Adsorbed Monomer Analog of a Common Polyelectrolyte

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The monomer analog of a common water-soluble charged macromolecule shows surface tilt and cooperative adsorption that would be expected for larger surfactant molecules—the small organic ion behaves as an embryonic surfactant. Yet the organic ion competes with inorganic ions (Na^+, Mg^{++}, etc.) for access to the surface, and therefore its tilt increases with the size of the competing co-ion. Similar ordering of charged units along a polyelectrolyte chain would be sterically frustrated. This suggests a new contribution to surface energetics when a charged macromolecule adsorbs. [S0031-9007(98)05926-2]

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The distribution of ions at the solid-water interface is a fundamental problem in nature and technology. Notions of screening point electrical charges, based on the classical "double layer" theories of Gouy-Chapman and Debye-Hückel [1,2], comprise still the most influential way of thinking about the problem—but this approach is founded on the minimalist assumption that ions possess neither size nor shape. The more realistic modeling of potentials of interaction has been the focus of most recent studies [3]. Here we focus on a different aspect, seldom considered: ions that are hydrophilic at the point of charge yet hydrophobic at the organic portion, such that electrical charge drags the remainder of the molecule into solution. For example, this is why most food dyes dissolve, why poly(styrene sulfonate) dissolves though polystyrene is insoluble in water, and so forth. Additional instances of local pockets of hydrophobicity in charged macromolecules involve proteins, DNA, and other synthetic polyelectrolytes in applications from foodstuffs to drug delivery. The scientific consequences of having partially nonpolar ions are fundamental in polymer physics, in biophysics, and in colloids.

We find that finite size and shape play essential roles. A small organic ion competes with inorganic ions (Na^+, Mg^{++}, etc.) for access to the surface and therefore its surface orientation shifts with the size of the competing co-ion. We suggest that this may give rise to frustrations in the adsorption of charged macromolecules. The organic ion, the 1,4-dimethylpyridinium cation (with molecular structure of P^+ is drawn in the inset of Fig. 1), was selected as the segmental analog of a common aqueous polyelectrolyte, alkylated poly(1,4-vinylpyridine). The P^+ was purchased from Aldrich and then purified by recrystallization, using precipitation with ethanol, until a clear white color was obtained. Keeping in mind the vulnerability of P^+ to oxidation, experiments were performed soon after recrystallization with care to minimize exposure to light and atmospheric oxygen. The inorganic salts (General Storage, pure grade, or Aldrich, purissim grade) were used as-received after control experiments showed no difference if they were baked first at 600 °C. The H_2O was double distilled and then further purified by passage through deionizing columns.

These molecules were allowed to adsorb from aqueous solution at 25 °C onto a flat, hydrophilic silicon crystal that had been oxidized controllably with oxygen plasma as described previously [4]. Adsorption was measured by polarized Fourier transform infrared spectroscopy in attenuated total reflection (FTIR-ATR) using a Biorad FTS-60 spectrometer equipped with a mercury-cadmium-telluride detector and a home-built adsorption cell [5]. The contribution of nonadsorbed species in solution to an ATR signal can be calibrated by using nonadsorbing surfaces and then subtracted quantitatively [4–6]. The effects described below are apparent even in the raw data, however. Neither the P^+ ions nor the polyelectrolyte analog, quaternized polyvinylpyridine, adsorbed except

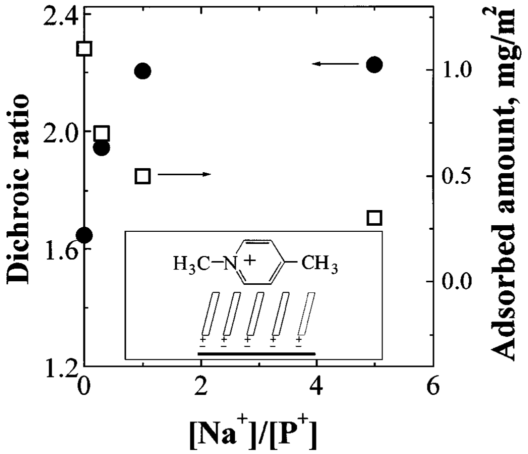

FIG. 1. Dependence of surface tilt on relative co-ion concentration. The dichroic ratio (circles; left axis) of the carbon-nitrogen stretch vibration at 1644 cm^{-1} of dimethylpyridinium (P^+) ions, adsorbed from D_2O onto oxidized silicon at $pH = 9.2$, and the amount adsorbed (squares; right axis) are plotted against the molar ratio of Na^+ to P^+ concentration in solution with $[P^+]$ fixed at 100 mM/ℓ. Inset shows the chemical structure of the P^+ ion and a cartoon of adsorbed P^+.

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above the isoelectric point [6]. In this case, the surface charge was negative; both the polyelectrolyte and the monomer analog adsorbed chiefly by electrostatic attraction to the surface of opposite charge.

Experiments therefore were conducted well above the isoelectric point (expected for oxidized silicon to be close to the known value for silica, $pH = 3$ to 3.4 [7,8]). In order to reduce overlap of the IR spectra of P^+ with those of water, we often used 99.9% D_2O (Sigma) rather than H_2O. The amount adsorbed was then ~10% less at a given pH, probably because of the known isotopic influence on the dissociation constant of surface silanol groups [9], but we verified that the results presented below did not depend on the choice of H_2O and D_2O solvent. In addition, fits of P^+ adsorption at low surface coverage to the classical Langmuir adsorption isotherm [2] implied the adsorption energy of $\sim 7k_BT$ ("low salt" conditions) and $\sim 3k_BT$ (in competition with 0.5 M NaCl).

We now consider tilt. The mean tilt (with respect to the surface) of these shaped ions was inferred from the dichroic ratio (D), defined as the ratio of infrared absorption in the p and s polarization directions [10–12]. Isotropy of an IR transition moment was equivalent to $D = 2.05$ for the refractive indices of our Si crystal and aqueous solutions. While D is this experiment was probably also influenced by residual roughness of the polished Si crystals (profilometry showed roughness up to 15 Å normal to the surface [6]), it is meaningful to compare relative values of D measured using the same crystal under different solution conditions. In the graphs discussed below, we analyze D of an in-plane stretch of the pyridine ring, the carbon-nitrogen stretch at 1644 cm^{-1} (its intensity was the highest of the IR absorption peaks), but the same effects were measured also for the weaker coupled carbon-carbon and carbon-nitrogen ring stretch at 1523 cm^{-1}. The band at 1644 cm^{-1} is directed along the symmetry axis of P^+ [6] and should reflect the molecular tilt.

Figure 1 shows the dependence of the P^+ dichroic ratio on the ratio of Na^+ to P^+ ions in solution; the concentration of P^+ was kept constant at 100 mmole/ℓ. The P^+ ions were preferentially parallel to the surface as long as the ionic strength was low and tilted more upright with increasing ionic strength. The dichroic ratio increased monotonically (with increasing proportion of Na^+) until reaching a plateau at the molar ratio $[Na^+]/[P^+] \sim 1$. This was accompanied by less P^+ adsorbed, the higher the Na^+ concentration, owing to competitive adsorption of Na^+ with P^+ for the surface, but the dichroic ratio of adsorbed P^+ remained constant. These observations were reversible when the salt concentration was subsequently lowered. Under vacuum conditions, pyridine molecules are known to stand straighter as the surface coverage increases [13], so these observations might at first seem unsurprising, but those systems lacked charge and were not free to equilibrate with a bulk reservoir. As we now discuss, the origin of molecular tilt was very different for the ions in aqueous environment.

To test the hypothesis that tilt reflected the presence of coadsorbed inorganic ions with the same charge, we varied the inorganic co-ion. (A co-ion is chemically different but carries the same charge). The P^+ ion is relatively bulky; it is roughly 3 by 8 by 9 Å in dimension, as gauged from the crystalline structure of a salt form of the ion [14], though these numbers can be expected to become slightly larger upon hydration in aqueous solution. It was conceivable that each pyridinium ring occupied more than a single adsorption site under low salt conditions—and that the smaller metal ions, in order to gain access to these occluded potential adsorption sites, forced the observed reorientation of P^+. Figure 2 shows the dichroic ratio plotted against the surface excess of P^+. For low salt (buffer conditions), one observes the preferentially parallel alignment also seen in Fig. 1. We found essentially the same result, $D \approx 2.2$, for a number of monovalent cations all with nearly the same hydrated radius in water (3.8, 3.6, and 3.3 Å, respectively, for Li^+, Na^+, and Cs^+ [1]). But the hydrated radius of Mg^{2+} is larger, 4.3 Å [1], and we expect its size in solution to be further enlarged at high pH by partial hydrolysis, so perhaps it is not surprising to have observed a larger dichroic ratio, $D \approx 2.9$. Parenthetically, we remark that these observations of the consequences of steric packing suggest a method by which an organic ion could be used to control the occluded area on an underlying surface (for

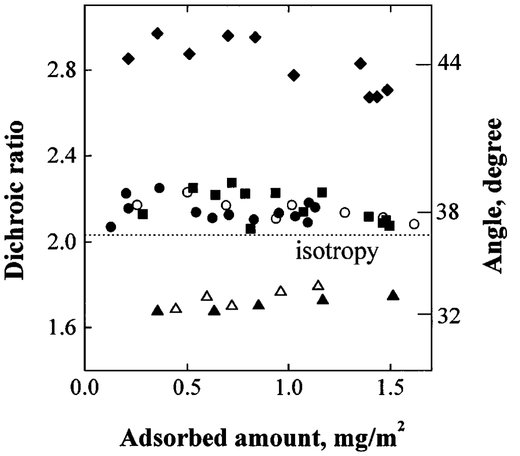

FIG. 2. Dependence of surface tilt on nature of the co-ion. The dichroic ratio (carbon-nitrogen stretch vibration at 1644 cm^{-1}) of dimethylpyridinium (P^+) ions adsorbed from D_2O onto oxidized silicon is plotted (left axis) against mass adsorbed. The various inorganic ions are indicated as buffer only (triangles), 0.1 M LiCl (open circles), 0.1 M CsCl (squares), 0.1 M NaCl (filled circles), and 0.01 M $MgCl_2$ (diamonds). The pH was 10.8. The tilt angle implied by this dichroic ratio (right axis) was estimated with the assumptions of azimuthal symmetry and no angular distribution. Isotropy is indicated by the dotted line.

example, access to channels through a lipid membrane) by switching the inorganic ion in solution.

Control experiments (Fig. 3) showed this to be general. As the observations presented above were at a particular pH, and pH controls the density of charged Si-O$^-$ groups on the solid surface, we checked whether tilt of P$^+$ ions depended on pH. This also served to check whether the observations might be influenced by adsorption of ions from the buffer solutions used to control pH, since the buffer ions were varied according to the pH that was desired (see caption of Fig. 3). In these control experiments, the pH was varied by several units, corresponding between pH 8.0 and 10.5 to an expected difference in surface charge of approximately a factor of 10 [15]. The dichroic ratio of the pyridinium rings proved to be nearly independent of pH.

We now discuss cooperative adsorption that suggested a structural transition at high surface coverage. Figure 4 shows a rounded step in the adsorption isotherm which occurred at P$^+$ surface coverage corresponding to a projected area of 33 Å^2 per molecule (1.2 mg m^{-2})—regardless of pH and ionic strength. This step was accompanied by a jump in the dichroic ratio, showing that the P$^+$ molecules tilted abruptly further away from the surface to accommodate the additional adsorbed amount. These data refer to P$^+$ in solution without added metal co-ions, at high P$^+$ concentration in solution, such that the surface coverage of P$^+$ reached larger values than in Figs. 1–3. Though the surface coverage cannot be interpreted literally because of uncertainties concerning roughness (see comments on surface roughness in the experimental section), it is similar in magnitude and slightly larger than the mean area of 20–25 Å^2 expected for Si-O$^-$ groups on silica [7], and also similar to the molecular area of ≈25 Å^2 expected from the crystal structure [14]. The step increase in amount adsorbed and in orientational order was coupled with hysteresis upon dilution after the step.

We considered the possibility that this originates in some kind of ion pairing of P$^+$ with negative surface charges. This would suggest that the surface charge density was, in each case, the same at the step, but experiments showed the step to occur at lower P$^+$ concentration, the higher the pH. Also, it is unclear why this mechanism would require the large observed increases of adsorbed amount (e.g., increase by a factor of 3 at $p\text{H} = 10.5$).

The conceivable explanation in terms of bilayer formation was explored carefully but considered unlikely for several reasons. First, ellipsometric measurements of dry P$^+$ films were performed. The results (not shown) also revealed an adsorption step but the maximum ellipsometric thickness observed, ≈9 Å, never exceeded the known size of the P$^+$ ion. Second, when we attempted displacement of adsorbed P$^+$ by exposure to a very high concentration of Na$^+$, 0.5 M NaCl in buffer

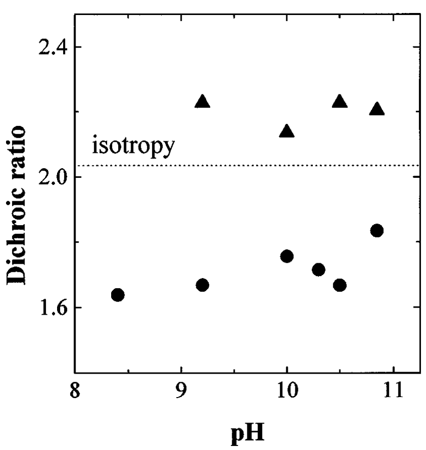

FIG. 3. Dependence of dichroic ratio on pH. The dichroic ratio (carbon-nitrogen stretch vibration at 1644 cm^{-1}) of dimethylpyridinium (P$^+$) ions, adsorbed from D$_2$O onto oxidized silicon, is plotted against pH under various conditions: Filled circles indicate adsorption from buffer solution without additionally added salt (2 mM Na$^+$); filled triangles indicate adsorption from 0.1 M NaCl solution. To control pH, the following buffer solutions were used: 1 mM sodium phosphate at $p\text{H} = 8.4$, 1 mM sodium borate at $p\text{H} = 9.2$, 1 mM sodium carbonate at pH 10.8, 1 mM mixed borate and carbonate at the other pH. Filled circles indicate adsorption from buffer solution without additionally added salt (2 mM Na$^+$). Filled triangles indicate adsorption from 01. M NaCl solution. The adsorbed amount was 0.8 mg m^{-2} except at $p\text{H} = 8.4$, where it was 0.6 mg m^{-2}. Isotropy is indicated by the dotted line.

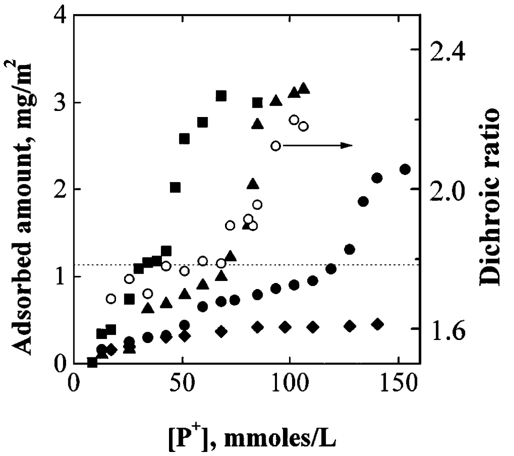

FIG. 4. Dependence of adsorption on P$^+$ solution concentration. The adsorbed amount of P$^+$ (left axis) and dichroism of the carbon-nitrogen stretch vibration at 1644 cm^{-1} (right axis, open circles), plotted against P$^+$ molar concentration in H$_2$O. Adsorption was at $p\text{H} = 11.5$ (squares), $p\text{H} = 10.5$ (triangles), $p\text{H} = 9.2$ (filled circles), and $p\text{H} = 8.0$ (diamonds). Except at $p\text{H} = 11.5$, where a mixture of sodium carbonate and NaOH was used, the pH was regulated by buffer conditions described in the legend of Fig. 2. No salt was added beyond the small amount required to establish buffer conditions (2 mM Na$^+$). Below, the step the adsorption was rapid and reversible, but, above the step, it was slow to equilibrate. It was technically unfeasible to wait longer than 30 min for equilibration at each data point. The dotted line indicates the surface coverage at the adsorption step, 1.2 mg m^{-2}.

solution, rapid displacement was observed in the prestep region but little displacement at higher surface coverage except when the solution was agitated. Finally, the films became significantly more hydrophobic when the surface coverage was high: The contact angle with water, $\theta = 5°-7°$ for surface coverage $<1\ \mathrm{mg\,m^{-2}}$, jumped to $\theta = 24°$ above the adsorption step. Bilayer formation would have produced a hydrophilic surface. Instead, these experiments suggest the formation of a P^+ monolayer comprised by pyridinium rings terminated with methyl groups.

It is interesting to find cooperative surface self-assembly in this molecule for which no micelle formation has been reported in the bulk; it is reminiscent of the surface crystallization often observed in traditional surfactants when they adsorb close to their critical micelle concentration (c.m.c.) [2,16]. Surface-induced order in an otherwise-isotropic liquid has also been observed in alkanes near the freezing temperature [17,18] and in liquid crystals near the isotropic-ordering transition temperature [19–21], though in those systems only within a degree or two of the bulk transition temperatures. Pursuing these analogies, we note an energetic advantage to the stacking of aromatic rings [22]. Ordering may be encouraged also by efficiency of steric packing (guided and locked in place by electrostatic attraction to the surface of opposite charge). The phenomenon seems analogous to the critical adsorption concentration, in which surfactants self-assemble at a surface at concentrations below the bulk c.m.c. [23]. Whatever the ultimate reason, these features of surface organization, which have been reported previously only for long hydrocarbon molecules, are reported here for a small organic ion, for what we believe to be the first time.

The relevance to macromolecular adsorption is simple and, we suggest, far reaching. If ions similar to P^+ are incorporated into a larger macromolecule (as, for example, into quaternized polyvinylpyridine chains), it is obvious that the packing cannot be the same. In particular, a strong confounding influence will be stereoregularity along the chain; the permissible orientation order will be largest for stereoregular sequences and least if chiral sequences along the chain backbone are random. The prominence of such chiral effects is obvious when one constructs the simplest ball-and-stick molecular models. Experiments similar to those reported in this paper, in which synthetic polyelectrolytes of variable tacticity were studied [6], confirm the expectation.

In fields from colloids to electochemistry and biochemistry, which also deal with the solid-liquid interface of aqueous solutions, we expect additional ramifications from this tendency of small organic ions to orient and order even at a disordered surface.

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