ELSEVIER
Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2008, **18**, 342–344

Mendeleev
Communications

Viscoelasticity of poly(vinylpyridinium chloride)/sodium dodecylsulfate adsorption films at the air–water interface

Alexey G. Bykov,[a] Shi-Yow Lin,[a] Giuseppe Loglio,[b] Reinhard Miller[c] and Boris A. Noskov*[d]

[a] *Chemical Engineering Department, National Taiwan University of Science and Technology, Taipei, 106 Taiwan*
[b] *Dipartimento di Chimica Organica, Universita degli Studi di Firenze, 50019 Sesto Fiorentino, Firenze, Italy*
[c] *MPI für Kolloid- und Grenzflächenforschung, Forschungcampus Golm, D14476 Golm, Germany*
[d] *Department of Chemistry, St. Petersburg State University, 198904 St. Petersburg, Russian Federation. Fax: +7 812 428 6939; e-mail: boris@BN1664.spb.edu*

DOI: 10.1016/j.mencom.2008.11.021

Measurements of the dynamic elasticity of an adsorption film of poly(vinylpyridinium chloride)/sodium dodecylsulfate (PVP/SDS) complexes indicate a structure transition in the film when the surfactant concentration approaches the concentration of PVP monomers and show that the rate of relaxation processes in polyelectrolyte/surfactant adsorption films is determined by the properties of the polymer chain.

Although interest in the solutions of complexes of polyelectrolytes and oppositely charged surfactants arose several decades ago,[1–3] adsorption layers of these systems have been investigated only for the last years.[3–5] The relation between the structure of molecules forming the complexes and the surface properties of the solution remains unclear. Recently, the neutron reflectivity and surface tensiometry data have given an opportunity to define two classes of polyelectrolyte/surfactant solutions, which differ significantly in the thickness of adsorption layer and the shape of adsorption isotherm.[6,7] At the same time, the dependences of surface rheological properties on surfactant concentration for these two classes of systems proved to be similar.[8,9] In this work, the surface rheological properties of mixed adsorption films of poly(vinylpyridinium chloride) (PVP) and sodium dodecylsulfate (SDS) were measured to clarify the influence of small changes in the pattern of interaction between the components on the dynamic surface properties. The transition between the two states corresponding to the above classes of the solution of PVP/SDS is possible by adding small amounts of NaCl.[10]

The measurements of complex dynamic dilational surface elasticity were performed by the oscillating barrier method, based on the simultaneous registration of the surface area harmonic oscillation in a Langmuir through and the corresponding oscillation of the surface tension. The experimental set-ups and procedures were described in detail elsewhere.[11,12]

Before use, SDS (Sigma–Aldrich) was purified by double recrystallization from ethanol. Sodium chloride (Merck) was purified from organic impurities by heating to 800 °C. Polyvinylpyridine (Polysciences) with a molecular weight of 50000 was used as received. For preparation of the solutions polyvinylpyridine was dissolved in an HCl solution at pH 3, then, SDS and hydrochloric acid were added to given concentration and pH values. Note that the hydrolysis of SDS in aqueous solutions can lead to the formation of dodecanol, which is characterized by a high surface activity. As a result, one can observe significant deviations of the surface pressure and elasticity from zero even at SDS concentrations a few orders of magnitude lower than the critical micellar concentration.[13,14] These effects depend on the purity of the original sample due to the autocatalysis of the SDS degradation and thus strongly irreproducible.[15,16] The test experiments showed that the influence of hydrolysis on the surface elasticity of pure SDS solutions did not exceed 30% within 5 h for our samples at least at concentrations lower than 0.1 mM.

All measurements of the solution properties were performed at pH 2 and a constant PVP concentration (0.01 wt%), with and without addition of NaCl. The dependence of the surface tension of mixed solution of PVP/SDS/NaCl (0.1 M) on surfactant concentration c (Figure 1) is close to the corresponding dependence obtained for this system earlier.[10] Deviations of the surface tension from the value for pure water occurred at $c = 10^{-7}$ M, *i.e.*, at a concentration several orders lower than for the solution of pure surfactant, which indicates the formation of PVP/SDS complexes with high surface activity at extremely low concentrations. At concentration $c < \sim 10^{-7}$ M, the equilibration time of the system was too long and measurements were difficult because equilibrium has not been achieved in five hours. In the range of SDS concentration from 10^{-7} to 2×10^{-5} M (Figure 1), the equilibrium surface tension decreased almost by 40 mN m^{-1} and further all changes did not exceed 2 mN m^{-1}. The range of abrupt changes of the slope of the surface tension isotherm usually is associated with the onset of the cooperative formation of surfactant aggregates on the polymer chains and is identified as critical aggregation concentration (CAC).[3,17] Taylor *et al.*[10]

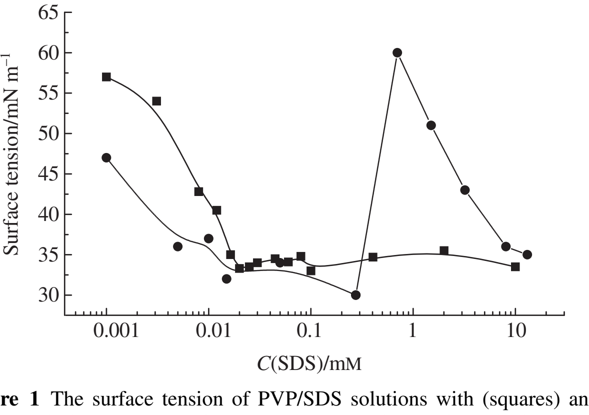

Figure 1 The surface tension of PVP/SDS solutions with (squares) and without (circles) 0.1 M NaCl *vs.* SDS concentration at the polyelectrolyte concentration 0.01 wt% in 5 h after the surface creation.

found the formation of a multilayer structure on the solution surface at $c > 1$ mM using neutron reflection.[10] However, changes in the adsorption layer thickness do not lead to noticeable changes of the surface tension isotherm for PVP/SDS/NaCl (0.1 M) solution, as well as for other systems.[18]

The surface tension isotherm for PVP/SDS solution without NaCl additives (Figure 1) only qualitatively agrees with the published dependence.[10] The discrepancy in the results can be interpreted by different degrees of polyelectrolyte ionization in the solutions, which brought about changes of the own surface activity of PVP. Unfortunately, Taylor *et al.*[10] did not mention the pH value of the investigated solution; therefore, the comparison can be done only qualitatively. At salt addition the ionization degree of the polyelectrolyte decreases, which leads to the weakening of polyelectrolyte–surfactant interaction and, hence, to the increase in surface tension. Therefore, the surface tension for PVP/SDS solutions without salt addition at concentration $c < 10^{-5}$ M is lower than that for the solution of PVP/SDS/NaCl (0.1 M) (Figure 1). A maximum on the surface tension isotherm appears with increasing concentration. This maximum is usually explained by the desorption of polyelectrolyte/surfactant aggregates at the saturation of polyelectrolyte by the surfactants molecules in the bulk solution.[6,19] Note that the precipitation of large aggregates from solution occurs at a concentration of SDS $c_0 \approx 0.7\times10^{-3}$ M, which corresponds to the equimolar ratio between PVP and SDS monomers. A further increase in the SDS concentration the aggregates grow step by step and even precipitate, leading to a temporary surface tension increase. Thereafter, the complexes are displaced by the increasing number of free SDS molecules in the bulk and consequently in the adsorption layer and the surface tension decreases down to values typical of a pure SDS layer. Finally, at $c > 0.01$ M, the surface tension stops changing with concentration and gets close to the surface tension for pure SDS micellar solution; in this case, surface properties become formed mainly by adsorbed surfactant molecules.[6,7]

The dependences of the real part of dynamic surface elasticity on SDS concentration for the investigated systems (Figure 2) are qualitatively close to the corresponding dependences of poly(styrenesulfonate)/dodecyltrimethylammonium bromide[8] (PSS/DTAB) and polydiallyldimethylammonium chloride/sodium dodecylsulfate[9] (PDMDAAC/SDS). In all cases, high dynamic surface elasticity exhibits itself in the range of low surfactant concentration, which at increasing of the concentration after a local maximum decreases abruptly in a narrow concentration range and further on approaches zero. Earlier, the high dynamic surface elasticity in the range of low concentrations was associated with the formation of two-dimensional structure in the surface layer both due to electrostatic interactions and segment–hydrocarbon tail of a surfactant molecule or segment–segment hydrophobic interactions that lead to the formation of two-dimensional nano- and microaggregates.[8,9] At concentrations two or three times lower than c_0, this structure decomposes and three-dimensional aggregates start to form in the surface layer. The adsorption film becomes loose and the surface elasticity decreases abruptly. The formation of three-dimensional aggregates (microgel) is confirmed by the strong increase of the ellipsometric signal due to the light scattering by aggregates in the surface layer at concentrations higher than the region of surface elasticity decrease.[9,20] At further increasing surfactant concentration complexes gradually desorb, the adsorption film grows enriched with free surfactant molecules and the surface elasticity approaches zero at frequencies less than 1 Hz. Results received in this work (Figure 2) can be explained in the same way. Particularly, one can assume that the surface elasticity decrease at $c \approx 1.6\times10^{-5}$ M for PVP/SDS/NaCl solution and at $c \approx 10^{-5}$ M for PVP/SDS solutions results from the formation of three-dimensional aggregates in the surface layer.

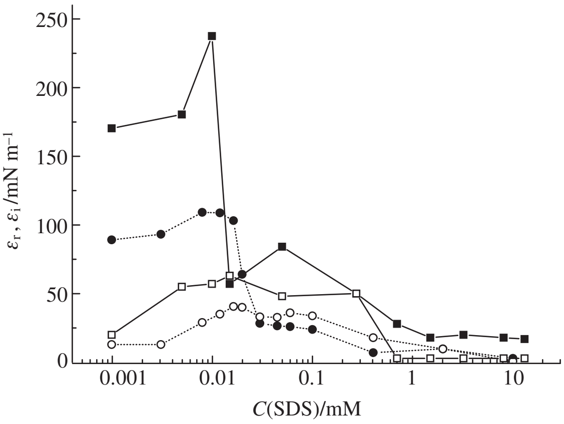

Figure 2 Concentration dependence of the real (solid symbols) and imaginary (open symbols) parts of the dynamic surface elasticity of PVP (0.01 wt%)/SDS with (circles) and without (squares) 0.1 M NaCl at the frequency of 0.14 Hz.

Despite that the dependences of the dynamic surface elasticity on concentration proved to be qualitatively the same for all investigated systems, the absolute values of the surface elasticity modulus are different. If in the range of local maximum the dynamic surface elasticity moduli for PVP/SDS/NaCl and PSS/DTAB solutions are close to each other (~110 mN m^{-1}), they are higher (~140 mN m^{-1}) for PSS/DTAB solution and anomalously high (~240 mN m^{-1}) for PVP/SDS solution. This indicates the influence of non-electrostatic factors, like the degree of hydrophobicity of polymer segments and the own rigidity of polymer molecules. At the same time, the difference between the two systems can be connected, at least partially, with the difference in the ionic strength of the solution. The addition of electrolyte (NaCl) screens the electrostatic repulsion between polyelectrolyte segments of the same charge, which leads to a decreased effective rigidity of the polymer chains and hence, to lower surface elasticity.

The main peculiarity of the system under investigation consists in the relatively high imaginary part of the complex surface elasticity, which for PVP/SDS/NaCl solution in the concentration range from 2×10^{-4} to 10^{-3} M is higher than the real part. The imaginary part is much lower than the real one for PSS/DTAB solutions and the adsorption film proves to be essentially elastic.[8] The imaginary part approaches the real one for PDMDAAC/SDS solutions only in a narrow concentration range.[9] The ratio of the two parts of the dynamic surface elasticity for PVP/SDS solutions is close to unity in the concentration range from 2×10^{-4} to 10^{-3} M and the adsorption film turns out to be viscoelastic at a frequency of 0.14 Hz. This means that relaxation processes with a charac-

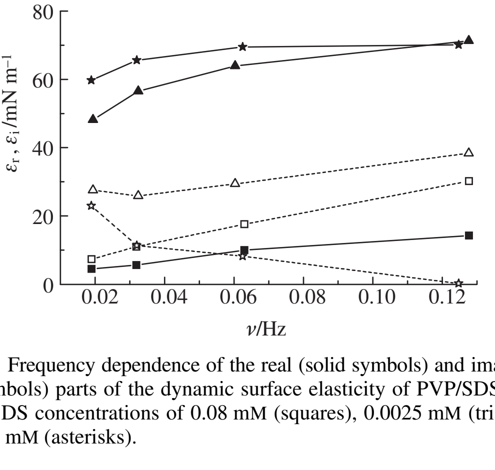

Figure 3 Frequency dependence of the real (solid symbols) and imaginary (open symbols) parts of the dynamic surface elasticity of PVP/SDS/0.1 M NaCl at SDS concentrations of 0.08 mM (squares), 0.0025 mM (triangles) and 0.001 mM (asterisks).

teristic time comparable with the period of the surface area oscillations, *i.e.*, $\tau \sim 10$ s, occur in the system. Indeed, the two parts of the dynamic surface elasticity strongly depend on the frequency of oscillation only at 2×10^{-5} M $< c < 10^{-3}$ M (Figure 3). A comparison between previously investigated polyelectrolyte/surfactant solutions show that the main relaxation time of the adsorption film depends on the properties of polyelectrolyte and determines its viscoelasticity. If one takes into account that the adsorption film is microheterogeneous in a broad concentration range, the relaxation processes can be attributed to the exchange of components between different surface microphases, and, hence, to the aggregate stability in the surface layer.

This work was supported by the National Taiwan University of Science and Technology (project no. NTUST-2007-R-06), the National Science Council of Taiwan and the Russian Foundation for Basic Research (joint project nos. 05-03-90580 and 08-03-00207), and the programme of the President of the Russian Federation ‘Leading Scientific Schools’ (NSh-3020.2008.3).

References

1 *Interaction of Surfactants with Polymers and Proteins*, eds. E. D. Goddard and K. P. Ananthapadmanabhan, CRC Press, Boca Raton, FL, 1993.

2 *Polymer-Surfactant Systems, Surfactant Science Series*, ed. J. C. T. Kwak, Marcel Dekker, New York, 1998, vol. 77.

3 E. D. Goddard, *Colloid Interface Sci.*, 2002, **256**, 228.

4 E. D. Goddard, *Colloid Surf.*, 1986, **19**, 255.

5 V. G. Babak and J. Desbrieres, *Colloid Polym. Sci.*, 2006, **284**, 745.

6 J. Penfold, R. K. Thomas and D. J. F. Taylor, *Curr. Opin. Colloid Interface Sci.*, 2006, **11**, 337.

7 D. J. F. Taylor, R. K. Thomas and J. Penfold, *Adv. Colloid Interface Sci.*, 2007, **132**, 69.

8 B. A. Noskov, G. Loglio and R. Miller, *J. Phys. Chem. B*, 2004, **108**, 18615.

9 B. A. Noskov, D. O. Grigoriev, S.-Y. Lin, G. Loglio and R. Miller, *Langmuir*, 2007, **23**, 9641.

10 D. J. F. Taylor, R. K. Thomas, J. D. Hines, K. Humphreys and J. Penfold, *Langmuir*, 2002, **18**, 9783.

11 A. V. Akentiev and B. A. Noskov, *Kolloidn. Zh.*, 2002, **64**, 149 (*Colloid J.*, 2002, **64**, 129).

12 B. A. Noskov, A. V. Akentiev, A. Yu. Bilibin, I. M. Zorin and R. Miller, *Adv. Colloid Interface Sci.*, 2003, **104**, 245.

13 V. G. Babak and J. Desbrières, *Mendeleev Commun.*, 2004, 66.

14 V. G. Babak and J. Desbrières, *Mendeleev Commun.*, 2005, 35.

15 K. Lunkenheimer and G. Czichocki, *Colloid Interface Sci.*, 1993, **160**, 509.

16 K. J. Mysels, *Langmuir*, 1986, **2**, 423.

17 E. D. Goddard, *Am. Oil Chem. Soc.*, 1994, **71**, 1.

18 N. J. Jain, P. A. Albouy and D. Langevin, *Langmuir*, 2003, **19**, 8371.

19 E. Staples, I. Tucker, N. Warren and R. K. Thomas, *Langmuir*, 2002, **18**, 5147.

20 C. Monteux, C. E. Williams, J. Meunier, O. Anthony and V. Bergeron, *Langmuir*, 2004, **20**, 57.

Received: 21st April 2008; Com. 08/3127