation amplitudes of surface tension ($\delta\gamma$) to the relative surface area ($\delta A/A$):

$$\varepsilon = \frac{A\delta\gamma}{\delta A} \quad (4)$$

If no relaxation processes occur in a strained surface layer, the film exhibits a pure elastic behaviour and the dynamic surface elasticity is equal to the static value. For a viscoelastic surface film, the ε value depends not only on the oscillation amplitudes of the surface tension and surface area, but also on the phase shift between these oscillations.

The dilational dynamic surface elasticity is a fundamental property of the surface. It is related to both the equilibrium characteristics of the interface and the kinetic coefficients of the relaxation processes being occurred. If all relaxation processes occur within the surface layer only, the dynamic surface elasticity can be treated as 2D analogue of the dynamic elasticity of the bulk phase. Generally, if interchange of (i) surfactant molecules between the surface layer and bulk phase or (ii) macromolecular segments between the proximal and distal regions of the surface layer is possible, this analogy becomes invalid and the expression for the dynamic surface elasticity should include kinetic parameters which characterize mass exchange between different regions of the two-phase system under study.[51, 52, 54–58]

The first expression for the dilational dynamic surface elasticity was derived by Lucassen and Hansen,[54] who studied diffusion-controlled kinetics of adsorption of a surfactant at the gas/liquid interface

$$\varepsilon = \varepsilon_0\frac{(1+\mathrm{i})/2\,\zeta}{1+(1+rmi)/2\,\zeta} \quad (5)$$

where

$$\varepsilon_0 = -\frac{\mathrm{d}\gamma}{\mathrm{d}\ln\Gamma}$$

γ is the surface tension, Γ is the surface excess (adsorption),

$$\zeta = \sqrt{\frac{D}{2\omega}}\left(\frac{\mathrm{d}c}{\mathrm{d}\Gamma}\right)$$

D is the diffusion coefficient of surfactant in the bulk phase and c is the surfactant concentration.

In the case of polymer solutions relation (5) can only be used for dilute solutions and in the initial step of adsorption where bulk-to-surface diffusional exchange of macromolecules is the major relaxation process. However, a drawback of reliable models for surface viscoelasticity also causes some authors to use the Lucassen–Hansen relationship for a wider concentration range where diffusional exchange can be neglected.[55, 56, 59, 60]

For more complex adsorption mechanisms, one should take into account the barrier to adsorption at the interface between the surface and sub-surface layers. Then, the expression for the dynamic surface elasticity takes the form [57]

$$\varepsilon = \varepsilon_0\frac{\mathrm{i}\omega\tau + (1+\mathrm{i})/2,\zeta}{1+\mathrm{i}\omega\tau + (1+\mathrm{i})/2\,\zeta} \quad (6)$$

where τ is the relaxation time of adsorption *per se* (τ is related to the kinetic coefficients of adsorption and desorption).

More general relations for the dynamic surface elasticity can be derived using nonequilibrium thermodynamics.[51, 52, 58, 61] These relations include the relaxation times of the processes occurring at the interface and corresponding relaxation forces as parameters. The thermodynamic approach is insufficient to estimate these quantities and one should use the structural and kinetic models for the system under study. For instance, theory of dilational surface viscoelasticity of solutions of linear flexible-chain polymers [58] is based on the Rouse model and on the reptation model by de Gennes.[62, 63]

An adsorption polymer film at the gas/liquid interface can be treated as consisting of a relatively dense region *I* near the gas phase (the thickness of region *I* is comparable with the size of monomer molecules) and a 'dilute' region *II* where 'loops' and 'tails' of polymer chains protrude into the solvent.[58] The surface tension of a polymer solution first of all depends on the concentration of chain segments in region *I*. In the case of uniform dilation (compression), the surface stress relaxation occurs by drawing polymer chains into region *I* or squeezing them out of region *I* to region *II*. For a low strain, a complete detachment of polymer chains from the surface or their bulk-to-surface transition are quite rare to occur and their influence can be ignored. Then, exchange of monomer molecules between regions *I* and *II* in the case of dilation (compression) of the liquid surface can be due to two processes:

— relaxation of internal stress in the chain and

— squeezing out (drawing in) a chain as a whole.

This makes it possible to derive the following expression for the dynamic surface elasticity of a polymer film for the case where the surface monolayer (proximal region of the surface layer) is formed by (i) polymer chains completely arranged on the surface and (ii) molecular fragments that form 'tails' and 'loops' in the distal region (*i.e.*, molecules characterized by one and two points corresponding to transitions from region *I* to region *II*) (Fig. 1):

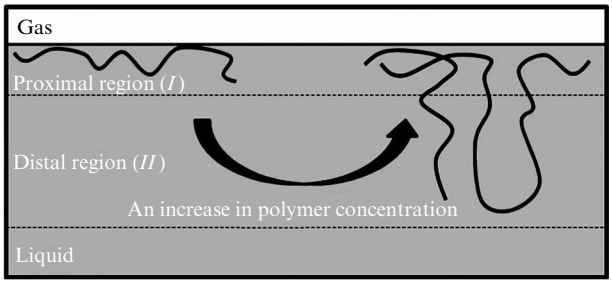


Figure 1. Formation of the distal region of the surface layer with increasing surface concentration of polymer chain segments: a schematic.[58]

$$\varepsilon = -\frac{\partial\gamma}{\partial \ln \widetilde{\Gamma}}\left[\frac{2\Gamma_3}{\pi\Gamma}{\sum}' \frac{8\mathrm{i}\tau_1\omega}{p^2\pi^2(1+\mathrm{i}\omega\tau_1/p^2)} + \right. \tag{7}$$

$$\left. + \left(1-\frac{2\Gamma_3}{\pi\Gamma}\right)\frac{\mathrm{i}\omega\tau_2}{1+\mathrm{i}\omega\tau_2}\right]$$

where the prime at the sum sign denotes summation over the odd numbers p; $\widetilde{\Gamma}$ is the number of monomer moles per unit surface area in the proximal region of the surface layer; Γ_3 is the number of monomer moles per unit surface area in region I belonging to chain segments with two points corresponding to transitions from region I to region II (so-called 'trains'); τ_1 is the relaxation time of internal stress in the chain, τ_2 corresponds to the motion of a chain segment as a whole in region I

$$\tau_1 = \frac{b^2 N_0^2}{2\pi^2 k_\mathrm{B} T B} \tag{8}$$

$$\tau_2 = \frac{N_2 L_2}{B\Gamma_2 a(\partial\Pi/\partial\Gamma)} \tag{9}$$

where b is the length of the chain segment; N_0 is the number of monomers in the chain segment in region I; k_B is the Boltzmann constant; T is absolute temperature; B is the polymer chain mobility; N_2 is the number of monomers in the chain segment with one point corresponding to transition from region I to region II; L_2 is the contour length of this chain segment; a is the average wall-to-wall distance for the 2D entanglement tube; Γ_2 is the number of monomer moles per unit surface area in region I belonging to chain segments with one point corresponding to transition from region I to region II; and Π is the surface pressure.

From expression (9) it follows that the relaxation time τ_2 decreases with increasing Γ and, correspondingly, the number of 'loops' and 'tails' protruding into the bulk phase.[58] At the same time, an increase in the number of 'loops' and 'tails' causes N_0 and, correspondingly, τ_1 to decrease, as follows from relation (8). As the number of 'loops' and 'tails' tends to infinity, the surface elasticity tends to zero.[58]

If chains are short enough and the number of adsorbed chains having more than one 'loop' ('tail') in region II is small, the surface stress relaxation at frequencies comparable with τ_2^{-1} will mainly occur through squeezing out (drawing in) particular chain segments out of (into) to region II. Then, the expression for the surface elasticity is reduced to an expression coinciding with the Maxwell rheological equation

$$\varepsilon = -\frac{\mathrm{d}\gamma}{\mathrm{d}\ln\Gamma}\,\frac{\mathrm{i}\omega\tau_2}{1+\mathrm{i}\omega\tau_2} \tag{10}$$

Approximation of experimental data on the dynamic surface elasticity by Eqn (10) provides additional information on the static and dynamic properties of the polymer chain. The quantity $\mathrm{d}\gamma/\mathrm{d}\ln\Gamma$ is an analogue to the Gibbs elasticity for solutions of low-molecular-mass surfactants; it characterizes the interaction between polymer chains in region I. The relaxation time τ_2 is related to the dynamic properties of the polymer through expression (9).

In a limiting case where the bulk concentration approaches zero and polymer chains are adsorbed irreversibly (no 'loops' and 'tails' are formed), Γ_2 tends to zero while τ_2 tends to infinity. The adsorption film thus exhibits pure elastic behaviour and the dynamic surface elasticity equals the static value, ε_0.

At high polymer concentrations in the bulk phase, the number of 'loops' considerably increases. As a consequence, τ_1 and τ_2 tend to zero. In this case, one can expect that the dynamic surface elasticity will also be close to zero. However, inter-chain interaction in the surface layer may lead to a low nonzero surface elasticity.

Thus, at low concentrations (macromolecules in the surface layer adopt a flat, almost 2D conformation), an increase in the surface concentration leads to stronger repulsion between adsorbed macromolecules and to an increase in the dynamic surface elasticity. As adsorption increases, a transition to the 3D structure of the surface film occurs and a more 'dilute' distal region of 'loops' and 'tails' is formed in addition to the more dense proximal region (see Fig. 1). As a result, the surface stress relaxation can occur through exchange of chain segments between different regions of the surface layer and the surface elasticity decreases. In this case, one can expect the appearance of a local maximum in the concentration and kinetic dependences of the dynamic surface elasticity, whereas the corresponding dependences of the surface tension will remain monotonic.

Maxwell's model (10) is often used to describe the surface elasticity of polymer solutions;[55,64–66] however, the relaxation mechanism is usually left out of consideration. It should be noted that not only exchange of chain segments between the distal and proximal regions of the surface layer but also the surface stress relaxation in a system with heterogeneous adsorption film through mass exchange between co-existing surface phases can lead to this model. If the surface area of a certain phase can be neglected, the expression for the dynamic surface elasticity takes the form[67]

$$\varepsilon = \varepsilon_0\frac{\mathrm{i}\omega/r}{1+\mathrm{i}\omega/r} \tag{11}$$

where r is the kinetic coefficient of mass transfer between phases in the surface layer.

If the surface areas of the co-existing phases are comparable, the experimentally measured total dynamic surface elasticity can be found using the following summation rule:[68]

$$\varepsilon = \sum_j \frac{\varepsilon_j}{F_j} \tag{12}$$

where ε_j is the dynamic surface elasticity of the phase j and F_j is the proportion of the surface area occupied by the phase j.

The relationships listed above are valid only for very low strains where the system′s response is proportional to strain. However, often the linear range is too narrow and one deals with a nonlinear response of the system even at the minimum strain attained in the rheological experiment; this complicates the interpretation of the surface rheological properties. In this case, the simplest approach is to expand the signal into a Fourier series using data on the first harmonic to describe the system.[69–71] The degree of nonlinearity can be evaluated using the total contribution of higher harmonics.[70] However, in this case partial loss of information on the relaxation processes from higher harmonics is possible. A more informative method is to analyze nonlinear oscillations of the surface tension using Lissajous patterns and the method of strain separation.[72–75] Nonlinear systems are of particular value for practice because many technological processes are accompanied by considerable deviations from the equilibrium and one can expect that system's response to dilation (compression) of the surface will be nonlinear.

III. Experimental methods

All methods of dilational surface rheology are based on a weak perturbation of a mechanical equilibrium in the system through dilation (compression) of the interface and subsequent registration of system's response. In the case of a low surface strain, from expressions (2) and (4) it follows that the response (surface tension increment) is determined by the dynamic surface elasticity. Modern experimental methods make it possible to determine the dynamic surface elasticity at frequencies of up to 2 MHz; the lower limit of the frequency range is only restricted by the measuring time. There are more than ten methods for measuring the dynamic surface elasticity corresponding to particular frequency ranges (Fig. 2) and procedures for application of a strain to the surface.

All high-frequency methods (>100 Hz) are based on measurements of parameters of capillary waves. Some authors (see, *e.g.*, Refs 76 and 77) state that the oscillating bubble method can also be used at frequencies >100 Hz; however, no reliable data on measurements of the dynamic surface properties using this method at high frequencies are available as yet. Difficulties are due to complexity in taking account of all hydrodynamic effects related to meniscus oscillations at high frequencies.[78,79] At the same time, propagation of linear capillary waves across the interface between two fluid phases can be described with high accuracy.

Assuming a homogeneous adsorption film, parameters of capillary waves are related to the dynamic surface properties by the following dispersion relation:[10]

$$(\rho\omega^2 - \gamma k^3 - \rho g k)(\rho\omega^2 - mk^2\varepsilon) - \varepsilon k^3(\gamma k^3 + \rho g k) + \\ +4\,\mathrm{i}\rho\eta\omega^3 k^2 - 4\eta^2\omega^2 k^3(m-k) = 0 \tag{13}$$

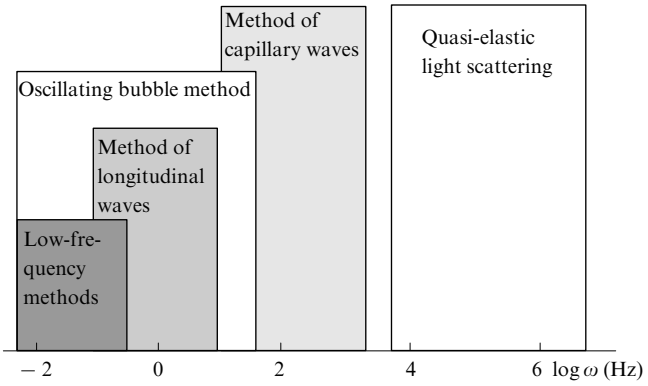


Figure 2. Different methods for measuring the dilational dynamic surface elasticity and corresponding frequency ranges.

where ρ is the density of the liquid, k is the complex wavenumber ($k = 2\pi/\lambda + \mathrm{i}\alpha$, λ is the wavelength, α is the damping coefficient of capillary waves), g is the free fall acceleration, $m = k + \mathrm{i}\rho\omega/\eta$ and η is the viscosity of the bulk phase.

Equation (13) can be obtained by solving a corresponding boundary-value problem for the equations of the dynamics of a viscous liquid[10] using the balance equations for the tangential and normal forces at the interface as boundary conditions; these equations relate the surface properties to the properties of the co-existing bulk phases. Having known the surface tension and parameters of capillary waves, the dynamic surface elasticity can be determined from Eqn (13).

Quasi-elastic light scattering by the interface is based on light scattering by high-frequency (from 10 kHz to 2 MHz) capillary waves that are spontaneously generated on the surface of a liquid owing to thermal fluctuations. Unfortunately, theoretical foundations of the method seem to be underdeveloped, which leads to errors in the determination of the surface rheological properties.[80] For instance, negative surface dilational viscosity values[81–83] of nearly equilibrium systems contradict the second law of thermodynamics.[51]

In the frequency range from ~ 30 to 1 000 Hz, the surface rheological properties are determined using capillary waves or capillary-gravity waves excited by a mechanical or electrical oscillator. In the former case, a thin rod oscillating up and down at a specified frequency is placed on the surface of a liquid.[12] In the latter case, a thin metallic plate is placed above the surface of a liquid and a high alternating voltage of about 500 V is applied to the plate. Capillary waves are excited at the edge of the plate under the action of electric field.[84]

Two main methods currently used for the detection of capillary waves are as follows. One method is based on reflection of a laser beam from the surface of a liquid.[84] A reflected beam goes to a photodetector. If the amplitude-to-wavelength ratio for capillary waves is much less than a unity, periodic displacements of the laser impact position from the average position are proportional to the capillary wave amplitude. By successively measuring the relative capillary wave amplitude at different distances from the oscillator one can determine the damping coefficient and the wavelength. In the other method,[12] parameters of

capillary waves are measured using a capacitive sensor (dynamic capacitor). From the dispersion relation (13) it follows that the capillary wave method for measuring dynamic surface elasticity with a reasonable accuracy works only at low ε values ($|\varepsilon| \leqslant 0.15\gamma$).[10]

At frequencies lower than $\sim$10 Hz, the surface elasticity can be measured by the longitudinal surface wave method,[85,86] which involves generation of longitudinal waves by oscillations of a moveable barrier in a Langmuir bath. Since in this case the shape of the liquid surface negligibly deviates from a flat surface, parameters of longitudinal waves are difficult to measure. Experimentally, this can be done by measuring the surface tension oscillations occurring as a result of propagation of longitudinal waves across the surface of the liquid. Small-amplitude surface tension oscillations are governed by the transverse capillary waves propagating along a direction that is perpendicular to the propagation direction of longitudinal waves. If the amplitudes of the two wave modes used are small, nonlinear interactions between them can be neglected.

Owing to experimental difficulties and complexity in interpretation of experimental data obtained by the capillary wave method, high-frequency methods of surface dilational rheology have been more rarely used in the last decade; most authors prefer simpler low-frequency methods. Yet another reason for popularity of the low-frequency methods consists in that the main relaxation processes in the adsorption polymer films usually occur at frequencies of about 1 Hz. In this case, high-frequency methods give only the limiting value of the dynamic surface elasticity. At frequencies $\leqslant$0.2 Hz, the longitudinal surface wavelength much exceeds the dimensions of the liquid surface in the cell (usually, a Langmuir bath), and the surface strain can be treated homogeneous. As a result, the surface tension oscillations due to dilation (compression) of the surface can be measured with ease by various methods and the surface elasticity can be determined from Eqns (2) and (4).

All low-frequency methods can conditionally be divided into two groups with respect to the shape of the surface of the solution under study. Using curved surface and the oscillating bubble (drop) methods, measurements can be done at small volumes of the solution under study. If the surface tension oscillations are determined from the shape of the oscillating drop at the tip of a thin capillary, measurements of the dynamic surface elasticity are possible if the volume of the solution under study is $\sim$10 μl. Recently, this advantage as well as commercially available equipment have made the surface rheology methods based on the determination of the shape of the oscillating bubble (drop) most popular.[37,48,56,64–66,71,79] However, the fact that the use of a curved interface leads to experimental difficulties, namely, if the surface tension is determined from the shape of the bubble (drop), the surface strain in the gravity field can not exactly correspond to uniform dilation (compression) and one should take into account the shear surface properties.[78] This fact is sometimes left out of consideration.

Yet another problem is due to strong perturbation of mechanical equilibrium near the surface at frequencies higher than $\sim$0.1 Hz.[79,87] In this case, the shape of the bubble (drop) can be influenced by inertial forces and internal friction in the liquid; oscillations may have a nonradial component and the classical Young–Laplace–Gauss equation is insufficient to describe the profile of the drop. One more fact rarely taken into account is as follows. The three-phase contact line at the capillary tip can be to some extent 'mobile', which makes the determination of the surface area of the meniscus difficult.[88] This effect provides an explanation for the influence of the capillary material on the results of the oscillating bubble (drop) measurements. If the determination of the surface tension is based on measurements of the pressure difference between the liquid and air bubble, the surface area of meniscus can be significantly reduced and the applicability conditions for the Young–Laplace–Gauss equation become less stringent. In this case, the available frequency range can be significantly extended; however, this faces new experimental difficulties due to the need for taking account of the elasticity of vessel walls, compressibility of the liquid, motion of the three-phase contact line and inhomogeneity of the liquid surface strain.

Methods of measurements of the rheological properties which are based on dilation (compression) of a flat liquid surface in a Langmuir bath are to a great extent free from drawbacks characteristic of the oscillating bubble (drop) method and allow one to attain higher accuracy. Dilation (compression) of a flat surface makes it possible to reduce the effect of the three-phase contact line and to carry out measurements at smaller amplitude of relative surface oscillations. The latter is of particular importance for the systems characterized by nonlinear response even under relative surface strains of the order of a few per cent. Surface oscillations can be due to barrier oscillations in the Langmuir bath or to oscillations of a ring immersed into the liquid.

The oscillating barrier method is well documented.[35,36] For instance, a fluoroplastic barrier in a Langmuir bath moves back and forth along flat edges of the bath, thus generating sinusoidal oscillations of the solution surface with specified frequency and amplitude. The surface tension oscillations are measured by the Wilhelmy plate method using a microbalance. The dilational surface elasticity can be measured by the oscillating barrier method only if the surface tension variations in the bath are uniform. Usually, this condition is met when the length of longitudinal surface waves in the bath much exceeds the dimension of the bath and the frequency is at most $\sim$0.2 Hz.

Surface elasticity measurements by the oscillating ring method were reported.[89,90] In this case, periodic dilation and compression of the liquid surface is carried out using a glassy ring with polished internal surface (to improve wetting). The axis of the ring is perpendicular to the liquid surface. Oscillations of the ring about this axis induce oscillations of the liquid surface as a result of periodic changes in the shape of the meniscus at the internal surface of the ring. The surface tension oscillations thus generated in the cell can also be measured by the Wilhelmy plate method using a microbalance. The oscillating ring method allows one to obtain more uniform liquid surface strain and the influence of shear viscosity on the results of measurements appears to be negligible even for highly viscous systems.

IV. Dilational surface rheology of solutions of nonionic polymers

Recently, methods of dilational surface rheology have been widely used in studies of solutions of random copoly-

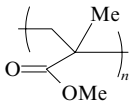
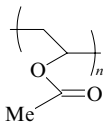
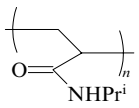
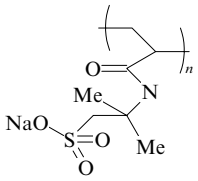
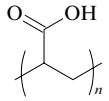
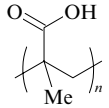
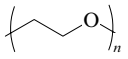
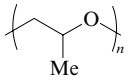
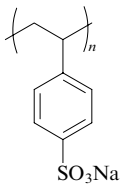
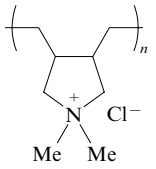
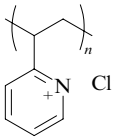
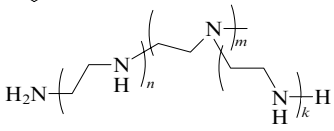
mers [91–94] and block copolymers [13, 14, 56, 95–98] because these compounds are utilized as stabilizers of foams and emulsions; solutions of nonionic homopolymers are studied more rarely.[35, 99–101] The structural formulas of polymers studied in Refs 102–151 are presented in Table 1. It should be noted that studies on the dilational rheological properties of spread polymer films on water surface were reported earlier than studies on the dilational surface rheology of polymer solutions.[102–105]

The air/water interface can be either good and bad solvent; this to a great extent predetermines the properties of a film.[106–109] For poly(methyl methacrylate) (PMMA) films, the interface is a bad solvent and the PMMA macromolecule adopts a pancake conformation. When the surface concentration of PMMA reaches a critical value, a fluid-to-glass transition is observed, accompanied by an abrupt increase in the surface elasticity.[108, 109] For polyvinyl acetate (PVAc) and poly(ethylene oxide) (PEO), the interface is a good solvent and macromolecules are freely distributed on the surface; an increase in the surface concentration leads to entanglement of polymer chains.[102, 110] In a detailed study of the dilational surface properties of PVAc films by the oscillating barrier method, electrocapillary waves and quasi-elastic light scattering, the surface viscoelasticity was investigated at frequencies from a few thousandths to a few tens of thousands of Hertz and the key surface stress relaxation times were estimated.[102] As the frequency increases, the surface dilational viscosity decreases and the real part of the dilational dynamic surface elasticity approaches the static elasticity value. It follows that main relaxation processes in the PVAc films occur at low frequencies (<1 Hz).

The dependence of the dynamic surface elasticity on the surface concentration of PEO appeared to be nonmonotonic (Fig. 3). The maximum in the plot can be associated with the beginning of formation of 'loops' and 'tails' (formation of the distal region in the surface layer). At low concentrations of the polymer, the adsorbed macromolecules adopt a flat (almost 2D) conformation in the surface layer. An increase in the surface concentration leads to stronger repulsion between adsorbed macromolecules and, hence, to an increase in the dynamic surface elasticity. Further increase in the surface concentration leads to transition to a 3D structure of the surface film where the distal region formed by 'loops' and 'tails' appears in addition to the more dense proximal region. As a result, the surface stress relaxation can occur through exchange of chain segments between different regions of the surface layer and the surface elasticity should decrease after passing through the local maximum. The difference between the real part of the dynamic surface elasticity and the static elasticity of PEO films at high surface concentrations of the polymer is indicative of slow relaxation processes in the surface layer. It follows that the formation of 'loops' and 'tails' begins near the maximum value of the dynamic surface elasticity, where it begins to differ from the static value,[111–113] rather than in the initial portion of the pseudoplateau in the plot of surface tension *vs.* surface concentration, as was assumed in a number of studies. This conclusion is consistent with neutron reflection data.[114]

A maximum in the surface elasticity -*vs.*-concentration plot was found in studies of poly(*N*-isopropylacrylamide) (PNIPAM) films.[115, 116] Higher surface elasticity values compared to those obtained for PEO were explained by

Table 1. Formulas of polymers studied.

Formula	Name	Ref.
	poly(methyl metacrylate) (PMMA)	108, 109
	polyvinyl acetate (PVAc)	102
	poly(*N*-isopropyl-acrylamide) (PNIPAM)	131
	poly(2-acrylamido-2-methyl-1-propane-sulfonic acid) sodium salt (PAMPS)	131
	polyacrylic acid (PAA)	90, 149
	polymethacrylic acid (PMA)	90
	poly(ethylene oxide) (PEO)	110
	poly(propylene oxide) (PPO)	98
	sodium polystyrene sulfonate (SPS)	127, 146
	polydiallyldimethyl-ammonium chloride (polyDADMAC)	88, 131
	poly(vinylpyridinium chloride) (PVPmCl)	151
	polyethylenimine (PEI)	150

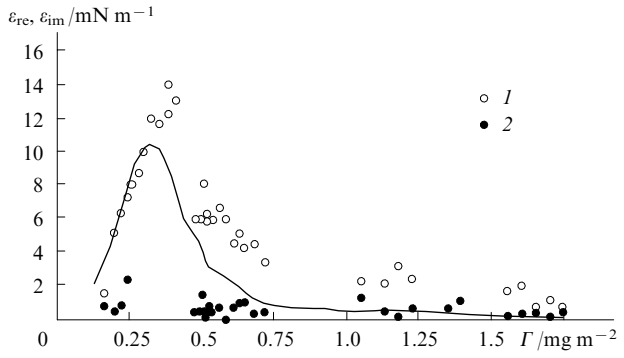


Figure 3. Real ε_{re} (*1*) and imaginary ε_{im} (*2*) parts of the dynamic surface elasticity plotted *vs*. PEO surface concentration (Γ) at 1 Hz; the solid line is the dependence of the static surface elasticity on Γ calculated from the surface tension isotherm.[110]

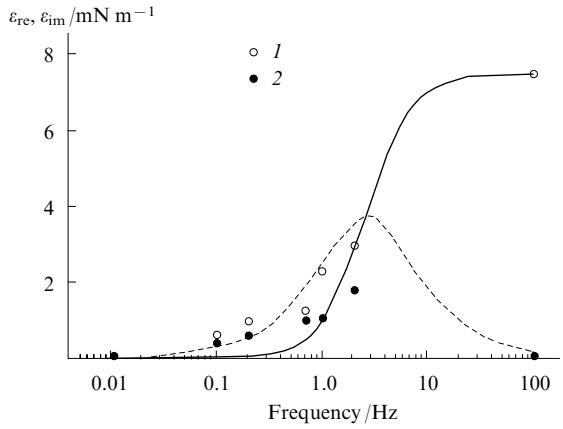


Figure 4. Frequency dependences of the real (*1*) and imaginary (*2*) parts of the dynamic surface elasticity of PEG solutions with a concentration of 0.001 mass %.
The real and imaginary parts of the surface elasticity were calculated using expression (10) and the experimental data taken from Ref. 35.

entanglement of polymer chains in the region of 'loops' and 'tails'.

Interest in the surface properties of polymer solutions is due to publications on dilational surface rheology of these systems. The concentration dependence of the dynamic surface elasticity of poly(ethylene glycol) (PEG) solutions[35] containing relatively low-molecular-mass PEG (< 4000) is nonmonotonic; it passes through a maximum equal to ~ 8 mN m^{-1} at a polymer concentration of 3×10^{-5} mas %. As in the case of spread polymer films, this maximum can be associated with the beginning of formation of 'loops' and 'tails' (formation of the distal region in the surface layer). Nevertheless, some differences between the dynamic surface properties of spread polymer films and adsorption polymer films should be pointed out. The dependences of the dynamic surface elasticity of the spread films of PEG, poly(propylene glycol) (PPG) and block copolymers of PEO and PPO on the surface pressure monotonically increase, pass through a maximum and then dissolution of the films begins. However, the surface elasticity of the adsorption films of these compounds pass through a maximum and then decreases; this indicates the formation of a less dense surface structure.[35,96,99] Besides, the dependence of the dynamic surface elasticity on the oscillation frequency and the noticeably large imaginary part of the dynamic surface elasticity for the adsorption films at high surface pressures point to the occurrence of low-frequency relaxation processes that do not manifest themselves in the spread films of PEG and block copolymers. Thus, the analogy between the spread films and adsorption films appears to be incomplete, and conclusions based on the results of studies on spread polymer films should be applied to adsorption films with care.

The viscoelastic behaviour of an adsorption film near the maximum value of the dynamic surface elasticity at ~ 0.1 Hz indicates that the relaxation time is close to the oscillation period. The results of measurements of the surface elasticity of PEG solutions in this region at different frequencies are shown in Fig. 4. This frequency dependence of the surface elasticity can be described using the Maxwell model. Since PEO chains are short, one can assume that the number of 'loops' and 'tails' per chain is also small (< 1). Then, the key parameters of the Maxwell model can be related to the dynamics of the polymer chain. The quantity $\partial\gamma/\partial \ln \Gamma$ (here, it equals 7.2 mN m^{-1}) is an important property of the surface layer; it is governed by the intermolecular interaction within this layer. For solutions of low-molecular-mass surfactants, this parameter can be determined from the surface tension isotherm using the Gibbs adsorption equation; however, this is impossible for polymer solutions. The relaxation time (0.06 s for a solution containing 0.001 mass % of PEG) is determined by both polymer chain parameters and by the packing type of macromolecular segments in the adsorption film.

As the molecular mass of the polymer increases, the local maximum of the surface elasticity is shifted towards lower concentrations as a result of higher surface activity; slow establishment of equilibrium in polymers with rather high molecular mass ($> 10\,000$) causes the local maximum of the surface elasticity to shift in the concentration range that is inaccessible to experimental studies ($\ll 10^{-4}$ mass %). At the same time, a local maximum appears in the kinetic curves of the dynamic elasticity of polymers with high molecular masses (Fig. 5) due to the same reasons as does the maximum in the concentration dependence.[100,101] As time passes, the surface concentration increases as a result of adsorption. The surface elasticity initially increases and then decreases upon the formation of 'loops' and 'tails'. The maximum surface elasticity value depends strongly on the degree of hydrophobicity of chain segments and can vary over a wide range. Recently, a local maximum in the kinetic dependence of the dynamic surface elasticity was also observed for natural nonionic polymers.[91] Conclusions based on the surface rheology data were confirmed by the results of the ellipsometry measurements[101,117] of the film thickness and adsorption value (see corresponding kinetic dependences in Fig. 6). It follows that adsorption does involve two key steps, namely, a fast first step with almost no changes in the adsorption film thickness (this corresponds to formation of a relatively dense proximal region of the surface layer) and a slower second step with the formation of 'tails' and 'loops' due to an increase in the film thickness at nearly constant adsorption value.

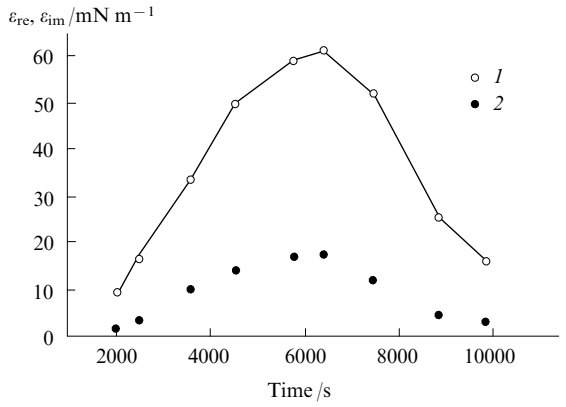


Figure 5. Kinetic dependences of the real (*1*) and imaginary (*2*) parts of the surface elasticity of PNIPAM solutions with a concentration of 0.0001 mass % at 0.14 Hz.
Experimental data were taken from Ref. 101.

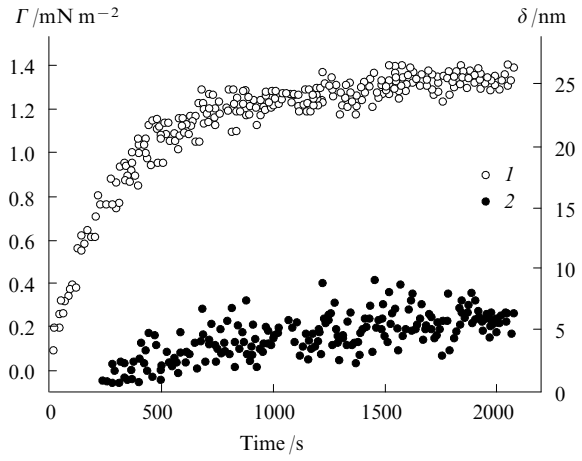


Figure 6. Kinetic dependences of Γ (*1*) and the surface layer thickness (δ) (*2*) for PNIPAM solutions with a concentration of 0.0001 mass %.
Experimental data were taken from Ref. 101.

The surface properties of more complex amphiphilic di- and triblock copolymers depend strongly on the block size ratio and on their degrees of hydrophobicity. The dependence of the dynamic surface elasticity of solutions of $PEO_{76}-PPO_{29}-PEO_{76}$ triblock copolymer on time (or on the surface pressure) exhibits two local maxima (Fig. 7) corresponding to transition of each type of blocks to the subphase.[96, 98] In the initial stage of adsorption the surface pressure dependence of the dynamic surface elasticity is identical to the corresponding dependence obtained for PEO solutions. It follows that the dynamic surface properties of the solution in this range of surface pressures are determined by more hydrophilic PEO segments. The second maximum in the dependences of the surface elasticity indicates that at high surface pressures, PPO segments are squeezed out of the dense proximal region of the surface layer to the 'dilute' distal region, thus participating in the formation of 'loops' and 'tails'; therefore, the classical polymer brush model is inappropriate for the description

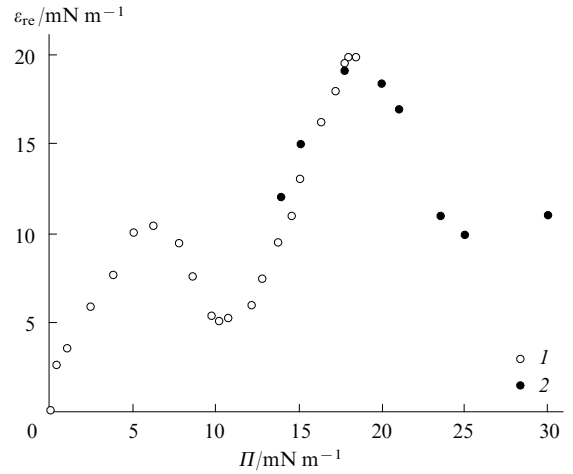


Figure 7. Real part of the surface elasticity plotted *vs.* surface pressure (Π): spread (*1*) and adsorption (*2*) $PEO_{76}-PPO_{29}-PEO_{76}$ films at 0.14 Hz.[98]

of the system in question. These results were confirmed by neutron reflection data.[118] Replacement of PPO segments by even more hydrophobic blocks leads to significant increase in the surface elasticity in the region of high surface pressures.[60] The dynamic surface properties of spread films of a diblock copolymer of PEO with hydrophobic polystyrene (PS) can be described by the model of a polymer brush with one block being fixed in the proximal region of the surface layer.[119]

Usually, adsorption films of amphiphilic polymers are characterized by a linear response to dilation (compression) of up to 10%. At the same time, spread films of insoluble polymers are characterized by nonlinear response even at low relative strain.[69] For instance, this result was obtained for PVAc, poly(octadecyl acrylate) and poly(vinyl stearate) spread films at high surface concentrations of these compounds.[69] The pseudoplastic behaviour observed is probably due to irreversible stretching of macromolecules in the direction perpendicular to the surface upon film compression. Another explanation consists in the onset of the anisotropy of the surface properties upon longitudinal compression (dilation) of spread films. In the course of dilation (after compression) the system has no time to recover the initial state and the surface pressure appears to be lower than prior to compression.

V. Dilational surface rheology of polyelectrolyte solutions

The surface properties of solutions of synthetic polyelectrolytes have been studied much less than those of, *e.g.*, protein solutions, which can also be treated as natural polyelectrolytes (polyampholytes).[18, 24, 25, 45, 120, 121] This is to a great extent due to low surface activity of most conventional polyelectrolytes. Only so-called polysoaps whose molecules contain a large number of hydrophobic groups exhibit rather high surface activity.[122, 123] Conventional synthetic polyelectrolytes having no extra hydrophobic chains can hardly be used as surfactants. Interest in the surface properties of polyelectrolyte solutions is due to other reasons, first of all, wide industrial use of complexes

of these compounds with low- and high-molecular-mass surfactants. Therefore, studies on the behaviour of charged macromolecules near the interface between two fluid phases (liquid/liquid, gas/gas) are currently important.

Low surface activity of synthetic polyelectrolytes is, in particular, due to very slow establishment of adsorption equilibrium at low ionic strength of solutions caused by the high electrostatic barrier of adsorption. In the initial step, adsorption of charged macromolecules causes the surface charge to increase and, as a consequence, further adsorption to slow down.[124–128] The barrier height and, hence, the adsorption rate depend strongly on the ionic strength of the solution and on the charge density of the polymer chain.[124–126] A noticeable decrease in the surface tension in the course of a routine experiment is only observed at high ionic strength of solutions.[127–130] The ionic strength increases with increasing polyelectrolyte concentration, which can lead to deviation of the surface tension from the bulk solvent value. Okubo[129,130] introduced the notion 'critical polyelectrolyte concentration' (CPC), which corresponds to the onset of abrupt increase in the surface pressure. Most synthetic polyelectrolytes are characterized by rather high CPC values, *e.g.*, $\sim$0.1 mass % for sodium polystyrene sulfonate (SPS) and a copolymer of poly(2-acrylamido-2-methyl-1-propanesulfonic acid) sodium salt with *N*-isopropylacrylamide (PAMPS–NIPAM).[127,131] The ionic strength of a solution can also be increased by adding an inorganic salt. For instance, at high NaCl concentrations, the surface tension of the SPS and PAMPS–NIPAM solutions decreases at a polyelectrolyte concentration of only $\sim$0.001 mass %.

At relatively low ionic strength of a solution corresponding to the appearance of surface activity for many polyelectrolytes (SPS, PAMPS–NIPAM, PDMDAAC) is relatively low, the dynamic surface elasticity slowly changes with time and can be as high as 80 mN m^{-1} for SPS solutions.[127,131] The real part of the surface elasticity appears to be much higher than the imaginary part. Such a pure elastic behaviour of the adsorption film indicates the absence of the distal region of 'loops' and 'tails' which is characteristic of adsorption films of nonionic polymers. Probably, electrostatic rigidity of polyelectrolyte chains due to repulsion between likely charged segments leads to high elasticity of the surface film and precludes the formation of 'tails' and 'loops' in the surface layer. For SPS solutions, the absence of the distal region of 'loops' and 'tails' in this concentration range was confirmed by neutron reflection data.[132] A study of solutions of a natural polyelectrolyte chitosan (its concentration was 0.026 mass %) also revealed a high surface elasticity of >40 mN m^{-1}.[122] Unlike synthetic polyelectrolytes, in this case the adsorption film exhibits viscoelastic behaviour which is transformed to pure elastic behaviour only at high concentrations of indifferent electrolyte.

As the ionic strength increases, the surface properties of polyelectrolyte solutions should approach those of solutions of nonionic polymers. First, according to the kinetic theory of adsorption, the electrostatic barrier vanishes at inorganic salt concentrations higher than 0.1 mol litre^{-1} and the adsorption rate of macromolecules is determined by the bulk-to surface diffusion.[124] Second, electrostatic repulsion between likely charged chain segments significantly decreases and macromolecules in the solution become more flexible and resemble molecules of amphiphilic nonionic polymers in properties. A study of PAMPS–NIPAM solutions confirmed the occurrence of such a transition upon an increase in the ionic strength of the solution.[131] The addition of NaCl to the PAMPS–NIPAM solution causes abrupt shortening of the equilibration time. As the system approaches the equilibrium state, the dynamic surface elasticity decreases, being at most 10 mN m^{-1}, and a local maximum appears in the kinetic dependences of the surface elasticity. For solutions of nonionic polymers, the appearance of a maximum in the kinetic dependences of the surface elasticity is due to the formation of the region of 'loops' and 'tails' in the surface layer. Therefore, one can assume that the adsorption film of PAMPS–NIPAM solutions in the presence of salt also consists of the proximal and distal regions.[131]

However, the dynamic surface properties of SPS solutions containing NaCl (up to a NaCl concentration of 1 mol litre^{-1}) are significantly different from those of solutions of nonionic polymers (Fig. 8), although the adsorption film thickness increases, as was shown by neutron reflection.[132] First, an increase in ionic strength causes accelerated formation of the surface layer only in the initial stage of adsorption.[127] It follows that the electrostatic barrier is not the only reason for slow establishment of the equilibrium values of the surface properties. Next, the dynamic surface elasticity slightly increases rather than abruptly decreases, as predicted by theory. The kinetic dependences of the surface elasticity of SPS solutions remain monotonic in the whole range of polyelectrolyte concentrations; this also contradicts the theory. Thus, no surface stress relaxation through exchange of chain segments between the proximal and distal regions of the surface layer (by analogy with nonionic polymers) does occur even at very low frequencies ($\sim$0.1 Hz). This behaviour can be explained taking into account hydrophobic interactions between macromolecules in the surface layer, which lead to formation of microaggregates near the interface.[127] In this case, individual chain segments can be embedded into aggregates;

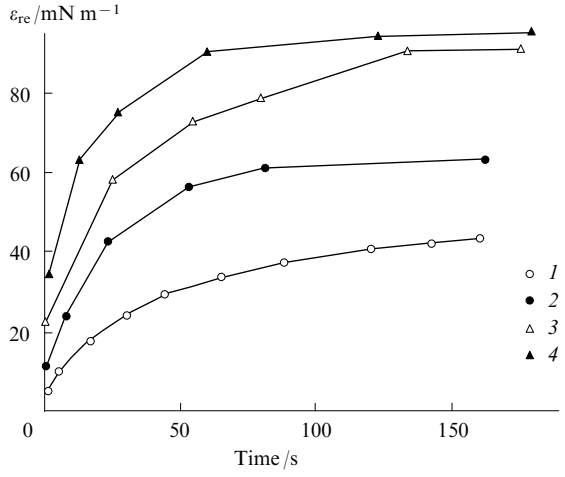


Figure 8. Kinetic dependences of the real part of the surface elasticity of SPS solutions at a concentration of 0.1 mass % and a frequency of 0.12 Hz; NaCl concentration: 0 (*1*), 0.1 (*2*), 1 (*3*) and 3 mol litre^{-1} (*4*).
Experimental data were taken from Ref. 127.

this precludes transition of chain segments from the bulk phase to the surface layer. Very slow changes in the surface properties was treated as indirect proof of heterogeneity of the surface layer.[128, 133] Microheterogeneity of SPS adsorption films was also confirmed by X-ray scattering data.[128]

The formation of microheterogeneous structure of adsorption films of hydrophobically modified chitosan through hydrophobic interactions between macromolecules upon the addition of inorganic salt led to an increase in the elasticity and to transition from viscoelastic to pure elastic behaviour of the adsorption films.[123]

PDMDAAC aqueous solutions in the presence of inorganic salt occupy an intermediate position between the PAMPS–NIPAM solutions whose dynamic surface properties are close to those of solutions of nonionic polymers and the SPS solutions with microheterogeneous surface layer.[131] An increase in the ionic strength of the PDMDAAC solutions is accompanied by a decrease in the equilibrium surface elasticity value and by the appearance of a maximum in the kinetic curve, thus indicating the formation of the distal region of the surface layer. However, the time taken to establish the equilibrium values of the surface properties exceeds the characteristic time of diffusion of macromolecules from the bulk; this may point to a more complex structure of the adsorption film.

Modified polyelectrolytes with long hydrophobic side chains (polysoaps) exhibit high surface activity compared to conventional synthetic polyelectrolytes.[122, 123] The surface tension of solutions of modified chitosan already decreases at concentrations of 0.0001 mass %. At low concentrations, the dynamic properties of adsorption films are close to those of films of other polyelectrolytes. High surface elasticity and pure elastic rheological behaviour indicate the formation of a rigid 2D film on the surface of the solution. As the bulk concentration of the polymer increases, the surface elasticity decreases and its real and imaginary parts take close values. This behaviour can be explained by the formation of the distal region of 'loops' and 'tails'.[123] An increase in the ionic strength at a polyelectrolyte concentrations of >0.001 mass % upon the addition of salt leads to an increase in the surface elasticity. The adsorption film now behaves as pure elastic system. However, the adsorption rate remains almost unchanged which can be due to formation of a microheterogeneous structure of the surface layer.

VI. Dilational surface rheology of solutions of polyelectrolyte/low-molecular-mass surfactant complexes

Recently, physical chemistry of solutions of polyelectrolyte/surfactant complexes has been developed intensively.[30, 39, 47, 134–167] By varying the concentrations, molecular masses and hydrophobicities of components, as well as the polymer chain rigidity and characteristics of surfactants one can vary the bulk and surface properties of aqueous solutions over a wide range. Probably, this is a reason for a wide use of solutions of polyelectrolyte–surfactant complexes in industry and medicine. Although for many applications the surface properties of mixed polymer/surfactant solutions are of greater importance than their bulk properties, until recently information on the structure of adsorption films of polyelectrolyte/surfactant complexes on water surface was mainly based on the results of surface tension measurements.[134, 135, 141]

Recently, the systems in question have been studied by powerful experimental methods including neutron reflectometry which provides unique information on the distribution of surfactant molecules and macromolecular segments along the normal to the interface.[30, 142, 143] However, this method is of limited use owing to relatively short time intervals and to a large neutron-beam cross section, which precludes the use of neutron reflection in the surface studies of heterogeneous films. This limitation is of particular importance because adsorption films of polyelectrolyte–surfactant complexes are characterized by high inhomogeneity.[88, 144–146] Dilational surface rheology is to a great extent free from these drawbacks. Recent studies showed that surface rheology methods are highly sensitive to formation of microaggregates in the surface layer of polyelectrolyte–surfactant solutions and allow one to study the mechanism of formation of adsorption films in these systems.[88, 90, 145–152]

Pioneering studies on dilational surface rheology of solutions of polyelectrolyte/surfactant complexes revealed (i) nonmonotonic changes in the dynamic surface elasticity with increasing surfactant concentration and (ii) dependence of the dynamic surface elasticity on the relative surface strain even at low strains ($\sim 1\%$).[145, 153–156] A Brewster angle microscopy study showed that these features can be due to the inhomogeneity of the adsorption film upon dilation (compression).[145]

Measurements of the dynamic surface elasticity of SPS–dodecyltrimethylammonium bromide (DTAB) and PDMDAAC–dodecyl sulfate (SDS) mixed solutions as function of time demonstrated very slow changes in the surface properties at low surfactant concentrations ($\leqslant 10^{-4}$ mol litre^{-1}).[88, 146] No equilibrium was established even a few hours after formation of the new surface. The real part of the dynamic surface elasticity monotonically increased with time and reached high values up to 140 mN m^{-1} for the PDMDAAC–SDS solutions. The imaginary part of the dynamic surface elasticity was much smaller and the adsorption film could be treated as pure elastic. The results obtained contradicted Goddard's model for polyelectrolyte–surfactant adsorption film[135, 141] and indicated the formation of 2D aggregates and a rigid film structure through electrostatic and hydrophobic interactions in the surface layer.[146] As the surfactant concentration increased to some critical value, the dynamic surface elasticities of the solutions with constant polyelectrolyte concentrations abruptly decreased several-fold (Fig. 9).

This fact was associated with the formation of 3D microaggregates in the surface layer, *i.e.*, with changes in the structure of the adsorption film.[146] Aggregation gave rise to a new mechanism of surface stress relaxation through mass exchange between the aggregates and the surrounding quasi-2D adsorption film and, therefore, to a decrease in the dynamic surface elasticity. The formation of microheterogeneous polyelectrolyte/surfactant adsorption film was confirmed by ellipsometry (Fig. 10).

The decrease in the surface elasticity was accompanied by a sharp increase in the ellipsometry signal (see curve *2* in Fig. 10) due to light scattering by the microaggregates formed in the surface layer. The other maximum in this curve is associated with an increase in the thickness of the surface layer and with the formation of a multilayer

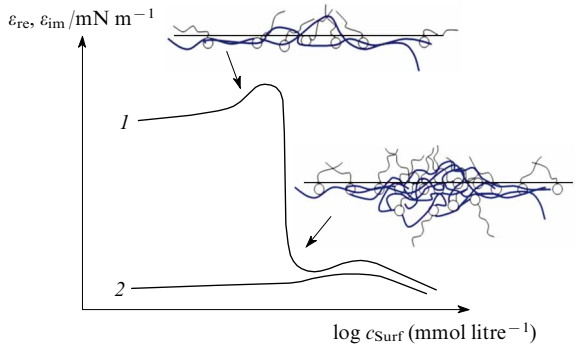


Figure 9. Changes in real (*1*) and imaginary (*2*) parts of the surface elasticity of solutions of polyelectrolyte–surfactant complexes with increasing surfactant concentration: a schematic.

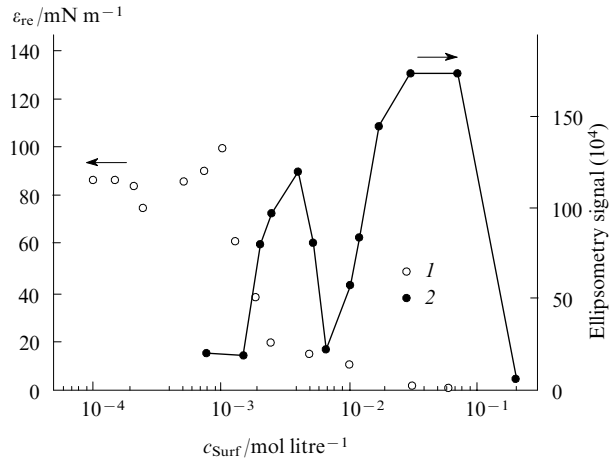


Figure 10. Real part of the surface elasticity (*1*) and ellipticity (*2*) of solutions of SPS–DTAB complexes containing 0.05 mass % of polyelectrolyte plotted *vs.* DTAB concentration (c_{Surf}). Experimental data were taken from Refs 144 and 146.

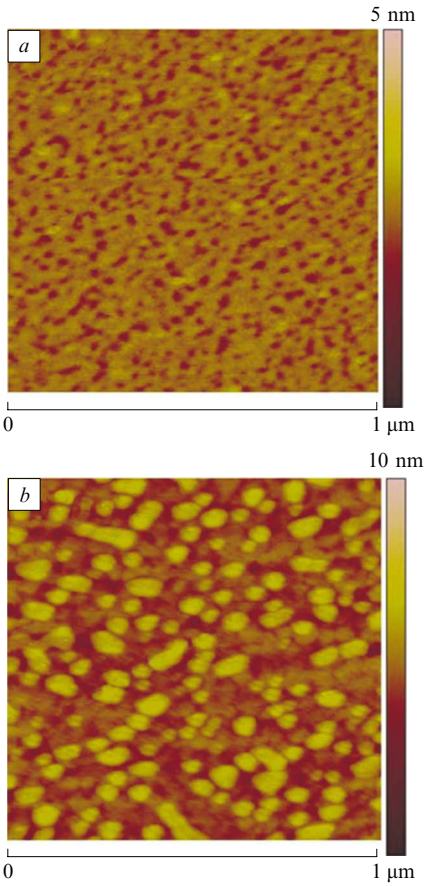


Figure 11. AFM images of SPS/DTAB adsorption films transferred to mica surface in the range of surfactant concentrations before (*a*) and after (*b*) abrupt decrease in the surface elasticity.[148]

structure. An atomic force microscopy study of SPS–DTAB adsorption films transferred onto mica substrate using the Langmuir–Blodgett technique revealed microaggregates (Fig. 11). At surfactant concentrations lower than the critical value (see above), the adsorption film was ~1.5 nm thick, which indicated a flat conformation of macromolecules in the surface layer without 'loops' and 'tails' (see Fig. 11 *a*). The presence of regions with relatively low surface density in the adsorption film at low surfactant concentrations is consistent with the adsorption film model proposed earlier.[146] At the surfactant concentrations higher than the critical value, individual aggregates (Fig. 11 *b*) with a characteristic size of 20 to 60 nm and a thickness of 2 to 2.5 nm (larger than the film thickness) were observed in the adsorption film. This thin film seems to be less dense than the film shown in Fig. 11 *a*; it should be characterized by lower elasticity.

Recently, similar dependences of the dynamic surface elasticity on the surfactant concentration with a local maximum and subsequent abrupt decrease in surface elasticity were obtained for solutions of many other polyelectrolyte/surfactant mixtures including polyacrylic acid (PAA)–DTAB,[90,149] polymethacrylic acid (PMA)–DTAB,[90] polyethylenimine (PEI)–SDS,[150] poly(vinylpyridinium chloride) (PVPmCl)–SDS[151] and carrageenan–DTAB.[156] These results point to similarity in the character of changes in the structure of the surface layer in all cases and to the formation of microaggregates in the adsorption film upon reaching some critical surfactant concentration. Differences between the systems studied mainly manifest themselves in the measured surface elasticity values, thus being of quantitative rather than qualitative character.

An increase in the ionic strength of solutions upon adding indifferent electrolyte (>0.1 mol litre^{-1}) led to changes in the dependences of the dynamic surface elasticity on the surfactant concentration and to acceleration of the adsorption film formation. At high ionic strength, the surface properties of PVPmCl–SDS–NaCl[151] and PDMDAAC–SDS–NaCl[152] solutions approached corresponding equilibrium values in less than an hour after the formation of a new surface even at low surfactant concentrations, which was indicative of reduction of the electrostatic barrier to adsorption. In the case of the SPS–DTAB and PDMDAAC–SDS solutions at low ionic strength an abrupt decrease in the surface elasticity occurred when the ratio of the concentration of surfactant molecules to the concentration of charged groups of polyelectrolyte was close to unity. For PVPmCl–SDS–NaCl and

PDMDAAC–SDS–NaCl solutions, this effect was observed at the surfactant concentrations ten times lower than the concentration of charged groups of the polyelectrolyte. Differences between the systems with high and low ionic strength also manifested themselves in the influence of the polyelectrolyte concentration on the decrease in the surface tension with increasing surfactant concentration. In the first case, the region of surfactant concentrations corresponding to the decrease in surface tension was almost independent of the polyelectrolyte concentration.[142, 143, 152] In the second case, this region as well as the region corresponding to abrupt decrease in the dynamic surface elasticity shifted towards higher surfactant concentrations with increasing the polyelectrolyte concentration.[146, 157, 158]

Thus, the critical surfactant concentration corresponding to the formation of microaggregates in the surface layer of solutions of polyelectrolyte–surfactant complexes, as well as the critical micelle concentration (CMC) of ionic surfactant, decreases with increasing the concentration of inorganic salt in the solution. However, in the case of solutions of complexes this behaviour seems to be due to the nonequilibrium state of the system at low ionic strength of the solution and at the surface lifetimes appropriate for experimental investigations. It follows that for solutions of complexes the determination of the critical aggregation concentration from the surface tension data may introduce large errors.[152]

For many systems, *e.g.*, PAA–DTAB, PMA–DTAB, PEI–SDS, PVPmCl–SDS and PVPmCl–SDS–NaCl solutions, reduction of the dynamic surface elasticity with increasing surfactant concentration is related to transition from the elastic to viscoelastic behaviour of the adsorption film.[90, 149–151] If at low surfactant concentrations the real part of the dynamic surface elasticity is more than ten times larger than its imaginary part, in the region of formation of 3D aggregates near the interface the real and imaginary parts take close values. Aggregation gives rise to a new surface stress relaxation mechanism involving exchange of surfactant molecules or macromolecular segments between microaggregates and the film. In this case, the Maxwell rheological model makes it possible to determine the main surface stress relaxation time which for many similar systems is of the order of 10 s (see Refs 90 and 151).

The influence of hydrophobic interactions on the formation of rigid structure of adsorption films of polyelectrolyte–surfactant complexes at low surfactant concentrations was studied taking solutions of chitosan–SDS complexes as examples.[122, 123, 159] The dynamic surface properties of this system were compared with corresponding results for solutions of hydrophobically modified chitosan (dodecylchitosan) in which the concentration of the $C_{12}H_{25}$ hydrophobic groups was the same as the concentration of SDS in the solutions of chitosan–SDS complexes. It was found that the dynamic surface elasticity and the surface activity of the dodecylchitosan solutions are much lower than those of solutions of the complexes. It follows that the distribution of SDS molecules along the polymer chain in the chitosan–SDS complex near the interface differs from the random distribution of the $C_{12}H_{25}$ groups in the dodecylchitosan adsorption film. In the adsorption films of the chitosan–SDS complexes, the SDS molecules can form compact clusters through hydrophobic interactions between themselves and segments of the polyelectrolyte molecules. This leads to higher elasticity compared to that of the hydrophobically modified chitosan film where the mobility of hydrophobic groups is restricted by their rigid bonds with the polymer chain.

The results obtained in studies on the dynamic surface properties of solutions of complexes between polyelectrolytes and surfactants with different-length hydrocarbon 'tails'[90, 149] also point to important role of hydrophobic interactions in the formation of rigid structure of adsorption films. An increase in the size of the hydrophobic group for solutions of mixtures of PAA with alkyltrimethylammonium bromides causes an increase in the dynamic surface elasticity in a wide range of surfactant concentrations. It should be noted that all measurements of the dilational surface elasticity of solutions of weak polyelectrolyte (PAA, PMA, PEI)–surfactant complexes were carried out at pH values of the solutions corresponding to complete dissociation of the polyelectrolytes. One can assume that investigation of the influence of the charge density in the polyelectrolyte on the surface properties of solutions of polyelectrolyte–surfactant complexes will provide additional information on the interaction between components in the adsorption films.

From the standpoint of research on the adsorption kinetics, measurements of the kinetic dependences of the dynamic surface elasticity of polyelectrolyte–surfactant solutions appeared to be much more informative than, *e.g.*, measurements of the kinetic dependences of the surface tension or adsorption value. The latter values vary monotonically with time in contrast to the kinetic dependences of the surface elasticity with one or two local maxima corresponding to structural changes in the adsorption film.[88, 90, 149, 150] For the PAA–DTAB, PMA–DTAB and PEI–SDS solutions, the first local maximum also corresponded to transition from linear to nonlinear response to small periodic surface strain with a relative amplitude of $\sim$3%. At short surface lifetimes, the surface tension oscillations were of pure harmonic character until the first maximum of the surface elasticity and then their character changed; a Fourier analysis of the measured signal revealed the appearance of higher harmonics.

Under compression of the surface film, after passing the maximum elasticity value, the surface tension reached some critical value and then remained almost unchanged, so almost flat portions appeared in the plots of surface tension *vs.* time (Fig. 12). Subsequent dilation of the film was again followed by an increase in the surface tension. The nearly flat portions in the surface tension oscillation curves can be due to formation of microaggregates in the surface layer after passing some surface concentration of the polyelectrolyte–surfactant complexes. The next compression step is accompanied by mass exchange between aggregates and the surrounding film. As a result, the local surface concentration in the film and the corresponding surface tension remain almost unchanged.

Further adsorption causes an increase in the number and/or size of aggregates in the surface layer and their interaction with one another and the surface elasticity thus increases again. Consequently, the surface pressure rises and a number of aggregates are squeezed out from the liquid surface. In that case, surface stress relaxation can occur through mass exchange between different layers in the

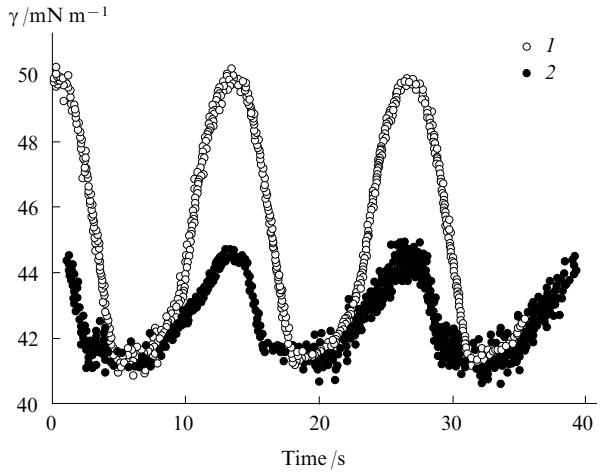


Figure 12. Surface tension (γ) oscillations for PAA–DTAB solutions (0.4 mmol litre^{-1}): 70 (*1*) and 90 (*2*) min after start of adsorption.
Experimental data were taken from Ref. 90.

adsorption film. The surface elasticity in turn decreases and a second maximum appears in its kinetic dependences. The formation of a multilayer structure in the concentration range corresponding to the kinetic dependences with two maxima was detected in a neutron reflection study.[160]

When studying the dynamic surface properties of solutions of polyelectrolyte–surfactant complexes at high surfactant concentrations, one should take into account the formation of macroscopic aggregates in the bulk phase. In this case, the surface properties can depend on the solution preparation procedure and vary over a period of a few days owing to the long-term establishment of the phase and sedimentation equilibria in the system.[161–164] For instance, freshly prepared PDMDAAC–SDS–NaCl solutions in the region of phase separation are characterized by relatively low surface elasticity and by nonlinear response of the system to weak surface dilation (compression); this can be due to penetration of aggregates into the surface layer.[152] A few days after preparation of the solution, the surfactant is embedded into macroscopic aggregates that precipitate on the bottom of the cell and the surface rheological properties take the values characteristic of the solutions with low surfactant concentration. Further increase in the surfactant concentration leads to dissolution of aggregates. If the surfactant concentration much exceeds the concentration of charged groups of the polyelectrolyte, the surfactant displaces complexes from the surface of the solution and the surface properties are governed by the excess surfactant molecules present in the surface layer. The dynamic surface elasticity at low frequencies ($\leqslant 1$ Hz) approaches zero and the surface tension becomes equal to the value characteristic of the micellar solution of the surfactant.

The results of studies on the rheological properties of adsorption films of polyelectrolyte–surfactant complexes at the oil/water interface appeared to be close to those reported for the air/water interface.[165–167] Abrupt changes in the structure of adsorption film and the formation of microaggregates in the surface layer were also observed at surfactant concentrations higher than some critical value.

VII. Dilational surface rheology of protein solutions

Recently, methods of dilational surface rheology have been successfully used to estimate the conformation of protein molecules near the liquid surface. In spite of a long story of research on the surface properties of proteins and importance of their results for solving many applied problems that are first of all related to the use of foams and emulsions, reliable data on the structure of protein films at the interface between two fluid phases are scarce. In the last fifteen years, modification of the secondary structure of proteins during adsorption on the surface of an aqueous solution has been assessed by optical methods. Most studies revealed minor changes in the reflection–absorption IR spectra or in circular dichroism spectra during adsorption of bovine serum albumin (BSA), β-lactoglobulin (BLG), lysozyme and ovalbumin, which make it possible to assess corresponding changes in the content of elements of the secondary structure.[31–33,168–170] Information on the tertiary structure of proteins in the surface layer is also insufficient. For instance, in recent works different points of view on the changes in the tertiary structure of lysozyme in the course of adsorption have been stated. On the one hand, it is stated that the tertiary structure of lysozyme in the surface layer is completely destroyed;[171,172] on the other hand, it was reported that the protein still has a globular structure near the air/solution interface.[30,173–175] Clearly, in some situations the available experimental methods are insufficient to study adsorption films consisting of macromolecules with complex structure on liquid surface. In this case, dilational surface rheology studies may provide additional information.

The dynamic surface properties of solutions of globular and non-globular proteins are significantly different. In the former case, the dynamic surface elasticity monotonically increases with time and can be as high as $\sim 70-90$ mN m^{-1}; in the latter case, (first of all, for β-casein solutions), the dynamic surface elasticity modulus is much lower (<20 mN m^{-1}) and its kinetic dependences exhibit two local maxima (Fig. 13). Interpretation of these dependences is facilitated when comparing them with the results obtained for solutions of block copolymers (these

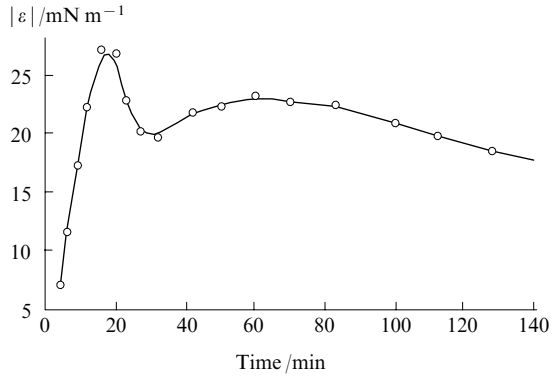


Figure 13. Kinetic dependence of the surface elasticity modulus of β-casein solutions at a concentration of 0.002 mg ml^{-1} and a frequency of 0.14 Hz.
Experimental data were taken from Ref. 176.

systems are also characterized by two maxima of the dynamic surface elasticity).[96] Indeed, since the β-casein molecule can be divided into two moieties characterized by different hydrophobicity and charge density, a diblock copolymer can be treated as rough model for β-casein.[177] Using an analogy with the dynamic surface properties of PEO–PPO–PEO solutions, two maxima of the surface elasticity of the β-casein solutions can be related to successive squeezing out of two molecular moieties which form 'loops' and 'tails' in the surface layer from the surface on an increase in the surface pressure.[176]

Additional proofs of the proposed mechanism of formation of β-casein adsorption films can be obtained by measuring the kinetic dependences of the dynamic surface elasticity of β-casein solutions containing small additives of ionic surfactants to probe the structure of the adsorption film.[178] Since the charge densities of the two moieties of β-casein molecule differ appreciably, one can expect that cationic and anionic surfactants will influence the maxima in the kinetic curve of the dynamic surface elasticity in different manner. This was indeed observed.[178] An increase in the hydrophobicity of the relatively hydrophilic moiety of β-casein molecule through the interaction with cationic DTAB influences the first maximum of the surface elasticity, thus leading to an increase in the surface pressure necessary to squeeze this molecular fragment out of the surface of the solution. Contrary to this, small additives of an anionic surfactant cause an increase in the surface pressure and surface elasticity in the region of the second maximum.

Changes in the character of the kinetic dependences of the dynamic surface elasticity upon addition of PNIPAM (a surfactant) to a β-casein solution allow one to monitor how the protein molecules are displaced from the surface of the solution by the surfactant.[179] At low PNIPAM concentrations, the kinetic dependences exhibit three rather than two peaks characteristic of β-casein; the third peak corresponds to displacement of the PNIPAM segments from the surface. This peak becomes more intense with increasing PNIPAM concentration, whereas the first two peaks gradually disappear. The shape of the second peak and corresponding surface pressure vary over a wide range; this is indicative of hydrophobic interactions between components in the surface layer.

The kinetic dependences of the dynamic surface elasticity of solutions of globular proteins are close to those of sols of charged silica nanoparticles with oppositely charged surfactants provided that the surfactant concentration is lower than the critical concentration corresponding to the onset of neutralization of nanoparticles by the surfactant molecules being adsorbed on them.[180] As for silica nanoparticles, the adsorption kinetics of globular proteins is first of all determined by the charge of adsorbed particles. With increasing the distance from the isoelectric point the adsorption rate considerably decreases.[181] The adsorption rate of globular molecules can be calculated within the framework of a model for diffusion of charged particles in the field created by the electric double layer near the interface.[182] As the ionic strength of the solution increases, the thickness of the double layer decreases and, therefore, the electrostatic barrier to adsorption also decreases. As a result, the influence of the charge of protein globules on the kinetic dependences of the dynamic surface properties weakens.[181, 182]

Considerable differences between the kinetic curves of the dynamic surface elasticity for solutions of non-globular and globular proteins suggest preservation of the tertiary structure of proteins in the latter case. If that is the case, the addition of strong denaturants that cause unfolding of protein globules in the solutions should lead to abrupt changes in the surface rheological properties and the kinetic dependences of the surface elasticity should become nonmonotonic.

At low concentrations of guanidine hydrochloride (GuHCl), the dynamic surface elasticity of BSA and BLG solutions slightly increases owing to an increase in the ionic strength of the solution, but the kinetic dependences of this quantity remain monotonic.[181, 183] However, as the GuHCl concentration exceeds some critical value, a local maximum appears in the kinetic dependences of the surface elasticity and these curves now resemble corresponding dependences obtained for solutions of amphiphilic polymers (Fig. 14). The dynamic surface elasticity near the equilibrium approaches a value of 15 mN m^{-1} for BSA solutions and 25 mN m^{-1} for BLG solutions. These values are somewhat higher than for solutions of amphiphilic polymers; this may be due to restricted mobility of protein molecules in the surface layer owing to, *e.g.*, disulfide bridges in the macromolecules. The critical concentration of GuHCl was ~0.65 mol litre^{-1} for BSA solutions and 0.25 mol litre^{-1} for BLG solutions, being somewhat lower than the values corresponding to the onset of unfolding of protein globules in the bulk phase. At the same time, ellipsometry and neutron reflection data indicate that for BLG solutions the critical concentration corresponds to the onset of considerable thickening of the adsorption film.[182, 184]

The addition of yet another strong denaturant, urea, to solutions of globular proteins also led to nonmonotonic kinetic dependences of the surface elasticity.[185] The surface pressure corresponding to the maximum dynamic surface elasticity is independent of the chemical nature of denaturant (GuHCl, urea, ionic surfactant), being characteristic of a given protein.

Ionic surfactants can also destroy the tertiary structure of proteins.[186–189] Measurements of the kinetic depend-

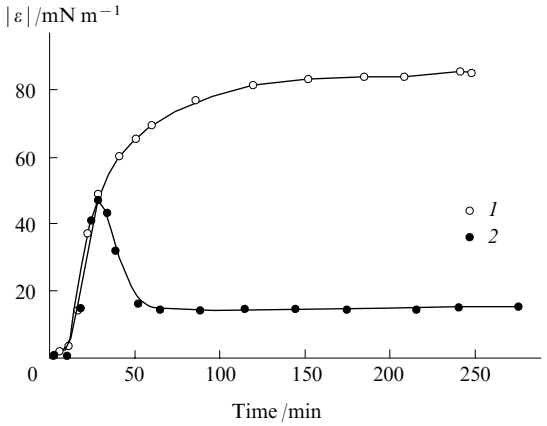


Figure 14. Kinetic dependences of the dynamic surface elasticity modulus of BSA solutions at a concentration of 0.03 μmol litre^{-1} and a frequency of 0.1 Hz; GuHCl concentration: 0 (*1*) and 4 mol litre^{-1} (*2*).
Experimental data were taken from Ref. 181.

ences of the dynamic surface elasticity allow one to obtain information on this process in the surface layer. The addition of DTAB to BSA and BLG solutions leads to nonmonotonic kinetic dependences if the surfactant concentration exceeds a value of $\sim$0.05 and 0.2 mmol litre^{-1}, respectively.[190] Unlike other denaturants, surfactants exhibit intrinsic surface activity and squeeze out protein and protein–surfactant complexes from the liquid surface at high concentrations. Therefore, at concentrations higher than CMC, the surface properties are determined by the excess surfactant molecules and the surface elasticity is close to zero. At low ionic strength, SDS cannot destroy the tertiary structure of the protein and the kinetic dependences of the surface elasticity are monotonic.[182, 190] However, an increase in the ionic strength to 0.4 mol litre^{-1} leads to destruction of the globular structure and to the appearance of a local maximum in the kinetic dependences of surface elasticity. The interaction of BSA with synthetic polyelectrolytes (SPS and PDMDAAC) also causes complexation and changes in the kinetic dependences of the dynamic surface elasticity.[191] If the protein and polyelectrolyte molecules bear opposite charges, the tertiary structure of the protein is partially destroyed in the surface layer; otherwise, polyelectrolyte forms a loose shell around the protein globule.

VIII. Conclusion

Methods of dilational surface elasticity have recently started to be used in studies of polymer solutions, but the results obtained offer great prospects for research on complex multicomponent systems. Progress in chemistry of liquid surface is to a great extent limited by a small number of available experimental methods. This is particularly pronounced in the case of systems with microheterogeneous surface where one should transfer films from the liquid surface to a solid surface in order to use various microscopy techniques. Unfortunately, not all transfer techniques are reliable and the film structure may be distorted in some cases. At the same time, measurements of the dilational dynamic surface elasticity as function of time allow one to monitor the formation of microaggregates in the film from the appearance of extrema in the kinetic curve and from generation of higher harmonics in the course of surface tension oscillations.

Local maxima of the dynamic surface elasticity may also appear as a result of formation of polymer bilayers or microaggregates near the interface as well as formation of the distal region of 'loops' and 'tails' in the surface layer. In the case of protein solutions, a local maximum appears upon destruction of the tertiary structure, thus illustrating unique capabilities of dilational surface rheology in studies of protein systems. The kinetic dependences of the dynamic surface elasticity of solutions of non-globular proteins or block copolymers can exhibit a number of local maxima corresponding to different steps in the formation of adsorption films. If a system in question contains more than one high-molecular-mass surfactant, conventional methods of surface chemistry are inconvenient to study the adsorption kinetics. At the same time, multi-peak kinetic curves of the surface elasticity make it possible to monitor how, *e.g.*, one component displaces some other component from the surface and to evaluate the interactions between macromolecules in the surface layer.

The drawbacks of methods of dilational surface rheology include a pronounced and in some cases nonestimable impact of hydrodynamic factors. For systems characterized by high values of the shear surface properties the method of oscillating barrier allows one to determine only the longitudinal surface dynamic elasticity representing the sum of the dilational and shear contributions. In this case, determination of the dilational surface properties requires that the shear surface properties be determined independently. When using the oscillating ring method, the influence of the shear surface properties is much less pronounced. The hydrodynamics of an oscillating meniscus near the capillary tip is much more complex than, *e.g.*, the hydrodynamics of propagation of small-amplitude longitudinal or transverse waves near a flat surface. This is a reason for a larger error of the methods of oscillating bubble compared to the methods of measurement of the surface dilational rheological properties on a flat liquid surface. The accuracy of measurements becomes of particular importance for essentially nonlinear systems[75] characterized by very narrow region of the surface oscillation amplitudes corresponding to linear behaviour. Also, adsorption of polymer films on liquid surfaces is characterized by slow establishment of equilibrium; therefore, determination of concentration dependences of the surface properties, first of all, the dynamic surface elasticity, seems to be senseless provided that there is no kinetic information on how these properties approach their equilibrium values.

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