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Influence of Charge Density and Coverage on Bound Fraction for a Weakly Cationic Polyelectrolyte Adsorbing onto Silica

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ABSTRACT: This work addressed the bound train fraction of an adsorbing model polyelectrolyte ((dimethylamino)ethyl methacrylate, DMAEMA), for variations in pH, which altered the relative charge densities of the polymer and substrate (silica). In addition to the weakly basic and acidic natures of the polyelectrolyte and substrate, respectively, this model system had the characteristic that adsorption was driven exclusively by electrostatic attractions. Therefore, at pH's where the polymer or the substrate was not charged, adsorption did not occur. At pH 6, which represented the extreme of a sparsely charged substrate and a densely charged polyelectrolyte with condensed counterions, the train fraction approached unity and was coverage-independent. At these conditions, the maximum bound train mass of 0.7 mg/m^2 exceeded previous reports for the maximum train mass of adsorbed nonionic polymers. At higher pH's, the substrate charge density increased while the polymer became sparsely charged. In this limit, the train fraction decreased and became coverage dependent, with loops and tails forming at crowded interfacial conditions, similar to previous observations for adsorbing nonionic polymers.

Introduction

When homopolymers adsorb at a liquid−solid interface, they form a combination of tails, loops, and trains, where the former extend into solution and the latter lie flat against the surface.[1−4] It is important to understand and to be able to predict the amount of trains or the extent of loops and tails so that appropriate molecules can be chosen for particular applications. This is especially the case with cationic polyelectrolytes, which play important roles as flocculants or as colloidal stabilizers, depending on their architectures and charge densities.

Attempts to quantify the adsorbed configurations of nonionic polymers such as poly(ethylene oxide) (PEO) in water or polystyrene in organic solvents have met with reasonable success. For instance, neutron scattering and reflectivity methods have quantified detailed concentration profiles in adsorbed layers[5,6] and NMR methods have been developed to quantify the bound or train fraction.[7,8] In general, for adsorbing nonionic homopolymers, it is understood that at starved interfaces, or on surfaces with coverages lower than that on the isotherm plateau, adsorbed chains lie flat, contributing to a large number of trains.[4,9,10] In the limit of low coverages corresponding to isolated chains, the train fraction approaches unity. Then as the surface coverage increases, it does so with increasing train mass (and a constant train fraction of unity) up to the point where the surface is filled with trains. The reported maximum train masses for nonionics such as PEO and poly(vinylpyrollidone) on silica are in the range 0.25−0.55 mg/m^2.[9] Additional chains can only adsorb to the surface through the generation of loops and tails. Hence, as the isotherm plateau is approached, the increase in total surface mass is accompanied by a decrease in train fraction, even though the train mass is nearly constant.[4,9] One interesting point borne out with nonionic homopolymers, but not confirmed with homopolymers in general (including polyelectrolytes), is that the dependence of train mass on adsorbed amount is independent of molecular weight.[4]

Analogous studies with polyelectrolytes are more difficult to find and more important to report, because a wide range of variables influences their adsorption. The huge number of parameters means that the results for one system may not translate directly to a system of different chemistry. In the case of electrostatically driven polyelectrolyte adsorption (one of many possible scenarios), one must consider the possible role of chemical attractions with the surface, solvent quality, and the influence of salt, which can screen interfacial repulsions (enhancing coverage) or compete for adsorption sites (reducing coverage.) Further, with weak polyelectrolytes, the pH of interest relative to the polymer's pK_a or pK_a range will determine the backbone charge density. At sufficiently high charge densities, counterions may condense, altering the behavior of the polymer.[11,12]

For adsorption which is aided by, if not exclusively driven by, electrostatic attractions, and where each segment is charged, adsorbed layers are generally expected to be flat, with a high train fraction.[13−17] In such situations, it has even been reported, or at least speculated, that the train fraction is always near unity. The strong segmental binding strength from the electrostatic attractions is thought to override any tendency for adsorbed chains to increase their entropy through the formation of loops and tails. Then, since loop and tail formation is suppressed, no effect of plateau coverage on molecular weight is observed.[18] Such a scenario is in stark constrast with nonionic systems where loop and tail formation lead to increased plateau coverage with molecular weight.[19,20]

The current work probes the adsorbed configuration and train mass of a model cationic polyelectrolyte

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((dimethylamino)ethyl methacrylate, DMAEMA) adsorbing onto a negatively charged surface (silica). Here, both the adsorbing polymer and the surface are weak bases and acids, respectively. Therefore, variations in pH accomplish changes in the charge density of the DMAEMA and the silica. The current work addresses a broad range of conditions, from the situation where the silica is sparsely charged and the polymer densely charged to that where the polymer contains no charge and the substrate ionization is high. Titration data, a discussion of charge density, and the role of counterion condensation for this system have been reported,[21] forming a foundation for the current work, which focuses on adsorbed chain configuration.

Several features of the current model system are worth noting: First, the current study compares polymeric and oligomeric versions of the same DMAEMA backbone chemistry, thus facilitating a clear distinction between situations where only trains and where loops and tails may form. Second, the sole driving force for DMAEMA adsorption on silica is electrostatic:[22] in the absence of chemical attractions between the polymer and surface, the relative charge spacing on the polymer vs that on the substrate is key in controlling adsorption. A quantitative examination of the relative charge distributions, taking counterion condensation into account, has been the subject of a previous work.[21] Finally, for the oligomer at low pH's of 6 or less, the DMAEMA is highly charged (even with its condensed counterions), and the silica charge is so sparse that even on the isotherm plateau, adsorbed oligomeric chains are separated (with one on each underlying surface charge) and noninteracting.[21] Hence, at pH's of 6 and below, the isotherm plateau for the oligomer represents isolated chains. Previously reported is a crossover at higher pH's to a regime where segmental repulsions limit the oligomer's surface coverage.

This study extends NMR solvent relaxation methods developed in the Cosgrove lab[7,8] to probe the bound train fraction in the model DMAEMA−silica system. The results for this polyelectrolyte system, taking into account what we have previously learned about acid−base and electrostatic bonds between the backbone and the surface, are then compared with the established behavior for nonionic homopolymers.

Materials and Methods

A pair of DMAEMA samples, one with molecular weight 31 300 and the other with molecular weight 2350, were provided as a gift from DuPont. We refer to the former as a polymer and the latter as an oligomer. Both had relatively low polydispersities of 1.1−1.3 as a result of the group transfer polymerization reaction used in their synthesis. The samples were provided in solutions of low-boiling polar organic solvents, which were removed prior to further study. For samples subject to study by NMR, D_2O was added, and then the organic solvents were removed by rotary evaporation. The process was repeated until no organic solvent peaks were apparent in the proton NMR spectrum. For experiments not requiring D_2O, a similar procedure was employed to replace the organic solvents with high-purity deionized water (Milli-Q). As a result of the use of D_2O in NMR studies, instead of pH, we report pD's.

A suspension of 12 nm silica particles (Ludox, DuPont) having a surface area of 230 m^2/g and a solids content of 30 wt % was employed as the substrate. Samples were purified by dialysis against DI water using a 6000−8000 molecular weight cutoff filtration membrane. Though the filter pores exceeded the colloidal diameter, it was possible to conduct the dialysis for a finite amount of time, after which ionic contaminants were removed (as shown by conductivity) and sufficient particles retained. After purification, NaCl was added back at a concentration of 10^{-3} M to yield a concentrated stock solution that did not form a repulsive gel. Dilution of this colloidal stock solution for experiments with an appropriate silica concentration typically gave NaCl concentrations as low as 10^{-5} M. In most studies, additional salt or buffering ions were added as needed. Typically NaOH was added to a KH_2PO_4 solution to yield a buffered solution of appropriate pH. These compounds were purchased from Fisher Scientific.

Electrophoretic mobility studies employed a DELSA 440 instrument from the Coulter Co. A Coulter EMPSL7 mobility standard (0.04 g/L of carboxylated polystyrene latex in 0.01 sodium phosphate buffer, pH 7) was employed for calibration.

Liquid-state proton NMR, using a GN-300 300 MHz FT-NMR spectrometer, was employed to characterize two features of DMAEMA adsorption: the adsorbed amount, leading to the adsorption isotherm, and the amount of DMAEMA in contact with the surface in the form of trains. Both experimental procedures have been described in detail in our previous paper.[22] It is important, however, to note that a benzene solution of tetrakis(trimethylsilyl)silane (TKS, purchased from Aldrich) with added chromium(III) acetonyl acetate was employed as an external standard in a sealed glass capillary tube. Also, a presaturation solvent suppression method[23] was applied to improve the dynamic experimental range.

In the case of adsorption isotherms, a series of calibration solutions (containing only DMAEMA and not silica) established the relationship between the amine methyl proton peak size and the free DMAEMA concentration. To generate adsorption isotherms, silica was added to the DMAEMA solutions of various concentrations, and after sonication, spectra were measured. Since constrained interfacial motions render adsorbed DMAEMA invisible in the NMR, the peaks from the free polymer were reduced. The remaining free polymer concentration was established from the calibration, and the adsorbed amount was calculated by difference, for each datum on an isotherm.

While the polymer's chemical shifts contain information about adsorption, solvent relaxation data (for the D_2O) provide an interpretation of the adsorbed configuration in the context of trains as opposed to loops and tails. Application of the solvent relaxation technique to probe polymer physics was first executed in the Cosgrove lab to characterize poly(ethylene oxide) and poly(vinylpyrollidone) adsorbing on silica.[7,8] More recently, we employed the method to probe the adsorbed configuration of a low molecular weight DMAEMA oligomer.[22] The current paper follows the approach in this previous work, which is summarized here.

The method is based on the principle that NMR relaxation times are a consequence of molecular mobility. For low molecular weight species such as solvents, rapid motion yields spin−lattice (T_1) and spin−spin relaxation times (T_2) that are inversely proportional to the correlation time. The constrained motions of adsorbed molecules lead to more efficient relaxations and hence faster (decreased) relaxation times, by up to several orders of magnitude. Hence, the exchange of solvent molecules between an interfacial environment and the bulk solution propagates the surface effect in an attenuated fashion throughout the entire solvent bath. The resulting enhanced rate of solvent relaxation, $R = 1/T_1$, is proportional to the amount of solvent constrained at the interface.

Both the silica−water interface and the interfacial environment consisting of DMAEMA trains adsorbed onto silica affect the solvent relaxation. We define R_0 as a reference relaxation rate corresponding to a silica dispersion (without DMAEMA) having the same surface area as that in an adsorption experiment (with DMAEMA). Indeed, the NMR solvent relaxation behavior of aqueous silica suspensions has been investigated both theoretically and experimentally.[24−27]

The specific relaxation rate is defined for convenience:

$$R_{sp} = \frac{R}{R_0} - 1 \qquad (1)$$

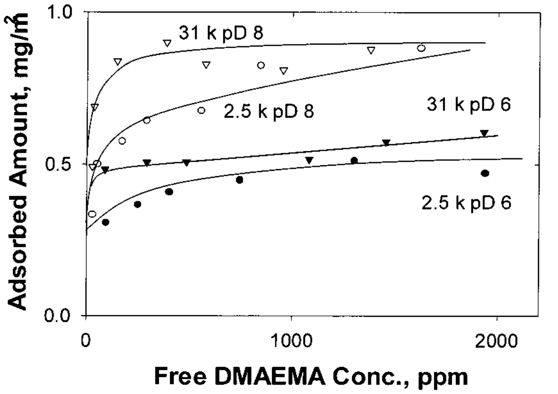

Figure 1. Adsorption isotherms for DMAEMA on 12 nm Ludox silica in D_2O. The nominal pD values correspond to the dilute region of each isotherm. The pD was roughly $^1/_2$ a unit higher when the free DMAEMA concentration was 2000 ppm.

In their careful investigation of PEO adsorption onto silica, van der Beek et al.[7] demonstrated the proportionality between the mass of bound trains and R_{sp} for a nonionic polymer on silica. The formalism was then extended to adsorbed poly(vinylpyrollidone). In both these cases, the train mass was proportional to R_{sp}, starting at zero coverage where the train fraction approached unity. For the weakly cationic polyelectrolyte, DMAEMA, similar results were found except for an insensitivity of R_{sp} to bound trains below 0.15 mg/m^2, where R_{sp} took on limiting values corresponding to those of the silica dispersions without added polymer.[22] This previous work focused exclusively on DMAEMA oligomers, whose capacity to form loops and tails was limited. The argument was therefore made that R_{sp} was proportional to train mass for DMAEMA, except in the low coverage limit, where the train fraction was the same below 0.15 mg/m^2 as it was above this sensitivity limit.

Results

Figure 1 compares the adsorption isotherms of the polymer and oligomer at 2 different pD's, which were controlled through the use of 0.01 M buffer solution containing NaOH and KH_2PO_4. The overall ionic strengths varied from 1.2×10^{-2} to 1.8×10^{-2} M, depending on the particular solution. We previously established that in this range ionic strength does not affect coverage.[22]

At each pH, the polymer coverage slightly exceeds that of the oligomer. More importantly, the polymer isotherms contain better-defined plateau regions and sharper initial increases in coverage as a function of concentration. This meets expectations for homopolymer adsorption,[4] where many individual groups along the adsorbing backbone contribute to the adsorption energy, as opposed to just a few for the oligomer. The higher coverage for the polymer suggests that loops and tails, in addition to trains, contribute to adsorbed mass, a possibility that is explored in greater detail below.

The feature in Figure 1, that the plateau adsorbed amount at pH 6 is less than that at pH 8, does not necessarily imply greater affinity between DMAEMA and the surface at pH 8. Instead, it is consistent with two separate ways of thinking about charge-driven adsorption. First, lower coverage is expected at pH 6 where the relatively sparse surface charge density and relatively high DMAEMA charge density mean that relatively few DMAEMA chains are needed to compensate the underlying surface charge, compared with pH 8. The explanation of the pH effect in Figure 1 must, however, go deeper since the surface charge is overcompensated on the isotherm plateau (which will be proven later) and since there is no chemical driving force for adsorption.

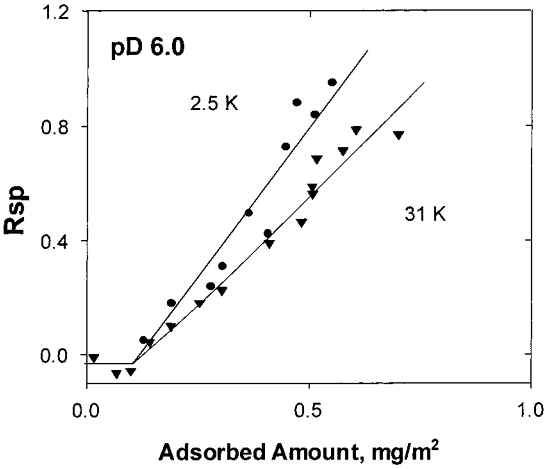

Figure 2. Specific solvent relaxation rate as a function of coverage for the polymer and the oligomer at a nominal pD of 6. This nominal pD corresponds to the dilute region of the isotherm and increased roughly $^1/_2$ a point above free solution concentrations of 2000 ppm, well on the plateau of the isotherm.

The influence of pH on the plateau coverage requires a second more general explanation that stronger binding occurs at pH 6, with a greater segmental adsorption energy or a greater number of segment−surface contacts per chain. This second explanation is consistent with the conclusions from our previous investigation:[21] It was revealed that, while single oligomers adsorbed on individual surface charges at pH 6, additional adsorption-induced silanol dissociation (on the order of 3−4 per oligomer) led to a minimum of 4−5 acid−base contacts per oligomer. In contrast, at pH 8, the DMAEMA is less densely charged, and the surface contains more intrinsic underlying charge. Our previous investigation found no additional adsorption-induced silanol ionization at pH 8, leaving approximately 2−3 acid−base interactions per oligomer.

While the coverages in Figure 1 suggest a more extended configuration of the adsorbed polymers compared with the oligomer, solvent relaxation data in Figure 2 quantify this effect. The data in Figure 2 correspond to points on two of the isotherms in Figure 1. The specific solvent relaxation rate, R_{sp}, is proportional to the adsorbed train mass, with the exception that below 0.15 mg/m^2 R_{sp} is insensitive to adsorption.[22] For higher coverages at pD 6, R_{sp} and hence the train mass vary linearly with the adsorbed amount. This suggests that the train fraction and, most likely, the adsorbed configuration are insensitive to coverage. Since R_{sp} is proportional to the adsorbed train mass, the slopes of the R_{sp} lines are roughly proportional to the train fraction. The steeper slope for the oligomer compared with the polymer suggests a higher train fraction for the former, consistent with expectations that the oligomer is less capable of forming loops and tails than the polymer. The observation of loops and tails in the polymer layer then explains the slightly higher coverages found for the polymer in Figure 1.

The insensitivity of R_{sp} to coverage in the low coverage limit was found for all adsorption runs and, as previously discussed,[22] does not imply a lack of train at low coverages. Indeed, in the low coverage limit, there is

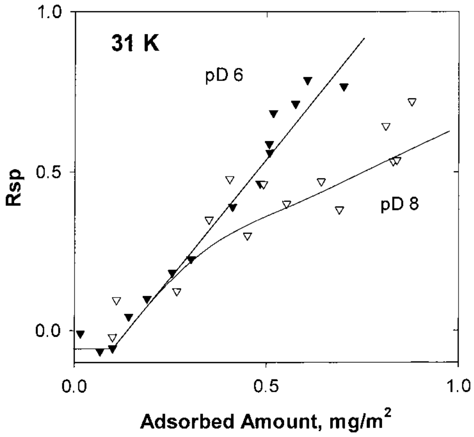

Figure 3. Influence of pD on the specific solvent relaxation rate for the 31K polymeric DMAEMA. The pD values are nominal, corresponding to the dilute end of the isotherm, similar to Figure 1.

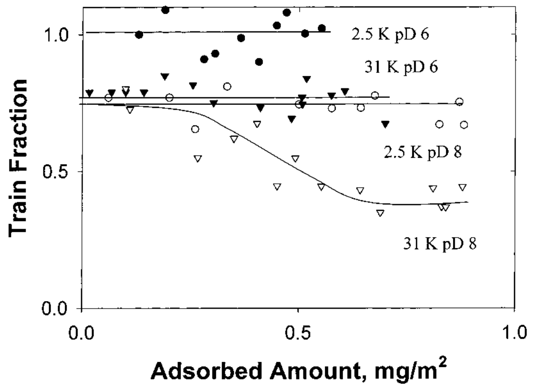

Figure 4. Train fraction as a function of coverage, corresponding to isotherm data in Figure 1.

the opportunity for the greatest amount of trains. Without at least some trains, no adsorption can take place. Above 0.15 mg/m^2, R_{sp} varies smoothly with coverage, motivating the assumption that the train mass varies continuously with a similar coverage dependence above and below 0.15 mg/m^2.

Figure 3 shows the influence of pH on R_{sp} for the polymer, with data points again corresponding to those on the isotherms in Figure 1. Compared with the configurations at pD 6, the polymer at pH 8 contains more loops and/or tails, except at the lowest coverages where the two are similar. At pD 6, the data are linear in R_{sp} above a coverage of 0.15 mg/m^2, indicating that polymer conformation, or at least the bound fraction, is insensitive to coverage. At pH 8, however, the data gradually turn over, indicating a decrease in the train fraction, or an increase in the amount of loops and tails, with increasing coverage.

Figure 4 summarizes the train fraction as a function of coverage for the oligomer and polymer at 2 different pH's, where adsorption was substantial. In generating Figure 4, it was assumed that the conditions giving the greatest slope in the R_{sp} vs coverage plots (which happened to occur for the oligomer at pD 6) corresponded to a train fraction of unity. A similar assumption was made for the low coverage limit for PEO adsorption on silica by the Cosgrove lab.[7] In the current study, not only was the train fraction the greatest for the oligomer at pD 6, it also was coverage independent, as indicated by the constant slope in Figure 2. The train fraction at coverages below 0.15 mg/m^2 was presumed to be the same as that at higher coverages, as previously discussed.

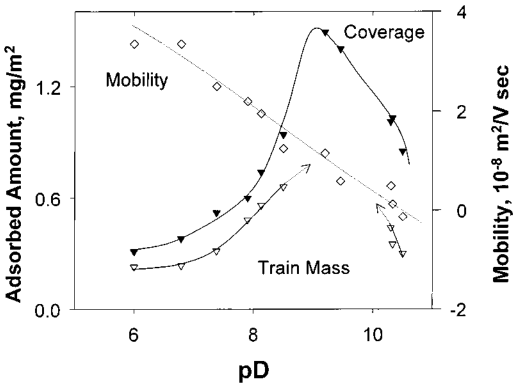

Figure 5. Coverage, train mass, and mobility near the isotherm plateau for 31K polymeric DMAEMA on 12 nm Ludox particles in 0.012−0.18 M ionic strength buffer. The pD's are the actual values, as opposed to the nominal ones reported in Figures 1−4.

In Figure 4, adsorption of the oligomer at pD 8 and adsorption of the polymer at pD 6 had rather large train fractions, with the bound fraction independent of coverage, in the range 0.75−0.8. At pD 8, however, the polymer's train fraction was coverage-dependent, starting with a train fraction near 0.75 at low coverages and decreasing to 0.4 at saturation. This suggests that for the polymer at pD 8 the amounts of loops and tails increase with coverage, similar to observations for nonionic homopolymer adsorption.[7] Conditions where the train fraction or conformation is coverage independent are likely to be those where adsorbed chains are noninteracting, for instance, chains adsorbed on a sparsely charged surface, discussed below. When the conformation depends on coverage, it suggests that adsorbed chains interact, which appears to be the case for the polymer at a pD of 8.

Figure 5 more closely examines the influence of pD on the polymer's coverage and interfacial configuration, for conditions corresponding roughly to the isotherm plateau. Mobility data are also included. (Data in Figure 5 correspond to a total polymer concentration of 4000 ppm which, after adsorption onto 4.6 m^2 of silica, gave remaining free solution concentrations of 3000−3600, depending on the plateau coverages for particular adsorption conditions.) The data for train mass are discontinuous near pD's of 9 and 10, because colloidal instability confounded determination of R_{sp} and, hence, train mass.

While a quantitative interpretation of the mobility data in Figure 5 are confounded by the small particle size relative to that of the polymer coil, the electrokinetic data still reveal an important fact about polymer adsorption on the isotherm plateau: Over the full range of pD's measured, polymer adsorption completely reverses the underlying surface charge, with the greatest reversal seen for the lowest pD's. This trend was also observed and interpreted more quantitatively for DMAEMA oligomer adsorbing onto large silica particles,[21] where the analysis was more straightforward. The prior results revealed a decreasing density of oligomeric DMAEMA−surface contacts as the pH was increased toward 8 or 9, a feature which is also likely to be present in the polymeric system. It is therefore worth noting that the polymer coverage and train mass exhibit maxima near pD 9, where the silica has a relatively

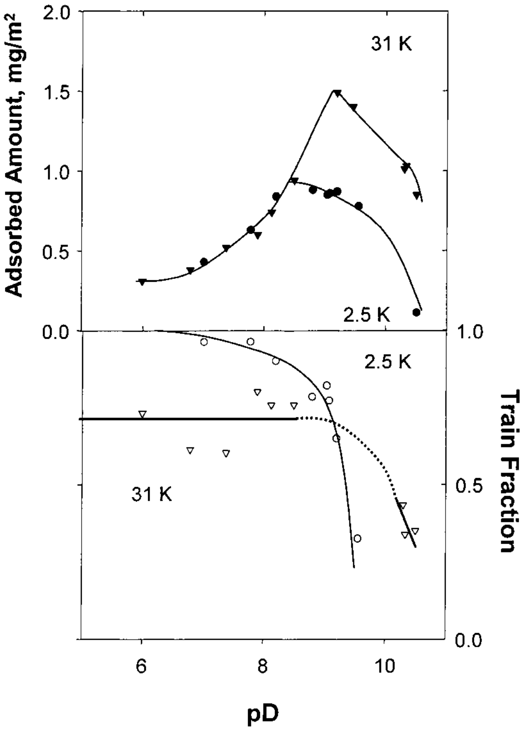

Figure 6. pD dependence of the coverage and train fraction for polymeric and oligomeric DMAEMA on the isotherm plateau on 12 nm Ludox particles.

large charge density and the DMAEMA is sparsely charged.

At the highest pH's in Figure 5, the train mass drops off more rapidly than does the total adsorbed amount, indicating that without charge the polymer loses its ability to anchor to the surface. Just before adsorption diminishes altogether, the layer contains many loops and tails. This interpretation is consistent with our previous reports of reduced electrostatic or acid–base interactions at higher pH.[21]

It is interesting to note in Figure 5 that the maximum observable train mass, occurring near pH 9 for the polymer, is about 0.7 mg/m^2. The value of 0.7 mg/m^2 slightly exceeds the oligomeric train mass on the isotherm plateau at pH 6, 0.6 mg/m^2 where the adsorbed layer was all trains. Our prior studies have shown that at pH 6 on the plateau of the isotherm the coverage was limited by sparse surface charge, and the tightly bound oligomers did not interact laterally on the surface. Therefore, a mass greater than 0.6 mg/m^2 must occur in the current study when the surface fills with trains. At pH's above 6 in the previous work, the condition of isolated chains broke down, and a situation was observed where lateral interactions among adsorbing chains limited the coverage. Therefore, the observation in Figure 5 of the maximum train amount (corresponding to the condition where the surface is filled with trains) of ~0.7 mg/m^2 is consistent with an oligomer mass of 0.6 mg/m^2 (with a train fraction of unity) just before the turnover from charge-limiting to surface-crowding regimes. For DMAEMA on silica, a monomer layer of DMAEMA corresponds to a mass near 0.7 mg/m^2.

The influence of pH on polymer configuration is made clearer in Figure 6, which compares the polymer and oligomer adsorbed mass and train fractions. In the limit of high pH, the oligomer's coverage approaches zero more quickly than does the polymer's, because the shorter oligomeric chains are limited in the lengths of loops and tails that can be formed. This is confirmed in the lower part of Figure 6 where the oligomer's train fraction drops more rapidly than that of the polymer as the pH is increased. These observations make sense if one recalls that only charged chains adsorb. When an adsorbing polymer bears a single charge, adsorption of one chain brings 31 300 molecular weight units to the interface, most of which forms two tails. When an oligomer bearing a single charge adsorbs, it brings 2300 molecular weight units to the surface, which contribute to two short tails. Qualitatively similar behavior was observed for the same polymer adsorbing on TiO_2,[28] indicating the dominance of polymer charge density over surface charge density on the adsorption behavior in this limit.

Discussion and Summary

This investigation demonstrated that DMAEMA oligomers and polymers adsorbing on negatively charged silica tend to adsorb in flat configurations at moderate pH's, where the polymer chain carries significant charge. At higher pH's, the polymer's charge is decreased. Though the silica is more densely charged under these conditions, the DMAEMA configuration is more extended, with fewer trains and more loops and tails. For the oligomer adsorbing at high pH, the configuration is relatively insensitive to coverage, while for the polymer, coverage influences the train amount at high pH.

Near pH 6 where the substrate charge density is low, both polymer and oligomer have large train fractions. In a previous study it was shown that, at pH 6, one oligomer adsorbed to each underlying surface charge, with each chain sufficiently far from its neighbors to effectively be isolated, even on the isotherm plateau. This is consistent with the current observations of a coverage-independent train fraction. Further, in the adsorbed state at pH 6, oligomer binding was found to be enhanced by secondary acid–base interactions, which formed as a result of localized silica deprotonation.

For polymer adsorption at pH 6, each coil is large enough to contact several surface charges, so that on the isotherm plateau polymer coils are not necessarily isolated. We suspect, however, that additional acid–base interactions occur for polymer adsorption roughly to the same extent that they have been shown to occur for oligomer adsorption. Hence, the observation of large train fractions for the adsorbing polymer at pH 6, in Figure 4, is consistent with expectations. The somewhat smaller train fraction for the polymer relative to that of the oligomer results from the polymer's capacity to form loops and tails, which increase its configurational entropy.

In the case of the oligomer at pH 6, it was observed that surface charge limited the ultimate coverage, with one oligomer adhering to each underlying surface charge on the plateau of the isotherm. The oligomers were too small to reach more than one surface site each, putting a cap on the observed coverage and giving rise to an interface with a patchy charge distribution. Since each polymer chain can access several surface charges at pH 6, different physics must be involved in determining that polymer's plateau coverage in the current study. It is therefore noted that the isotherm plateau for the polymer increases slightly with concentration at high concentrations while for the oligomer it is more nearly flat. At the highest coverages for the polymer at pH 6, interchain repulsion or surface filling must ultimately cap the coverage.

At pH 8, the silica contains a relatively large density of negative surface sites, while the DMAEMA is slightly charged. Our previous investigation revealed that under these conditions adsorbed oligomers had relatively few (2−3) contact points, compared with pH 6, explaining the lower train fraction in the current study. In the limit of high pH, the DMAEMA charge vanishes, and adsorption no longer occurs. As this limit is approached from the side of lower pH, the adsorbed polymer layers contain substantial amounts of loops and tails.

Prior studies focusing on the adsorption of nonionic polymers such as PEO indicated that polymers adhered to the surface in a relatively flat conformation until the point where the surface was nearly saturated with trains. At higher coverages, loops and tails were found in adsorbed layers, and the train mass did not increase further with coverage. For these nonionics, after the surface saturated with trains, the interfacial mass increased substantially but only through the formation of loops and tails. Further, the coverage at which the surface filled with trains (and after which loops and tails began to form) could be relatively small, on the order of 0.25 mg/m^2, but as large as 0.55 mg/m^2.

While the qualitative picture is similar for charge-driven adsorption, the quantitative details with DMAEMA are strikingly different. High train fractions are found, and there is little effect of coverage on the formation of loops and tails, for most situations. Indeed, for DMAMEA, the surface capacity for trains alone was about 0.7 mg/m^2, substantially more than the reported surface capacity for PEO trains, 0.25 mg/m^2. Yet, if one considers the dimensions of adsorbed DMAEMA segments, with an oligomer able to occupy 1−2 nm,[2,21] train coverages of 0.7 mg/m^2 are quite plausible. The fundamental difference between DMAEMA and PEO adsorption on silica must then stem from the stronger interactions between charged segments and the surface ($\sim$4 kT)[29] for the former, compared with $\sim$1 kT for each silica−PEO contact. Further, substrate ionization can occur to accommodate a large number of such contacts for DMAEMA.

In the limit of high pH where the polymer charge is sparse, DMAEMA adsorption is more quantitatively consistent with the behavior previously observed for nonionics. Here, once the DMAEMA coverage reaches 0.2−0.3 mg/m^2, the train fraction begins to decrease as the coverage further increases and loops and tails are generated.

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(29) The approximate value of 4 kT adsorption energy for each charged segment was estimated from integration of a Debye−Huckel force profile to determine the work to bring a positive charge to a negatively charged surface, where it finally resides in a region of −100 mV. Variations in the final position of the positive charge will affect this value.

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