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2003 J. Phys.: Condens. Matter 15 S219

(http://iopscience.iop.org/0953-8984/15/1/328)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) S219–S224 PII: S0953-8984(03)55272-9

Polyelectrolyte–surfactant complexes at interfaces and in bulk

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Received 28 October 2002
Published 16 December 2002
Online at stacks.iop.org/JPhysCM/15/S219

Abstract

We have investigated the interactions between anionic polyelectrolytes and a cationic surfactant at the air/water interface and in bulk, for increasing surfactant concentrations. Mixed aggregates are formed at the air/water surface at extremely low surfactant concentrations. Above a critical aggregation concentration, a viscosity drop indicates that polymer chains undergo a rapid collapse. At higher surfactant concentrations, light scattering shows the existence of larger structures, which are surprisingly monodisperse. Their size increases with surfactant concentration. During this bulk evolution, surface tension remains constant, suggesting that the surface aggregates remain unchanged.

1. Introduction

Interaction between polymers and surfactants is an important field of interest [1]. In particular, mixed aqueous solutions have been extensively studied but are far from being completely understood. Their properties strongly depend on the polymer and surfactant types, leading to different macroscopic behaviours.

In the case of polyelectrolyte and surfactant of opposite charge, the electrical charges play an important role, which still needs to be investigated. Previous studies on surface rheology and foam stability [2] of such solutions also evidenced the role of the polymer backbone flexibility. In this paper, we first present results on adsorption at the air/water interface of polyelectrolytes/DTAB mixtures for polymers of different backbone rigidity. Moreover, because complexation in bulk or at a surface is generally related, we also describe several bulk properties of these solutions.

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0953-8984/03/010219+06$30.00

2. Materials and methods

Here, we have used dodecyltrimethylammonium bromide (DTAB), a cationic surfactant. It was recrystallized three times before use. Two water-soluble linear anionic polyelectrolytes are used: sodium carboxymethylcellulose (carboxyMC) and DNA. CarboxyMC is a block copolymer [3] with random partial substitution of the hydroxyl groups by hydrophilic carboxymethyl groups. The fraction of ionized monomers (degree of substitution DS) is 1.23, leading to counterion condensation. Mononucleosomal calf thymus DNA was prepared by digestion of nucleosomal DNA [4], leading to monodisperse fragments containing 146 base pairs. We have added 20 mM NaBr in the DNA solutions in order to avoid unbinding of the double-helix strands. DNA has a rigid backbone with an intrinsic persistence length $l_p^{int} = 50$ nm; carboxyMC is more flexible ($l_p^{int} \sim 10$ nm). The actual persistence lengths are larger because they contain a contribution of the electrostatic charges, which decreases when salt is added. Most of the experiments reported here will be related to carboxyMC and more details can be found in [5]. More data on other polymers will be given in forthcoming publications.

Surface tension experiments were performed at room temperature (20–25 °C) using a Wilhelmy method (open frame) or a pendant drop tensiometer. The viscosity of the solutions was measured using capillaries. Quasi-elastic and static light scattering measurements have been performed on a spectrometer using a vertically polarized argon-ion laser ($\lambda = 514.5$ nm). The temperature was controlled at 25 °C. The scattered light was detected at scattering angles ranging from 30° to 150°. Using a correlator we deduced the normalized scattered electric field autocorrelation function $g(t)$ and calculated a diffusion coefficient $D(q) = 1/\tau q^2$, with τ the characteristic decay time of $g(t)$.

3. Experimental results and discussion

3.1. Surface properties

The polymer concentration C_p is 0.127 g l^{-1} for carboxyMC and 0.35 g l^{-1} for DNA. The adsorption kinetics of the mixed and pure surfactant solutions were studied while varying the surfactant concentration C_S; the equilibrium surface tensions are plotted in figure 1. Surface tensions of the mixed solutions are well below the pure surfactant ones, underlining strong interactions between DTAB and the polymers at the surface even at very low surfactant concentrations. This surface tension lowering results from polymer and surfactant adsorption at the surface caused by electrostatic interactions between the polyanion and the cationic surfactant. The surface tension levels off above the critical aggregation concentration (CAC) and the gap between CAC and CMC is a measure of the strength of the attraction between polymer and surfactants. For carboxyMC, the CAC plateau is much larger than for DNA (almost two surfactant concentration decades). This is as expected from the difference in backbone rigidity, the flexible chains being able to wrap around surfactant micellar aggregates and rigid ones not [6]. At higher concentrations, the surface tension approaches that of the pure surfactant solutions, meaning that the surface layer probably only contains surfactant.

3.2. Bulk properties

It is accepted that cooperative complexation in bulk starts at the CAC (0.1 mM for carboxyMC and 0.9 mM for DNA), far below the critical micelle concentration (CMC) of the surfactant (15 mM for DTAB). At this stage, micelles may start to form [7] and decorate the carboxyMC

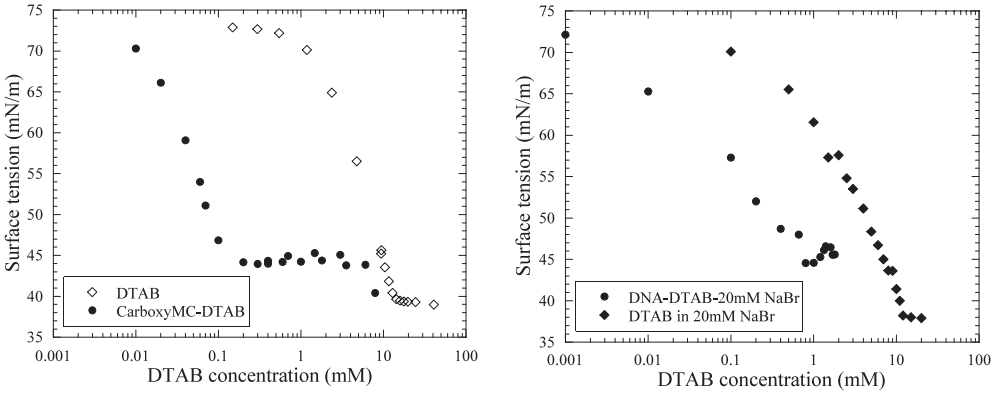

Figure 1. Equilibrium surface tensions of mixed carboxyMC/DTAB (left) and DNA/DTAB/20 mM NaBr (right) layers versus C_S.

chains [8], whereas the microstructure of the aggregates is unknown for DNA. When the surfactant concentration is increased, the solutions evolve from clear to cloudy and undergo a macroscopic associative phase separation (9 mM for carboxyMC, 2.1 mM for DNA). Furthermore, no precipitate redissolution occurs, even up to twice the CMC. This is as observed for other polyelectrolytes with a high charge density [9].

At the carboxyMC concentrations used, the pure polymer solutions are in the semi-dilute regime, where polymer chains overlap but do not entangle and the solution viscosities are not high. In the concentration range studied, the viscosity of the pure surfactant solutions is equal to that of water. Then, any change in viscosity will reflect a change in polymer chain conformation (extension or shrinkage). For surfactant-free (or salt-free) solutions, the polyelectrolyte chains are in an extended conformation. When surfactant (or salt) is added, the viscosity decreases from the pure polymer solution value down to that of water. For all concentrations and especially below CAC, the viscosity with DTAB is below that with salt (figure 2, left), showing that a small amount of surfactant is more efficient than salt for recoiling the chains. This may be due to the additional hydrophobic effects. Above 0.1 mM for carboxyMC, the polymer/salt solution viscosity decreases: salt screens the electrostatic repulsions between the polymer charges; the reduction in chain size is such that they no longer overlap. The chain undergoes a shrinkage process, equivalent to a partial collapse phenomenon [10], less rapid with salt than with surfactant. Then, the viscosity evolves from the semi-dilute to the dilute regime and decreases accordingly. The viscosity reaches a value close to that of water around $C_S = 1$ mM but no turbidity is observed yet. The viscosity decrease is therefore not due to the precipitation of the complexes. This chain collapse above the CAC is similar to that found for other polymers and in particular for long DNA chains with DTAB (figure 2, right). The DNA chain starts from an extended conformation at low DTAB concentration and evolves towards a globular state at high C_S. In addition, coexistence of coils and globules clearly appears at intermediate concentrations [11]. This phenomenon does not occur for the very rigid polymers, in particular for the short DNA fragments also used in this study (the length of the DNA corresponds to the persistence length).

The polymer conformation depends on l_p, which is also affected by the electrostatic repulsions in the polyelectrolyte chain itself. Our choice of a low polymer concentration allowed us to start from semi-dilute carboxyMC solutions and to reach easily a conformation of isolated polymer globules by adding surfactant. Since the interaction between the polymer

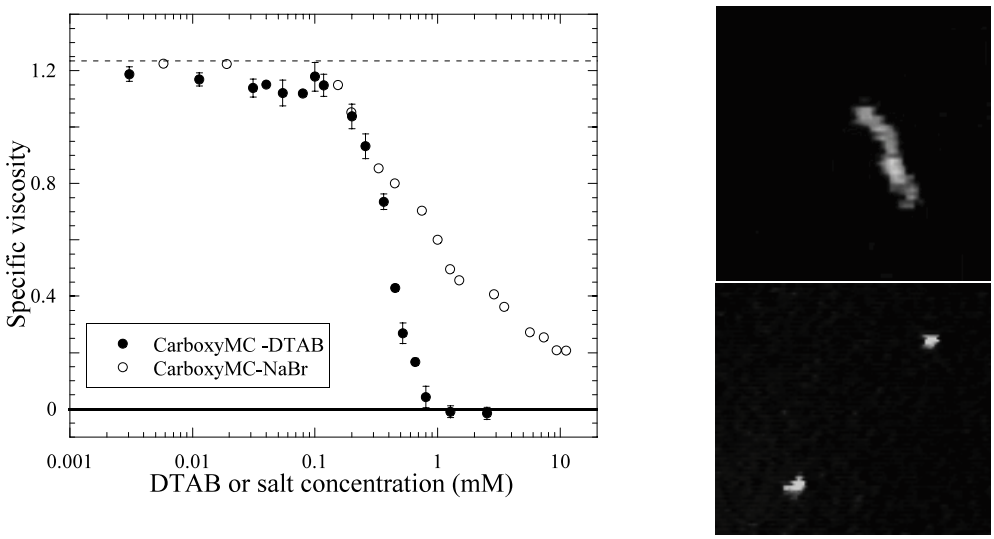

Figure 2. Left: specific viscosity of polymer aqueous solutions $(\eta - \eta_0)/\eta_0$, η_0 being the water viscosity, as a function of added surfactant or salt concentration at 26 °C. The dashed line corresponds to the polymer alone, the full line to water. Right: fluorescence images of T4 DNA molecules (166 000 base pairs); top: DNA in 20 mM NaBr solution, moving freely in solution; bottom: DNA in 1.9 mM DTAB, 20 mM NaBr, DNA is in a globular conformation [12].

and surfactant is dependent on C_S, the structure of the polymer/surfactant complex might also depend on C_S: polymer chains decorated by micelles close to the CAC, possibly evolving towards a denser packing of micelles linked by the polymer chains as in assemblies of neutral/polyelectrolyte diblock copolymers and DTAB [13]. In the case of DNA, the microstructure is still unknown, even at the CAC.

3.3. The vicinity of the precipitation boundary

By using dynamic light scattering before the precipitation zone ($C_S < 9$ mM for carboxyMC and $C_S < 2.1$ mM for DNA) we have obtained information on the origin of the turbidity increase in the solutions. The autocorrelation functions $g(q, t)$ (figure 3) are single-exponential functions. The same diffusion coefficient is deduced at each scattering angle. Because the diffusion coefficient $D(q)$ is independent of scattering vector, no internal modes are present, the objects are rigid-like. The diffusion coefficient D decreases when DTAB concentration increases. Assuming that scattering is due to polymer/surfactant aggregates, and applying the Stokes–Einstein formula, we deduced their hydrodynamic radius R_H. The hydrodynamic radius increases with C_S, $C_S >$ CAC (figure 4). The size of the complexes does not change over periods of months. For carboxyMC, the smallest value corresponds to the size of the polymer chain in concentrated salt solution (1 M NaBr), i.e. the size of the collapsed chain, confirming the collapse mechanism postulated above. For DNA, the smallest value corresponds to a rod with a length equal to the persistence length as expected. The larger sizes correspond to aggregates containing more than one chain. Complementary light scattering determinations (aggregate gyration radius and volume for carboxyMC) [5] showed that the aggregates are spherical.

The remarkable monodispersity of the aggregates is not observed for carboxyMC at the smallest concentrations: the autocorrelation function is not a single exponential and the relaxation time distribution is relatively broad.

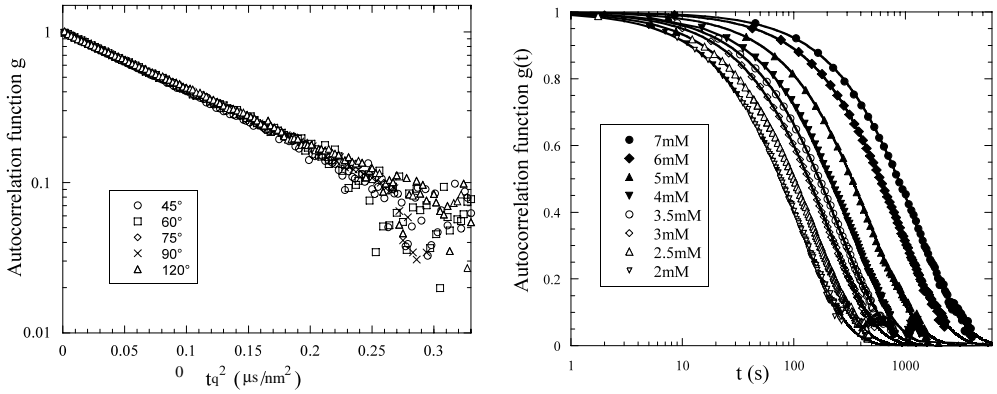

Figure 3. Left: autocorrelation functions for a 4 mM DTAB/carboxyMC solution, at different scattering angles, versus tq^2. Right: autocorrelation functions of the same system for different DTAB concentrations. The curves are single-exponential fits.

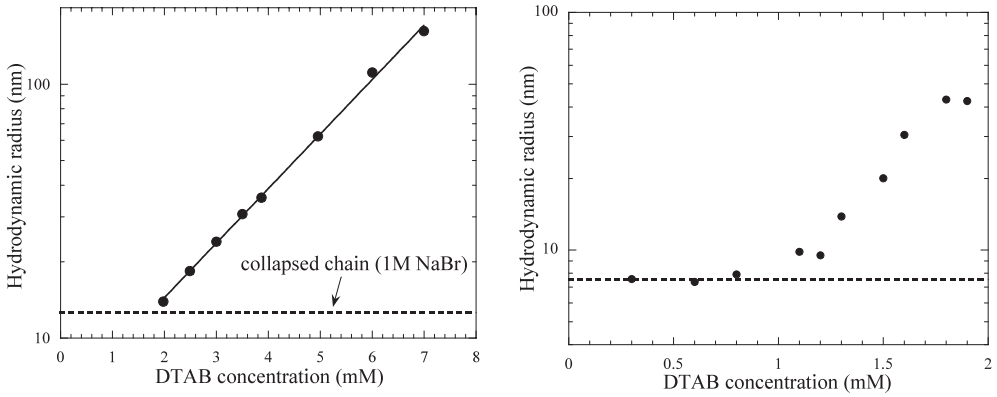

Figure 4. Evolution of apparent hydrodynamic radii of the aggregates. Left: carboxyMC/DTAB system. The full line is an exponential fitting. Right: DNA/DTAB system. The dotted line corresponds to the R_H-value of the rod-like DNA, whose length is the persistence length.

This concentration range, where the viscosity drops and in which we observe broad size distributions, could correspond to the range where coexistence of globules and more or less extended structures was shown in the DTAB/long DNA system. Upon increasing C_S, the width of the distribution decreases until the regime of single-exponential decay of $g(t)$ is reached. It is remarkable that the aggregates are monodisperse, even for carboxyMC, although the chain distribution is rather broad. It is then obvious that the size and the shape of the aggregates are only determined by a specific surfactant organization. Similar well-defined aggregates controlled by electrostatic interactions have recently been described (aggregates of block copolymers and DTAB [13], of anionic and cationic surfactants [14], of DNA and lipids [15]). Neutron scattering experiments are in progress to improve our knowledge of the microstructures of the studied aggregates.

4. Conclusions

Adding a cationic surfactant to a polyelectrolyte of opposite charge can dramatically alter the physical properties of the solution. We evidenced strong interactions between DTAB and polyanions of different backbone rigidities. At the interface, a surface tension lowering due to coadsorption occurs, although the polymers are non-surface-active alone. Complexation occurs at the interface even at very low surfactant concentrations. In the bulk, a strong cooperative binding process of surfactant and polymer occurs at the CAC: in the case of carboxyMC, the complexes are polymer chains decorated by surfactant micelles. Above CAC, a rapid collapse process of the flexible polyelectrolyte chains induced by surfactant occurs until the size of the collapsed polymer chain is reached. Afterwards, a growth of polymer/surfactant complexes is observed until the precipitation boundary is reached. The bulk complexes are remarkably monodisperse, although the polymer itself can be far from well defined in length. Rigid polymers such as our short DNA fragments do not undergo the collapse phase. Very flexible polymers, such as polyacrylamide sulfonate, despite showing the collapse phase, and forming the large polymer/surfactant aggregates like carboxyMC and DNA, do not show precipitation when the polymer concentration is comparable to those used here (around 100 ppm). Precipitation is only observed in more concentrated polymer solutions [16]. More work is under way to provide an understanding of the role of the polymer backbone rigidity and to elucidate the microstructures of these original monodisperse aggregates, which form before the precipitation boundary.

Acknowledgments

We thank S Désert for his assistance with light scattering measurements (SCM/CEA-Saclay) and F Livolant's group for allowing preparation of DNA to be carried out in her laboratory.

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