Selective co-deposition of anionic silica particles at hydrophobic surfaces from formulations of oppositely charged polymers and surfactants

Wei Wang [a,1], Eric S. Johnson [b], Tommy Nylander [a], Pete Ellingson [c], Beth Schubert [c], Lennart Piculell [a,*]

[a] Physical Chemistry, Kemicentrum, Lund University, Box 124, SE-221 00 Lund, Sweden
[b] Procter & Gamble, Sharon Woods Technical Center, 11511, Reed Hartman Highway, Cincinnati, OH 45241-2422, USA
[c] Procter & Gamble, Winton Hill Business Center, 6100 Center Hill Avenue, Cincinnati, OH 45224, USA

G R A P H I C A L   A B S T R A C T

Amphiphilic polyions selectively mediate "mismatched" co-deposition of hydrophobic particles on charged surfaces and *vice versa*
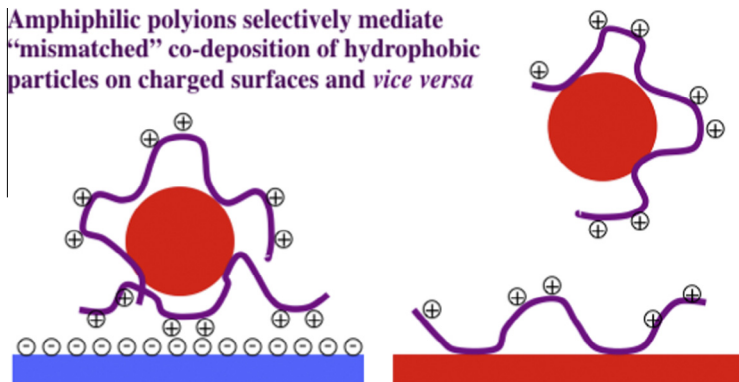
A B S T R A C T

The surface-selective surface deposition of anionic hydrophilic silica particles from aqueous polymer–surfactant formulations was investigated by in-situ null-ellipsometry. The formulations, with or without silica particles, contained anionic sodium dodecylsulfate (SDS) and a cationic polymer, cationic hydroxyethyl cellulose (cat-HEC) or a copolymer of acrylamide and methacrylamidopropyl trimethylammonium chloride (AAm/MAPTAC). Surface deposition from the formulations onto model surfaces of either anionic hydrophilic, or hydrophobized, silica was induced by controlled dilution of the formulations into the coacervation region, and was monitored with time by ellipsometry. The dilution simulated a rinsing process in a typical application. In all cases a steady-state surface layer remained after extensive dilution. An enhanced deposition from the silica-containing formulations was found on the hydrophobized silica surface, indicating a substantial co-deposition of silica particles. Much less co-deposition, or none at all, was found on hydrophilic silica. The opposite trend, enhanced co-deposition on hydrophilic silica, was previously found in similar experiments with hydrophobic silicone oil droplets as co-deposants (Clauzel et al., 2011). The amphiphilic cationic polymers evidently favor a "mismatched" co-deposition of anionic particles to hydrophobic surfaces, or *vice versa*. The findings suggest a strategy for surface-specific delivery of particles to surfaces.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Modern personal care and detergent formulations should ideally perform a complex series of tasks at a target surface (hair, fabric) [1–3]. Typically, the formulation should first clean the surface, by removing soil. At a later stage, however, certain benefit agents should deposit from the formulation onto the surface. These agents could be, for instance, a perfume or a conditioning agent, such as a cationic polymer or silicone oil [1,2,4–6]. At the next level of performance, these benefit agents should be deposited *selectively* at certain target surfaces [7,8]. Taking hair-care as an example, one would like to deposit conditioning agents selectively to damaged parts of the hair to provide conditioning where it is needed the most.

A strategy commonly used to achieve the above performance is based on the well-known complexation and associative phase separation ("coacervation") that take place in aqueous mixtures of charged surfactants with polyions of opposite charge (see several recent reviews [9–13]). Thus, to a formulation that contains a large concentration of a cleaning anionic surfactant, one adds a cationic polymer at a concentration much inferior, on a charge equivalence basis, to that of the anionic surfactant. If certain criteria of the polycation and the surfactant are met, net negatively charged soluble complexes, containing excess surfactant, are formed in such a system [14–18]. In systems containing sufficiently hydrophobic polycations, which are able to bind excess surfactant by hydrophobic association, detailed phase diagram studies indicate that these complexes are thermodynamically stable [16,17]. However, owing to the strong attraction between the oppositely charged "macroions" (the polycation and the surfactant aggregate), kinetically trapped stable dispersions can also be produced for many systems in a region of excess surfactant, depending on the details of the mixing process [18–21]. In either case, when the formulation is diluted, as in a rinsing step in a cleaning application, the bulk surfactant concentration will decrease and the excess surfactant will gradually leave the complex in accordance with the surfactant–polyion binding isotherm. At some point, the net charge of the complex becomes sufficiently low so that an associative phase separation occurs, and a concentrated "coacervate" phase separates out of the solution [1]. This phase separation by dilution can give rise to an enhanced surface deposition, as has been confirmed in several previous studies, involving a number of different polycations, on both negatively charged and hydrophobic surfaces [8,22–27].

The surface-depositing coacervate can, furthermore, be used as a vehicle to co-deposit other particles in the formulation, which should carry out specific beneficial functions at the surface [1,6]. The underlying idea is that the polyion–surfactant complexes should adsorb at the particle surface and, eventually, give rise to a particle–surface attraction. Again, studies of model systems have shown that this strategy works, but that the quantitative success of the co-deposition depends strongly on the detailed choice of the polyion [8,24]. Basically, the polycation has to be slightly hydrophobic in order to bind an excess of anionic surfactant, but if it is too hydrophobic, it binds surfactant too willingly, and the region of phase separation and strong deposition becomes too narrow for practical purposes.

The aim with the present study is to obtain a better molecular understanding of the co-deposition phenomenon, which can serve as a guide to optimize the formulations to obtain selective deposition of particles depending on the properties of the surface. In a recent study from our laboratories, we investigated polycation–surfactant deposition and co-deposition of silicone oil droplets on both hydrophilic (anionic) silica and hydrophobized silica, for formulations of a range of different polyions of differing hydrophobicity [8]. A striking observation was that both the polymer–surfactant deposition, and the co-deposition of silicone oil droplets, were quantitatively different on hydrophobic and hydrophilic surfaces. Specifically, it was found that for some of the polyions, a co-deposition of the *hydrophobic* silicone oil seemed to occur selectively to the *hydrophilic* silica surface, but not to the hydrophobized surface. This remarkable finding suggests that one may indeed obtain a selective co-deposition at certain surfaces. The pattern that seemed to emerge was that a better co-deposition occurred if there was a "mismatch" between the particle and the surface with respect to hydrophobicity.

The present study is undertaken to further the mechanistic understanding of a selectivity of deposition with respect to the surfaces properties. We will test the mismatch hypothesis by exploring whether the substrate surface properties control the deposition pattern also for *hydrophilic* (anionic) silica particles as "co-deposants". The size of the silica particles is chosen to be similar to that of the silicone oil droplets used in two previous studies [8,24]. Two cationic polymers are investigated, one polysaccharide derivative and one synthetic vinyl co-polymer; these were the ones that gave rise to the most pronounced selectivity as regards silicone oil co-deposition in our previous study [8].

2. Materials and methods

2.1. Materials

An acrylamide/methacrylamidopropyl trimethylammonium chloride (AAm/MAPTAC), copolymer was synthesized by Procter & Gamble and obtained as a stock solution at a weight concentration of ca. 6.5%. The synthesis procedure and the physical properties of the copolymer are described in Ref. [25]. In the synthesis, the monomer weight ratio was 80:20 (neutral/cation) resulting in a charge content of 1.1 mmol charges per g dry polymer. Trimethylammonium hydroxyethyl cellulose chloride UCARE LR-30M (cat-HEC), was obtained from Amerchol Corporation and purified as described in Ref. [27]. Sodium dodecyl sulfate (SDS) was received from BDH. The critical micelle concentration of SDS in water is 8.3 mmol/L at room temperature [28]. Silica particles Bindzil® 1420DI, kindly donated by AkzoNobel, were received as a 20 wt% aqueous dispersion. Dynamic light scattering (DLS) measurements (Malvern Nano ZS) on a dilution series of the silica particles in 1 mM NaCl gave a hydrodynamic radius of 15 ± 1 nm at infinite dilution. A surfactant-stabilized silicone oil emulsion (droplet hydrodynamic radius 18 nm; see Refs. [8,24] for characteristics of the emulsion) from Dow Corning was used in a few experiments.

P-type boron doped silicon wafers with a thermal silicon oxide layer of 270–300 Å purchased from SWI (Semiconductor Wafer, Inc.) and cut to appropriate size (approx. 1×4 cm) were used as substrate for the adsorption studies. The substrates were treated with water:ammonia (25%, aq):hydrogen peroxide (30%, aq) 5:1:1 at 80 °C for 5 min followed by water:hydrochloric acid (37%):hydrogen peroxide (30%, aq) 5:1:1 at 80 °C for 5 min. After thorough rinsing with water the surfaces were stored under ethanol (abs.). Prior to use, a surface was dried under flow of nitrogen and then plasma cleaned for a minimum of 5 min using a Harrick Scientific Corp., model PDC-3XG (30 W, 0.03 torr). This resulted in a hydrophilic surface as obvious from complete wetting by water. In order to obtain hydrophobized surfaces, hydrophilic plasma-cleaned substrates were gas-phase silanized by placing substrates and a few mL of chlorodimethyloctylsilane in desiccator and lowering the pressure. The substrates were kept at reduced pressure for 14–18 h at room temperature. After the silanization was completed the substrates were rinsed by sonication 3 times