

Interaction between silica in the presence of adsorbed poly(ethyleneimine): correlation between colloidal probe adhesion measurements and yield stress

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Received 8th March 2010, Accepted 10th June 2010

DOI: 10.1039/c003973j

The interaction forces between silica surfaces with adsorbed layers of polyethyleneimine (PEI) were measured using colloidal probe microscopy as a function of solution conditions and PEI molecular weight. The surface coverage of polymer, as determined from optical reflectometry, was a significant factor influencing the extension of the chains away from the interface and also the development of adhesion between the surfaces. For the high molecular weight PEI (70 kDa), the adhesion passed through a maximum as a function of pH. The magnitude and position of this maximum was dependent on the surface excess of adsorbed PEI. The greatest adhesion was observed for the highest surface coverage of 0.88 mg m^{-2} at pH 11 where the force–distance curves on approach indicated the presence of a significant steric layer. Furthermore, the forces on separation under these conditions indicated strong bridging of PEI chains across the interface contributing to the enhanced adhesion. However, at lower surface coverage, no bridging was observed but the adhesion was still significantly greater than in the absence of an adsorbed layer of PEI. The adhesion at lower surface coverage was indicative of a charge-patch mechanism. The measured values of adhesion correlated very well with the observed yield stress of concentrated dispersions of silica in the presence of adsorbed layers of PEI. Thus, the molecular mechanisms probed during surface forces measurements can be used to predict the ensemble behaviour of the many particles dispersed in an aqueous medium which is of particular importance in minerals processing.

Introduction

Polyelectrolytes are often used to mediate the interactions between particulates in concentrated suspensions. They can be found in a number of diverse industries such as waste-water treatment, paper-making and mineral processing to name a few.¹ Ultimately, the stability of a colloidal suspension will be a balance between the forces due to the overlap of the charged surface electrical double layers, the dispersion forces, and the forces due to the presence of the polyelectrolyte. The ability to stabilize a suspension, or conversely cause particle aggregation, can be finely tuned simply through alteration of solution conditions such as ionic strength and pH in the absence of adsorbed polyelectrolyte. However, the stability will be profoundly affected when polyelectrolyte is added to the suspension, particularly if it adsorbs at the solid–liquid interface. The resultant potential energy of interaction can be difficult to predict as complex and competing factors such as the polymer molecular weight, charge and concentration in solution, all influencing the surface excess. The adsorbed amount will govern the extension of the polyelectrolyte away from the interface, a factor which may aid in stabilizing the system

through the introduction of a steric repulsive force or induce aggregation through bridging of chains.^{2,3}

Understanding how to achieve the ideal surface coverage of polyelectrolyte for a given application by judicious control over solution conditions has hence been researched heavily from both a theoretical and experimental stand point.^{4–8} Ionic strength plays a key role, with intermediate concentrations screening charge on the polymer backbone allowing closer approach of chains and hence higher adsorbed amounts. However at very high ionic strengths, charged polymer segments compete with co-ions for available binding sites typically reducing the surface excess. Charge density of the polymer is another factor influencing the adsorbed amount. pH is particularly important for polyelectrolytes whose charged groups are weakly ionisable.⁹ High charge density gives rise to low adsorbed amounts and a flat conformation at the interface as the polyelectrolyte molecules assume the role of counter-ions in the electrical double layer. Adsorption proceeds until the surface charge is neutralized although in most practical cases, a kinetically stable charge reversal is observed. This has been confirmed through mean-field calculations^{3,10,11} as well as experimentally verified and forms the basis of the polyelectrolyte multilayer technique.¹² Lower charge density on the polymer however results in a higher adsorbed amount and the formation of a steric layer.¹³ Many of these theoretical predictions of polyelectrolyte adsorption and layer conformation have been experimentally verified using direct surface forces measurement.^{14–22}

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However the picture of the adsorbed layer is complicated further if the structure of the polyelectrolyte is branched rather than linear. Polyethyleneimine (PEI) is often used in a branched form for application as a flocculating agent. Recent studies investigating the adsorption of PEI to silica as a function solution conditions have helped clarify the structure at the interface.^{23,24} Claesson *et al.* investigated the conformation of PEI as a function of solution conditions with the surface forces apparatus.²⁵ They showed that there was a significant difference in the extension of the polymer layer away from the interface with pH. A subsequent study by Poptoshev and Claesson investigated the concentration dependence on the observed surface forces between glass.²⁶ By choosing appropriate polymer concentration, the surface excess could be varied resulting in significant differences in the magnitude of the adhesion upon separation of the surfaces. Neutron techniques have also been used to study the interaction between silica surfaces in the presence of PEI.²⁷ GISANS showed that silica nanospheres exhibited a long range repulsion in bulk solution.

The yield stress of a suspension is a measure of the resistance of the structured fluid to flow. It is dependent upon a number of geometric factors including the size, shape and concentration of particles. Furthermore, the yield stress measures the strength and nature of the inter-particle forces in a flocculated structure. Previously, the yield stress of a concentrated suspension of silica in the presence of PEI was investigated as a function of pH, molecular weight and most importantly, the surface coverage of polymer.²⁸ It was observed that at low surface coverage, the yield stress was greater than in the absence of adsorbed PEI and a charge-patch attraction mechanism was proposed. Furthermore, at high surface coverage the yield stress was a maximum, with polymer bridging proposed as the dominant mechanism. In this study, the aim is to conclusively elucidate the molecular mechanisms involved in the development of the increased yield stress between concentrated silica suspensions through the use of colloidal probe measurements of the surface forces on approach and separation. Of particular interest is the form of the adhesive interaction at elevated pH.

Experimental section

Materials

Milli-Q water was used in the preparation of solutions. pH was adjusted using an appropriate amount of HCl or NaOH. A background electrolyte, NaCl (Sigma Aldrich, Australia), was used in all experiments.

Branched polyethyleneimine (PEI) with molecular weights of 600 and 70 000 Da from PolySciences Inc were used as received. PEI of molecular weight 70 000 comes in the form of a 30% aqueous solution (polydispersity 17 ± 5.2) while the 600 Da PEI has a purity of more than 99% (polydispersity 1.08). PEI contains primary, secondary and tertiary amine groups in approximately 1 : 2 : 1 25/50/25 ratio.

Oxidised silicon wafers from Peregrine Semiconductor Australia (Homebush Bay, Australia) were used for the adsorption measurements using optical reflectometry as well as the surface forces measurements.

Methods

Optical reflectometry (OR) was used to determine the surface excess and adsorption kinetics of PEI to silica as a function of molecular weight, ionic strength, concentration of polymer and pH. In OR,^{29–31} silicon wafer with a well defined oxide layer (107 nm) is used as the substrate. A polarized laser beam is passed through a 45° prism onto this reflective silica surface. The laser beam is reflected back through another 45° prism into the detection system where the parallel (p) and perpendicular (s) components are measured. Changes in the optical properties due to an adsorbing species will alter the ratio of the p and s components. This ratio can be converted to a surface excess by using a four layer optical model (silicon : silica : adsorbing species : solvent) if the refractive indices and layer thicknesses are accurately known.³² The refractive indices used in calculating the sensitivity factor were $n_{\text{Si}} = 3.8$, $n_{\text{SiO}_2} = 1.46$, $n_{\text{PEI}} = 1.36$ and $n_{\text{water}} = 1.33$ with the refractive index increment (dn/dc) for PEI of 0.21 mL g⁻¹ used.²³ Using this technique, the adsorption of PEI to silica is performed under well defined hydrodynamic conditions with the incident laser beam striking the surface at the stagnation point with a constant flow of polymer solution supplied to the liquid cell. Thus the adsorption is diffusion limited. Hence, OR gives valuable information regarding the surface excess and adsorption kinetics.

Colloidal probe microscopy was used to measure the surface forces between adsorbed layers of PEI on silica surfaces on approach and separation. A silica sphere of radius 10 μm was attached to the end of an atomic force microscope cantilever with a small amount of epoxy according to the method of Ducker *et al.*^{33,34} Standard, contact Si₃N₄ cantilevers (Veeco, USA) were used for all force measurements in this study. The data were typically collected using the 200 μm long, triangular shaped cantilever with a spring constant of 0.29 N m⁻¹ as measured by the thermal noise method.³⁵ The typical surface forces measurement using this technique has been described extensively elsewhere.³⁶ The adsorption of PEI was undertaken using different solution conditions in order to vary the adsorbed amount. However, all surface forces measurements were taken in polymer free, pH adjusted electrolyte solution at a temperature of 23 °C. For the measurement of the adhesion between the polymer coated surfaces, the maximum applied load and unloading rate were held constant and as such, no potential time dependent behaviour was investigated here.^{37,38}

For the yield stress measurements, 50 wt% samples of silica dispersion were prepared. A base solution was first prepared by adding accurately measured amounts of PEI to distilled water. The solution was then made alkaline (pH ≈ 12) by adding about 1 ml of 1 M NaOH. The additive concentration was measured in terms of dry weight percent or dwb% (g of additive per 100 g of oxides). Measurement in dwb% will make it convenient to interpret the result as the same number of dwb% for different molecular weight PEI will mean they have approximately the same number of amine groups. A measured amount of oxide was then added to the solution. The dispersion was then sonicated with a sonic probe for 1 ½ min to produce a homogenous dispersion. Approximately 60 g of dispersion was prepared for

each sample. The dispersion was allowed to equilibrate for at least 4 hours prior to any measurements. The pH of the prepared dispersions ranged from 7.5 to 10.7. In order to minimize dilution, 1 M to 5 M HCl was then used to reduce the pH of the dispersions. At higher pH, localised flocculation can occur in the vicinity of the acid droplet, and was redispersed by sonicating. The Brookfield DV-II+ viscometer was used to measure the yield stress of the samples. The viscometer has a spring torque of 0.7187 mN m at 100% scale reading. The method employed to measure the yield stress was the vane technique.³⁹ A four-blade vane was immersed in the flocculated slurry and rotated at a slow speed of 0.3 rpm. The maximum torque was recorded and used to calculate the yield stress.

Results and discussion

Prior to the surface forces measurements, a thorough study of the surface excess and adsorption kinetics of PEI to the silica substrate was undertaken as a function of a range of solution conditions. A previous study investigating the yield stress of a silica suspension in the presence of PEI revealed a strong influence on the adsorbed amount of polymer.²⁸ The equilibrium surface excess was measured as a function of 70 kDa molecular weight PEI solution pH and is shown in Fig. 1. The polymer concentration was constant throughout this series of adsorption experiments at 50 ppm and the background electrolyte concentration was 0.01 M. The adsorbed amount increases significantly with pH as the negative charge of the silica surface increases as expected. Furthermore, increasing pH reduces the charge density on the PEI resulting in a more extended conformation of the polymer immobilized at the interface and increased layer thickness in agreement with previous studies investigating weak polyelectrolyte adsorption to an oppositely charged interface.^{2,20,40} The adsorbed amount reaches a maximum of 0.9 mg m^{-2} at pH 10. This is significantly greater than monolayer coverage indicating that under these conditions, the polymer chains extend significantly away from the interface.

The effect of ionic strength on the adsorption of PEI to silica was also investigated. Understanding how the surface excess varies with the background electrolyte concentration is

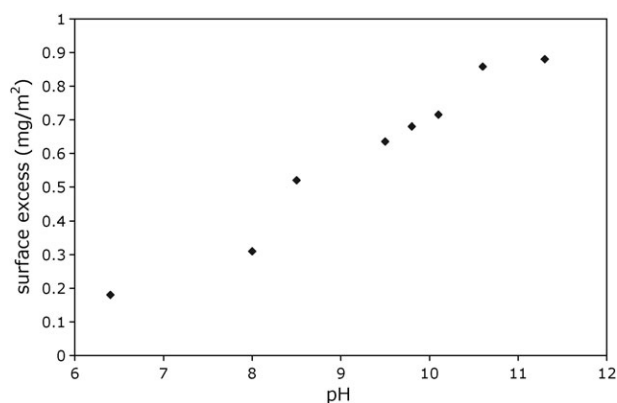


Fig. 1 Adsorbed amount of PEI on silica as a function of pH. Adsorption was undertaken with a polymer concentration of 50 ppm with an ionic strength of 0.01 M NaCl.

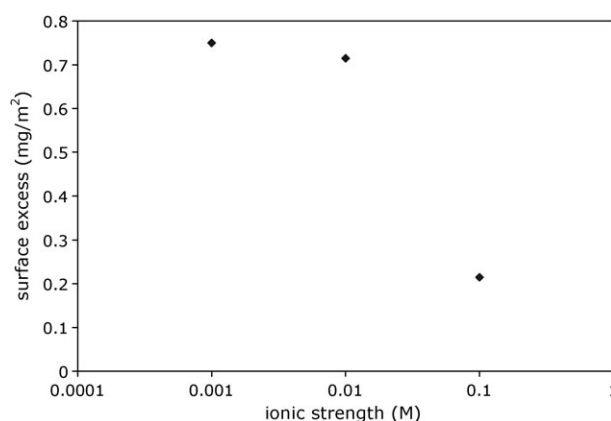


Fig. 2 Adsorbed amount of 70 kDa PEI at pH 10 as a function of background electrolyte (NaCl) concentration. Adsorption measurements were performed using a solution of PEI with a concentration of 50 ppm.

important as it aids in demonstrating the relative affinity of the polyelectrolyte for the surface and points to the presence or absence of any non-ionic interactions such as hydrogen bonding. If adsorption of PEI is driven purely by electrostatics, then it may be expected that the surface excess will decrease as the concentration of co-ions in solution compete for the available surface binding sites. Fig. 2 shows the adsorbed amount of 70 kDa PEI at pH 10 as a function of the concentration of NaCl. At this pH, PEI has a very low charge, however, it can be seen that the surface excess decreases significantly with increasing ionic strength suggesting that the adsorption is predominantly due to ionic interactions. To definitively rule out any non-ionic interactions, much higher electrolyte concentrations are necessary which is problematic for reflectometry due to large refractive index gradients within the measurements cell. Furthermore, with increasing ionic strength, the PEI chains may be expected to collapse toward a more compact conformation potentially increasing the amount of polymer which may be adsorbed through geometric considerations. However, this is clearly not the case as shown in Fig. 2 then it is likely that the main driving force for adsorption is electrostatics.

The adsorption of 70 kDa PEI to silica, in terms of surface excess, agrees qualitatively with predictions from theory as a function of the polymer charge, surface charge and ionic strength.² Furthermore, by simply changing the solution conditions, a significant range of surface coverage may be easily achieved. Importantly, it is not just the adsorbed amount of polymer that will only influence the adhesion, but the extension of the chains away from the solid–liquid interface will be the dominant factor. The influence of molecular weight of PEI on the adsorbed amount was also investigated. An increase in surface excess with increasing molecular weight under the same adsorption conditions was observed consistent with previous studies.²³

Based upon the measured surface excess determined through OR, appropriate conditions were chosen for the subsequent surface forces measurements in order to compare and contrast with the observed yield stress values of the concentrated silica dispersions in the presence of PEI at various surface coverage.

Fig. 3 shows the surface forces as a function of distance for the approach of a silica sphere to a silica substrate in the presence of adsorbed layers of 70 kDa PEI. Two different surface excesses were chosen, firstly, the maximum surface coverage of 0.9 mg m^{-2} by adsorbing the polymer at pH 10.5 and the lower surface excess of 0.60 mg m^{-2} was achieved through adsorption at pH 8.5. After adsorption, the polymer solution was replaced with an electrolyte solution of equivalent pH. Subsequently, the pH of the solution was reduced to the lowest value and then sequentially increased up to the maximum value. Furthermore, the response of the polymer layer to pH cycling was investigated by performing measurements as the pH was decreased to investigate reversibility. Force curves were recorded in PEI free solution by injecting a pH adjusted NaCl solution with a concentration of 0.01 M as shown in Fig. 3. Hence, any repulsive force due to overlapping electrical double layers should decay rapidly with a Debye length of the order of 3 nm.

Clearly, the force curves in Fig. 3a decay much more slowly with distance indicating that the repulsive force is not purely of electrostatic origin. It is therefore likely that a combination of electrostatic and steric forces, often termed electrosteric,^{16,41} is responsible for this greater than expected force. This is indeed

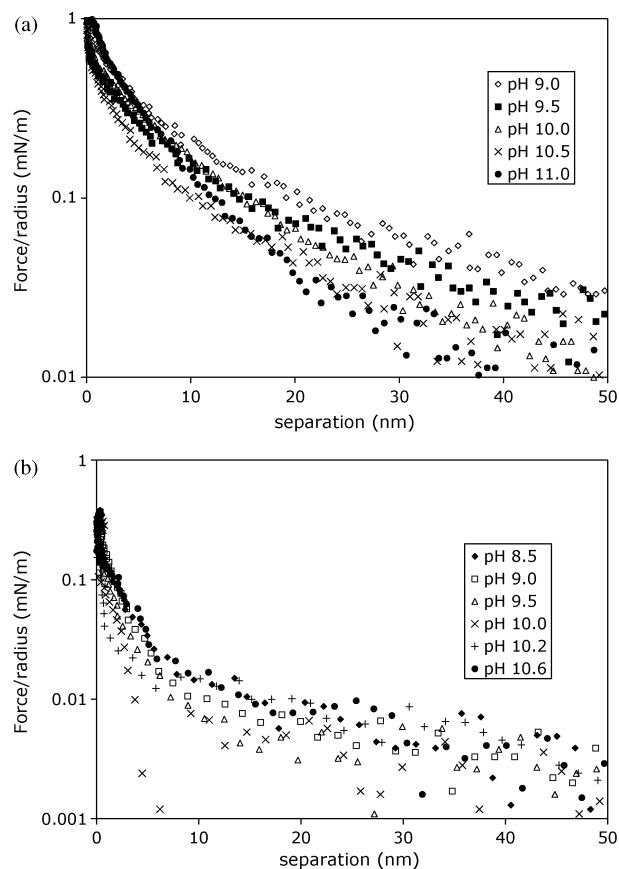


Fig. 3 Surface forces on approach for the interaction between a flat silica substrate and silica colloidal probe both with adsorbed layers of PEI with a molecular weight of 70 kDa. Top shows the forces when the surface excess is 0.88 mg m^{-2} and bottom when the surface excess is 0.60 mg m^{-2} . All forces were recorded in a pH adjusted solution of NaCl with a concentration of 0.01 M.

supported by investigation of the extent of the forces on approach as a function of pH. There is a reduction of the magnitude of the force as the pH of the solution is increased. Hence, the reduced force can be rationalized by considering the abundance of positive charge on the PEI chains which also decreases as the pH of the solution increases. Furthermore, previous zeta potential measurements using the same polyelectrolyte adsorbed on silica show that the overall charge changes from positive to negative in this pH region for a similar surface excess of PEI.²⁸ At pH 11, where the PEI chains are essentially uncharged, there is a fundamental change in the shape of the force–distance curve, indicating that the origin of the force is now due to a steric interaction.^{17,18,20,40,42,43}

Interestingly, the profile of the force–distance curves shown in Fig. 3b where the surface excess is substantially lower (0.6 mg m^{-2}) is significantly different in shape and magnitude to the higher surface coverage case. Here, the forces decay very rapidly with distance, with approximately the correct Debye length as predicted from the Poisson–Boltzmann equation of 3 nm for a 1 : 1 electrolyte with a concentration of 0.01 M. This suggests that the polymer layer is adsorbed in a flat conformation with only a limited extension away from the interface in direct contrast to the significant steric interaction force at higher surface coverage. At pH 10–10.2, there is a short-ranged jump into contact which corresponds to the approximate point of zero charge observed in zeta potential measurements previously.²⁸ Thus this very low net charge suggests that the forces on approach at this short separation are dominated by dispersion forces and not a bridging interaction which would act at greater surface separations.²⁶ At the even lower surface coverage of 0.18 mg m^{-2} , achieved through adsorption of the 70 kDa PEI at pH 6.5, the forces on approach continue to decrease in extent and magnitude as shown in Fig. 4. Here, the pH was held constant for the surface forces measurements.

Fig. 5 shows the forces on approach at pH 10.5 on increasing and decreasing pH cycle runs for the highest surface coverage. The extent of the repulsive forces are essentially the same to

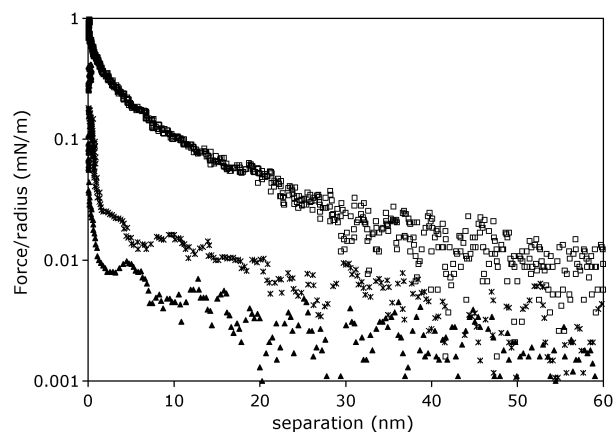


Fig. 4 Forces on approach between silica surfaces with adsorbed layers of 70 kDa PEI at different surface excess at pH 10 and 0.01 M background NaCl solution. Open squares are $\Gamma = 0.88 \text{ mg m}^{-2}$, crosses are $\Gamma = 0.60 \text{ mg m}^{-2}$ and closed triangles are $\Gamma = 0.18 \text{ mg m}^{-2}$. The scatter in the forces below 0.01 mN m^{-1} is due to thermal noise.

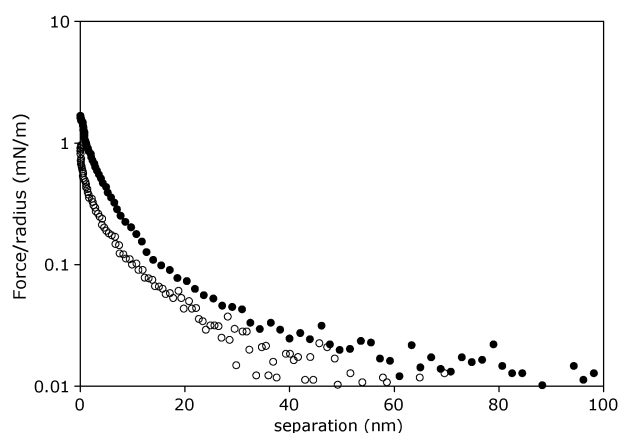


Fig. 5 Comparison of the forces on approach between 70 kDa PEI coated silica surfaces at pH 10.5. Open circles are for the increasing part of the pH cycle whilst closed circles are after the pH has been reduced from higher pH.

within experimental error however the magnitude at short separations is slightly greater when the pH is decreasing demonstrating that the order of the measurements in terms of pH does not significantly influence the overall interaction. It is possible, however, that the dissolved silicate species may interact with the PEI chains at the elevated pH leading to a change in conformation. Although at pH greater than 10 some dissolution of silica may be possible, the almost reversible nature of the force profiles shown in Fig. 5 suggests little change to either of the silica surfaces due to elevated pH. This is perhaps due to an equilibrium between the pH adjusted salt solution and silicate species already achieved prior to injection into the AFM cell as the solutions were stored in a glass flask.

Surface forces measurements between the silica surfaces with adsorbed PEI were also performed as a function of molecular weight. Fig. 6 shows example force–distance curves for 600 Da and 70 000 Da at two different pH values. The PEI was adsorbed under similar solution conditions for both polymers, that is, from a 50 ppm polymer solution in 0.01 M

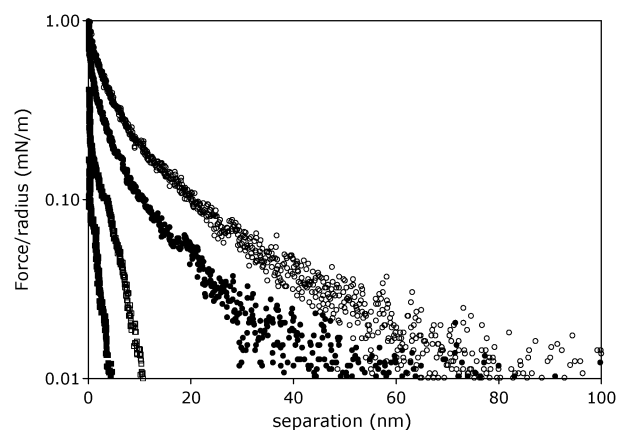


Fig. 6 Surface forces on approach between PEI coated silica surfaces as a function of pH in 0.01 M NaCl solution. High molecular weight (70 000 Da) at pH 9 (open circles) and at pH 10.5 (filled circles), low molecular weight (600 Da) at pH 9 (open squares) and at pH 10.5 (closed squares).

NaCl with the pH adjusted to 10.5. This leads to adsorbed amounts of 0.36 mg m^{-2} and 0.88 mg m^{-2} for the 600 Da and 70 000 Da molecular weights, respectively, representing the highest surface coverage of polymer for each molecular weight. Fig. 6 shows that the polymer layer is flat for the low molecular weight PEI covered surfaces which may be expected for such a short chain polymer with the forces on approach decaying as predicted with DLVO theory. Again, as for the higher molecular weight polymer, the force is greatest for the lowest pH in agreement with zeta potential measurements.²⁸

The surface forces on approach presented in Fig. 4–6 show some very interesting trends. In summary, the greater the adsorbed amount of PEI on silica, the greater the repulsive or stabilizing force irrespective of the solution conditions during measurement. In particular, high surface coverage of polymer results in an electrosteric force which acts over greater than 100 nm however increasing the pH reduces the charge on the polymer and hence the extent of this force. For low surface coverage, achieved through either the use of a lower molecular weight PEI or by adsorbing to silica at a lower pH, a weaker interaction force is observed presumably due to a decreased electrostatic interaction and less chain overlap and compression at short separations. At the high ionic strength used in this study, this results in a rapidly decaying repulsive force.

Based upon the surface forces data on approach, it is tempting to suggest that the low surface coverage conditions will lead to a more unstable suspension as the PEI coated silica particles will be able to approach to a much closer range under Brownian motion than for the high coverage, electrosterically stabilized silica. The adsorption of PEI results in charge reversal of the silica particles. For low coverage the overcompensation of positive charge is quite minimal as reflected in the zeta potential measurements and hence the kinetic barrier to aggregation is small in the absence of a significant steric force.²⁸ Thus, it is likely then that there is some correlation between surface potential and yield stress of the concentrated suspension in this pH region and at low surface excess. Such conditions are typical for charge-patch flocculation⁴⁴ and therefore the relatively strong inter-particle attractive force should manifest in an increased yield stress.

The yield stress of concentrated silica suspensions treated with PEI for two different molecular weights, as shown in Fig. 7, was determined as a function of surface excess and pH. The polymer used in these experiments is identical to those used in force measurements. Yield stress can be related to the interaction potential between particles. There has been a considerable amount of work relating the yield stress to the particle pair DLVO interaction potential or force for a range of oxide dispersions including this silica.^{45–47} This is indicated by the linear decrease in the yield stress with the square of the zeta potential. As long as the flocculated network structure occupied the whole volume of the container, the majority of the particles in the network will have two-nearest neighbors except those particles at the network junctions. Also as long as there is no formation of agglomerates (forming a clear layer of supernatant on the surface) the particulate microstructure in the network can be regarded as the same at any pH. The yield stress was measured directly with a vane viscometer. The vane

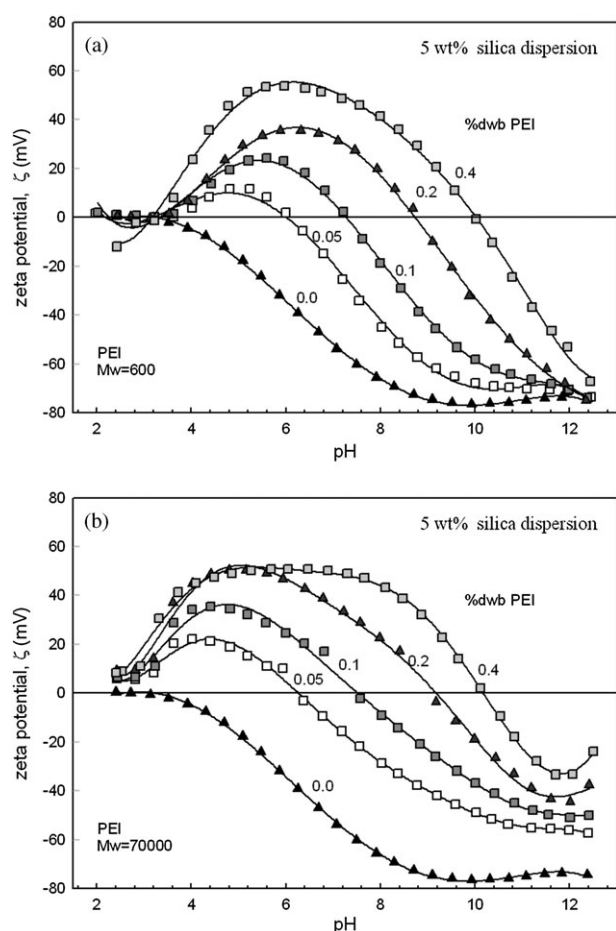


Fig. 7 The yield stress-pH behaviour of 50 wt% silica suspensions under the influence of PEI of (a) M_w 600 and (b) M_w 70000. Reproduced with permission from ref. 28

is immersed in the dispersion and rotated slowly at speed less than 1 rpm. The measured yield stress was found to be independent of rotational speed at less than 1 rpm.

For a given surface coverage, the yield stress goes through a maximum with pH for both the low molecular weight and high molecular weight PEI. There is a good agreement between the maximum yield stress and the minimum in the repulsive force measured using colloidal probe for the low surface coverage case. However, Fig. 7 shows that the overall maximum in the yield stress occurs at the maximum surface coverage where the forces on approach are highly repulsive due to the electrostatic adsorbed layer. Thus, it seems likely that there is more than one mechanism which can explain the measured yield stress data. Therefore, in order to reconcile these observations, the surface forces on separation were also measured to provide more information.

The surface forces or adhesion were measured as the silica surfaces were separated as a function of pH, surface coverage and molecular weight. Fig. 8 shows two typical force-distance profiles on separation. All adhesion data measured could be characterized by one of these two profiles. In Fig. 8, it is obvious that there are two types of adhesive interactions. The first is what is termed “primary adhesion” where after a strong enough restoring force is exceeded as the surfaces are

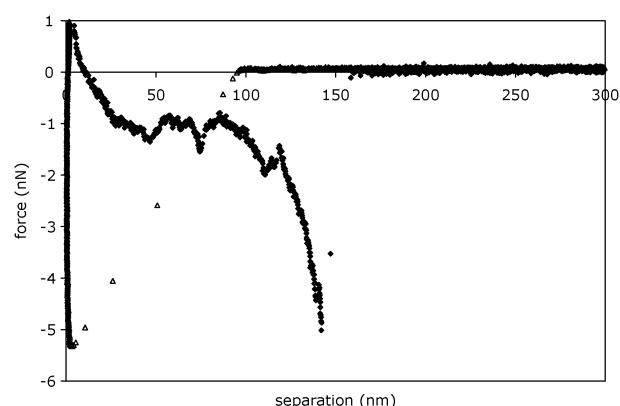


Fig. 8 Typical adhesion measured between 70 kDa PEI coated silica surfaces. Open symbols show the measured pull-off force as a function of separation at low surface coverage and high pH, closed symbols show the pull-off high surface coverage and high pH.

separated, the force returns to baseline levels. This is characteristic of charge-patch aggregation and is indeed observed only when the surface coverage of PEI is low. This is supported by the forces on approach where at low surface coverage, the extension of the polymer layer into solution is minimal allowing intimate contact between the silica surfaces. The polymer layer has a flat conformation and there are available binding sites on both surfaces for a limited number of segments of the PEI chains to attach across the interface. The rest of the polymer molecule is tightly held and does not detach upon separation of the surfaces. The second profile shows that many contacts are made during loading and that many polymer chains can bridge between the surfaces on separation leading to the characteristic saw tooth pattern in the pull off force-distance profile. Typically, this type of force curve was observed only for the 70 kDa PEI at pH where the charge on the polymer was low, that is greater than 10. The polymer in this case is approaching poor solvency preferring an environment rich in polymer segments. The maximum extension of the polymer chains is of the order of the contour length of the polymer however the possibility of “pulling” a network of polymer molecules into solution from the interface cannot be discounted. The polydisperse nature of this sample may also contribute to the slightly larger than predicted chain extension lengths.

The maximum pull-off force between the PEI coated silica surfaces was hence measured from the global minimum in these force-distance curves as is shown in Fig. 9 for the high molecular weight sample. Whilst previous studies have indicated that there is some rate dependency of the measured adhesion values, in all measurements here, care was taken to maintain a constant maximum applied load and unloading rate. The dynamic adhesion effects are currently under investigation for this system. However for surfaces with adsorbed polymer layers with only minimal extension, it is expected that the inter-diffusion of chains across the interface will be limited leading to no strong increase in adhesion as a function of time in contact.^{38,40,48} The same trend is observed between the colloidal probe adhesion measurements and the yield stress data as a function of surface coverage and pH by comparison

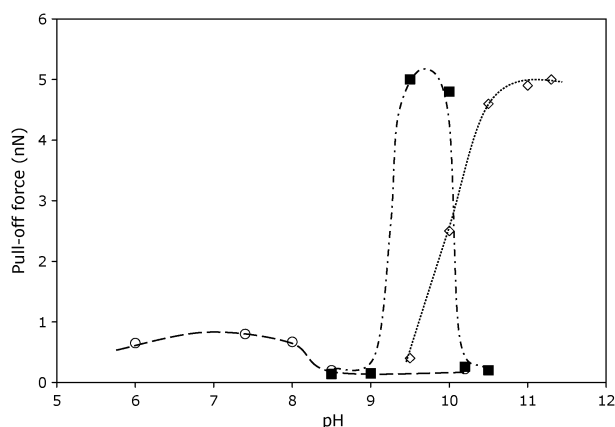


Fig. 9 Maximum pull-off force on separation of silica surfaces coated with 70 kDa PEI as a function of pH. The surface excess of PEI on the silica surfaces was varied: 0.18 mg m^{-2} (open circles), 0.60 mg m^{-2} (filled squares) and 0.88 mg m^{-2} (open diamonds). Lines are to guide the eye.

of Fig. 7 and 9. That is, the position of the maximum in both the yield stress and adhesion with respect to pH increases as the surface coverage of PEI increases. In addition, the overall magnitude of the yield stress scales well with the measured adhesion values determined from the colloidal probe technique under similar conditions of pH and surface coverage. Furthermore, for situations at less than full coverage of polymer, the maximum in the pull-off measurement corresponds well with the minimum in the magnitude of the repulsive surface forces on approach. At full surface coverage, the pull-off force increases with pH in agreement with the reduction in the electrostatic stabilization force observed on approach of the PEI covered surfaces.

Interestingly, the maximum pull-off force seems to be independent of surface coverage. However, as shown in Fig. 8, there is a fundamental difference in the adhesion profile between low coverage and high coverage. Hence, simply using the pull-off force as an indicator for adhesion is not sufficient. In order to account for the difference in adhesion profile, the area between the force–distance curve and baseline was integrated to give the adhesion energy. Fig. 10 shows the adhesion energy as a function of surface coverage and pH. Whilst the maximum in pull-off force with surface coverage agrees well with the yield stress data as shown in Fig. 7, the converted data to adhesion energy increases monotonically. This perhaps indicates that there is some rate dependency of the adhesion energy data at high surface coverage consistent with a bridging mechanism of adhesion together with chain entanglement as described previously. These dynamic effects are currently under further investigation.

The pull-off force and adhesion energy was also measured for the silica surfaces with adsorbed layers on the low molecular weight (600 Da) PEI as a function of pH. The surface excess of PEI was determined to be 0.38 mg m^{-2} using optical reflectometry by adsorbing at pH 10.5. It is therefore expected then that both the pull-off force and adhesion energy will be significantly lower than in the high molecular weight case if the surface excess and adsorbed layer thickness dominate the interaction. This is indeed the outcome as shown in Fig. 11.

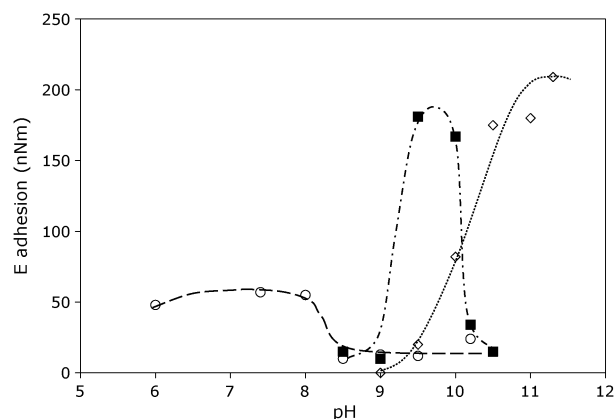


Fig. 10 Adhesion energy on separation of silica surfaces with adsorbed layers of 70 kDa PEI as a function of surface coverage and pH. The surface excess of PEI on the silica surfaces was varied: 0.18 mg m^{-2} (open circles), 0.60 mg m^{-2} (filled squares) and 0.88 mg m^{-2} (open diamonds). Lines are to guide the eye.

The magnitude of the adhesion reaches a maximum at pH 10 of 25.9 nN m , much less than the highest adhesion reached with the 70 000 Da PEI functionalized surfaces of greater than 200 nN m . Furthermore, as the contour length of the low molecular weight polymer is significantly shorter, there are fewer opportunities to develop a significant bridging force and hence there is a close correlation between the pull-off force and adhesion energy.

The adhesion measurements performed using the colloidal probe technique between bare silica surfaces showed no significant adhesion over the solution conditions investigated in this study. Clearly, the presence of an adsorbed layer of PEI acts to promote an increase in adhesion in the pH range of 6–11. This qualitatively agrees with the observations of yield stress. In the absence of PEI, no significant yield stress was observed however it was significantly increased with an adsorbed layer, regardless of the polymer conformation and surface excess. The colloidal probe adhesion measurements between two silica surfaces serve to directly highlight the molecular mechanisms occurring in a concentrated suspension.

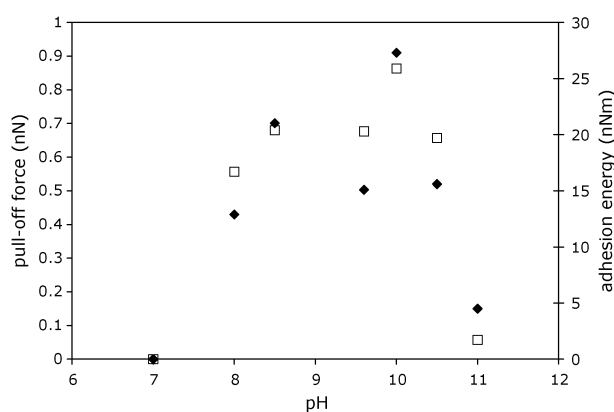


Fig. 11 Pull-off force (closed diamonds) and adhesion energy (open squares) between silica surfaces with adsorbed layers of low molecular weight (600 Da) PEI as a function of pH.

Conclusions

The influence of PEI molecular weight, surface coverage and pH on the molecular scale adhesion measurements between silica surfaces closely correlates with yield stress measurements of the corresponding system of a concentrated silica dispersion. Very high surface excess of PEI results in the greatest adhesion, particularly at elevated pH where PEI is essentially uncharged through a polymer chain bridging mechanism. By controlling the adsorbed amount through adsorption at varying pH, the adhesion interaction could be tuned to give lower adhesion where a charge-patch mechanism is suggested. These different mechanisms for the development of the adhesion interaction are supported by the surface forces data on approach of the silica surfaces as a function of surface coverage where at low adsorbed amounts, only electrostatic repulsive forces are observed whereas at high adsorbed amounts a steric or electrosteric interaction force is measured. Hence, both the forces on approach and separation provide insight into the behaviour of a suspension in the presence of polymer. This is particularly relevant at high solids content where the particles are always in relatively close contact and kinetic energies are capable of overcoming any energy barrier to flocculation.

Acknowledgements

Shaun Howard is gratefully acknowledged for the instruction in the use of the optical reflectometer. Helpful discussions with Tim Senden and Vince Craig, ANU, are also acknowledged.

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