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## Polyelectrolyte adsorption

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**Résumé.** — L'adsorption de polymères non chargés à partir d'une solution est maintenant assez bien comprise : on dispose d'informations sur la structure de la couche adsorbée, ainsi que sur l'effet des principaux paramètres tels que masse moléculaire des chaînes, effets du solvant et des interactions polymère-surface. On observe une certaine convergence entre théories et expériences. Par contre l'adsorption de polyélectrolytes est loin d'être comprise parce qu'elle est très complexe. En plus des paramètres mentionnés ci-dessus, il faut considérer trois autres variables qui décrivent les propriétés électrostatiques de la surface adsorbante, celles du polyélectrolyte, et la concentration de petits ions. La théorie en est encore à ses débuts, d'autant plus que certains des états observés sont peut-être métastables. Nous présentons les questions importantes dans ce domaine, et nous passons en revue les résultats expérimentaux. Nous discutons aussi quelques approches qui semblent actuellement prometteuses.

**Abstract.** — The adsorption of uncharged polymers is, due to numerous efforts over past decades, fairly well understood. Some insight exists into the structure of the adsorbed layer, and the effect of the important parameters molecular weight, solvency and polymer/surface interaction has been investigated. Theory and experiment are beginning to converge. The polyelectrolyte adsorption process, however, is far from understood, because it is so very complex. In addition to the aforementioned parameters, three more variables are involved, namely the electrostatic properties of the adsorbent surface, those of the polyelectrolyte, and the concentration of small ions. It is the aim of this contribution to highlight important questions and to review the available experimental data. Theory is still in its infancy, the more so since some data are indicative of metastable states. Some promising approaches will be discussed.

### 1. Introduction.

Flexible polymers have a large number of internal degrees of freedom. The structure and shapes they assume are therefore strongly influenced by external force fields and the study of these effects is a very rewarding one. Much attention has been given to the behaviour of uncharged flexible polymers at phase boundaries. These systems therefore may serve as a useful reference for a discussion of polyelectrolyte adsorption. Let us summarize a few relevant results.

It is widely accepted that physisorption of individual macromolecules to an adsorbent (substrate) occurs through multiple anchoring points, separated by chain sections sticking out into the solution as « loops » (attached at both ends) and « tails » (attached at one end). The adsorbed molecules interpenetrate laterally to an extent determined by the surface density of available adsorption sites, the strength of the segment/surface interaction, and the

strength of the effective segment/segment interaction. A *segment density profile* normal to the interface develops, which is the resultant of all these forces, and which for physisorbed polymers, falls monotonously with increasing distance until the polymer concentration in the solution is reached.

The shape of this profile has been studied experimentally by neutron scattering [1-4]. An alternative is to study the thickness of the adsorbed layer, operationally defined in terms of a particular experiment: optical techniques (ellipsometry [5], reflectometry [6]), hydrodynamic techniques (diffusion of colloidal particles [7], flow through capillaries [8], electrokinetics [9]) and « disjoining pressure » techniques (surface forces balance [10], osmotic pressure of concentrated colloidal dispersions [11]) have all been used to measure thickness. Especially the latter two techniques have revealed thick adsorption layers for high molecular weight polymers: values up to 200 nm have been found [12]. There is

now much evidence that these large values are a consequence of the presence of long tails [13].

Theoretical approaches found useful starting points in theories for polymer solutions, be it either a version of the classical mean field theory [14] or (for good solvents) the scaling theory [15]. The main focus has been on profile shapes. In addition, detailed calculations on conformations were carried out within the mean field approximation [16]. Among other things, these calculations showed that « tails » arise naturally as a consequence of the adsorption layer.

A further important theoretical result for uncharged chains is that the molecular weight dependence of several observables (adsorbed amount, thickness) is rather different for good and for poor (theta-) solvents. In good solvents the adsorbed amount is nearly constant (provided the molecules are long enough [14, 15]) and the thickness increases rather strongly when the layers approach saturation [12]. In theta solvents, however, the adsorbed amount increases continuously and the thickness increases much more gradually [12, 14]. The rather general mean field theory has been quite successful in rationalizing a large variety of data. The reason for this, not entirely anticipated, success is now somewhat better understood with the help of a generalized polymer solution model initiated by Schaefer [17, 18]. A critical review of the available data has recently appeared [19].

Let us now turn to polyelectrolytes. Here the situation is much less consolidated. A reasonable first-order theory for the expansion of isolated coils in dilute solution was only recently proposed [20]. We know now that highly charged polyions are rather stiff at low ionic strength. On top of this, there is the already classical problem of the electrical double layer close to the polyion and its relation to titration data and zeta-potentials [21]. For semi-dilute solutions of polyions, there is at best a number of conjectures [22], the concentrated solution is far from understood. It is therefore not surprising that only little theoretical work on adsorption has been done. Also the number of meaningful fundamental studies with well-defined polyelectrolytes on well-defined substrates is regrettably small. Nevertheless we will try to draw some conclusions from the studies carried out so far.

## 2. Theory.

A logical way towards an adsorption theory for charged polymers is to start from one for uncharged polymers and to incorporate the electrostatic free energy in the partition function. The neutral polymer theory takes the changes in conformation upon adsorption (hopefully correctly) into account, and all that is added is the electrostatic segment/segment and segment/surface interactions.

Hesselink was the first to carry out such a program [23]. However, he based his calculations on the theory of Hovee [24] who had simplified the free energy function considerably by dropping the shape of the segment density profile as a variable: he assumed it was exponential and thereby obtained an implicit equation containing only the fraction of bound segments and the adsorbed amount as variables. Hesselink had to do a similar thing: he assumed a simple two-step function for the density profile consisting of a « surface layer » (density  $\rho_s$ ) and a « loop layer » (density  $\rho_l$ ). He fixed  $\rho_l$  on the value of the average density of a free coil according to Hermans and Overbeek [25]. In this way the thickness is retained as a variable. Although this may seem reasonable, one is completely misled by the preassumed profile shape. In fact, thicknesses were predicted of the order of microns, larger even than that of the extended chain length of the molecules.

The essential step is to allow the profile to adjust itself. This can be done easily in a mean field lattice model as used by Roe [26] and by Scheutjens [14] and was indeed done by Van der Schee [27, 28]. The important finding is that for strongly repelling, charged, segments the free energy minimum corresponds to a very *thin* layer rather than to a swollen one. Although this may seem surprising, it is completely in line with the result for uncharged polymers that in good solvents the profile decays more steeply than in poor solvents [14, 16]. In other words, water (dilute saline solution) is an extremely good solvent for polyions. An example of a profile is shown in figure 1, where for comparison we also show the profile for a neutral, but otherwise similar polymer.

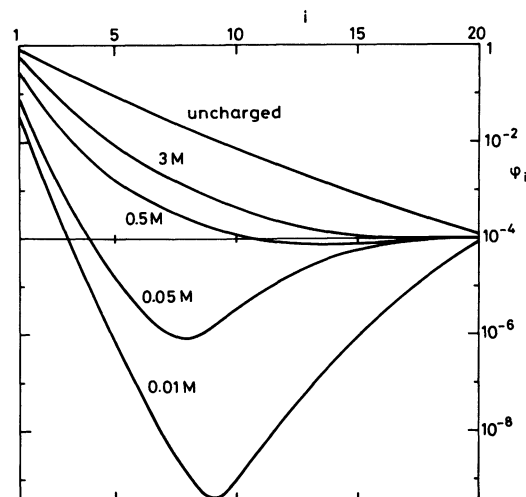


Fig. 1. — Segment density (volume fraction) profiles of a strong polyelectrolyte near an uncharged surface, calculated by the Van der Schee theory. For comparison, the profile for an uncharged polymer is also shown. Salt concentrations are indicated at each curve. Chain length 2 000 segments.  $\phi_i$ : volume fraction;  $i$ : distance from wall.

Two observations should be made here. First, the calculations are done under the assumption that the electrostatic contributions to the polyion rigidity play a minor role at the surface, in other words, the chain is apparently flexible. This may be questionable in view of the strong stiffening effects observed in the bulk solution. However, (i) due to the accumulation of polymer at the surface, screening effects are enhanced and the chain is presumably less stiff, (ii) the fact that a flat structure is predicted means that the conformational entropy plays a minor role, so that an inaccurate estimate of that contribution to the total free energy has little effect on the position of the free energy minimum.

Secondly, for the calculation of the electrical contributions the spatial distribution of all charges must be known, and since the polymer segments are placed on a lattice the question arises whether or not the polymer charges and/or the countercharges should be « smeared out » or not. The answer is that it does not matter very much : the result is independent of the assumptions made here. It seems justified to take a closer look at the Van der Schee model [27].

As we have already mentioned, adsorption layers at low ionic strength are thin, much thinner than for the corresponding uncharged polymers. Consequently, most observables (adsorbed amount, thickness) depend little on molecular weight. On neutral, or identically charged surfaces, adsorption occurs only if segments experience some non-electrostatic attraction by the substrate. As a rule adsorption isotherms are of the « high affinity » type ; adsorption increases with increasing salt concentration and decreasing polymer charge density. In the same direction, molecular weight effects become more pronounced.

On an oppositely charged surface the amount adsorbed is close to (but slightly higher than) the amount of surface charge that the polymer can compensate, so that charge reversion occurs as a

result of adsorption. The adsorption of weak polyelectrolytes is further complicated by the fact that their charge density is influenced by the local environment, i.e. the charge density of the polyion may increase or decrease upon adsorption. This case has been studied (using the Van der Schee model) by Evers [29]. An interesting observation is that the adsorbed amount as a function of pH for a weak polyelectrolyte adsorbing on an oppositely charged surface goes through a maximum (Fig. 2). This is because charging the polymer initially results in a stronger polymer/surface attraction and concomitant increased adsorption, but this increase is more than off-set by the strong lateral repulsion which builds up when the polymer charge density increases further.

### 3. Experimental data.

Before discussing experimental data it should be emphasized that a comparison with theoretical results is only meaningful if the data obtained corresponds to an adsorption equilibrium. Below we shall discuss a few observations which suggests that metastable states (rather than a well-defined equilibrium) may sometimes occur. A second remark concerns the interaction between small counterions and the polyion. Theoretically, this interaction is supposed to be purely electrostatic, without any change in the hydration state of the ions, etc. However, it is well known that many ions, especially the divalent metal ions have a strong tendency to interact specifically with negative charged groups, notably carboxylic groups [30]. Specific interactions can have large effects on polyion adsorption but general models cannot easily cope with them.

Finally let us consider a selection of experimental data for a few simple polyelectrolytes.

### 4. Polystyrene sulphonate (PSS).

PSS is a highly charged, well defined strong polyion. Its adsorption on silica [31], hematite [32], polystyrene latex (both positive and negative) [33],  $\text{CaCO}_3$  [34] and single crystals of polyoxymethylene (POM) [32, 35] and on platinum [36, 37] has been studied.

Two remarkable results are worth mentioning. Firstly, segment density profiles on PS latex have been measured by neutron scattering [33] for two molecular weights ( $74 \times 10^3$  and  $780 \times 10^3$ , respectively) and an ionic strength of 0.5 M. Both profiles show that most of the polymer is confined in a *thin* layer (2 and 15 nm, respectively). Corresponding profiles for uncharged polymers would be expected to be at least 4 times thicker (Fig. 3). Secondly, the adsorption of PSS on POM (neutral) and on silica (negative) at an ionic strengths of about 0.5 M was hardly dependent on molecular weight, whereas at

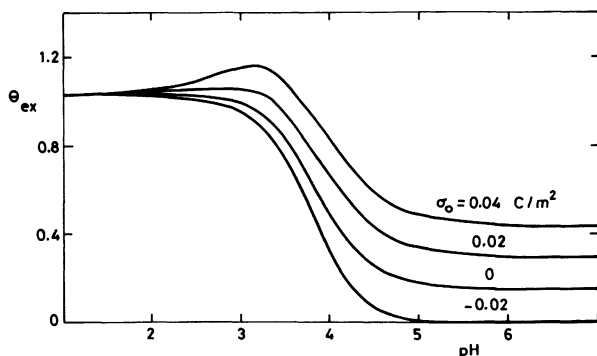


Fig. 2. — Adsorbed amount  $\theta_{ex}$  of a weak polyacid with  $pK_0 = 4$  as a function of pH for various surface charge densities  $\sigma_0$ . Chain length 500 segments, salt concentration 1 M (from Ref. [29]).

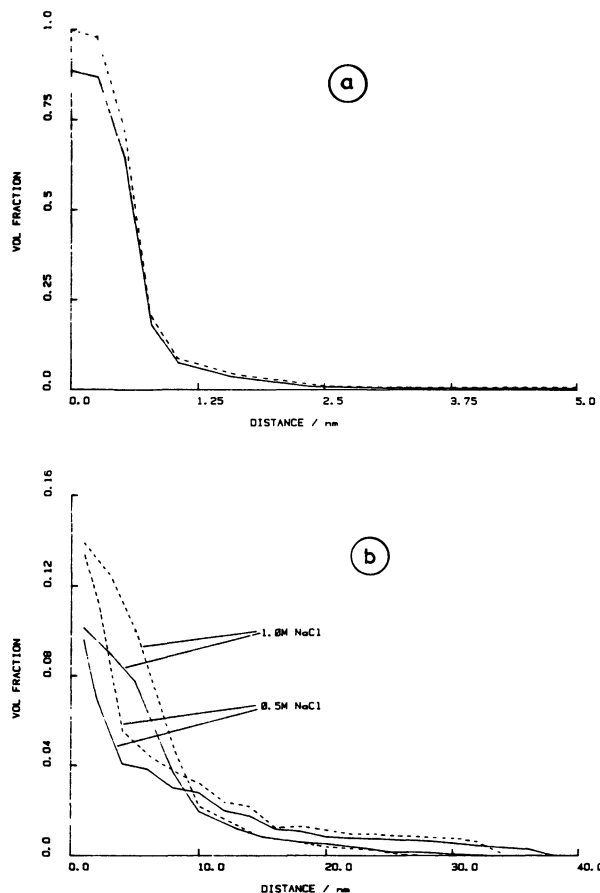


Fig. 3. — Segment density profiles obtained by small angle neutron scattering (from Ref. [33]). a) PSS ( $MW 74 \times 10^3$ ) adsorbed from 0.5 M NaCl : (—) on positive PS latex, (---) on negative PS latex. b) PSS ( $MW 780 \times 10^3$ ) adsorbed from 0.5 and 1.0 M NaCl, respectively : (—) on positive PS latex, (---) on negative PS latex.

ionic strength of 2 to 3 M the molecular weight effect was very pronounced (Fig. 4). The effects of ionic strength on the adsorbed amount and the segment density profiles are in agreement with the Van der Schee theory. An unexplained feature, however, is the shape of the adsorption isotherms on silica and on POM : these do not show the steep initial rise and almost horizontal plateau which is so characteristic for well fractionated polymers adsorbing on well-defined substrates. Instead, the adsorption increases much more gradually and a distinct plateau was not found in the concentration range studied (Fig. 5). The theory never gives isotherms of this shape [35]. It has been pointed out by Silberberg that adsorption on neutral surfaces, or on surfaces of like charge, is weakened by the electrostatic repulsion between the molecules and by the entropy loss of the counterions, and that this might lead to a rounded isotherm. However, this aspect has been fully accounted for in the theory discussed here, and is in fact responsible for the low adsorption at low ionic strength. Yet,

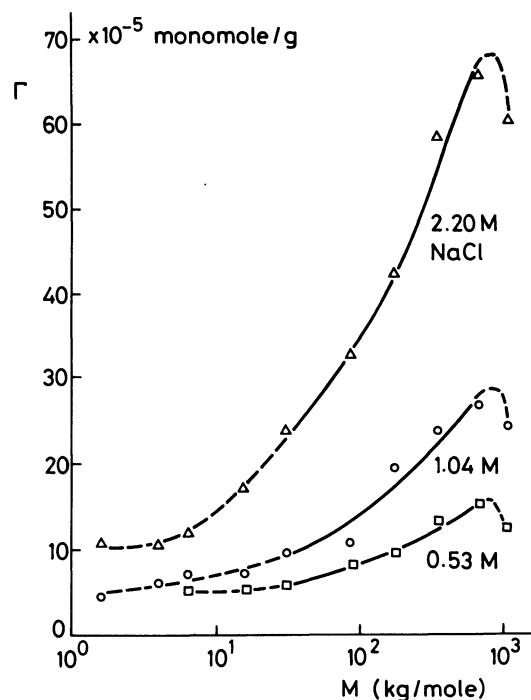


Fig. 4. — Adsorption of PSS on POM crystals as a function of molecular weight, at three NaCl concentrations (the points corresponding to the highest MW are not reliable since the MW of the corresponding sample was not correct) (from J. Papenhuijzen, thesis, Wageningen 1985 ; see also Ref. [35]).

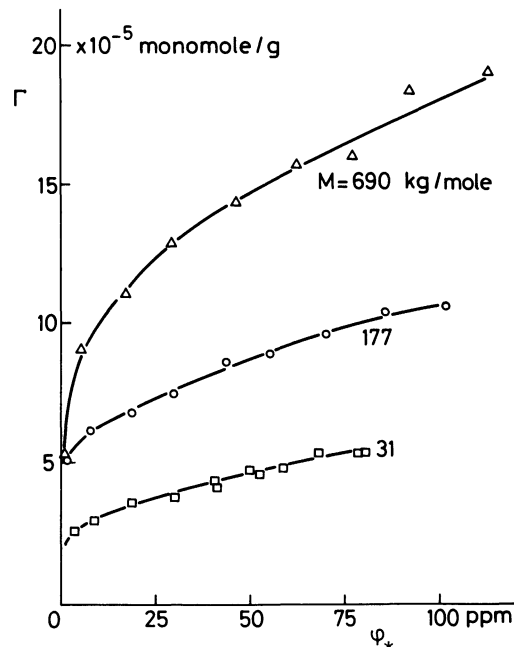


Fig. 5. — Adsorption isotherms of PSS on POM crystals from 0.53 M NaCl solution, for three molecules weights (from J. Papenhuijzen, thesis Wageningen 1985 ; see also Ref. [35]).

calculated isotherms are always of the high-affinity type with a well defined plateau.

A possible explanation is that the adsorbed polyelectrolyte layer is laterally strongly inhomogeneous; this effect is totally ignored in the theory. One might expect that this leads to adsorption isotherms which have more in common with those of monomers, i.e. a more rounded shape.

With respect to thickness of the adsorbed layers, the data are less conclusive. Ellipsometric thicknesses have been obtained for PSS on platinum. Thicknesses decreasing from 80 nm in  $10^{-1}$  M salt to 30 nm in 4.17 M NaCl were reported, for a molecular weight of about  $10^6$ . Hydrodynamic thicknesses have been determined by dynamic light scattering for PS latex; they were (for the comparable molecular weight  $780 \times 10^3$ ) of the order of 40 nm and only slightly dependent on ionic strength. The decrease of (ellipsometric) thickness with increasing salt concentration observed on platinum was not in agreement with a simple scaling picture [37] (Fig. 6).

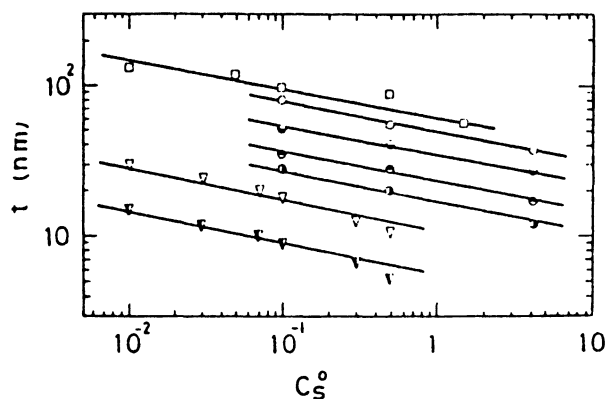


Fig. 6. — Double-logarithmic plots of ellipsometric thickness,  $t$  on platinum, as a function of salt concentration ( $M$ )  $C_s^0$ , for various PSS samples (circles) a polyacrylic acid sample (squares) and two maleic acid-ethyl vinyl ether copolymers (triangles) (from Ref. [37]). Solid lines are drawn with a slope of  $-0.2$ .

### 5. Polylysine (PL).

PL is a strong polybase (intrinsic  $pK_0 \approx 10.6$ ) which can be obtained in well defined fractions with a narrow molecular weight distribution. Its adsorption on glass [38], PS latex [38] and silver iodide (AgI) crystals [27, 39] was studied in detail, and some results on mica were obtained [40].

As with PSS, the adsorbed amount at low ionic strength was found to hardly depend on molecular weight [38, 39] thus corroborating again a central theoretical result. Also, the enhancing effect of ionic strength on adsorption was very similar to that observed for PSS (Fig. 7). A variable which could be additionally studied was the surface charge density; on glass, adsorption is almost proportional to the charge density [38] (Fig. 8), whereas on AgI adsorp-

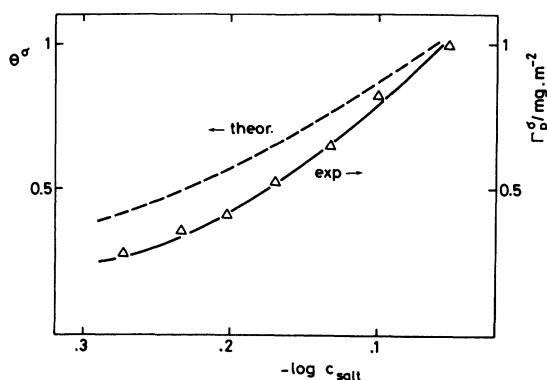


Fig. 7. — Effect of ionic strength on the adsorption of PL on negative AgI. Full curve: experiments (chain length 300 monomers,  $pAg = 11$ ,  $pH = 6$ ). Dashed curve: Van der Schee theory (chain length 300 segments) (from Ref. [39]).

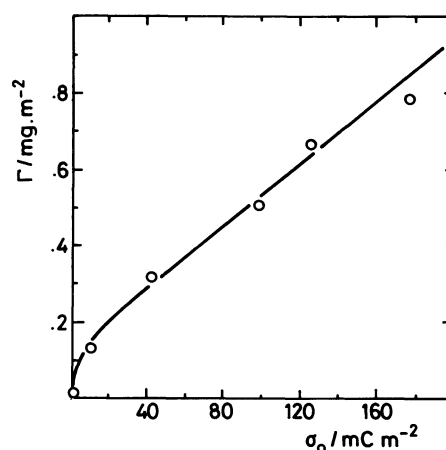


Fig. 8. — Adsorption of poly-L-lysine on silica (aerosil  $0 \times 50$ ) as a function of  $\sigma_0$  in 0.01 M NaBr (from B. C. Bonekamp, thesis, Wageningen 1984).

tion was already found on a slightly positive surface, but increased likewise as the surface became first less positive and then more negative [39]. Such behaviour is intuitively expected and also in line with the Van der Schee theory.

Further information on the conformation of adsorbed PL was obtained from conductivity studies. Adsorption in all cases tended towards a slight superequivalency with respect to the charged groups on the surface, which is consistent with a rather, but not entirely, flat conformation [38]. However, the question whether or not long tails can develop at plateau adsorption cannot be answered from these data. There is a strong need for reliable thickness measurements.

Some information on thickness is obtained from measurements carried out with a surface force balance, for mica surfaces covered with PL (molecular weight  $9 \times 10^4$ ) in dilute  $KNO_3$  [40]. After

incubation of the bare mica with the PL solution a repulsion was first observed at a distance of 120 nm. When the surfaces were brought together and then separated again, a force/distance curve was obtained which did not extend beyond 25 nm (Fig. 9). Apparently, the structure of the layer had changed as a result of compression. The authors explained their finding by assuming that some long, but metastable, tails or loops had been formed during the adsorption process. When forced over the barrier, these loops or tails can adsorb, thus reducing the « steric » thickness of the polymer layer. In this context, it is interesting to note that the Van der Schee-theory predicts, for adsorption on an oppositely charged surface, a repulsive zone in the electrical potential, situated at the periphery of the adsorbed layer (Fig. 10) [27]. This repulsive zone might provide the barrier that stabilizes the metastable tails. A recent theoretical paper seeks to describe the process leading to this situation in terms of sequential adsorption [41].

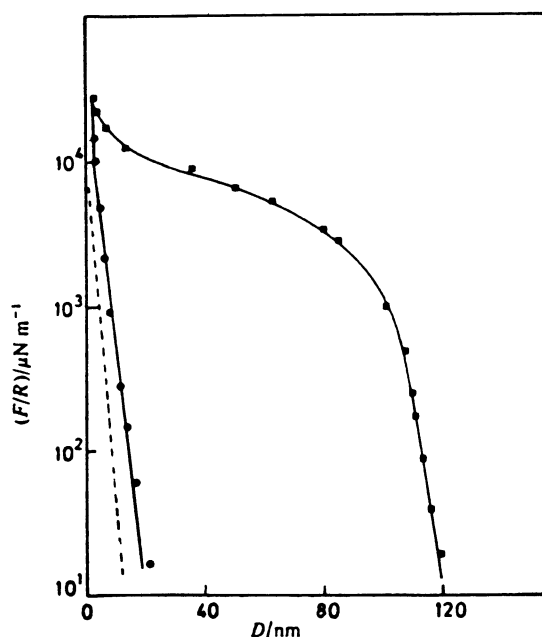


Fig. 9. —  $(F/R)$  versus distance ( $D$ ) for two mica surfaces in poly-L-lysine solution ( $10 \text{ mg/dm}^3$ ) at  $10^{-3} \text{ M KNO}_3$  and  $\text{pH} = 3$ . Squares : first approach ; circles : first withdrawal. Dashed curve : electrostatic force between bare mica surfaces in  $10^{-3} \text{ M KNO}_3$  and  $\text{pH} 3$  (from Ref. [40]).

The reversibility issue is also at stake in a few experiments for PL on AgI where, after initial adsorption, the surface charge of the AgI was suddenly changed in order to produce desorption. Short chains did indeed desorb fully within an hour, but for long chains desorption was extremely slow and, although followed for several days, never came to completion during an experiment [42]. We may

conclude with the caveat that the effect of sample history on polyelectrolyte adsorption data should not be overlooked.

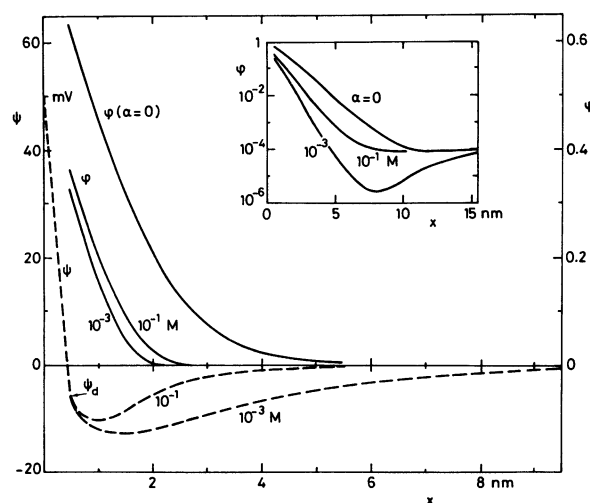


Fig. 10. — Electrical potential (dashed curves) and segment density profiles (full curves) for a strong polyelectrolyte adsorbing on an oppositely charged surface at  $10^{-1}$  and  $10^{-3} \text{ M}$  electrolyte, respectively. The inset shows segment density profiles on a semi-logarithmic scale (see also Fig. 1). Chain length : 100 segments.

## 6. Polyacrylic acid (PAA) and polymethacrylic acid (PMA).

PAA and PMA are well known weak polyacids. Adsorption of PAA on  $\text{TiO}_2$  [43, 44] has been studied. Some adsorption took place on negative  $\text{TiO}_2$  ( $\text{pH} 9.8$ ) but the adsorption increased much by making the surface more positive [43]. Very weak adsorption of PMA on negative AgI was also observed and could be increased by making the AgI more positive [44] (Fig. 11). Some attention in these studies was given to the effect of divalent metal ions

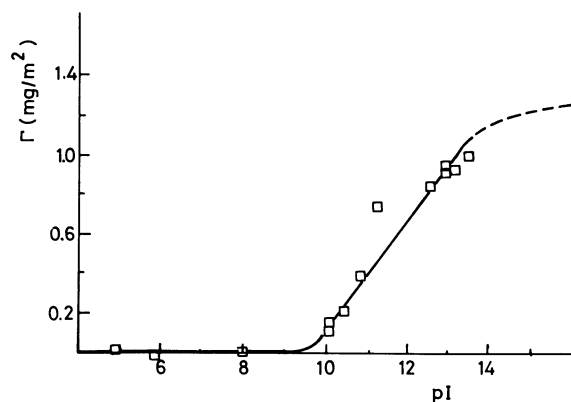


Fig. 11. — Adsorption of PMA from  $16.5 \text{ mmol KNO}_3$  on AgI as a function of concentration of potential determining ion ( $\text{I}^-$ ) (from Ref. [44]).

(Ca<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>) on adsorption. It was very generally found that in the presence of such ions adsorption was strongly enhanced [43, 44]. This is consistent with the finding that the charge density of PAA in solution is strongly reduced by these ions. As we have seen, that is a favourable situation for adsorption. More systematic data on adsorption of weak polyelectrolytes are most welcome, especially with respect to the effects of pH and surface charge.

### Conclusions.

Adsorption layers of neutral, long polymers are usually thick and fluffy, but polyelectrolytes form thin and compact layers. In this respect, polyelectrolytes may be considered as polymers adsorbing from

an extremely good solvent. Only at very high ionic strength, electrical interactions are sufficiently suppressed and the adsorption is more like that of uncharged polymers. These conclusions can be drawn from experimental data, but are also in good agreement with a mean field lattice theory proposed by Van der Schee. It is not yet clear to what extent long tails are formed as a result of adsorption. Some thickness data are indicative of such tails, but they may well be metastable, because an electrostatic barrier blocks their adsorption. Such a situation is reminiscent of what happens in electrostatically stabilized colloidal dispersions and calls for description of adsorption in terms of a process rather than an equilibrium.

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