

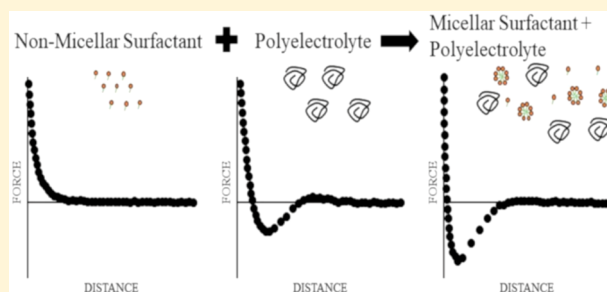
Colloidal Depletion and Structural Force Synergism or Antagonism in Solutions of Mutually Repelling Polyelectrolytes and Ionic Surfactants

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Supporting Information

ABSTRACT: Depletion and structural forces were measured between a silica sphere and plate in solutions containing sodium polyacrylate (Na-PAA) anionic polyelectrolyte and sodium dodecyl sulfate (SDS) anionic surfactant using colloidal probe atomic force microscopy, at high pH where the two species are electrostatically repelling from each other and from the silica surfaces. Measurements were performed for a range of SDS and Na-PAA concentrations to span conditions where only one of the species or both of the species would exert a detectable depletion or structural force when present in a single-component solution. In mixed solutions, conditions were identified (i) where depletion attraction was synergistically enhanced or antagonistically weakened relative to single component solutions; (ii) where the range of the depletion attraction was significantly extended and the repulsive structural force barrier was eliminated, due to simultaneous depletion of both species over different length scales; and (iii) where one species was the dominant depletant and forces in mixtures were indistinguishable from those in a single component solution of the dominant depletant. Force measurements were interpreted with the aid of pyrene solubilization assays of SDS micellization and dynamic light scattering investigation of the state of assembly of the polyelectrolyte or surfactant. The variety of colloidal force effects were attributed to ionic strength and excluded volume effects of Na-PAA on SDS micellization, ionic strength effects of SDS on Na-PAA chain clustering in solution, and ionic strength effects on the counterion contribution to polyelectrolyte osmotic pressure. While prior studies have shown that depletion force synergism occurs when polymers and surfactants form mixed complexes, this work shows that it can occur in noncomplexing mixtures as well, and it indicates the variety of effects that should be taken into account when attempting to predict forces in such mixtures.



■ INTRODUCTION

Most commercially important complex fluid formulations are multicomponent, often in the form of colloidal suspensions, foams, or emulsions with continuous phases incorporating polymers, surfactants, cosurfactants, nanoparticles, or other species to achieve the required product performance. This investigation is motivated by the mismatch between the widespread technological use and the incomplete understanding of colloidal forces and stability in multicomponent complex fluids. Along with the forces described by Derjaguin–Landau–Verwey–Overbeek (DLVO) theory,¹ many non-DLVO forces may operate in the presence of macromolecules, including, for example, steric forces,^{2,3} bridging forces,⁴ and oscillatory structural forces,^{5–8} the first attractive minimum of which is known as the depletion force.^{9–13} Depletion and structural forces between suspended particles are caused by macromolecules, micelles, nanoparticles, or similar nanoscale objects in solution or co-suspension. They arise from packing

constraints imposed on these objects in the narrow gap between surfaces. The depletion force is caused by exclusion of those objects, which may be referred to as “depletants”, from the intersurface gap upon sufficiently close approach of the two interacting surfaces. The resulting osmotic pressure difference between the bulk and the gap produces a stress that would drive the surfaces together: an apparent attraction force to act in addition to van der Waals attraction.

Theoretical understanding of the depletion force has expanded greatly^{14–19} since the original Asakura and Oosawa model,^{9,10} but inspection of this foundational model provides useful insights into how the force may respond to changes in solution conditions. The magnitude of the depletion

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interaction energy was assumed directly proportional to the osmotic pressure Π of the bulk solution. This model, expressed in terms of the interaction between a sphere of radius a and a flat plate as a function of surface-to-surface separation distance h gives the depletion interaction energy $\phi_{\text{dep}}(h)$ as²⁰

$$\phi_{\text{dep}}(h) = -\pi\Pi a(2\Delta - h)^2 \quad h < 2\Delta \quad (1)$$

$$\phi_{\text{dep}}(h) = 0 \quad h > 2\Delta \quad (2)$$

The range of the interaction is dictated by a depletion layer thickness Δ that equals the radius of the depletant, r , in the case of uncharged, nominally spherical depletants. An electrostatic exclusion zone around charged depletants increases Δ to an extent that scales with the Debye length κ^{-1} . Experiments with hard, charged spherical depletants indicate²⁰ that $\Delta \approx r + 5\kappa^{-1}$. Factors that would increase the osmotic pressure of a depletant in solution, the size of the depletant, or the thickness of the double layer would tend to strengthen the depletion attraction. The latter two factors would also increase its range.

Whereas the osmotic pressure of an ideal, nonionic macromolecule at molar concentration ρ_{om} is

$$\Pi = RT\rho_{\text{om}} \quad (3)$$

Counterion contributions increase the osmotic pressure of a polyelectrolyte that has a net charge $|z|$ in the presence of a 1:1 salt at bulk concentration ρ_{os} to

$$\Pi = RT \left[(|z| + 1)\rho_{\text{om}} + 2\rho_{\text{os}} \left(1 - \sqrt{\frac{|z|\rho_{\text{om}}}{\rho_{\text{os}}} + 1} \right) \right] \quad (4)$$

Typically, $|z| \gg 1$ and polyelectrolytes accordingly tend to yield stronger depletion forces than uncharged depletants at similar number concentrations mainly because of their greater osmotic pressures.^{20–22}

Adding background electrolyte diminishes the counterion osmotic pressure contribution, ultimately decreasing the osmotic pressure to that of the uncharged macromolecule, eq 3, in swamping electrolyte conditions. This directly weakens the magnitude of the depletion force. By decreasing the Debye length, electrolyte addition also decreases Δ . This decreases the range and further weakens the magnitude of the depletion force in accordance with eqs 1 and 2.

While salt-induced weakening of the depletion force would diminish the attractive component of the net force between surfaces, increasing background electrolyte concentration of course also weakens the electrostatic double layer repulsion between charged surfaces. Hence, depending on the relative contributions of double layer and depletion forces in a particular system, the net effect of salt addition could be to either increase or decrease the depth of any attractive force minimum that may occur in the force profile.

Depletion forces have been measured and predicted for solutions containing a single type of depletant, including spherical^{23,24} or nonspherical²⁵ nanoparticles, nonionic polymers,^{26–29} polyelectrolytes,^{21,30} and ionic surfactant micelles.^{15,31} Depletion forces in single-depletant systems were recently reviewed.³² Depletion forces in multicomponent systems are seldom investigated, but there are prior studies for solutions of mutually attractive species. Tulpar and co-workers³³ first observed synergistic enhancement of the depletion force between a silica sphere and a flat silica plate caused by the charged supramolecular assemblies that form by

complexation of Pluronic F108 poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) nonionic triblock copolymers with anionic sodium dodecyl sulfate (SDS) surfactants. Further examination of that system showed that synergistic enhancement of both depletion attraction and the first repulsive barrier of the oscillatory structural force was confined to a finite range of surfactant-to-polymer concentration ratios, which depended on the electrolyte concentration.³⁴ Synergism was due primarily to the osmotic pressure enhancement associated with the pseudopolyelectrolyte formed by polymer/surfactant complexation and, depending on electrolyte concentration, an increase in depletant size relative to either uncomplexed polymers or surfactant micelles.³⁴ Synergistic enhancement of depletion and structural forces in a mixture of poly(acrylic acid) and silica nanoparticle depletants has been attributed primarily to increased depletant size resulting from polymer adsorption to the nanoparticles.¹⁷

Synergistic force enhancements in the above-mentioned binary systems were directly attributable to the mutual attraction between the two components that produced new, “binary depletants” by complexation or adsorption. The current work is the first attempt to determine how depletion and structural forces may be altered in the presence of two mutually repelling depletants that have no tendency to form complexes. Colloidal probe atomic force microscopy (CP-AFM) was used to measure the net force profile between a negatively charged silica sphere and silica plate in the presence of aqueous solutions of sodium poly(acrylate) anionic polyelectrolyte (Na-PAA) and anionic SDS surfactants at elevated pH where electrostatic repulsions prevent polymer/surfactant complexation^{35,36} and adsorption to silica.³⁷ Because of their ionic nature, each component contributes ionic strength effects that have multiple consequences in the mixtures. Altered charge screening in the mixtures alters surfactant micellization and dipole-driven polyelectrolyte clustering in solution. These effects are revealed by pyrene solubilization assays of micellization and by dynamic light scattering, and they significantly alter depletion and structural forces. These ionic strength effects act in parallel with simple screening of the double layer repulsion between charged silica surfaces and the contribution of the Debye length to the depletion length. The net effect is that, despite the lack of complexation, SDS and Na-PAA mixtures can exhibit synergistic enhancement or antagonistic reduction of depletion and structural forces, depending on the concentrations of the two species. The results provide guidance for the interpretation and prediction of colloidal forces in complex mixtures. This may be particularly challenging, because whenever colloidal forces are synergistically or antagonistically altered by mixing components, as opposed to merely exhibiting additive contributions from each component, the mixed system behavior cannot be predicted from the behaviors exhibited by either species acting in a single-component system in the absence of the other.^{17,38}

■ EXPERIMENTAL SECTION

Materials. Sodium polyacrylate (M_n 60 000) was purchased from Polymer Source, Inc. Sodium dodecyl sulfate was purchased from Sigma-Aldrich (BioXtra grade, >99% purity) and used as received. SDS purity was confirmed by the absence of a minimum in the surface tension isotherm near the critical micelle concentration (CMC). All solutions containing SDS were prepared on the day of the experiment to minimize hydrolysis to dodecanol. Pyrene (>99% GC) was

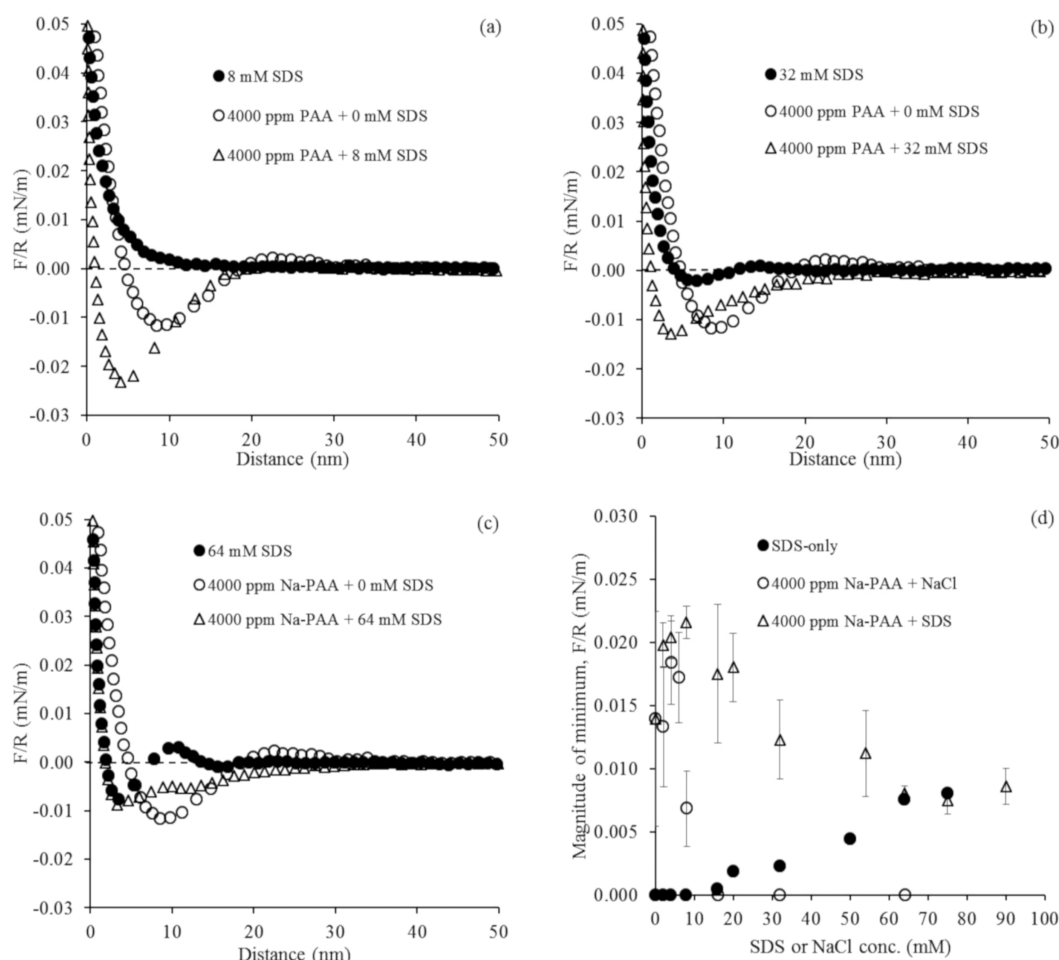


Figure 1. Representative normalized force profiles for selected SDS concentrations with 4000 ppm of Na-PAA: (a) 8 mM SDS, (b) 32 mM SDS, and (c) 64 mM SDS. (d) Summary plots for the magnitude of the primary minimum in the net force profiles for various SDS concentrations in the presence of 0 or 4000 ppm of Na-PAA and for various NaCl concentrations in the presence of 4000 ppm of Na-PAA. Except for data corresponding to varying NaCl concentrations with no SDS, the NaCl concentration was 0.1 mM. The same data for 4000 ppm of Na-PAA with no added SDS is repeated in panels (a)–(c) to facilitate comparison.

purchased from Sigma-Aldrich. Sodium chloride (Biotechnology grade) was purchased from VWR Life Science. Water for all experiments was purified to 18.2 M Ω cm resistivity using a Thermo-Fisher Barnstead Nanopure Diamond system. Unless otherwise noted, all experiments were conducted at pH 10 in the presence of 0.1 mM NaCl. Solutions were adjusted to pH 10 by NaOH (Fisher Scientific) and were checked for stable pH for the duration of experiments.

Methods. Colloidal Probe Atomic Force Microscopy. We used the CP-AFM technique³⁹ to measure the interaction force between a spherical silica probe particle and a flat silica plate using a Bruker Multimode VIII atomic force microscope in contact mode. Silica colloidal probe cantilevers were prepared by attaching a silica sphere (10 μ m nominal diameter, Corpulcular Inc.) to the end of a tipless silicon nitride cantilever with reflective gold coating on the back side (Bruker MLCT-O10, B, nominal spring constant 0.02 N/m) using a UV-curable epoxy glue (Norland optical adhesive 63). This cantilever was cured and cleaned via UV-ozone ProCleaner (Bioforce Nanosciences) for 1 h after attachment, and cleaned again immediately before every experiment by 20 min of further treatment. The spring constant for each cantilever was measured using the thermal tuning method.⁴⁰ The diameters of the colloidal probes were determined to be 8.7 ± 0.5 μ m by scanning electron microscopy (Hitachi 2460-N), which also confirmed that no epoxy had migrated onto the probe to influence forces. Flat plates for force measurements were silica discs with 0.5 nm RMS roughness, purchased from CVI Laser Optics. These surfaces were cleaned prior to each experiment by soaking first

in NOCHROMIX (Godax Laboratories) mixed with sulfuric acid and then 6 N HCl (BDH Chemicals) for 20 min each and last in 10 mM NaOH for 30 min with extensive water rinses between each step.⁴¹ The AFM fluid cell (Bruker Model MTFML) was cleaned in purified water followed by 200 proof ethanol (Pharmco) and then dried using a nitrogen jet. Fluid cell tubing was bath sonicated (Branson 1200) in purified water prior to each experiment for 2 min and thoroughly rinsed to remove any adsorbed polymers or surfactants from the previous experiment. Cleanliness was verified prior to each experiment by measuring the highly reproducible double layer repulsion between the bare silica probe and the bare disc in 0.1 mM NaCl solution, with adhesion prevented by hydration forces.

For each experiment, approximately 10 times the liquid cell volume of the solution of interest was pumped through the liquid cell. After filling, the system was allowed to equilibrate for 15 min before measuring forces. The sphere-to-plate approach and retract speeds were kept below 60 nm/s to decrease the hydrodynamic force on the cantilever to the point where it would not influence measured force curves.⁴² For each solution composition, forces were measured at five different locations on the disc surface and an average force curve was calculated. All measurements were conducted at 22 ± 2 °C. All forces were normalized by the colloidal probe radius.

Pyrene Solubilization Assay. A pyrene solubilization assay^{43,44} was performed using ultraviolet–visible spectrophotometry (Cary 300) following the protocol described previously³⁴ in order to determine the effect of Na-PAA on SDS micellization. The SDS CMC was determined from plots of solubilized pyrene concentration as a

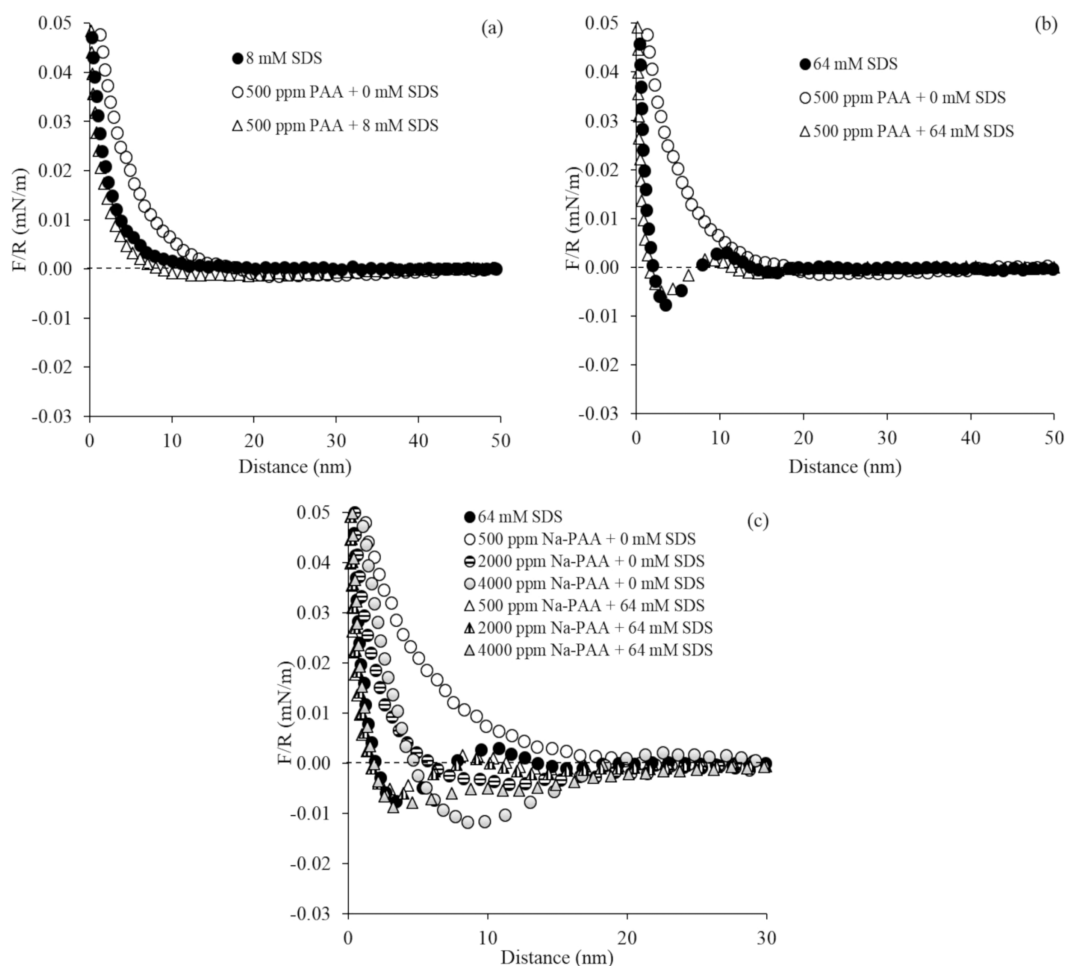


Figure 2. Representative normalized force profiles for selected SDS concentrations with 500 ppm of Na-PAA: (a) 8 mM SDS and (b) 64 mM SDS. (c) Comparison of force profiles for mixtures and single component solutions at 64 mM SDS for 0, 500, 2000, and 4000 ppm of Na-PAA. The NaCl concentration was 0.1 mM.

function of SDS concentration, in the presence of a fixed Na-PAA concentration (varied from 0 to 6000 ppm).

Dynamic Light Scattering. Dynamic light scattering (DLS) was performed with solutions containing 500 ppm (0.0083 mM) or 4000 ppm (0.067 mM) Na-PAA with varying SDS and NaCl concentrations using a Malvern Zeta Sizer Nano ZS instrument at 173° backscatter angle. Distributions of translational diffusion coefficients obtained from DLS analysis provide information on the relative amounts of free PAA chains and SDS micelles as well as any effects on the assembly of Na-PAA into clusters. All DLS samples were filtered by 0.45 μ m poly(ether sulfone) syringe filters and measured at 23 ± 0.1 °C. Autocorrelation functions were fitted for translational diffusion coefficient distributions using the CONTIN algorithm.

RESULTS AND DISCUSSION

Force Curve Analysis: Effect of SDS and Na-PAA Concentration. Force profiles were measured in solutions containing 500 or 4000 ppm of Na-PAA with varying SDS concentrations at pH 10 with 0.1 mM NaCl as background electrolyte. These are plotted together with profiles measured in single component SDS or Na-PAA solutions to compare the magnitude and range of the depletion attraction and the repulsive structural force barrier (Figures 1 and 2). Forces for Na-PAA/SDS mixtures plotted in Figure 1a–c are representative profiles obtained from a single experiment conducted by changing the solution composition in the liquid cell, using the

same silica sphere and plate and without allowing the liquid cell to become dry.

In the absence of Na-PAA, the force profile for 8 mM SDS with 0.1 mM NaCl was purely repulsive, with an exponential decay length of 3.1 nm, similar to the 3.4 nm Debye length expected for an 8.1 mM solution of 1:1 electrolytes (Figure 1a). This was just below the CMC, and as expected, SDS acted as a fully dissociated 1:1 electrolyte, consistent with prior literature.^{15,31,33} In the absence of SDS, 4000 ppm of Na-PAA produced an attractive depletion force with a minimum in the net force profile at 8.6 nm in apparent separation distance, as well as a repulsive barrier with a maximum at 23 nm originating from the structural force associated with the sorting of Na-PAA chains in the gap between silica surfaces. When 8 mM SDS was added to the 4000 ppm Na-PAA solution, the minimum in the attractive force deepened significantly and moved to smaller separation distance. Note that a shortcoming of the CP-AFM method is the difficulty in determining the absolute position of surface contact, or zero separation distance. If any materials were to adsorb, resulting steric forces could shift the apparent zero separation distance, but it was verified by ellipsometry (Beaglehole Picometer, using procedures detailed elsewhere^{45,46}) that neither PAA nor SDS adsorbed to silica under the current conditions, consistent with prior literature.⁴³ Thus, changes in separation distance

associated with key force profile features were meaningful in this system.

To examine whether SDS-induced changes in force profiles could be attributed solely to electrolyte effects associated with SDS addition, forces were also measured for 4000 ppm Na-PAA solutions in the presence of NaCl concentrations ranging from 0.1 to 64 mM. The magnitudes of any observed force minima were plotted as a function of NaCl concentration (Figure 1d). Since 8 mM NaCl decreased the magnitude of the attractive minimum produced by 4000 ppm of Na-PAA, rather than increasing it, the deepening of the attractive minimum observed upon 8 mM SDS addition cannot be attributed to increased screening of the double layer repulsion by the addition of 8 mM SDS acting simply as a 1:1 electrolyte. The deepening indicates enhanced depletion attraction. The likely causes for this effect will be discussed below. The force profile in the mixture is clearly not the sum of the profiles for single component SDS and Na-PAA solutions, and the magnitude of the attractive depletion minimum in the mixture is greater than the sum of the minima observed in the individual solutions. The effect of the mixture on the depletion force is synergistic.

Increasing the SDS concentration beyond the CMC to 32 mM (Figure 1b) in the absence of Na-PAA produced an attractive depletion well at ~ 7 nm and a mild repulsive structural barrier at ~ 15 nm caused by SDS micelle depletants. The mixture of 32 mM SDS and 4000 ppm of Na-PAA shifted the position of the attractive minimum to ~ 4 nm, which was a smaller separation distance than either the SDS or Na-PAA by itself. Although the depth of the minimum was similar to that in the SDS-free Na-PAA solution, the shape of the attractive portion of the force profile was distinct from either single-component solution. The repulsive barriers produced by SDS and Na-PAA in their single-component solutions were absent. Instead of repulsive barriers, the attraction persisted out to distances where the Na-PAA repulsive barrier had occurred. The net effect of mixing 32 mM SDS and 4000 ppm of Na-PAA was to eliminate any long-range repulsive barriers and broaden the range over which the net force was attractive: from ~ 1 to 25 nm for the mixture, compared with ~ 4 to 12 nm for 32 mM SDS and ~ 6 to 18 nm for 4000 ppm of Na-PAA. This represents an antagonistic effect of mixing on the repulsive structural force barrier.

Further increasing SDS concentration to 64 mM (Figure 1c) in the absence of Na-PAA increased both the depth of the depletion attraction minimum and the height of the repulsive barrier due to the increased concentration of micellar depletants. The mixture of 64 mM SDS and 4000 ppm of Na-PAA showed a broad attractive regime in the force profile, with no repulsive barrier, qualitatively similar to the mixture with 32 mM SDS. Whereas the location of the minimum and the onset of attractive forces in the mixture with 32 mM SDS shifted to a smaller separation distance, and the minimum deepened relative to SDS-only solutions, in the case of 64 mM SDS, the location and depth of the attractive minimum in the mixture were now indistinguishable from the 64 mM solution of SDS alone, as was the separation distance at which the force first became attractive (~ 2 nm). The key difference between the mixture and the solution of SDS alone was the broadening of the attractive regime.

The depth of the attractive minimum for 4000 ppm of Na-PAA varied nonmonotonically with increasing SDS concentration (Figure 1d). The error bars in Figure 1d were obtained by averaging three independent CP-AFM experiments using

fresh silica probes and plates for all the SDS and NaCl concentrations. Increasing from 0 to 8 mM SDS nearly doubled the depth of the minimum in 4000 ppm Na-PAA solutions. Under these conditions, SDS by itself produced no attractive force.

Beyond 8 mM SDS, the depth of the attractive minimum in mixtures with 4000 ppm of Na-PAA decreased with increasing SDS concentration. In the absence of Na-PAA, increasing SDS concentration beyond 8 mM increased the depth of the attractive minimum as the micellar depletant concentration increased. The depth of the attraction in mixtures exceeded that in the solutions of SDS alone until 64 mM SDS, where the depths became equal. Compared to SDS-free solutions of Na-PAA, the attraction was deeper for the mixtures up through 20 mM SDS, with a similar depth at 32 mM SDS. For 64 mM SDS and beyond, the depth of the attractive minimum in the mixture was less than it was in the solution of PAA alone but it remained finite (matching that produced in the concentrated SDS solutions). The weakening of the depth of PAA-induced depletion forces by addition of concentrated SDS represents an antagonistic mixture effect.

Nonmicellar SDS behaves as a fully dissociated 1:1 electrolyte. To help interpret electrolyte effects, force profiles were also measured, and the magnitudes of the attractive minima plotted, for 4000 ppm Na-PAA solutions with no SDS but with increasing NaCl concentrations (Figure 1d). The depth of the attractive minimum first increased with increasing NaCl concentration up to 4 mM. This is due to screening of double layer repulsions between silica surfaces: weakening the double layer repulsion between the silica surfaces made the net force more attractive. Contrary to the effect of adding SDS, when adding NaCl beyond 4 mM, the attractive minimum became less deep, despite the increased double layer screening, and there was no attraction in the force profiles at all for NaCl concentrations of 16 mM and above. Thus, the depletion attraction was weakened and ultimately eliminated by background electrolyte swamping the counterion contribution to the polyelectrolyte osmotic pressure, according to eq 4).

Figure 2a,b shows representative force profiles for 500 ppm Na-PAA/SDS mixtures containing 0, 8, or 64 mM SDS and the corresponding single-component solutions. Without SDS, 500 ppm of Na-PAA did not produce an attractive minimum in the force profile, which was dominated by the double layer repulsion. There was a very shallow, but reproducible, minimum in the force profile for 500 ppm of Na-PAA and 8 mM SDS (Figure 2a). The strong synergistic depletion force enhancement observed for 4000 ppm of Na-PAA and 8 mM SDS was not observed for 500 ppm of Na-PAA. The appearance of a shallow depletion force minimum in this mixture was likely due in part to the enhanced screening of the double layer repulsion between silica surfaces caused by the higher ionic strength of the mixture relative to either of the single-component solutions. The weakened repulsion would reveal more of the depletion force induced by Na-PAA. That depletion force may also have been somewhat strengthened in the mixture for reasons to be discussed in the pyrene solubilization and dynamic light scattering sections below.

The force profiles with 64 mM SDS were similar with and without 500 ppm of Na-PAA (Figure 2b). Unlike the force profile for 4000 ppm of Na-PAA and 64 mM SDS (Figure 1c), the force profile obtained for 500 ppm of Na-PAA and 64 mM SDS retained a weakened but finite repulsive structural force barrier. Figure 2c shows the effect of Na-PAA concentration on

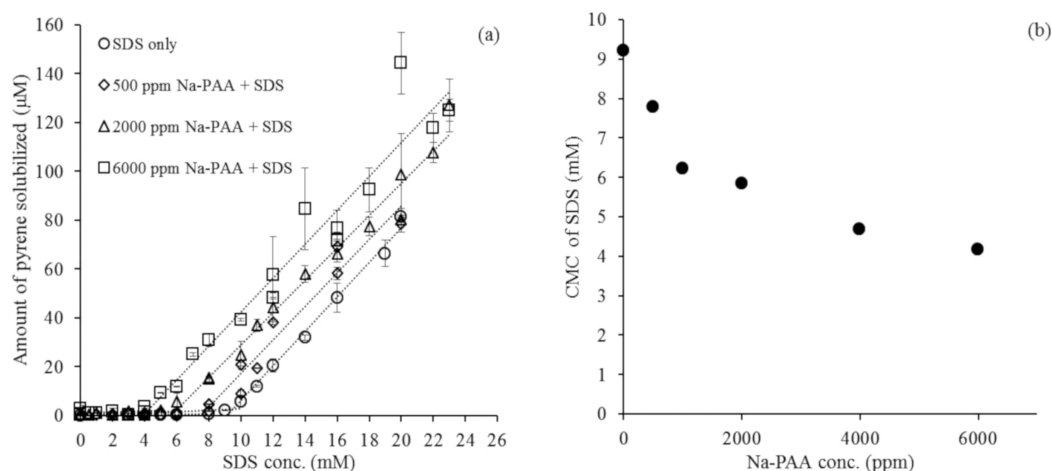


Figure 3. (a) Pyrene solubilization in solutions of varying SDS concentrations containing a fixed Na-PAA concentration (selected concentrations shown for clarity). (b) CMC of SDS as a function of Na-PAA concentration. Each solution contained 0.1 mM NaCl.

force profiles for a constant 64 mM SDS concentration. For comparison in the absence of SDS, increasing the Na-PAA concentration from 500 to 2000 and again to 4000 ppm increased the depth of the depletion attraction minimum. With 64 mM SDS, the depth of the attractive minimum was similar to the solution of 64 mM SDS alone, for all three Na-PAA concentrations. This indicates that SDS micelles dominated the depletion attraction at small separation distances. The repulsive barrier at larger separation distance decreased in magnitude as the Na-PAA concentration increased, ultimately disappearing with 4000 ppm of Na-PAA to be replaced by the broad attractive regime noted above.

Characterization of the Na-PAA/SDS System. Interpretation of these varied effects of mixtures, some of which enhanced and others suppressed depletion or structural forces, requires further examination of the solution contents themselves. First, pyrene solubilization assay results will be reported to investigate the effect of Na-PAA on SDS micellization, since any change in CMC would change the concentration of micellar depletants. Dynamic light scattering results will then be reported to gain confirmatory information about conditions where both SDS micelles and Na-PAA chains coexist and to investigate the role that PAA chain clustering in solution may play in these mixtures.

Pyrene Solubilization Assay. Pyrene is sparingly soluble in water but is readily solubilized in surfactant assemblies. The CMC is identified as the surfactant concentration at which the solubilized pyrene concentration increases abruptly. Furthermore, the slope of solubilized pyrene concentration vs surfactant concentration, i.e., the solubilizing power, is sensitive to different modes of surfactant self-assembly and aggregation numbers and can distinguish free micelles from polymer-bound assemblies.^{36,43} Assays were conducted by increasing SDS concentration while holding the Na-PAA concentration constant. These were repeated for several Na-PAA concentrations, as well as for solutions with no Na-PAA (Figure 3a). Addition of Na-PAA did not affect the solubilizing power ($6.5 \pm 0.5 \mu\text{M}$ pyrene per mM SDS). This not only confirms that SDS and Na-PAA did not form complexes under these conditions but also indicates that the micelle aggregation number was unaffected by Na-PAA.

Addition of Na-PAA did decrease the SDS CMC in a systematic manner (Figure 3b), from 9 to 4 mM as the Na-

PAA concentration increased from 0 to 6000 ppm. (The CMC in the absence of Na-PAA is comparable but somewhat larger than the 8.3 mM value typically reported for low ionic strength conditions, reflecting the tendency of CMC values to depend on the measurement method.) Promotion of micellization results from the sodium counterions dissociated from Na-PAA. Increased screening of headgroup repulsions decreases the CMC, just as occurs with the addition of simple electrolytes to solution. Similar results were reported previously for polyelectrolytes and ionic surfactants that have the same sign of charge,^{47,48} including PAA and SDS at high pH where no complexation occurs.³⁶

The CMC reduction caused by Na-PAA likely played an important role in the depletion force synergism. With 4000 ppm of Na-PAA, the CMC was decreased to 4.7 mM. This is noteworthy, as the force measurements indicated that the effect of SDS on the attractive force profile in 4000 ppm Na-PAA solutions was indistinguishable from that of NaCl up to 4 mM (Figure 1d). Those effects were explained simply by screening of the double layer repulsion. Beyond 4 mM, whereas further NaCl addition weakened the depletion attraction, the attraction was further strengthened by SDS addition up to 8 mM, and remained stronger in mixtures than in solutions of Na-PAA alone until 32 mM SDS. With a decreased CMC and no change in aggregation number, the SDS micelle concentration would be greater in the mixtures with Na-PAA. Part of the enhanced depletion attraction measured for 4000 ppm of Na-PAA and 8 mM SDS was likely due to the contribution from SDS micellar depletants, a result of the decreased CMC. In addition, the decrease in CMC to 7.8 mM in the presence of 500 ppm of Na-PAA would result in a very small concentration of SDS micelles which would add a small contribution to the depletion force.

The change in the CMC caused by Na-PAA addition must also change the degree to which adding SDS alters the solution ionic strength and double layer repulsions, compared to solutions that have no Na-PAA. Since the degree of counterion binding to SDS micelles is reported to be ~ 0.77 ,^{34,49,50} the incremental increase in solution ionic strength provided by dodecyl sulfate anions and Na^+ counterions is smaller above the CMC than below. While SDS does incrementally increase ionic strength above the CMC, its contribution must be less in solutions containing Na-PAA than in solutions of SDS alone

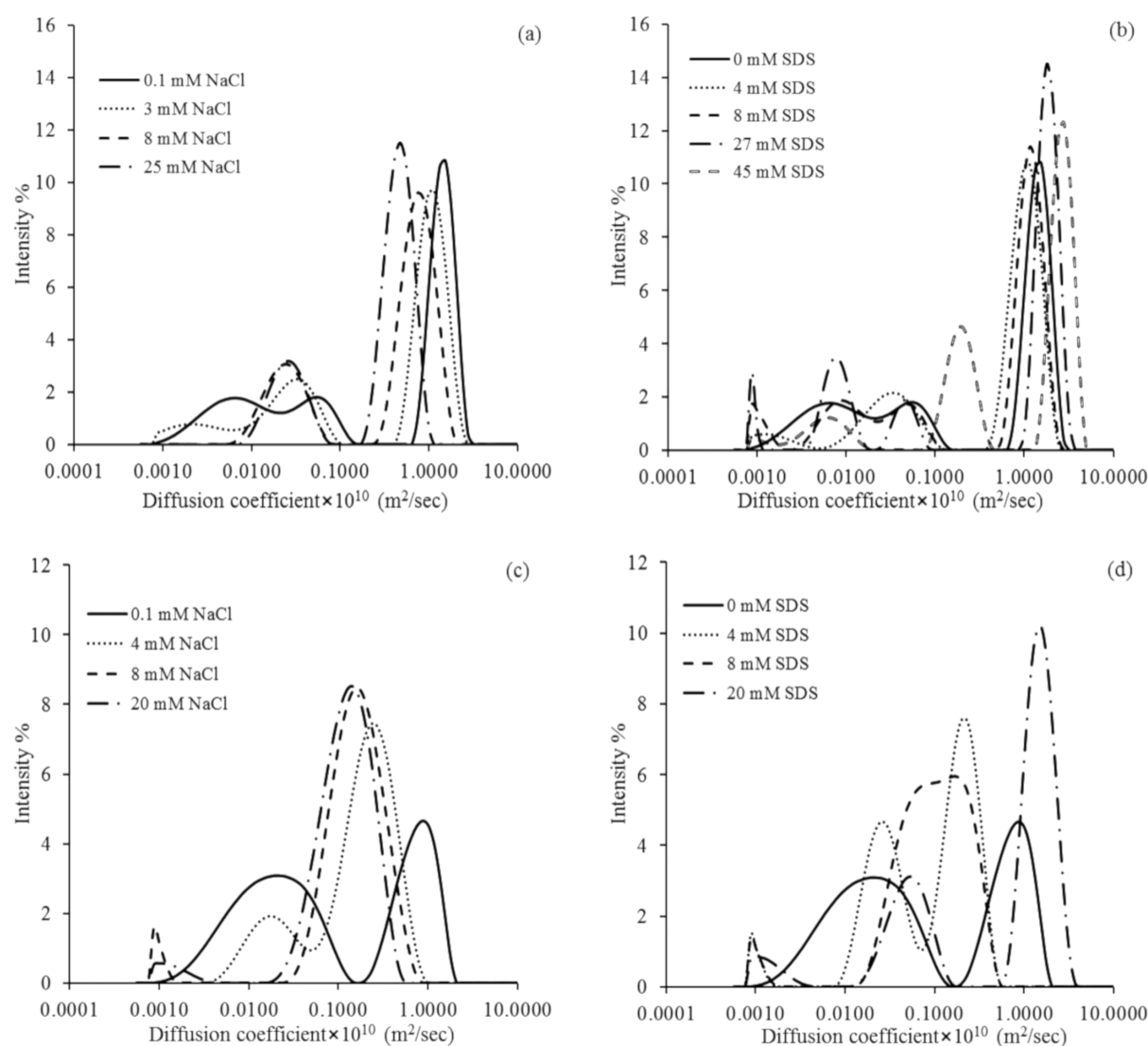


Figure 4. Diffusion coefficient distributions of (a) 4000 ppm of Na-PAA at varying NaCl concentrations, (b) 4000 ppm of Na-PAA at 0.1 mM NaCl and varying SDS concentrations, (c) 500 ppm of Na-PAA at varying NaCl concentrations, and (d) 500 ppm of Na-PAA at 0.1 mM NaCl and varying SDS concentrations.

because the CMC is lower. The SDS contribution to ionic strength was calculated for solutions with 0, 500, or 4000 ppm of Na-PAA, based on the measured CMC values and the reported aggregation number⁵¹ (78) and degree of Na⁺ counterion binding to SDS micelles (77%). The calculation employed the model of Pashley and Ninham,⁵² which states that micelles do not contribute to ionic strength. Tadmor and co-workers⁵³ have similarly reported that polyelectrolytes only contribute to the effective Debye length governing double layer forces via their dissociated monovalent counterions. Calculated ionic strength values are summarized in [Supporting Information section I](#).

Since 4000 ppm of Na-PAA decreased the CMC, the contribution to ionic strength from 8 mM SDS was decreased from 8 mM in the absence of Na-PAA to only 5 mM when added to 4000 ppm of Na-PAA. This would slightly weaken the double layer screening effect (favoring a more repulsive/less attractive net force), but it would also allow a greater counterion contribution to the polyelectrolyte osmotic pressure (favoring a stronger depletion attraction). The net outcome of these effects, as well as the addition of micellar

depletants, was observed ([Figure 1a](#)) to be a strengthened depletion attraction in the mixture of 8 mM SDS and 4000 ppm of Na-PAA.

In the presence of 4000 ppm of Na-PAA, the contribution of 64 mM SDS to the solution ionic strength is merely 11.5 mM. Clearly, 64 mM SDS should not be expected to eliminate depletion forces in the manner that 64 mM NaCl did ([Figure 1d](#)). In fact, the depth of the attractive minimum for 4000 ppm of Na-PAA with ionic strength near this 11.5 mM value is significantly weakened relative to the attractive force measured for Na-PAA in the presence of just 0.1 mM NaCl ([Figure 1d](#)). The weakening (but not elimination) of PAA-induced depletion forces combined with the abundance of SDS micelles at 64 mM SDS produced a depth of the attractive minimum in the mixture that was similar to the case of 64 mM SDS acting alone, but significantly less than 4000 ppm of Na-PAA acting alone. This represents an antagonistic effect of the mixture on the depletion force. The broadened attractive regime measured in the mixture ([Figure 1c](#)) suggests that PAA and SDS micelles contribute depletion forces over different separation distance scales.

Dynamic Light Scattering. Depletion and structural forces observed in different concentration regimes can be influenced by multiple factors, including ionic strength effects on the polyelectrolyte osmotic pressure and the relative contributions of SDS micelles and Na-PAA chains as depletants. The concentration of free Na-PAA chains is influenced by their tendency to form noncovalent clusters in a concentration dependent manner.^{54–56} Driven by dipole/dipole correlations, this polyelectrolyte clustering is favored by increasing polyelectrolyte concentration and is disrupted by increasing ionic strength. Should multichain clusters form, this would decrease the concentration of free Na-PAA chains to act as depletants. The relatively low concentration, large size, and likely polydisperse character of clusters may be such that they do not contribute significantly to depletion or structural forces. DLS was used to determine intensity weighted diffusion coefficient distributions (Figure 4) in an attempt to identify the presence and relative amounts of free Na-PAA chains, clusters, and SDS micelles under conditions relevant to the force measurements.

Since SDS exerts incremental ionic strength effects, DLS measurements were first performed with solutions of Na-PAA and NaCl to investigate the role of ionic strength. For the baseline low ionic strength condition of 0.1 mM NaCl, the diffusion coefficient distribution for 4000 ppm of Na-PAA (Figure 4a) displayed a well-defined mode at a larger diffusion coefficient and a broad mode (resolved by CONTIN as apparently bimodal) with diffusion coefficients 1–3 orders of magnitude smaller. The latter is the slow, or “extraordinary”, mode caused by polyelectrolyte clustering.⁵⁴ Free chains coexist with clustered chains. With increasing NaCl concentrations up to 25 mM, the free chain mode remained well-defined and shifted to smaller diffusion coefficients as expected from screening of interchain electrostatic repulsions.^{55–57} Concurrently, the extraordinary mode shifted from apparently bimodal to a single, less disperse mode that remained well separated from the free chain mode. Since SDS never would contribute to ionic strength by more than 20 mM under conditions considered in this study, this suggests that free chains and clusters coexisted in all the solutions examined in the force measurements for 4000 ppm of Na-PAA.

When SDS was added to 4000 ppm Na-PAA solutions containing 0.1 mM NaCl (Figure 4b), the surfactant behaved similarly to NaCl for concentrations below the CMC, screening interchain repulsions and shifting the free chain mode to smaller diffusion coefficients, while preserving the extraordinary mode clusters. The situation became more complex when increasing beyond the CMC (4.7 mM). The faster diffusion coefficient mode shifted to larger values. This is best interpreted as the coexistence of SDS micelles and free Na-PAA chains that could not be resolved in the autocorrelation function. The slow mode remained for all SDS concentrations up to the maximum considered (45 mM). At 45 mM SDS, the distribution was resolved into three distinct modes: with the fastest mode shifting to higher diffusion coefficient values, retention of the extraordinary mode for the lowest diffusion coefficients, and with a well-resolved mode in between. That “new” mode occurred at diffusion coefficients comparable to the free PAA chain mode observed in 25 mM NaCl, and was thus interpreted as arising from free chains in the mixture with SDS. The fastest mode was attributed to SDS micelles. Trends with regard to changing values of average diffusion coefficients associated with each

mode were systematic with regard to increasing NaCl or SDS concentration, and trends illustrated for the selected distributions discussed here are representative of overall trends in the system at multiple concentrations (Supporting Information section II).

DLS results help interpret forces measured in the various concentration regimes. For 4000 ppm Na-PAA mixtures with SDS above the CMC, the depletion attraction was enhanced relative to solutions of Na-PAA alone or SDS alone until 32 mM, at which point the attraction nearly matched that in the Na-PAA solution but still exceeded that in the SDS solution. At 64 mM, the depth of the attraction became indistinguishable from that in solutions of SDS alone. This is consistent with the coexistence of micelles and free PAA chains at the higher SDS concentrations. Coexistence of micelles and free chains also produced the broadened region of attraction in the force profiles (Figure 1), where the data suggested that PAA chains and micelles contributed to depletion forces at larger and smaller separation distances, respectively.

Dissociation of PAA chains from clusters may also have played some role to increase the contribution of PAA chains as depletants when the SDS concentration was increased, based on the tendency of the clusters to become relatively less important in the distribution with increasing ionic strength. Weighting the contributions of each mode by the integrated area under the peaks, and calculating the ratio of areas for clusters and free chains, the clusters decreased in relative abundance from $A_{\text{cluster}}/A_{\text{free}} \sim 0.65$ to 0.35 as the ionic strength increased to 25 mM (Supporting Information section III).

Diffusion coefficient distributions for 500 ppm Na-PAA solutions with increasing NaCl concentration but no SDS (Figure 4c) similarly indicated a fast mode from free chains and a broad extraordinary mode arising from clusters. With increasing NaCl, the free chain mode progressed systematically to smaller diffusion coefficients as expected from increased screening, while the extraordinary mode weakened until at 20 mM, there was only evidence for a single, free-chain mode. SDS behaved similarly to NaCl below the CMC (Figure 4d), shifting the free chain mode to smaller diffusion coefficients and weakening the relative contribution from the extraordinary mode. Above the CMC, evidence of SDS micelles appeared as a shift in the fast mode to larger diffusion coefficients. The mode corresponding to smaller diffusion coefficients was now more in line with free PAA chains than with the extraordinary mode clusters. The relatively high concentration of SDS micelles in 500 ppm Na-PAA and SDS mixtures beyond 20 mM SDS, as represented by the high intensity weighting of the micelle (fast) peak in the diffusion coefficient distribution, is consistent with the force profile in the mixture being very similar to that in SDS only solutions (Figure 2b). Both would be dominated by SDS micellar depletants at high SDS concentration.

Adding NaCl produced a more severe disruption of the extraordinary mode clusters for 500 ppm of Na-PAA: adding just 8 mM NaCl decreased the relative abundance of clusters $A_{\text{cluster}}/A_{\text{free}}$ from ~ 1 to ~ 0.1 (Supporting Information section III). Thus, the appearance of a shallow minimum in the mixture of 500 ppm of Na-PAA and 8 mM SDS may have been caused in part by an increased concentration of free chains to serve as depletants upon SDS addition, relative to the solution of Na-PAA alone.

Table 1. Summary of Mixture Effects on Force Profiles for 4000 ppm of Na-PAA in Different SDS Concentration Regimes

below CMC ($C_{\text{SDS}} \leq 4.7 \text{ mM}$)	somewhat above CMC ($4.7 \text{ mM} < C_{\text{SDS}} < 32 \text{ mM}$)	well above CMC ($C_{\text{SDS}} \geq 32 \text{ mM}$)
synergistically enhanced attraction	synergistically enhanced attraction	broadened attraction regime with primary minimum depth in mixtures matching those in SDS solutions; loss of structural force barrier
cause: Screened double layer repulsion; little effect on Na-PAA depletion forces	causes: increased micelle abundance due to decreased CMC overcomes decreased polyelectrolyte osmotic pressure; reduced Na-PAA clustering increases free chain concentration and enhances depletion forces.	cause: depletion of micelles and PAA at different distances

Summary of Force Profile Interpretations for 4000 ppm Na-PAA Solutions. Force measurements and complementary probes of the state of SDS and Na-PAA in solution indicate several distinct mechanistic processes that contribute to different extents in different concentration regimes. The effects of the mixture on net force profiles, and depletion and structural forces in particular, can be quite different according to the concentration regime. The key force observations and contributing mechanistic phenomena are summarized in Table 1 for the 4000 ppm Na-PAA solutions.

■ CONCLUSIONS

Force profiles measured by colloidal probe AFM between negatively charged silica surfaces in aqueous solutions of Na-PAA, SDS, and their mixtures indicated several distinct concentration regimes within which mixtures yielded synergistic or antagonist effects on depletion and structural forces relative to single-component solutions. The origins of synergistic depletion force enhancement in this system, where the polyelectrolyte and surfactant are electrostatically mutually repellent, are distinct from those of depletion force synergism in previously studied systems involving complexation of the different components,^{33,34} where it was the formation of those complexes that produced the synergism. In the current system of highly charged anionic polyelectrolytes and anionic surfactants, no complexes form, but an interplay of several factors contributes to a variety of effects on forces.

Below the normal CMC, SDS behaves as a 1:1 electrolyte and screens electrostatic double layer repulsions. The effect of SDS to act as a simple electrolyte, which would diminish the counterion contribution to polyelectrolyte osmotic pressure and thus the magnitude of the depletion attraction, is offset by a decrease in CMC caused by the incremental increase in counterion concentration provided by Na-PAA polyelectrolytes. The resulting increased abundance of micelles, which act as depletants together with polyelectrolyte chains, synergistically enhances the magnitude of depletion forces in the mixtures relative to either single-component solution. This effect is strengthened as the polyelectrolyte concentration is increased.

Above the CMC, SDS addition still increases ionic strength, but the incremental effect is far weaker than it is below the CMC. Thus, depletion forces remain strong in Na-PAA solutions containing micellized SDS. They are stronger in Na-PAA mixtures with SDS than the depletion forces that operate with the same molar concentration of NaCl, since an excess of the simple electrolyte strongly suppresses the depletion force by reducing polyelectrolyte osmotic pressure. Depletion forces originating from the polyelectrolyte remain strong in SDS solutions at concentrations where simple electrolyte addition would have eliminated them. This preservation of polyelectrolyte-induced depletion forces in SDS solutions also may be augmented by partial dissociation of polyelectrolyte clusters

with increasing ionic strength, which increases the concentration of free chains to act as depletants. SDS addition well in excess of the CMC produces attractive depletion force minima that are similar in magnitude to those measured in the absence of the polyelectrolyte, but the repulsive structural force barrier that is exhibited by either single-component solution is also eliminated. Instead of a repulsive barrier at longer range, the force profiles exhibit broad regions of purely attractive forces. This is attributed to distinct contributions from depletion of micelles and of polyelectrolyte chains occurring over different separation distance ranges.

The net forces acting between negatively charged surfaces in this system of mutually repelling, nonadsorbing anionic polyelectrolytes and anionic surfactants deviate quantitatively from either single-component system, in terms of the magnitudes of attractive depletion force wells and/or repulsive structural barriers, and at higher surfactant concentrations they deviate even qualitatively, with well-formed structural force barriers present in both single-component solutions at longer range entirely eliminated and replaced with broad ranges of attraction. Awareness of the simultaneous effects of incremental ionic strength increases, polyelectrolyte-induced surfactant micellization, and polyelectrolyte cluster disruption on colloidal depletion and structural forces in this type of surfactant/polyelectrolyte mixture will aid in the formulation of colloidal suspensions where forces must be controlled to engineer colloidal stability, phase behavior or rheology. These effects reflect a subtle interplay between the roles of ionic surfactants and polyelectrolytes as both depletants and as sources of counterions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.langmuir.9b02143](https://doi.org/10.1021/acs.langmuir.9b02143).

Calculated ionic strength of Na-PAA/SDS mixture as a function of SDS concentrations, diffusion coefficient trends and relative contributions of extraordinary and fast modes from DLS (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Israelachvili, J. *Intermolecular and Surface Forces*; Elsevier, 2011.
- (2) Liang, W.; Tadros, T. F.; Luckham, P. F. Flocculation of Sterically Stabilized Polystyrene Latex Particles by Adsorbing and Nonadsorbing Poly(acrylic Acid). *Langmuir* **1994**, *10* (2), 441–446.
- (3) Napper, D. Steric Stabilization. *J. Colloid Interface Sci.* **1977**, *58* (2), 390–407.
- (4) Lu, C.; Pelton, R. PEO Flocculation of Polystyrene-Core Poly(vinylphenol)-Shell Latex: An Example of Ideal Bridging. *Langmuir* **2001**, *17* (25), 7770–7776.
- (5) Biggs, S.; Dagastine, R. R.; Prieve, D. C. Oscillatory Packing and Depletion of Polyelectrolyte Molecules at an Oxide-Water Interface. *J. Phys. Chem. B* **2002**, *106* (44), 11557–11564.
- (6) Théodoly, O.; Tan, J. S.; Ober, R.; Williams, C. E.; Bergeron, V. Oscillatory Forces from Polyelectrolyte Solutions Confined in Thin Liquid Films. *Langmuir* **2001**, *17* (16), 4910–4918.
- (7) Fielden, M. L.; Hayes, R. A.; Ralston, J. Oscillatory and Ion-Correlation Forces Observed in Direct Force Measurements between Silica Surfaces in Concentrated CaCl₂ Solutions. *Phys. Chem. Chem. Phys.* **2000**, *2* (11), 2623–2628.
- (8) Christov, N. C.; Danov, K. D.; Zeng, Y.; Kralchevsky, P. A.; Von Klitzing, R. Oscillatory Structural Forces due to Nonionic Surfactant Micelles: Data by Colloidal-Probe AFM vs Theory. *Langmuir* **2010**, *26* (2), 915–923.
- (9) Asakura, S.; Oosawa, F. Interaction between Particles Suspended in Solutions of Macromolecules. *J. Polym. Sci.* **1958**, *33* (126), 183–192.
- (10) Asakura, S.; Oosawa, F. On Interaction between Two Bodies Immersed in a Solution of Macromolecules. *J. Chem. Phys.* **1954**, *22* (7), 1255–1256.
- (11) Milling, A. J.; Vincent, B. Depletion Forces between Silica Surfaces in Solutions of Poly(acrylic Acid). *J. Chem. Soc., Faraday Trans.* **1997**, *93* (17), 3179–3183.
- (12) Piech, M.; Walz, J. Y. Depletion Interactions Produced by Nonadsorbing Charged and Uncharged Spheroids. *J. Colloid Interface Sci.* **2000**, *232* (1), 86–101.
- (13) Kralchevsky, P. A.; Danov, K. D.; Anachkov, S. E. Depletion Forces in Thin Liquid Films due to Nonionic and Ionic Surfactant Micelles. *Curr. Opin. Colloid Interface Sci.* **2015**, *20* (1), 11–18.
- (14) Mao, Y.; Cates, M. E.; Lekkerkerker, H. N. W. Theory of the Depletion Force due to Rodlike Polymers. *J. Chem. Phys.* **1997**, *106* (9), 3721–3729.
- (15) James, G. K.; Walz, J. Y. Experimental and Theoretical Investigation of the Depletion and Structural Forces Produced by Ionic Micelles. *Colloids Surf., A* **2014**, *441*, 406–419.
- (16) Piech, M.; Walz, J. Y. Direct Measurement of Depletion and Structural Forces in Polydisperse, Charged Systems. *J. Colloid Interface Sci.* **2002**, *253* (1), 117–129.
- (17) Ji, S.; Walz, J. Y. Synergistic Effects of Nanoparticles and Polymers on Depletion and Structural Interactions. *Langmuir* **2013**, *29* (49), 15159–15167.
- (18) Chatterjee, A. P.; Schweizer, K. S. Influence of Solvent Quality and Thermal Fluctuations on Polymer-Mediated Depletion Interactions. *Macromolecules* **1999**, *32* (3), 923–934.
- (19) Chatterjee, A. P.; Schweizer, K. S. Microscopic Theory of Polymer-Mediated Interactions between Spherical Particles. *J. Chem. Phys.* **1998**, *109* (23), 10464–10476.
- (20) Odiachi, P. C.; Prieve, D. C. Effect of Added Salt on the Depletion Attraction Caused by Non-Adsorbing Clay Particles. *Colloids Surf., A* **1999**, *146* (1–3), 315–328.
- (21) Pagac, E. S.; Tilton, R. D.; Prieve, D. C. Depletion Attraction Caused by Unadsorbed Polyelectrolytes. *Langmuir* **1998**, *14* (18), 5106–5112.
- (22) Biggs, S.; Prieve, D. C.; Dagastine, R. R. Direct Comparison of Atomic Force Microscopic and Total Internal Reflection Microscopic Measurements in the Presence of Nonadsorbing Polyelectrolytes. *Langmuir* **2005**, *21* (12), 5421–5428.
- (23) Herman, D.; Walz, J. Y. Adsorption and Stabilizing Effects of Highly-Charged Latex Nanoparticles in Dispersions of Weakly-Charged Silica Colloids. *J. Colloid Interface Sci.* **2015**, *449* (0), 143–151.
- (24) McKee, C. T.; Walz, J. Y. Interaction Forces between Colloidal Particles in a Solution of like-Charged, Adsorbing Nanoparticles. *J. Colloid Interface Sci.* **2012**, *365* (1), 72–80.
- (25) Piech, M.; Walz, J. Y. Analytical Expressions for Calculating the Depletion Interaction Produced by Charged Spheres and Spheroids. *Langmuir* **2000**, *16* (21), 7895–7899.
- (26) Rudhardt, D.; Bechinger, C.; Leiderer, P. Direct Measurement of Depletion Potentials in Mixtures of Colloids and Nonionic Polymers. *Phys. Rev. Lett.* **1998**, *81* (6), 1330–1333.
- (27) Ruths, M.; Yoshizawa, H.; Fetters, L. J.; Israelachvili, J. N. Depletion Attraction versus Steric Repulsion in a System of Weakly Adsorbing Polymer-Effects of Concentration and Adsorption Conditions. *Macromolecules* **1996**, *29* (22), 7193–7203.
- (28) Kuhl, T. L.; Berman, A. D.; Hui, S. W.; Israelachvili, J. N. Part 2. Crossover from Depletion Attraction to Adsorption: Polyethylene Glycol Induced Electrostatic Repulsion between Lipid Bilayers. *Macromolecules* **1998**, *31* (23), 8258–8263.
- (29) Kuhl, T. L.; Berman, A. D.; Hui, S. W.; Israelachvili, J. N. Part 1. Direct Measurement of Depletion Attraction and Thin Film Viscosity between Lipid Bilayers in Aqueous Polyethylene Glycol Solutions. *Macromolecules* **1998**, *31* (23), 8250–8257.
- (30) Sharma, A.; Tan, S. N.; Walz, J. Y. Effect of Nonadsorbing Polyelectrolytes on Colloidal Interactions in Aqueous Mixtures. *J. Colloid Interface Sci.* **1997**, *191* (1), 236–246.
- (31) James, G. K.; Walz, J. Y. Experimental Investigation of the Effects of Ionic Micelles on Colloidal Stability. *J. Colloid Interface Sci.* **2014**, *418*, 283–291.
- (32) Briscoe, W. H. Depletion Forces between Particles Immersed in Nanofluids. *Curr. Opin. Colloid Interface Sci.* **2015**, *20* (1), 46–53.
- (33) Tulpar, A.; Tilton, R. D.; Walz, J. Y. Synergistic Effects of Polymers and Surfactants on Depletion Forces. *Langmuir* **2007**, *23* (8), 4351–4357.
- (34) Lele, B. J.; Tilton, R. D. Control of the Colloidal Depletion Force in Nonionic Polymer Solutions by Complexation with Anionic Surfactants. *J. Colloid Interface Sci.* **2019**, *553*, 436–450.
- (35) Wang, C.; Tam, K. C. Interactions between Poly(acrylic Acid) and Sodium Dodecyl Sulfate: Isothermal Titration Calorimetric and Surfactant Ion-Selective Electrode Studies. *J. Phys. Chem. B* **2005**, *109* (11), 5156–5161.
- (36) Maltesh, C.; Somasundaran, P. Evidence of Complexation between Poly(acrylic Acid) and Sodium Dodecyl Sulfate. *Colloids Surf.* **1992**, *69* (2–3), 167–172.
- (37) Berglund, K. D.; Timko, A. E.; Przybycien, T. M.; Tilton, R. D. Use of Nonionic Ethylene Oxide Surfactants as Phase-Transfer Catalysts for Poly(acrylic acid) Adsorption to Silica against an Electrostatic Repulsion. *Prog. Colloid Polym. Sci.* **2003**, *122*, 56–66.
- (38) Ji, S.; Walz, J. Y. Depletion Forces and Flocculation with Surfactants, Polymers and Particles - Synergistic Effects. *Curr. Opin. Colloid Interface Sci.* **2015**, *20* (1), 39–45.
- (39) Ducker, W. a.; Senden, T. J.; Pashley, R. M. Direct Measurement of Colloidal Forces Using an Atomic Force Microscope. *Nature* **1991**, *353* (6341), 239–241.
- (40) Green, C. P.; Lioe, H.; Cleveland, J. P.; Proksch, R.; Mulvaney, P.; Sader, J. E. Normal and Torsional Spring Constants of Atomic Force Microscope Cantilevers. *Rev. Sci. Instrum.* **2004**, *75* (6), 1988–1996.
- (41) Braem, A. D.; Biggs, S.; Prieve, D. C.; Tilton, R. D. Control of Persistent Nonequilibrium Adsorbed Polymer Layer Structure by Transient Exposure to Surfactants. *Langmuir* **2003**, *19* (7), 2736–2744.

- (42) Tulpar, A.; Walz, J. Y. Simultaneous Measurement of Structural and Hydrodynamic Forces between Colloidal Surfaces in Complex Fluids. *Colloids Surf., A* **2007**, *300*, 268–280.
- (43) Braem, A. D.; Prieve, D. C.; Tilton, R. D. Electrostatically Tunable Coadsorption of Sodium Dodecyl Sulfate and Poly(ethylene Oxide)-B-Poly(propylene Oxide)-B-Poly(ethylene Oxide) Triblock Copolymer to Silica. *Langmuir* **2001**, *17* (3), 883–890.
- (44) Kim, J.; Domach, M. M.; Tilton, R. D. Pyrene Micro-partitioning and Solubilization by Sodium Dodecyl Sulfate Complexes with Poly(ethylene Glycol). *J. Phys. Chem. B* **1999**, *103* (48), 10582–10590.
- (45) Saigal, T.; Riley, J. K.; Golas, P. L.; Bodvik, R.; Claesson, P. M.; Matyjaszewski, K.; Tilton, R. D. Poly(ethylene Oxide) Star Polymer Adsorption at the Silica/aqueous Interface and Displacement by Linear Poly(ethylene Oxide). *Langmuir* **2013**, *29* (12), 3999–4007.
- (46) Riley, J. K.; Matyjaszewski, K.; Tilton, R. D. Electrostatically Controlled Swelling and Adsorption of Polyelectrolyte Brush-Grafted Nanoparticles to the Solid/liquid Interface. *Langmuir* **2014**, *30* (14), 4056–4065.
- (47) Velegol, S. B.; Tilton, R. D. Specific Counterion Effects on the Competitive Co-Adsorption of Polyelectrolytes and Ionic Surfactants. *J. Colloid Interface Sci.* **2002**, *249* (2), 282–289.
- (48) Velegol, S. B.; Tilton, R. D. A Connection between Interfacial Self-Assembly and the Inhibition of Hexadecyltrimethylammonium Bromide Adsorption on Silica by Poly- L -Lysine. *Langmuir* **2001**, *17* (1), 219–227.
- (49) Nishikido, N. Estimation of Micellar Charge or Aggregation Number from Conductivity and Counterion-Activity Measurements. *J. Colloid Interface Sci.* **1983**, *92* (2), 588–591.
- (50) Evans, H. C. 117. Alkyl Sulphates. Part I. Critical Micelle Concentrations of the Sodium Salts. *J. Chem. Soc.* **1956**, 579.
- (51) Kim, J.-H.; Domach, M. M.; Tilton, R. D. Effect of Electrolytes on the Pyrene Solubilization Capacity of Dodecyl Sulfate Micelles. *Langmuir* **2000**, *16* (26), 10037–10043.
- (52) Pashley, M.; Ninham, B. Double-Layer Forces in Ionic Micellar Solutions. *J. Phys. Chem.* **1987**, *91* (1), 2902–2904.
- (53) Tadmor, R.; Hernández-Zapata, E.; Chen, N.; Pincus, P.; Israelachvili, J. N. Debye Length and Double-Layer Forces in Polyelectrolyte Solutions. *Macromolecules* **2002**, *35* (6), 2380–2388.
- (54) Muthukumar, M. Ordinary–extraordinary Transition in Dynamics of Solutions of Charged Macromolecules. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113* (45), 12627–12632.
- (55) Sedláč, M. The Ionic Strength Dependence of the Structure and Dynamics of Polyelectrolyte Solutions as Seen by Light Scattering: The Slow Mode Dilemma. *J. Chem. Phys.* **1996**, *105* (22), 10123–10133.
- (56) Sedláč, M. Domain Structure of Polyelectrolyte Solutions: Is It Real? *Macromolecules* **1993**, *26* (5), 1158–1162.
- (57) Brown, W.; Fundin, J.; Miguel, M. da G. Poly(ethylene Oxide)-Sodium Dodecyl Sulfate Interactions Studied Using Static and Dynamic Light Scattering. *Macromolecules* **1992**, *25* (26), 7192–7198.