Colloids and Surfaces A: Physicochem. Eng. Aspects 368 (2010) 84–90

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Surfactant effects on colloidal interactions: Concentrated micellar solutions of nonionic surfactant

M. Nayeri, R. Karlsson, J. Bergenholtz*

Department of Chemistry, University of Gothenburg, SE-412 96, Göteborg, Sweden

ARTICLE INFO

Article history:
Received 16 April 2010
Received in revised form 6 July 2010
Accepted 15 July 2010
Available online 23 July 2010

Keywords:
Total internal reflection microscopy
Latex
Nonionic surfactant
Micelles
Colloid stability
Interaction potential
Triton X-100
$C_{12}E_5$

ABSTRACT

The effect of nonionic surfactants on interaction energies between polystyrene latex or silica spheres and a flat glass surface has been studied using total internal reflection microscopy (TIRM). The measurements reveal that both Triton X-100 and $C_{12}E_5$ contribute to the Debye screening length, an effect that is essentially removed on first exposing the surfactants to ion-exchange resin. Whereas particles can be embedded in Triton X-100 concentrations at least as high as 285 times the critical micelle concentration, the same particles become elastically tethered at intermediate separations from the glass surface in somewhat less concentrated micellar solutions of $C_{12}E_5$. The elastic energy is caused by a connecting structure between the particle and glass surface, which remains intact on dilution and on lowering the ionic strength of the solvent.

1. Introduction

Surfactants are widely used for modifying the surface chemistry of colloidal particles [1,2], for imparting extra stability to dispersions [3,4], and, more generally, for tuning colloidal interactions [5,6]. In this context nonionic surfactants play an important role because many times the interactions of ionic surfactants, their micellar solutions or mesophases with charge-stabilized colloidal particles are too strong, leaving limited regions of miscibility [7–10]. Systems of oppositely charged particles and surfactant typically require bilayer-structured adsorption of surfactant to produce some limited stability against aggregation [7] and like-charged particles and surfactants demix at rather modest concentrations [8,11–13]. In contrast, small colloidal particles can be embedded in solutions of nonionic surfactant, even fairly concentrated ones [9,14–16]. Such nonionic surfactants, being relatively insensitive to ionic strength and pH, provide a robust means for sterically stabilizing colloidal particles through adsorption [17–19]. However, the interaction becomes temperature dependent [14,20], following roughly the behavior of the neat surfactant solution.

The stabilizing effect adsorption of nonionic surfactant has on colloidal particles is well known [3,17–19,21], as is the depletion interaction that may set in beyond the critical micelle concentration (CMC) in somewhat more concentrated surfactant solutions [5,22,23]. More generally, however, colloidal stability and interactions are expected to be sensitive to the presence of microstructure around them [8,14,24]. For example, once colloidal surfaces are saturated by surfactant, further interaction with a structured surroundings composed of the same surfactant is expected to be unfavorable. Indeed, colloidal particles partition preferentially in less structured phases in phase separated systems, as is found for instance in depletion-induced phase separation. One may expect also that the interactions among colloids should depend on the type and density of structures formed in the surrounding solvent [25] and that more complex behavior is exhibited when, e.g., more complex micellar structures are formed. Such structural forces owing to charged globular micelles have been observed indirectly [26] and directly in surface forces measurements [27–29]. While the effect of nonionic surfactant on interaction forces have been studied for concentrations around the CMC, showing that the nature of the surface is important and that the surfactant has little effect on the electrostatic screening [30–32], data on more concentrated nonionic surfactant solutions are scarce.

Rutland and Christenson [33] report a long-range repulsion at surfactant concentrations far exceeding the CMC but still in the micellar (L_1) phase, which remains unexplained. These measurements were made with the surface forces apparatus (SFA), which provides exquisite distance resolution but detects rather

---

* Corresponding author. Tel.: +46 31 786 9078; fax: +46 31 772 1394.
E-mail address: jbergen@chem.gu.se (J. Bergenholtz).

0927-7757/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2010.07.016

large forces. An alternative technique for directly studying interactions is total internal reflection microscopy (TIRM) [34,35]. It is ideally suited for detecting the weak interactions (of order k_BT) most relevant to colloidal stability. This has been amply demonstrated in studies of, e.g., electrostatic [36–39], depletion [40–45], and steric interactions [46,47], as well as interactions mediated by critical fluctuations in the solvent [48]. In this work we probe the effect of bulk solution structure on colloidal-level interactions by TIRM. We examine the interaction between a colloidal sphere and a plane glass surface in aqueous solutions of nonionic surfactants. In one case the surfactant is known to form small globular micelles [49,50] and in the other case studied the surfactant forms threadlike micelles on increasing concentration [51–53]. The focus of the study is the effect of large surfactant concentrations, far in excess of the CMC, up to ≈300 × CMC, where the particle–surface separations may presumably be brought in proximity of microstructural length scales of significance in the micellar system.

In what follows, we begin by describing the in-house-built TIRM instrument, which is based on set-ups described in the literature [39,54–56]. Results are then presented for interaction energies in the presence of concentrated micellar solutions of the surfactants Triton X-100 and $C_{12}E_5$. The sensitivity of the technique reveals that both of these contribute to the ionic strength of the solution, an effect that is removed through ion exchange. We find that particles can be kept suspended above glass surfaces in high concentrations of Triton X-100 but that particles become elastically tethered at intermediate separations in $C_{12}E_5$ solutions for concentrations exceeding about 6 mM.

2. Experimental

2.1. Reagents and sample preparation

The nonionic surfactant *t*-octylphenoxy polyethoxy ethanol with an average of 9.5 ethylene oxide units per molecule (Triton X-100, TX-100), which is a Dow Chemicals product, was obtained from MP Biomedicals. Penta(ethylene glycol) dodecylether ($C_{12}E_5$) was obtained from Nikko Chemicals. Both surfactants were either used as received, or, following Oberdisse and Porte [57], aqueous stock solutions of surfactant were placed in contact with a mixed-bed ion-exchange resin (Amberlite IRN-150, Sigma–Aldrich) until a constant conductivity was measured. Oberdisse and Porte have found surfactant loss during ion exchange to be less than 2%. MilliQ water, filtered using 0.45 μm Nylon syringe filters (Acrodisc, Pall), was used in preparing all dispersions and surfactant solutions. In addition, in preparing $C_{12}E_5$ solutions, nitrogen gas was first bubbled through the solvent to minimize the aging that has been reported for $C_{12}E_5$ solutions in contact with air [58,59]. Solutions were usually used in measurements within one or two days. In a few cases, systems were fluorescently labeled using FM1-43 (Molecular Probes, Invitrogen), a predominantly hydrophobic molecule that fluoresces when embedded in apolar environments. Solutions of FM1-43 were introduced in the sample cell after flushing the cell with salt solutions of the same ionic strength as used in preparation of samples.

The TIRM measurements were done on crosslinked spherical polystyrene particles with a diameter of 10.0 ± 0.4 μm (Polysciences Inc.). They were obtained as a stock dispersion at a weight concentration of 2.64%. According to the manufacturer, these are stabilized by strongly acidic sulfate groups and a minimal amount of surfactant is present in the stock dispersion. Measurements were also made on silica spheres with a nominal diameter of 5.00 ± 0.35 μm (Sigma–Aldrich), which were received as a 5 wt% aqueous dispersion. Since TIRM operates on single particles, it is necessary to ensure that very few particles enter the TIRM cell.

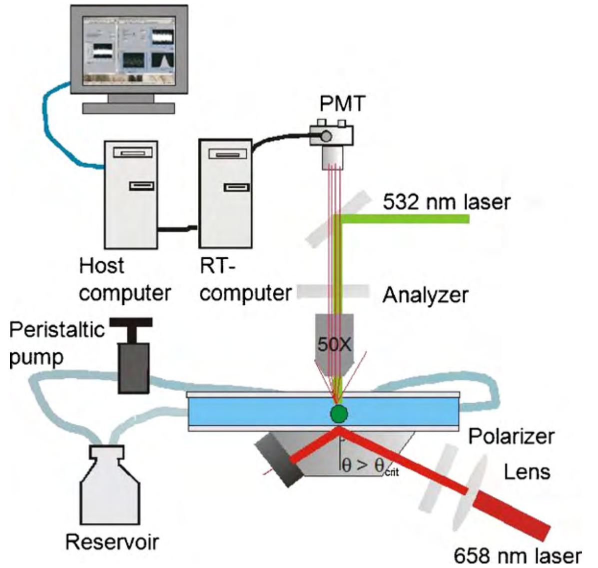

Fig. 1. Schematic drawing of the experimental TIRM set-up used in this work and as described in the text.

Typically 30 mL of stock dispersion, diluted to concentrations of approximately 1×10^{-7}, was added to a reservoir connected by tubing to the TIRM sample cell. To introduce surfactant, aliquots of concentrated (L_1) surfactant solution were added to the reservoir, in this way raising the surfactant concentration in steps. Homogeneous solutions were obtained after stirring the contents of the reservoir and pumping the solution through while keeping a particle in place with an optical tweezer (see below). Low-iron, soda lime glass slides (Fisher's Finest Premium, Fisher Scientific) serve as surfaces in the experiments. They were soaked for 1 h in pH 14 NaOH solution after which they were rinsed with copious amounts of water and ethanol and finally dried.

2.2. Methods

Refractive index measurements on surfactant solutions at different concentrations were made at a wavelength of $\lambda \approx 680$ nm with a Reichert AR600 (Leica). These are required, at least in principle, for determining the proper decay length β^{-1} of the evanescent scattering by the particle through [60],

$$\beta = \frac{4\pi}{\lambda}\sqrt{\left(n_1 \sin\theta\right)^2 - n_2^2} \qquad (1)$$

where λ is the vacuum wavelength of the light source and n_1 and n_2 are the refractive indices of the glass slide and the solvent in the cell, respectively. For the TX-100 solutions a refractive index increment of 0.130 cm^3/g was extracted from near-linear refractive index data as a function of surfactant concentration. An identical analysis for $C_{12}E_5$ solutions resulted in a refractive index increment of 0.125 cm^3/g, which is in reasonable agreement with data in the literature [32,61]. From these values and Eq. (1) one concludes that neglecting surfactant effects on the refractive index results in separation distances in error by no more than ≈3 nm at the highest surfactant concentrations. For fluorescence microscopy a Leica DMI6000B inverted fluorescence microscope was used. A mercury arc lamp was used in conjunction with the I3 Leica filtercube in order to excite the FM1-43 dye.

The TIRM measurements were made with an in-house-built instrument, shown schematically in Fig. 1. The present design is based on descriptions of TIRM set-ups in the literature [39,54–56]. A Zeiss Axiolab-A microscope with a Zeiss Epiplan 50×-magnification, long-working-distance objective serves as