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Adsorption of Ionizable Polymers on Ionic Surfaces: Poly(acrylic acid)

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Received August 20, 1982

ABSTRACT: The adsorption behavior of ionized poly(acrylic acid) on tribasic calcium phosphate surfaces from aqueous solutions has been studied by Fourier transform infrared spectroscopy. Measurements included the amount adsorbed, a parameter proportional to fraction of surface-bound repeating units, and the extent of water-induced desorption. Results indicate that the cationic nature of the adsorbing surface is the main driving force for the intense and largely irreversible adsorption of the anionic polyelectrolyte. Another important factor in the adsorption behavior is the collective drag of macromolecules toward the surface through segmental interactions in solution. Collective surface migration of chains is most prominent in solutions of high concentration or molecular weight. Such adsorbates are partly desorbable and contain low fractions of surface-bound repeating units. The intensity of collective drag decreases significantly in concentrated solutions with ionization of side groups and screening of the surface potential by addition of monovalent ions to the solvating medium.

Introduction

The adsorption of polymer molecules on surfaces has been a phenomenon of scientific and technological interest over the past few decades. The problem has been analyzed experimentally with different techniques for various substrate/adsorbate systems. An extensive review of experimental work has been organized by Lipatov and Sergeeva. Several authors have made important contributions in the theoretical treatment of the problem but primarily for the case of adsorption from dilute solutions.[2–14] The issues of scientific concern include (1) the amount of macromolecular material that is isothermally adsorbed by substrates from melts or solutions, (2) the intensity of substrate/adsorbate interaction and its relation to adsorption stability, (3) the conformational transitions undergone by chains in the adsorbed layer and their effect on molecular motion, and (4) the substrate properties and macromolecular variables that control all of the above features of adsorption. The adhesion of organic macromolecules to metals, ceramics, and biological tissues and the control of interface-related properties in composite materials are two examples where adsorption phenomena become technologically relevant.

The classical hypothesis of polymer adsorption from solution on impenetrable surfaces envisions the process as one involving conformational distortion of molecular coils. This distortion is caused by interactions between repeating units and surface sites and is accompanied by a loss of entropy in the polymeric coil. An example is the elongation and lateral contraction of a Gaussian chain as it spreads to interact with the substrate's active sites. There is a great deal of discussion in the literature concerning the nature of the adsorbed film based on experiments that measure its thickness and weight. One concept proposed is that of multilayer adsorption, in which chains do not necessarily change their shape. A similar idea is the adsorption of macromolecular aggregates rather than single molecules.[16,17] Others have envisioned the formation of attached segments and unadsorbed loops[18] explaining why the thickness of the adsorbed layer exceeds that of a monolayer of flatly attached chains. Conformational distortion into a rather elongated state has been supported by experimental measurements[19] of the fraction of functional groups attached to the surface (e.g., more than 30%). The effect of solution variables (solvent, temperature, and molecular weight) and nature of the substrate on amount adsorbed has also been investigated (e.g., see ref 20–27). Even though there are exceptions, adsorption usually increases with molecular weight, and it is inversely proportional to solution intrinsic viscosity (it decreases with solvent power). Generally speaking, experimental work on adsorption has been more common in nonionic polymers. Earlier experimental work on polyelectrolyte adsorption has been reviewed by Fontana.[28] For adsorption of ionic polymers,

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0024-9297/83/2216-1143$01.50/0

factors such as degree of ionization, the substrate's charge density, and ionic strength of the solvent have been identified as important variables. For example, adsorption has been observed to decrease with degree of ionization[29,30] and to increase sometimes with ionic strength of the solvent. The observed trends and interpretations have varied. However, a common view has been that the effect of degree of ionization and ionic strength on polymer coil dimensions is the primary factor controlling adsorption.

Theoretical treatments of polymer adsorption have covered both nonionic and ionic macromolecules. Generally speaking, a high-affinity type of isotherm has been predicted for adsorption from dilute solutions. That is, adsorption rises sharply and then levels off beyond a certain concentration. In Silberberg's work[5] the adsorbed layer consists of consecutive segment "trains" attached to the surface separated by "loops" of segments dangling in solution. The free energy change associated with the loop-to-train transition was calculated, and the system's overall change in internal energy identified as a controlling factor. Hoeve, Dimarzio, and Peyser[9] considered chain flexibility as a parameter in the equations describing partition functions. The results indicated that the ability to form a considerable number of loops depends directly upon molecular flexibility and that the size and number of loops are directly related to the free energy of adsorption. Hoeve derived an isotherm that does not reach a limiting value of adsorption; its slope decreases with concentration but remains positive. This treatment takes into account the effects of solvent power by evaluating the free energy change associated with coil expansion and interacting loops. Hesselink[31,32] combined Hoeve's considerations with the effects of electrostatic interactions in order to predict isotherms for polyelectrolyte adsorption. As in previous treatments, several free energy changes associated with the adsorption process are considered: ΔF_1, the conformational free energy change for a random coil in solution adsorbing into a series of trains and loops; ΔF_2, the free energy change associated with interactions of adsorbed segments with the surface and solvent; and ΔF_3, a term describing the interaction of loops. In addition to these three terms, Hesselink considered the electrical free energy change of a double layer formed upon adsorption of charged segments on a charged surface, ΔF_4, and the adsorption energy of uncharged segments on a charged surface, ΔF_5. The total free energy change upon adsorption is therefore given by

$$\Delta F = \sum_{i=1}^{5} \Delta F_i \tag{1}$$

Some of the predictions of this theory will be discussed in the context of experimental data.

Our experimental work has been carried out with a molecularly versatile polymer and over a reasonably wide concentration range. The macromolecule used was poly(acrylic acid) (PAA) in moderately concentrated aqueous solutions, adsorbing on surfaces of the ionic solid tribasic calcium phosphate. PAA, a water-soluble polymer, is essentially nonionic in neutral solutions but is easily converted to a polyelectrolyte through base-induced ionization of its carboxyl side groups to carboxylate anions. It is well-known that ionization of polymers leads to distention of the macromolecular coil as a consequence of Coulombic repulsions among repeating units bearing electrical charge. Addition of electrolytes to the solvating medium, on the other hand, can screen ionic repulsion and thus lead to coil contraction. Ionization of side groups can also transform the macromolecule into a rigid-rod chain due to interactions with counterions. The work of Oosawa[33] is a good review on the behavior of polyelectrolytes in solution. Selection of an aqueous PAA system in our study has thus allowed us to manipulate conformations and flexibility in adsorbing chains. In addition to a quantitative analysis of adsorption as a function of concentration and molecular weight, an aspect of special interest in our study has been the hydrolytic stability of adsorbed layers. The analytical technique used has been Fourier transform infrared spectroscopy (FT IR) coupled with attenuated total reflection (ATR). As explained below, the use of these spectroscopic tools was important given the aqueous nature of our experimental system.

Experimental Section

Sample Preparation. Poly(acrylic acids) with viscosity-average molecular weights of ~250 000 and ~50 000 were obtained from Polysciences Inc. These polymers were purified by solvation in *p*-dioxane followed by precipitation with benzene. Precipitated polymers were vacuum-dried and then redissolved in *p*-dioxane in order to carry out a coarse fractionation of molecular weight by precipitation with *n*-heptane. The first 20 wt % fraction precipitated was discarded (high molecular weight material), and the last 20 wt % fraction left in solution (low molecular weight material). The precipitated middle fraction of 60 wt % contained the material used for adsorption experiments. The experimental fraction was vacuum-dried, washed several times with double-distilled water, and stored as a concentrated stock solution.

Aqueous solutions of 0.85 mol of monomer/L (0.61 mg/mL), 0.62 mol/L (0.45 mg/mL), 0.40 mol/L (0.29 mg/mL), and 0.28 mol/L (0.20 mg/mL) were prepared from the stock solution. Sample solutions of each concentration were neutralized by addition of different amounts of NaOH in order to produce various degrees of polyacid ionization. Alkali additions were 0.2, 0.4, or 0.6 mol of NaOH per mole of monomer (C(a) = 0.2, 0.4, or 0.6). NaCl was used as a screening electrolyte in partly neutralized PAA and added in amounts of 0.1 or 0.5 mol per mole of NaOH used for neutralization (C(s) = 0.1 or 0.5).

Adsorption Experiments. The adsorbent used was tribasic calcium phospahte (TCP) from Fisher Scientific. The stoichiometry of this ionic solid is approximately $Ca_{10}(OH)_2(PO_4)_6$. Adsorption was induced by exposure of 5-mL solution samples to 0.175 g of the adsorbent for 8 h. These exposures were carried out in ground glass sealed vessels while the slurry was stirred. The 8-h period was found to be sufficient to reach adsorption equilibrium. Three specimens were used for data collection from each adsorption experiment: (1) the PAA solution prior to TCP exposure, (2) solution/TCP slurries after the adsorption period, and (3) the supernatant liquid left in centrifuged slurries after the adsorption period. TCP powders collected after centrifugation were washed with distilled water and vacuum-dried. Dried material (0.05 g) was exposed to 25 mL of double-distilled water for 24 h without agitation and then recovered by filtration. The purpose of pure water exposure was to induce PAA desorption.

Spectroscopic Data Collection. Liquid and powder samples were analyzed with a Nicolet 7199 FT IR spectrophotometer. Analysis of liquids involved reflectance measurements using a 4× beam condenser with an internal reflection attachment. This attachment was equipped with a liquid microsampling cell and a germanium, 45° internal reflection element of dimensions 10 × 5 × 1 mm (all reflection attachments were manufactured by Harrick Scientific). In all cases, the intense water absorbance centered about 1653 cm^{-1} was digitally subtracted from spectra. The results of this compensation are illustrated in Figure 1a–c for a sample solution. Powder samples were examined in transmission using KBr pellets. Typical spectra obtained for water-exposed and unexposed powders are shown in Figure 1d,e. The wavenumber location and assignments for bands of interest have been summarized in Table I.

Results and Discussion

Data Analysis and General Observations. Infrared absorbance measurements on original solutions and supernatant liquid after substrate centrifugation were used

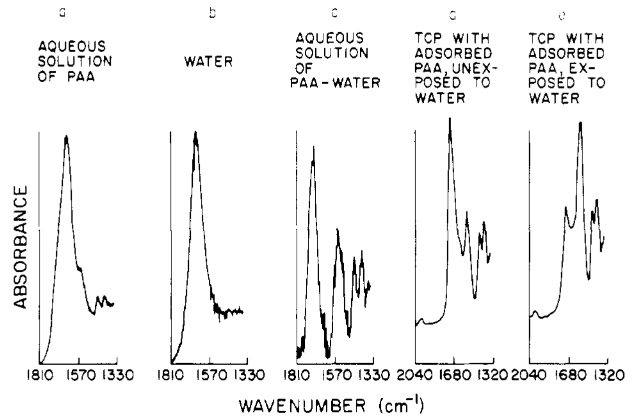

Figure 1. (a–c) FT IR spectra showing the result of digital subtraction of water absorbance from that of poly(acrylic acid) aqueous solutions. After subtraction, the polymer's ν(C=O), $\nu_{asym}(COO^-)$, and $\delta(CH_2)$ peaks are clearly revealed. The spectrum of irreversibly adsorbed polymer (e) contains a higher concentration of ionized side groups (COO–, 1560 cm^{-1}) relative to (d) (the spectrum of the adsorbate before exposure to water).

Table I
Infrared Bands Used in Experimental Measurements

wavenumber, cm^{-1}	assignment
2925	$\nu(CH_2)$
1710	ν(C=O)
1560	$\nu_{asym}(COO^-)$
1450	$\delta(CH_2)$
700-500	ν(P-Ca)

to calculate the parameter Γ, which measures the amount of adsorbed PAA. Using Beer's law, we write this parameter as

$$\Gamma = (A_s - A_l)/B_0\epsilon_{\delta(CH_2)}L \tag{2}$$

where the A values are digitally integrated absorbances due to the $CH_2(\delta)$ (bending) mode in PAA's repeating unit. A_s denotes absorbance in the original polymer solution and A_l corresponds to absorbance in the supernatant liquid. The constant B_0 is number of grams of adsorbent (substrate) per milliliter of polymer solution, and $\epsilon_{\delta(CH_2)}$ and L represent the infrared band's extinction coefficient and the beam's path length, respectively. The constant $\epsilon_{\delta(CH_2)}L$ was calculated from an experimental plot of A_s for the $\delta(CH_2)$ mode vs. polymer concentration. Since we used ATR as opposed to transmission, L should be fixed as it is determined by optical constants and the quality of reflecting crystal/liquid contact. For liquid samples, it should be appropriate to assume, as we have, that the extent of this contact is reproducible in the various measurements. Thus, Γ has units of grams of polymer adsorbed per gram of adsorbent, and polymer that is not adsorbed by the substrate is experimentally defined as material remaining in the supernatant liquid after centrifugation of the slurry.

The amount of polymer desorbed into water from TCP powders, Γ', was calculated from the expression

$$\Gamma' = \Gamma - A_{p_2}/b\epsilon \tag{3}$$

The parameter $A_{p_2}/b\epsilon$ measures the amount of polymer per gram of substrate that remained adsorbed after exposure to pure water. A_{p_2} is the ratio of integrated absorbances corresponding to the $\nu(CH_2)$ (stretching) mode in PAA and the ν(P–Ca) mode in TCP for substrate with adsorbed polymer after water exposure, b is the thickness of the KBr pellet, and ϵ is an effective extinction coefficient necessary to obtain a value of grams of polymer per gram of substrate. ϵ was calculated from spectroscopic measurements on KBr pellets of thickness b' containing the TCP powder with adsorbed polymer before exposure to water (subscript 1)

$$\epsilon = A_{p_1}/b'\Gamma \tag{4}$$

$$A_{p_1} = (A_{\nu(CH_2)})_1/(A_{\nu(Ca-P)})_1 \tag{5}$$

The amount of polymer desorbed was also calculated as a weight fraction desorbed, D, given by

$$D = (A_p/b' - A_{p_2}/b)/(A_{p_1}/b') \tag{6}$$

The use of Beer's law in calculations of Γ' is justified on the basis that linear plots of absorbance vs. concentration were obtained for the $\nu(CH_2)$ mode in PAA solutions using the ATR technique. Degree of ionization in PAA, α, was measured through integrated absorbances corresponding to carbonyl group stretching in COOH groups (A_{1710}) and asymmetric carboxylate ion stretching (A_{1560}). The parameter α is given by

$$\alpha = \frac{A_{1560}(\lambda_{1560}/\lambda_{1710})}{A_{1560}(\lambda_{1560}/\lambda_{1710}) + A_{1710}} \tag{7}$$

where the λ's are correction factors that account for the fact that beam penetration in internal reflection is a function of the radiation's wavelength.[34]

A parameter of great interest in polymer adsorption is the fraction of repeating units within an adsorbed layer that are "bound" through some interaction with sites on the adsorbent's surface. Experimentally, it is difficult to obtain an absolute measurement of this fraction unless this interaction is highly specific and produces a spectroscopic fingerprint. In our experimental system, one may postulate at least two types of interactions that could directly bind or decrease the thermal motions of repeating units near the adsorbing surface. One is hydrogen bonding of COOH groups; another could involve Coulombic attraction between ionized side groups (carboxylate groups) and cationic sites on the TCP surface such as calcium ions. This last possibility would result in a strong, long-range interaction of polymer segments with the surface. Using spectroscopic data, we calculated the parameter p', which in our opinion quantifies the trend in fraction of surface-bound repeating units through ionic interactions. The parameter p' is given by

$$p' = \frac{C_b}{C_t} \approx \frac{XA_sy}{C_t} \tag{8}$$

where C_b is the concentration of bound repeating units, C_t is the concentration of adsorbed repeating units, A_s is the integrated absorbance of carboxylate ion stretching in the supernatant liquid, and y is a factor that normalizes the largest p' values to unity. X is given by

$$X = \frac{C_{pls}\alpha_{pls}L_{lps}}{C_s\alpha_sL_s} \tag{9}$$

where the subscripts pls and s refer to the powder–liquid slurry and supernatant liquid, respectively. All C's are measured from the appropriate $\delta(CH_2)$ peaks, and the form of the p' expression (eq 8) can be justified as follows. The absorbance due to asymmetric carboxylate stretching in the supernatant liquid and in the powder–liquid slurry can be written as

$$A_s = C_f\epsilon_fL_s \tag{10}$$

$$A_{pls} = (C_f\epsilon_f + C_{af}\epsilon_{af} + C_b\epsilon_b)L_{pls} \tag{11}$$

where C_f is the concentration of free carboxylate side

Table II
Increase in Poly(acrylic acid) Degree of Ionization upon Addition of the Adsorbing Substrate Tribasic Calcium Phosphate

soln concn, mol/L	mol of NaOH/ mol of COO^-	α_0[a]	α'[b]	$\Delta\alpha$[c]
0.85	0.0	0.0	0.17	0.17
0.85	0.2	0.16	0.26	0.10
0.85	0.4	0.47	0.50	0.03
0.62	0.0	0.0	0.19	0.19
0.62	0.2	0.27	0.46	0.19
0.62	0.4	0.53	0.67	0.14
0.62	0.6	0.75	0.81	0.06
0.40	0.0	0.0	0.21	0.21
0.40	0.2	0.31	0.53	0.22
0.40	0.4	0.53	0.56	0.03
0.40	0.6	0.72	0.80	0.08
0.28	0.0	0.0	0.27	0.27
0.28	0.2	0.23	0.41	0.18
0.28	0.4	0.41	0.56	0.15
0.28	0.6	0.61	0.71	0.10

[a] Degree of ionization in original solution. [b] Degree of ionization after substrate addition. [c] $\alpha' - \alpha_0$.

groups, C_{af} refers to free carboxylate groups that are part of the adsorbed layer, and C_b corresponds to substrate-bound carboxylates. ϵ's and L's represent the respective extinction coefficients and path lengths. If one assumes that all extinction coefficients are similar in magnitude, then one can write

$$XA_s = A_{pls} \tag{12}$$

$$C_t\alpha' = C_{af} + C_b \tag{13}$$

$$C\alpha'' = C_f + C_t\alpha \tag{14}$$

where C and α'' are the repeating-unit concentration and degree of ionization in the original solution, respectively, and α' is the degree of ionization in the adsorbed layer. Substituting eq 10, 11, 13 and 14 into eq 12, one obtains the expression

$$C_b = \frac{XA_s - (C\alpha'')\epsilon_f L_{pls}}{L_{pls}(\epsilon_b - \epsilon_f)} \tag{15}$$

Equation 15 justifies the use of (8) as an indication of trends in the extent of the adsorbate's interaction with the surface. XA_s is equal to the carboxylate ion absorbance of the powder–liquid slurry (A_{pls}). Therefore, increasing values of p' partly reflect the existence of greater concentrations of carboxylate side groups in adsorbed macromolecules relative to those that remained in the supernatant liquid. There are at least two different interpretations for increasing values of p', that is, for increasing concentration of ionic side groups in the adsorbed layer. One is that electrostatic attraction between the surface and polymeric segments fractionates the solution with preferential adsorption of the most highly ionized chains. Another interpretation is that acidic carboxyl groups near the surface are ionized by basic ions of the substrate, thus creating ion-pair interactions at the interface. In either case, high measured values of p' should provide an index of ionic interaction between the substrate and repeating units in the adsorbate. A final comment on p' is the fact that it does not account for repeating units bound to the substrate by nonionic interactions such as hydrogen bonding.

Two general observations from our spectroscopic data are important in the interpretation of results. First of all, we found that TCP induces ionization of COOH groups in PAA. This effect is revealed by data presented in Table II. The additional ionization measured in supernatant liquids relative to original solutions could result from extraction of basic ions from the TCP lattice (e.g., OH^- and PO_4^{-3}) upon contact with the acidic solution. As expected from this argument, increasing pH in original solutions due to PAA preneutralization reduces the extent of TCP-induced ionization ($\Delta\alpha$ values in Table II). This suggests lower solubility of the adsorbent in media of greater basicity. The role of substrate solvation in adsorption is discussed in a subsequent section. Secondly, the measured values of Γ are fairly high compared to those for nonionic polymers on common substrates such as glass, carbon, alumina, and silica. Γ values tend to be below 0.15 g/g and often are a few milligrams per gram. The range 0.10–2.2 g/g for PAA on TCP implies a high adsorption affinity in our experimental system.

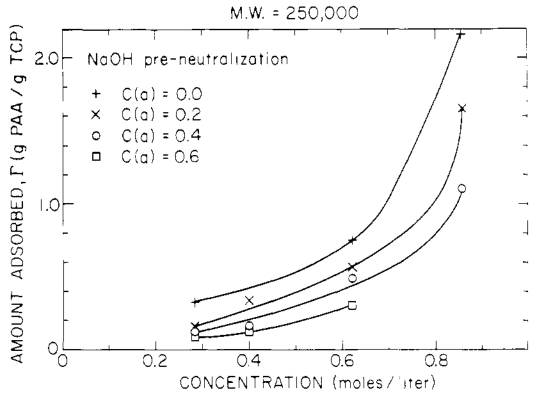

Figure 2. Amount of poly(acrylic acid) adsorbed from solution per gram of tribasic calcium phosphate as a function of concentration. Each curve corresponds to a different degree of preneutralization of the polyacid with NaOH.

Adsorption: Effect of Concentration and Molecular Weight. Adsorption isotherms plotted from Γ measurements are shown in Figure 2. This family of curves points out a strong sensitivity of adsorption to solution concentration beyond a certain value. The curves show a rather steep rise in Γ as solution concentration is raised between 0.62 and 0.85 mol/L. This behavior is different from the high-affinity isotherms predicted by most theoretical treatments for dilute solutions. These theories predict isotherms in which Γ rises sharply with concentration and then levels off.[5] This is similar to a classical Langmuir isotherm in which there is progressive occupation of surface sites by individual molecules until saturation is achieved. Such a model does not describe the behavior observed in the concentration range studied. Instead, adsorption appears to involve collective motion of molecules toward the adsorbent's surface. As solution concentration is raised, the topology of interaction among chain segments must drag rapidly increasing amounts of material toward the adsorbing surface. The familiar chain entanglements are interactions that would intuitively create collective motion of molecules in solution toward the substrate. However, other types of segment–segment interactions could also lead to molecular drag: for example, intermolecular secondary bonding or the existence of high-density segmental nodes throughout the macromolecular solutions. In the context of segment–segment interpenetration, collective drag should be enhanced by increasing molecular weights at a given solution concentration. This effect is revealed by experimental results plotted in Figure 3. Γ values for 0.85 mol/L solutions prepared from PAA of 250 000 average molecular weight are considerably higher than those for polymer of 50 000 molecular weight. The effects of

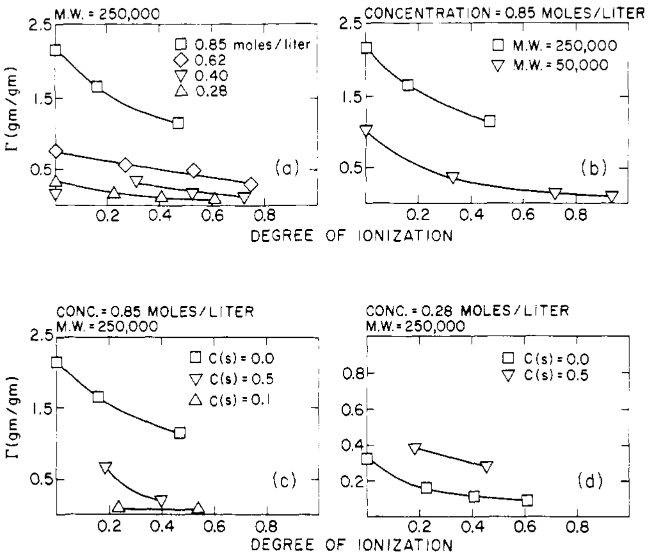

Figure 3. Plots of amount of poly(acrylic acid) adsorbed from solution per gram of substrate as a function of the polymer's degree of ionization (as measured spectroscopically): (a) effect of concentration; (b) effect of molecular weight; (c) effect of added electrolyte in the most concentrated solution; (d) effect of added electrolyte in the most dilute solution.

Table III
Viscosity of 0.85 mol/L PAA Solutions as a Function of Degree of Ionization (α) and Added NaCl (C(s))

viscosity, P	α	C(s)	viscosity, P	α	C(s)
9	0.00	0.0	83	0.54	0.1
34	0.16	0.0	23	0.19	0.5
78	0.47	0.0	44	0.40	0.5
34	0.24	0.1			

preneutralization and added electrolyte on adsorption were found to be sensitive to concentration, and this provides further insight on the role of collective drag.

Adsorption: Effect of PAA Ionization. Figure 3 summarizes results obtained for Γ with increasing α. In attempting to explain the observed decrease in Γ with increasing α, one must consider the conformational changes that are brought about by ionization of the polymeric coil. Ionization by NaOH leads to the coil's expansion due to electrostatic repulsion between negatively charged side groups. Experimentally, a good indication of the more extended and rigid conformations is the drastic rise in solution viscosity produced by preionization (Table III). The intramolecular repulsions that extend the chains may also act at the intermolecular level and reduce the extent of segment–segment bonding or interpenetration. Thus, one may interpret the deposition of less material on the substrate with increasing α as the result of less collective drag among the highly extended and rigid chains. This effect is more easily visualized assuming that, prior to ionization, secondary bonding is an important mode of segment–segment interaction. In this context, when ionization occurs, electrostatic repulsions disrupt secondary bonds and macromolecular drag in adsorption becomes less effective. An alternative explanation for less drag is that a high entanglement density among rigid and extended chains reduces molecular migration toward the adsorbing surface. A decrease in Γ with increasing degrees of ionization has been observed in other experiments[28,29] and explained in terms of the greater surface area occupied by extended chains. Hessenlink's theory[32] predicts the effect but suggests a different explanation. That is, highly charged segments find it difficult to adsorb on a surface containing a significant charge of the same sign due to the initial coverage of the substrate by preattached segments. On the basis of our results, we suggest that the effect of α on segment–segment interactions in solution is an important factor in adsorption. This is justified on the basis that the effect should be more pronounced in the most concentrated solutions and may therefore explain the observed decreasing sensitivity of Γ to α in solutions of concentrations below 0.85 mol/L.

Table IV
Spectroscopically Measured Degree of Ionization (α) as a Function of Added NaOH and NaCl

mol of NaOH/mol of COO$^-$	mol of NaCl/mol of COO$^-$	soln concn, mol/L	deg of ionization (α)
0.2	0.0	0.85	0.16
0.4	0.0	0.85	0.42
0.2	0.5	0.85	0.18
0.4	0.5	0.85	0.40
0.2	0.0	0.28	0.23
0.4	0.0	0.28	0.41
0.6	0.0	0.28	0.61
0.2	0.5	0.28	0.18
0.4	0.5	0.28	0.45
0.6	0.5	0.28	0.60

Adsorption: Effect of Added Electrolyte. Figure 3 shows the effect of added NaCl (C(s) = 0.5) on Γ values for the least concentrated solution. The observed increase in adsorption agrees with experimental results on another system.[29] Added NaCl affects the polyion's conformation since the mobile ions screen electrostatic repulsions acting on chain segments. The consequence is some contraction of the expanded polyion and thus a partial recovery of entropy. One may also view this effect as a decrease in solvent power of the aqueous medium. The concept has been treated in theoretical work reviewed by Eisenberg and King,[35] and it is experimentally revealed by a decrease in viscosity upon addition of salts to polyelectrolyte solutions (see Table III). The smaller radii of gyration in the presence of electrolyte may explain the enhanced Γ values for adsorption from dilute solution. That is, more macromolecules can occupy the available surface sites for adsorption. On the basis of previous arguments, we also expected enhanced adsorption of ionized PAA with added electrolyte from the most concentrated solution, the reason being that a screening salt should reverse the effect of chain ionization on collective drag. As discussed below, the effect of NaCl on surface potential can provide an explanation for the low Γ values measured for the most concentrated solution.

Interestingly, a small addition of electrolyte (C(s) = 0.1) to the most concentrated solution leads to a decrease in the amount of adsorbed polymer by nearly an order of magnitude. This observation is shown in Figure 6, and it is in contrast to the enhanced adsorption measured in the most dilute solution. As indicated by data in Table IV, the degrees of polymer ionization are not significantly changed by NaCl addition to explain the observed decrease in Γ. One possible origin of this effect is electrostatic screening of the cationic substrate by free Cl$^-$ ions. The chemisorption of these ions could decrease the attractive potential exerted by a positively charged surface on polyanions in solution. The concept has been illustrated in Figure 4. In this figure, chain segments are shown within cylindrical shells described by Katchalsky et al.[36,37] These shells represent the idea that counterions which are not fixed at a side group can be localized along the potential valley of the macroion (small cylinder) or be mobile in a free volume domain (large cylinder). Upon adsorption, the

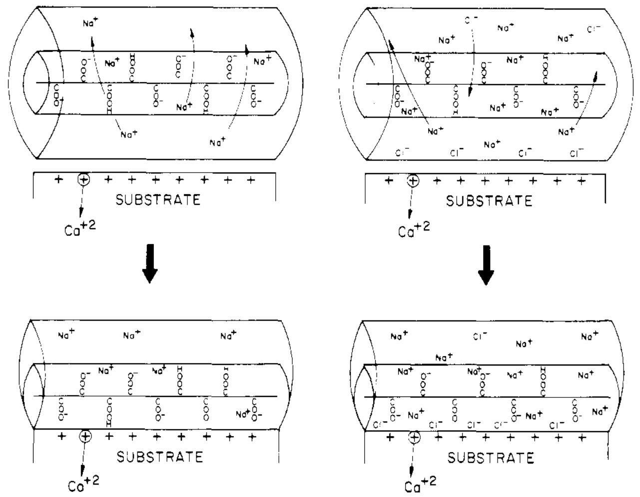

Figure 4. (a) Schematic representation of adsorption for a PAA macroion segment on the cationic surface of TCP (the Na^+ counterion distribution is distorted upon adsorption. (b) A similar representation showing electrostatic screening of the cationic substrate by Cl^- ions from added electrolyte.

spatial distribution of counterions is distorted, and interaction with the cationic surface reduces the electrical free energy of chain segments. If the solution is not dilute, the strong electrostatic force drags many chain segments by collective migration. On the other hand, if the surface is screened by added electrolyte, a strong, long-range electrostatic force no longer acts on chain segments. Under these conditions, segments near the surface could eventually displace Cl^- ions and become adsorbed. However, the collective drag effect does not take place due to the weak surface potential in the electrolyte-screened substrate. In the more dilute solution (0.28 mol/L), surface-site screening may not occur since the amount of NaCl required to achieve $C(s) = 0.1$ or 0.5 is much smaller than that for solutions of 0.85 mol/L concentration. Therefore, the relatively small number of mobile ions added are likely to interact with polyion segments and would not be available for surface screening. In the concentrated solution, the greater amounts of NaCl added can lead to electrostatic screening of the substrate.

One needs to postulate a physical reason for substrate screening by chloride ions. As pointed out earlier, our spectroscopic data indicate that PAA becomes neutralized upon contact of solutions with the pulverized substrate (Table II). This must result from solvation of basic ions (PO_4^{3-} and OH^-) from the substrate's surface due to contact with the acidic solution. If a charge equivalent of Ca^{2+} ions does not dissolve simultaneously, the implication is adsorption of the polyanion on a positively charged adsorbent surface (see Figure 5). We infer this to be the case since none of our solutions, even the most concentrated, exhibited any gelation. Gelation would indicate a significant release of Ca^{2+} from the substrate (we know from other work in our laboratories that PAA solutions can gel with small amounts of $Ca(OH)_2$). In a previous study[38] with a similar substrate (hydroxyapatite) actual measurements revealed the release of phosphate ions upon adsorption of organic polyphosphonates. Thus, in our solutions with added electrolyte, we would expect available Cl^- ions in solutions to rapidly form a Stern and diffuse double layer on the cationic surface. These layers then decrease the electrostatic driving force for adsorption of the anionic polymer. If solvation of substrate basic ions into the acidic polymer solution raises the surface potential for adsorption, this potential should decrease at higher pH (with incresing α). However, as α increases, the polymer's charge density increases as well, thus favoring adsorption. The combination of these two opposing effects could explain the general trend in all solutions for Γ values to level off with increasing α. In this context, it is also relevant to point out that the electrical potential of ionized segments can reach a limiting value beyond a critical amount of alkali addition.[33] That is, beyond a certain degree of ionization, additional counterions "condense" to form ion pairs with macroion segments. Once a limiting chain segment potential is reached, changes in adsorption driving force would only be controlled by the effect of α on surface potential. The moderate increase in Γ observed at $C(s) = 0.5$ is probably the result of conformational contraction induced by the added salt. A fivefold increase in the ratio of NaCl to COO^- equivalents would make conformational changes more significant. Polyelectrolytes are also known to precipitate or "salt out" from solutions of high ionic strength. Thus, the increased adsorption might be the consequence of collective drag or precipitation as segment–segment interactions are enhanced by higher ionic strength in the solvent.

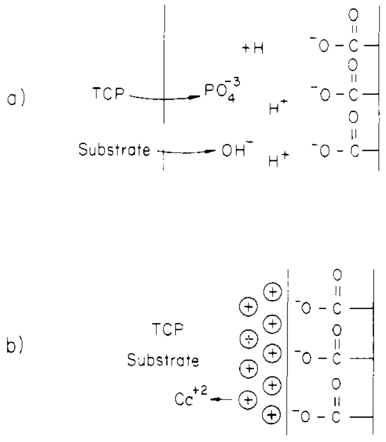

Figure 5. (a) Basic ions, OH^- and PO_4^{3-}, are preferentially dissolved from the TCP substrate upon contact with acidic solutions of PAA. (b) Basic ion extraction creates a positive space charge on TCP surfaces, which stabilizes adsorbed segments of the negatively charged macroion.

Our interpretation of results points out the importance of strong substrate potentials in the attraction of polymeric adsorbate even from concentrated solutions that can produce collective drag. Generally speaking, the postulated cationic nature of the TCP surface in acidic solutions may explain the high values of Γ measured in our experiments for the negatively charged polyelectrolyte. This is consistent with Hesselink's theory,[32] which predicts the adsorption of a negatively charged polymer to be significantly higher on cationic surfaces than on neutral or negative ones, especially if the nonionic adsorption energy per segment is small. In the context of Hesselink's theory, our observed decrease in adsorption with added screening electrolyte also suggests that charge interaction is the main driving force for adsorption. The isotherm predicted by the theory has the form

$$\frac{N_a}{A\delta} = \frac{N_f}{V} \exp\left[\nu \left\{ \epsilon + \ln (1 - \phi_0) + 2\chi\phi_0 - \frac{\tau\alpha\kappa\sigma}{2ne} - b\sigma(3\sigma - 2\sigma_0) \right\} \right] \quad (16)$$

where N_a is the number of adsorbed molecules, A is the surface area, δ is approximately the thickness of a segment, N_f is the number of molecules after adsorption in a solution of volume V, ν is the number of segments per polymer chain, and ϵ is the nonionic adsorption energy per segment.

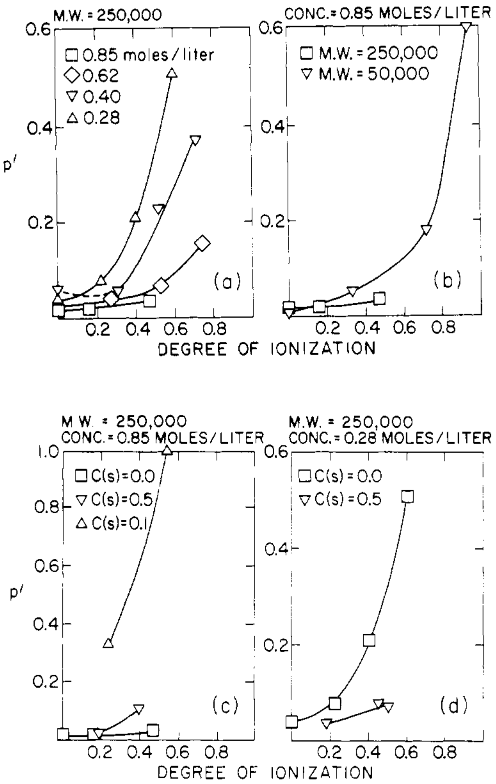

Figure 6. Plots of a parameter proportional to fraction of substrate-bound repeating units (p') as a function of degree of ionization in PAA (as measured spectroscopically): (a) effect of concentration; (b) effect of molecular weight; (c) effect of added electrolyte in the most concentrated solution; (d) effect of added electrolyte in the most dilute solution.

The electrostatic terms relevant to our discussion are τ, which is -1 or $+1$, depending on the anionic or cationic nature of the adsorbing polymer, κ^{-1} (the thickness of the double layer), n (the number of monovolent ions per cm^3 far from the surface), e (the protonic charge), and σ (the surface charge density) (σ_0 is the surface charge at the surface prior to adsorption).

Fraction of Bound Repeating Units and Polymer Desorption. Figure 6 shows plots of the calculated parameter p' as a function of α, revealing also the effects of concentration, electrolyte addition, and molecular weight on this variable. As discussed earlier, the calculation of p' is an attempt to quantify the trends in fraction of surface-bound repeating units within the adsorbate. The most general observation is the inverse relationship between Γ and p'. This observation corroborates our earlier interpretation of substantial adsorption being the result of collective drag as a consequence of segmental interactions in the presence of a strong attractive surface potential. When the collective motion of macromolecules toward the surface is substantial, one would expect only a small fraction of bound repeating units within the adsorbate. The experimental data indicate low values of bound fraction in adsorbates from solutions of high molecular weight polymer, high concentration, or low concentration but with added electrolyte. All these types of solutions led to large amounts of adsorbed polymer. A decrease in bound fraction with increasing concentration has been predicted theoretically. However, in previous experimental work by Thies,[39] a marked dependence of bound fraction on concentration was not observed for poly(methyl methacrylate) adsorbed on alumina and silica. Killman[40] confirmed this finding but also observed, as we have, a decrease in bound fraction with increasing concentration for polystyrene and poly(vinylpyrrolidone).

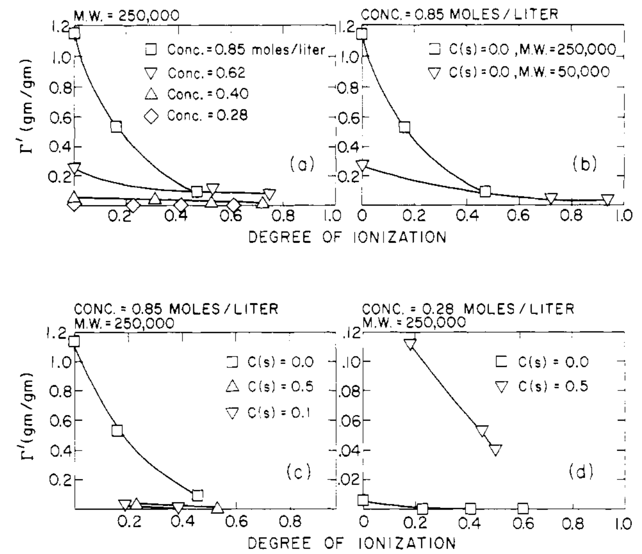

Figure 7. Plots of amount of PAA desorbed into pure water (per gram of substrate) after 24 h as a function of PAA degree of ionization prior to adsorption: (a) effect of concentration; (b) effect of molecular weight; (c) effect of added electrolyte in the most concentrated solution; (d) effect of added electrolyte in the most dilute solution.

The specific effect of α on p' suggests some interesting features about ionic polymer adsorption. The relevant data, shown in Figure 6, reveal an increase in bound fraction with α at all concentrations. This correlation can be interpreted as a greater driving force for adsorption in individual molecules or segments as their electrical free energy and rigidity increase. The rise in electrical free energy is, of course, the result of increasing ionization in segments that are only partly screened by Na$^+$ counterions. It is intriguing that p' values do not exhibit a tendency to level off with increasing α. This effect was expected on the basis of limiting values of chain segment potential and decreasing surface potential with α. One may speculate that even at constant segment potential, chain flexibility and thus entropy continue to drop due to Coulombic interactions between side groups and counterions. Therefore, entropy loss upon adsorption may not be as significant in rigid chains, this creating a stronger enthalpic driving force for chain interaction with the surface. According to the data, the sensitivity of p' to α is greatest in the more dilute solutions. The origin of this effect is not clear; however, one may suggest that effective charge densities in concentrated media could be lowered by mechanisms such as the clustering of ions.

An important experimental result obtained in our study is the correlation between values of Γ', the amount of PAA desorbed from the substrate into pure water after adsorption, and the bound repeating unit fraction parameter, p'. Figure 7 shows Γ' plots as a function of α and all other solution variables studied. Curves of weight fraction desorbed as a function of p' were also generated from some of the data and are shown in Figure 8. For solutions of intermediate and high concentration, there is an apparent correlation between weight fraction desorbed and p'. Adsorbates with the highest fractions of bound repeating units (according to p' calculations) seem to produce the most hydrolytically stable adsorbed layers. It also follows from Γ' data that solutions which were earlier claimed to produce large quantities of adsorbate by collective drag contain the largest amount of material that is easily desorbable into pure solvent (water). Within experimental limitations and conditions, adsorption of PAA on TCP from the most dilute solution seems to be irreversible over

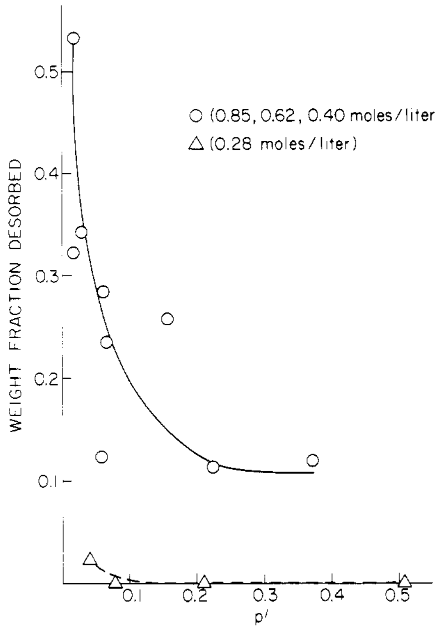

Figure 8. Plots of the adsorbate's weight fraction desorbed into pure water after 24 h as a function of a parameter proportional to substrate-bound repeating units (p').

a wide range of p' values. In this solution, adsorption could be better described as a strong surface attachment of individual coils even at very low values of p'. In this context, the rapidly rising values of desorbed fraction with decreasing p' for more concentrated solutions is interpreted as an indication of adsorbed aggregates that do not directly bond to the surface. Figure 1 shows characteristic portions of infrared spectra from TCP powders containing adsorbed PAA before and after exposure to pure water for 24 h. The most salient feature after water exposure is the intensification of COO^- absorbance relative to that associated with COOH groups. This implies that the most strongly bound macromolecules on the adsorbent's surface are highly ionized. The observation is in agreement with our finding that powder–liquid slurries always revealed higher concentrations of ionized repeating units than supernatant liquids. It also justifies our approach of using degree of ionization in adsorbed layers as an experimental indicator of trends in surface-bound repeating units.

Conclusions

The adsorption behavior of ionized poly(acrylic acid) on tribasic calcium phosphate surfaces is affected significantly by the substrate's electrostatic potential as well as the polymer's conformation and intermolecular association in aqueous solution. Generally, large amounts of the anionic polyelectrolyte are adsorbed due to the cationic nature of the substrate in acidic media. As long as a strong adsorbate/substrate attractive potential exists, the adsorption process is controlled by collective drag of macromolecules toward the surface. This collective drag occurs under conditions that produce segment–segment association in solution unless the surface potential is reduced by screening electrolytes. Thus, high concentration or molecular weight in solutions of flexible chains (molecules with low degrees of ionization) lead to large amounts of adsorbed polymer. Chains within this type of adsorbate only contain a small fraction of surface-bound repeating units and desorb easily into media of pure solvent. On the other hand, less collective drag and thus less adsorption is observed from solutions of low concentration or those containing chains in rigid and extended conformations. These adsorbates contain, however, small or undetectable amounts of desorbable polymer.

Acknowledgment. Partial support for this work from NIH Grant DE05945 is greatly appreciated. We also acknowledge the use of laboratory facilities at our previous affiliations in the Department of Materials Science and Engineering and the Department of Biological Materials at Northwestern University.

Registry No. PAA sodium salt, 9003-04-7; TCP, 12167-74-7.

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