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Measurement of depletion interaction in semi-dilute solutions of worm-like surfactant aggregates

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Abstract. — The force as a function of separation is measured between two mica surfaces coated with adsorbed bilayers of cetyltrimethylammonium bromide (CTAB) and immersed in aqueous solutions of elongated and semi-flexible micelles of CTAB. For the range of concentrations studied, where the ionic strength is kept constant, the worm-like micelles form a transient network similar to an entangled polymer solution (semi-dilute regime). The electrical double-layer repulsion between the adsorbed bilayers is preceded at larger separations by an attraction with two distinct regimes. The first one is the strongest and is attributed to a complete depletion of micelles. As predicted by the theory, the range of the interaction is reduced while the strength is increased as the volume fraction is increased. The second regime appears at larger separations where an oscillation-like shape is superimposed on a weak attractive background. It is suggested that the attraction results from an orientation depletion of the anisotropic micelles aligning along the surfaces. The oscillatory behavior is further evidenced with measurement of the structure factor by SANS.

The stability of colloidal suspensions may be affected by the addition of polymers [1] or other nanometric particles. In presence of non-adsorbing polymers, flocculation was observed as early as 1938 [2], later interpreted [3] in terms of depletion forces due to the imbalance in the compressive osmotic pressure acting on the surface of one colloid. A rich background both in theory and in experiment has elaborated the concentration dependence of this depletion attraction in polymer solutions [4-7]. Other nanometric particles such as micelles [8, 9] may play a similar role to polymers. Recently in solutions of globular charged micelles, the depletion force profile was directly measured [10, 11] using a surface force apparatus (SFA) [12]. Unfortunately, attempts to determine the force-distance profile in non-adsorbing polymer medium have failed. To date the only portion of such a profile to be known is *via* adhesion measurements [7]. The profile can be provided with a SFA, but as the sensitivity of the device requires concentrations of at least a few per cent, full equilibrium conditions are rarely met. Measurements are hindered by the slow exclusion of the polymer from the narrow gap coupled with viscoelastic properties. Force profiles in solutions of linear particles non-adsorbing remain to be measured.

In the present study, the difficulties associated with polymers are in part overcome by the use of "living" polymers, linear and flexible micelles which can break and recombine [13]. Unlike regular polymer solutions for which equilibrium only applies to the configurational freedom, the polydispersity and the mean length of the chains are not fixed but in thermal equilibrium, as aggregates continuously exchange material due to the rapid reversibility of self-assembly process [13]. In the semi-dilute regime, the chain length of the entangled micelles is dependent on concentration and not constant as for regular polymers [13]. The key advantage of their labile nature is that the polydispersity can be adapted to release any conformation restrictions, induced by confinement, and so any equilibrium is more rapidly achieved than for regular polymers. As a result both the range and magnitude of the depletion interaction can be expected to differ from a real polymer system. Indeed, in dilute regime the local average length of confined micelles is predicted to decrease with surface separation [14]. Further, the persistence length of those semi-flexible objects ($l_p = 15\text{-}20\text{ nm}$) is larger than classical macromolecules. This property may affect the interaction profiles inducing structural effects and even phase transitions upon confinement. Finally, although the equilibrium statistics of living polymer solutions are quite well described by scaling laws, the exponents depart from those expected for regular polymers [13].

In our previous study on depletion, the system was comprised of globular micelles of cetyltrimethylammonium bromide (CTAB) [10, 11]. At relatively weak ionic strength (about 0.05 M for KBr solutions [15, 16]) these micelles undergo a transition in shape and size, becoming elongated to thin flexible cylinders with lengths up to a few micrometers. All experiments reported here were carried out at fixed ionic strength (0.1 M KBr; Pronalys, analar grade) for which the binding equilibrium is barely affected over a large range of CTAB (Kodak) concentrations [15, 16], and at 30 °C, above the Krafft temperature of the solutions. Force-distance measurements between mica surfaces immersed in these solutions (from the c.m.c up to 12 wt % in CTAB) were performed with a SFA [12]. Care was taken to assure that full equilibrium of the viscoelastic system had been attained at each separation. When one surface is moved, viscous drag forces prevent the other surface from following instantaneously and sufficient time for reequilibration must be allowed, otherwise force profiles may become hysteretic under compression or decompression. If the surfaces are approached too quickly, the chains do not have sufficient time to relax from their entanglement and migrate outwards from the confinement towards the reservoir. In a restricted equilibrium, rapid measurements mean that no longer is the chemical potential constant, rather it is the number of chains which is now fixed, giving rise to a repulsion [14]. Equilibration times are of the order of a few seconds at the lowest concentrations but increase notably with the volume fraction, Φ , to the order of minutes for most viscous solutions. Thermodynamic equilibrium in this extreme case is unattainable: for $\Phi > 0.12$, a change in surface separation of about 1 nm requires an equilibrium time of around one minute, increasing at small separations, so that the inherent thermal drift of the surfaces hinders both reliable calibrations and so force profiles.

Comparison of the contact position in micellar solutions with that of bare mica indicates that both mica surfaces have an adsorbed charged CTAB bilayer in direct agreement with previous observations [10, 11, 17]. At small separations ($< 15\text{ nm}$) the interaction is always exponentially repulsive (Fig. 1c), as expected for an electrical double-layer interaction with no apparent contribution from charged micelles. Further, it changes little with CTAB concentration. Indeed, the screening length, κ^{-1} , is almost completely determined by the added salt whereas the dissociated counterions Br^- from the surfactant and free CTA^+ ions are a small correction [11]. A fit to the electrostatic repulsion by a linearized Poisson-Boltzmann approximation indicates that the decay-length decreases from 1.1 to 0.9 nm over the concentration range studied, in agreement with predictions [17].

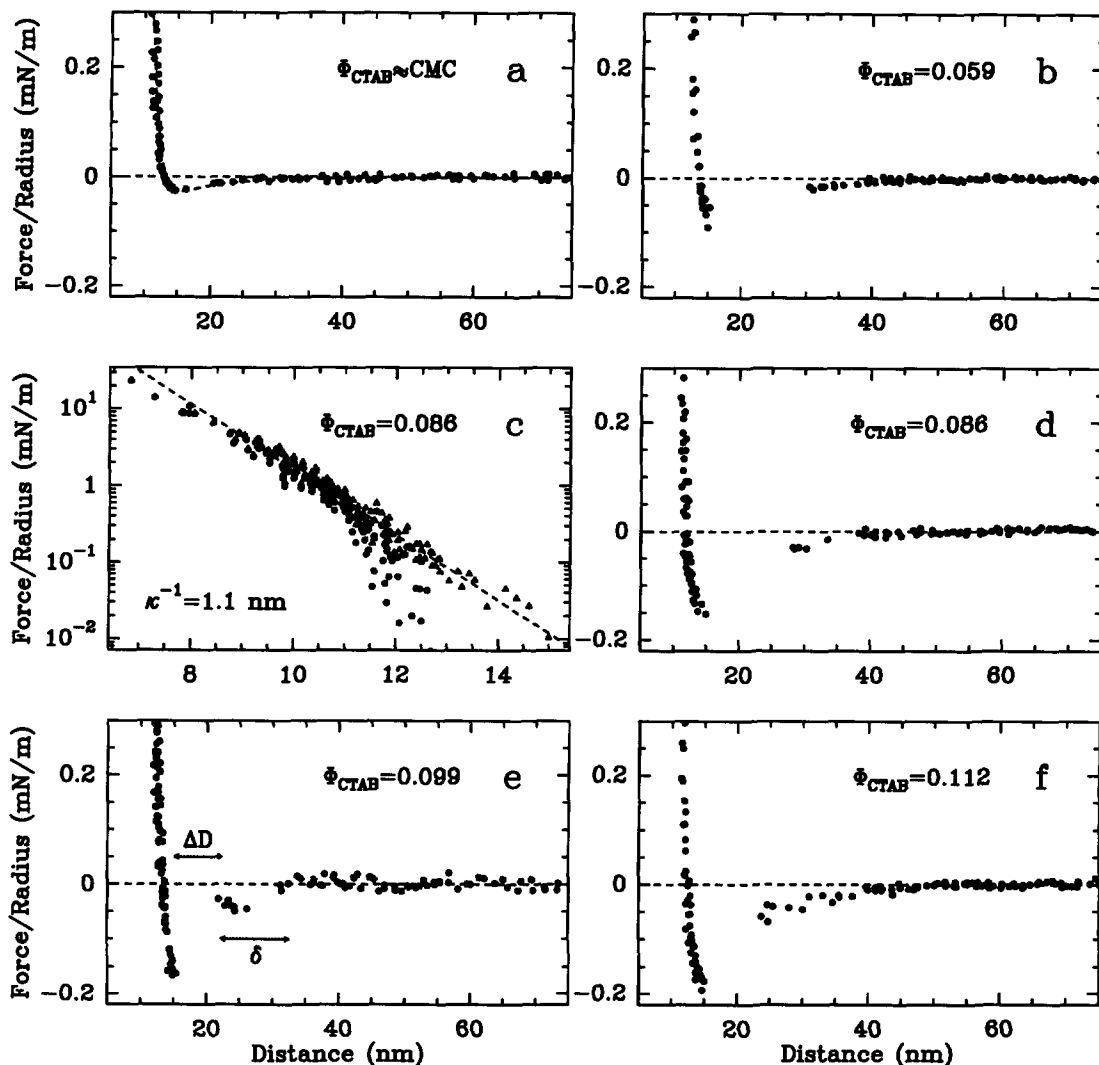


Fig. 1. — Measured force F (normalized by the mean radius of curvature R of the surfaces) as a function of surface separation between crossed mica cylinders, each coated with an adsorbed bilayer of CTAB (thickness ≈ 3.1 nm), and immersed in worm-like micellar solutions of CTAB at constant ionic strength (added $[KBr] \approx 0.1$ M). All curves are the superposition of at least three inward and outward runs. (a) At the c.m.c. the attractive minimum around 15 nm is due to the competition between the attractive dispersion forces and the double-layer repulsion (the dashed line is the best-fit numerical solution). (b-f) As the CTAB weight fraction, Φ , increases, this minimum deepens due to depletion in micelles. (c) After subtraction of the dispersion forces and the constant F_d/R (depth of the depletion minimum; see text), the resulting force (triangles) is purely exponential as expected for an electrical double-layer repulsion. (e) The oscillation-like shape (δ range) which superimposes on the attractive regime at larger separations is supposed to be due to an orientation depletion of the semi-flexible polymers aligning along the surfaces.

At larger separations the force deviates from a pure exponential repulsion to reveal a secondary minimum located at ≈ 15 nm which is present at all concentrations. Near the c.m.c.

(Fig. 1a) this minimum is shallow, ≈ 0.025 mN/m and remains steady up to about $\Phi = 0.02$. The depth is consistent with the expected contribution of van der Waals attraction, within the experimental error. However, at larger weight fractions (semi-dilute regime), the secondary minimum deepens (an order of magnitude stronger at $\Phi = 0.112$, the largest weight fraction reported; Fig. 1f), initially broadening and finally contracting as the concentration is increased. At weight fractions above 0.04, the attractive part of the force profile is no longer purely monotonic as a weak repulsion is superimposed, as exemplified at $\Phi = 0.1$ between 21 and 32 nm (Fig. 1e). This marks the barrier between two distinct regimes each showing a different dependency upon Φ . Unlike the secondary minimum, the regime preceding the barrier at larger separations evolves slowly with Φ . Its range appears to be almost steady with a mean value of $\delta \approx 10.5 \pm 1.5$ nm; the uncertainty arises from difficulties in assigning precisely the beginning of this shallow attraction. The intrinsic device instability for attractive regimes renders accurate determination of the profile shape difficult. Indeed, at small concentrations, the repulsive barrier is low while at larger Φ , despite larger magnitudes, the increasing relaxation time defeats accurate measurement (compare the noise in the data between Figs. 1a and 1e).

Strong similarities with the force profiles observed previously in concentrated solutions of spherical micelles [10] suggest that structural effects are also present in these worm-like systems. In the former study, the oscillatory profile indicates a degree of local order correlations between the non-adsorbing aggregates. Upon addition of salt, correlations are progressively reduced as the related structural effects vanish when the diffuse layers are compressed [11], but may still be in effect at sufficiently high surfactant concentrations [18]. This is confirmed by SANS performed on the instrument PAXY at Laboratoire Léon- Brillouin (CEN-Saclay, France) for CTAB in D₂O-0.1 M KBr (Fig. 2). In the low wavevectors range where the structure factor dominates, a broad peak highlights the persistence of correlations at the highest studied concentrations, for which the force profiles display the most pronounced oscillatory shape. The peak location (inset Fig. 2) and the period of the oscillation (Fig. 1e) give comparable lengths, though direct correspondence is not straightforward. A simple model would be to describe the micelles as assemblies of flexible strings of connected rigid rods, each rod with a length comparable to the persistence length. As discussed by Auvray, confinement of dilute solutions of rigid rods between hard walls induces an orientation depletion [19]. Due to lack of space, anisotropic objects tend to align along walls for gaps smaller than their long axis, and hence their local density is reduced. For more concentrated bulk solutions, in addition to a similar depletion effect, local ordering near walls is expected as interactions between anisotropic particles would aid to their alignment. Such a collective behavior is then consistent with the observed structural effect superimposed on an attractive background. Note that such a mechanism is likely to be favored in living polymers systems since labile worm-like micelles can adapt their average length and polydispersity in order to release the confinement constraint.

The main result of the present study, which is the concentration dependence of the deepest minimum, is now discussed. This behavior is of interest as a comparison with regular polymers confined between hard walls. Conformation of regular flexible and non-adsorbing polymers in good solvent and in semi dilute regime has been calculated by Joanny *et al.* [6]. For narrowing gaps, the midpoint density of polymer segments decreases below some separation and vanishes completely at a critical separation of $\pi\xi$, where ξ is the average mesh-size of the entanglement. When the chains are fully depleted from the gap, the deficit in osmotic pressure, $\Pi_{\text{osm}} \approx k_B T / \xi^3$, causes the two plates to attract. In the limit of two identical spherical walls of large radius R , so that $R \gg \pi\xi$, the attractive force is a linear function of the separation D :

$$F \propto -\pi R(\pi\xi - D)k_B T / \xi^3, \quad D \leq \pi\xi \quad (1)$$

Note that equation (1) uses the Derjaguin approximation which relates the force, $F(D)$,

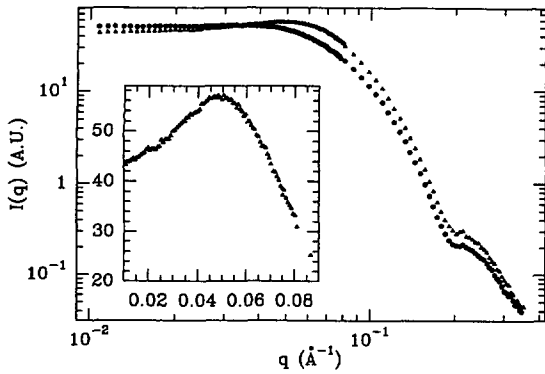


Fig. 2

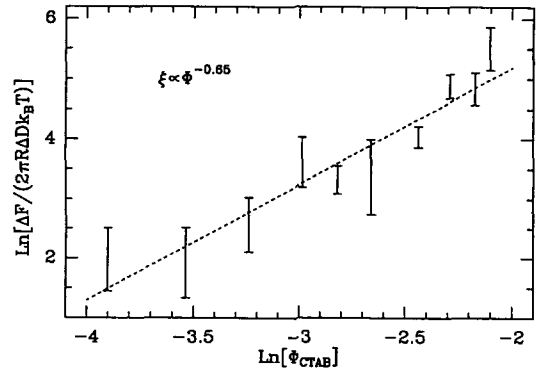


Fig. 3

Fig. 2. — SANS pattern from a 6% (dots) and 10% (triangles) solution of CTAB in D_2O with 0.1 M KBr. The log-log scale highlights the different regimes encountered for the variation of the scattered intensity with q [25]. At the largest q , $I(q)$ varies as $q^{-1} \exp(-R_c^2 q^2/2)$, where R_c is the radius of the micellar cylinder, and then follows the Porod limit (q^{-4}). At the lowest q , the entangled network of the worm-like chains gives a flat profile for $I(q)$. In the intermediate q -range, the bump in the structure factor (enlarged in the inset, drawn on a linear scale) highlights the presence of correlations at high surfactant concentrations.

Fig. 3. — Scaling law for the mesh-size of the entanglement, as extracted from the depth $(F_s - F_d)/R$ of the secondary minimum and the depletion range (ΔD) observed in the force-distance profile. The error bars reflect the uncertainty in the measurements between different runs and different experiments at the same CTAB concentration.

between two spheres and the surface free energy of interaction, $E(D)$, of two parallel plates ($F(D) = \pi R E(D)$). Since ξ varies with the polymer volume fraction as $\Phi^{-\alpha}$ ($\alpha \approx 3/4$), the range of the depletion interaction decreases also as $\Phi^{-\alpha}$, while the adhesion, $F(D = 0)$, increases as $\Phi^{2\alpha}$ when the chain concentration increases.

A very different picture is predicted in the case of adsorbing polymers: first a rapid increase in surface adsorption for infinitesimal volume fraction [20], then followed by a plateau at larger concentrations [21]. This results in a decrease in the cross-bridging attraction because of excluded effects in the gap. There, the range and strength of the attraction are not determined by the solution concentration but instead are rather sensitive to the coverage and thickness of the adsorbed amount which depend essentially on the solvent quality and on the mean chain length in dilute regime.

In regards to the two different situations, only the depletion one is consistent with the observed concentration dependence of a deepening minimum: as illustrated in figure 1, this attractive regime is characterized by a contracting range together with an increasing strength as Φ increases. Complete depletion of living polymers is thus expected to be achieved as soon as the separation between the walls is smaller than a few ξ . In the SFA, the two crossed cylinders (mean radius $R \approx 2$ cm) of molecularly smooth mica surfaces are geometrically equivalent to two spheres of radius $2R$ approaching each other when $D \ll R$. Under this approximation equation (1) predicts for the force:

- (i) a linear profile after subtraction of the dispersion contribution. This cannot be checked as either the remaining forces are too small and noisy to enable a reliable fit (at low Φ), or the

- whole attractive profile is inaccessible due to the mechanical instability of the device and appears discontinuous in the recorded data at higher concentrations ($\Phi \geq 0.05$);
- (ii) a scaling behavior of the volume fraction both for the range and the adhesion. The coefficient α is predicted to be 0.77 for real polymers with strong excluded volume, and 0.5 in regimes of weak excluded volume where mean-field exponents are expected instead [22]. For a pure depletion origin of the interaction over the interval ΔD (Fig. 1e) ranging between the locations of the structural oscillation-like maximum (free energy density at the maximum: $F_s/2\pi R$) and the secondary minimum (depth: $F_d/2\pi R$), equation (1) gives:

$$\frac{F_s - F_d}{2\pi R \Delta D k_B T} \propto \xi^{-3} \propto \Phi^{3\alpha} \quad (2)$$

Over the dilution range studied, the best linear fit of equation (2) plotted on a log-log scale (Fig.3) gives a slope of 1.95 ± 0.15 , i.e. $\alpha \approx 0.65 \pm 0.05$. Although the fit is carried out over one decade of dilution only with a large scatter in the data, the value extracted for this exponent is reasonable. It falls in the range 0.6-0.8 obtained for a large variety of worm-like micellar systems [13]. It appears smaller than the result ($\approx 3/4$) obtained by dynamic light scattering for the same system and over a larger dilution range [13], but comparable to the result obtained by fringe-pattern photobleaching recovery techniques, where exponents have been shown to be very dependent on the ionic strength [23]. Fit procedures applied onto the double layer repulsion occurring at small separations, typically between 8 and 15 nm, indicate that the corresponding force profiles are well described (Fig. 1c) by a law $F(D)/R = A \exp(-\kappa(D - 2T_{\text{bil}})) - A_{\text{Ham}}/6D^2 - B$, where A is a constant related to the surface potential, $\kappa^{-1}(\Phi)$ is the decay length in very good agreement with the theoretical prediction, T_{bil} is the thickness of a CTAB bilayer adsorbed on each surface ($2T_{\text{bil}} \approx 6.2$ nm), $A_{\text{Ham}}(D)$ is the effective Hamaker function, and $-B(\Phi)$ is a constant always very close to the adhesion force, $F_d(\Phi)/R$, within the experimental accuracy. This result means that ΔD describes almost the full range of the depletion attraction, or equivalently, that the effective hard wall radius for the mica surfaces with their adsorbed charged bilayers, $R_{\text{eff}} = R + \delta R$, has been incremented by half the minimum location, $\delta R \approx 15/2$ nm, in the presence of charged aggregates [10]. In other words, at large separations ($D = \infty$), owing to the electrostatic interaction between the charged walls and the ionic micelles, the density of polymer segments vanishes within a layer of thickness, δR , around each wall. Thus the specific excess of free energy becomes zero for separations smaller than $2\delta R$ and the corresponding force between the two spheres becomes a constant equal to $2\pi R \Delta E(D = 2\delta R)$. According to equation (1), the range of the depletion interaction scales linearly with ξ . A linear fit of the log-log curve of ΔD vs. Φ provides a slope of -0.63 corroborating well the preceding value for α .

In order to compare the measured depletion range, ΔD , and the mesh-size, ξ , light-scattering was carried out. In the semi-dilute regime, at small scattering vectors ($q\xi < 1$), the correlation length of the flexible chains can be extracted from the angular distribution of the scattered intensity. For concentrations less than 3% the expected Ornstein-Zernike law was followed [24, 25]. At $\Phi = 0.03$, this gives an estimated ξ of 13.5 ± 2.0 nm, while the force measurements indicate an interaction range $\Delta D = 21 \pm 2$ nm. In contrast, at higher concentrations no reliable value for ξ can be extracted from the observed too small slope of the angular distribution of the intensity. The range of the depletion appears smaller in the semi-dilute regime of living polymers than the theoretical one predicted for real non-adsorbing polymers ($k\xi$ with $k = 1 - 2$ instead of π). Such a deviation may find its origin in the labile nature of the worm-like aggregates, being able to change their length distribution upon confinement [14], and hence capable to delay their depletion from between the walls. Note also that quantitative comparison with theory is uneasy. Indeed, the dilution range accessible with a SFA coincides with a regime

where several characteristic lengths are comparable, whereas the theory considers the mesh-size of the network as being the dominant length. Here, the mesh-size, the persistence length, and the mean separation between micelles become similar at high concentrations as evidenced by the structure factor. Further, the scaling behavior of ξ as a function of Φ can be altered before the concentrated regime is attained. Indeed, at the ionic strength retained in this study, the overall micelle size is not much larger than the persistence length [16, 24], and a cross-over to marginal solvent may be suspected at some concentrations [26].

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