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Adsorption of Weak Polyelectrolytes on Amphoteric Oxide Surfaces

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The adsorption of a weakly cationic polyelectrolyte (poly(dimethylaminoethyl methacrylate), (AMA) and a weakly anionic polyelectrolyte (carboxymethylcellulose, CMC), were studied as a function of pH. As substrates we used the (amphoteric) metal oxides TiO_2 and Fe_2O_3 . Adsorption of CMC on to colloidal particles was determined from the solution depletion; adsorption of AMA was followed by a reflectometric method. In addition, layer thicknesses were measured. These were determined from the increase in hydrodynamic radius of diffusing colloidal particles. For proper data interpretation, the effects of free polymer on diffusion were also carefully analysed, and it was found that the friction on small particles is intermediate between that exerted by the pure solvent, and that expected on the basis of solution viscosity.

The adsorbed amounts showed in both cases a downward trend with increasing polymer charge density, in agreement with an ion-exchange mechanism of adsorption that is expected if electrostatics dominate. AMA displays a maximum adsorbed amount at the point where the polymer charge density becomes so low that electrostatics as the driving force for adsorption vanishes. For CMC there could also be a maximum (at low pH) but there are, as yet, no data at sufficiently low pH. The adsorbed amounts of CMC were insensitive to the molecular weight. Layer thicknesses of adsorbed CMC, however, increased markedly with molecular weight. This may indicate partially irreversible adsorption of CMC.

KEY WORDS Adsorption, polyelectrolyte, carboxymethylcellulose, layer thickness, oxide, light scattering

INTRODUCTION

Electrostatic interactions play an important, if not dominant, role in the adsorption of polyelectrolytes; this seems to be an almost trivial observation. However, when it comes to understanding polyelectrolyte-solid interactions in detail, it is not always easy to see how electrostatics affect these. Partly, this is due to the fact that the electrostatics may give rise to both attraction and repulsion in the same system, and the balance between the two may be quite subtle [1]. Another complicating factor is that if the charge is due to reversible proton transfer reactions, the number of charged groups present in the system is not fixed; it may vary as a result of adsorption. Such effects can sometimes be studied experimentally [2], but they are not easily predicted quantitatively.

On the basis of existing data, a number of theoretical models describing polyelectrolyte adsorption equilibria have been developed over the last two decades [3–7]. The simplest of

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these models assigns a charge density to both the surface and the substrate which cannot vary upon adsorption. For the case that electrostatics is the sole interaction present in the system, these models predict that polyelectrolyte adsorption is essentially a kind of ion exchange process, whereby small counterions are exchanged for macroions at the surface. As a result, the adsorbed amount is determined by the amount of charge exchanged per m^2 . This must of course remain constant as the charge density on the polymer decreases, so that the adsorbed mass must increase. On closer inspection of theoretical results one finds that in fact the surface charge is always slightly overcompensated, for entropic reasons [5,7]. The increase in adsorbed amount with decreasing charge density cannot go on indefinitely, as the macromolecules need at least some charge to compete successfully with the salt ions. Therefore the adsorption passes through a maximum at low polymer charge density; decreasing the charge even further results in a rapid reduction in adsorbed mass.

More refined models have been constructed to take into account the presence of weakly dissociating acid or base groups on the polymer, as well as effects of finite ion size and non-electrostatic interactions between polymer and substrate, but none of these extensions led to qualitatively different trends predicted for the adsorbed amount (at low ionic strength) as a function of pH. We note in passing that non-electrostatic effects become much more important at high ionic strength, to the effect that adding salt enhances rather than reduces adsorption when a non-electrostatic adsorption mechanism is present.

As to the structure of the adsorbed layers, most models predict that polyelectrolytes have a strong tendency to form very thin layers, with flat polymer conformations. Adding salt or reducing the charge density leads to gradual thickening of the layers, but thicknesses comparable to those for uncharged polymers are not easily reached.

Over the past ten years, a number of systematic experimental studies have appeared as well as some reviews [8,9]. Most of the data seem to be consistent with the ion exchange aspect of polyelectrolyte adsorption, showing a maximum at low polymer charge density. However, the effects of added salt and the shape of adsorption isotherms do not follow the predictions very well. In addition, the data on adsorbed layer thickness were often hard to reconcile with the idea of flat conformations [10]. As the empirical basis developed, more weaknesses of the models became apparent, and revisions seem to be needed.

In the present paper, we present experimental results on the adsorption of weak polyelectrolytes on the surface of insoluble metal oxides TiO_2 and Fe_2O_3 . Both are typical amphoteric oxides, which carry a net positive charge at low pH, and a net negative charge at high pH. The point of zero charge (pzc) is for TiO_2 located somewhere in the pH range 4–6, depending on the solid structure; for Fe_2O_3 we used haematite, for which has its pzc at ~ 8.5 [11]. We give results for both the adsorbed amount and the layer thickness of the adsorbed polymer. We compare these data with theoretical predictions, pointing out to what extent the latter are adequate.

EXPERIMENTAL METHODS

Determination of Adsorbed Amounts

The most widely used method to study adsorption is the so-called depletion method, whereby a solution of the adsorbate is brought into contact with the adsorbent, and the change in concentration after equilibration is determined by some convenient analytical

method. In order to have a detectable concentration change, the surface area of the adsorbent must be sufficiently large; for this reason one often uses adsorbent in the form of a colloidal dispersion. This depletion method has the disadvantage that the relevant surface area must be determined separately, which is not always very reliable. Also, the method is not suitable to follow the adsorption as a function of time, when adsorption occurs rapidly. In this paper we present data for polyelectrolyte adsorption on rutile and on haematite particles determined with the depletion method.

We also employed a newer technique, namely reflectometry, which has sufficient accuracy to determine very small adsorptions, and the rapidity of a typical optical signal. The set-up is sketched in Figure 1. A small He-Ne laser produces a linearly polarized incident beam [1]. The beam passes through a prism [2] into the cell and is reflected by the adsorbent [3], a small strip of monocrystalline silicon covered with a thin dielectric film. In the present experiments, this was a film of sputtered TiO_2 , with a thickness of approximately 25 nm. Upon reflection, the beam undergoes a change in its state of polarization. The reflected beam leaves the cell and is split into its two principal polarization components I_p and I_s by the beam splitter [4]. The intensity of each of these two components is finally detected by photodiodes [5], and their ratio $I_p/I_s \equiv S$ is determined electronically [6]. Upon adsorption, S changes by a small amount from its value S_0 for the bare surface to $S_0 + \Delta S$. The plane of polarization of the incident beam is usually chosen such that $S_0 \approx 1$, since this gives optimum sensitivity.

The success of this technique in determining adsorption hinges on the fact that the reflecting silicon wafer carries a dielectric film which acts as an optical spacer between the silicon and the solution, thereby creating a phase difference between the beam reflected at the solution/film interface and the beam reflected at the film/silicon interface. This has two effects: the reflectivity for the parallel polarized (p-)component is enhanced, and ΔS can become very near to linear in the adsorbed amount. Of course, it is necessary for

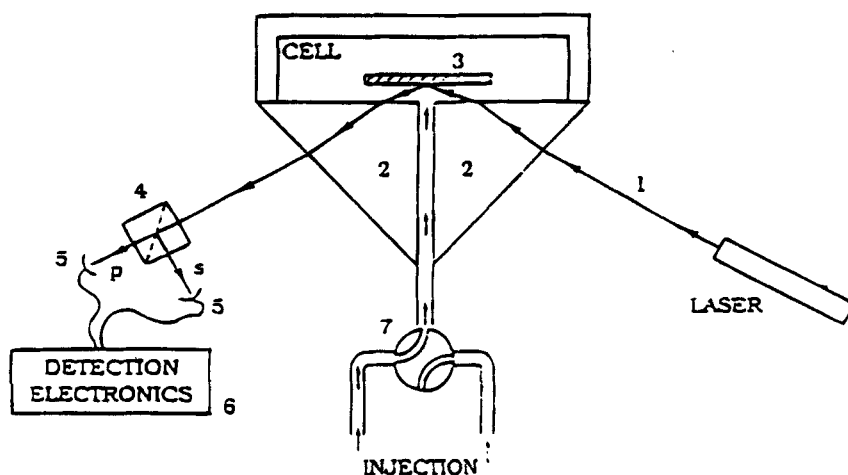


FIGURE 1 Schematic overview of the reflectometry set-up, top view. (1) incident laser beam; (2) glass prism; (3) reflecting substrate; (4) polarizing beam splitter; (5) photodiodes; (6) analog divider circuit.

the adsorbed polymer layer to have a refractive index significantly different from that of the solvent, but for organic solutes in water this is invariably the case. Conditions for optimum sensitivity and linearity, both in water and in organic solvents and for a range of refractive index values for the dielectric film have been specified in a recent description of the technique [12]. These conditions were determined from calculations using the standard theory for optical reflection from multilayered interfaces [13]. It is perhaps useful to note that adsorbed amounts for polyelectrolytes typically span the range between 0 and 1 mg/m², so that a suitable technique must be able to detect 0.05 mg/m². Since the reflectometric spot has an area of about 1 mm² this corresponds to 50 pg of deposited material to be detected, and this is easily achieved by the reflectometer! Moreover, the adsorption is measured under conditions of a constant flow of polymer solution, which ensures that the adsorbed amount corresponds to the imposed concentration of free polymer.

Adsorbed Layer Thicknesses

In order to characterize adsorbed polymer layers further, it is often useful to measure their thickness, since this quantity gives some indication of the extent to which the polymer chains protrude away from the substrate into the solution. The protruding chain sections perturb tangential solvent flow already at extremely low densities. The so-called 'hydrodynamic thickness' δ_h , defined in terms of reduced tangential flow [14,15] is therefore very sensitive to such structural details. A straightforward way to determine δ_h is to measure the increase in diffusion radius (from a to $a + \delta_h$) that spherical colloidal particles undergo when they get covered with adsorbed polymer. The idea is to use the Stokes-Einstein equation:

$$D = \frac{kT}{6\pi\eta(a + \delta_h)} \quad (1)$$

where D is the diffusion coefficient, η the viscosity of the medium, T the temperature and k Boltzmann's constant. Such measurements can be readily carried out with very dilute particle dispersions; the polymer taken up by the particles is then negligible as compared to the total amount in solution. Equipment to measure D from the intensity fluctuations in light scattered by particles in Brownian motion (quasi-elastic light scattering, QELS) is fairly standard and commercially available. We used a light scattering set-up manufactured by ALV, Mainz, Germany, equipped with a 35 mW He-Ne laser as the light source and an ALV-5000 digital autocorrelator.

A problem arising from the use of Equation 1 for determining δ_h is that free polymer in the solution not only influences the adsorption (thereby determining δ_h) but also affects the hydrodynamic friction (represented by η) experienced by the diffusing polymer-covered particles. The Stokes-Einstein equation is based on the assumption that for length scales of the order of the diffusing object, the surrounding medium can be considered as a continuum. This is entirely correct when the medium is a simple liquid, and the particle size in the colloidal range (> 1 nm). In that case, η can be taken to be the liquid's kinematic viscosity. However, in a polymer solution this condition may not be fulfilled at all, in particular when the polymer molecular weight is high. It is tempting to use for η the bulk shear viscosity of the polymer solution as determined by viscometry but this is not always correct. A way to deal with this is to represent the friction exerted by dissolved polymer on small

colloidal particles by using an effective 'diffusional viscosity' for η in Equation 1, which could be somewhere in between the viscosity of the solution and that of the solvent and has to be determined from diffusion measurements (i.e., light scattering).

Several authors have investigated this problem [16–21]. The general findings are that the 'diffusional viscosity' is indeed in between the solution's shear viscosity and the solvent viscosity, more or less proportional to the solution shear viscosity, and dependent on the size of the colloidal particle. Differences between 'diffusional' and ordinary solution viscosity are particularly pronounced for aqueous polymer and polyelectrolyte solutions [16,17,20], but less so for polymers in organic solvents [21]. The effect has also been analyzed theoretically, but so far this has not led to a useful alternative for Equation 1 [18,22,23]. Most treatments consider the limit where the particles are small, so that they experience only a small extra friction from the free polymer. In this limit, the motion of the polymer is much slower than that of the particles, so that the polymer is usually regarded as immobile. This leads to the prediction that the diffusion coefficient of the particles becomes negligibly small when their size becomes large. Of course this cannot be right: for (very) large particles the polymer is mobile and the solution should behave as a continuum so that the diffusion coefficient is expected to correspond to the macroscopic shear viscosity of the solution. Since our particles are neither large nor small, we cannot apply theoretical models. Consequently, we must take an empirical approach and determine 'diffusional viscosities' experimentally for particles of (approximately) the size used in the adsorption measurement. Moreover, these particles have to be inert (non-adsorbing) so that the reduction in D that they experience as a function of polymer concentration can be unequivocally related to the effective viscosity, (i.e., $\delta_h = 0$). One can then use these viscosities to get δ_h from data for adsorbing particles of similar size.

That such corrections are indeed substantial, even to the extent that qualitatively wrong conclusions result when they are not properly taken into account, is illustrated by some layer thickness data for a neutral water-soluble polymer (hydroxyethylcellulose, HEC, molecular weight of 330,000, with on average 1.9 ethylene oxide units per glucose monomer). Ordinary shear viscosity data for this polymer, as well as effective diffusional viscosities from light scattering data using non-adsorbing (inert probe) silica particles (radius of 285 nm), are presented in Figure 2. In order to prevent adsorption in this case, diffusion measurements were performed at pH 11. As can be seen, the effective 'diffusional' viscosity is well above that of the solvent, but still substantially lower than the shear viscosity. The effect of using different choices for η on the thickness of the adsorbed layer, now measured at pH = 3, is presented in Figure 3. Up to a free polymer concentration of 20 mg/L, the chosen value of η does not seem to matter, but differences cannot be ignored at higher concentrations. As is clear from the figure, the data obtained taking $\eta = \eta_{water}$ ('solvent viscosity') suggest a very strong increase in layer thickness; when η is taken from viscometric data ('viscometry'), the upward trend turns into a downward trend with increasing concentration, which is inconsistent with any adsorption model. Only when the data are evaluated by means of the inert probe diffusion data do we get a reasonable curve.

MATERIALS

As polyelectrolytes we used one cationic polymer (poly-[N,N-dimethylaminoethyl methacrylate], denoted as AMA) and one anionic polymer, CMC. AMA is a typical flex-

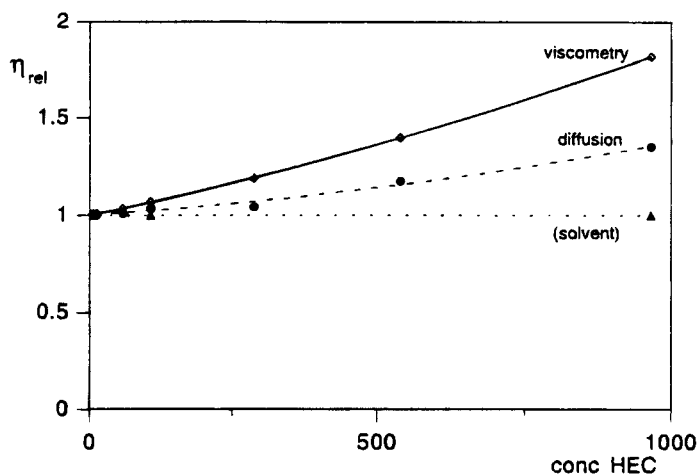


FIGURE 2 True shear viscosity and effective diffusional viscosity as determined from inert probe diffusion, both taken relative to the solvent viscosity and plotted as a function of polymer concentration in aqueous solutions of HEC. Bare particle radius: 285 nm.

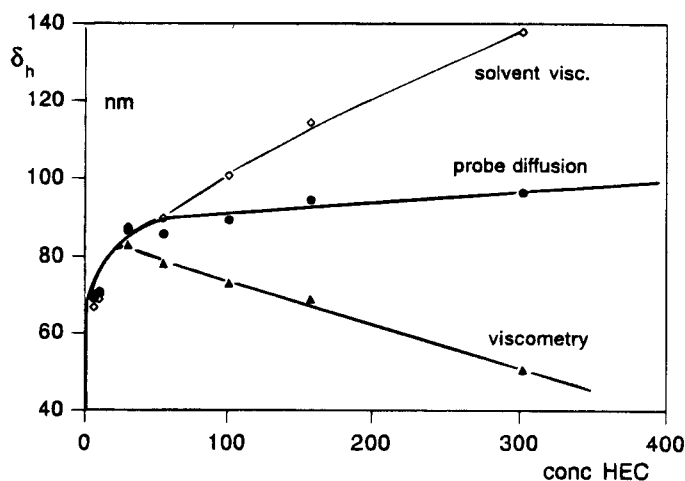


FIGURE 3 Hydrodynamic thickness of adsorbed HEC layers, as determined from light scattering, for three different choices of the viscosity in the Stokes-Einstein equation, Equation 1.

ible vinyl polymer. It was prepared by anionic polymerization and therefore presumably has a fairly narrow molecular weight distribution. Unfortunately, it adsorbs from tetrahydrofuran (THF) on Styragel columns so that we cannot report size exclusion (SEC) data. The molecular weight of this polymer was 20 kg/mol. CMC, which has a less flexible backbone (its 'bare' persistence length is about 5 nm), was prepared from alkali treated cotton linters by heterogeneous reaction with monochloro acetic acid. Various CMC samples were prepared, all from the same cellulose source. These polymers are presumably rather polydisperse. Their molecular weights have been determined from the intrinsic vis-

cosities in aqueous solution at pH 3.0 and 0.01 M NaCl; Mark Houwink constants for these conditions are $a = 0.92$ and $K = 8.1 \times 10^{-6} \text{ m}^3\text{kg}^{-2}$ [24]. Molecular weights (as sodium salts) and degrees of substitution (ds-average number of carboxy methylgroups per glucose unit) are summarized in Table I. Concentrations of CMC in aqueous solution are readily determined by means of colorimetry [25].

As solids we used titanium dioxide (TiO_2) and iron oxide (Fe_2O_3). Titanium dioxide was available in the form of colloidal rutile particles, and as sputtered films on silicon wafers, with a less well-defined crystal structure. The electrochemical surface properties of these two types of TiO_2 are slightly different: rutile has its point of zero charge (determined both from potentiometric titration and from electrophoresis) at pH 6, whereas the sputtered TiO_2 has an isoelectric point (determined from streaming potential measurements) close to pH 4. Iron oxide was available as a colloidal haematite dispersion with almost spherical, monodisperse particles; their radius was about 42 nm. Furthermore, we used colloidal silica particles of two different sizes (Ludox particles, with radius 18.2 nm, and 'Stöber' silica spheres of 285 nm) as inert probes in light scattering studies.

TABLE I

Characteristics of CMC samples used in this study. Viscosity-average molecular weights M_v were determined using $K = 8.1 \cdot 10^{-6} \text{ m}^3 \text{ kg}^{-2}$ and $a = 0.92$ as Mark Houwink constants.²⁴

Sample	degree of substitution	$[\eta]$ (m ³ /kg)	M_v (kg/mole)
CMC-1	0.99	0.10	500
CMC-2	0.99	0.39	400
CMC-3	0.99	1.12	120
CMC-4	0.99	1.40	30
CMC-5	0.75	—	500
CMC-6	1.25	—	500

RESULTS AND DISCUSSION

Adsorbed Amounts

In Figure 4 we present the adsorbed amount Γ of AMA on sputtered TiO_2 as a function of pH, from buffered solutions with two different ionic strengths. We first note that at high pH no adsorption occurs. Since AMA carries weakly cationic tertiary amine groups, it loses most of its positive charge as the pH increases from 6 to 8. Hence, at high pH we are dealing with an effectively neutral polymer. These data imply that AMA in its neutral state has no attractive interactions with TiO_2 . Adsorption starts abruptly upon lowering the pH to a certain point. For the case of low ionic strength this is at a higher pH (~ 9.5) than for the case with 0.1 M NaCl. This reflects the competition between partly charged AMA molecules and sodium ions for the negatively charged surface sites. The polymer chain needs to have a certain minimum amount of charge before it can win this competition, and more charge needs to be present at higher concentrations of sodium in the solution. As soon as the balance tips over in favour of the polyelectrolyte, adsorption rises rapidly with increasing charge, i.e. decreasing pH.

However, Γ cannot rise indefinitely; at some point nearly all sodium ions are replaced, and the amount of polymer charge that can accumulate will be dictated by the amount of surface charge. Hence, if the charge per polymer chain is increased further, the number of

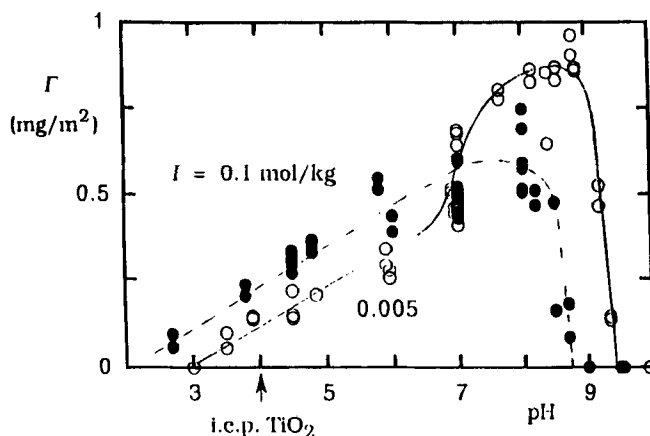


FIGURE 4 Amount of adsorbed AMA from 10 mg/kg solutions on sputtered TiO_2 films as a function of pH, from buffered salt solutions, at two different ionic strengths (indicated). The isoelectric point (i.e.p.) is also indicated (arrow).

adsorbing chains will decrease, and so does the adsorbed amount. Indeed do we see a rather dramatic decrease between pH 9 and 7 for the case of low salt concentration. The other curve decreases likewise, albeit less dramatically. From pH 6 downwards, the charge on the polymer is almost constant. Yet, we observe a further decrease of Γ in this direction. This is caused by the fact that the charge on the surface of TiO_2 goes down as we approach the isoelectric point (indicated by the arrow).

It is remarkable that, in this range, the added salt enhances adsorption, whereas at high pH it had a reducing effect. We ascribe this to the fact that polymer is adsorbed to the point where it just slightly overcompensates the surface charge. Overcompensation is also found from electrokinetic data, which invariably show a reversal of charge: bare TiO_2 is negative at $\text{pH} > 4$ but TiO_2 covered with the polycationic polymer is positively charged. This excess of positive charge has to be small, as it leads to repulsion between the chains in the adsorbed layer. However, as this repulsion is weakened by the screening effect of added electrolyte, a higher excess charge, and more adsorption becomes possible.

Finally, we note that the adsorbed amount goes all the way to zero as the pH is lowered sufficiently. Since negative charge is removed from the surface, this is no surprise. The surprise, however, is that adsorption still occurs beyond the pzc, i.e. in the range where the net overall charge of bare TiO_2 is positive. In this range, theoretical models will predict from the overall electrostatic repulsion that adsorption is only possible by a non-electrostatic mechanism. Since the result at high pH tells us that AMA cannot interact with TiO_2 by other than electrostatic forces, we have to assume that some electrostatic attraction is still possible despite the overall positive charge. We can rationalize this when we take into account that the TiO_2 surface is amphoteric, and that its net charge is actually a sum of positive and negative charges, and that the density of these charges is pH-dependent. Not only does this imply that there are still negative sites in the range $\text{pH} < \text{pzc}$ (although decreasing in number when the pH drops) but also that the presence of a positively charged macromolecule near the surface facilitates the formation of negative sites and hampers the formation of positive ones. Hence, locally the pzc may be shifted to lower pH. Thus, both the

facts that these surfaces are heterogeneous (amphoteric), and that their charge can be adjusted, can contribute to the observed adsorption at $\text{pH} < \text{pzc}$. Heterogeneous surfaces with adjustable site distributions have been considered theoretically [26], but only for the case of short-ranged, non-electrostatic interactions. Therefore, a more quantitative analysis has to await the elaboration of an electrostatic equivalent for these theories.

In Figure 5 we show the pH-dependence of the adsorption (this time determined with the depletion method) of our polyanionic polymer, CMC, from NaCl solution. Figure 5a is for colloidal haematite as the substrate, and Figure 5b gives data for TiO_2 (colloidal rutile). Again, we observe a decrease in Γ , as the charge on the chain increases, i.e. this time in the direction of increasing pH. The lowest pH for which we have data is 3, which is about the pK of the carboxymethyl group [27]. Hence, the polymer is still considerably charged at this pH, and we should have to take data down to $\text{pH} \sim 1$ to see whether or not a maximum occurs. There is another difference: at very high pH, where both oxide surfaces are well into the range of negative charge the adsorption does not show any tendency to vanish, as it did for AMA at low pH. A possible reason for this is that CMC can also interact with TiO_2 through short range, non-electrostatic forces, most likely through hydrogen bonding of the vicinal OH-groups with specific groups on the surface. This conclusion is supported by the fact that neutral polysaccharides can also adsorb from water onto metal oxides [28], whereas several other neutral water-soluble polymers do not [29].

The data in Figure 5 show that there is hardly any effect of the degree of substitution even though the ion exchange mechanism would predict so: a higher degree of substitution implies more charge, and, hence, a lower adsorption. Presently we have no explanation for this.

We finally found that the adsorbed amounts as presented in Figure 5 do not detectably depend on the length of the CMC chains. This trend is found more often with polyelectrolytes [9,30,31]. For neutral polymers, a dependence on molecular weight is nearly always present [9], and usually ascribed to the capability of flexible polymers to form loops and loose ends ('tails'). We thus tend to infer that polyelectrolytes, when they adsorb, do so in fairly flat configurations on the surface, tails being relatively unimportant. Indeed do theoretical calculations support this conclusion [5,8], but the experimental evidence is less clear. Some results obtained with the surface force apparatus [32], as well as neutron scattering [33] data do indeed confirm the existence of very flat adsorption layers. However, data on flocculation rates are at variance with this [34].

Layer Thickness

We therefore decided to measure hydrodynamic thicknesses for CMC adsorbed on haematite as a function of pH and molar mass. In order to do this, we first had to evaluate the effect of polymer in solution on the diffusion of inert colloidal probe particles. It was found that CMC does not adsorb on silica at any pH, so that silica particles are suitable as inert probes. In Figure 6 we give both the shear viscosity of CMC solutions ($M \sim 360\text{K}$) at pH 10 and in 0.01 M NaCl for various concentrations plotted and the 'diffusional' viscosity as obtained from QELS for particles with a radius of 285 nm and 18.2 nm, respectively. It is remarkable that, at the highest polymer concentration, the measured shear viscosity overestimates the effect of polymer on diffusion by as much as a factor of 4 for the small particles, and that for the large particles there is still a discrepancy, although much smaller. Similar corrections were determined for lower pH's.

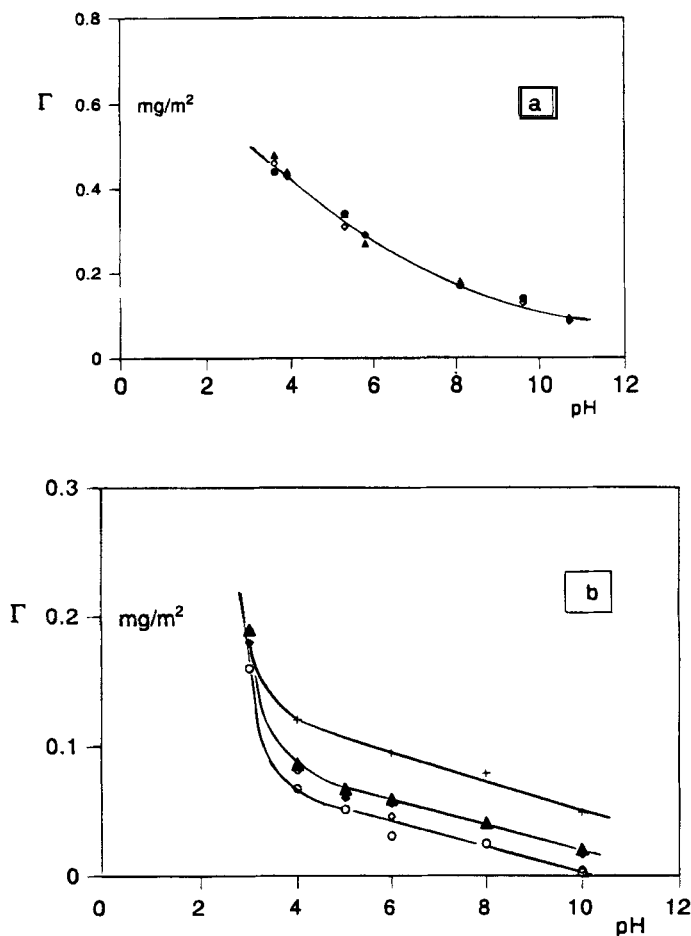


FIGURE 5 Plateau adsorbed amounts (at polymer concentrations of ~ 100 mg/L) of CMC (500 kg/mol) for various degrees (ds) of carboxymethylation on amphoteric oxides as a function of pH; (a) on haematite as the adsorbent at 0.01 M NaCl; diamonds: $ds = 0.75$, circles: $ds = 0.99$, triangles: $ds = 1.25$; (b) on rutile as the adsorbent at various concentrations of added NaCl; crosses: 1M NaCl ($ds = 1.25$); filled symbols: 0.1 M NaCl (triangles: $ds = 1.25$, diamonds: $ds = 0.75$); open symbols: 0.01 M NaCl (diamonds: $ds = 1.25$, circles: $ds = 0.75$).

Next, CMC was adsorbed onto colloidal haematite particles (with a bare radius of 42 nm) and the diffusion coefficient was determined. In order to convert these data into layer thicknesses the effect of the free polymer has to be taken into account. As demonstrated above, this effect depends on the size of the diffusing particle in a way which is, as yet, not fully understood. Moreover, we have no data for diffusion of inert particles of exactly 42 nm, and the effective radius of the particles increases as a result of adsorption. In order to correct in a reasonable way for the free polymer effect, we decided to use an interpolation formula that gives the effective diffusion viscosity η_{eff} for particles with radii between 1 and 600 nm. We construct this formula on the basis of our data for two particle sizes (Fig. 6) and impose as constraint that the effective viscosity in the limit of small particles must approach the solvent viscosity η_0 , whereas the large particle limit has to be

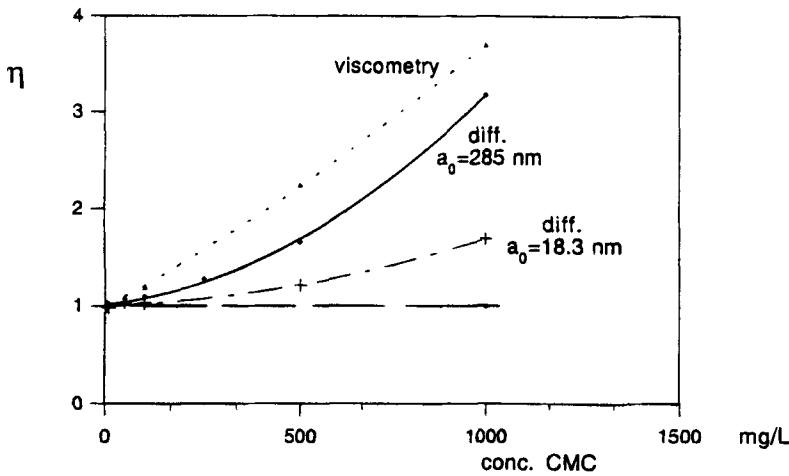


FIGURE 6 Relative viscosities (with respect to water) of CMC solutions as determined by viscometry, diffusion of inert probe particles of 285 nm radius, and diffusion of inert probe particles of 18.2 nm radius, respectively. The (solvent) reference level is also indicated.

given by the measured shear viscosity. We denote the formula as $\eta_{eff}(a, \eta_{rel})$. It turns out that η_{eff}/η_0 increases with particle size approximately as a power law; e.g., for CMC (500K) we find:

$$\frac{\eta_{eff}}{\eta_0} = a^{0.21} \tag{2}$$

We realize that there is no theoretical basis for this expression (other than that the correct limits are observed) but presently we have no better way to carry out the correction for free polymer.

Finally, the corrected particle size a is given by:

$$\frac{D_0}{D} = \frac{\eta_{eff}(a, \eta_{rel})a}{\eta_0 a_0} \tag{3}$$

where D_0 refers to diffusion of a bare particle in solvent and D to diffusion of a particle with an adsorbed layer in a polymer solution; a_0 the radius of the bare particle. The layer thickness δ_h is simply found from $\delta_h = a - a_0$.

The results for four CMC samples with $ds = 0.99$ different in (average) chain length, at pH 3 and in 0.01 M NaCl, are shown in Figure 7. As can be seen, substantial thicknesses are found; the lowest molecular weight produces layers that have a thickness of about 8 nm, independent of concentration, and for the longest chains we find thicknesses as high as 48 nm.

These results cannot easily be reconciled with the picture of flat adsorption that models tend to predict for low ionic strength and appreciable polymer charge density. This is the more surprising since the adsorbed amounts appear to follow these predictions quite reasonably, i.e., clear dependences on pH and ionic strength, and hardly any dependence on chain length. Hence, the layers that are formed by polymers of different molecular

weight contain the same amount of polymer but their hydrodynamic thicknesses at high concentration are widely different. This would suggest a structure with mainly trains and (small) loops having average sizes independent of molecular weight; loops and trains together largely determine the adsorbed amount. The layer thickness must then be determined by a very dilute periphery of long tails, and these are formed more easily from long chains. One possibility is that these tails are the remnants of configurations that the molecules had in solution, and that become partly fixed as a result of some irreversibility of the adsorption. Indeed additional measurements (not presented here) show that the layer thickness depends on the (pH-) history of the samples, which suggests that the adsorption is at least partially irreversible. This may be due to the strength of the ionic bonds that hold the polymer on the oxide surface.

It would therefore make sense to compare the thicknesses reached at high concentration with the size of free polymer coils. A reasonable estimate of this size is the hydrodynamic radius R_h of an equivalent sphere that is readily obtained from the intrinsic viscosities $[\eta]$ using the standard expression $4/3\pi R_h^3 = [\eta]M / k N_{av}$, where $k = 2.5$ is the Einstein coefficient for the viscosity of a dispersion of spheres and N_{av} is Avogadro's number. We find radii of 8, 20, 41, and 48 nm for the CMC samples 30K, 120K, 400K, and 500K, respectively. These are almost equal to the (corrected) thicknesses reached by these samples in CMC solutions of 1000 mg/L, which corroborates the picture sketched above.

CONCLUSIONS

Polyelectrolytes have a strong tendency to adsorb on amphoteric metal oxides. To a large extent this is due to electrostatic effects. As long as the polymer is sufficiently charged (beyond a few percent of charged groups) adsorption occurs on surface sites of opposite charge. Moreover, adsorption can even occur under conditions where the net charge of the

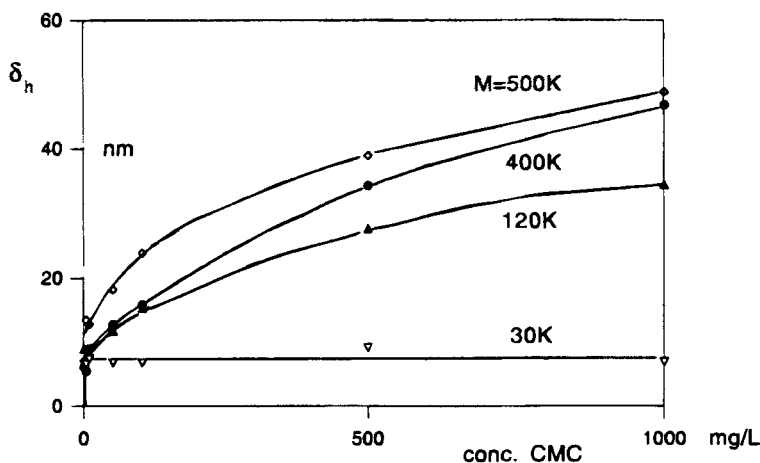


FIGURE 7 Hydrodynamic layer thicknesses of CMC samples with degree of substitution of 0.99 and various molecular weights onto colloidal haematite particles at pH 3 and 10^{-2} M NaCl.

bare oxide surface is not opposite to that of the polymer. Since the surface can adjust its charge density locally, and can provide suitable groups even when the net charge is in the repulsive range, adsorption can still occur. This situation is not unlike that of adsorption onto a neutral heterogeneous surface where adsorption is predicted to occur in spite of an average repulsive potential [26].

Both poly(dimethylaminoethyl methacrylate) and carboxymethylcellulose display the typical pH dependence that is expected on the basis of a largely electrostatic adsorption mechanism. In addition, CMC would seem to benefit from a non-electrostatic mechanism.

The thickness of adsorbed polyelectrolyte layers can be readily determined by means of diffusion measurements on colloidal particles. However, the friction factor in the Stokes-Einstein equation that is used to evaluate the data should be considered carefully. Neither the solvent viscosity, nor the viscosity of the polymer solution in which the colloidal particles diffuse provide the appropriate value. It is necessary to determine the effective friction by means of inert (non-adsorbing) probe particles of approximately the same size as the adsorbent particles.

In this way we obtained hydrodynamic layer thicknesses for CMC adsorbed on haematite as a function of polymer concentration and molecular weight. Substantial layer thicknesses are found. Moreover, the data display a clear dependence on molecular weight which is absent in the adsorbed amount data. This result is contradictory to the picture of flat adsorption that emerges from theory for the case of low ionic strength and high polymer charge density. We interpret the thickness in terms of a very dilute periphery of long tails that form during adsorption in a presumably irreversible manner.

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References and Notes

1. H. G. M. van de Steeg, M. A. Cohen Stuart, A. de Keizer, and B. H. Bijsterbosch; *Langmuir* **8**, 2538 (1992).
2. B. C. Bonekamp, J. Lyklema; *J. Colloid Interface Sci.*, **113**, 67 (1986).
3. H. A. van der Schee and J. Lyklema; *J. Phys./Chem.*, **88**, 6661 (1984).
4. O. A. Evers, G. J. Fleer, J. M. H. M. Scheutjens, and J. Lyklema; *J. Colloid Interface Sci.*, **111**, 446 (1986).
5. M. R. Böhmer, O. A. Evers, and J. M. H. M. Scheutjens; *Macromolecules* **23** 2288 (1990).
6. M. Muthukumar; *J. Chem. Phys.* **86**, 7230 (1997).
7. R. Varoqui, A. Johner, and A. Elaissari; *J. Chem. Phys.*, **94**, 6873 (1991).
8. M. A. Cohen Stuart, G. J. Fleer, J. Lyklema, W. Norde, and J. M. H. M. Scheutjens; *Adv. Colloid Interface Sci.*, **34**, 477 (1991).
9. G. J. Fleer, M. A. Cohen Stuart, J. M. H. M. Scheutjens, T. Cosgrove, and B. Vincent; "Polymers at Interfaces", Chapman & Hall, London 1993, Ch. 5 (neutral homopolymers) and Ch. 7 (polyelectrolytes).
10. G. Durand-Piana, F. Lafuma, and R. Audebert; *J. Colloid Interface Sci.*, **119**, 474 (1987).
11. L. G. J. Fokkink, A. de Keizer, and J. Lyklema; *J. Colloid Interface Sci.*, **127**, 116 (1989).
12. J. C. Dijt, M. A. Cohen Stuart, and G. J. Fleer; *Adv. Colloid Interface Sci.*, **50**, 79 (1994).
13. W. N. Hansen; *J. Optical Soc. Am.*, **58**, 380 (1968); J. Lekner, "Theory of Reflection", Martinus Nijhoff Publ., Dordrecht (1987).
14. Th. van den Boomgaard, T. A. King, Th. F. Tadros, H. Tang, and B. Vincent; *J. Colloid Interface Sci.*, **66**, 68 (1978).

15. M. A. Cohen Stuart, F. H. W. H. Waajen, T. Cosgrove, T. L. Crowley, and B. Vincent; *Macromolecules*, **17**, 1825 (1984).
16. G. S. Ullmann, K. Ullmann, R. M. Lindner, and G. D. J. Phillies; *J. Phys. Chem.*, **89**, 692 (1985).
17. G. D. J. Phillies, G. S. Ullmann, and K. Ullmann; *J. Chem. Phys.*, **82**, 5242 (1985).
18. G. D. J. Phillies; *Macromolecules*, **20**, 558 (1987).
19. G. D. J. Phillies; *J. Chem. Phys.*, **93**, 5029 (1989).
20. W. Brown and R. Rymden; *Macromolecules*, **19**, 2942 (1986).
21. W. Brown and R. Rymden; *Macromolecules*, **21**, 840 (1988).
22. A. R. Altenberger, M. Tirrell, J. Dahler; *J. Chem. Phys.*, **84**, 5122 (1986).
23. R. I. Cukier; *Macromolecules*, **17**, 252 (1983).
24. J. Brandrup, E. H. Immergut; *Polymer Handbook*, 3rd Ed., Wiley, 1989.
25. M. Dubois, K. A. Gilles, J. K. Hamilton, P. A. Rebers, and F. Smith; *Anal. Chem.*, **28**, 350–356 (1956).
26. D. Andelman and J. F. Joanny; *J. Phys II France*, **3**, 121 (1993).
27. F. H. Chowdhury and S. M. Neale; *J. Polym. Sci., A* **1**, 2881 (1963).
28. N. K. Khoshla, R. P. Bhagat, K. S. Ghandi, and A. K. Biswas; *Colloids Surfaces*, **8**, 321 (1984).
29. J. M. Kleijn and J. Lyklema; *Colloid Polym. Sci.*, **265**, 1105 (1987).
30. J. Marra, H. A. van der Schee, G. J. Fleer, and J. Lyklema, in "Adsorption from Solution", eds. R. H. Ottewill, C. H. Rochester, and A. L. Smith, Ac. Press. 245 (1983).
31. J. Papenhuijzen, H. A. van der Schee, and G. J. Fleer; *J. Colloid Interface Sci.*, **104**, 530 (1985).
32. M. A. Dahlgren, P. M. Claesson, and R. Audebert; *Nordic Pulp Paper Res. J.*, **8**, 1 (1993).
33. T. Cosgrove, T. M. Obey, and B. Vincent; *J. Colloid Interface Sci.*, **111**, 409 (1986).
34. Y. Adachi, M. A. Cohen Stuart, and R. G. Fokkink, *J. Colloid Interface Sci.*, submitted (1994).