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Surface Forces between Adsorbed Quaternarized Poly(2-vinylpyridine) Layers: Molecular Rearrangements and Bridging Interactions

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ABSTRACT: The surface forces between quaternarized poly(2-vinylpyridine) (QP2VP) layers adsorbed onto mica have been measured over a range of solution pH conditions. It was found that QP2VP overcompensates the mica's negative charge, resulting in a positively charged interface. The surface potential at the mica/polyelectrolyte interface is a balance of the charge on the adsorbed polyelectrolyte and the charge on the underlying mica surface. It was also found that, below and near the pK_a of the polyelectrolyte, segment−segment repulsion results in the polyelectrolyte adopting a conformation with significant extension into solution. Interpenetration of the extended chains leads to a bridging attraction. At high pH a decrease in the polyelectrolyte charge density decreases segment−segment repulsion, resulting in a compact adsorbed conformation where no bridging attractive jump is observed. An adhesion is measured between adjacent layers under all pH conditions, regardless of the presence of an attractive jump in. Here the important distinction is made between an attractive force caused by the overlap of anchored polyelectrolyte chains extending into solution and chain entanglement that occurs due to molecular rearrangements when polyelectrolyte layers are under compression.

Introduction

Polyelectrolytes are used widely industrially for wastewater treatment, dewatering of sludge byproducts in mining, paper making, and many more economically important processes. Polyelectrolytes have proven useful in colloidal systems since they are able to adsorb at and alter the properties of an interface such as surface charge and the adhesion between colloidal particles. Being able to control the potential at an interface by either increasing the net charge or neutralizing the charge at that interface enables the control of surface forces between individual particles in colloidal solutions. An examples of this is when surface charge is increased by a polyelectrolyte; this increases the electrostatic repulsion between particles which can lower the viscosity of a colloidal solution. The neutralizing charge at an interface can conversely reduce the electrostatic repulsion between particles which can then result in the flocculation and settling of a colloidal dispersion.[1]

Polyelectrolyte adsorption can alter close-range surface forces by acting as a steric barrier to flocculation. Under certain conditions, the interpenetration of polyelectrolyte chains between neighboring particles can lead to a bridging attractive force causing flocculation. Åkesson et al. explain bridging as polyelectrolyte chains crossing over the midplane between neighboring surfaces, leading to an attraction between the surfaces.[2] Both steric and bridging forces are strongly dependent on the adsorbed conformation of the polyelectrolyte, where a compact adsorbed layer may not allow interpentration and thus bridging, resulting in a purely repulsive steric force. Conversely, a polyelectrolyte layer in an extended conformation may allow significant interpenetration and attractive bridging. The relationship between polyelectrolyte conformation and surface forces is of great importance to the effective application of polyelectrolytes to real world processes.

Several studies into the way in which polyelectrolytes alter the interaction forces between surfaces have been made using the surface forces apparatus (SFA).[3−5] These studies have found that the addition of polyelectrolytes alter the surface forces between two mica surfaces, and the mica charge can be neutralized with relatively low concentrations of polyelectrolyte. It has also been found that strong attractive bridging forces are present at polyelectrolyte concentrations less than 20 ppm.

Early investigations of surface forces between adsorbed polyelectrolyte layers[4,5] involved poly((3-(methacrylamido)propyl)trimethylammonium chloride), i.e., MAPTAC, and poly((2-(propionyloxy)ethyl)trimethylammonium chloride), i.e., PCMA,[6,7] which are both high charge density, cationic polyelectrolytes with one charge per monomer unit. In both studies, each polyelectrolyte was allowed to adsorb from a low salt (10^{-4} M KNO_3) solution and was found to neutralize mica surfaces at low concentrations, 10 and 20 ppm, respectively. Upon further increase in polyelectrolyte concentration, the reappearance of a double-layer repulsion was limited since further adsorption is hindered by the large polyelectrolyte population already at the mica surface.

The two studies mentioned above[4−7] concluded that both MAPTAC and PCMA adsorb in a relatively flat conformation. It was proposed that the polyelectrolyte molecules were rodlike in solution and adsorbed as such. The long-range surface forces were shown to be caused solely by the overlap of adjacent electrical double layers. There was little or no force due to the interpenetration of the adsorbed layers except when the layers were brought into close association (<20 nm) where a bridging force was measured.

In another study, Marra and Hair[8] allowed poly(2-vinylpyridine) (P2VP) to adsorb to mica surfaces at low pH = 3.6. At this pH the basic pyridine functional

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groups along the polymer backbone are protonated, resulting in a strongly charged polyelectrolyte. Similar to previous studies, P2VP was found to adsorb in a flat conformation and neutralized the mica surfaces. The resulting surface forces were well described by electrical double-layer theory at long range, and a strong attractive force was exhibited at closer range. The separation at which a hard wall repulsion was found was once again small, and the adhesion between the layers when in contact was large. In this work after initial adsorption occurred the pH was increased, resulting in the neutralization of the polyelectrolyte. The adsorbed conformation was proposed to change due to a decrease in the repulsion between polyelectrolyte segments and a decreased affinity of the segments for the oppositely charged mica surface. Steric forces were seen at surface separations of up to 120 nm, and the strong adhesions exhibited earlier now disappeared.

To investigate the effect of charge density of a polyelectrolyte on surface forces between adsorbed polyelectrolyte layers, Claesson et al. investigated several copolymers of the cationic 2-(propionyloxyethyl)trimethylammonium chloride, i.e., CMA, and the neutral acrylamide, i.e., AM. These copolymers ranged in charge density from 10 to 100% charge.[9] Adsorbed layers of these particular low charge-density polyelectrolytes were found to extend into solution, giving rise to weak bridging attraction. This attraction was found to increase with the charge density of the adsorbed polyelectrolyte. The thickness of the adsorbed layer was also found to depend on the charge density of the polyelectrolyte, the adsorbed layer becoming thicker as the charge density on the polyelectrolyte decreases.

In the study presented here, we have used the surface forces apparatus (SFA) to investigate the forces between layers of the cationic polyelectrolyte quaternarized poly(2-vinylpyridine) or QP2VP adsorbed onto mica. QP2VP is known to adsorb strongly to negatively charged silica surfaces over a broad range of solution pH conditions.[10] This work has shown that the surface excess and conformation of adsorbed QP2VP depend strongly on pH. It was found that the surface excess of the polyelectrolyte increases with pH, and the polyelectrolyte conformation is more extended at low pH and adopts a more compact conformation at high pH. How the above adsorption characteristics of QP2VP affect the interaction forces between two surfaces is the subject of the work we are presenting here.

Another important factor when considering the surface forces between adsorbed polyelectrolyte layers is how the compressibility of these layers affects surface interactions. For example, geometric constraints on colloidal particles such as occur in high volume fraction sols can lead to conformation changes of adsorbed polyelectrolyte and subsequent changes in the surface forces. Observations of polyelectrolyte layer compressibility have been made by Luckham[11] and Marra.[8] Our work also addresses this important issue.

Experimental Section

Materials. Ruby muscovite mica was obtained from S & J Trading and was cleaved in order to obtain several molecularly smooth single crystals 1 cm^2 in area and ~1−2 μm thick.

Water used in all solutions was obtained from a Milli-Q Plus water purification system, which was fed by a reverse osmosis water purification system. The final pure water obtained had a resistivity of 18.2 MΩ•cm. All chemicals used for preparing solutions or cleaning were AR grade. Sodium iodide (ICN Biomedicals Inc.), hydriodic acid (Merck Pty Ltd.), and both nitric acid and sodium hydroxide (APC Seven Hills) were all used as received. RBS 35 Detergent was supplied by Pierce. AR grade ethanol (APC Seven Hills) was redistilled from an all Pyrex still. Nitrogen gas (BOC Gases) was filtered through a hydrocarbon moisture trap.

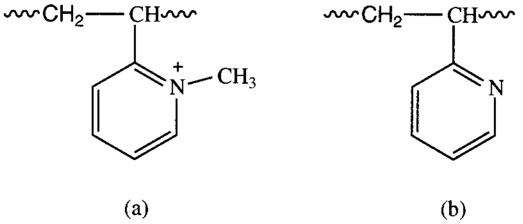

Figure 1. Structure of the repeat units of quaternarized poly(2-vinylpyridine): (a) nonquaternarized residues comprising 24% of the total chain and (b) quaternarized residues comprising 76% of the residues containing iodide counterions. (a) and (b) are arranged in a statistical distribution along the polyelectrolyte backbone.

The polyelectrolyte used in this study was quaternarized poly(2-vinylpyridine) (QP2VP) and was a gift from Dr. Alain Hill of Bristol University. It is illustrated in Figure 1 and is comprised of vinylpyridine monomers which are quaternarized by methyl iodide such that 76% of the repeating units bear a permanent positive charge statistically distributed along the polyelectrolyte backbone. The remaining 24% of the monomer units bear ionizable vinylpyridine groups. These groups have a pK_a of around 5.25, which is that of pyridine[12] and was confirmed by a simple titration. The charge on the polyelectrolyte can come from both the nonquaternarized amide groups which protonate at low pH and also from the permanently charged quaternarized pyridinium moieties. The average number of repeat units on this polyelectrolyte is 170, resulting in a molecular weight of 36 000 g mol^{-1}.

Cleaning Procedures. All internal parts of the surface forces apparatus except for the magnet assembly were sonocated in 1% RBS detergent solution for 1 h, soaked in 10% nitric acid overnight, and then soaked in ethanol overnight. Each part was rinsed with copious amounts of Milli-Q water between each soaking, and prior to assembly each part was rinsed with redistilled ethanol and blown dry with purified nitrogen gas. This procedure was repeated for the cleaning of the magnet assembly, but no nitric acid was used. Glassware was soaked in a 10% w/w aqueous NaOH solution for 30 min and then rinsed with copious amounts of Milli-Q water just prior to use.

Apparatus. All measurements obtained in this study were made using a modified Mk IV surface forces apparatus (SFA). The use of the surface forces apparatus for measuring colloidal interactions is well described elsewhere.[13] Essentially, two thin sheets of back-silvered mica are each glued to a hemicylindrical silica disk. The disks are then mounted in a crossed cylinder conformation in the SFA.

The molecularly smooth mica is back-silvered to a transmittance of ~5%, and white light is shone normally through the surfaces. This light undergoes multiple reflections between the two surfaces which, upon transmittance, exhibits an interference pattern known as fringes of equal chromatic order (FECO). Measurement of the spacing between successive fringes, when viewed in a spectrograph, yields the separation between the mica surfaces[13,14] with an accuracy of ~±0.1 nm. Separations are always quoted as the mica−mica separation, and zero surface separation is defined as mica−mica contact.

The lower surface is mounted on a double cantilever spring of known force constant. From the deflection of this spring a force can be measured. The crossed cylinder configuration of the two mica surfaces is the mathematical equivalent to a sphere on a flat. The radius of curvature (R) is measured from the profile of the FECO interference pattern. Both parallel and perpendicular radii are measured by placing a dovetail prism in the path of the light exiting the SFA.[15] The geometric mean of the radii is used to calculate the free energy of interaction from the interaction force (*F*) using the Derjaguin approximation,[16] $F/R = 2\pi G_f$ where G_f is the free energy of interaction so all force profiles will be plotted as *F*/*R*.

In a typical SFA experiment, the surfaces are moved normally to each other by a mechanical motor for coarse movement and a piezo electric crystal (to which the top surface is mounted) for fine separation adjustment. In our modified SFA a magnetic force transducer (MFT) is employed instead of the piezoelectric crystal for fine motor adjustment. The operation of the magnetic force transducer entails the attachment of a magnet to the lower surface, and a magnetic transducer with a variable current supply is fastened to the underside of the SFA cell.[17] A variable magnetic field is produce by the transducer, which then applies a force to the magnet attached to the lower surface which allows us to adjust surface separation over a range of 0−2 μm. The sensitivity is equivalent to that obtained using a piezoelectric crystal, i.e., subnanometer sensitivity in movement. Advantages of the MFT over the piezoelectric crystal are that its response is extremely linear, it is nonhysteretic, and it is less prone to drift through thermal conduction.

In our modified SFA, a reduced volume cell was used which requires 50 cm^3 to entirely immerse the surfaces. This allows smaller volumes of solution to be used, thus minimizing the amount of costly polyelectrolyte used in each experiment.

In the acquisition of force profiles, the measurement of the surface separation and the movement of the surfaces were achieved manually. The surfaces were brought together by gradually increasing the voltage applied to the MFT. This was done slowly enough so that, after each increase in voltage to the MFT, the system was allowed relax before the next voltage increase. The slow approach of the surfaces maximizes the ability of the adsorbed layers to rearrange and minimizes velocity-dependent effects on the force curves, thus yielding a force curve as close to equilibrium as possible.

Experimental Protocol. Interaction forces were measured between physisorbed polyelectrolyte layers which were formed by allowing QP2VP to adsorb onto bare mica surfaces from a stock solution which was adjusted to pH 4.0. This stock solution was made prior to commencement of the experiment and contained 100 ppm of QP2VP with a background electrolyte concentration of 1×10^{-4} M NaI at pH 6.3. Adjustments in pH where made using solutions of hydriodic acid and sodium hydroxide. The surfaces were allowed to equilibrate with the polyelectrolyte solution for a minimum of 2 h before measurements were taken to allow sufficient time for adsorption of the polyelectrolyte. Further pH adjustments were made by draining the SFA cell, leaving a droplet in between the mica surfaces and introducing new stock solution adjusted to the required pH.

Results

Note that all force profiles presented in the Results section are shown as semilog plots where *F*/*R* is on a logarithmic scale and surface separation is plotted linearly. This aids visual identification of electrical double-layer forces that decay exponentially with separation and thus appear linear on a semilog plot. Also note that zero surface separation is defined as mica−mica contact.

pH = 4. The forces measured between mica surfaces onto which QP2VP had been allowed to adsorb at pH 4.0 are shown in Figure 2. At separations greater than 10 nm the force profile is linear on a semilog plot and is well described by DLVO theory. A fit to the data at long range, using the nonlinear Poisson−Boltzmann equation,[18] yielded a surface potential (ψ_0) of 125 mV and a Debye length (κ^{-1}) of 15 nm. The Hamaker constant used in the DLVO calculations was 2.2×10^{-20} J.[13] This potential is calculated assuming that the outer Helmholtz plane (OHP) is defined as the mica−mica contact. This is an approximation given that the adsorbed layer is itself a source of charge, but nonetheless, such a fit gives an indication of relative changes in ψ_0 and κ^{-1}. The implications of this are discussed below.

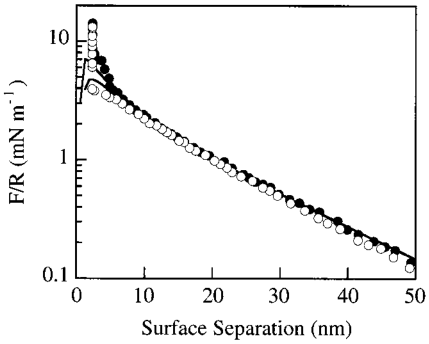

Figure 2. Semilog plot of normalized force vs surface separation between mica surfaces with adsorbed QP2VP at pH 4.0. The two force profiles are those obtained on initial (filled circles) and subsequent (open circles) compressions of the adsorbed QP2VP layers. The solid curves represent the DLVO theoretical fit to the experimental data. The upper and lower limits are for constant charge and constant potential boundary conditions, respectively. Adhesions measured were 42 mN m^{-1} on both decompressions. Both jump outs were measured from the position of the hard wall.

At surface separations of less than 5 nm it can be seen that the forces measured between the adsorbed polyelectrolyte layers deviate significantly from DLVO predictions. An additional close-range repulsion was measured where the force profile is stepped. This close-range repulsion is most likely steric or electrosteric due to contact between the adsorbed polyelectrolyte layers.

At a surface separation of 2.3 nm, an increase in applied load to 14 mN m^{-1} resulted in no further compression of the adsorbed layers. Therefore, this intersurface spacing we denote as the position of the repulsive hard wall. The position of this hard wall repulsion indicates the presence of a compressed polyelectrolyte layer of 1.15 nm on each surface.

On decompression of the layers (i.e., application of a force in the outward direction) the surfaces were observed to jump apart, indicative of a strong attractive force between the two surfaces. From the separation at which the surfaces come to rest after they “jump out” and the spring constant, an adhesive force of 42 mN m^{-1} was calculated. It should be noted that upon decompression the two surfaces remained at their hard wall separation, and it is from this position that they jumped apart.

The surface forces between the polyelectrolyte layers was measured again, shortly after the first compression. The results are shown in Figure 2 represented as open cirlces. The data for initial and subsequent compressions overlay each other at large surface separations. However, the step measured between 2 and 5 nm on first compression of the polyelectrolyte layers is no longer present. This is shown more clearly in Figure 3. This figure highlights that, where on first compression there was a step in the force profile between 4.5 and 2.5 nm, on second compression the surfaces were observed to jump from 4.5 nm surface separation to 2.5 nm, indicating that an attractive force is now present. A hard wall repulsion was present at 2.3 nm, as for the first compression. On decompression the surfaces were found to jump out from 2.3 nm the position of the hard wall, and an adhesion of 42 mN m^{-1} was measured from the

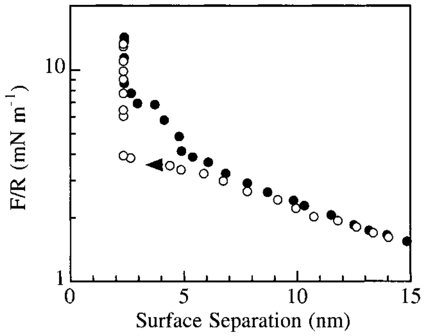

Figure 3. This is the same data as that in Figure 2 except on an expanded scale, illustrating the detail of the force profiles upon compression of QP2VP layers at pH 4.0. The two force profiles are those obtained on initial (filled circles) and subsequent (open circles) compressions of the adsorbed QP2VP layers. The arrow indicates the presence of an attractive jump into contact on the second compression.

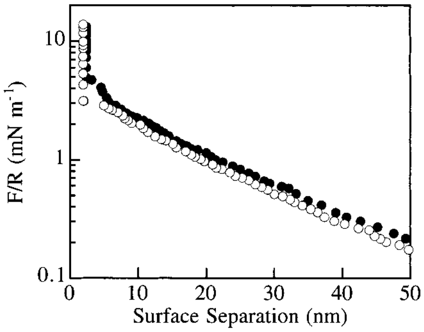

Figure 4. Semilog plot of normalized force vs surface separation between mica surfaces with adsorbed QP2VP at pH 6.2. The two force profiles are those obtained on initial (filled circles) and subsequent (open circles) compressions of the adsorbed QP2VP layers. The adhesion measured was 32 mN m^{-1} on decompression. Both jump outs were measured from the position of the hard wall.

jump distance. This adhesion is unchanged from that measured on the initial decompression of the surfaces.

Subsequent force curves not shown here were similar to the force curve obtained on the second compression of the polyelectrolyte-coated surfaces. The form of the force curve and the adhesion remained constant.

pH = 6. The adsorbed polyelectrolyte layers were exposed to polyelectrolyte solution at pH 6 and allowed to equilibrate. The forces measured between these layers on first and subsequent approaches are presented in Figure 4. Once again the force profiles are linear at large surface separations (on a semilog plot) in agreement with DLVO predictions, with a calculated surface potential of 103 mV (κ^{-1} = 17 nm).

At small surface separations (Figure 5) an identical trend was found at pH = 6.2 to that observed at pH = 4.0 with a step between 2 and 5 nm and a hard wall repulsion at a surface separation of 2.1 nm. Upon subsequent compression of the polyelectrolyte layers the repulsive step was no longer present; an attractive force was found instead, where the surfaces jumped into the hard wall position at 1.9 nm. Once again the position of the attractive jump in was the same as the position of the onset of the repulsive step. The adhesion on first decompression was 32 mN m^{-1}. No change in this value was measured on subsequent decompressions.

pH = 8.5. The forces measured between two surfaces with adsorbed QP2VP equilibrated at pH 8.5 on first and subsequent approaches is presented in Figure 6.

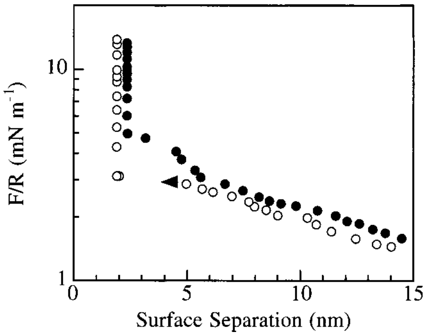

Figure 5. This is the same data as that in Figure 4 except on an expanded scale illustrating the detail of the force profiles upon compression of QP2VP layers at pH 6.2. The two force profiles are those obtained on initial (filled circles) and subsequent (open circles) compressions of the adsorbed QP2VP layers. The arrow indicates the presence of an attractive jump into contact on the second compression. This attractive jump was not observed on initial compression. Adhesions measured were 32 mN m^{-1} on both decompressions. Both jump outs were measured from the position of the hard wall.

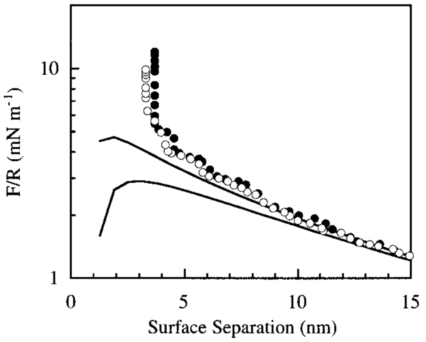

Figure 6. Semilog plot of normalized force vs surface separation between mica surfaces with adsorbed QP2VP at pH 8.5. The two force profiles are those obtained on initial (filled circles) and subsequent (open circles) compressions of the adsorbed QP2VP layers. The solid curves represent the DLVO theoretical fit to the experimental data. The upper and lower limits are the constant charge and constant potential boundary conditions, respectively. Adhesion on first decompression was 10 mN m^{-1} and decreased to 4 mN m^{-1} on subsequent decompressions. Both jump outs were measured from the position of the hard wall.

The force profiles obtained once again follow trends exhibited at lower pH conditions where the force profile is linear at large surface separation where an additional repulsion is measured at close range. The calculated surface potential under these conditions was 98 mV with κ^{-1} = 13 nm. Interestingly, at small surface separations, the form of the force profile measured between the adsorbed layers at pH 8.5 is significantly different to those obtained in solutions of lower pH. The position of the hard wall is at a surface separation of 3.3 nm as compared to 1.9 nm—2.3 nm at lower pH's. Also, at pH 8.5, instead of a single large step, there appear to be several smaller steps. In addition, the force profile obtained on initial compression of the polyelectrolyte layers is the same as that measured for subsequent compressions, with no attractive jump into contact of the two polyelectrolyte-coated surfaces. These results are different to those obtained at lower pH's where initial and subsequent compressions of the polyelectrolyte layers are different, and subsequent compressions exhibit an attractive jump from about 5 nm surface separation to 2 nm surface separation.

Table 1. Surface Potential of Adsorbed QP2VP Layers As Measured at Several Polyelectrolyte Concentrations[a]

[QP2VP] (ppm)	potential (mV)
20	80 ± 2
50	100 ± 2
100	103 ± 5

[a] The surface potentials were obtained by fitting DLVO theory to the force profiles measured between adjacent QP2VP layers which were allowed to adsorb at each polyelectrolyte concentration.

Not only is the close-range attractive jump no longer present, but the adhesive force measured is only 10 mN m^{-1} on initial decompression. Subsequent decompressions gave a measured adhesive force of 4 mN m^{-1}. This again is a very different result to that obtained under low-pH conditions. At pH's 4 and 6, there was no difference between the adhesion measured on initial and subsequent decompressions.

Dependence of Surface Potential on Polyelectrolyte Concentration. To determine the sign of the charge originating from the mica/polyelectrolyte interface, a series of experiments were performed where the force profiles between polyelectrolyte layers were measured as a function of polyelectrolyte concentration. The surface potentials obtained for polyelectrolyte layers on mica which were allowed to adsorb from background polyelectrolyte concentrations of 20, 50, and 100 ppm are presented in Table 1.

Note that the surface potential of bare mica under the same solution conditions was measured by us and found to be −103 mV.

By increasing the concentration of polyelectrolyte in solution, the amount of adsorption onto mica is known to increase.[7,19] Thus, an increase in the amount of adsorbed polyelectrolyte leads to a greater number of positively charged species in the interfacial region. The data in Table 1 show that the magnitude of the surface potential increases with polyelectrolyte surface excess. This trend can only be achieved if the net surface potential is positive as a result of polyelectrolyte adsorption; i.e., the surfaces are overcompensated.[7,19]

Discussion

Effect of Solution pH on Surface Potential. We have established that when QP2VP adsorbs onto mica, the surface potential is net positive since the QP2VP's positive charge dominates the negative charge of the underlying mica surface (see results above). This positive surface potential was found to be dependent on solution pH. As the solution pH was altered from 4.0 to 6.2 and finally to 8.5, the potential of the surfaces was found to decrease significantly from +125 to +103 mV, with only a small decrease to +97 mV, respectively. This unusual trend is due to the effect solution pH has on both the surface excess and charge of the polyelectrolyte and the charge on the mica surface.

It has been shown previously[10] that the adsorption of QP2VP onto a negatively charged surface increases with solution pH as a result of the increasing electrostatic attraction between the surface and the polyelectrolyte. This alone should lead to an increase in net surface charge as dominated by the positively charged QP2VP. The polyelectrolyte is comprised of both quaternarized and nonquaternarized pyridine moieties along its backbone in a statistical distribution, 76% being the monomers quaternarized by methyl iodide and 24% of the residues being nonquaternarized pyridine (see Figure 1). The quaternarized moieties have a permanent positive charge insensitive to pH, but the nonquaternarized moieties have a pK_a of 5.25 and are positively charged at low pH and neutral at high pH. As the solution pH is increased, the charge on the adsorbed QP2VP decreases as these nonquaternarized pyridinium ions deprotonate, which would be a factor decreasing the net positive charge at the interface.

The underlying mica surface will contribute to the effective interfacial potential. Mica is known to acquire a surface charge through the dissolution of potassium ions from within its crystal lattice resulting in a residual negative charge.[20−22] At low pH, protons adsorb to the surface, partially neutralizing the negative charge. As the solution pH is increased, the number of protons associated with the mica decreases, and the negative charge on the mica surface increases.

In summary, although the surface excess of QP2VP increases with pH, any expected increase in surface potential is offset by the decrease in polyelectrolyte charge density and the increased negative charge on the underlying mica surface.

It is quite unusual that 24% of the monomer units of QP2VP can have such a significant affect on the surface charge given that 76% of the monomers have a permanent positive charge. However, it is important to emphasize that associated with the QP2VP are iodide counterions residual from the quaternarization process (see above), and in addition, all our experiments were performed with a background salt of 10^{-4} M NaI. The iodide counterion has been found to strongly screen the charge of pyridinium ions.[10] Sudhölter and Engberts[23] found that iodide counterions bind to 1-methylpyridinium surfactant headgroups with an efficiency of 83%. This implies that the pyridinium ions which make up 76% of the monomer units on QP2VP may contribute as little as 10−20% of the polyelectrolyte's total charge density. The remaining charge originates from protonation of the nonquaternarized pyridine side groups. Hence, at low pH where protonation is maximized, the total charge density on QP2VP is expected to be no greater than 50%. At high pH, the charge density of QP2VP is low and is solely due to the quaternarized groups.

In our calculations of the surface potential we have assumed that the outer Helmholtz plane (OHP) is located at mica−mica contact. It has been noted that workers elsewhere have chosen the position of the OHP as being the position of the hard wall repulsion. However, this assumes that there is a dense layer on each surface which is impermeable to ions and that that no charge originates from within this layer. This is not the case for adsorbed polyelectrolytes. Furthermore, in polyelectrolyte systems, one must also consider further extension of charged loops and tails into solution and contribution from these segments to the net surface potential.

There is no 2-dimensional plane of charge from which an electrical double layer emanates, but rather a 3-dimensional layer of charge that has varying charge density and permeability to counterions. Clearly, precise placement of an OHP in a polyelectrolyte system, when fitting experimental data to DLVO theory, is extremely difficult. Hence, caution must be exercised when interpreting absolute values of surface potentials associated with polyelectrolytes at interfaces. All that can be discussed with certainty are trends such as changes in the surface potential with pH.

The interaction forces measured between mica surfaces exposed to 100 ppm of QP2VP at pH = 4 as shown in Figure 2 agree with DLVO theory only at separations above 5 nm. The Debye length as calculated by fitting the nonlinear Poisson−Boltzmann equation is 15 nm. In a 10^{-4} M monovalent salt solution at pH 4, the Debye length is expected to be 22 nm. Given that our fitted Debye length is significantly less than this, the polyelectrolyte itself must be contributing to the total salt concentration through any unassociated counterions and/or extension of the polyelectrolyte into the diffuse region of the double layer.

Short-Ranged Forces upon Compression of Adsorbed QP2VP Layers. At both pH 4.0 and 6.2 it was found that, on initial compression of the QP2VP layers, the repulsive force is greater than that predicted by DLVO theory as a result of an electrosteric repulsion between the two layers. This repulsion increases upon further compression until it reaches a plateau; i.e., the force profile is stepped. The step ranges over surface separations of 2−5 nm. Further increases in the applied load are unable to compress the layers; i.e., they have reached their hard wall separation at which point the repulsive force increases sharply. The step in the force profile indicates that, over the surface separations where this occurs, there is little or no resistance to compression of the polyelectrolyte loops and tails that extend into solution. On subsequent compressions, this step is no longer present. Instead, over 2−5 nm surface separation, there now exists an attractive force. The surfaces jump from a separation of 5 nm to their hard wall separation, i.e., 2 nm.

We believe this attractive force is bridging attraction between the QP2VP layers. A bridging attractive force between adsorbed polyelectrolyte layers is in fact expected to be exhibited in our QP2VP system since a cationic polyelectrolyte is adsorbed onto negatively charged mica. In such systems, where the surfaces have a strong affinity for the adsorbed polyelectrolyte, it has been found that an attractive force is present at small surface separations (<20 nm) which is greater in range than van der Waals dispersion forces.[5,7,9] In our system, an attractive force was detected at surface separations of 5 nm. Figure 2 contains the DLVO prediction of the interaction forces in the QP2VP system and predicts an attractive force at a surface separation of 2 nm. This is clearly much lower in range than the attractive force we measure.

Bridging forces have been found to be relatively weak in some overcompensated systems as we have with our QP2VP system, compared to nearly compensated systems where bridging has been found to be strongly attractive.[9] This trend has been found to vary both with charge density of the polyelectrolyte and with each different polyelectrolyte used.[7] It should be reiterated that it has already been established that QP2VP, although in principle has a high charge density, in reality, much of its charge is screened by the associated iodide counterions (see above). Therefore, a bridging attraction between layers of adsorbed QP2VP is not an unusual result.

There is still the question of why the force profile on first compression of the polyelectrolyte layers exhibits a step and no bridging attraction, whereas subsequent compressions all lead to a bridging attractive force. We believe that, before any compression of the adsorbed QP2VP layers, there are a large number of loops and tails extending into solution, acting effectively as a steric barrier, as measured. The initial approach of the adsorbed layers results in the irreversible compression of some of these loops and tails. The steric barrier is thereby removed, but there is sufficient extension into solution to give rise to bridging attraction. The fact that this history-dependent behavior occurs shows that the quasi-equilibrium conformation of the polyelectrolyte when adsorbed from solution is significantly different from the one irreversibly (over several hours) adopted when the two adsorbed layers were put under compressive load. Many loops and tails containing positive charge which extended into solution initially remain in closer association to the negatively charged mica surface once they are forced into that conformation by compression, as has been seen elsewhere.[8,11]

As shown by the data in Figure 6, the form of the force profile at pH 8.5 is different to what is measured at pH 4.0 and 6.2. At pH 8.5, there is no single step in the force profile, on initial compression of the QP2VP layers. In addition, the compressional force profiles for initial and subsequent compression of the adsorbed layers are indistinguishable, and there is no sign of an attractive jump into the hard wall position, as was observed under low-pH conditions.

The force profile, on initial inspection, appears monotonic with a deviation from DLVO theory longer range than seen at lower pH; i.e., the deviation commences at a surface separation of 10 nm as compared to 5 nm for pH 4 and 6.2. Surprisingly, on closer inspection, at surface separations less than 10 nm, the force profile seems to consist of a series of small steps. Another observation is that the position of the hard wall occurs at a surface separation of 3.3 nm, whereas at pH 4 and pH 6.2, the hard wall was at around 2 nm.

From previous spectroscopic data[10] it is known that QP2VP adsorbs strongly onto a negatively charged surface with significant extension into solution. This spectroscopic data also show that the adsorption of QP2VP is pH-dependent, the surface excess increasing with solution pH. This is consistent with our force profile data. When the solution pH is at 8.5, the adsorbed amount increases, and correspondingly the layer thickness increases, resulting in an increased hard wall separation. This is illustrated in Figure 6, which contains a comparison of the force profiles at all values of solution pH studied.

Another manifestation of the increased adsorbed amount of QP2VP at pH 8.5 is the range over which the force profile deviates from DLVO theory. This range, as stated above, is greater than at lower values of solution pH. The small steps in the force profile over this range are caused by the folding of adsorbed polyelectrolyte loops and tails extending into solution from the interface under compressional load.

Perhaps the most interesting difference between the force profile at pH 8.5 and those obtained at lower pH's is the absence of a bridging attraction. As already described above, in an overcompensated system, bridging attraction occurs when there is significant extension of polyelectrolyte chains into solution. Although at pH 8.5 there is a greater extension of the polyelectrolyte layers into solution than at lower pH's, the absence of a bridging attraction is most likely due to the high packing density of the adsorbed QP2VP. It should be borne in mind that a solution pH of 8.5 is significantly above the pK_a of the vinylpyridine moieties of QP2VP.

Consequently, as detailed above, at pH 8.5 the polyelectrolyte charge density is low, thus minimizing segment−segment repulsion. This facilitates a relatively compact conformation of the adsorbed polyelectrolyte chains, thereby inhibiting bridging.

Short-Ranged Forces upon Decompression of Adsorbed QP2VP Layers. Upon decompression of the layers (i.e., application of a force in the outward direction) the surfaces were observed to jump apart, indicative of a strong attractive force between the two surfaces, regardless of solution pH. The surfaces jumped apart from their hard wall separation.

The adhesions measured between the adsorbed polyelectrolyte layers were found to decrease significantly with increasing solution pH. At pH 4.0 the adhesion was 42 mN m^{-1}, and when the solution pH was increased to 6.2, the adhesion dropped to 32 mN m^{-1}. When the pH was further increased to 8.5, the adhesion dropped further.

It has been discussed above that at low solution pH the adsorbed polyelectrolyte is able to adopt an open conformation which allows chain interpenetration between neighboring polyelectrolyte layers. This gives rise to the bridging attraction discussed above. However, it should be emphasized that the force of adhesion will have contributions from both chain interpenetration and segment−segment attraction facilitated by compression of the layers. As solution pH is increased, the degree of chain interpenetration will decrease since the polyelectrolyte becomes more compact on the surface, as detailed above. Thus, we measure a drop in the force of adhesion with increasing solution pH. This drop is most pronounced at pH 8.5. This is not surprising given that there was no attractive bridging force measured on compression of the layers, as described above, indicating that chain interpenetration is minimal.

An interesting result is that, at pH 8.5, the magnitude of the adhesive force measured upon initial separation of the surfaces was 10 mN m^{-1}. For all subsequent decompressions the adhesion was significantly less, i.e., 4−5 mN m^{-1}. This effect can be related to the packing density of the polyelectrolyte on the surface and segment−segment interaction. We have already stated that at high pH QP2VP adsorbs in large surface excess onto mica, giving rise to a relatively compact layer. We have also discussed how this is due to the decrease in polyelectrolyte charge density. The high packing density of QP2VP at pH 8.5 prohibits a bridging attraction, also discussed above. However, the fact that an adhesion is measured upon decompression implies that some chain entanglement can occur but only when the QP2VP layers are in close contact. The drop in the measured adhesion after initial compression of the QP2VP layers implies that the degree to which this entanglement occurs is reduced. It appears that the first compression of the polyelectrolyte layers facilitates attractive segment−segment interactions within each adsorbed layer. Hence, fewer chains are available for entanglement between neighboring layers, and so the adhesion is reduced.

At pH 4 and 6.2, this difference between the adhesions measured on first and subsequent decompressions is not observed. Given that at these pH values the polyelectrolyte charge density is significantly higher that at pH 8.5, there will be resistance to chain entanglement when the layers are under compression. Thus, the measured adhesion is dominated by the bridging attraction between polyelectrolyte chains that extend into solution. We are making the distinction here between an attractive force that occurs between anchored polyelectrolyte chains extending into solution and chain entanglement that occurs due to molecular rearrangements when polyelectrolyte layers are under compression.

Conclusions

We have shown that polyelectrolyte quaternarized poly(2-vinylpyridine) (QP2VP) adsorbs in significant amounts to mica under a range of pH conditions. The polyelectrolyte layer was found to overcompensate the surface charge on the mica surface. The net surface potential is a balance between the pH-sensitive charge density of the polyelectrolyte and the mica surface. Under all pH conditions the long-range surface forces between two surfaces with adsorbed QP2VP were well described by DLVO theory.

At small surface separations (<10 nm) the force profiles deviate from the DLVO prediction. Near or below the pK_a of the ionizable groups of QP2VP, the charging up of the polyelectrolyte restricts its packing density and polyelectrolyte chains extend into solution. This facilitates a bridging attraction between the two polyelectrolyte-covered surfaces. At solution pH's significantly above the polyelectrolyte's pK_a, the increased packing density and decreased charge density of QP2VP inhibit bridging since there is insignificant extension of the polyelectrolyte chains into solution. The surfaces do not undergo an attractive jump into contact.

Upon decompression of the QP2VP layers an adhesion force was measured. We acknowledge that this adhesion is a result of the bridging between two polyelectrolyte-covered surfaces as they are brought into close proximity. However, even at high pH where QP2VP does not extend significantly into solution, an adhesion was measured. We believe that there is an important distinction to be made with regards to the mechanism by which bridging occurs. When considering polyelectrolyte bridging, it is important to distinguish between an attractive force that occurs due to the interpenetration of anchored polyelectrolyte chains extending into solution and chain entanglement that occurs due to molecular rearrangements when polyelectrolyte layers are under compression.

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