

Dynamic Friction by Polymer/Surfactant Mixtures Adsorbed on Surfaces

Linmao Qian,[†] Magali Charlot, and Eric Perez*

Laboratoire de Physique Statistique de l'Ecole Normale Supérieure, UMR8550, 24 rue Lhomond, 75231 Paris Cedex 05, France

Gustavo Luengo,* Anne Potter, and Colette Cazeneuve

L'Oreal Recherche, 1 Avenue Eugène Schueller, 93601 Aulnay sous Bois, France

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A cationic polyelectrolyte was adsorbed on mica from highly concentrated solutions. The friction and surface force behaviors of the adsorbed layers in aqueous media were studied using a new homemade surface force apparatus (SFA). The long-range repulsions produced by the pure cationic polymer at low salt concentration indicate that the chains are in an extended conformation. The addition of anionic surfactant or of salt condenses the cationic polymer chains as evidenced by the much shorter range of the repulsions. These forces are, for both conformations, a combination of steric and double-layer forces. During sliding, the friction forces produced by the adsorbed layers increase monotonically with the load. A strong dependence of these forces on the sliding speed is noticeable for the extended conformations, while the dependence vanishes in the coiled conformations. This study shows the important role of the conformational state of adsorbed polymer chains on their tribological properties.

Introduction

Neutral or charged polymers display various adsorption properties depending on their flexibility, on the solvent, and on the surface characteristics. They play an important role in industrial applications. The presence of polymers on surfaces has been extensively researched in view of understanding and controlling the surface forces of steric nature and the tribological properties of surfaces. In general, the interest is focused on the protection of the underlying surfaces against wear and/or the improvement of their friction properties.^{1,2} Therefore, the interaction of highly charged macromolecules (polyelectrolytes) adsorbed on a surface is of great interest from both fundamental and applied points of view.^{3,4} Furthermore, in many industrial applications such as washing, emulsification, painting, and cosmetology, among others, these systems can be made more complex with the incorporation of free surfactants that can modify the polymer and compete for adsorption.

It is nowadays accepted that the adsorption of these systems is governed by electrostatic forces that largely depend on the surface charge density and the ionic strength of the solution.⁵ When a surfactant is added to a polyelectrolyte solution, their association is further complicated by the presence of a surface. The polymer conformation at the surface is a delicate balance of various interactions and yet far from being predictable. There is however an interest in understanding the molecular conformations which the polymer and the surfactants can take near the surface in contrast to the bulk.

The use of surface experimental techniques becomes necessary to probe the structure of the surface adsorbed layer and the extension of the polymer in the solution. Neutron reflec-

tivity^{6,7} has proved to be very adequate to measure the profile of adsorbed layers. The conformation of adsorbed molecules and the density of the layer determine the nature of the forces involved between such layers. In those situations, atomic force microscopy (AFM)⁸ and measurements with a surface force apparatus (SFA)⁹ were shown to be excellent experimental techniques. Much of the SFA work has been directed toward the understanding of the forces involved at the mica surface.^{10–12}

Brushes of polyelectrolytes could be formed on mica by adsorption of a copolymer onto hydrophobic surfaces¹³ or from Langmuir–Blodgett deposition.¹⁴ Numerous SFA studies involving adsorbed layers of polyelectrolytes involved low concentrations (0.001–0.01%) and long adsorption times (overnight).^{15–19} These studies have concluded that, from a low concentration and a long adsorption time, highly charged polyelectrolytes adsorb flat on surfaces of opposite charge, and the resulting interaction is essentially double-layer forces. If the polyelectrolyte is adsorbed from a higher concentration, steric interactions set in.¹⁷ Polyelectrolytes with a low charge density do not adsorb as flat layers and give rise to steric repulsions.^{15,18}

In the cosmetic industry, today's shampoos do more than cleanse hair but are expected to provide also additional benefits, such as conditioning, ease of combing, a soft feel, and a nice appearance. A variety of cationic polymers are often formulated in association with surfactants to provide the conditioning effect. However, in shampoos, the adsorption process takes place during a limited amount of time (minutes) with highly concentrated solutions, and it is of interest to know the nanotribological behavior of such layers. The aim of the present work is to study systems of industrial interest which involve highly charged polyelectrolyte layers resulting from adsorption for a limited amount of time (5 min) and from a highly concentrated solution (1%), conditions close to shampoo formulations used to promote conditioning of hair. With a homemade surface force apparatus^{20,21} capable of measuring normal and shear forces

* To whom correspondence should be addressed. E-mail: perez@lps.ens.fr (E.P.); gluengo@recherche.loreal.com (G.L.).

[†] Present address: Tribology Research Institute, Southwest Jiaotong University, Chengdu 610031, Sichuan Province, China.

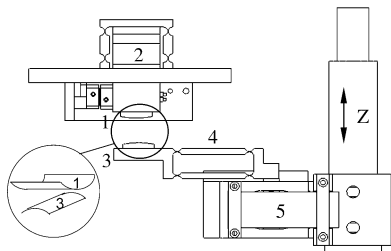


Figure 1. Schematic drawing of the apparatus. The lower surface is fixed to the normal force spring attached to a piezoelectric bimorph system, allowing for horizontal translation. The upper surface is attached to a stiff spring system (10^4 N/m). Any friction force applied to the upper surface displaces it horizontally. Its movement is measured by capacitance plates. A piezoelectric translator allows the distance between the surfaces to be changed by moving the lower surface relative to the upper one. This distance is measured by multiple-beam interferometry.

simultaneously, surface forces and friction forces were measured to understand the nanotribological properties of adsorbed layers made of a mixture of a polyelectrolyte and a surfactant. The study provides information on how the polyelectrolyte conformation can affect its dynamics under shear.

Materials and Methods

The selected cationic polymer is a quaternary ammonium derivative of hydroxyethyl cellulose (HC), pure grade from Union Carbide, with a molecular weight (MW) of 400000 and a cation content of 1 mequiv/g ($\sim 2/3$ of the monomers are charged). The friction and surface force properties were studied either with the polymer alone or with the addition of an anionic surfactant, lauryl ether sulfate (TA1). Ultrapure water from an Elgastat Maxima unit with a resistivity of 18.2 M Ω /cm and a maximum level of total organic carbon of 3 ppb was used, ensuring the lowest possible level of contamination. The KNO₃ was Merck Suprapure. We investigated the adhesion and friction of two aqueous systems containing either 1% HC or 1% HC + 10% TA1.

Surface Force Measurements. All the adhesion and friction experiments were made with a homemade two-dimensional SFA that has been thoroughly described previously.²⁰ As in the now classical SFA,⁹ the apparatus involves two curved molecularly smooth mica surfaces which are horizontal, with a curvature radius $R \approx 2$ cm, arranged in a crossed cylinder geometry (Figure 1). The distance D between the surfaces is controlled by a two-stage micrometric unit and a piezotranslator.

The friction forces are measured between the two surfaces (1 and 3) of Figure 1. The upper surface (1) is attached to a system of springs and capacitance plates (2) which can measure the bidimensional friction forces with an accuracy of ~ 10 μ N in the version of the setup which was used. The lower surface (3) is attached by means of a spring (4) (used to measure the load) to a piezoelectric bimorph system (5) that generates a bidimensional lateral movement to create friction. Strain gauges on the bimorph elements can measure lateral displacement. The bimorph system is attached to a three-stage vertical translation that controls the distance between the surfaces. The fine translation stage (not shown) consists of a piezotranslator that has a repeatability of 1 nm on a travel distance of 12 μ m. The distance D is measured by multiple-beam interferometry to within ± 1 –2 Å . The load, i.e., the normal force between the surfaces, is measured by the spring (4). With a spring constant $K \approx 700$ N/m, the accuracy of the normal force determination is ~ 2 μ N.

The mica used in the measurements is the highest quality, optically clear muscovite green mica. Ethanol of spectroscopic

grade was used in the cleaning procedures. Mica was cleaved down to 2–5 μ m, cut into pieces (0.8×0.8 cm), put onto a back-sheet to avoid surface contamination, and silvered from the backside. Just before an experiment two equally thin mica sheets were glued, silvered side down, onto two cylinder disks in a cross configuration.

At the beginning of each experiment, to check the cleanliness of the mica surfaces and calibrate the zero distance, the mica-carrying disks were brought into contact in air. Surfaces which showed a smooth, distinctive jump into adhesive contact were considered to be free of debris and other types of contamination. The fringe positions were recorded to calibrate the zero distance.

Subsequently, the two disks were taken out from the apparatus and immersed into the respective HC aqueous solution for 5 min at 20 $^{\circ}$ C. The samples were then rinsed statically for 1 min in a 1 mM KNO₃ aqueous solution to remove the physical adsorption layer of HC. KNO₃ aqueous solution was chosen to eliminate very long range electrostatic repulsions that occur between charged surfaces across pure water. Then, the drained but still wet mica surfaces were put back into the apparatus. Finally, 100 μ L of 1 mM KNO₃ aqueous solution was introduced between the two surfaces and formed a meniscus. A small beaker full of water was introduced into the apparatus to reduce the evaporation of the meniscus and limit the subsequent possible changes of salt concentration.

After equilibration for 2 h, force–distance profiles were measured during approach and separation of the surfaces. Immediately after, friction force measurements were performed using a triangular voltage input signal to move the surfaces at constant speed as is common in tribological measurements. The travel distance of one cycle was 200 μ m, which is much larger than the size of the contact region. The highest frequency used is 1 Hz, i.e., much below the resonance frequency (50 Hz). The drift of the separation distance was often around 5 nm/min, and a correction was applied to keep track of the load. The effects of the speed and load on friction were investigated for the two systems studied. At least two separate experiments were performed and three curves per experiment obtained for each case to ensure the reproducibility of the measurements.

Results

Normal Forces. Before any friction measurements were done, normal forces were measured as a function of distance in each experiment. This provides some information about the film structure, helps to define the conditions at which friction forces will be measured, and helps to analyze the friction behavior later on.

In a first series of experiments, HC polymer was adsorbed from an aqueous solution containing 1% HC as described above. Figure 2 shows the force–distance profiles. An exponential repulsive force starts from a separation of 500 ± 100 nm with a decay length of 83 ± 16 nm (circle plots). This variability of the range and decay length of the force is due to the evaporation of water from the meniscus whose salt concentration is very sensitive to the evaporation given its small volume. This effect of salt concentration will be illustrated and discussed further below with the use of high salt concentrations. Upon compression, the repulsion rises gradually, and was measured up to a value of $F/R = 40$ mN/m, corresponding to a polymer thickness of ~ 6 nm (solid circle). The measured force–distance profiles, plotted on a semilogarithmic scale, appear to be linear over a distance range of 20–500 nm. No adhesion force was measured for the polymer HC. The approach and separation curves followed the same path (showing no hysteresis behavior), as shown in the Figure 2.

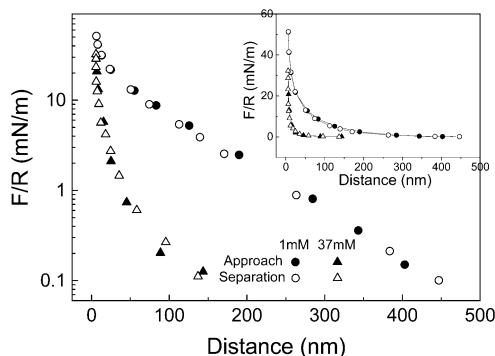


Figure 2. Normal forces vs distance between two surfaces coated with a layer of HC polymer (adsorbed from a 1% w/w solution) in 10^{-3} M KNO_3 (circles) and in 37 mM KNO_3 (triangles).

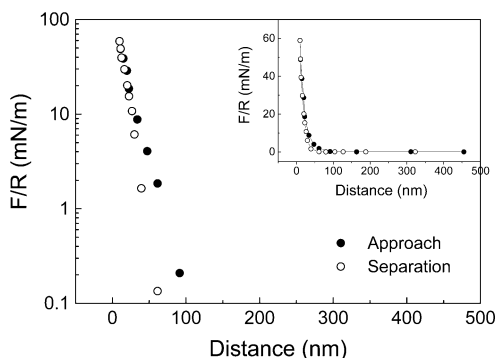


Figure 3. Normal forces vs distance between two surfaces coated with an adsorbed layer of a mixture of HC polymer with anionic surfactant in 10^{-3} M KNO_3 .

When several hours was allowed for the evaporation, the decay lengths were shorter (not shown), suggesting a condensation of the adsorbed polymer layer. To confirm this explanation, one separate experiment was done in which the HC layers were adsorbed in the same conditions, but the forces were measured in a much higher salt concentration (37 mM KNO_3). A large change of properties was observed as shown in Figure 2 (triangle plots). The forces extended to a much shorter range, ~ 150 nm, with nonexponential variations, suggesting that the polymer layer shrunk to a smaller size. Therefore, the effect of salt is to strongly compact the polyelectrolyte molecules.

The addition of an anionic surfactant (TA1) to the polyelectrolyte in 1 mM KNO_3 changed the force profile dramatically (in comparison to that of Figure 2, polyelectrolyte in 1 mM KNO_3) as can be seen in Figure 3. On approaching the surfaces, no repulsive force was detected until a distance of ~ 100 nm was reached; the force–distance profile was then much steeper and still exponential with a decay length of 12 ± 4 nm. It needed application of a force of about 50 mN/m to decrease the gap to $D = 8$ nm. In contrast to the pure HC, a small hysteresis behavior was noticeable (Figure 3) between the approaching and separating branches of the curves.

Thus, the addition of the anionic surfactant considerably changed both the extent and compressibility of the adsorbed layers by condensing the charged polymer HC. No adhesion force was observed in this case.

Friction Forces. Once the force–distance profile was known, it was easy to adjust the load applied to the surfaces. The friction forces were measured for various loads and surface separations. Figure 4 shows a typical frictional trace, over the 200 μm travel distance, for highly compressed HC layers (at 2 mN load) with about 6 nm thickness at a sliding velocity of 19 $\mu\text{m/s}$. A friction force of about 200 μN can be deduced from this trace. The

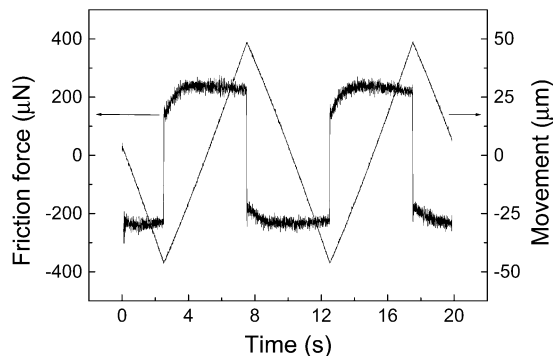


Figure 4. Lateral movement (triangular signal) of the lower surface as probed by the strain gauges which are glued on the piezoelectric bimorphs (scale on the right). Friction force traces (scale on the left). Because the mechanical parts cannot be aligned to better than a small fraction of a degree,²¹ some correction has to be applied to keep the same load during the lateral movement. This correction introduces some error which manifests itself as a nonhorizontal baseline as shown in the friction trace.

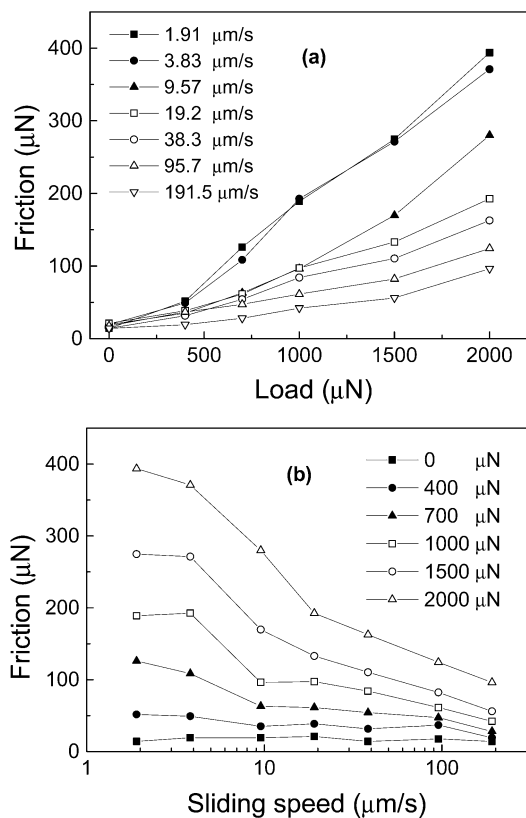


Figure 5. (a) Friction force vs load for HC in 10^{-3} M KNO_3 . (b) Same data plotted as friction force vs sliding speed.

displacement of the lower surface probed by the strain gauges is also shown.

Various loads were applied ranging from 400 to 2000 μN . The friction force measurements with HC layers in 1 mM KNO_3 solution over the distance range of 6–400 nm between the surfaces yielded the curves shown in Figure 5a. The highest load was 2000 μN , because, above this value, some surface damage occurred frequently. This could be seen at first from the friction traces that showed an irreversible change of friction behavior; as the damage increased, it could be seen from the interference fringes, which revealed a deformation of the surfaces.

The friction of polymer HC in 1 mM salt concentration is highly sensitive to the sliding speed. The experimental points

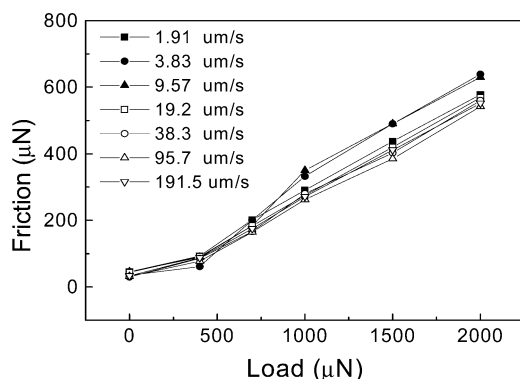


Figure 6. Friction force vs load for HC in 10^{-3} M KNO_3 measured 6 h after the normal force measurements (i.e., 6 h allowed for evaporation, relative to Figure 5a).

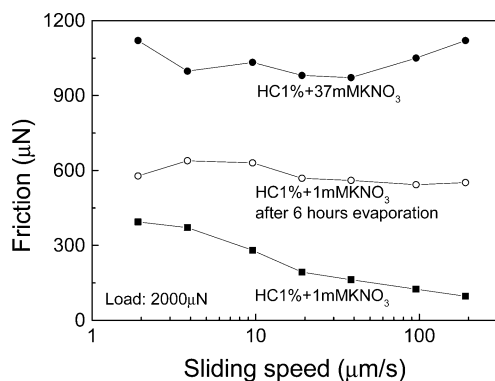


Figure 7. Friction force vs speed at a load of 2 mN for HC in 1 mM KNO_3 , in 1 mM KNO_3 after 6 h of evaporation, and in 37×10^{-3} M KNO_3 .

of Figure 5a are replotted in Figure 5b as the friction force versus shear speed. They show that the friction force decreases monotonically with the logarithm of the speed. When the sliding speed increases from 1.91 to 191 $\mu\text{m/s}$, the friction forces decrease by about 80%. Some variability was observed in this decrease of the friction forces with speed. This was correlated with the time allowed for water evaporation from the meniscus. When more time was allowed for evaporation, the friction force showed a smaller decrease with speed.

Figure 6 shows the friction forces measured after evaporation was allowed to proceed for 6 h. While the sliding speed increased by 100-fold, the friction forces only varied by about 15%. In a way similar to that observed with the normal forces, more time allowed for water evaporation from the meniscus means a higher salt concentration. To probe more rigorously the effect of salt concentration, one experiment was performed with a much higher salt concentration, i.e., 37 mM KNO_3 . The friction forces became almost independent of sliding speed as can be seen in Figure 7, confirming that the friction dependence on speed of this polymer was highly sensitive to salt concentration. In addition, the level of friction forces increased with salt concentration: at a load of 2 mN, the friction forces were more than twice as high in 37 mM salt compared to 1 mM salt solution (Figure 7).

In low salt concentration (1 mM KNO_3), adding 10% anionic surfactant TA1 to the 1% cationic polymer HC dramatically changed the friction behavior (Figure 8) compared to that of the pure 1% HC (Figure 5a). The friction force was still approximately linear with the load, but the effect of speed on friction was strongly decreased as compared to that of pure HC in 1 mM salt. At low speed (1.91 $\mu\text{m/s}$), the friction force was almost similar to that with pure HC polymer. However, at high

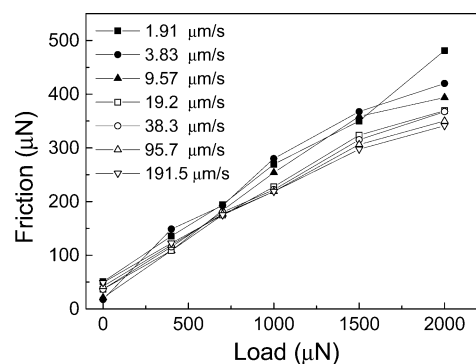


Figure 8. Friction force vs load for 1% HC + 10% TA1 in 10^{-3} M KNO_3 .

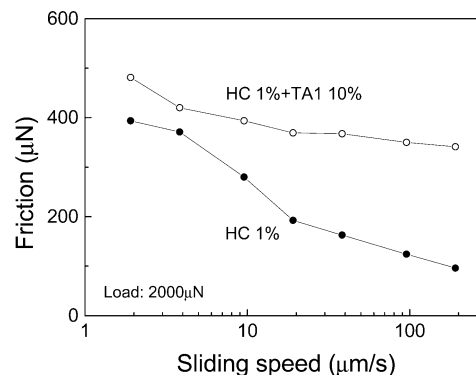


Figure 9. Friction force vs speed at a load of 2 mN for 1% HC in 10^{-3} M KNO_3 and 1% HC + 10% TA1 in 10^{-3} M KNO_3 .

TABLE 1: Effect of the Speed on the Friction Coefficients

speed ($\mu\text{m/s}$)	1% HC + 1 mM KNO_3	1% HC + 1 mM KNO_3 (6 h of evaporation)	1% HC + 37 mM KNO_3	1% HC + 10% TA1 + 1 mM KNO_3
1.91	0.19	0.28	0.33	0.21
3.83	0.18	0.33	0.31	0.20
9.57	0.13	0.31	0.33	0.19
19.2	0.09	0.27	0.31	0.17
38.3	0.08	0.27	0.32	0.17
95.7	0.05	0.26	0.30	0.16
191.5	0.04	0.27	0.31	0.15

speed, the decrease in the friction force was much smaller: when the sliding speed increased from 1.91 to 191 $\mu\text{m/s}$ (100 times), friction forces decreased by only $\sim 30\%$ (see Figure 9). This shows that the anionic surfactant TA1 strongly affects the structure of the polymer layer as already observed in the normal forces.

Addition of the anionic surfactant produces effects both on the normal force–distance profile and on the friction behavior. These effects share several common features with those obtained by adding salt: the layer thickness is highly contracted and the friction becomes insensitive to the sliding speed. However, the level of friction force is higher in high salt concentration as can be seen from Figure 7. This figure shows the friction forces at a 2 mN load at various sliding speeds for 1% HC in 1 mM KNO_3 and 1% HC + 10% TA1 in 1 mM KNO_3 .

The friction forces vary approximately linearly as a function of load. One can therefore use Amontons's law to calculate a friction coefficient. The friction coefficients corresponding to the different situations are listed in Table 1. The decrease of friction coefficient for a 100-fold increase of speed is $\sim 80\%$ for 1% HC in 1 mM salt, $\sim 13\%$ after evaporation, 5% in 37 mM salt, and $\sim 28\%$ with surfactant in 1 mM salt. The effect of the salt is to increase the level of friction and to suppress its dependence on the speed. The effect of adding the surfactant

does not reduce the friction coefficient but reduces the dependence on the speed. With a decrease of the friction coefficient with speed (1% HC + 1 mM salt), one should expect a stick–slip behavior. However, the friction traces did not display evidence for a proper stick–slip in any of the results. In general, these polymers do not give stick–slip on hair, and that is why they are used as conditioning agents.

Discussion

The conformation of a polyelectrolyte chain in an aqueous solvent depends on several factors related to the repulsive forces between the cationic charges of the polymer.²² It is well known that highly charged polyelectrolytes are in an open conformation at low salt concentration because of the electrostatic intramolecular repulsion when the distance between two successive charges is small enough. The reference distance is the Bjerrum length (the distance at which two unit charges have an interaction of $\sim k_B T$ in water is ~ 0.7 nm).²² Conversely, in high salt concentration, the repulsion between charges is screened and thermal fluctuations tend to coil the chains.²² Here, two-thirds of the HC monomers are charged, which, with a monomer length of ~ 1.2 nm, results in a mean distance of ~ 1.8 nm between the charges. This is longer than the Bjerrum length but sufficiently close to it, so that the polyelectrolyte conformation will be open. In the dilute regime, highly charged polyelectrolytes adsorbed on a surface are expected to have a flat conformation as was reported^{17,23} because the cationic monomers are attracted to the negatively charged surface. The resulting surface interactions are essentially double-layer forces.¹⁷ Conversely, polyelectrolytes with low charge density do not lie flat on the surface¹⁵ and result in surface forces with mainly steric repulsions. Many studies have been reported in which the layer was adsorbed from a polyelectrolyte solution of concentration on the order of 0.001%.^{16–19} This concentration contrasts markedly with our surface force measurements in which the polymer concentration is 2–3 orders of magnitude higher. The consequence is that our highly charged cationic polyelectrolyte molecules do not lie flat on the negatively charged mica surface because of the competition between the adsorbing molecules and excluded volume effects between them.^{23–24} The layer thickness is therefore higher because the chains extend into solution. In the case of HC with low salt concentration, the regime is semidilute: a simple calculation based on the size of a stretched polymer chain can give an order of magnitude of the maximum concentration of the dilute regime. With a contour length of $0.8 \mu\text{m}$ (obtained from the molecular weight 4×10^5 and the monomer size 1–1.5 nm), this concentration turns out to be on the order of $10^{-4}\%$. The 1% concentration used in the present experiments is at least 3 orders of magnitude larger, and the system is therefore clearly in the semidilute regime. When mixed with the surfactant, the resulting radius of gyration of the polymer R_g is estimated further below (~ 25 nm) and the concentration used still corresponds to a semidilute regime. This trend to be in the semidilute regime in a wide range of low concentrations is a fairly general property of polyelectrolytes. In this regime, the polymer chains are close to each other. The present polymer concentration which is orders of magnitude above the onset of the semidilute regime explains why the adsorbed molecules do not lie flat on the surface, and why there is a long distance repulsion. This is a strong difference from the dilute regime in which the force–distance profile generally follows that of a double-layer repulsion.²⁵ Here, the experimental results have shown that surfactants and salts can have strong effects on the force–distance profiles and on the friction properties of the charged polymer.

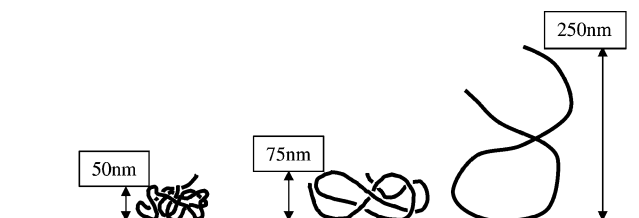


Figure 10. Extension of the $0.8 \mu\text{m}$ long polyelectrolyte chains in three cases: 250 nm for the pure polymer in 1 mM KNO_3 , 75 nm for the polymer in 37 mM KNO_3 , 50 nm for 1% HC + 10% TA1 in 10^{-3} M KNO_3 .

Normal Forces. For the pure cationic polymer 1% HC at low salt concentration, the molecule is expected to be extended with a large size (Figure 10). This is illustrated in the normal force–distance profiles by a very long range of the repulsive force of ~ 500 nm (Figure 2). The forces vary exponentially with distance with a decay length of ~ 80 nm. This is nearly an order of magnitude larger than the Debye length corresponding to the 1 mM KNO_3 solution (9.6 nm). Therefore, the forces can only be a mixture of steric and double-layer repulsions. The distance range of the force ($\sim 0.5 \mu\text{m}$) is on the order of the length of the chain molecule, showing that the molecules are in a fairly extended conformation. When the salt concentration is higher (37 mM), the range of the repulsion is strongly reduced (Figure 2) and the layer is compacted to ~ 20 nm at a much lower force (5 mN/m) than in low salt concentration (20 mN/m). However, the force–distance profile displays a large difference from the double-layer forces corresponding to 37 mM salt concentration (which would have a decay length of ~ 1.5 nm). Here also, the repulsion results from a mixture of steric and double-layer forces. The range of the force (~ 150 nm) indicates that the HC polymer extends less in the solution in agreement with ref 14. All of this shows that the chains are in a different conformation at high salt concentration: they are coiled because of the screening of intramolecular repulsions. The addition of 10% anionic surfactant into the cationic polymer solution changes considerably the normal force curves for 1 mM KNO_3 . Because the anionic charges of the surfactant reduce the repulsion between the cationic charges of the polymer molecules, the latter will be condensed and have a small size (Figure 10). This is illustrated in Figure 3 by the short range (100 nm) of the repulsive force. It is consistent with another study of mixtures of polyelectrolytes with surfactants having opposite charge in which a collapse of the chains was induced by the introduction of the surfactant.²⁶ This behavior is fairly similar to the effect of adding salt. Therefore, the addition of surfactant of opposite charge shares, with the addition of salt, the feature of condensing the polymer layer by screening the charges or by neutralizing them.

The normal forces are clearly dominated by steric interactions. A first examination of them shows that they have a longer range in low salt concentration than in a high one or with added surfactant. This is not surprising because the polyelectrolyte is supposed to be in a relatively extended conformation in low salt concentration while it is in a more condensed one when the repulsions between the charges are screened by ions in a more concentrated salt solution, or by the surfactant. In the case of end-grafted polymers on a surface in the mushroom regime, the interaction is expected to vary as $\exp(-D/R_g)$, where D is the distance and R_g the radius of gyration of the polymer. Although the polymer is adsorbed instead of grafted, it is interesting to analyze the forces relative to the radii of gyration R_g or to the mean end-to-end distance R_F of this polyelectrolyte, considering that the polymer remains confined during the

experiments. It should also be noted that the theory for polyelectrolytes is far less developed than that for neutral polymers and that one is therefore limited to very crude estimates. An estimate of R_g and R_F of the polymer can be made using equations given in ref 24. For a weakly charged polyelectrolyte (or a polyelectrolyte in which the charges are strongly screened), the mean end-to-end distance is given by $R_F = (l_{\text{eff}}d)^{0.2}L^{0.6}$, where l_{eff} is the persistence length (~ 1.3 nm), d the chain diameter (1 nm), and L the contour length ($0.8 \mu\text{m}$). This leads to an R_F of about 58 nm. Other sources state that²⁷ $R_F = 0.1M^{0.5}$ nm for cellulose derivative polymers in water, which gives a value of 63 nm in good agreement with the above estimate. These polyelectrolytes can be considered as Gaussian chains²⁴ whose R_g is related to R_F by $R_g = R_F/6^{1/2}$.²⁸ This gives $R_g \approx 25$ nm. It is of interest to compare the range of the forces to $2R_F$. The values obtained (150 nm for 1% HC in 37 mM salt and 100 nm for 1% HC + 10% TA in 1 mM salt) are close to $2R_F$. When the surfactant is added (1% HC + 10% TA), the decay length of the interactions (12 nm) is not close to the R_g value. In the case of the pure polymer in low salt concentration, R_F is estimated in a different way. For a highly charged polyelectrolyte, ref 24 proposes $R_F = (l_{\text{eff}}L)^{0.5}$. Skolnick et al.²⁹ and Schneider et al.³⁰ obtain persistence lengths for a similar type of polymer (carboxymethyl cellulose with similar molecular weight and salt concentrations) which, for a 1 mM salt concentration, correspond to ~ 46 nm. This gives $R_F \approx 0.19 \mu\text{m}$ and $R_g \approx 78$ nm. The value of $2R_F$ is close to the range of the forces ($0.5 \mu\text{m}$). Interestingly, the R_g value is close to the decay length (83 nm). Although we have adsorbed layers and not end-grafted polymers, the similarities observed between these parameters are interesting.

Therefore, our experiments contrast most studies made with polymers adsorbed from a low concentration in which either the charge density is high and the polymer is adsorbed flat on the surfaces or the charge density is low and the adsorbed polymer has some extension in the bulk solution.^{15–19} Here, it extends considerably in solution. Our findings agree with ref 17 in which an increase of polyelectrolyte concentration leads to the apparition of steric forces.

Friction Forces. The friction traces (Figure 4) show a first increase of the friction force over a distance of $30 \mu\text{m}$, after which it reaches a constant value similarly to that in ref 31. The confinement has a strong effect on viscosity: the bulk shear viscosity of 1% HC concentration is very low and almost independent of the shear rate: $0.04 \text{ Pa}\cdot\text{s}$.³² The measured friction forces F can be used to calculate the effective viscosity by using the equation $\eta = FD/Av$. Here, D is the film thickness, A is the contact area, and v is the shear speed. The effective viscosity is plotted as a function of shear rate (defined as v/D) in Figure 11.

This shows that the confinement increases the viscosity by several orders of magnitude, in agreement with the results from refs 33 and 34. The increase of viscosity with confinement is likely to result from enhancement of the interpenetration of the chains from one surface to the other. At 1 mM salt concentration, the friction force is spectacularly sensitive to the sliding speed. As the chains have an extended conformation, they are likely to orient themselves along the shear direction. By doing this, they reduce their interpenetration and therefore the friction force. The decrease of the friction force with speed contrasts markedly with the observations of ref 18 in which an increase of the friction force with the scan rate (and therefore the speed) was observed. However, a comparison is difficult because the polyelectrolyte layers of this reference were adsorbed from a

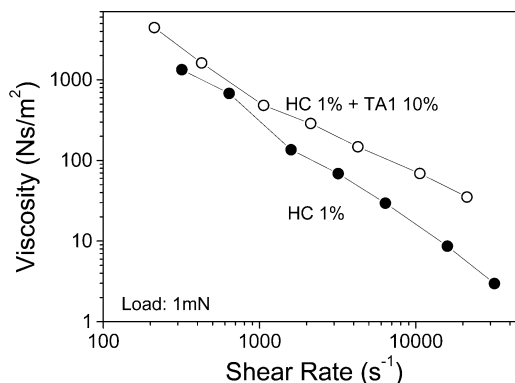


Figure 11. Effective viscosity vs shear rate for 1% HC in 10^{-3} M KNO_3 and 1% HC + 10% TA1 in 10^{-3} M KNO_3 .

very low concentration solution (20 ppm) and the friction forces were measured in the polymer solution. The uncoiled conformation of the molecules in the present case contrasts with the coiled conformation of the molecules (1% HC + 10% TA), which should be much less sensitive to shear speed. It is indeed observed that, at high salt concentrations, i.e., when the molecules are coiled, the dependence of the friction force on the speed has almost disappeared (Figure 7). Therefore, the strong correlation between the salt concentration, the distance range of the normal force, and the speed dependence of the friction forces together provide a consistent picture of the layer structure and properties: extended conformations produce friction forces highly dependent on speed, in contrast to coiled conformations.

The effect of adding surfactant is qualitatively similar to that of adding salt: the dependence of friction force on the sliding speed decreases (by 30%), but it does not disappear as is the case with salt addition. The normal forces also show features similar to those obtained by adding salt: the range of forces is strongly decreased. The origin of the difference between friction forces with the surfactant and at high salt concentration is not clear. A possible explanation would be that the surfactant, because of its mobility, acts as a lubricant on the polymer chains. Altogether, the strong correlation between the polyelectrolyte conformation, stretched or coiled, produced by salt or surfactant, and the speed dependence of the friction forces gives a very consistent picture of the tribological properties of charged polymers.

The decrease of the friction forces observed with a speed increase of two decades leaves a question open regarding the speed at which the friction is the maximum. At ultralow speeds, the friction forces are known to increase with speed: ref 35 states that a low friction force at ultralow speeds must be a general effect because the chains have the time to relax their stress by spontaneous conformational change. It should therefore be expected that lower sliding speeds should have revealed a maximum in the friction forces. In this case, the rate of evaporation of water unfortunately did not allow these ultralow speeds to be used.

Conclusion

When adsorbed from a highly concentrated solution, polyelectrolytes on mica surfaces having opposite charge produce thick adsorbed layers in which the polymer at the surface is not in a flat conformation. At low salt concentration, the layers produce very long range repulsive forces because polymer molecules are in an extended conformation. These repulsions result from a mixture of steric and double-layer forces. At high

salt concentration, the polyelectrolyte chains condense and the range of repulsive forces decreases substantially. In low salt concentration, the addition of an ionic surfactant also contributes to condense the layer. This gives rise to repulsive forces of much shorter range than with the polyelectrolyte alone.

When two surfaces covered with the polyelectrolyte layers are slid against each other, the friction forces vary approximately linearly with the load so that friction coefficients can be deduced. At low salt concentration, the friction forces between pure polyelectrolyte layers are highly dependent on the sliding speed. One expects extended chains to easily orient along the shear direction and reduce their interpenetration. This causes the friction force to decrease by as much as 80% when the speed is increased in the range of micrometers per second to hundreds of micrometers per second. When the polymer chains are compacted by a much higher salt concentration, the dependence on the sliding speed disappears. The effect of adding surfactant to the polyelectrolyte in solutions with low salt concentration is also to condense the polymer layer by neutralizing it, as illustrated by the smaller range of repulsion forces. The friction forces are also less sensitive to the sliding speed. By showing consistently that adsorbed coiled polymers produce friction forces which are fairly insensitive to the sliding speed while extended polymer chains do the opposite, the results clearly give information on the dynamics of chain molecules under shear in relation to their conformation.

Controlling a sensorial effect such as hair smoothness implies understanding the phenomena from many different scales: from the macroscopic to the nanoscopic level. It is at this latter level that nanotribology may help relate cosmetics and molecular structure. The present study has allowed some of the complex phenomena occurring in cosmetic conditioners in which the interplay of polymers, surfactants, and water is a complex equilibrium of surface forces and tribology to be captured. This approach can be extended to solve many questions related to cosmetology.

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