Mendeleev Commun., 2003, 13(6), 256–258

Dynamic surface elasticity of sodium poly(styrenesulfonate) solutions

Sergey N. Nuzhnov,[a] Reinhard Miller[b] and Boris A. Noskov*[a]

[a] *Department of Chemistry, St. Petersburg State University, 198904 St. Petersburg, Russian Federation.*
Fax: +7 812 428 6939; e-mail: boris@bn1664.spb.edu
[b] *MPI für Kolloid- und Grenzflächenforschung, Forschungcampus Golm, D14476 Golm, Germany*

10.1070/MC2003v013n06ABEH001813

The surface viscoelastic properties of aqueous sodium poly(styrenesulfonate) solutions show that the relaxation of surface stresses by monomer exchange between the proximal and distal regions of the surface layer does not occur in solutions of this typical strong polyelectrolyte.

Polyelectrolytes soluble in water are widely used in various industries. However, information on the behaviour of charged macromolecules in the surface layer of solution is limited[1] because of the absence of reliable experimental techniques for studying the surface properties of polymer systems. Recently, neutron reflectivity made it possible to determine the distribution of polyelectrolyte segments in the surface layer.[2,3] At the same time, almost nothing is known on the dynamics of charged macromolecules at the liquid surface.

We applied mechanical relaxation spectrometry to studies of the non-equilibrium surface properties of aqueous solutions of a typical strong polyelectrolyte, sodium poly(styrenesulfonate) (PSS). This experimental technique was successfully used in a study of the relaxation mechanism of surface stresses in the adsorbed films of nonionic surface-active homopolymers.[4–6]

Surface viscoelastic properties were determined by means of capillary waves and the oscillating barrier method. The damping coefficient α and the length λ of capillary waves are related to the complex dynamic surface elasticity ε, which reflects both elastic and viscous surface properties, *via* the dispersion equation (1),[5] where ω is the angular frequency, γ is the surface tension, $k = 2\pi/\lambda + \mathrm{i}\alpha$ is the wave number, g is the gravitational acceleration, $m^2 = k^2 - \mathrm{i}\omega\rho/\mu$, μ is the shear viscosity of the bulk solution, ρ is the liquid density and h is the liquid depth in the trough.

The capillary wave characteristics were measured by the electrodynamic method, which is based on the application of a non-contact capacity wave probe. The experimental procedure was described in detail elsewhere.[5,7,8] The surface tension was measured by the Wilhelmy plate method.

Only relatively low values of the dynamic surface elasticity (< 20 mN m^{-1}) can be measured by the capillary wave method with reasonable accuracy.[7] At a higher surface elasticity, we used the oscillation barrier method. It is based on the detection of surface tension oscillations caused by periodical compression and expansion of the liquid surface in a Langmuir trough. If the oscillation frequency is less than ~0.2 Hz, the surface tension changes with time homogeneously, and ε can be found from the ratio of the oscillation amplitudes of the surface tension and the surface area.[9]

PSS (Aldrich) with the average molecular mass 70000 was purified by dialysis using cellulose membranes (Sigma). Sodium chloride was purified by heating in an oven to remove organic impurities. Fresh twice-distilled water was used for the preparation of solutions.

Before measurements, the surface of the test solution was swept by moving barrier and cleaned with a Pasteur pipette. The time of cleaning was taken as the time of the interface formation.

An important property of PSS adsorption films consists in the extremely slow equilibration process. The surface tension of PSS solutions in the concentration range 0.01–3 wt% did not reach equilibrium within 5 h. Note that in this concentration range the surface tension of nonionic polymer solutions reaches equilibrium in less than one minute.[5,6] We used the measurements of capillary wavelength for longer registration of the surface tension. The corresponding results are less sensitive to changes of the liquid level in the trough due to evaporation. The wavelength is approximately proportional to the cubic route of surface tension according to the dispersion equation of capillary waves.

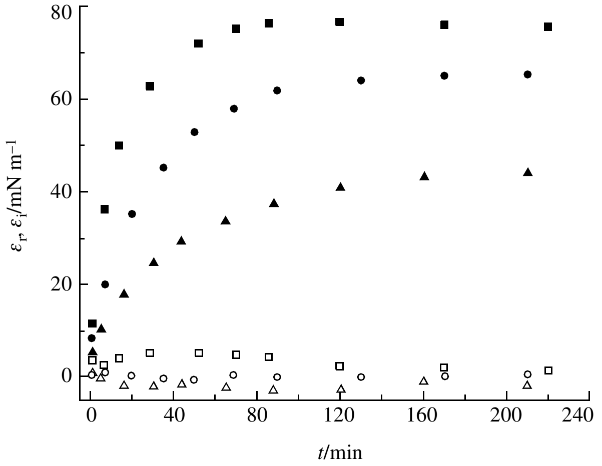

Figure 1 Kinetic dependence of the real (solid symbols) and imaginary (open symbols) parts of the dynamic surface elasticity at a frequency of 0.12 Hz and PSS concentrations of 0.2 (triangles), 0.6 (circles) and 1 wt% (squares).

As shown by wavelength measurements the equilibration process in PSS adsorption films exceeds two days. The rates of surface tension and wavelength decrease drop with concentration. The values of λ and γ for low-concentration solutions ($c < 0.01$ wt%) did not differ from the value for water during several hours after interface formation. These data probably resulted in a conclusion about the zero surface activity of PSS.[10,11]

Unlike the wavelength, the damping coefficient of capillary waves is mainly determined by the surface viscoelasticity. It follows from the dispersion equation that the function $\alpha(\varepsilon)$ is non-monotonic.[7] The kinetic dependence of the damping coefficient has a local maximum in the concentration range between 0.1 and 0.5 wt%. At lower concentrations the damping coefficient increases monotonically with time and remains constant at $c < 0.01$ wt% within the limits of experimental error during the time of measurements. At $c > 0.7$ wt% the damping coefficient increases only slightly with time. This behaviour indicates that the dynamic surface elasticity of PSS solutions increases with time and concentration. Direct calculations of the surface elasticity confirm this conclusion. However, the precision of these calculations decreases significantly with increasing $|\varepsilon|$, and for $|\varepsilon| > 20$ mN m^{-1} only rough estimates can be obtained.

$$\varepsilon = \varepsilon_\mathrm{r} + \mathrm{i}\varepsilon_\mathrm{i} = \frac{\rho\omega^2[\rho\omega^2 - (\gamma k^3 + \rho gk)\tanh(kh)] + 4\mathrm{i}\rho\mu\omega^3k^2 + 4\mu^2\omega^2k^3[m\tanh(kh) - k]}{mk^2[\rho\omega^2 - (\gamma k^2 + \rho gk)\tanh(kh)] + k^3(\gamma k^3 + \rho gk)}, \qquad (1)$$

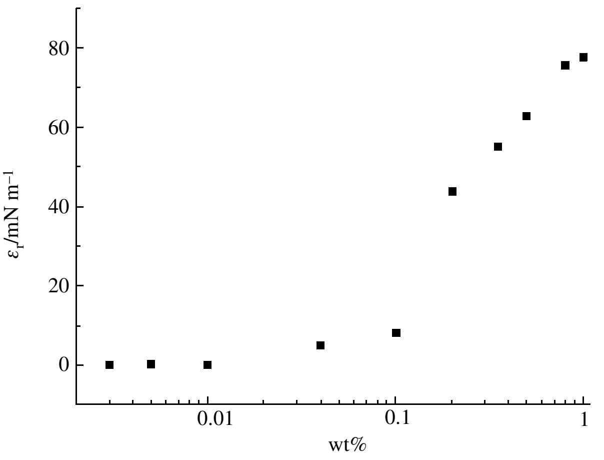

Figure 2 The real part of the dynamic surface elasticity of PSS solutions 4 h after the fresh surface formation *vs.* concentration.

The low sensitivity of the damping coefficient to the surface elasticity at high $|\varepsilon|$, which is characteristic of PSS solutions, follows from the dispersion equation (1).[7]

Therefore, we used the oscillating barrier method to study higher concentrated PSS solutions. Figure 1 shows the kinetic dependences of both components of the dynamic surface elasticity of PSS solutions at a frequency of 0.12 Hz. For all solutions ε_r increases with time and ε_i does not differ from zero in the error limits. The limit value of the real part of dynamic surface elasticity increases with concentration and approaches 75 mN m^{-1} at $c \geq 1$ wt%. Both components of the dynamic surface elasticity do not depend on frequency in the studied range 0.01–0.2 Hz.

Thus, the viscoelastic properties of PSS adsorption films differ from those observed in nonionic polymer adsorption films. First, the dynamic surface elasticity in the latter case deviates from zero in the whole concentration range accessible to measurements, while one can discover the surface viscoelastic properties of PSS films only at concentrations higher than 0.01 wt% (Figure 2). Second, the equilibration times of the surface layer of PSS solutions are several orders of magnitude higher than those of nonionic polymers. Note that the slow polyelectrolyte adsorption due to an electrostatic barrier was observed earlier.[1,12] Third, the surface elasticity of relatively concentrated PSS solutions ($c > 0.1$ wt%) exceeds the values for nonionic polymer solutions by more than one order of magnitude. In this case, the modulus of dynamic surface elasticity does not exceed 5 mN m^{-1} in the whole concentration range for macromolecules with a molecular mass higher than 10000.[4–6] This difference can be connected with different relaxation mechanisms of the surface stresses in polyelectrolyte solutions and the solutions of polymers without electrolytic dissociation. For polyelectrolyte solutions, the measured surface elasticity equals to the Gibbs modulus; therefore, it can be determined in principle using the self-consistent field (SCF) theory.[14]

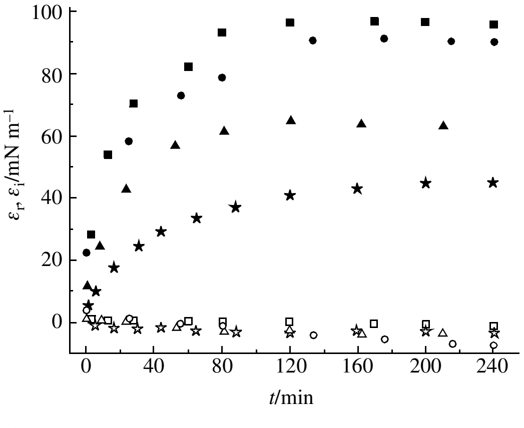

Figure 3 Kinetic dependence of the real (solid symbols) and imaginary (open symbols) parts of the dynamic surface elasticity of 0.1 wt% PSS solutions at a frequency of 0.12 Hz and NaCl concentrations of 0 (asterisks), 0.1 (triangles), 1 (circles) and 3 mol dm^{-3} (squares).

The surface layer of nonionic polymer solutions consists of a relatively concentrated proximal region and a region of loops and tails protruding into the bulk solution (distal region). The relaxation of surface stresses upon surface compression (expansion) proceeds at the expense of segment exchange between the proximal and distal regions of the surface layer.[5,13] As a result, a low surface elasticity is observed at frequencies lower than the reverse characteristic time of this exchange.[4–6] For polyelectrolyte solutions without inorganic salts, as it follows from the SCF theory, the adsorbed macromolecules do not form loops and tails because of an increased rigidity due to electrostatic repulsion between the segments.[2,3,12,14] If the ionic strength increases, for example, on the addition of an inorganic salt, the repulsion forces become screened. This allows the formation of the distal region of the surface layer, as confirmed by neutron reflectometry.[2,3] Simultaneously, this leads to a decrease in the electrostatic adsorption barrier, and calculations according to the SCF and Kramer rate theories show that the adsorption rate has to increase by several orders of magnitude.[12] Then, one can expect that the dynamic surface properties of PSS solutions have to approach the properties of nonionic polymer solutions.

To test this hypothesis, we measured the kinetic dependences of the dynamic surface elasticity at different NaCl concentrations (Figure 3). Salt addition led to a significant increase of the rate of ε_r changes only at the initial stage of adsorption. In all cases, the changes in surface viscoelastic properties proceeded during several hours after surface formation in contradiction to the results of calculations.[12] This indicates that the electrostatic adsorption barrier is not the only reason for the slow changes of surface properties with time. The imaginary part of the dynamic surface elasticity was close to zero as in the case of PSS solutions without the salt. Moreover, the addition of the salt led to a small increase of maximum ε_r values in contradiction to the above assumption. Therefore, the increase of the ionic strength does not lead to the appearance of an additional mechanism of surface stress relaxation. This could indicate the absence of loops and tails; however, neutron reflectometry leads to the reverse conclusion.[2,3] A more probable explanation of the results obtained can be connected with the restricted mobility of charged macromolecules in the surface layer even on the addition of a salt, for example, due to aggregate formation. Theodoly *et al.*[1] also assumed the formation of aggregates in the adsorbed film of PSS solutions in order to explain the results of X-ray surface scattering. Another argument in favour of the microheterogeneity of PSS adsorption films stems from the slow surface tension relaxation at a high salt content. The slow relaxation is characteristic of microheterogeneous surface films, it was considered as indirect evidence for surface aggregation.[1,15] The formation of aggregates in the bulk phase of strong polyelectrolyte solutions is well known, and it cannot be explained until now.[16] One can assume that this process in the surface layer and the bulk phase has the same reason, for example, hydrophobic interactions.

In conclusion, the dynamic surface properties of strong polyelectrolyte solutions differ significantly from those of the solutions of nonionic homopolymers. This distinction can be connected with the peculiarities of the polyelectrolyte surface layer structure, for example, with the formation of microheterogeneous surface films.

This work was supported by the Russian Foundation for Basic Research (grant no. 03-03-32366), President of the Russian Federation (Leading Scientific Schools, grant no. NSh-789.2003.3) and the programme ‘High School Research on Priority Directions of Science and Engineering’ (project no. 203.06.06.035).

References

1 O. Theodoly, C. E. Williams and R. Ober, *Eur. Phys. J. E.*, 2001, **5**, 51.
2 H. Yim, M. S. Kent, A. Matheson, M. J. Stevens, R. Ivkov, S. Satija, J. Majewski and G. S. Smith, *Macromolecules*, 2000, **33**, 6126.
3 H. Yim, M. S. Kent, A. Mathewson, M. J. Stevens, R. Ivkov, J. Majewski and G. S. Smith, *Macromolecules*, 2002, **35**, 9737.
4 B. A. Noskov, A. V. Akentiev, G. Loglio and R. Miller, *Mendeleev Commun.*, 1998, 190.
5 B. A. Noskov, V. A. Akentiev, G. Loglio and R. Miller, *J. Phys. Chem. B.*, 2000, **104**, 7923.
6 B. A. Noskov, V. A. Akentiev and R. Miller, *J. Colloid Interface Sci.*, 2002, **255**, 417.
7 B. A. Noskov, *Adv. Colloid Interface Sci.*, 1996, **69**, 63.
8 B. A. Noskov and D. O. Grigoriev, *Langmuir*, 1996, **12**, 3399.
9 A. V. Akentiev and B. A. Noskov, *Kolloidn. Zh.*, 2002, **64**, 149 (*Colloid J.*, 2002, **64**, 129).
10 T. Okubo, *J. Colloid Interface Sci.*, 1988, **125**, 386.
11 D. J. F. Taylor, R. K. Thomas and J. Penfold, *Langmuir*, 2002, **18**, 4748.
12 M. A. Cohen Stuart, C. W. Hoogendam and A. Keizer, *J. Phys.: Condens. Matter*, 1997, **9**, 7767.
13 B. A. Noskov, *Colloid Polym. Sci.*, 1995, **273**, 263.
14 G. J. Fleer, *Ber. Bunsenges. Phys. Chem.*, 1996, **100**, 936.
15 D. Vollhard, *Adv. Colloid Interface Sci.*, 1993, **1**, 247.
16 M. Sedlák, *J. Chem. Phys.*, 2002, **116**, 5236; 5246; 5256.

Received: 17th June 2003; Com. 03/2139