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ScienceDirect
Mendeleev Commun., 2016, **26**, 64–65
Mendeleev Communications

Dynamic surface elasticity of the mixed solutions of DNA and cetyltrimethylammonium bromide

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DOI: 10.1016/j.mencom.2016.01.025

The dilational dynamic surface elasticity of the mixed solutions of DNA and a cationic surfactant was measured for revealing the mechanisms of adsorption and surface stress relaxation, which are different from those of polyelectrolyte/surfactant solutions studied earlier due to the high persistence length of DNA molecules.

Interest in the properties of the mixed solutions of polyelectrolytes and oppositely charged surfactants is caused by various industrial applications of these systems.[1–5] Attention was focused on the mixed solutions of DNA and cationic surfactants due to the potential usefulness of the DNA/surfactant complexes for the transfer of genetic materials to the cells.[6–8] Although the structure of polyelectrolyte/surfactant complexes in a bulk phase can be studied in detail,[9,10] information on the adsorption layer structure is scarce due to a limited number of suitable experimental procedures. Recently, it has been shown that, unlike other modern techniques, for example, neutron reflection method,[1,7,8] the methods of dilational surface rheology can give information on the microstructure of adsorption layers in the solutions of synthetic polyelectrolytes and surfactants.[11,12] In this work, we were the first to apply an oscillating barrier method to the mixed solutions of DNA and the cationic surfactant, cetyltrimethylammonium bromide (CTAB),[†] in order to compare their dilational surface properties with those of the mixed solutions of synthetic polyelectrolytes and oppositely charged surfactants.

The concentration dependence of the surface tension of DNA/CTAB solutions qualitatively agrees with published data.[6–8] Some quantitative discrepancies between the data can result from different molecular weights of DNA, a higher surface activity of DNA/CTAB complexes, as compared with that of DNA/dodecyltrimethylammonium bromide,[5] and different salt concentrations. The surface tension of DNA/CTAB solutions is lower than that of pure CTAB solutions from very low concentrations of about 0.1 μM up to the concentrations close to the CMC of CTAB thereby indicating the formation of DNA/surfactant complexes of high surface activity (Figure 1). The breakpoint of the concentration dependence at about 0.08 mM CTAB corresponds to the critical aggregation concentration (CAC) – the beginning of the cooperative binding of surfactant molecules by DNA in the bulk phase. At lower concentrations, the complex formation mainly occurs in the surface layer and the amount of the bound surfactant in the bulk does not exceed a few percents of DNA phosphate groups.[6] At concentrations higher than 0.05 mM, the solutions become turbid and visible aggregates appear in the bulk phase. In this case, the aggregation in the bulk phase is preferred to the complex formation at the interface leading to the depletion of the surface layer by the surfactant and DNA/surfactant complexes and thereby to an increase in the surface tension.[6,8] At CTAB concentrations higher than 1 mM, the surface tension approaches the values for pure CTAB solutions.

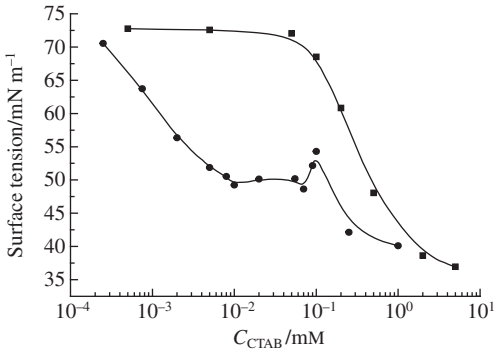

Figure 1 Surface tension as a function of surfactant concentration for (■) pure CTAB and (●) mixed DNA/CTAB solutions.

A similar behavior was also found for the mixed solutions of synthetic polyelectrolytes and oppositely charged surfactants, where the persistence length and charge density differ strongly from the values for DNA.[13,14] At the same time, the dynamic surface properties of DNA/CTAB solutions significantly differ from the properties of other polyelectrolyte/surfactant solutions. The imaginary part of the complex dynamic surface elasticity is much smaller than the real one for all of the investigated solutions. Therefore, only the results for the real part are discussed below. Unlike the corresponding data for the mixed solutions of synthetic polyelectrolytes and surfactants, all the kinetic dependences of the real part of the dynamic surface elasticity are monotonic (Figure 2). The characteristic equilibration time (~1 h) remained almost unchanged when the surfactant concentration was increased from 0.00075 to 0.07 mM. Note that the characteristic diffusion time from the bulk phase to the surface is proportional to the

[†] CTAB (Sigma-Aldrich) was twice recrystallized from an ethyl acetate–ethanol mixture before use. Calf thymus DNA (M_w = 10^7 Da, 16 kbp) and Trizma base from Sigma were used without purification. Sodium chloride was preheated at about 750 °C for the elimination of organic impurities. The stock solutions were prepared in water produced by a Milli-Q purification system (Millipore). DNA fibers were dissolved in a 10 mM Tris-HCl buffer solution with pH 7.6 containing 20 mM NaCl to keep the double helix intact. The final concentration of DNA was 50 μM (in nucleotide units). The concentrations of the cationic surfactants were varied in a range of 0.0001 – 3 mM. The experimental procedures for measuring surface tension by the Wilhelmy plate method and complex dynamic dilational surface elasticity by the oscillating barrier method were described elsewhere.[11,12] The frequency and amplitude of the surface area oscillations were 0.1 Hz and 3%, respectively. The measurements were carried out at 20±0.5 °C.

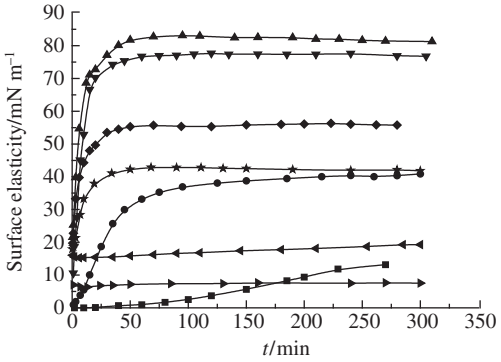

Figure 2 Kinetic curves of the dynamic surface elasticity of mixed DNA/CTAB solutions at different CTAB concentrations: (■) 0.00025, (●) 0.00075, (▲) 0.008, (▼) 0.02, (◆) 0.055, (★) 0.07, (◀) 0.09, (▶) 0.25 mM.

square of the inverse concentration.[4] This means that the rate of CTAB diffusion does not influence the rate of formation of DNA/CTAB complexes at the interface and the latter quantity is determined by the adsorption of DNA. A slight change of the surfactant concentration from 0.07 to 0.09 mM close to the CAC results in an increase in the adsorption rate by more than an order of magnitude and the dynamic surface elasticity remains constant during the time of measurements at higher concentrations. This abrupt transition indicates changes in the adsorption mechanism, and it can be related to the abrupt increase of CTAB binding to DNA molecules in the bulk. Beyond the CAC, the DNA/surfactant complexes are mainly formed in the bulk phase and adsorbed fast at the interface leading to the fast growth of the concentration of hydrophobic groups in the surface layer. Below the CAC, the slow decrease of the surface tension with the surface age is mainly a consequence of the slow adsorption of individual components and their interaction at the interface. Note that the increase in the adsorption rate close to the CAC is more gradual for other polyelectrolyte/surfactant solutions.[11]

The dynamic surface elasticity changes nonmonotonically with surfactant concentration. Below the CAC, the surface elasticity rises with CTAB concentration up to 85 mN m^{-1} (Figure 3). Note that the dynamic surface elasticity of a pure CTAB solution does not exceed 5 mN m^{-1} at a frequency of 0.1 Hz in the whole concentration range. The changes of the surface elasticity below the CAC obviously indicate the increase in surface concentration and the gradual formation of a rigid surface layer structure. The growth of CTAB concentration up to about 3CAC results only in slight changes of the surface elasticity in the error limits, but a further increase leads to an abrupt drop of this quantity. This effect could indicate a strong decrease of the surface concentration, but our preliminary atomic force microscopy data on the adsorption layers transferred onto a solid surface (not shown) do not support this explanation and display even the formation

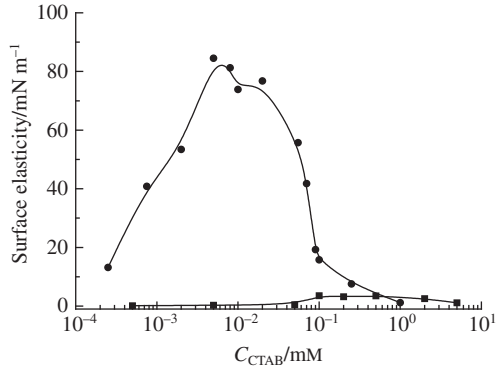

Figure 3 Dynamic surface elasticity as a function of surfactant concentration for (■) pure CTAB and (●) mixed DNA/CTAB solutions.

of bilayers of DNA/surfactant complexes at the interface in this concentration range. Moreover, the neutron reflectivity of similar systems also does not confirm the decrease of the surface concentration at least in the range of transparent solutions.[7,8]

The decrease of the dynamic surface elasticity on growing surfactant concentration has already been observed for the mixed solutions of synthetic polyelectrolytes and surfactants as a result of the formation of microaggregates in the adsorption layer.[11,13] In this case, a new relaxation mechanism appears in the surface layer due to the exchange of polymer segments and surfactant molecules between the aggregates and the surrounding adsorption layer, and the surface elasticity starts to diminish. This relaxation mechanism also leads to the nonmonotonic kinetic dependence of the dynamic surface elasticity when the formation of microaggregates in the surface layer occurs in the course of adsorption. This nonmonotonic kinetic dependence was not previously observed for DNA/CTAB solutions, and the data in Figure 2 do not corroborate this relaxation mechanism. It is more probable that the formation of multilayers results in a looser three-dimensional structure of the adsorption layer as compared with the layers at lower CTAB concentrations, and mechanical relaxation can occur at the expense, for example, of a change in the layer thickness. At the same time, Figures 2 and 3 do not exclude the formation of microaggregates in the surface layer. The high rigidity of DNA molecules (high persistence length) can hinder the matter exchange between different parts of the adsorption layer, and the kinetic dependence of the dynamic surface elasticity can remain monotonic in this case. The results show that the surface dilational rheological properties of DNA/CTAB solutions differ from those of previously studied solutions of complexes between oppositely charged synthetic polyelectrolytes and surfactants and indicate a different mechanism of mechanical relaxation in the surface layer. The observed peculiarities can be connected with the high persistence length of DNA molecules.

This work was supported by the St. Petersburg State University (research grant no. 12.38.241.2014) and the Russian Foundation for Basic Research (project nos. 14-03-00670_a and 15-53-45043 IND_a). The authors are grateful to the Center for Chemical Analysis and Materials Research for the assistance in the DNA sample analysis.

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Received: 18th June 2015; Com. 15/4652