

**Adsorption of polyelectrolytes and charged
block copolymers on oxides
Consequences for colloidal stability**

Foar ús Heit

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**Adsorption of polyelectrolytes and charged
block copolymers on oxides
Consequences for colloidal stability**

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Stellingen

De beschrijving van ladingen in het SF-model voor polyelectrolytadsorptie is niet discreet genoeg.

Dit proefschrift, hoofdstukken 2, 3, 4 en 5.

Geladen diblokcopolymeren met twee wateroplosbare blokken vormen bij adsorptie nooit een dikke én sterk geladen laag.

Dit proefschrift, hoofdstukken 4 en 5.

In de tijd stabiele multilagen van polyelectrolyten zijn niet stabiel in thermodynamische zin.

Dit proefschrift, hoofdstuk 6.

Het ontstaan van peuken bij het hakken van glasvezels duidt op een te sterke interactie tussen de glasvezelfilamenten.

Het onder de aandacht brengen van misstanden door middel van publieks-onvriendelijke acties werkt averechts.

Het houden van schapen brengt rust in een stressvol bestaan.

De ware kattenliefhebber onderscheidt slechts twee soorten: lieve katten en katten met karakter.

Het beste begin van de dag is een goede nachtrust.

Het groepsgevoel wordt versterkt door zich af te zetten tegen een andere groep, de "tegenpartij".

Thee leent zich beter tot koffiepraat dan koffie omdat thee over het algemeen in grotere hoeveelheden en heter geschonken wordt.

Nederlands is uitstekend geschikt om wetenschap in te bedrijven.

Stellingen behorend bij het proefschrift:

"Adsorption of polyelectrolytes and charged block copolymers on oxides: consequences for colloidal stability" van N. G. Hoogeveen, Landbouwwuniversiteit Wageningen, 2 februari 1996.

1. Introduction	1
1.1 General	1
1.2 Colloidal stability	2
1.3 Adsorption of polymers	4
1.4 Kinetics, equilibrium and reversibility	6
1.5 Aim of the study	7
1.6 Outline of the thesis	7
1.7 References	8
 2. Polyelectrolyte adsorption on oxides: kinetics and adsorbed amounts	 11
2.1 Introduction	11
2.2 Materials and methods	14
2.2.1 Polymers	14
2.2.2 Substrate	15
2.2.3 Other reagents	16
2.2.4 Reflectometry	16
2.2.5 Reproducibility	17
2.3 Results and discussion	18
2.3.1 Kinetic curves	18
2.3.2 Initial adsorption rate	19
2.3.3 Adsorbed amount	25
2.4 Conclusions	36
2.5 References	38
 3. Polyelectrolyte adsorption on oxides: reversibility and exchange	 41
3.1 Introduction	41
3.2 Materials and methods	43
3.2.1 Materials	44
3.2.2 Reflectometry	44
3.2.3 SCF model calculations	45
3.3 Results	45
3.3.1 Reversibility upon dilution	45
3.3.2 Reversibility upon pH-changes	47
3.3.3 Exchange of polymers differing in chain length - theoretical predictions	50
3.3.4 Exchange of polymers differing in chain length - experimental data	52
3.3.5 Competition between neutral polymers and polyelectrolytes	62
3.4 Discussion	64
3.5 Conclusions	66
3.6 References	67

4. The adsorption of charged block copolymers with two adsorbing blocks	69
4.1 Introduction	69
4.2 Materials and methods	71
4.2.1 Block copolymers - polymerisation	71
4.2.2 Block copolymers - characterisation	74
4.2.3 Adsorbent	78
4.2.4 Other reagents	78
4.2.5 Reflectometry	79
4.2.6 SCF-model calculations	79
4.3 Results and discussion	80
4.3.1 Homopolymer adsorption	80
4.3.2 Block copolymer adsorption	84
4.3.3 Effect of block copolymer composition	85
4.3.4 Sequential adsorption experiments	87
4.3.5 Comparison with theoretical calculations	89
4.4 Conclusions	91
4.5 References	92
5. Charged (block co)polymers as stabilisers and flocculants of oxides	95
5.1 Introduction	95
5.2 Materials and methods	97
5.2.1 Materials	97
5.2.2 Methods	98
5.3 Results	99
I. Results for PVP ⁺	99
5.3.1 Adsorption experiments	99
5.3.2 Streaming potential measurements	101
5.3.3 Effect on the colloidal stability	102
II. Results for HMA-AMA block copolymers	104
5.3.4 Adsorption experiments	104
5.3.5 Streaming potential measurements	107
5.3.6 Stability measurements	109
5.4 Discussion	112
5.4.1 Electrostatic stabilisation	112
5.4.2 Steric stabilisation	113
5.4.3 Electrosteric stabilisation	113
5.4.4 Bridging flocculation	114
5.4.5 Mosaic flocculation	115
5.4.6 Charge neutralisation	115
5.5 Conclusions	116
5.6 References	116

6. The formation and stability of multilayers of polyelectrolytes	
6.1 Introduction	119
6.2 Materials and methods	120
6.2.1 Materials	120
6.2.2 Reflectometry	121
6.2.3 Electrophoretic mobility	122
6.2.4 Hydrodynamic layer thickness measurements	122
6.3 Results and discussion	123
6.3.1 Experimental information on multilayer formation	123
6.3.2 Conditions for multilayer formation	125
6.3.3 Stable Multilayers	132
6.4 Conclusions	135
6.5 References	136
Summary	137
Samenvatting	141
Curriculum vitae	145
Nawoord	147

Chapter 1 Introduction

1.1 General

Metal oxides and silicates are by far the most common minerals found in the earth's crust. The use of metal oxides for industrial applications is very diverse, due to the variety of their properties. Huge amounts of oxides are used as raw materials for the production of glass (SiO_2 , Na_2O , CaO , Al_2O_3) and cement (CaO , SiO_2 , Al_2O_3 , Fe_2O_3). Smaller amounts are used in many industrial and household goods like fluorescent lamps (Al_2O_3 , Y_2O_3), ceramic condensers (BaTiO_3), television screens ($\text{Y}_2\text{O}_2\text{S}$, Fe_2O_3 , CoAl_2O_4), catalysts (V_2O_5), batteries (PbO_2), cosmetics (ZnO_2), paper (clay, TiO_2), paint (TiO_2 , Fe_2O_3 , PbO_2 , MnO_2 , ZnO), etc.

Often oxide layers are prepared from colloidal suspensions. For example, fluorescent bulbs and tubes are coated with a layer of oxidic particles, using flow deposition from a concentrated dispersion (sludge). After deposition the solvent is removed by heating and a thin dry coating remains. In order to produce layers with the desired properties it is mandatory to use stable dispersions, as shown in Fig. 1.1. Fig. 1.1a represents the stable situation, which leads to the formation of dense homogeneous layers, whereas in Fig. 1.1b the dispersion is unstable, resulting in more open, coarse, and inhomogeneous layers.

For the production of paper, oxides (clay, TiO_2) are used as fillers to

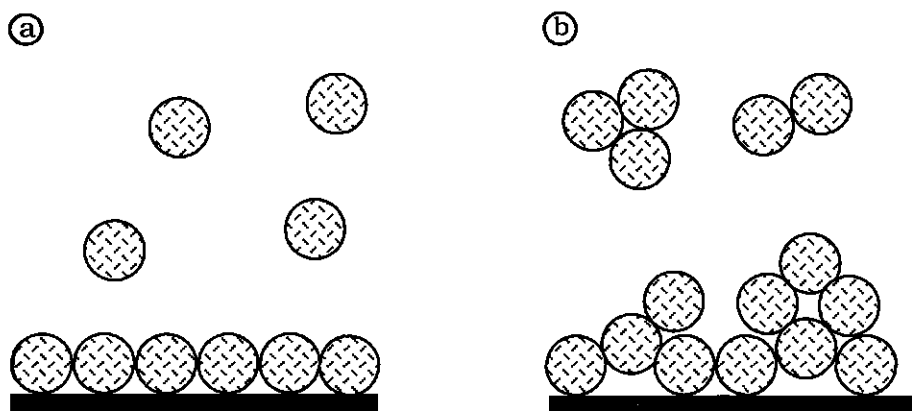


Figure 1.1 The structure of a thin film of oxidic particles formed from a stable dispersion (a) and an unstable dispersion (b).

improve the optical and printing properties. In this case, a somewhat unstable dispersion is required because aggregates of oxidic material are more easily retained by the relatively rough fibre mat.

The examples mentioned above illustrate the importance of the colloidal stability and the need to control it and, if necessary, to modify it. Few systematic studies have been carried out to study the colloidal stabilisation of aqueous oxide dispersions; a lack of knowledge exists in this field. The aim of the present investigation is therefore to study how the colloidal stability of aqueous dispersions can be influenced.

1.2 Colloidal stability

The size of oxidic particles in a dispersion ranges from 10^{-9} to 10^{-5} m, which is the typical size range of colloidal particles. These dispersions are in principle unstable, since the particles attract each other due to van der Waals forces. In order to impart colloidal stability it is necessary to provide some sort of repulsion between the particles. In aqueous solutions there are two main ways to do this: *electrostatically* and *sterically* (Fig. 1.2)¹.

In aqueous solutions oxidic particles usually carry a charge due to the protonation or deprotonation of surface groups. The acquired charge depends on the pH and the ionic strength in the solution, and on the nature of the oxide. Oxides can be characterised by their tendency to take up or release protons. A measure for this tendency is the position of the pH at which the net surface charge is zero (the so-called iso-electric point

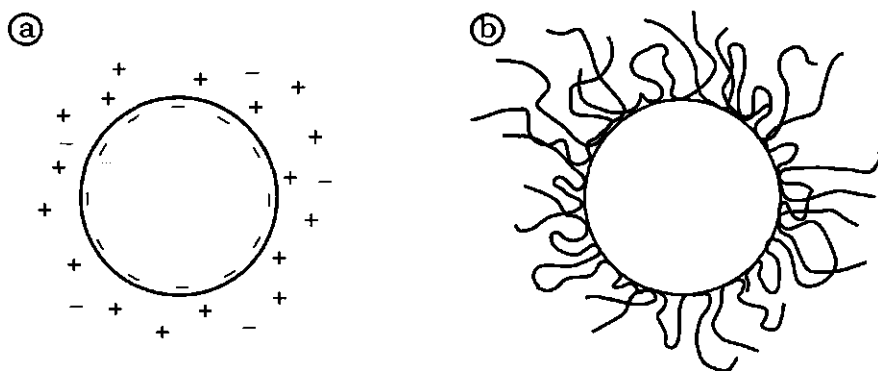


Figure 1.2 Electrostatically (a) and sterically (b) stabilised particles.

or i.e.p.). We thus may distinguish between acidic oxides (such as SiO_2 , i.e.p. ≈ 2), basic oxides (for example, Fe_2O_3 , i.e.p. ≈ 9), or amphoteric oxides (e.g., TiO_2 , i.e.p. ≈ 6).

The presence of charge on the surface of a particle leads to the formation of a diffuse layer of countercharge (Fig. 1.2a), which ensures electroneutrality. When charged particles approach each other, these diffuse layers overlap, which causes a repulsive force, which counteracts the attractive van der Waals forces. The thickness of the diffuse layer depends on the concentration of ions in the medium; at low ionic strength very thick double layers can be found. Electrostatic stabilisation works best when thick highly charged diffuse layers are formed, i.e., when the particles are strongly charged and at a low ionic strength. The dispersion will, however, become unstable close to the iso-electric point (i.e.p.), or when the ionic strength is high.

Steric stabilisation is brought about by adsorbing molecules on to the surface. These molecules form a protective sheath (Fig. 1.2b) which prevents the particles from approaching too closely, since an overlap of the steric layers results in a strong repulsion. The ensuing stability depends on the thickness of the steric layer. Long thin molecules like polymer chains, which can form thick adsorbed layers, are particularly suited as stabilisers. Polymers are long chain molecules that are built from a large number of repeating units, called monomers or segments.

Several kinds of polymers can be used, e.g., neutral polymers, charged polymers (polyelectrolytes) and also copolymers, which are polymers consisting of more than one type of monomer. This type of polymer is interesting since it allows to combine two or more favourable properties into one polymer. Depending on the way the monomers are arranged in a copolymer one distinguishes *random copolymers* (e.g., with a structure AABAABBBBA), *diblock copolymers* (AAAAAABBBBBB), and *alternating copolymers* (ABABABABAB), where A and B represent different monomer types.

Diblock copolymers are expected to be very effective stabilisers for dispersions in non-aqueous systems (e.g., the classical "oily" paints)². From theoretical and experimental studies it has been concluded that the best stability is imparted by a block copolymer with one block that anchors strongly on the surface (the *anchor* block), and one block which protrudes far into the solution (the *buoy* block)³⁻⁵. The respective lengths of the blocks are important: a long buoy block is favourable because it

gives a thick layer, but the anchor block should not be too short in order to obtain secure attachment to the surface. In such systems there is an optimum anchor-to-buoy block ratio, where both the adsorbed amount and the stabilising effect is maximal.

Above, we have indicated that stabilisation of colloids can occur via an electrostatic or a steric mechanism. When (charged) oxidic particles are stabilised by adding (charged) polymer molecules to them, both mechanisms could play a role, because the polyelectrolyte chains are charged but could also provide a steric effect. It now depends on the relative importance of both contributions whether we call the stabilisation *electrostatic*, *steric* or *electrosteric*.

1.3 Adsorption of polymers

Previously, we described how one can modify the stability of particles by adsorbing polymer molecules on to them. Their effectiveness depends largely on the amount of polymer which adsorbs and on the structure of the adsorbed layer. These variables are determined by the interactions governing the adsorption.

Polymer molecules only adsorb at a surface if this process leads to a decrease of the total free energy. For neutral polymers the major contribution to the adsorption energy is the non-electrostatic interaction with the surface, arising from, e.g., hydrogen bonding or hydrophobic interactions. The strength of this non-electrostatic interaction is determined solely by the types of polymer, substrate and solvent. We found that most neutral polymers do not adsorb strongly on oxides from an aqueous environment. Hence, these neutral polymers are not very well suited to act as steric stabilisers for oxidic dispersions.

For charged polymers, also electrostatic interactions affect the affinity for the charged oxide surface. When both polymer and substrate carry groups with the same charge sign, the adsorption is counteracted, whereas the adsorption is stimulated when the signs are opposite. Since the amount of charge on the oxide surface and on the polyelectrolyte can be modified rather easily by adjusting the pH and/or the ionic strength of the solution, we are able to control the adsorbed amount to some extent. For this reason we chose to work with charged polymers.

We studied both homopolyelectrolytes and charged diblock copolymers consisting of one neutral block and one charged block, in order to

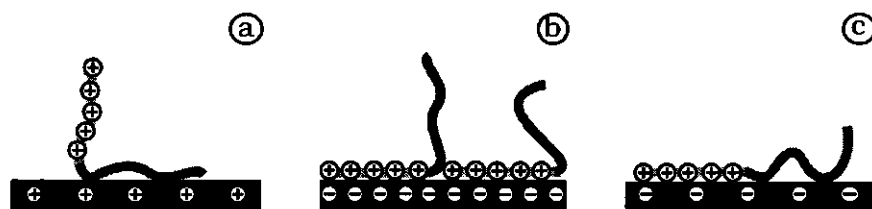


Figure 1.3 Three possible conformations of block copolymers consisting of a charged block and a neutral block adsorbed on oxides.

evaluate the potential of such copolymers as stabilisers for inorganic oxidic particles. Such a block copolymer can have three possible conformations when it adsorbs on a substrate, as illustrated in Fig. 1.3.

In Fig. 1.3a, the surface is positively charged, so that the charged block is repelled by the surface. If the neutral block adsorbs sufficiently strong (high affinity) and the charged one sticks out into solution, both electrostatic and steric stabilising mechanisms could be active, leading to electrosteric stabilisation.

In Fig. 1.3b the surface is negatively charged. Now the charged block adsorbs, due to the favourable electrostatic interaction with the surface. If the charged block adsorbs more strongly than the neutral block it may displace the neutral block from the surface. The latter block will then form uncharged hairs which could cause steric stabilisation. Whether or not there is also an electrostatic contribution to the stability of the system depends on the net charge in the system, *i.e.*, the sum of the surface charge and the adsorbed charge.

In Fig. 1.3c an intermediate situation is sketched in which both blocks adsorb on the surface and no hairs protrude into the solution. In this case no steric stabilisation takes place and it depends on the net charge, whether or not the system is (electrostatically) stable.

From the discussion of Fig. 1.3 we can deduce some important parameters which determine the effect of adsorbed (block co)polymers on the stability of a dispersion. For steric stabilisation it is important to have many long tails sticking out into solution. Therefore, knowledge about the *structure* of the layer (which block protrudes into the solution, how thick is the layer) and about the *adsorbed amount* is needed. Electrostatic contributions are mainly determined by the net charge of the system; structural aspects of the layer will then be less important. The net charge is given by the sum of the *surface charge* and the *adsorbed polymer charge*

(i.e., the adsorbed amount times the charge per polymer molecule). When the net charge is zero the surface charge is precisely compensated by the adsorbed charge (*charge compensation*).

1.4 Kinetics, equilibrium and reversibility

Another important parameter which must not be neglected is time. Several processes take place immediately after mixing polymer and dispersed particles. The mixing of both solutions takes some time, but the adsorption of polymer onto the particles is usually even slower. Moreover, when the particle dispersion is unstable, the formation of aggregates in the solution is also a time-dependent process. The kinetics of these various processes can be very important for the outcome of an experiment. For example, if the formation of aggregates is very fast compared to the adsorption process, then some aggregates will be formed before the system can be stabilised, and these aggregates are not easily redispersed.

The adsorption can in itself be thought of to consist of three processes: transport of polymer from the bulk of the solution to the surface of the particle, attachment to the surface, and reorganisation of the adsorbed molecule. By measuring the kinetics of adsorption under various conditions, one could deduce which of these steps is most time-consuming.

When the outcome of an experiment depends on the kinetics of the various steps the system is not in equilibrium. In principle every system strives to attain equilibrium, which is characterised by a minimum free energy. The kinetics of a process determine, however, how fast the equilibrium state is attained. Up to date, there is no theoretical model yet describing the kinetics of polyelectrolyte adsorption. There do exist several theoretical models for the equilibrium properties of polyelectrolytes in solution and at interfaces². Such theoretical models are very useful since they can help us understand the system better. A comparison between theory and experiment is only justified when it has been established that the experimental system has reached its equilibrium state.

A way to check whether or not equilibrium is attained is by looking at the reversibility of the process (see Ch. 3). For example, when after adsorption the pH and/or the ionic strength of the medium are changed, the system has to adapt itself to the new situation. Then the adsorption

after this indirect route can be compared with direct adsorption under the required conditions. When the system is in equilibrium both results should be identical.

1.5 Aim of the study

The aim of this study is to find out how the addition of charged polymers affects the stability of oxidic dispersions. Moreover, we want to know how this effect on the stability is related to the adsorption properties of the charged polymers.

The central items are:

- How does the final adsorbed amount depend on the experimental parameters (pH, ionic strength, block copolymer composition)?
- What is the structure of the adsorbed layer and how does it depend on the experimental parameters?
- How does the presence of a layer of adsorbed polymer affect the stability of oxidic dispersions?
- Can we use charged polymers and/or charged block copolymers to control the stability of oxidic dispersions?
- Are the systems in equilibrium?
- How well do theoretical (equilibrium) models predict the results?

In order to answer these questions the adsorption properties of charged polymers on oxides and their effect on the stability of oxidic dispersions were systematically investigated. Well-defined oxide substrates and well-characterised polymer samples were used to limit the number of uncertainties in the experiments.

1.6 Outline of the thesis

In Chs. 2 and 3 we describe the adsorption behaviour of strong and weak *homopolyelectrolytes* on oxides.

In Ch. 2 we study how the kinetics of the adsorption and the final adsorbed amount depend on typical electrostatic parameters such as the pH and the ionic strength of the solution. Also, we examine how the polymer and surface charges determine the adsorbed amount. We show that upon adsorption *overcompensation* of the surface charge is found. The overcompensated surface charge is partly neutralised by an adjustment of the surface and polymer charges.

In Ch. 3 we look at the reversibility of polyelectrolyte adsorption and examine whether or not adsorbed polyelectrolyte molecules can be displaced by other polymer molecules coming from the solution (exchange). We show that the systems under investigation are not very reversible due to slow reconfiguration processes on the surface and evaluate how this affects the structure of the adsorbed layer, for which we present a model.

In Ch. 4 the synthesis and the properties of a new type of *charged block copolymer* are described. We investigate the adsorption of these molecules on oxides and deduce in what conformation the block copolymers are adsorbed.

In Ch. 5 we examine the effect of polyelectrolytes and charged block copolymers on the colloidal stability of oxide dispersions. Upon adsorption of these additives both stabilisation and destabilisation can occur, depending on the dosage and the properties of the additives. These observations are translated into some recommendations for better control of the colloidal stability in the presence of charged (block co) polymers.

Finally, in Ch. 6, we exploit the fact that upon adsorption of strongly charged polyelectrolyte molecules overcompensation of the surface charge occurs. Because of this overcompensation, addition of positively and negatively charged polyelectrolytes (in alternated order) to a solid surface leads to the formation of multilayers of polyelectrolytes.

Such multilayers can be used to study the complexation between anionic and cationic polyelectrolytes, since the (electrostatic) interaction between both polymers determines the stability and the stoichiometry of the multilayer structure. Knowledge about the interactions between polyelectrolytes might be informative for the behaviour of complex (industrial) dispersions where more than one type of polyelectrolyte is present.

1.7 References

- (1) D.H. Napper, *Polymeric stabilization of colloidal dispersions*, Academic Press, London, 1983.
- (2) G.J. Fleer, M.A. Cohen Stuart, J.M.H.M. Scheutjens, T. Cosgrove, and B. Vincent, *Polymers at interfaces*, Chapman & Hall, London, 1993.
- (3) C.M. Marques and J.F. Joanny, *Macromolecules*, 1969, **22**, 1454.
- (4) O.A. Evers, J.M.H.M. Scheutjens, and G.J. Fleer, *J. Chem. Soc.*

Faraday Trans., 1990, **86**, 1333.

(5) D.T. Wu, A. Yokohama, and R.L. Setterquist, *Polymer J.*, 1991, **23**, 711.

Chapter 2 Polyelectrolyte adsorption on oxides: kinetics and adsorbed amounts

We have investigated the adsorption of strong polyelectrolytes (quaternised polyvinyl pyridine (PVP⁺) and quaternised dimethylaminoethyl methacrylate (AMA⁺)) and of a weak polyelectrolyte (AMA) onto TiO₂ and SiO₂, using reflectometry. Two characteristic properties, *i.e.*, the initial adsorption rate and the adsorbed amount, were studied as a function of ionic strength and pH. Also the effects of the molar mass of the polymers, of the type and valence of the ions, and of the surface charge and the segment charge were investigated.

We find that the initial adsorption rate is usually determined by the rate of transport to the surface, and therefore by the diffusion coefficient, which depends on the size of the molecule. A polyelectrolyte chain is swollen due to the internal electrostatic repulsion of the charged segments. The repulsion can be decreased (and thus the diffusion coefficient increased) either by an increase of the salt concentration or by a reduction of the segment charge, *e.g.*, by changing the pH for weak polyelectrolytes.

The adsorbed amount is determined by a balance between the interactions in the system. For PVP⁺ adsorbing on TiO₂, these interactions are mainly electrostatic, but on SiO₂ also a non-electrostatic affinity of PVP⁺ for the surface plays a role. The adsorption of AMA⁺ and AMA on TiO₂ is purely electrostatic. Upon adsorption of AMA⁺ the surface is found to adjust its charge. In the case of adsorption of AMA both the surface and the segment charge are regulated. This regulation process reduces the build-up of the electrostatic potential on the surface, and enables more polymer molecules to adsorb.

2.1 Introduction

Polyelectrolyte adsorption is a widely studied subject because of its relevance to many industrial applications^{1,2}. The adsorption mechanism can be thought of as a three-step process: (i) transport from the bulk to the surface, (ii) attachment to the surface, and (iii) rearrangements in the adsorbed layer. The latter process is often quite slow; it could be

responsible for the sometimes claimed irreversibility of polyelectrolyte adsorption³⁻⁵. During the initial stages of the adsorption we only see steps (i) and (ii). When all polymer arriving at the surface immediately adsorbs, the adsorption rate is transport-limited. This occurs in the initial stages of the adsorption of several neutral polymers on SiO_2 ⁶. As the adsorption proceeds, the surface becomes increasingly covered with polymer. At a certain point the adsorption will be hindered. The rate of adsorption then depends also on the attachment process. At an even higher coverage, the rate becomes independent of the transport process and the attachment is completely rate-limiting until the plateau value is reached.

Usually, only the plateau value of the adsorbed amount is studied. The adsorbed amount is determined by the balance between all interactions in the system. The electrostatic ones, which play a key role in polyelectrolyte adsorption, are (i) the interaction between the substrate and the polymer segments, and (ii) the mutual interaction between the charged segments, which always opposes adsorption. On an oppositely charged surface, these interactions favour a flat conformation, in which the segments are mainly situated in trains. In such a conformation the interaction between the segments and the surface is maximised. When the surface charge is compensated, i.e., when the adsorbed charge is just equal to the surface charge, the electrostatic attraction of the segments with the surface is balanced by the repulsion in the adsorbed layer. In many cases the surface charge is overcompensated. The extra polymer charge then causes a net electrostatic repulsion, which at low ionic strength can be very high. This repulsion prevents strong overcompensation of the surface charge at low ionic strength⁷.

Because of the importance of the electrostatic interactions, polyelectrolyte adsorption depends strongly on electrostatic parameters such as the surface charge and the polymer charge, which can both depend on the pH, and the ionic strength. However, also a non-electrostatic affinity for the surface and the solvent quality may play a role. This makes the adsorption of polyelectrolytes a complicated phenomenon. We can illustrate this by focusing on the effects of the ionic strength and the segment charge of a polymer.

Polyelectrolytes adsorbing on an oppositely charged surface experience both an electrostatic attraction with the surface (favouring adsorption) and an electrostatic repulsion within the layer (counteracting adsorption). Therefore, the effect of addition of salt can be rather diverse. Some

authors find the adsorbed amount to increase upon addition of salt^{3,8-10}, others find it to decrease^{8,10}, and even a maximum as a function of the ionic strength has been reported¹¹. Van de Steeg *et al.*¹² showed that the presence of a strong non-electrostatic affinity favours an increase of the adsorbed amount upon addition of salt. It is therefore important to know whether the adsorption is purely electrostatic, or whether other interactions are also present.

Several authors describe the effect of the segment charge of polyelectrolytes adsorbing on oppositely charged surfaces. As discussed above, highly charged polyelectrolytes adsorb till charge compensation. When the segment charge is lowered, more polymer molecules have to adsorb to compensate the surface charge, which leads to a higher adsorbed amount. This continues until at a certain charge a maximum is found; further reduction weakens the electrostatic bond with the surface too much, and the adsorbed amount decreases. Such a maximum in the adsorbed amount as a function of the segment charge was found both experimentally^{8,10,13,14} and theoretically^{12,15}.

In this chapter we study the adsorption of polyelectrolytes on oxides. The main questions in our investigation are:

- (i) Is the rate of adsorption initially limited by the attachment process or is it determined by the transport in solution?
- (ii) How is the adsorption influenced by typical electrostatic parameters like pH and the ionic strength?
- (iii) Do the polymer and surface charge change as a result of adsorption, and if so, how does this affect the adsorption?
- (iv) Is the adsorption determined by electrostatics alone, or are there additional driving forces?

In order to answer these questions, we measured for strong and weak polyelectrolytes the amount adsorbed on oxides as a function of time. We consider two characteristic parameters: (i) the initial adsorption rate, which gives insight into the transport and attachment properties of polyelectrolytes for a bare surface and (ii) the adsorbed amount after 20 min., which is indicative for the adsorption capacity, and therefore tells something about the interactions in the system. The ionic strength and the pH were the main variables in the experiments. In some cases, however, we also varied the type and valence of the cations, the substrate, the type and the molar mass of the polymer, and the segment and surface charge.

2.2 Materials and methods

2.2.1 Polymers

We used quaternised polyvinyl pyridine (PVP⁺, Rochrom, the Netherlands), and untreated and quaternised polydimethylaminoethyl methacrylate (AMA and AMA⁺, respectively). The structural formulas of these polymers are given in Fig. 2.1. AMA was synthesised by Dr. Arnold's group in Halle (Germany) by anionic polymerisation, and AMA⁺ (trade name Kounan Floc K-53PS) was a gift from Dr. Y. Adachi in Tsukuba (Japan).

Both PVP⁺ and AMA⁺ carry a constant charge of one elementary charge per segment, indicated by the superscript "+", whereas AMA bears tertiary amine groups giving it a pH-dependent charge. We measured this charge as a function of pH by a potentiometric titration method. The results are presented in Fig. 2.2 for AMA in solutions of 0.009 and 0.08 mol/kg KNO₃, respectively. Two observations can be made: (i) the pH-range over which the amine groups are titrated is much broader than for monomeric species, and (ii) the pK_a , which is the pH where half of the groups is charged, shifts to a higher value at higher ionic strength. Both effects result from the fact that the segments are connected in a chain. In such a chain when a group is charged, its electric field hampers the titration of neighbouring groups. Upon addition of salt, the electrostatic interaction is screened, which makes the charging of the groups easier.

Some characteristics of the polymers are listed in Table 2.1. The molar mass M_s per segment and the molar mass M_w of the polymer for PVP⁺ include the counterion (Br⁻). For AMA and AMA⁺ the counterion is not

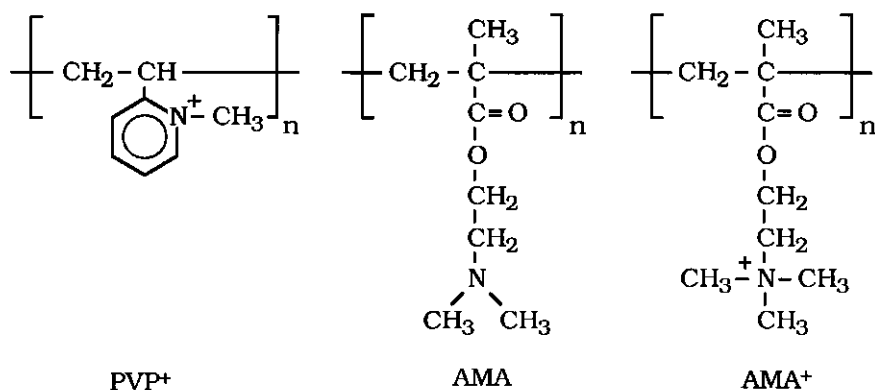


Figure 2.1 Structural formulas of polydimethylaminoethyl methacrylate (AMA), its quaternised form (polytrimethylammoniumethyl methacrylate, AMA⁺), and quaternised poly-2-vinyl pyridine (poly-1-methyl-2-vinylpyridinium, PVP⁺).

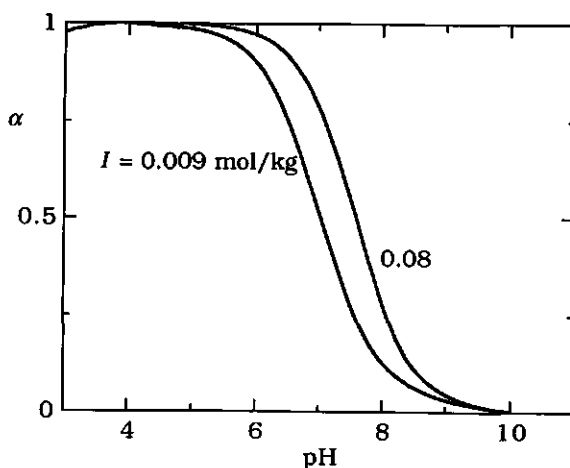


Figure 2.2 Titration data of AMA at two KNO_3 concentrations (indicated).

included in M_s and M_w . The value for M_w/M_n of PVP^+ was specified by the supplier. For AMA this ratio is not known, but since the polymer was made by anionic polymerisation we expect it to be rather monodisperse. The values for the refractive index increments dn/dc were measured with a differential refractometer. Due to differences in the refractivity of charged and uncharged groups, dn/dc for AMA was found to depend on the degree of dissociation; it varied from $0.14 \text{ cm}^3/\text{g}$ (uncharged) to $0.21 \text{ cm}^3/\text{g}$ (charged). For PVP^+ and AMA^+ dn/dc is $0.21 \text{ cm}^3/\text{g}$, independent of pH.

The polymer concentration in all experiments was 10 mg/kg .

2.2.2 Substrate

We used strips of silicon wafers bearing thin layers of TiO_2 or SiO_2 as the

Table 2.1 Characteristics of the polyelectrolytes

polymer	M_s (g/mol)	M_w (kg/mol)	M_w/M_n	charge	dn/dc (cm^3/g)
PVP ⁺	200	2.8	1.13	constant	0.21
PVP ⁺	200	11.6	1.07	constant	0.21
PVP ⁺	200	120	1.03	constant	0.21
AMA ⁺	172	ca. 6×10^3	polydisperse	constant	0.21
AMA	157	20	monodisperse	variable	0.14-0.21

adsorbent. The wafers, which are of the Czochralsky-type, were obtained from Aurel GmbH (Germany). A TiO_2 layer of about 25 nm was deposited by reactive sputtering of Ti in an oxygen atmosphere. This was carried out at Philips Laboratories in Eindhoven (The Netherlands). A SiO_2 layer of about 100 nm was formed by thermal oxidation at 1000 °C for 1 hour. The iso-electric points (i.e.p.) of these layers are around $\text{pH} = 4$ (TiO_2) and $\text{pH} = 2$ (SiO_2), as determined from streaming potential measurements. The i.e.p. found for TiO_2 is lower for most crystalline forms of TiO_2 . Probably the TiO_2 layer is amorphous. The strips were cleaned with an UV-ozone oxidation procedure, and could be used and cleaned many times.

2.2.3 Other reagents

All experiments were carried out in a buffer solution. We employed a barbital-acetate buffer for the pH-range of 3 - 8.5, and a glycine buffer at $\text{pH} > 8.5$. Because these buffers contain only monovalent ions, the ionic strength of the buffer solutions can be kept constant when the pH is varied. The ionic strength of the buffer solutions was 0.005 mol/kg. Sometimes extra salt (LiCl , NaCl , CsCl , or MgCl_2) was added.

2.2.4 Reflectometry

The adsorption measurements were performed in a reflectometer with a stagnation-point flow-cell as described by Dijt *et al.*¹⁶. For this geometry the transport of particles to a collector has been described by Dabros and van de Ven¹⁷. The flux J of polymer to the surface depends on the kinematic viscosity ν of the solution, the diffusion coefficient D of the polymer, and the difference $c_b - c_s$, where c_b and c_s are the concentrations in the bulk and near the surface, respectively¹⁶

$$J = k\nu^{1/3}D^{2/3}(c_b - c_s) \quad (2.1)$$

Here, k is a constant for a given set-up. It depends on a dimensionless streaming intensity parameter $\bar{\alpha}$, on the radius R of the inlet tube and the Reynolds number Re , according to¹⁶

$$k = \frac{0.776(\bar{\alpha}\text{Re})^{1/3}}{R} \quad (2.2)$$

The principle of reflectometry is as follows⁶. A laser emits a polarised beam, which is reflected by the silicon wafer in the reflectometric cell. The reflected light is splitted up into its parallel and perpendicular components, which are detected separately by means of photodiodes. The

signal S is then defined as

$$S = f \frac{R_p}{R_s} \quad (2.3)$$

where f is an apparatus constant and R_p and R_s are the reflectivities of the parallel and the perpendicular components. Upon adsorption of polymer on the oxide layer the signal changes by an amount ΔS . The relative change in the reflectometer signal $\Delta S/S_0$ is proportional to the adsorbed amount Γ , provided Γ is not too high¹⁶

$$\Gamma = \frac{1}{A_s} \cdot \frac{\Delta S}{S_0} \quad (2.4)$$

The sensitivity factor A_s was calculated using the method of Hansen¹⁸, which is based on the matrix formalism of Abeles. This factor depends on the thickness d_{ox} of the oxide layer and on the indices of refraction: n_{Si} for silicon, n_{ox} for the oxide layer, and n_s for the solution. Also, the refractive index increment dn/dc of the polymer (Table 2.1), the angle of incidence θ_i and the wavelength λ of the laser beam must be known. The values used were $n_{Si} = 3.8$, $n_{ox} = 1.46$ (SiO₂) or 2.3 (TiO₂), $n_s = 1.33$, $\lambda = 632.8$ nm, $\theta_i = 75^\circ$, $d_{ox} = 113$ nm (SiO₂) or 25 nm (TiO₂). For this set of parameters, A_s is in the range 0.019 to 0.027 m²/mg.

2.2.5 Reproducibility

The measurements were performed in duplicate. The error between two measurements taken the same day is usually less than 10 %, and mainly due to baseline drift. The initial adsorption rate is hardly affected by a slow baseline drift and is therefore better reproducible. When the experiment is repeated days later, the outcome can quantitatively differ from the first result, but the trends are similar. The reasons for this variation are not quite clear. An illustration of this phenomenon is found in Fig. 2.8. The curve for AMA⁺ (triangles) was measured in one day and the deviations are less than 10 %. The results for AMA (open and filled circles) are compilations of many experiments spread over many days. Here the error can be as large as 30 %.

Another source of errors is pH drift. The pH was measured with an accuracy of ± 0.05 . In regions where the adsorbed amount depends very strongly on the pH, even a small drift causes a significant inaccuracy in the curves. In Fig. 2.8, this could cause the spread around pH = 7.

2.3 Results and discussion

2.3.1 Kinetic curves

In Fig. 2.3 we present typical examples for the time-dependent adsorption $\Gamma(t)$ of PVP⁺ onto TiO₂ at pH = 8 from solutions containing varying amounts of LiCl. In Fig. 2.3a the initial part is given and Fig. 2.3b gives the adsorption behaviour for longer timescales. The curve for $I = 0.1$ mol/kg lies above the curves for lower and higher ionic strengths. Clearly, the adsorbed amount passes through a maximum as a function of ionic strength. This maximum will be discussed later in more detail.

From such "kinetic" curves two characteristic values can be extracted: the initial adsorption rate $(d\Gamma/dt)_0$ and the "final" adsorbed amount. The adsorbed amount usually reaches a constant value after 20 minutes. There are cases, however, especially for adsorption on TiO₂ at high ionic strengths, for which a slow increase is still observed after 20 minutes. The value after 20 minutes is therefore not necessarily an equilibrium value, but we assume that it is an adequate measure of the total amount adsorbing on a substrate.

In the following figures these characteristic values are plotted, whereby each point is obtained from one "kinetic" curve as shown in Fig. 2.3. First,

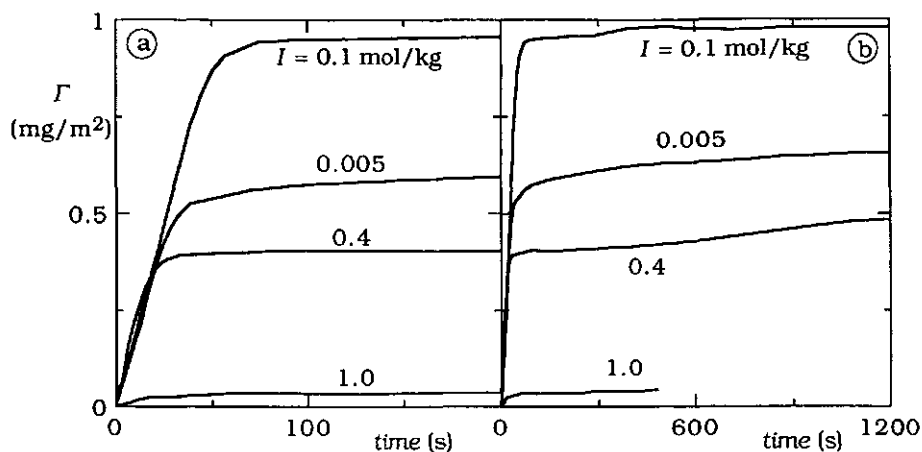


Figure 2.3 The initial part (a) and the curve for longer timescales (b) of typical adsorption data of PVP⁺ on TiO₂ at different ionic strength. The polymer concentration was 10 mg/kg and the ionic strength 0.005, 0.1, 0.4, and 1 mol/kg, as indicated. In all experiments a buffer solution with an ionic strength of 0.005 mol/kg is present; for solutions with a higher ionic strength LiCl was added.

we illustrate the influence of the ionic strength and the pH on the initial adsorption rate and discuss it in terms of the rates of the transport and attachment processes. Secondly, we present the adsorbed amount after 20 minutes and analyse it in terms of the interactions present in the system.

2.3.2 Initial adsorption rate

Effect of ionic strength

Figure 2.4 illustrates the effect of the ionic strength I on the initial adsorption rate of PVP⁺ ($M_w = 3$ K or 120 K) at pH = 8 onto TiO₂ (open symbols) and SiO₂ (filled symbols). For TiO₂, the initial adsorption rate increases slightly with ionic strength until at a certain point it drops to zero. For SiO₂, a monotonic increase with ionic strength is observed. The curves for TiO₂ and SiO₂ are the same for low ionic strength, indicating that in this region the adsorption rate is independent of the nature of the substrate. The use of a smaller PVP⁺ molecule leads to a considerably higher initial slope, but the drop for TiO₂ sets in at a lower ionic strength.

In order to explain these data, it is important to know which step is rate determining and how this step is affected by the ionic strength and the pH. As we have described before, the adsorption is transport-limited when all polymer molecules arriving at the surface adsorb onto it. The

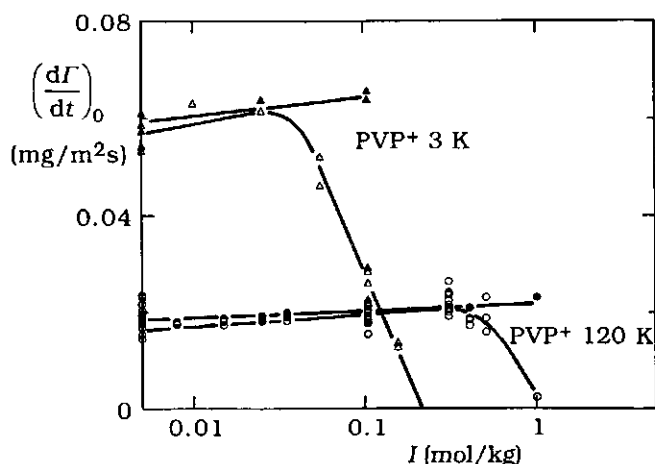


Figure 2.4 The effect of the ionic strength at pH = 8 on the initial adsorption rate of PVP⁺ with a molar mass of 3 K (triangles) and 120 K (circles), respectively. The substrates used were TiO₂ (open symbols) and SiO₂ (filled symbols). The ionic strength of the buffer solution was 0.005 mol/kg and monovalent ions were added to increase it to the plotted value. The polymer concentration was 10 mg/kg.

adsorption rate $d\Gamma/dt$ is then equal to the theoretical flux J , which for the stagnation-point flow-cell is given by Eqs. 2.1 and 2.2. When the attachment process is slow, the adsorption rate will be smaller. We can account for this smaller rate by defining a probability β that a molecule near the surface adsorbs onto it. The initial adsorption rate $(d\Gamma/dt)_0$ is then given by

$$(d\Gamma/dt)_0 = \beta J \quad (2.5)$$

The value of β distinguishes between the transport-limited case ($\beta = 1$) and the attachment-limited case ($\beta < 1$). Note that when β is close to but not equal to 1, the transport rate still strongly influences the adsorption, although we define the adsorption to be attachment-limited.

The transport rate is affected by all variables in Eq. 2.2, i.e., v , D and $c_b - c_s$. In the initial stages, c_s is essentially zero. The bulk concentration c_b is kept constant at 10 mg/kg. This concentration is quite low so that the solution viscosity ν is almost that of water and therefore we do not expect any effect of the factor $\nu^{1/3}$ in Eq. 2.1. The diffusion coefficient D , however, is influenced considerably by the pH and the ionic strength. A polyelectrolyte coil is swollen due to the internal electrostatic repulsion between its charged segments. When salt is added, this repulsion is screened and the polymer coil shrinks, leading to a higher value of D . For polymers with a pH-dependent charge, like AMA, the repulsion can also be reduced by a decrease in the segment charge upon variation of the pH, which also results in a higher diffusion coefficient.

For transport-limited conditions, we expect an increase in the adsorption rate with increasing ionic strength. For the adsorbent SiO_2 , this is indeed found over the entire range of I . For TiO_2 , however, we see that $(d\Gamma/dt)_0$ drops above $I = 0.3$ mol/kg and $I = 0.02$ mol/kg for PVP⁺ samples with molar masses of 120 K and 3 K, respectively. Apparently, on SiO_2 the adsorption is transport-limited over the whole ionic strength range, whereas on TiO_2 this applies only up to a certain ionic strength. A clear indication that the adsorption at low ionic strength is really transport-limited comes from the observation that in that region the curves on TiO_2 and SiO_2 are identical: the adsorption rate is then independent of the nature of the substrate.

In this transport-limited region, we expect the diffusion coefficient to be the main variable. We find an increase in the adsorption rate by a factor of 1.22 over the range $I = 0.005$ to 1 mol/kg, which implies an increase in the diffusion coefficient by a factor of $(1.22)^{3/2} = 1.35$. According to

Odijk's theory¹⁹, the radius of gyration of a polyelectrolyte molecule decreases by a factor of 1.2 upon increasing the ionic strength from 0.005 to 1 mol/kg. Assuming $D \sim 1/R_g$, the decrease in the diffusion coefficient is of the same order of magnitude as the factor found experimentally. The theoretical calculations apply to a polymer with 600 repeating units and a persistence length of 1 nm, which is representative for PVP⁺ with a molar mass of 120 kg/mol.

Kowblansky and Zema²⁰ found that the diffusion coefficient of a partly hydrolysed polyacrylamide, with 66% charged groups and a molar mass of 1500 K, increases by a factor of 1.6 upon increasing the ionic strength from 0.1 mol/kg to 1 mol/kg. This higher value is probably related to the higher molar mass (for longer polymers Odijk's theory predicts a stronger dependence of the radius of gyration on the ionic strength), but also the intrinsic stiffness of PVP⁺ could be responsible for the smaller change in D ; upon increase of I an extended conformation is maintained, even though the repulsion is decreased.

The much higher initial adsorption rate for PVP⁺ of low molar mass ($M_w = 3$ K) is due to the increased diffusion coefficient for this short molecule. Polymer solution theory²¹ states that the diffusion coefficient scales with the molar mass of the polymer as $D \sim M_w^{-\gamma}$. For neutral polymers in a good solvent the value of γ is known: $\gamma = 0.5$ for relatively short chains (where Gaussian statistics apply) and $\gamma = 0.6$ for long chains (which are swollen through the excluded volume effect). This swelling is expected to be even stronger for polyelectrolytes because of the internal electrostatic repulsion. Our data suggest $\gamma \approx 0.5$ for PVP⁺ ($M_w = 3$ K - 120 K). Hence, no additional swelling is detected. Probably, these samples are still in the low-molecular-weight range.

On TiO₂, the attachment process becomes rate limiting at high ionic strength. In general, two different reasons for reduced attachment can be envisioned:

- (i) The polyelectrolyte could in principle adsorb on the surface, but it cannot get into contact. This happens when there is a steric barrier, *e.g.*, by already adsorbed polymers, or an energetic barrier. During the initial stages of the adsorption, the surface is essentially bare, which excludes steric hindrance. An electrostatic potential barrier, however, is possible when the polyelectrolyte and the surface have the same charge sign. This potential barrier will be lower when the ionic strength is increased.
- (ii) An other reason might be that the attraction of the polyelectrolyte to

the substrate is too small. When a polyelectrolyte hits a surface, it forms a number of contacts. After this initial contact the molecule unfolds, thereby increasing the number of contacts and maximising the interaction with the surface. When the adsorption energy per contact is small, the initial gain is small and some molecules might desorb before they can secure their position by the unfolding process. In this case there is not really a barrier present, but from all polymer molecules bumping against the surface only a few stick.

In the case of PVP⁺/TiO₂ at pH = 8, as in Fig. 2.4, the polymer and the substrate are oppositely charged, which excludes the existence of a potential barrier. The observed drop in the adsorption rate at high ionic strength must therefore be caused by too low an (effective) adsorption energy. This is probably related to competition of small cations for the charged surface sites, which thereby weaken the electrostatic attraction of the polymer to the surface. From the fact that salt ions act as displacers, we can conclude that the attraction to the surface for PVP⁺/TiO₂ is mainly electrostatic. This displacement of PVP⁺ by salt ions depends on the molar mass. For short chains ($M_w = 3$ K) the attachment to the surface is already affected at $I > 0.02$ mol/kg, whereas for longer ones ($M_w = 120$ K) an ionic strength higher than 0.3 mol/kg is needed.

For PVP⁺ adsorbing onto SiO₂, salt ions cannot displace the polymer from the surface (see also Fig. 2.7). In this system, a significant non-electrostatic attraction exists, which keeps the overall attraction high, even when the electrostatic component is weakened. Such a non-electrostatic contribution has also been found for other quaternary amine groups, such as tetraalkyl ammonium salts adsorbing on silica^{22,23}, and is thought to originate from hydrophobic bonding.

Effect of pH

In Fig. 2.5 the initial adsorption rates of AMA and AMA⁺ onto TiO₂ are plotted as a function of pH. The salt concentrations are 0.005 mol/kg (open symbols) or 0.1 mol/kg (filled symbols, only AMA). For AMA⁺, two different regions can be distinguished. Below the i.e.p. of TiO₂ (pH = 4), the rate is low (region 1), above pH = 4 the rate is a little higher and about constant over the whole pH-range (region 2). For AMA, the curve is more complicated and a third region is found. After an initial increase at pH < 4 (region 1), the rate stays constant up to pH = 6 and then an increase is observed, which is rather strong at $I = 0.005$ mol/kg and only weak for

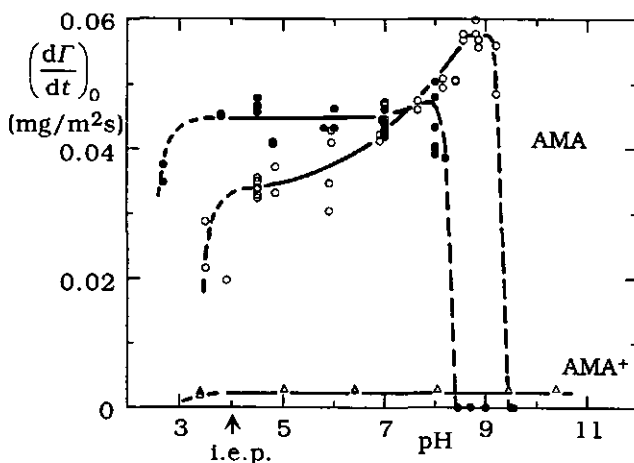


Figure 2.5 The effect of pH on the initial adsorption rate of AMA (circles) and AMA⁺ (triangles) on TiO₂. The ionic strength was 0.005 mol/kg (open symbols). For AMA also a curve at an ionic strength of 0.1 mol/kg (filled symbols) is presented. The polymer concentration was 10 mg/kg and the buffer concentration was 0.005 mol/kg.

The curves can be split up into regions depending on whether the attachment step or the transport step is supposed to be rate limiting. These regions are represented by dashed and solid parts of the curve, respectively (see text).

$I = 0.1$ mol/kg (region 2). Beyond a certain pH (≈ 8 for $I = 0.005$ and ≈ 9 for $I = 0.1$ mol/kg) the rate suddenly drops to zero (region 3).

When the results for AMA⁺ are compared with those for AMA the most striking feature is the much lower rate of adsorption for the former. This originates from the high molar mass ($M_w \approx 6 \times 10^3$ K) of AMA⁺, which corresponds to a small diffusion coefficient.

The diffusion coefficient of AMA⁺ is not affected by the pH, since it bears a constant charge. Therefore, for transport-limited adsorption of AMA⁺ the adsorption rate must be independent of pH. A constant rate of adsorption is found at pH > 4, i.e., when the substrate is negatively charged. From the fact that the rate is independent of the surface charge of the adsorbent TiO₂ (as long as it is negatively charged) we can infer that the adsorption rate is transport-limited in the whole range of pH > 4.

At pH < 4, the net charge of both TiO₂ and AMA⁺ is positive. In this case both mechanisms for a reduced attachment, as described above, can hinder adsorption and the rate is attachment-limited. Despite the unfavourable electrostatic interaction, adsorption does occur, which points to a net attraction between polymer and surface. The nature of this

attraction can be non-electrostatic, but it can also result from an electrostatic interaction if the charge distribution on the surface is heterogeneous. We discuss the nature of this attraction later.

Upon closer inspection of the effect of the pH on the adsorption rate of AMA onto TiO_2 , we can again interpret region 1 to be attachment-limited and region 2 to be transport-limited. Region 3, which is non-existent for AMA^+ , must be due to the variation of the segment charge with the pH. At high pH, AMA is deprotonated. From the titration behaviour (Fig. 2.2), we see that at $\text{pH} = 8$ and $I = 0.1 \text{ mol/kg}$ the segment charge in the bulk is only 12%, and at $\text{pH} = 9$ and $I = 0.005$ only 3%, which causes the electrostatic attraction to the surface to become rather small and the adsorption attachment-limited. In this situation the small cations take over in compensating the surface charge. The polyelectrolyte does not adsorb below a certain segment charge, *i.e.*, above a certain pH. At high ionic strength this desorption pH is lower, due to the higher concentration of competing salt ions. From the observation that at high pH AMA does not adsorb (see also Fig. 2.8), whereas AMA^+ does, we infer that the adsorption of AMA and AMA^+ results from electrostatic interactions: no significant non-electrostatic interactions occur.

In region 1, the net charge of both TiO_2 and AMA is positive and a potential barrier hinders adsorption. At high ionic strength this barrier is lowered, leading to an increase of the sticking probability β (see Eq. 2.5) and a lower pH for the transition of attachment-limited region (region 1) to transport limitation (region 2).

In region 2 the transport process is the determining factor and the observed behaviour is most likely caused by changes in the diffusion coefficient upon variation of the pH. The titration data of AMA (Fig. 2.2) can be compared with the observed changes in the adsorption rate. For $4 < \text{pH} < 6$ the initial adsorption rate (Fig. 2.5) and the degree of dissociation (Fig. 2.2) are approximately constant. For higher values of the pH there is a large change in the initial adsorption rate, which coincides with the region where deprotonation of AMA takes place. The adsorption rate of AMA at $I = 0.005 \text{ mol/kg}$ increases from 36 to $56 \times 10^{-3} \text{ mg/m}^2\text{s}$ between $\text{pH} = 6$ and $\text{pH} = 9$, which corresponds to an increase in the diffusion coefficient by a factor of 1.9. In this pH range the charge of the polymer drops from 90 % to 3 %. At $I = 0.1 \text{ mol/kg}$, the smaller rate increase from $\text{pH} = 6$ to $\text{pH} = 8$ amounts to a change in the diffusion coefficient by a factor of 1.1, which goes along with a decrease of the charge from 97% to

26%.

An important effect of the segment charge was also observed by Kowblansky and Zema²⁰, who found that the diffusion coefficient for a partly hydrolysed polyacrylamide depends strongly on the degree of hydrolysis, and therefore on the polymer charge. For polymers with a degree of hydrolysis of 0.6% and 66%, respectively, the diffusion coefficient changed by a factor of 1.6 at $I = 0.1$ mol/kg and by a factor of 1.3 at $I = 0.5$ mol/kg. From both Kowblansky's work and ours, we find that the effect of the segment charge is smaller at high ionic strength. This is to be expected since at higher ionic strength the repulsion between the charged segments in the chain is screened. However, the factor by which the diffusion coefficient increases is smaller for AMA (this work) than for PAM²⁰. This might be caused by two effects: (i) the molar mass of the PAM samples used in ref. [20] is much larger than that of our AMA, and (ii) the charges on PAM are relatively close to the backbone, whereas for AMA they are more distant and give rise to a smaller internal repulsion. The effect of screening by salt ions can also be deduced from a comparison of the initial adsorption rates at low and high ionic strength (at a constant segment charge). At pH = 4 AMA is fully charged at both ionic strengths. Going from the lower curve to the upper one at pH = 4, the increase of $(d\Gamma/dt)_0$ corresponds to an increase in the diffusion coefficient by a factor of 1.6.

2.3.3 Adsorbed amount

In this section the adsorbed amount of polyelectrolyte as a function of the ionic strength and the pH is discussed. As mentioned earlier, we take the amount after 20 min. as representative for the plateau value of the adsorption isotherm. The effect of the ionic strength was studied for PVP⁺ adsorbing on both TiO₂ and SiO₂. In these experiments besides the salt concentration also the type of cation (Fig. 2.6) and the molar mass were varied (Fig. 2.7). The effect of the pH on the adsorption was investigated for AMA and AMA⁺ adsorbing on TiO₂ (Fig. 2.8). From the adsorption properties of the constantly charged AMA⁺ we find the effect of the pH on the surface charge, whereas from a comparison between AMA and AMA⁺ we can deduce the effect of the segment charge on the adsorption. We discuss how the various parameters influence the adsorption and thereby interpret some main trends.

Effect of ionic strength

Figure 2.6 illustrates the effect of the addition of salt on the adsorption of PVP⁺ ($M_w = 120$ K) at pH = 8 onto TiO₂ as a function of the concentration of several cations: LiCl, NaCl, CsCl and MgCl₂. In all cases also a buffer with an ionic strength of 0.005 mol/kg was present. Addition of monovalent cations causes an increase in the adsorbed amount until a maximum is found around $I = 0.2$ mol/kg. At still higher I the adsorption decreases steeply to zero around $I = 1$ mol/kg. No influence of the type of (monovalent) ion is observed. When MgCl₂ is added, only a decrease in the adsorbed amount is found. No adsorption is left when the Mg²⁺-concentration exceeds 0.03 mol/kg.

As discussed before, for adsorption on TiO₂ the principal interactions are electrostatic. A net electrostatic repulsion arises when overcompensation of the surface charge occurs. Addition of salt screens this repulsion, which tends to increase the adsorbed amount. The electrostatic attraction between polymer and surface, however, is also weakened, because the cations compete with the polymer for the negative surface sites. This gives a tendency to decrease the adsorbed amount. It is difficult to predict what the net effect will be. In Fig. 2.6 we see that the adsorption in the presence of monovalent ions passes through a

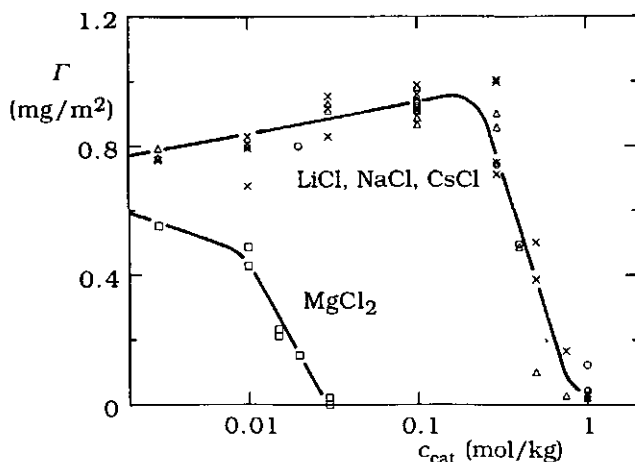


Figure 2.6 The effect of the ionic strength and the type of cation on the amount of PVP⁺ ($M_w = 120$ K) adsorbed onto TiO₂ at pH = 8. The cations added were LiCl (triangles), NaCl (circles), CsCl (crosses) and MgCl₂ (squares). In all cases a buffer solution with an ionic strength of 0.005 mol/kg was present. The polymer concentration was 10 mg/kg.

maximum. Apparently, at low I the repulsion is affected most strongly, whereas at higher I the attraction disappears.

When the type of the ion (at given valence) has a significant effect on the adsorption of a polyelectrolyte, the ion must have a specific interaction with either the polyelectrolyte or the substrate. In our system several monovalent cations were used and no effect is found. We infer that there is no specific interaction between Li^+ , Na^+ , or Cs^+ and TiO_2 . For MgCl_2 we have an asymmetric combination of ions. In this case the screening of the negative surface sites by Mg^{2+} (and thus of the attraction) will be enhanced, whereas the effect on the repulsion in the adsorbed layer (due to Cl^-) is identical. Therefore, the adsorption is less than in the presence of a monovalent salt. Whether or not Mg^{2+} has a specific interaction with TiO_2 could only be seen when several divalent cations are used. We have not carried out such experiments.

Figure 2.7 illustrates the effects of chain length for PVP⁺ (3 K, triangles, and 120 K, circles) and substrate (TiO_2 , open symbols, and SiO_2 , filled symbols) on the (monovalent) salt dependence at pH = 8. The upper solid curve, for PVP⁺ 120 K on TiO_2 , is reproduced from Fig. 2.6 (without data points). For SiO_2 as the substrate the adsorbed amount increases monotonically with ionic strength. For $M_w = 120$ K this increase is gradual till $I \approx 0.3$ mol/kg and then it becomes steeper. A smaller polymer gives a similar shape of the curve, but the total adsorbed amount is less. The curves for PVP⁺ on TiO_2 display a maximum. For $M_w = 3$ K this maximum is situated around $I = 0.05$ mol/kg, and for $M_w = 120$ K it is found around 0.3 mol/kg.

The attraction of a polyelectrolyte to a substrate can be either electrostatic, non-electrostatic, or result from a combination of these two. As seen above, the adsorption of PVP⁺ on TiO_2 is mainly electrostatic in nature. In this case desorption occurs at high I . Adsorption on SiO_2 , however, is enhanced by addition of salt over the entire range of the ionic strength. Apparently, in this case there is also a non-electrostatic interaction. At high salt concentration the overall attraction remains high, even though the electrostatic part of the attraction is screened. The screening of the electrostatic repulsion is now the dominant effect and this gives rise to a higher adsorbed amount. A similar trend was found for polystyrene sulfonate (PSS^-) adsorbing on polyoxymethylene crystals⁹. For this system a non-electrostatic attraction is the only driving force for adsorption.

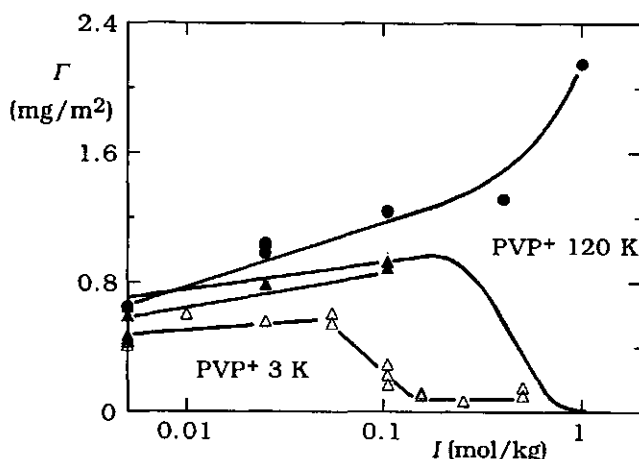


Figure 2.7 The effect of ionic strength on the adsorbed amount of PVP⁺ at pH = 8 with a molar mass of 3 K (triangles) and 120 K (circles), respectively. The substrates used were TiO₂ (open symbols) and SiO₂ (filled symbols). The curve for PVP⁺ ($M_w = 120$ K) on TiO₂ is the same as in Fig. 2.6; for clarity the data points are omitted. The ionic strength of the buffer solution was 0.005 mol/kg and monovalent ions were added to increase it to the desired value. The polymer concentration was 10 mg/kg.

For both substrates the curve for PVP⁺ 3 K lies below the one for PVP⁺ 120 K. The reason is that a smaller polymer adsorbs with less segments in contact with the surface, and therefore can compete less effectively with the cations. The attraction is thus weaker for the shorter polymer. Since the decrease in the adsorbed mass for TiO₂ at high ionic strengths results from the competition between polymer and salt ions, the maximum occurs at a lower ionic strength for the smaller polymer, because of the lower number of contacts with the surface. The decrease in the adsorbed amount beyond the maximum is gradual for the short polymer and rather steep for the long one. This gradual decrease in the adsorbed mass upon reduction of the segmental adsorption energy is typical for oligomers; PVP⁺ 3 K is a very short chain, containing only 14 monomeric units.

Effect of the pH

In Fig. 2.8 we present the results for AMA and AMA⁺ adsorbed onto TiO₂ as a function of pH. These data allow us to investigate the effects of the surface charge and the polymer charge. The ionic strength was 0.005 mol/kg (AMA and AMA⁺) and 0.1 mol/kg (only AMA). For AMA⁺ a virtual linear dependence of the adsorbed amount on pH is obtained over the

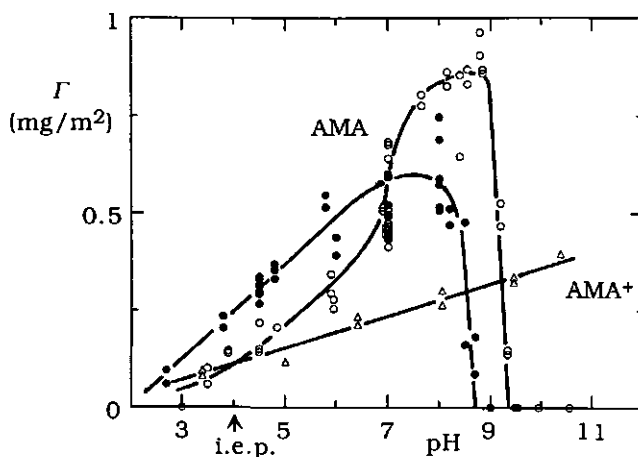


Figure 2.8 The effect of pH on the amount of AMA (circles) and AMA⁺ (triangles) adsorbed onto TiO₂. The ionic strength was 0.005 mol/kg (open symbols). For AMA also a curve with an ionic strength of 0.1 mol/kg (filled symbols) is given. The polymer concentration was 10 mg/kg and the buffer concentration 0.005 mol/kg.

whole pH range. For AMA at $I = 0.005$ mol/kg, the adsorption increases slowly until it shoots up around $\text{pH} = 7$. Around $\text{pH} = 8.5$ a maximum is reached, after which the adsorption drops to zero. Addition of salt enhances the adsorption at $\text{pH} < 7$. At $\text{pH} > 7$, however, the amount is lower and a shift in the maximum to a lower pH value (around 7.5) is observed. Surprisingly, at $\text{pH} < \text{i.e.p.}$ also some adsorption occurs, although both the surface charge and the polymer charge are positive.

Effect of the surface charge

The pH affects both the segment charge of AMA and the surface charge of TiO₂. In order to separate these two factors we consider first the adsorption of the constantly charged AMA⁺. The adsorbed mass of this polymer (and also of other constantly charged polyelectrolytes like PVP⁺ and PSS⁻ adsorbing on TiO₂) increases linearly with the pH (Fig. 2.8). Such a linear dependence on the pH was also reported by Gebhardt and Fuerstenau²⁴ for polyacrylic acid adsorbing on hematite. The adsorbed charge σ_{ads} for a polymer with a molar mass per segment M_s and a degree of dissociation α is given by

$$\sigma_{\text{ads}} = \Gamma \frac{F\alpha}{M_s} \quad (2.6)$$

where F is the Faraday constant. For AMA^+ $\alpha = 1$, since it has one elementary charge per segment. When we assume that charge compensation occurs $\sigma_{\text{ads}} = -\sigma_{0p}$, where σ_{0p} is the surface charge in the presence of adsorbed polymer. From the linear dependence of the adsorbed mass with pH it follows from Eq. 2.6 that σ_{ads} and σ_{0p} also depend linearly on the pH. This is somewhat peculiar since from titration data of oxidic particles (rutile, hematite)²⁵ we know the surface charge of bare particles to vary with pH according to the Gouy-Chapman theory:

$$\sigma_0 \propto \sinh\left(\frac{\text{pH}^0 - \text{pH}}{2}\right) \quad (2.7)$$

where the i.e.p is denoted by pH^0 . The relation given by Eq. 2.7 is only linear when the pH is close to the i.e.p., i.e., at low surface charge. Apparently, the adsorbed polymer influences the dissociation of the surface groups. In the presence of adsorbed AMA^+ the formation of anionic surface groups is stimulated and the formation of cationic groups is impeded. The net effect is a shift in the i.e.p. to a lower value and an expulsion of protons. Such an expulsion of protons upon adsorption of cationic polyelectrolytes has been measured experimentally^{26,27}. This charge regulation has two effects: (i) it makes the surface more negative, and (ii) it enhances the adsorption since, at the same adsorbed amount, less overcompensation of the surface charge, and thus less unfavourable repulsion occurs.

The question remains why the surface charge σ_{0p} in the presence of polymer is linear with the pH. This might be explained by considering the properties of the Stern-layer. In the simplest concept, the Stern-layer is a charge-free layer next to the surface, with a thickness equal to the size of the counterions. It then acts as a molecular condenser, for which the electrostatic potential drop is linear in the surface charge σ_0 :

$$\psi_0 - \psi_s = \sigma_0 \frac{d}{\epsilon} \quad (2.8)$$

where ψ_0 and ψ_s are the potentials at the surface and the solution side of the Stern layer, respectively, and d and ϵ are the thickness and the dielectric permittivity of the Stern layer.

When adsorption of charged species in the Stern layer occurs, this layer is no longer free of charge. However, the Stern layer may now be viewed upon as consisting of two layers, each of which can be treated as a condenser, with charges σ_{0p} for the inner condenser and $\sigma_{0p} + \sigma_{\text{ads}}$ for the outer, respectively. The adsorbed charge σ_{ads} is supposed to be

located on the dividing plane. The total potential difference over both layers is then given by

$$\psi_0 - \psi_s = \sigma_{0p} \frac{d_1}{\epsilon_1} + (\sigma_{0p} + \sigma_{ads}) \frac{d_2}{\epsilon_2} \quad (2.9)$$

where the subscripts 1 and 2 denote the inner and outer layer, respectively. The amount of charge in the diffuse part of the double layer σ_d equals the amount of uncompensated charge, i.e., $\sigma_d = -(\sigma_{0p} + \sigma_{ads})$. Using Hückel's linearisation $\psi_s = \sigma_d / \epsilon \kappa$ for low potentials, Eq. 2.9 can be rewritten as

$$\psi_0 = \sigma_{0p} \frac{d_1}{\epsilon_1} - \sigma_d \left(\frac{d_2}{\epsilon_2} - \frac{1}{\epsilon \kappa} \right) \quad (2.10)$$

When there is full charge compensation, $\sigma_d = 0$, and the second term of Eq. 2.10 vanishes. In that case σ_{0p} is linear in ψ_0 and, hence, in pH. Also when $\sigma_d \neq 0$, σ_{0p} is still approximately linear in ψ_0 when the second term is small (small overcompensation) or when it is constant. For adsorption of AMA^+ on TiO_2 overcompensation of the surface charge is found, but most of the surface charge is assumed to be compensated in the Stern layer and therefore the adsorbed mass depends linearly on the pH.

To get an estimate of the amount of induced surface charge ($\sigma_i = \sigma_{0p} - \sigma_0$), we use the data of Gebhardt and Fuerstenau²⁴. These authors measured the adsorption of polyacrylic acid (PAA) on hematite as a function of pH in the presence of 1 mM NaClO_4 . Evers *et al.*¹⁵ converted Gebhardt's data for the adsorbed amount as a function of pH into the adsorbed amount as a function of the surface charge by using potentiometric titration data of bare hematite particles. Evers *et al.* only used data in a narrow pH-region (6 - 9) close to the i.e.p. of bare hematite ($\text{pH}^0 = 9$). Since in this region Eq. 2.7 may be linearised, they obtained a linear relation between the adsorbed amount and the bare surface charge. We choose a different approach and plot the adsorbed charge instead of the adsorbed amount against σ_0 (not shown here), using Eq. 2.6. We assumed $\alpha \approx -1$, corresponding to one elementary charge per segment, which is nearly the bulk value in this pH-range (6 - 9) for polyacrylic acid. We obtain the following relation between the adsorbed σ_{ads} and the bare surface charge σ_0

$$\sigma_{ads} = \sigma_{ads}^0 - 3.0\sigma_0 \quad (2.11)$$

where σ_{ads}^0 is the amount of adsorbed charge in the i.e.p., i.e., where the bare surface has no net charge; this parameter was found to be -0.05

C/m^2 . Note that this linear relation is only found for the pH-region around the i.e.p. of hematite. When we assume charge compensation to occur ($\sigma_{op} = -\sigma_{ads}$), the induced surface charge σ_i is given by

$$\sigma_i = \sigma_{op} - \sigma_0 = -\sigma_{ads}^0 + 2.0\sigma_0 \quad (2.12)$$

This expression shows that below the i.e.p. of Fe_2O_3 the induced surface charge upon adsorption is at least twice the bare surface charge. Moreover, at the i.e.p. of the bare particles all charge is induced. We conclude that charge regulation leads to appreciable higher adsorbed amounts; this effect cannot be neglected for oxidic systems. This regulation, however, only takes place under the influence of adsorbed polymer; it can therefore not be the driving force for adsorption.

We now return to the question why adsorption of AMA and AMA^+ occurs at $pH < i.e.p.$, *i.e.*, on a net positively charged surface. In other words, what is the nature of the attraction in this case? Several authors^{11,24,28} who find adsorption of charged species on a surface in its i.e.p. claim that this can only result from a non-electrostatic interaction. This is probably correct for a homogeneous surface with a homogeneous charge density. In such a system, the surface charge is zero in the i.e.p., and therefore any interaction causing adsorption must be of a non-electrostatic nature. However, since uncharged AMA (at high pH) does not adsorb onto TiO_2 , we can not ascribe the adsorption at $pH < i.e.p.$ to a non-electrostatic interaction.

In our opinion it is more realistic for an oxidic surface like TiO_2 to use a model of the surface with discrete sites (bound hydroxyl groups)²⁹. Depending on the pH and the local electrostatic potential, these sites can be negative, positive or neutral. Far from the surface only the net charge is important, *e.g.*, for colloidal interactions; then the surface can be considered to be homogeneously charged and the "homogeneous" model is appropriate. Closer to the surface, however, the heterogeneity shows up. Adsorption is a very short-range process, and it is therefore affected by the heterogeneity. This is especially important in the i.e.p. because at this point, even though the net charge is zero, there are still negatively and positively charged sites. A charged molecule can now, in principle, adsorb by a purely (local) electrostatic mechanism. This adsorption, however, will cause the electrostatic potential to become positive, which eventually will prevent other polymer molecules to adsorb. A charge regulation process, as described above, can reduce this potential and thereby enhance adsorption. In our opinion, the significant adsorption of AMA^+ in and

below the i.e.p. is caused by a heterogeneous charge distribution, which is the driving force for adsorption, and this adsorption is enhanced by a charge regulation process.

Effect of the polymer charge

The amount of AMA adsorbed on TiO_2 as a function of pH is not only affected by changes in the surface charge, but also by changes in the segment charge. At low ionic strength, two very pronounced effects appear: (i) around $\text{pH} \approx 7$ the adsorption of AMA goes up and (ii) around $\text{pH} \approx 9$ it drops to zero. Both effects are related to the titration behaviour of AMA. Deprotonation of AMA means that more molecules have to adsorb in order to compensate the surface charge. But since AMA is bound only electrostatically to TiO_2 , it requires a minimum segment charge to adsorb. Above $\text{pH} = 9.5$ this condition is no longer fulfilled and no adsorption occurs. This behaviour agrees completely with both experimental^{8,10,13,14} and theoretical results^{12,15}.

At high ionic strength, the maximum occurs already at $\text{pH} = 7.5$ (and it is less pronounced), since the extra salt ions help to displace the polymer. At low pH the effect of addition of salt is an increase in the adsorption. Here the lateral repulsion is reduced more strongly than the polymer-surface attraction. A possible reason is the heterogeneity effect. On a heterogeneously charged surface the polymer can attach to several negative sites in close proximity, thereby locally regulating the surface charge. A monovalent ion cannot do this and such ions can then compete less effectively with the polymer. When the overall surface charge increases, the heterogeneity effect becomes less important.

We can analyse the deprotonation effect a little further. If the adsorbed macroions compensate the surface charge σ_{0p} exactly, the adsorbed amount is obtained from Eq. 2.6 by equating σ_{0p} and $-\sigma_{\text{ads}}$:

$$\Gamma = - \frac{M_s \sigma_{0p}}{F\alpha} \quad (2.13)$$

Here, we use the assumption of charge compensation even though we know that overcompensation occurs. This assumption is not too bad, however, at low ionic strength since the extent of overcompensation is only small in that case.

We now use Eq. 2.13 to calculate the degree of dissociation α of AMA in the adsorbed layer from σ_{0p} and Γ . The adsorbed amount is simply measured, but for σ_{0p} this is not so easy because it is affected by the

adsorbing polyelectrolyte. For AMA^+ , which has a constant charge of one elementary charge per segment ($\alpha = 1$), we can find σ_{0p} directly from Eq. 2.13. Assuming that AMA induces the same amount of charge as AMA^+ , we can insert this value for σ_{0p} in Eq. 2.13 to find α for AMA. It is then given by

$$\alpha = \frac{M_s \Gamma_q}{M_{sq} \Gamma} = 0.92 \frac{\Gamma_q}{\Gamma} \quad (2.14)$$

where Γ_q and M_{sq} are the adsorbed amount and the segmental molar mass for the quaternised AMA^+ , and Γ and M_s are the corresponding quantities for AMA. The assumption that AMA induces the same countercharge is probably valid at low pH, where the segment charge on AMA is relatively high. When α decreases at higher pH, the induced countercharge will be less for AMA than for AMA^+ , which leads to an overestimate of the segment charge.

In Fig. 2.9 the degree of dissociation in the surface layer and in the bulk are plotted as a function of pH, as indicated. The solid curve was calculated from Eq. 2.14 and from the adsorbed amounts of AMA^+ and AMA in Fig. 2.8. At low pH the segment charge on the surface is considerably lower than the bulk value, demonstrating the deprotonation due to the electrostatic potential in the adsorbed layer. At a certain pH,

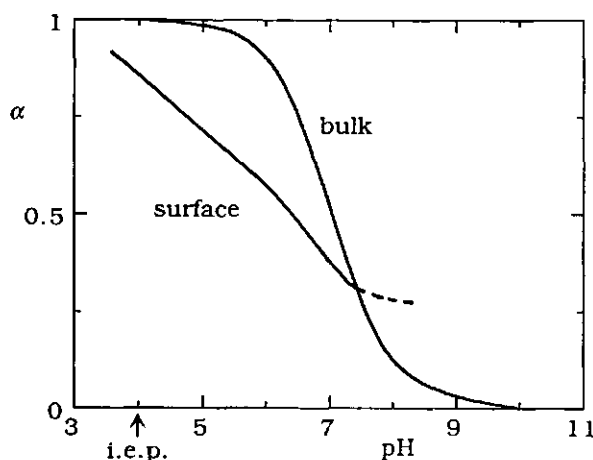


Figure 2.9 The effect of the pH on the degree of dissociation α in the adsorbed layer and in the bulk, as indicated. The curve for α in the adsorbed layer was calculated using Eq. 2.14 and the curves for Γ_q (AMA^+) and Γ (AMA) at $I = 0.005$ mol/kg in Fig. 2.8. The curve for α in the bulk solution is the same as that in Fig. 2.2 at $I = 0.009$ mol/kg.

the curves cross. This pH coincides with the maximum adsorbed mass for AMA. Here, charge compensation no longer takes place, since the attraction has become too weak and part of the surface charge is compensated by small ions. Then the calculation of α using Eq. 2.14 is no longer justified. Although we cannot determine α from Eq. 2.14 at higher pH values we expect the segment charge to be higher than in the bulk because now the adsorbed polymer feels a negative potential, since the adsorbed charge is smaller than the surface charge.

The value calculated for α is an average value. The degree of dissociation is not the same throughout the adsorbed layer. Close to the surface the segment charge will be highest, since there the electrostatic attraction with the surface is optimal. The segments in loops and tails will be less strongly charged, because the strong repulsion makes this unfavourable. Such a distribution is confirmed by experiments by Trau *et al.*³⁰, who used an evanescent wave technique to study the charge and the conformation of an acrylamide copolymer on SiO₂. They concluded that in the adsorbed layer the average segment charge was smaller than in the bulk, which agrees well with our finding of a lower segment charge in adsorbed layers of AMA. They also found that the charged segments in the adsorbed layer were predominantly situated near the surface.

Effect of the type of polyelectrolyte

In order to examine the effect of the type of polymer, we have to know which polymer is preferentially adsorbed. Since PVP⁺ and AMA differ both in molar mass and in chemical structure, this is not easy to predict. Therefore we carried out sequential adsorption experiments in which first one type of polymer was adsorbed for 20 min. after which the other one was injected. If the second polymer adsorbs more strongly than the first one, it is expected to completely displace the first polymer. If, however, the first polymer adsorbs preferentially, nothing would happen upon addition

Table 2.2 Preferentially adsorbing polyelectrolytes

system pH	AMA/PVP ⁺ 3 K		AMA/PVP ⁺ 120 K	
	8	4	8	4
$I = 0.005 \text{ mol/kg}$	PVP ⁺	AMA	PVP ⁺	AMA
$I = 0.1 \text{ mol/kg}$	AMA	AMA	PVP ⁺	AMA

of the second polymer. We checked the preference for adsorption on TiO_2 at $\text{pH} = 4$ and 8 , and at $I = 0.005$ and 0.1 mol/kg for AMA competing with $\text{PVP}^+ 3 \text{ K}$ and 120 K , respectively. The results are summarised in Table 2.2.

By comparison of the experiments for AMA/ $\text{PVP}^+ 3 \text{ K}$ and AMA/ $\text{PVP}^+ 120 \text{ K}$, we are able to distinguish between a preferential adsorption due to the length of the polymer, or due to its structure. At $\text{pH} = 4$, AMA always adsorbs preferentially over PVP^+ , whereas at $\text{pH} = 8$ this trend is reversed, except for the combination AMA/ $\text{PVP}^+ 3 \text{ K}$ at high ionic strength. Under those conditions ($\text{pH} = 8$, $I = 0.1$ mol/kg, see also Fig. 2.7) $\text{PVP}^+ 3 \text{ K}$ hardly adsorbs, since this short polymer cannot compete sufficiently with the salt ions. The general trend is therefore that PVP^+ adsorbs preferentially at $\text{pH} = 8$. However, when the quaternised AMA^+ is used instead of AMA, we found that AMA^+ adsorbs preferentially at $\text{pH} = 8$ (not shown here). This indicates that when the net charges on both polymers are equal, there is a preference for AMA. The preference of PVP^+ over AMA at high pH must therefore be due to the deprotonation of AMA. The degree of dissociation of AMA in the bulk at $\text{pH} = 8$ is about $0.1 - 0.3$, depending on the ionic strength, whereas PVP^+ has a constant charge of 1 elementary charge per segment. The electrostatic interaction of PVP^+ with the surface is thus much stronger than for AMA, and PVP^+ is therefore preferentially adsorbed.

The preference of AMA over PVP^+ when both polymers are fully charged could in principle be due to the existence of non-electrostatic interactions. We found, however, that AMA has no significant non-electrostatic interactions with TiO_2 . Thus, the reason why AMA adsorbs more strongly can only be related to structural differences between the polymers. The charged group on AMA is located in the rather flexible side-chain, whereas the charge on PVP^+ is situated close to the backbone. Therefore the charged groups on AMA can get closer to the charged sites on the surface, and thus obtain a more favourable electrostatic interaction.

2.4 Conclusions

In this study the adsorption of polyelectrolytes onto oxides has been investigated by means of reflectometry. The effects of ionic strength and pH were studied for PVP^+ on TiO_2 and SiO_2 , and for AMA and AMA^+ on TiO_2 , respectively. Two important parameters were determined: the initial

adsorption rate and the adsorbed amount after 20 min.

The initial adsorption rate is determined by (i) the transport from the bulk to the surface and (ii) the attachment to the surface. For adsorption on a bare surface the transport process is rate limiting, unless the adsorption energy becomes too low, or when there is an electrostatic potential barrier, *e.g.*, for a polyelectrolyte adsorbing on a surface with the same charge sign. As a consequence, a variation of the ionic strength or the pH influences the adsorption rate mainly through its effect on the diffusion coefficient. This diffusion coefficient is low for a highly charged polyelectrolyte in a solution with a low salt concentration, because the polyelectrolyte coil is strongly swollen due to the internal repulsion between the charged segments. This repulsion is reduced, and thus the transport rate enhanced, by either increasing the ionic strength or decreasing the segment charge (*i.e.*, raising the pH).

The adsorbed amount is determined by the balance between all interactions in the system. These can be electrostatic and non-electrostatic. When the salt concentration is increased, all electrostatic interactions are screened. Since these interactions can be both attractive and repulsive, it depends on their relative importance whether the adsorbed amount increases or decreases. For PVP⁺ on oppositely charged TiO₂ an initial modest increase is found, followed by a decrease to (almost) zero at high ionic strength. In this case the attraction to the surface is mainly electrostatic. Differences between various monovalent metal ions (ion-specific effects) are absent. On SiO₂, PVP⁺ experiences an additional strong non-electrostatic interaction, resulting in a monotonic increase of the adsorbed amount with ionic strength.

The adsorption of AMA⁺ and AMA onto TiO₂ is a purely electrostatically driven process, since uncharged AMA (at high pH) does not adsorb. The adsorption of AMA⁺ depends linearly on pH. From this we infer that surface charge is regulated by the adsorbing polyelectrolyte. At pH = 4, which corresponds to the i.e.p. of the bare surface, the adsorption is not zero. In our opinion the driving force for adsorption of AMA and AMA⁺ on (net) uncharged TiO₂ is the heterogeneity of the surface charge distribution, assisted by charge regulation of the surface.

The effect of the segment charge is demonstrated by the pH-dependence of the adsorption of AMA, which can adjust its degree of protonation. We find a maximum in the adsorbed amount as a function of the pH, which points to two antagonistic effects. With increasing pH (i)

more molecules are needed to compensate the surface charge (higher Γ) and (ii) the electrostatic attraction to the surface is weakened (lower Γ). At low pH the first effect is dominant, at high pH the second.

From a comparison between the adsorbed amounts of AMA and its quaternised analogue AMA⁺ the segment charge of AMA in the polymer layer on the surface can be deduced. Upon adsorption of a weak polyelectrolyte on oxides, both the polymer and the surface adjust their charge. The difference between the segment charge in the adsorbed layer and in the bulk arises from the electrostatic potential in this layer due to overcompensation of the surface charge.

When PVP⁺ and AMA compete for adsorption, the preference depends on the pH. At high pH, where AMA is deprotonated, PVP⁺ adsorbs more strongly. When the net charges on both polymers are equal, AMA adsorbs preferentially. This is probably related to the fact that AMA has a flexible spacer between the charged group and the polymer backbone.

2.5 References

- (1) *Handbook of water-soluble gums and resins*; R.L. Davidson, Ed.; McGraw-Hill book company: New York, 1980.
- (2) *Polyelectrolytes for water and wastewater treatment*; W.L.K. Schwoyer, Ed.; CRC Press, Inc.: Boca Raton (Florida), 1981.
- (3) P.A. Williams, R. Harrop, G.O. Phillips, G. Pass, and I.D. Robb, *J. Chem. Soc., Faraday Trans. I*, 1982, **78**, 1733.
- (4) M.C. Cafe and I.D. Robb, *J. Colloid Interface Sci.*, 1982, **86**, 411.
- (5) J. Meadows, P.A. Williams, M.J. Garvey, R.A. Harrop, and G.O. Phillips, *Colloids Surfaces*, 1988, **32**, 275.
- (6) J.C. Dijt, M.A. Cohen Stuart, J.E. Hofman, and G.J. Fleer, *Colloids Surfaces*, 1990, **51**, 141.
- (7) H. Tanaka, L. Ödberg, L. Wågberg, and T. Lindström, *J. Colloid Interface Sci.*, 1990, **134**, 219.
- (8) G. Durand, F. Lafuma, and R. Audebert, *Progr. Colloid Polym. Sci.*, 1988, **266**, 278.
- (9) J. Papenhuijzen, G.J. Fleer, and B.H. Bijsterbosch, *J. Colloid Interface Sci.*, 1985, **104**, 530.
- (10) B. Popping, A. Deratani, B. Seville, N. Desbois, J.M. Lamarche, and A. Foissy, *Colloids Surfaces*, 1992, **64**, 125.
- (11) H.G.M. van de Steeg, A. de Keizer, M.A. Cohen Stuart, and B.H.

- Bijsterbosch, *Colloids Surfaces A*, 1993, **70**, 77.
- (12) H.G.M. van de Steeg, M.A. Cohen Stuart, A. de Keizer, and B.H. Bijsterbosch, *Langmuir*, 1992, **8**, 2538.
- (13) T.K. Wang and R. Audebert, *J. Colloid Interface Sci.*, 1988, **121**, 32.
- (14) J. Blaakmeer, M.R. Böhmer, M.A. Cohen Stuart, and G.J. Fleer, *Macromolecules*, 1990, **23**, 2301.
- (15) O.A. Evers, G.J. Fleer, J.M.H.M. Scheutjens, and J. Lyklema, *J. Colloid Interface Sci.*, 1986, **111**, 446.
- (16) J.C. Dijt, M.A. Cohen Stuart, and G.J. Fleer, *Adv. Colloid Interface Sci.*, 1994, **50**, 79.
- (17) T. Dabros and T.G.M. van de Ven, *Colloid Polym. Sci.*, 1983, **261**, 694.
- (18) W.N. Hansen, *J. Optical Soc. Am.*, 1968, **58**, 380.
- (19) T. Odijk, *J. Polym. Sci., Polym. Phys. Ed.*, 1977, **15**, 477.
- (20) M. Kowblansky and P. Zema, *Macromolecules*, 1982, **15**, 788.
- (21) P.-G. de Gennes, *Scaling concepts in polymer physics*, Cornell University Press, Ithaca, 1979.
- (22) J.C.J. van der Donck, Ph.D. Thesis, Eindhoven University, 1992.
- (23) M.W. Rutland and R.M. Pashley, *J. Colloid Interface Sci.*, 1989, **130**, 448.
- (24) J.E. Gebhardt and D.W. Fuerstenau, *Colloids Surfaces*, 1983, **7**, 221.
- (25) L.G.J. Fokkink, A. de Keizer, and J. Lyklema, *J. Colloid Interface Sci.*, 1989, **127**, 116.
- (26) B.C. Bonekamp and J. Lyklema, *J. Colloid Interface Sci.*, 1986, **113**, 67.
- (27) M. Sidorova, T. Golub, and K. Musabekov, *Adv. Colloid Int. Sci.*, 1993, **43**, 1.
- (28) J. Lyklema, *Colloids Surfaces*, 1989, **37**, 197.
- (29) T. Hiemstra, W.H. van Riemsdijk, and G.H. Bolt, *J. Colloid Interface Sci.*, 1989, **133**, 91.
- (30) M. Trau, F. Grieser, T.W. Healy, and L.R. White, *Langmuir*, 1992, **8**, 2349.

Chapter 3 Polyelectrolyte adsorption on oxides: reversibility and exchange

We studied the reversibility of the adsorption of polyelectrolytes on oxides by deliberately creating non-equilibrium situations, either by changing the experimental conditions or by performing exchange experiments. Subsequently, we monitored the return to the equilibrium situation.

Our measurements indicate that polyelectrolyte adsorption on oxides is only partially reversible, due to the strong (electrostatic) interaction with the surface, which slows down reconfiguration processes. This interaction is weakened, and thereby the reversibility enhanced, by the addition of salt.

A model for the structure of adsorbed layers, allowing little reconfiguration, shows that heterogeneous layers are formed.

3.1 Introduction

In Ch. 2 we considered the adsorption of polyelectrolytes on charged surfaces, paying special attention to the role of various interactions. For a comparison with theory, however, it is also crucial to know whether the adsorption reaches equilibrium. Polyelectrolytes on oppositely charged surfaces probably do not have a very high mobility, because of their strong electrostatic attraction to the surface. It is then questionable whether the adsorption may be considered as a reversible process. In most experimental studies¹⁻⁴ the system is tacitly supposed to have reached its equilibrium situation and, hence, the results are often compared to equilibrium theories⁵. Some authors, however, changed the conditions in the system (pH, ionic strength) after adsorption and monitored the relaxation to a new equilibrium situation. These experiments usually indicate a very slow and incomplete response of the adsorbed layer when a desorption step is involved⁶⁻⁸. Meadows *et al.*^{7,8} even used such a strategy to enhance the adsorbed amount.

In order to gain more insight in this matter, we decided to study the reversibility of polyelectrolyte adsorption. The notion of reversibility is coupled to the timescale of the experiment. We can distinguish three different cases:

- complete reversibility, which means that the relaxation from a non-equilibrium situation towards equilibrium is too fast to be measured and the system is always in equilibrium.
- partial reversibility, where the relaxation process takes place during the experiment.
- irreversibility, for which on the timescale of the experiment no relaxation is found.

The reversibility of a system can not only be studied by changing the experimental conditions, but also by following the exchange between polymers of different length, *e.g.*, by using a polydisperse sample. Theory predicts that, from dilute solutions, the longest molecules adsorb preferentially⁵. Therefore, in equilibrium a polydisperse sample is fractionated with the longer molecules adsorbed and the smaller ones in solution. However, kinetically the smaller molecules adsorb first due to their higher diffusion coefficient, after which they have to be displaced by the longer ones. The composition of the adsorbed layer will depend on whether or not exchange occurs, which might have important consequences for the properties of dispersions in contact with polydisperse (industrial) polymer samples.

The exchange process may be thought of as to consist of the following processes which possibly may occur simultaneously: (i) attachment of long molecules, (ii) rearrangements in the adsorbed layer, and (iii) desorption of the small molecules. Displacement can take place in two ways as proposed by Dijt *et al.*⁹: either by direct contact, whereby an incoming polymer molecule displaces some small molecules when it adsorbs (*i.e.*, during step (i)), or after reconfiguration of the large molecule on the surface (*i.e.*, during step (ii)).

A number of exchange studies has been reported for polyelectrolytes¹⁰⁻¹⁵. Tanaka *et al.*¹⁰ studied the exchange of a cationic polyacrylamide (c-PAM) with fluorescent probes against unlabeled c-PAM of the same molar mass. They found a large effect of the molar mass on the exchange rate. For c-PAM with a low molar mass ($M_w = 10$ kg/mol) up to 60 % was found to be exchanged in 40 days, whereas for c-PAM with a high molar mass ($M_w = 7 \times 10^3$ kg/mol) no exchange could be observed.

Experiments using polyelectrolytes differing only in molar mass were reported by several authors¹¹⁻¹⁴. These experiments indicate that the ionic strength plays an important role. At low ionic strength the exchange is very slow and, hence, the adsorbed layer consists of mainly small

molecules. At high ionic strength, however, exchange of small molecules by longer ones does indeed take place.

The competition between chemically different polymers was studied by Adam and Robb¹⁵ for two polyelectrolytes and by De Laat and Van den Heuvel¹⁶ for a combination of a polyelectrolyte and a neutral polymer. In these cases, not only the length of the polymer, but also the interaction of the segments with the surface is different.

In this paper we examine the reversibility and the exchange of polyelectrolytes on oxides, with particular emphasis on the role of electrostatic interactions. The main questions addressed here are:

- How reversible is the adsorption?
- Which steps determine the rate of exchange?
- How are the reversibility and the exchange rate affected by the experimental conditions, *i.e.*, pH and ionic strength?

In order to answer these questions, we measured the reversibility of polyelectrolyte adsorption upon dilution, and upon changes in the pH. This may give insight in the rates of the desorption and of the reconfiguration process in the adsorbed layer. In addition, exchange studies were carried out. Two cases were considered: (i) exchange between polyelectrolytes differing in chain length only, and (ii) competition between a polyelectrolyte and a neutral polymer.

3.2 Materials and methods

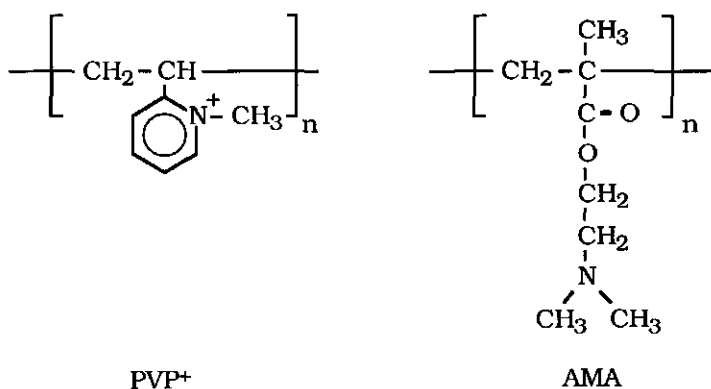


Figure 3.1 Structural formula of polydimethylaminoethyl methacrylate (AMA) and quaternised poly-2-vinyl pyridine (poly-1-methyl-2-vinylpyridinium, PVP⁺).

3.2.1 Materials

The materials used are the same as in Ch. 2, in which we described the adsorption properties of polyelectrolytes on oxides. Here, we will therefore only give the main characteristics of the materials. For more detailed information the reader is referred to Ch. 2.

The polyelectrolytes were quaternised polyvinyl pyridine (PVP⁺) and polydimethylaminoethyl methacrylate (AMA). The structural formula of these polymers is given in Fig. 3.1. Some characteristics of the polymers are collected in Table 3.1. The polymer concentration in single-component systems was 10 mg/kg; in the mixtures it was varied.

Table 3.1 Important properties of the polyelectrolytes.

polymer	M_s (g/mol)	M_w (kg/mol)	M_w / M_n	charge	dn/dc (cm ³ /g)
PVP ⁺	200	2.8	1.13	constant	0.21
PVP ⁺	200	11.6	1.07	constant	0.21
PVP ⁺	200	120	1.03	constant	0.21
AMA	157	20	monodisperse	variable	0.14-0.21

As the adsorbent we used strips of silicon bearing thin layers of TiO₂ (25 nm) or SiO₂ (100 nm). The iso-electric points (i.e.p.) of these layers are around pH = 4 (TiO₂) and pH = 2 (SiO₂), as determined from streaming potential measurements.

In all experiments a barbital-acetate buffer solution with an ionic strength of 0.005 mol/kg was present. Sometimes extra salt (NaCl) was added.

3.2.2 Reflectometry

The adsorption measurements were carried out in a reflectometer equipped with a stagnation-point flow-cell as described by Dijt *et al.*¹⁷ In the stagnation-point the flux J of polymer to the surface depends on the kinematic viscosity ν , on the diffusion coefficient D of the polymer, and on c_b and c_s , which are the polymer concentrations in the bulk and near the surface, respectively¹⁸

$$J = k\nu^{1/3}D^{2/3}(c_b - c_s) \quad (3.1)$$

Here, k is constant for a given set-up and flow rate.

The relative change in the reflectometer signal ΔS with respect to the initial value S_0 is proportional to the adsorbed amount Γ , provided that Γ is not too high¹⁸

$$\Gamma = \frac{1}{A_s} \frac{\Delta S}{S_0} \quad (3.2)$$

The sensitivity factor A_s was calculated using the method of Hansen¹⁹. It is proportional to the refractive index increment dn/dc of the polymer solution (see Table 3.1); values for A_s ranged from 0.019 to 0.028 m²/mg. More details can be found in Ch. 2.

3.2.3 SCF model calculations

The self-consistent-field (SCF) theory of Scheutjens and Fleer has been extended to the adsorption of charged polymers on charged surfaces by Israëls *et al.*²⁰. This theory, being a mean-field theory, allows for a gradient perpendicular to the surface only: all variations parallel to the surface are smeared out. The system is modelled by a lattice in which each lattice cell contains either a solvent molecule, a polymer segment, a salt ion, or an adsorbent entity. Non-electrostatic interactions are represented by Flory-Huggins χ parameters, whereas electrostatic interactions are implemented using a multilayer Stern model. More detailed information on the SCF-theory can be found in a recent monograph by Fleer *et al.*⁵

All calculations were done using a cubic lattice, with lattice spacing $d = 0.6$ nm. The relative dielectric permittivity was taken as $\epsilon_r = 80$. All χ -parameters were chosen to be 0 (athermal solvent).

3.3 Results

In this section the reversibility and the exchange properties of polyelectrolytes are described. First, the reversibility of the adsorption upon dilution and upon changes in the pH is discussed. Second, the exchange of polyelectrolytes is treated.

3.3.1 Reversibility upon dilution

In Fig. 3.2 some results for desorption upon dilution are shown. These curves are typical examples of the (time-dependent) information obtained from the reflectometer. The curves consist of an initial steep part followed

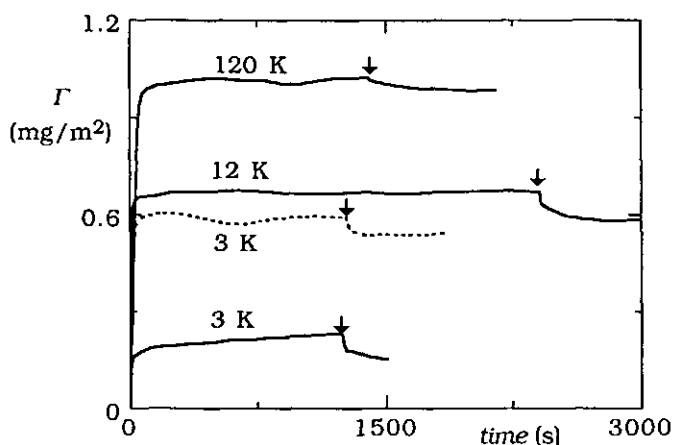


Figure 3.2 Desorption upon dilution of PVP⁺ with molar masses of 120, 12 and 3 kg/mol, denoted as 120 K, 12 K and 3 K, respectively. The preceding adsorption (left of the arrows) of 10 mg/kg PVP⁺ till plateau coverage onto TiO₂ was carried out from a buffer solution at pH = 8 and ionic strengths of 0.025 mol/kg (dotted curve) and 0.1 mol/kg (solid curves). Desorption was initiated by switching to a pure buffer solution (without any polymer) at the moment indicated by the arrows.

by a levelling off to a plateau value. Then, at a certain point (indicated by the arrow) the injected flow is switched from a polymer solution to a pure buffer solution. Some desorption is observed in all cases (9% for PVP⁺ 3 K at $I = 0.025$ mol/kg, and 34%, 13 % and 3 % for PVP⁺ 3 K, 12 K and 120 K at $I = 0.1$ mol/kg, respectively), although never a decrease to zero is found. The desorbed amount is smaller for longer molecules and at lower ionic strength.

When the adsorption would be entirely reversible, one would expect the adsorbed amount to decrease to zero upon dilution. A drop to zero, however, is never found on the timescale of the experiment (about 10 min.). Although this might suggest an irreversible adsorption, this is not necessarily the case. Dijt *et al.*²¹ showed that desorption is extremely slow for polymers, because they often adsorb according to a high affinity adsorption isotherm. Due to the high affinity, the concentration of free polymer near the surface, in equilibrium with any adsorbed amount below saturation, is extremely low ($c_s \approx 0$), even when the adsorption is completely reversible. These free molecules have to diffuse away from the surface before more polymer can desorb. The rate of desorption is therefore limited by the transport step ($c_b = 0$ and $c_s \approx 0$ in Eq. 3.1).

Since the desorption is transport-limited, no information about the detachment rate can be obtained (as long as it is faster than the transport). According to this approach, the dependencies of the desorption on the molar mass and the ionic strength might simply be due to differences in the shape of the adsorption isotherm. This is corroborated by the fact that for a longer polymer, which has a higher affinity, a lower desorption rate is found. Therefore, on the basis of the results displayed in Fig. 3.2, it is not possible to draw any conclusions about whether or not the adsorption is reversible.

3.3.2 Reversibility upon pH-changes

It is well known that the surface charge of oxides, and, therefore, the adsorbed amount of polyelectrolytes, depends on pH. When, after adsorption at a certain pH, the solution is changed to a solution with a different pH, one expects that in the reversible case the adsorbed amount adjusts to the new circumstances. The time needed for such an adjustment provides information about the rate of equilibration.

In Fig. 3.3 the reversibility of the adsorption of the strong polyelectrolyte PVP⁺ ($M_w = 120$ kg/mol) upon cycling the pH from 4 to 8 and from pH = 8 to 4 and from pH = 8 to 4 to 8 is presented. In Figs. 3.3a and b the ionic strengths are 0.005 mol/kg and 0.1 mol/kg, respectively. Since TiO₂ becomes more negative when the pH is increased from 4 to 8, the plateau

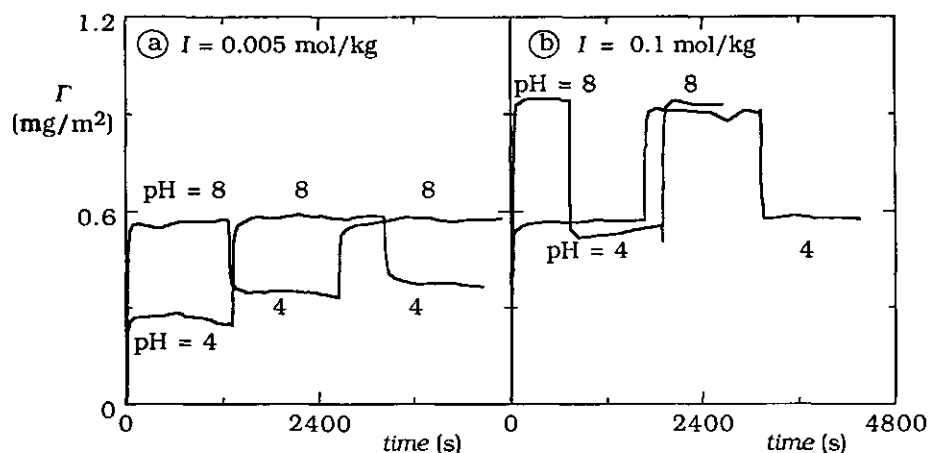


Figure 3.3 Reversibility of the adsorption of PVP⁺ on TiO₂ upon changing the pH from 8 to 4 to 8 and from 4 to 8 to 4. The ionic strength was 0.005 mol/kg (a) and 0.1 mol/kg (b). The polymer concentration was 10 mg/kg.

level for adsorption at $\text{pH} = 8$ is higher than at $\text{pH} = 4$. After lowering the pH from 8 to 4, desorption is always observed. At $I = 0.1 \text{ mol/kg}$, the plateau level for adsorption at $\text{pH} = 4$ is reached, whereas at $I = 0.005 \text{ mol/kg}$ the adsorbed amount remains higher than expected. Upon increasing the pH from 4 to 8, at both ionic strengths the plateau level for adsorption at $\text{pH} = 8$ is reached, irrespective of the sample history.

Clearly, the adsorption at $I = 0.005 \text{ mol/kg}$ is less reversible than at $I = 0.1 \text{ mol/kg}$. Upon changing the pH from 8 to 4, the surface charge of TiO_2 becomes less negative. A surplus of positive charge will be created at the surface, causing a high electrostatic potential. This potential is the driving force for desorption. The desorption process can be thought of as a two-step process: (i) reconfiguration of the adsorbed layer and (ii) detachment from the surface. In the reconfiguration process both the break-up of bonds and formation of other bonds occur, whereas in the detachment process bonds are only broken. The rate at which reconfiguration and detachment takes place depends on the strength of the interaction and on the number of bonds. When the bond is of an electrostatic nature, it is weakened by the presence of salt ions. Therefore, an adsorbed polyelectrolyte at a high ionic strength is more loosely attached and can adjust itself rather easily to the new circumstances, whereas at a low ionic strength the situation is frozen. Such a hypothesis was also proposed by Meadows *et al.*⁷, who stated that desorption will only take place as long as the lateral repulsion is higher than the desorption energy.

Another explanation for a slow desorption was put forward by Cafe and Robb⁶. They suggested that, in order to desorb, the polyelectrolyte has to diffuse from the surface through the adsorbed layer to the bulk solution. Since there is a surplus of charge in the adsorbed layer, it forms a barrier for polymer segments which were previously attached to the surface.

A remarkable observation is that, upon switching the pH from 4 to 8, the adsorbed amount always attains the level corresponding to adsorption taking place at $\text{pH} = 8$. This does not necessarily mean that the adsorption is fully equilibrated at $\text{pH} = 8$. The conformation of the layer could still be different for the two cases, even though the adsorbed amount is the same.

The reversibility upon changes in pH for the weak polyelectrolyte AMA on TiO_2 is illustrated in Fig. 3.4. We have chosen to present the raw data (the relative change in the reflectometer signal $\Delta S/S_0$), since during the experiment dn/dc of the polyelectrolyte changes with pH , so that the

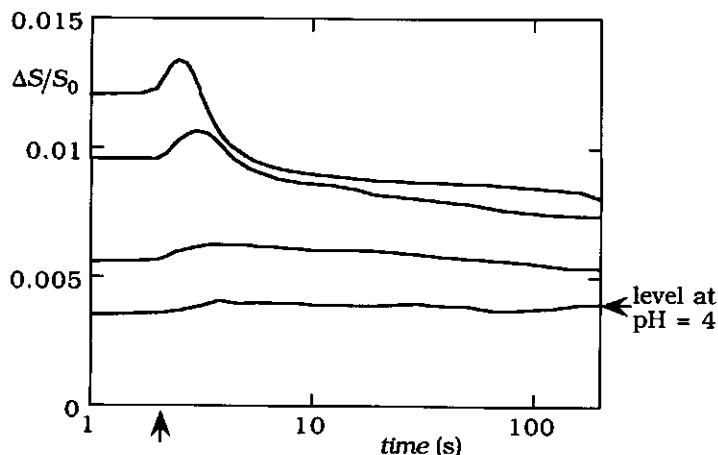


Figure 3.4 Reversibility of the adsorption of AMA on TiO_2 upon switching (at $t = 0$) from a 10 mg/kg polymer solution at $\text{pH} = 7$ to a buffer solution at $\text{pH} = 4$ (indicated by the vertical arrow). The ionic strength was 0.005 mol/kg. The adsorbed amount of AMA at $t = 0$ was varied by limiting the time for adsorption: the initial values are 0.13, 0.20, 0.35 and 0.44 mg/m^2 , respectively. The latter value corresponds to full coverage. The adsorbed amount corresponding to adsorption at $\text{pH} = 4$ is indicated by the horizontal level.

sensitivity factor A_s is not constant. The conversion into adsorbed amounts is therefore not straightforward. In the experiment, AMA was first adsorbed to a certain coverage at $\text{pH} = 7$ from a buffer solution ($I = 0.005$ mol/kg). For example, in the top curve AMA was adsorbed to full coverage (0.44 mg/m^2). At a certain moment, indicated by the vertical arrow, the polymer solution at $\text{pH} = 7$ is replaced by a buffer solution at $\text{pH} = 4$. A rapid increase in signal is observed (note the logarithmic timescale) followed by a slower decrease, both of which are larger at a higher initial coverage. The lowest curve only displays a small increase in the signal. The final value attained in this curve is equal to the value for direct adsorption at $\text{pH} = 4$ (indicated by the horizontal arrow).

When the pH is switched from 7 to 4, the surface charge becomes less negative, whereas the polymer becomes increasingly positively charged. Both give rise to a surplus of positive charge on the surface, which acts as the driving force for desorption. Then why is the signal shown to increase initially? This feature is not due to additional adsorption (as at first one would be inclined to believe), but due to a change in A_s . From Eq. 3.2 we find $\Delta S/S_0$ to be proportional to the adsorbed amount Γ times the

sensitivity factor A_s . When the pH changes from 7 to 4, the polyelectrolyte at the surface becomes increasingly charged, which results in a higher value for dn/dc and thus in a higher value for A_s . The increase due to a change in dn/dc amounts to about 11% of the total signal. This value is in good agreement with the change in dn/dc , as expected on the basis of the titration data for adsorbed AMA (see Ch. 2), assuming a linear dependence of dn/dc on the degree of dissociation of AMA.

The subsequent decrease in the signal is due to desorption. For a reversible system, the value for pH = 4 (indicated) should be reached. All the curves, except for the lowest one (which already has the value for pH = 4), decrease in time. According to our classification the adsorption is only partially reversible; for a completely reversible system the desorption should have been immediate. In Fig. 3.4 only the first part of the desorption is rather quick. The amount of polymer that desorbs quickly is larger when initially more polymer was adsorbed.

For an explanation we can again invoke the two hypotheses for slow desorption mentioned above. Cafe and Robb⁶ suggested that the electrostatic potential on the surface, due to the surplus of charge, would act as a barrier for desorption. In that case we would expect the desorption to be the slowest for the highest electrostatic potential, i.e., at the highest initial coverage. Clearly this is not found.

Our hypothesis was that the desorption rate depends mainly on the number of bonds and the strength of these bonds. At a high initial coverage the number of bonds a molecule has with the surface is lower than at a lower coverage. Now, initially less bonds have to be broken in order to desorb. Also, the electrostatic potential, which is the driving force for desorption, is high at a high coverage. Therefore the desorption rate is initially high. At a lower coverage the desorption slows down, since then the polymer has more bonds with the surface and also the electrostatic potential becomes lower. This is what we find experimentally.

3.3.3 Exchange of polymers differing in chain length - theoretical predictions

In order to establish whether or not a system is reversible, one needs to know the equilibrium situation. Theoretical predictions for the exchange of neutral molecules were presented by Dijt *et al.*⁹ We are not aware, however, of any predictions for pairs of charged chain molecules. Therefore we used the self-consistent mean-field theory of Israëls *et al.*²⁰

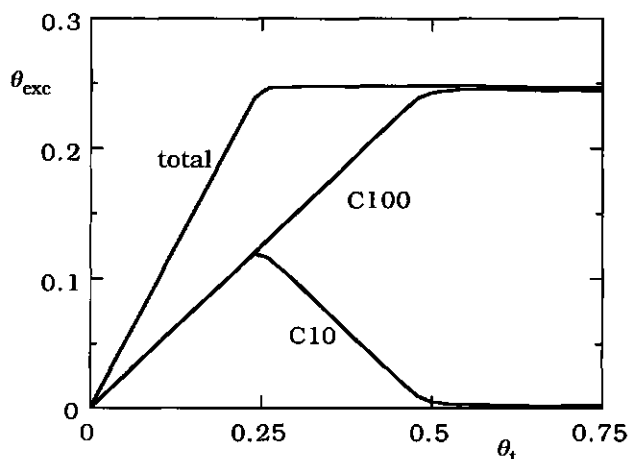


Figure 3.5 Theoretical predictions for the total excess adsorbed amount and the individual amounts for polyelectrolytes consisting of 10 (C10) and 100 (C100) segments, adsorbing from a 1 : 1 (mass ratio) mixture of C10 and C100. The surface charge is 0.25 elementary charge per site, which is equivalent to -0.11 C/m^2 at a lattice spacing $d = 0.6 \text{ nm}$. The polyelectrolyte segments are fully charged. For more details see text.

to calculate the equilibrium state for systems containing equal amounts of the polyelectrolytes C10 and C100, consisting of 10 and 100 segments, respectively, and carrying one elementary charge per segment. The surface charge was taken to be negative, with 0.25 elementary charges per surface site, which for a cubic lattice with a lattice spacing of 0.6 nm corresponds to a surface charge density of about -0.11 C/m^2 . This charge is taken as fixed, unlike in the experimental system, where it can adjust itself. Also, since a mean-field approximation is used, no lateral heterogeneities are possible. All χ -parameters were chosen to be zero: only electrostatic interactions are considered. For the volume fraction of salt in the system we used $\phi = 0.001$. This can be converted into an ionic strength by multiplying ϕ by a constant which, for the chosen lattice spacing, equals $7.7 \times 10^3 \text{ mol/m}^3$.

In Fig. 3.5 theoretical predictions for the excess adsorbed amounts of both C10 and C100 and their combined adsorbed amount as a function of the total amount θ_t of polyelectrolyte in the system are presented. All quantities are given in equivalent monolayers. The curves can be split up in three regions ($0 < \theta_t < 0.25$ (region 1), $0.25 < \theta_t < 0.5$ (region 2) and $\theta_t > 0.5$ (region 3)). In region 1, C10 and C100 adsorb completely on the surface due to their high-affinity isotherms. This is indicated by the slopes

which are 0.5 for both components and 1 for the total amount. For C10 the complete adsorption ends at $\theta_t = 0.25$, where the surface charge is just compensated. Further adsorption of both components would cause overcompensation, resulting in a high unfavourable electrostatic potential. Therefore, in regions 2 and 3 the total adsorbed amount remains constant at the level of charge compensation. The composition on the surface, however, changes in region 2, showing the preference for the long molecules. The adsorbed amount of C100 increases with the added amount (the slope is still 0.5), thereby displacing C10 from the surface. The exchange coefficient $d\Gamma_{10}/d\Gamma_{100} = -1$, where the subscript denotes the chain length, as was also found theoretically for pairs of neutral polymers⁹. In region 3, the surface charge is almost completely compensated by C100. No further increase of the adsorption occurs.

When we assume that the adsorption is completely reversible, we can easily convert the initial part of Fig. 3.5 ($\theta_t < 0.5$) into a "dynamic" curve, by changing the abscissa into a time-axis, since in that part the adsorption is transport-limited. In that case θ_t represents the total amount of polymer transported to the surface, which is equal to the flux J times t . The system depicted in Fig. 3.5 has equal amounts of small and long molecules and would therefore represent a mixture with $J_{10} = J_{100}$.

It is, however, questionable whether the data in Fig. 3.5 are relevant for the behaviour of our experimental system, since the theoretical surface charge is fixed, whereas for the experimental system it is not. A fixed surface charge means that the adsorption stops when charge compensation is attained, whereas in many experimental systems an overcompensation of the bare surface charge is found (see Ch. 2).

3.3.4 Exchange of polymers differing in chain length - experimental data

PVP⁺ adsorption on TiO₂ from mixtures

Figure 3.6 shows the adsorption kinetics of PVP⁺ ($M_w = 120$ kg/mol, denoted as 120 K) and of bimodal mixtures of PVP⁺ on TiO₂ at pH = 8 at two ionic strengths. In Fig. 3.6a the ionic strength is 0.025 mol/kg and the mixture consists of molecules with a molar mass of 3 kg/mol (3 K) and 120 kg/mol (120 K), whereas in Fig. 3.6b the ionic strength is 0.1 mol/kg and the molar masses of the components are 12 kg/mol (12 K) and 120 kg/mol (120 K). The mixtures were prepared in such a way that the ratio

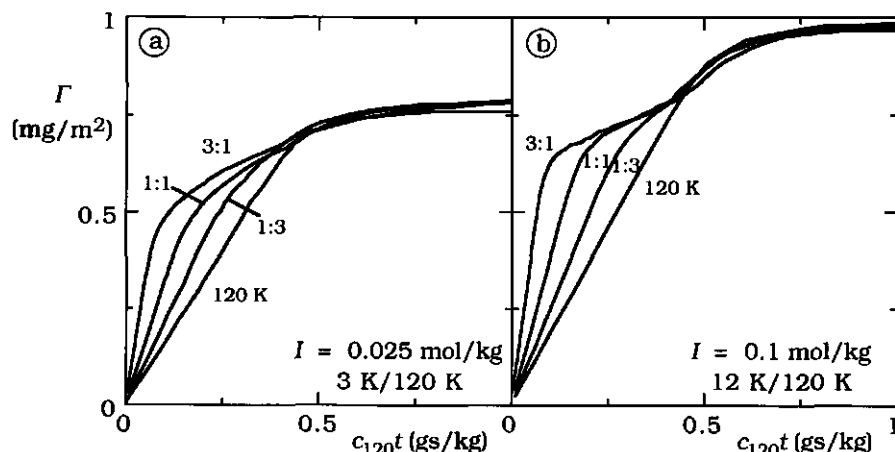


Figure 3.6 The adsorption of PVP⁺ 120 K and of mixtures of PVP⁺ 3 K and 120 K at $I = 0.025$ mol/kg (a), and 12 K and 120 K at $I = 0.1$ mol/kg (b). These data are for pH = 8 and the adsorbent TiO₂. The mixtures were prepared in such a way that the ratio between the initial transport rates of the small and the long molecules was 3 : 1, 1 : 1 and 1 : 3, as indicated. To enable a comparison between the curves for the mixtures and for 120 K, the abscissa axis was scaled by plotting it as $c_{120}t$, where c_{120} is the concentration of PVP⁺ 120 K.

between the initial transport rates ($\sim D^{2/3}c$) of the small and the long molecules was 3:1, 1:1 and 1:3. In Fig. 3.6 the time-dependent adsorption curves are scaled by plotting the x-axis as $c_{120}t$, where c_{120} is the concentration of PVP⁺ 120 K in the mixture. In this way the initial flux J_{120} of the long molecules to the surface is identical in all samples (see Eq. 3.1).

In Fig. 3.6, the curves show an initial linear part with a gradual transition around 0.5 mg/m² (Fig. 3.6a) and 0.6 mg/m² (Fig. 3.6b) to a second straight part, which has a lower slope. Next, the curves for the mixtures coincide with the one for the longest polymer (120 K) adsorbing from a single component system. In this part there are no small molecules left on the surface and only further adsorption of the long molecules is seen.

The fact that all curves eventually come together to a single curve has great significance. It indicates that the adsorption rate of the long molecules is independent of the temporary presence of small molecules on the surface. The curve for 120 K therefore also represents the adsorption of the long molecules in the mixture. When we subtract this curve from

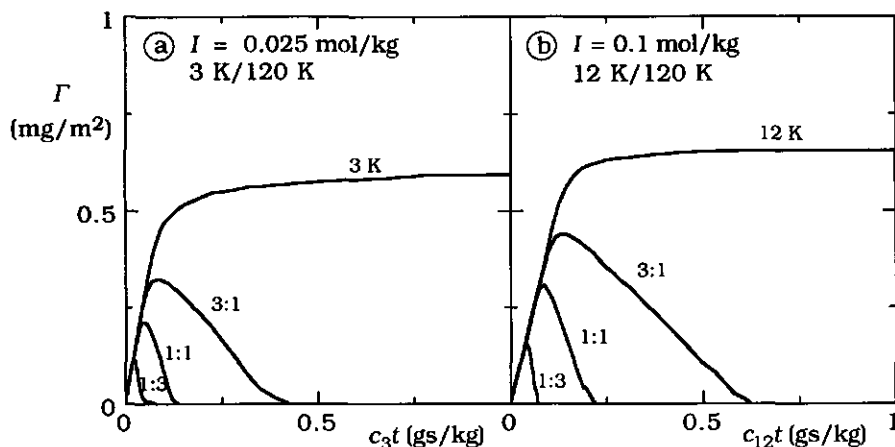


Figure 3.7 The adsorption of the small molecules from single-component systems and from the mixtures presented in Fig. 3.6. The data for the mixtures were obtained by subtracting the curve for 120 K from the mixture curves in Fig. 3.6a and 3.6b, respectively. Other parameters as in Fig. 3.6.

the curve for the mixture, the evolution of the adsorbed amount of the small molecules as a function of time remains. These amounts are plotted in Figs. 3.7a and b. In addition, data for the small molecules in a single-component system are shown in Fig. 3.7. The curves are plotted as a function of c_3t (Fig. 3.7a) or $c_{12}t$ (3.7b), c_3 and c_{12} being the concentration of the small molecules in the mixture. Now the initial flux of the small molecules to the surface is identical for all curves. All curves have a linear initial part which coincides with the curve for small polymers adsorbing from a single-component system. At a certain point a maximum adsorbed amount is reached in the mixture, after which the molecules start to desorb from the surface. The desorption rate is more or less constant, until no small molecules are left on the surface.

We will now try to interpret the curves in Figs. 3.6 and 3.7. In the linear initial sections the adsorption rates of both the small and the long molecules are constant. These initial rates are equal to those for the adsorption of a single-component system on a bare surface. In Ch. 2 we have shown that the initial adsorption rate for single-component systems is equal to the flux of molecules to the surface (transport-limited adsorption). Therefore initially both components adsorb independently, in agreement with the theoretical data in Fig. 3.5, their adsorption rates being determined by the rate of transport only. Hence, the total initial

adsorption rate of a mixture of polymer molecules with length i can be generally expressed by

$$(d\Gamma/dt)_0 = \sum_i J_i = k \sum_i c_i D_i^{2/3} \quad (3.3)$$

Equation 3.3 implies that the initial adsorption rate of a component is proportional to its concentration. This feature was already used to scale the abscissa in Figs. 3.6 and 3.7.

The linear part of the curves for the mixtures (Fig. 3.6) ends at a certain adsorbed amount. At that point the adsorption rate of the small molecules is reduced due to the already adsorbed polymer molecules and, hence, their adsorption is attachment-limited.

In the second linear part of the curve the adsorption of the long molecules proceeds undisturbed by the presence of small molecules. The small molecules, however, are displaced from the surface. The desorption rate of the small molecules is found to be more or less constant. Generally, the adsorption rate of a mixture containing two polymers with length i and j , where $j > i$, can be written as

$$d\Gamma/dt = d\Gamma_i/dt + d\Gamma_j/dt = (d\Gamma_j/dt)(1 + d\Gamma_i/d\Gamma_j) \quad (3.4)$$

where $d\Gamma_i/d\Gamma_j$ is the exchange coefficient, as introduced in the discussion of Fig. 3.5. The values for the exchange coefficient are given in Table 3.2.

Table 3.2 Exchange coefficients for various systems

mixture	$d\Gamma_s/d\Gamma_l$ ($I = 0.025$ mol/kg)	$d\Gamma_s/d\Gamma_l$ ($I = 0.025$ mol/kg)
3 : 1	-0.65	-0.76
1 : 1	-0.59	-0.73
1 : 3	-0.37	-0.52

Let us now consider the displacement process in more detail. As noted before, displacement can occur both by "direct contact" (an adsorbing long molecule rapidly bumps off some small molecules) and by subsequent reformation (the spreading molecule displaces some additional molecules)⁹. These mechanisms are pictured schematically in Fig. 3.8. With respect to the reformation, two cases can be distinguished: the completely reversible case, where the reformation is very fast, and the partly reversible case, where the reformation is slow on the timescale

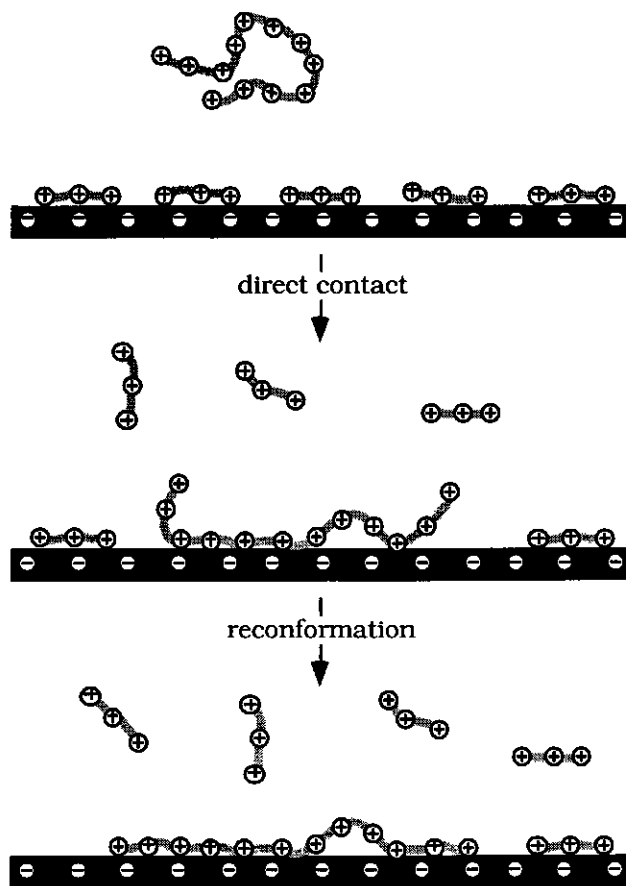


Figure 3.8 Schematic representation of the displacement process by direct contact and by reformation.

of the experiment. In a completely reversible system, a long molecule will displace an equal mass of smaller molecules, resulting in an exchange coefficient of -1 (see Eq. 3.4). When the unfolding is slow, however, displacement occurs mainly by direct contact. In that case less small molecules can be displaced per long molecule. This has several consequences: (i) the absolute value for $d\Gamma_i/d\Gamma_j$ is lower than unity, (ii) an overpopulation of small molecules with respect to equilibrium exists on the surface, and (iii) the displacement is completed at a higher total coverage. The existence of an overpopulation can be checked experimentally by stopping the supply of long molecules. This gives the adsorbed long molecules time to unfold, which may then cause some

desorption of small molecules so that a decrease in the total adsorbed amount is observed. We have carried out such an experiment for the systems at hand (not shown here), and indeed some desorption occurred on the timescale of the experiment. Therefore, we can conclude that the investigated systems are partly reversible, which results in an overpopulation of small molecules during exchange.

There are two main differences between the exchange of the low ionic strength system (3 K/120 K) and the high ionic strength one (12 K/120 K). First, the absolute values of the exchange coefficients are smaller at low ionic strength (Table 3.2). Second, PVP⁺ 3 K is desorbed only just before the long molecules reach their plateau value, whereas at high ionic strength the desorption is complete already at 0.2 mg/m² below the plateau value of the long molecules (see Fig. 3.6). These differences both point to a slower reconfiguration at low ionic strength, which is probably due to the stronger electrostatic bonds between the polymer molecule and the surface at low *I*. Such a conclusion was also drawn from the response of the system upon changing the pH (Figs. 3.3 and 3.4).

Next, we analyse the desorption rate of the small molecules in more detail. As discussed above, the reconfiguration is slow and the displacement occurs mainly by direct contact. The question is why the rate of desorption by the "direct contact" process is constant, rather than exponentially decaying as expected on the basis of a simple first order process. We propose the following explanation. As implied by Eq. 3.4, a constant desorption rate is obtained whenever (at constant $d\Gamma_j/dt$) the exchange coefficient $d\Gamma_i/d\Gamma_j$ is constant. The exchange coefficient is determined by the number of small molecules with which an incoming large molecule interacts, *i.e.*, on its "interaction area" A_i multiplied by the local number density ρ_s of the small molecules. The number N_d of small molecules which is displaced by direct contact is then given by

$$N_d = A_i * \rho_s \quad (3.5)$$

The number density of small molecules is not simply given by its adsorbed amount, since part of the surface is blocked by long molecules. The number density ρ_s of N_s small molecules on a total area A_t corrected for the area A_b blocked by long molecules is given by

$$\rho_s = \frac{N_s}{A_t - A_b} \quad (3.6)$$

This density remains constant throughout the displacement process, since the adsorbed molecules cannot move laterally over the surface.

Sequential adsorption experiments of PVP⁺ 12 K on TiO₂

Sequential adsorption experiments were carried out using the 12 K/120 K system at $I = 0.1$ mol/kg. PVP⁺ 12 K was preadsorbed to a certain coverage, and left to age. All preadsorbed layers were aged for 20 min; the saturated layer in the presence of the polymer solution and the undersaturated layers in the presence of a buffer solution. After ageing, the surface was exposed to a 10 mg/kg solution of 120 K. In Fig. 3.9 we present this latter part of the curve, where $t = 0$ represents the point where the solution is switched to PVP⁺ 120 K.

As in Fig. 3.6, the curves in Fig. 3.9 display an initial linear part from the preadsorption level up to $\Gamma \approx 0.7$ mg/m². In this range the adsorption rate is equal to the transport-limited adsorption rate for 120 K on a bare surface, even though PVP⁺ 120 K adsorbs on the partly coated surface. Above $\Gamma \approx 0.7$ mg/m² a second linear part with a lower slope is found, indicating that some exchange takes place. Beyond that the curves level off to a plateau value. However, this plateau level is *higher* than the value for the adsorption of 120 K on a bare surface; the ones with a preadsorbed amount of about 0.5 mg/m² reach the highest final total adsorbed amount.

Clearly, these systems are not reversible at these timescales. This is unexpected, since in Fig. 3.6b we find that 120 K can completely displace

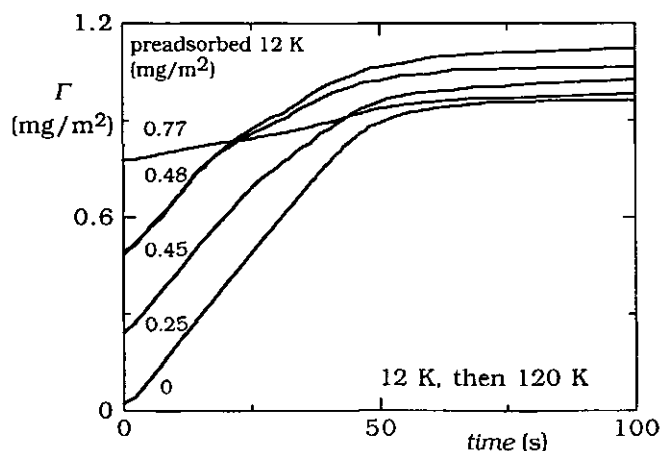


Figure 3.9 The adsorption of PVP⁺ 120 K at pH = 8 and at $I = 0.1$ mol/kg onto bare TiO₂ and onto TiO₂ with preadsorbed PVP⁺ 12 K. The amounts of PVP⁺ 12 K at $t = 0$ are 0, 0.25, 0.45, 0.48 and 0.77 mg/m², respectively, where the latter value corresponds to full coverage.

12 K when the polymers are supplied in a mixture. The major difference between this experiment and the one presented in Fig. 3.6b, is the ageing of the adsorbed layer prior to exposure to the second polymer. During ageing, adsorbed molecules may adjust their conformation so that they probably lie flatter on the surface, with more segments contacting it. The stronger bonding with the surface then makes it harder to displace the preadsorbed molecules: the system will be less reversible.

One may wonder why the total adsorbed amount and, hence, the total adsorbed charge is higher when PVP⁺ 120 K adsorbs on a precoated surface than when it does so on a bare surface. A higher total adsorbed amount was observed, however, in all experiments in which undersaturated layers of PVP⁺ on TiO₂ were aged for some time after which more polymer was supplied, even when in both steps the same polymer sample was used. One possible explanation is that the charge adjustment is more efficient in the experiments with an ageing step. In Chs. 2 and 4 we show that the amphoteric TiO₂ adjusts its charge upon adsorption of polyelectrolytes. This charge adjustment will be most efficient when the molecules are in close contact with the surface, i.e., in a flat conformation. Since during the ageing process the layer of 12 K changes its conformation to a flatter one, this might cause a greater adjustment of the surface charge. As a result, more polymer could possibly adsorb. An experimental check on this mechanism would be to follow the kinetics of proton release after covering the surface with a fixed amount of polymer (below saturation).

Exchange of PVP⁺ on SiO₂

We investigated the exchange between PVP⁺ 3 K and 120 K on SiO₂ at pH = 8 and at an ionic strength of 0.025 mol/kg, both by sequential adsorption experiments and by adsorption from a mixture. The curves for the mixture and for the sequential experiment are presented in Fig. 3.10. They are compared to the curves for the single-component systems of PVP⁺ 3 K and of PVP⁺ 120 K adsorbing on a bare surface.

The curves for only 3 K, for only 120 K, and for the mixture display the familiar initial linear part due to transport-limited adsorption, whereby the slopes are given by Eq. 3.1 for the single-component systems and by Eq. 3.3 for the mixture. After the initial part, however, there is no second linear part which would indicate an exchange as found in Figs. 3.6 and 3.9. This is also not found for the sequential adsorption experiment.

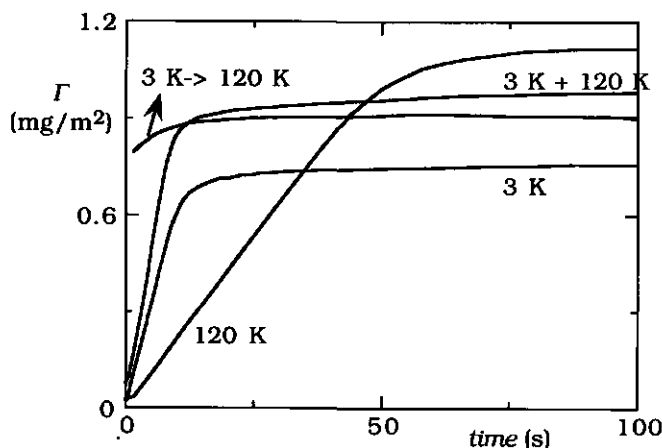


Figure 3.10 The adsorption of PVP⁺ 3 K and PVP⁺ 120 K from single-component solutions and from a mixture of these on a bare surface. Further, the adsorption of PVP⁺ 120 K on a surface precoated with PVP⁺ 3 K is presented. The experimental conditions were: pH = 8, $I = 0.025$ mol/kg, polymer concentration 10 mg/kg. The mixture consisted of 10 mg/kg PVP⁺ 3 K and 10 mg/kg PVP⁺ 120 K.

Moreover, the plateau values of the curves for the mixture and for the sequential experiment do not correspond to the one for PVP⁺ 120 K.

Evidently, the adsorption of PVP⁺ on SiO₂ is not reversible on this timescale. The reason for the lack of displacement probably is the stronger bond between PVP⁺ and SiO₂. In Ch. 2 it was already noted that PVP⁺ adsorbs on SiO₂ not only by an electrostatic mechanism but also by a non-electrostatic interaction between the polymer segments and the surface, which is probably some sort of a hydrophobic effect.

The plateau values for the mixture, and for the adsorption of 120 K on a surface precoated with 3 K, remain lower than for PVP⁺ 120 K adsorbing on a bare surface. It is strange that the adsorbed amount cannot exceed $\Gamma = 0.9$ mg/m² when the adsorbed layer consists of many small and some long molecules (in the sequential experiment), whereas it can do so if only long molecules are present (in the experiment with only 120 K). Apparently, the presence of adsorbed small molecules limits the final total adsorbed amount and, hence, the final total adsorbed charge. The structure of the layer must therefore be different.

We tentatively put forward a model for the adsorbed layer to interpret these features for SiO₂ (Fig. 3.11). We assume that the reconfiguration process is very slow, as was concluded before (for TiO₂) in the discussion

of Figs. 3.6 and 3.7. When the molecules do not spread over the surface, their conformation in the adsorbed state reflects the one in solution. Upon adsorption of a polyelectrolyte molecule, local overcompensation of the surface charge is found as sketched in Fig. 3.11. The presence of the molecule prevents the adsorption of other molecules nearby, due to the strong lateral electrostatic repulsion. The density with which the molecules can be packed on the surface determines the total adsorbed charge. In Fig. 3.11 the density has been chosen such that adsorbed charge exceeds the surface charge as is often found experimentally. This excess of charge will be neutralised by charge regulation of the surface or by coadsorption of simple ions (not included in Fig. 3.11).

Since an adsorbed charged molecule blocks part of the surface, this implies that in the plateau of the adsorption isotherm the surface is only partially filled. For long molecules this results in a rather heterogeneous layer (Fig. 3.11b), whereas for small molecules the layer is more homogeneous, since the inhomogeneities are smaller. Also, smaller molecules adsorb in a flatter fashion, since their conformation in solution is more rodlike. Therefore they cover the surface more efficiently, as will

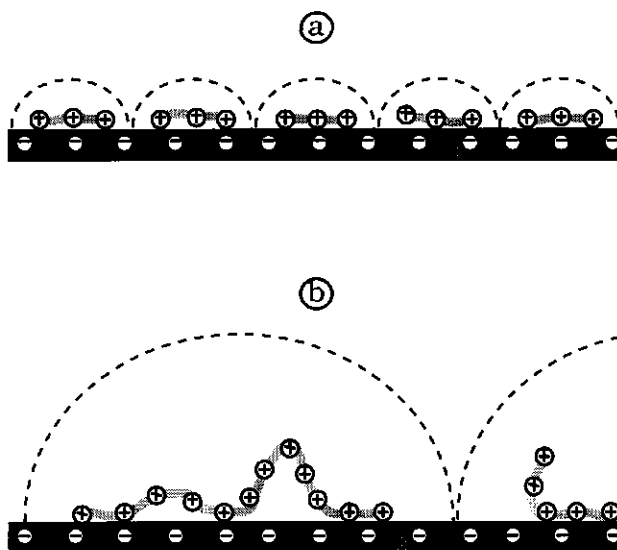


Figure 3.11 Schematic representation of the adsorbed layer of small (a) and large (b) polyelectrolyte molecules. Adsorption results in a local overcompensation of the surface charge, which blocks part of the surface for incoming molecules. The heterogeneity is stronger for longer chains.

be confirmed during the discussion of Fig. 3.12. We conclude that for adsorption of polyelectrolytes differing in length, the layer structure can be very different, when the reconfiguration is very slow. Such a heterogeneous structure cannot be described with the mean-field approximation used in the theoretical calculations described above.

On the basis of this model for the adsorbed layer we expect that the presence of adsorbed small molecules, which cover the substrate more efficiently than longer molecules, will limit the final adsorbed amount upon exposure to long molecules (sequential adsorption experiment). A lower final value for the sequential adsorption experiment (and for the mixture) compared to the plateau level for the long molecules was indeed found on SiO_2 . On TiO_2 (Fig. 3.9), however, the total adsorbed amount is higher for the sequential adsorption experiment. Apparently, small adsorbed molecules can block the surface more efficiently on SiO_2 than on TiO_2 . Above, we ascribed this higher adsorbed amount on TiO_2 to an easier adjustment of the surface charge, in the presence of (small) molecules with a flat conformation. The ability to adjust the surface charge (i.e., the double layer capacitance) is much less for SiO_2 than for TiO_2 ²². Therefore, this charge regulation mechanism is less efficient for SiO_2 .

3.3.5 Competition between neutral polymers and polyelectrolytes

Our last data set comprises sequential adsorption experiments on SiO_2 where a polyelectrolyte (PVP⁺ 3 K or 120 K) is first adsorbed to plateau coverage, after which a neutral polymer polyethylene oxide (PEO) with a molar mass of 23 K, is injected. In Fig. 3.12 the results of these experiments at pH = 4 (Fig. 3.12a) and pH = 7 (Fig. 3.12b) are presented. The ionic strength was 0.005 mol/kg. At both pH's also the curve for PEO adsorbing on a bare surface is included. As for Fig. 3.4, the reflectometric data could not be converted into an adsorbed mass since dn/dc for PVP⁺ and PEO is different.

The dependence on the pH for adsorption on a bare surface is as expected: the adsorbed amount of the neutral PEO is not very much influenced by the pH, whereas the adsorption of PVP⁺ increases with increasing pH. When PEO is added to a surface coated with PVP⁺ at pH = 4, some extra adsorption is found both for PVP⁺ 3 K and 120 K. At pH = 7 addition of PEO leads to a slight increase for a substrate covered with PVP⁺ 120 K, but for PVP⁺ 3 K no extra adsorption seems to occur. The

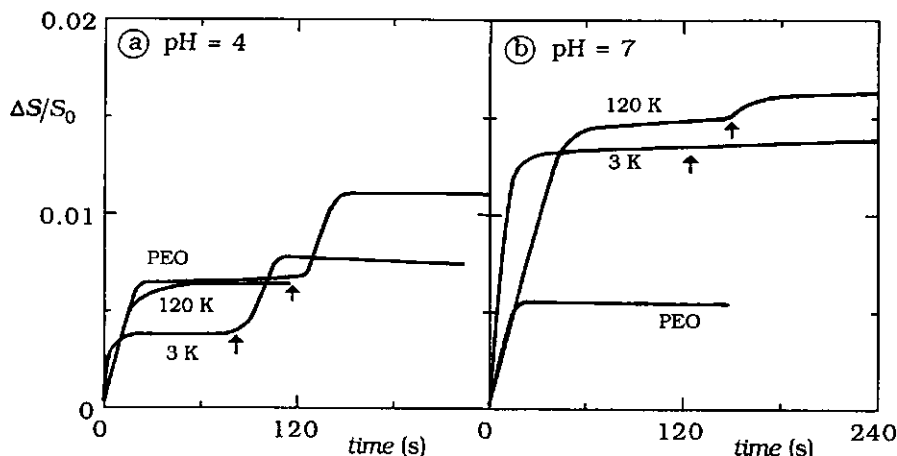


Figure 3.12 Sequential adsorption experiments of PVP⁺ (120 K and 3 K) and PEO (23 K) at pH = 4 (a) and pH = 7 (b) onto SiO₂. Other parameters: polymer concentration 10 mg/kg, buffer concentration 0.005 mol/kg.

extra (PEO) adsorption at pH = 4 seems to be almost independent of the molar mass of PVP⁺ in the first step.

The fact that at low pH both PVP⁺ and PEO can be co-adsorbed on the surface, thereby forming a mixed layer, is probably due to the different driving forces for adsorption (see also Ch. 4). The polyelectrolyte PVP⁺ adsorbs as long as there is a net electrostatic attraction. At the plateau coverage, the surface is only partially covered (see Fig. 3.11). The neutral PEO adsorbs because of its non-electrostatic interaction with the substrate. The amount of PEO adsorbed reflects the amount of free area left, and therefore PEO can be used as a probe for the structure of the polyelectrolyte layer. At pH = 4 the amount of PEO adsorbed in the second step of the experiment is about the same for surfaces covered with PVP⁺ 3 K and 120 K, but it remains lower than on a bare surface. Apparently, both PVP⁺ 3 K and 120 K are able to screen part of the surface for adsorption of PEO. The efficiency with which the surface is screened is higher for PVP⁺ 3 K than for PVP⁺ 120 K: with an adsorbed amount, which is half of that for PVP⁺ 120 K, it blocks the same amount of surface. At pH = 7 the adsorbed amounts of PVP⁺ 3 K and 120 K are higher and a greater part of the surface is screened. Again, the screening of PVP⁺ 3 K is more efficient, since no more PEO can attach to the surface, whereas on a surface covered with PVP⁺ 120 K adsorption of PEO still occurs. Obviously, smaller molecules screen the surface much more efficient than

long molecules, as was also concluded from the PVP⁺ exchange experiments on SiO₂ (Fig. 3.10) and illustrated in the model for the adsorbed layer (Fig. 3.11).

3.4 Discussion

The reversibility of polyelectrolyte adsorption can be studied by changing the conditions stepwise, thereby creating a non-equilibrium situation. The rate at which relaxation to equilibrium occurs determines the reversibility of the system. We explored several ways to investigate the reversibility of polyelectrolyte adsorption. We shall now summarise the most important observations, and put forward a model for the exchange process.

The reversibility upon dilution is difficult to assess because all our polymers have a high-affinity adsorption isotherm, which leads to a very slow desorption rate, even though locally there may be full thermodynamic equilibrium²¹.

The reversibility upon changes of the pH proved to be much more informative. The ionic strength influences the reversibility considerably. At $I = 0.1$ mol/kg, the adsorption of PVP⁺ (120 K) is reversible within 5 min, whereas at low ionic strength ($I = 0.005$ mol/kg) the adsorbed amount corresponding to the new pH-value is not reached in 30 min. The reversibility of AMA at $I = 0.005$ mol/kg was checked as a function of the initial coverage. The experiments indicate that, initially, the desorption is fast but later the process slows down. The level for adsorption at the new pH is not reached in 30 min.

Another estimate of the reversibility of the adsorption is obtained from the exchange of polymers. We performed two types of experiments: simultaneous adsorption from bimodal mixtures and sequential adsorption experiments. From the experiments on TiO₂ with mixtures of PVP⁺ molecules differing in chain length, we found that at a higher ionic strength the exchange is faster. The rate of the desorption of small molecules is constant, which indicates that displacement of small molecules occurs mainly by "direct contact", i.e., an incoming molecule rapidly displaces a number of molecules upon attachment. This is probably caused by the slow reconfiguration of PVP⁺. For the adsorption of PVP⁺ 120 K on TiO₂, which is precoated with PVP⁺ 12 K, we found that the final total adsorbed amount is *higher* than for adsorption of PVP⁺ 120 K on a bare surface. This is probably due to an ageing of the precoated

layer, leading to a more extensive charge regulation. The plateau level for PVP⁺ 120 K on SiO₂ precoated with PVP⁺ 3 K, however, was *lower* than the value for PVP⁺ 120 K adsorbing on a bare surface. This is due to the absence of charge regulation combined with a more efficient surface coverage by smaller molecules.

The sequential adsorption experiments of the polyelectrolyte PVP⁺ and the neutral polymer PEO show that PEO can be used as a probe for the space left on the surface after PVP⁺ has adsorbed. At pH = 4 the same amounts of PEO adsorb on surfaces precoated with PVP⁺ 3 K and with 120 K, even though the adsorbed amount for PVP⁺ 120 K is twice as high as for PVP⁺ 3 K. This indicates that the shorter PVP⁺ 3 K covers the surface more efficiently than PVP⁺ 120 K.

From all these observations, we can deduce a scenario for the exchange of polymers and indicate which steps determine the rate of exchange and how these steps are influenced by the various parameters. Exchange consists of the following steps: (i) attachment of incoming molecules, (ii) reconfiguration of the adsorbed layer and (iii) desorption of displaced molecules. From our experiments, we conclude that the reconfiguration in all our systems is very slow. Since, for reconfiguration, bonds must be broken and new bonds formed, the reconfiguration rate depends on the strength of the bond and the number of bonds with the surface. For polyelectrolytes adsorbing on oppositely charged surfaces the bonds are usually electrostatic (ion pairs); the strength of such bonds is mainly determined by the distance between the charged groups on the surface and the polymer, and by the ionic strength, although other (non-electrostatic) interactions can also play a role. The number of bonds is determined by the degree of dissociation, by the degree of polymerisation of the polymer, and by the conformation of the molecule on the surface. Other factors which limit the conformation rate are spatial constraints like pinning processes and entanglements in the layer, or limited available space on the surface, especially at high coverage.

When reconfiguration is slow so that desorption slows down, the attachment of new polymer molecules creates a surplus of charge on the surface. This leads to an electrostatic barrier which hinders the attachment of newly arriving molecules. De Laat *et al.*¹² have shown that this barrier is highest for a molecule which carries a high charge, i.e., a long polyelectrolyte. This can lead to fractionation of a polydisperse sample such that at low ionic strength the intermediate fraction is

primarily adsorbed^{11,12}. For the longest molecules the barrier is too high to allow them to participate in the exchange process. The barrier is lower at high ionic strength, which facilitates the participation of the longer molecules¹². The adsorbed fraction is then shifted to a higher mean molar mass.

We finally return to the main question of this work: How reversible is the adsorption of polyelectrolytes? Our observations and also a variety of literature data^{7,8,10,12,14} indicate that polyelectrolyte adsorption is not very reversible. In some cases, it may take a very long time before equilibrium is attained, especially at low ionic strength. It is therefore questionable whether experimental results can be interpreted fully with theoretical (equilibrium) theories, especially with respect to the structure of the adsorbed layer. This structure is important for characteristic properties like the layer thickness²³ or the flocculation rate²⁴.

3.5 Conclusions

The reversibility of a system determines whether or not equilibrium is attained. We studied the reversibility of the system in three ways: (i) by dilution, (ii) by changing the pH and (iii) by exchange processes.

All the experiments show that the reversibility is better at high ionic strength; at low ionic strength usually no reversibility occurs on the timescale of the experiments (30 min). Sequential adsorption experiments of PVP⁺ molecules differing only in chain length indicate that on TiO₂ the ageing of preadsorbed (small) molecules makes it harder to remove them. Mixed layers of small and long molecules attain on TiO₂ a *higher* and on SiO₂ a *lower* adsorbed amount than the plateau level for a sample of long molecules only.

The reconfiguration of the adsorbed layer was found to be very slow and to be the rate-limiting step for the relaxation process. Due to the slow reconfiguration a barrier is created for incoming polyelectrolyte molecules. A qualitative picture was put forward for the structure of the adsorbed layer, taking the limited reconfiguration of the adsorbed molecules into account. It shows that the layer can be rather heterogeneous, in particular for long polyelectrolyte molecules. In this picture, there is still free area available on the surface. Even at the plateau adsorbed amount neutral polymer molecules can attach. These latter molecules can thus serve as a probe for the amount of area left.

We conclude that the adsorption of polyelectrolytes is only partially reversible on practical timescales. Especially the structure of the adsorbed layer is in many cases far from its equilibrium structure.

3.6 References

- (1) G. Durand, F. Lafuma, and R. Audebert, *Progr. Colloid Polym. Sci.*, 1988, **266**, 278.
- (2) J. Papenhuijzen, G.J. Flier, and B.H. Bijsterbosch, *J. Colloid Interface Sci.*, 1985, **104**, 530.
- (3) B. Popping, A. Deratani, B. Seville, N. Desbois, J.M. Lamarche, and A. Foissy, *Colloids Surfaces*, 1992, **64**, 125.
- (4) H.G.M. van de Steeg, A. de Keizer, M.A. Cohen Stuart, and B.H. Bijsterbosch, *Colloids Surfaces A*, 1993, **70**, 77.
- (5) G.J. Flier, M.A. Cohen Stuart, J.M.H.M. Scheutjens, T. Cosgrove, and B. Vincent, *Polymers at interfaces*, Chapman & Hall, London, 1993.
- (6) M.C. Cafe and I.D. Robb, *J. Colloid Interface Sci.*, 1982, **86**, 411.
- (7) J. Meadows, P.A. Williams, M.J. Garvey, R.A. Harrop, and G.O. Phillips, *Colloids Surfaces*, 1988, **32**, 275.
- (8) J. Meadows, P.A. Williams, M.J. Garvey, and R. Harrop, *J. Colloid Interface Sci.*, 1992, **148**, 160.
- (9) J.C. Dijt, M.A. Cohen Stuart, and G.J. Flier, *Macromolecules*, 1994, **27**, 3219.
- (10) H. Tanaka, L. Ödberg, L. Wågberg, and T. Lindström, *J. Colloid Interface Sci.*, 1990, **134**, 219.
- (11) A.W.M. de Laat and G.L.T. van den Heuvel, *Colloids Surfaces*, 1995, accepted.
- (12) A.W.M. de Laat, G.L.T. van den Heuvel, and M.R. Böhmer, *Colloids Surfaces*, 1995, accepted.
- (13) D.R. Bain, M.C. Cafe, I.D. Robb, and P.A. Williams, *J. Colloid Interface Sci.*, 1982, **88**, 467.
- (14) R. Ramachandran and P. Somasundran, *J. Colloid Interface Sci.*, 1987, **120**, 184.
- (15) U.S. Adam and I.D. Robb, *J. Chem. Soc., Faraday Trans. I*, 1983, **79**, 2745.
- (16) A.W.M. de Laat and G.L.T. van den Heuvel, *Colloids Surfaces A*, 1993, **70**, 179.
- (17) J.C. Dijt, M.A. Cohen Stuart, J.E. Hofman, and G.J. Flier, *Colloids*

Surfaces, 1990, **51**, 141.

(18) J.C. Dijt, M.A. Cohen Stuart, and G.J. Fleer, *Adv. Colloid Interface Sci.*, 1994, **50**, 79.

(19) W.N. Hansen, *J. Optical Soc. Am.*, 1968, **58**, 380.

(20) R. Israëls, J.M.H.M. Scheutjens, and G.J. Fleer, *Macromolecules*, 1993, **26**, 5405.

(21) J.C. Dijt, M.A. Cohen Stuart, and G.J. Fleer, *Macromolecules*, 1992, **25**, 5416.

(22) T. Hiemstra, J.C.M. de Wit, and W.H. van Riemsdijk, *J. Colloid Interface Sci.*, 1989, **133**, 105.

(23) P.F. Luckham and J. Klein, *J. Chem. Soc., Faraday Trans. I*, 1984, **80**, 865.

(24) Y. Adachi, M.A. Cohen Stuart, and R. Fokkink, *J. Colloid Interface Sci.*, 1994, **167**, 346.

Chapter 4 The adsorption of charged block copolymers with two adsorbing blocks

We have investigated the adsorption of diblock copolymers consisting of uncharged water-soluble dihydroxypropyl methacrylate (HMA) and positively charged dimethylaminoethyl methacrylate (AMA). As the substrate we used TiO_2 and SiO_2 . Adsorbed amounts of the block copolymers and of the homopolyelectrolyte AMA were determined by means of reflectometry, as a function of pH, ionic strength and block length ratio. These results are compared with theoretical calculations using the self-consistent-field (SCF) theory of Scheutjens and Fleer extended for charged block copolymers.

We find that the adsorption behaviour of charged block copolymers is essentially different from that of neutral block copolymers, because the electrostatic interactions, including an induced interaction, play a key role. This induced interaction influences the dissociation of the surface groups, thereby reducing the build-up of the electrostatic potential on the surface. When the composition of the block copolymer is varied a maximum in the adsorbed amount is observed, which is similar to that found for adsorption of polyelectrolytes with varying segment charge. Also, depending on the pH charged block copolymers can adsorb with both blocks in contact with the surface, whereas neutral block copolymers usually have one anchoring block.

Qualitative agreement is found between the experimental and theoretical results.

4.1 Introduction

Uncharged block copolymers are well known for their stabilising abilities^{1,2}, arising from their conformation on the surface. Usually, one block is preferentially adsorbed (anchor), leaving the other block protruding into the solution (buoy). When the buoy block is swollen in the solvent, particles covered with such a layer will repel each other and thus be sterically stabilised.

The adsorption of neutral block copolymers depends on the anchor-to-buoy length ratio. It is customary to distinguish two regimes³. For a

relatively long anchor the adsorbed amount is limited primarily by the available area for the anchor (anchor regime). In this regime the adsorbed amount therefore increases when the anchor block becomes smaller. When the buoy blocks are relatively long, their lateral repulsion will become important. Now, the adsorbed amount results from a balance between anchoring energy and lateral repulsion of the buoy (buoy regime). In this regime, a decreasing anchor length will reduce the adsorbed amount. The resulting picture is that upon variation of the block copolymer composition a maximum in the adsorbed amount is found. Theoretically, this was found by Marques and Joanny³ using scaling arguments, and by Evers *et al.*⁴ using a self-consistent mean-field theory; it was verified experimentally by Wu *et al.*⁵.

For charged block copolymers there are also electrostatic interactions to be reckoned with, which could change the picture sketched above considerably. Two cases can be distinguished. On equally charged or uncharged surfaces no adsorption will occur unless there is an adsorption energy which can overcome the electrostatic repulsion. On oppositely charged surfaces, however, adsorption is stimulated by the electrostatic contributions. Usually, compensation or slight overcompensation of the surface charge is found. This means that the adsorbed amount Γ is approximately inversely proportional to the segment charge τ of the polyelectrolyte

$$\Gamma \propto -\frac{\sigma_0}{\tau} \quad (4.1)$$

where σ_0 is the surface charge density.

Equation 4.1 indicates that at given σ_0 the adsorbed amount will rise when the segment charge is reduced. This goes on until at a certain point a maximum in the adsorbed amount is found: further reduction of the charge weakens the electrostatic attraction between polymer and surface too much. Using a self-consistent mean-field theory, such a maximum was predicted by Evers *et al.*⁶ and by Van de Steeg *et al.*⁷ for polyelectrolytes with a high and a low surface affinity, respectively. It has also been found experimentally by Wang and Audebert⁸ and Blaakmeer *et al.*⁹.

The aim of this investigation is to study the adsorption of block copolymers consisting of one charged and one uncharged block. To our knowledge, this is the first study on the adsorption properties of such block copolymers. We were especially interested in the possibility to form

a charged buoy layer on a surface, where the uncharged block would adsorb and the charged block would not. For this reason we used a copolymer consisting of one positively charged block and one neutral water-soluble block, where the latter has a non-electrostatic affinity for the surface. Depending on the surface charge we can then envisage three possible situations (see also Fig. 1.3). Firstly, on a positively charged surface, the charged block is repelled so that a charged buoy layer may be formed. Secondly, on a negatively charged surface the charged block can anchor and we might have a neutral buoy layer. Thirdly, an intermediate situation is possible in which both blocks adsorb on the surface so that a mixed layer builds up, without clear anchor-buoy characteristics.

The electrostatic interactions in the system are influenced by the salt concentration and the pH. It is necessary to vary these parameters as well as the block copolymer composition to obtain a coherent picture.

The main questions are therefore: (i) how is the adsorption affected by the pH, the salt concentration and the block copolymer composition, and (ii) in what conformation do block copolymers adsorb on the surface under various conditions.

In order to answer these questions we measured the adsorbed amount as a function of pH, salt concentration and composition, using reflectometry. As substrates we used the oxides SiO_2 and TiO_2 , which have a pH-dependent charge density. For obtaining insight in the conformation of adsorbed charged block copolymers we performed experiments where the surface was exposed sequentially to neutral and charged homopolymers. The experimental results are compared with theoretical calculations using a self-consistent mean-field lattice model.

4.2 Materials and methods

4.2.1 Block copolymers - polymerisation

The block copolymers were synthesised by the group of Dr. Arnold in Halle (Germany) by sequential anionic copolymerisation of protected glyceryl methacrylate with dimethylaminoethyl methacrylate (AMA). Subsequent hydrolysis of the protecting group yields a block copolymer of dihydroxypropyl methacrylate (HMA) and AMA. The HMA block carries hydroxyl groups, which make it water-soluble and enable the formation of hydrogen bonds with the oxide surface. The AMA block contains tertiary amine groups that are positively charged over most of the practical pH-range.

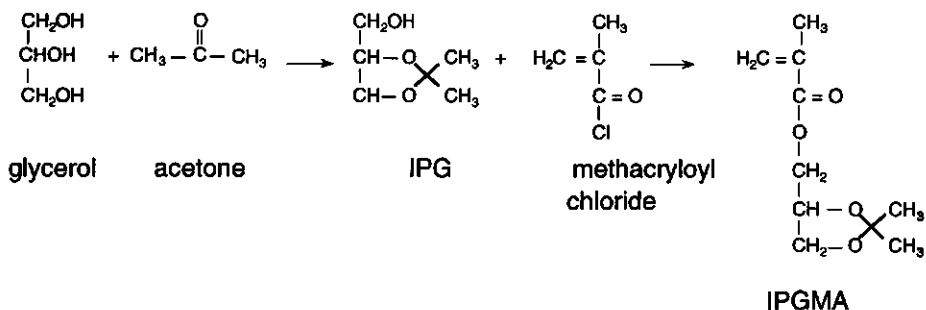


Figure 4.1 Reaction scheme for the synthesis of the monomer IPGMA. First, glycerol reacts with acetone to isopropylidene glycerol (IPG), which is then esterified with methacryloyl chloride to form isopropylidene glycerol methacrylate (IPGMA).

AMA can be polymerised directly by anionic polymerisation (after proper purification) but HMA cannot, because it has active hydrogen atoms. The hydroxyl groups were therefore protected by forming an acetal, (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate (isopropylidene glycerol methacrylate, IPGMA), which is easily hydrolysed after its polymerisation¹⁰. The synthesis of IPGMA is shown in Fig. 4.1. First, isopropylidene glycerol (IPG) was prepared following a slightly modified version of the method described by Newman *et al.*¹¹. Subsequently, the required methacrylate monomer was synthesised by reacting IPG with methacryloyl chloride in triethylamine. The obtained IPGMA was distilled twice under vacuum and then stored over CaH_2 at 4° C.

Before use in the polymerisation the monomers dimethylaminoethyl methacrylate (AMA, purchased from Fluka) and IPGMA were stored for several days over CaH_2 . Directly before introducing the monomer into the reactor, remaining traces of H_2O were removed by use of a triisobutylaluminium solution in hexane. This solution ($\approx 10\%$) was added dropwise to the monomer, until the yellow-green colour, due to the formation of a monomer-aluminiumalkyl complex, remained, thus indicating that water was no longer present. The hexane was removed at low pressure, after which the monomer was distilled *in vac.* at 40 - 50° C.

The polymerisation, summarised in Fig. 4.2, was carried out in tetrahydrofuran (THF) under ultra pure argon atmosphere in glass reaction vessels that had been cleaned by heating under vacuum. The solvent was first dried over sodium and distilled once. Shortly before the polymerisation, THF was further purified by adding polystyryllithium and then distilled into the reactor under reduced pressure.

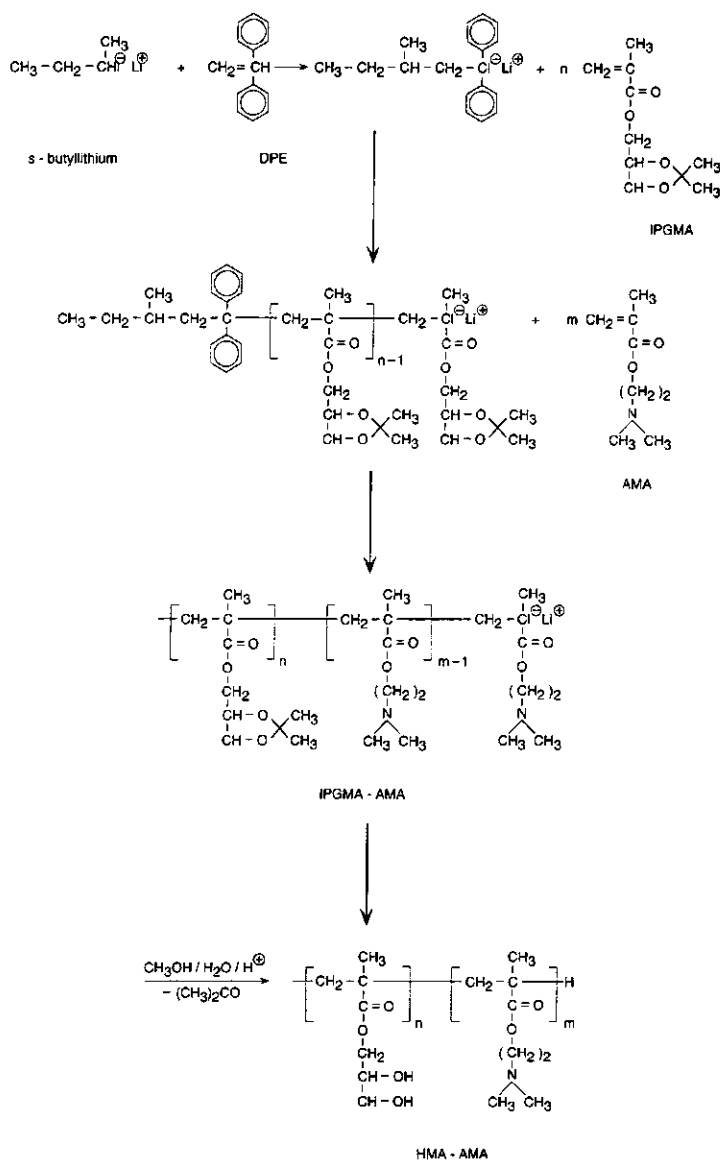


Figure 4.2 Reaction scheme for the synthesis of HMA-AMA diblock copolymers. First, *s*-butyllithium reacts to 1,1-diphenylethylene (DPE) (initiation). The resulting molecule then reacts to isopropylidene glycerol methacrylate (IPGMA), whereby the first block is formed. At a certain point dimethylaminoethyl methacrylate (AMA) is introduced and the block copolymer of IPGMA and AMA is formed. The polymerisation is terminated by addition of methanol, after which IPGMA is converted into dihydroxypropyl methacrylate (HMA), by hydrolysis of the protecting group.

As the initiator, *s*-butyllithium was used, which had been prepared by reacting *s*-butyl chloride with lithium in cyclohexane under inert gas.

In the first step of the polymerisation *s*-butyllithium reacted to 1,1-diphenylethylene (DPE) (initiation) in the presence of LiCl. DPE was purified by titration with *s*-butyllithium and subsequent vacuum distillation. Anhydrous lithium chloride (LiCl 99.99%, Aldrich) was first dried for two days at 100°C under vacuum after which a 0.5 molar solution in THF was prepared for use in the polymerisation. LiCl, DPE and *s*-butyllithium were injected in molar ratios 5 : 2 : 1 through a septum, using a syringe.

After 15 min. of reaction, the monomer IPGMA was added dropwise, and the first block was formed. After 20 min. the second monomer AMA was added and the block copolymer of IPGMA and AMA was formed. After 15 more minutes of reaction, the polymerisation was stopped by addition of methanol. The temperature during the polymerisation was kept between -60 and -40°C.

The total molar mass of the block copolymer and the ratio of the block lengths can be controlled by choosing the initiator/IPGMA/AMA ratio. Two sets of polymerisations were carried out. In the second set the initiator/IPGMA/AMA ratio was chosen such as to achieve a total molar mass for the block copolymers of 20 K, while varying the block length ratio.

In order to determine the lengths of the IPGMA block (Table 4.1), samples were taken from the reactor before addition of AMA. The IPGMA polymer so obtained was precipitated and characterised by size exclusion chromatography (SEC).

The IPGMA-AMA block copolymer solutions (5 - 6%) were concentrated by evaporation to about 30% of the initial volume. The IPGMA blocks were then hydrolysed by means of aqueous HCl solution (pH = 1 - 2). After about 3 days of continuous stirring the hydrolysis of the acetal groups into dihydroxypropylgroups was complete. Remaining solvent was removed by evaporation.

4.2.2 Block copolymers - characterisation

Size Exclusion Chromatography

The SEC analyses were carried out in THF at room temperature with Styragel as the stationary phase. The polymer in the eluent was detected by differential refractometry and viscometry. Calibration was based on

Table 4.1 Characteristics of IPGMA blocks in the IPGMA-AMA block copolymers.

M_n IPGMA (K)	M_w/M_n IPGMA	projected mol fraction IPGMA (%)
2.7	1.09	100
2.7	1.09	60
22.0	1.03	95
22.2	1.03	90
19.9	1.08	75
11.9	1.05	50
7.1	1.05	25
-	-	0

polystyrene standard samples. Unfortunately, only IPGMA polymers could be analysed in this way. AMA-containing polymers adsorbed on the Styragel column and could not be studied with SEC. In Table 4.1 the properties of the IPGMA blocks in the block copolymers (before hydrolysis) are listed. Also included are the projected mol fractions of the IPGMA block in the block copolymer.

Infrared spectroscopy

Infrared spectra of the solid AMA homopolyelectrolyte (a), the HMA homopolymer (b), and of a block copolymer (c) consisting of 75% HMA and 25% AMA in KBr are shown in Fig. 4.3. In the spectrum of the AMA homopolymer (Fig. 4.3a) a strong band at 1726 cm^{-1} is found. This band appears in all three spectra and is due to the ester functionality (carbonyl group). Furthermore, in Fig. 4.3a the contribution from several CH stretch vibrations around $2970 - 2770\text{ cm}^{-1}$ is clearly visible as well as a small absorption at 3435 cm^{-1} , which is probably due to residual water. The peaks below 1600 cm^{-1} in the so-called fingerprint region we will not assign.

In the spectrum of the homopolymer HMA (Fig. 4.3b) both the strong OH stretch vibration around 3450 cm^{-1} and the ester functionality are prominent. The CH stretch vibrations (although still present) are somewhat obscured by the broad OH stretch band.

In the spectrum of the block copolymer (Fig. 4.3c), besides the bands characteristic for HMA and AMA, new bands appear at 2697 and 2519 cm^{-1} , respectively, which we assign to hydrogen bonds between the amine

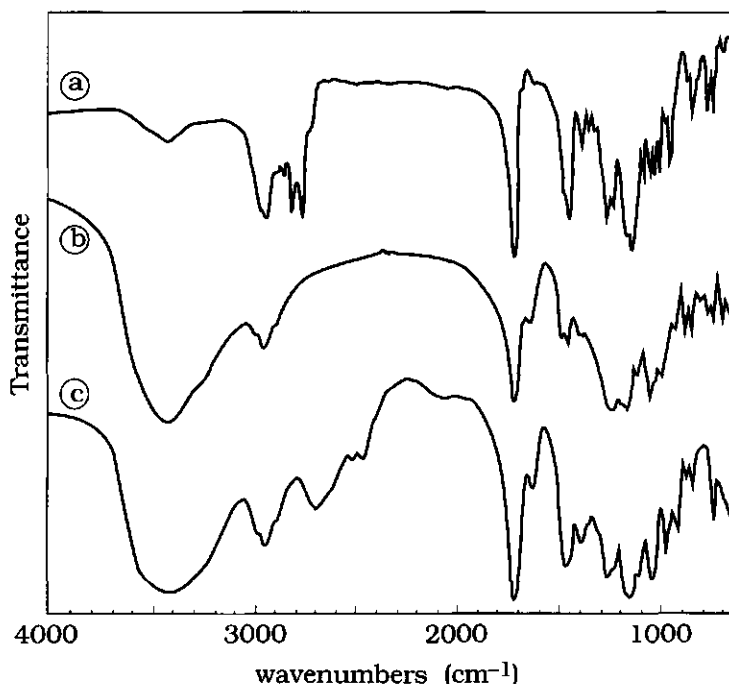


Figure 4.3 Transmission IR spectrum of (a) the homopolyelectrolyte AMA, (b) the homopolymer HMA and (c) the 75/25 HMA-AMA diblock copolymer in dry KBr. The most important peaks are at 3450 cm^{-1} (OH-stretch vibration), in the range $3000 - 2700\text{ cm}^{-1}$ (CH-stretch vibrations) around 2700 and 2520 cm^{-1} (H-bonding), and at 1730 cm^{-1} (carbonyl stretch vibration).

groups on the AMA block and hydroxyl groups on the HMA block. In the dry state the block copolymer is probably folded in such a way that AMA and HMA can interact with each other.

Proton titrations

Proton titrations provide information on the charging behaviour of the block copolymer. Also, we can use this technique to check whether hydrolysis of the ester groups occurs, since upon hydrolysis carboxylic acid groups form which are titrated around $\text{pH} = 4.8$. Although we did find that the monomer of AMA is hydrolysed rather quickly, we did not see any hydrolysis in the block copolymers, except for the HMA homopolymer. Since the polymers prove stable against hydrolysis (even when we tried to invoke hydrolysis by deliberately adding base), it must mean that the HMA in the homopolymer must be hydrolysed somewhat before polymerisation

took place. The increased stability in the block copolymers against hydrolysis is probably due to some kind of steric protection provided by the chain structure.

Having established the stability of AMA against hydrolysis we now consider its properties as a polybase. In Fig. 4.4 we present proton titration curves for the AMA homopolymer dissolved in a 0.009 and a 0.08 mol/kg KNO_3 solution, respectively. The measured proton charge is expressed as a fraction of the total amount of amine groups present. Clearly, the polymer charge is formed entirely between $\text{pH} = 5 - 10$, which rules out any contribution from acidic groups.

Most tertiary amine groups have pK_a values around 10. For a monomeric amine this would imply that it is 50% protonated at $\text{pH} = 10$. Obviously, this is not the case for our polymer. In fact, at $\text{pH} = 10$ the charge is very close to zero. Two effects are responsible for this. First, the *intrinsic* pK_a of the amine group of AMA is lower than expected. The monomer of AMA has a pK_a of 8.4, according to the manufacturer. The second effect is the dependence of the *apparent* pK_a of a functional group in a polymer chain on the degree of dissociation. Since the segments are connected in a chain the charging of a group will be hindered by the electrical fields of charged neighbouring groups. Protonation will therefore occur at a lower pH. The smaller the salt concentration and the larger the degree of protonation, the stronger these electrical fields are, and therefore

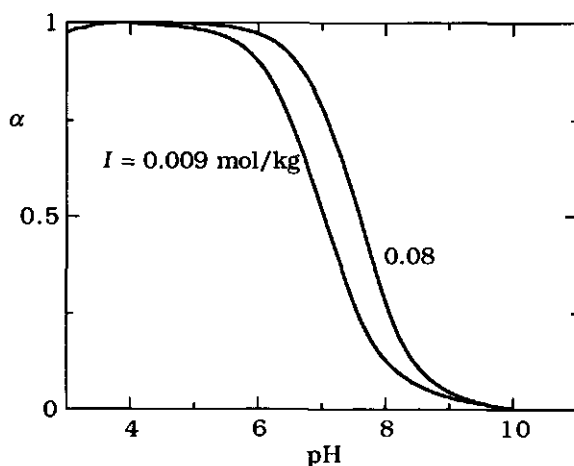


Figure 4.4 Acid-base titration of AMA in aqueous solution, at two ionic strengths ($I = 0.009$ and 0.08 mol/kg, as indicated). The measured charge is expressed as the degree of protonation α of the total number of proton-accepting (amine) groups.

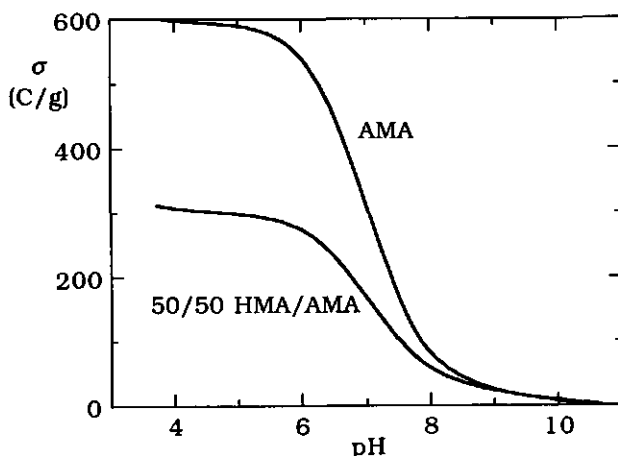


Figure 4.5 Acid-base titrations of aqueous solutions of a 50/50 HMA-AMA diblock copolymer and a AMA homopolymer, respectively. The measured charge is expressed as the total charge σ per g of polymer. The total charge of the block copolymer is approximately half that of the homopolymer.

the downward shift of the pH at which a given protonation is reached.

In Fig. 4.5 we give the titration data of the homopolymer AMA and the 50/50 HMA-AMA diblock copolymer; the charge σ is expressed here per unit weight of the polymer. Again, there is no evidence of acidic groups. The total charge of the block copolymer is at any pH half of that of AMA, because the neutral block does not contribute to the charge.

4.2.3 Adsorbent

We used strips of silicon wafers with thin top layers of SiO_2 or TiO_2 as the adsorbing surface. The wafers are of the Czochralsky-type and were purchased from Aurel GmbH (Germany). A SiO_2 layer of ca. 100 nm was formed by thermal oxidation at 1000 °C for 1 hour. A TiO_2 layer of ca. 25 nm was deposited by reactive sputtering of Ti, which was done at Philips Laboratories in Eindhoven (The Netherlands). The iso-electric point (i.e.p.) of the TiO_2 layer is around pH = 4, as determined by streaming potential measurements. The i.e.p. of SiO_2 was found to be around pH = 2. Prior to use the adsorbents were cleaned with an UV-ozone oxidation procedure. The strips could be used and cleaned many times.

4.2.4 Other reagents

All experiments were carried out in a buffer solution. A barbital-acetate

buffer was used in the pH range 3 - 8.5, and a glycine buffer was employed at pH > 8.5. These buffers contain only monovalent ions. The ionic strength of the buffer solutions was 0.005 mol/kg. Sometimes an additional amount of NaCl was added to yield an ionic strength of 0.1 mol/kg.

The polymer concentration was 10 mg/kg (10 mg polymer per kg solvent) in all experiments.

4.2.5 Reflectometry

The adsorption measurements were carried out in a reflectometer with a stagnation-point flow-cell as described by Dijt *et al.*¹². For not too high adsorbed amounts, the relative change in the signal, $\Delta S/S_0$, is proportional to the adsorbed amount Γ ¹²:

$$\Gamma = \frac{1}{A_s} \cdot \frac{\Delta S}{S_0} \quad (4.2)$$

The sensitivity factor A_s was calculated using the method of Hansen¹³, which is based on the matrix formalism of Abeles. This factor depends on the thickness d_{ox} of the oxide layer and on the indices of refraction: n_{Si} for silicon, n_{ox} for the oxide layer, and n_s for the solvent. Furthermore, the refractive index increment dn/dc of the polymer, the angle of incidence θ_i and the wavelength λ of the laser beam must be known. The values used were $n_{Si} = 3.8$, $n_{ox} = 1.46$ (SiO₂) or 2.3 (TiO₂), $n_s = 1.33$, $\lambda = 632.8$ nm, $\theta_i = 75^\circ$, $d_{ox} = 113$ nm (SiO₂) or 25 nm (TiO₂). Since there are differences in the refractivity of charged and uncharged segments, dn/dc was found to be pH-dependent, varying from 0.14 cm³/g to 0.20 cm³/g. The resulting values of A_s are in the range 0.019 to 0.027 m²/mg.

4.2.6 SCF-model calculations

The self-consistent-field (SCF) theory of Scheutjens and Fleer, developed originally for adsorption of homopolymers, has been extended to the adsorption of charged block copolymers on charged surfaces¹⁴. The system is represented by a lattice in which each lattice cell contains either a polymer segment, a salt ion, an adsorbent entity or a solvent molecule. In the simplest version of the theory only a gradient perpendicular to the surface is allowed: all variations parallel to the surface are smeared out (mean-field approximation). The non-electrostatic interactions are accounted for by Flory-Huggins χ -parameters. The electrostatic interactions are implemented using a multilayer Stern model, which can

be considered as a discrete version of the Poisson-Boltzmann equation. More detailed information on the SCF-theory can be found in a recent monograph by Fleer *et al.*².

All calculations were carried out using a cubic lattice, with a lattice constant $d = 0.6$ nm. The relative dielectric permittivity of the solvent (water) was taken as $\epsilon_r = 80$, whereas for all other substances (polymer, ions and adsorbent) $\epsilon_r = 4$. All χ -parameters were chosen to be 0, except for the χ_s -parameter of the neutral block with the surface. Zero solvency parameters imply a good solvent for both blocks of the polymer.

4.3 Results and discussion

4.3.1 Homopolymer adsorption

To get a better understanding of the adsorption behaviour of block copolymers, the adsorption of the corresponding homopolymers should be studied first. Since our homopolymer HMA, intended to be uncharged, is partly hydrolysed, only results for the charged homopolymer AMA are given. (See also Chs. 2 and 3 for more detailed information on the kinetics of the adsorption and the adsorbed amount, and on the reversibility of the adsorption process).

In Fig. 4.6 the amount of AMA adsorbed on TiO_2 as a function of pH at two ionic strengths is given. Both curves show an increase in the adsorbed amount with increasing pH. At a certain pH it reaches a maximum and then it drops rapidly to zero. Addition of salt enhances the adsorption at $\text{pH} < 7$. At $\text{pH} > 7$, however, the adsorbed amount decreases and a shift in the maximum to lower pH is observed.

In order to explain these experimental findings, it is necessary to consider the balance of the attractive and repulsive interactions in the system, which governs the adsorption of polyelectrolytes on a charged surface. The most important interactions are:

- the electrostatic interaction between a polymer segment and an adsorbent molecule, which can be either repulsive (when both charges have the same sign) or attractive (when they have opposite signs). Note that for a heterogeneously charged surface (i.e., with both positively and negatively charged groups) repulsive and attractive interactions can be present at the same time.
- the non-electrostatic attraction between a polymer segment and an adsorbent molecule (e.g., through H-bonding).

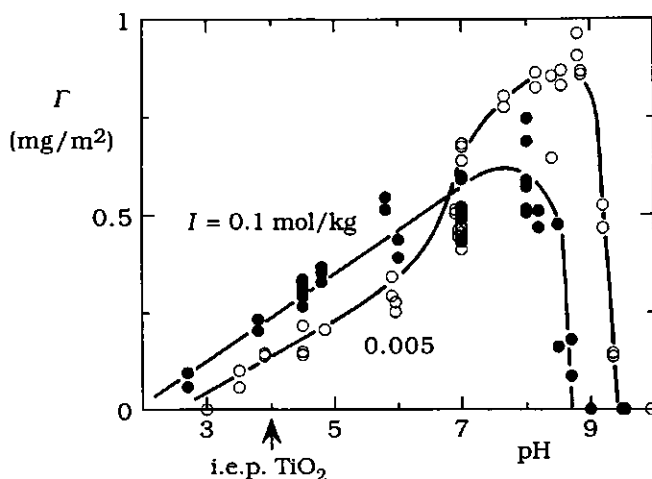


Figure 4.6 The effect of the pH on the adsorbed amount of the homopolyelectrolyte AMA onto TiO_2 . The ionic strength was 0.005 mol/kg (open symbols) and 0.1 mol/kg (filled symbols). The polymer concentration was 10 mg/kg and the buffer concentration 0.005 mol/kg.

- electrostatic and non-electrostatic interactions between polymer segments within the adsorbed layer. For a polymer in a good solvent these interactions are repulsive.

There is an additional interaction possible if the surface possesses dissociative groups on the surface, as is the case for oxides. The surface charge of oxides can be considered as originating from proton transfer reactions between the surface and the bulk solution. Both negative and positive charges can thus be formed; their sum is the net surface charge¹⁵. The proton transfer equilibria are not only determined by the intrinsic pK_a of the surface groups, but also by the electric potential which these groups experience, *i.e.*, by charges in their immediate surroundings. When there is a surplus of positive charge nearby, *e.g.*, after adsorption of a positively charged polyelectrolyte, the apparent pK_a will be shifted toward higher values. Locally, the surface charge becomes more negative, thereby reducing the build-up of a high positive electrostatic potential on the surface (charge regulation, see Ch. 2). Indeed, it has been found in several studies^{16,17} that oxide surfaces expel or take up protons upon adsorption of a polyelectrolyte. This induced interaction can enhance the adsorption, but it can not be the sole driving force for adsorption.

The occurrence of such an induced electrostatic interaction, in

combination with a non-electrostatic (or even electrostatic) attraction might explain the significant adsorbed amount of polyelectrolytes on oxides in the i.e.p.; in this case the direct electrostatic attraction is due to the heterogeneity of the surface charge (which is overall zero). Such adsorption can be seen in Fig. 4.6 and has also been found by several others¹⁸⁻²⁰. The driving force for adsorption in the i.e.p. is usually interpreted to be of a non-electrostatic nature^{18,21}. Another possibility, though, is the presence of a heterogeneous charge distribution, as discussed in more detail below.

In most theoretical models, the simplified picture of a surface as a homogeneously charged flat plate is used. However, the adsorption behaviour of polyelectrolytes on oxides in the i.e.p. might be better understood by taking into account a heterogeneous charge distribution. In the i.e.p. there are both negatively and positively charged sites on the surface, even though the overall surface charge is zero. The occurrence of oppositely charged patches offers a distinct possibility for polyelectrolytes to adsorb on surfaces where there is no net charge. An analogous situation of uncharged polymers adsorbing on overall non-adsorbing surfaces with energetic heterogeneity was studied theoretically by several groups²²⁻²⁴. In such a system with a distribution of adsorption energies on the surface, the patch size was found to be especially important. On very large patches the contact with non-adsorbing surface sites is minimised and the adsorbed amount is proportional to the amount of adsorbing surface²⁴. When the patches become smaller adjacent non-adsorbing sites also affect the adsorption. In an analogous way a distribution of the charges on the surface, in combination with the induced interaction described above, may well lead to an electrostatic attraction between polymer and surface which is substantially stronger than expected on the basis of the average surface charge alone.

The effect of addition of salt is very complicated, since both attractive and repulsive electrostatic interactions are present in the system. The adsorbed amount can now increase or decrease depending on the relative importance of the electrostatic factors for adsorption. It is very difficult to estimate the strength of the electrostatic interaction and the effect of salt on it. However, we can predict the relative effect of salt on the electrostatic attraction upon variation of the segment charge in a polyelectrolyte.

The electrostatic attraction of a polyelectrolyte to the surface depends on the number of charged segments in contact with the surface. Added

salt will compete with these segments for the surface charge, thereby weakening the attraction. For a highly charged polyelectrolyte this attraction will be weakened less than for a polyelectrolyte with a low segment charge.

The electrostatic repulsion depends on the electrostatic potential in the adsorbed polymer layer. A high potential will arise when overcompensation of the surface charge occurs. Now two cases can be distinguished:

- When no overcompensation occurs, the electrostatic repulsion will not be very high and the salt effect is mainly determined by its effect on the electrostatic attraction with the surface. Addition of salt will reduce the adsorbed amount. This reduction will be more strongly when the segment charge is small.
- When overcompensation of the surface charge is found, the electrostatic repulsion becomes an important factor. Addition of salt can have a strong effect on the electrostatic repulsion when the electrostatic potential is high, as it can be for highly charged polyelectrolytes. Thus, for a polyelectrolyte with a high segment charge the attraction is not affected strongly by the salt concentration, whereas the repulsion will be affected more strongly. The result is an increase of the adsorbed amount upon addition of salt. For polymers with a low segment charge the effect of salt on the attraction will become more important and the screening of the repulsion becomes of minor relevance. This means that a smaller increase, or even a decrease in the adsorbed amount can be observed. Indeed, this behaviour was found by Durand *et al.*²⁵ for the adsorption of cationic polyacrylamides on montmorillonite. They observed that for a cationic monomer content (τ) of 1% the adsorbed amount decreased with increasing salt concentration. For $\tau = 5\%$ they found no salt effect, whereas for highly charged polyacrylamides ($\tau = 13\%$ and $\tau = 30\%$) the adsorbed amount increased with increasing salt concentration.

From the balance of the interactions described above we seek an explanation for the observed effects of pH and ionic strength. The significant adsorption of the homopolyelectrolyte at and even below the i.e.p. points to a strong (non-electrostatic and/or heterogeneous) attraction between surface and polyelectrolyte. Increasing the pH leads to an increasingly negative charge on the surface, which enhances the adsorption. At a certain pH also the polymer groups will be affected by the pH. Deprotonation leads to a smaller charge on the polymer which has

two opposite effects:

- More molecules are needed to compensate the surface charge (see Eq. 4.1). This effect causes the steep increase in the adsorbed amount at $\text{pH} = 7$ at low ionic strength.
- The electrostatic attraction between polymer and surface is weakened. This gives rise to the sharp decrease in the adsorbed amount at $\text{pH} > 8.5$ (low ionic strength) and at $\text{pH} > 7.8$ (high ionic strength).

Evidently, uncharged AMA does not stick to TiO_2 . Hence, there can be hardly any non-electrostatic interaction. We therefore ascribe the adsorption at $\text{pH} \leq \text{i.e.p.}$ to an electrostatic attraction on a heterogeneously charged surface, as discussed above. The adsorption is probably further enhanced by charge regulation of the oxide surface, as was discussed in Ch. 2.

Upon addition of salt all electrostatic interactions are screened. At $\text{pH} > 7$ the interaction between surface and polymer, which is weakened due to deprotonation of the polymer, is lessened even more by salt screening, causing a decrease in the adsorbed amount and a shift of the maximum towards lower pH. At $\text{pH} < 7$, the effect of screening is reversed. Now adding salt enhances the adsorbed amount since in this pH-range the adsorption is suppressed by the strong electrostatic repulsion within the adsorbed layer, which effect is stronger than that of the decreasing attraction between polymer and surface. The direction of the salt effect agrees with what is predicted above for a polyelectrolyte with a varying charge, namely that the adsorbed amount decreases more strongly as the polyelectrolyte becomes more weakly charged.

We conclude that for the homopolyelectrolyte AMA the adsorption depends markedly upon pH and salt concentration because these parameters affect the balance between the attractive and repulsive interactions in the system.

4.3.2 Block copolymer adsorption

Figure 4.7 shows the adsorption of two HMA-AMA block copolymers as well as that of the homopolyelectrolyte AMA as a function of pH at two different ionic strengths. The curve for the homopolyelectrolyte is the same as presented in Fig. 4.6 and is included here for comparison. The block copolymers follow the same trends as AMA, although the adsorbed amount is considerably higher. Another feature is that at $\text{pH} < 3$ and at $\text{pH} > 9$ (low ionic strength) there still is a significant adsorption of the

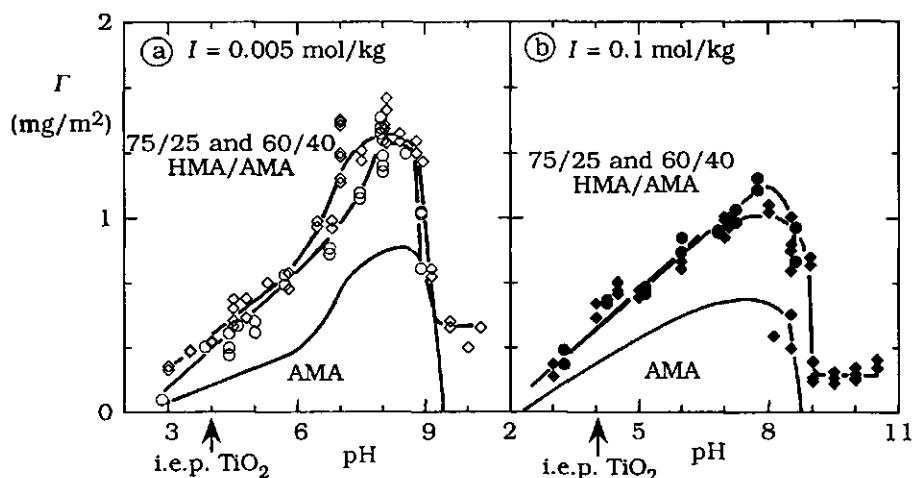


Figure 4.7 The effect of pH on the adsorbed amount of the homopolyelectrolyte AMA ($M_w = 20$ K) and of the block copolymers (60/40 HMA-AMA ($M_w = 4$ K); circles and 75/25 HMA-AMA ($M_w = 20$ K); diamonds) on TiO₂. The ionic strength was 0.005 mol/kg ((a), open symbols) and 0.1 mol/kg ((b), filled symbols). The experimental curve for AMA is identical to that in Fig. 4.6. Other parameters see Fig. 4.6.

block copolymer, whereas the adsorption of AMA is almost zero under these conditions. Apparently, the adsorption is enhanced by the uncharged HMA. In the intermediate pH-range, also the AMA-block is able to adsorb, thereby following the charge on the surface. Since in the block copolymer only the AMA block attributes to the charge compensation, more molecules have to adsorb, leading to much higher adsorbed amounts.

4.3.3 Effect of block copolymer composition

Figure 4.8 illustrates the influence of the block copolymer composition on the adsorption behaviour. The experiments were performed on both TiO₂ and SiO₂, at pH = 4.5 and pH = 7, and for two ionic strengths. All the data of Fig. 4.8 apply to block copolymers with a constant chain length ($M_w = 20$ K). However, their composition is different (see Table 4.1).

Starting at high AMA content, an increased adsorption is observed when the charged block becomes smaller. In almost all curves a maximum is reached, after which, at still smaller AMA block lengths, the adsorbed amount decreases again. Only in the experiment performed on TiO₂ at pH = 4.5 and at a low ionic strength is such a maximum absent. In all cases the adsorbed amount at pH = 7 is higher than that at pH = 4.5. The effect

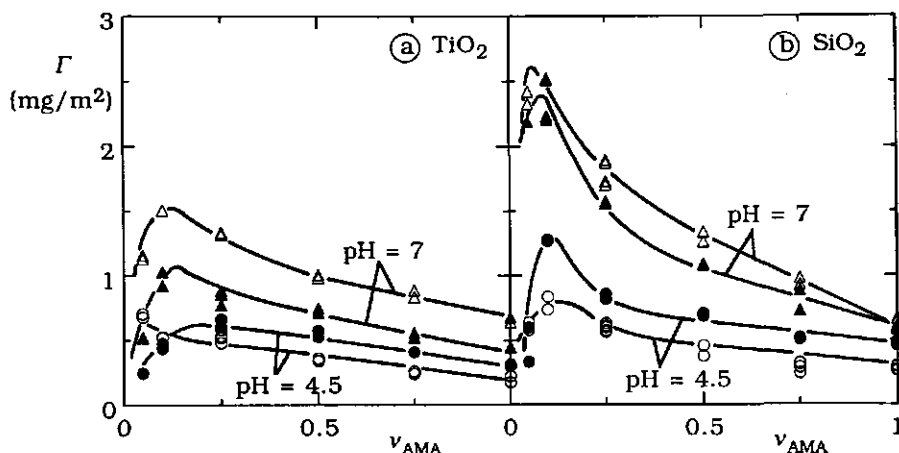


Figure 4.8 The effect of the block copolymer composition on the adsorbed amount on TiO_2 (a) and SiO_2 (b) at pH = 4.5 and at pH = 7, as indicated. The experiments were performed at low ionic strength (0.005 mol/kg; open symbols) and at high ionic strength (0.1 mol/kg; filled symbols). The molecular weight of the block copolymers is constant, $M_w = 20$ K, other parameters as in Fig. 4.6.

of added salt is quite complicated. At pH = 7 it causes a decrease in the adsorbed amount, whereas at pH = 4.5 the effect depends on the composition: for block copolymers with a high AMA content the adsorption is increased, for relatively small AMA blocks it is reduced.

The strive for charge compensation by the charged block is the main reason for the existence of the maximum. When the AMA block becomes smaller, more molecules do adsorb. At a certain composition (around 10% AMA) a maximum is found since further reduction of the length of charged block weakens the electrostatic attraction to the surface too much. This is the same behaviour as found in the case of homopolyelectrolyte adsorption at high pH.

The effects of pH and ionic strength for the block copolymer are comparable to the trends found for the homopolymer AMA (Fig. 4.6) and can be explained along the same lines. At pH = 7 the surface charge is much more negative than at pH = 4.5, which causes an increase in the adsorption of the AMA block and thus of the block copolymer.

Upon salt addition all electrostatic interactions are weakened. At high pH a decrease of the adsorption is found similar to that in the homopolyelectrolyte. There the electrostatic attraction between surface and polymer will be affected most. At low pH this attraction is also

screened, but now the electrostatic repulsion within the adsorbed layer, which opposes the adsorption, is weakened even more, leading to an increase in the adsorbed amount. Only for small AMA blocks, which have a weak electrostatic attraction with the surface, does the adsorption decrease, thereby shifting the maximum to higher AMA-content. Again we find the direction of the salt effect in agreement with our prediction that the adsorbed amount will be reduced more strongly for polymers with a smaller charge.

4.3.4 Sequential adsorption experiments

The question is still open which block in the block copolymer is attached to the surface. We performed sequential adsorption experiments to see whether a charged polymer does in fact displace a neutral polymer or vice versa. As the neutral polymer we used a sample of the polysaccharide dextran with a molecular weight of 500 K. The charged polymer was the homopolyelectrolyte AMA. In a sequential adsorption experiment one polymer was allowed to adsorb first, after which the other was added. The expectation is that nothing will happen when the first polymer adsorbs preferentially, whereas complete displacement occurs if the second polymer has a higher affinity for the surface, eventually leading to the

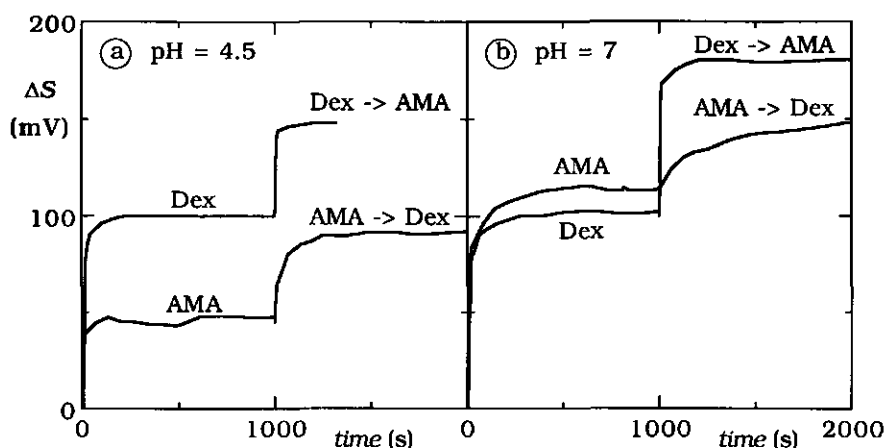


Figure 4.9 Sequential adsorption experiments on TiO_2 of the neutral polysaccharide dextran (Dex) and the homopolyelectrolyte AMA at pH = 4.5 (a) and pH = 7 (b). The change in signal ΔS , is proportional to the adsorbed amount (see Eq. 4.2). Other parameters: ionic strength 0.005 mol/kg, $M_w(\text{Dextran}) = 500 \text{ K}$, $M_w(\text{AMA}) = 20 \text{ K}$, polymer concentration 10 mg/kg, and buffer concentration 0.005 mol/kg.

adsorption level of the second polymer. Such displacement processes are known to occur for many pairs of neutral polymers²⁶.

In Fig. 4.9 we present the results of the experiments at pH = 4.5 and pH = 7.0 at an ionic strength of 0.005 mol/kg. Surprisingly, we observe in all cases an increase in the adsorbed amount upon addition of the second polymer. Also, the final level depends on the order of polymer addition, indicating that there is no equilibrium on this time scale (15 min.). The effect of the pH on the adsorption of the polymers on a bare surface is as expected. The adsorption of dextran is not influenced by the pH, since it is a neutral polymer, whereas for AMA the adsorption varies with pH. For AMA added to a surface covered with dextran the same trend is found. On a surface with preadsorbed AMA, however, more dextran does adsorb at low pH.

Clearly, there is no absolute preference for either polymer on the surface. Both polymers adsorb and a mixed layer on the surface is formed. The reason for the lack of preference probably lies in the different driving forces for adsorption. The neutral polymer adsorbs because of its non-electrostatic interaction with the surface. Since dextran cannot screen the surface charge the polyelectrolyte will adsorb over the dextran layer, by an electrostatic mechanism. AMA, not having a strong affinity to the surface, adsorbs solely because of the charge on this surface. Once charge compensation or a slight overcompensation is attained, the adsorption of AMA stops, leaving a partly covered surface (see also Ch. 3). On this surface dextran molecules can still attach, depending on the amount of space left. At high pH more AMA is adsorbed, leaving less room for dextran. Such behaviour was also observed by De Laat and Van den Heuvel²⁷ for sequential adsorption of polyvinyl alcohol and polyacrylic acid on BaTiO₃ dispersions.

If formation of a mixed layer is the general pattern for mixtures of charged and uncharged homopolymers, we may expect that adsorption of the block copolymer also leads to a mixed layer. The AMA block is in contact with the surface, and the conformation of the HMA block, which has a non-electrostatic affinity to the surface, depends on the amount of space left on the surface and thus on the adsorbed amount of the block copolymer. For low adsorbed amounts the HMA block can adopt a relatively flat conformation, whereas at high adsorbed amounts it will be forced into loops and tails.

4.3.5 Comparison with theoretical calculations

The experimental results may be compared with calculations using a self-consistent mean-field theory¹⁴. In Fig. 4.10, which is the theoretical counterpart of Fig. 4.8, the effect of composition on the adsorbed amount is shown. The calculations were performed for a block copolymer C_nN_{100-n} with a constant total length of 100 segments, n of which are charged (C) and $100 - n$ neutral (N). The charged segments carry a constant positive charge of one elementary charge per segment. The neutral block has a non-electrostatic affinity for the surface, corresponding to an adsorption energy of 0.5 kT per segment ($\chi_{sN} = 0.5$). All other χ parameters were chosen to be zero. The curves were calculated for an uncharged surface ($\sigma_0 = 0 \text{ C/m}^2$) and for two oppositely charged surfaces ($\sigma_0 = -0.02$ and -0.05 C/m^2). The theoretical surface charge is fixed, which means that, unlike in the experimental system, it does not adjust itself to the pH. The volume fraction of salt in the bulk solution is $\phi_s = 0.001$ (a) or 0.01 (b). This can be converted into an ionic strength by multiplying ϕ_s by $7.7 \times 10^3 \text{ mol/m}^3$. The conversion factor depends on the lattice spacing, which in our case was chosen as 0.6 nm .

Figure 4.10 shows that block copolymer adsorption is different for an

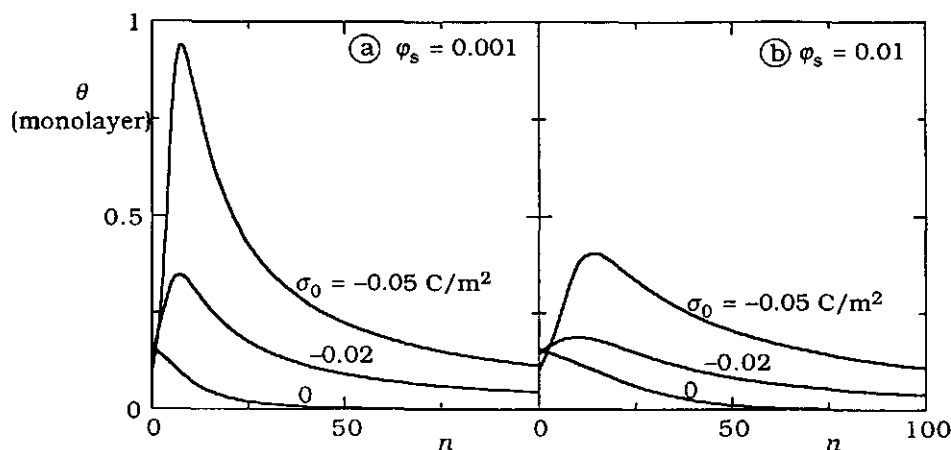


Figure 4.10 Theoretical results for the effect of the composition on the adsorption of the block copolymer C_nN_{100-n} at low ($\phi_s = 0.001$, (a)) and high salt concentration ($\phi_s = 0.01$, (b)), for three values of the surface charge σ_0 : 0 C/m^2 , -0.02 C/m^2 , and -0.05 C/m^2 , as indicated. The neutral block has a non-electrostatic affinity for the surface ($\chi_{sN} = 0.5$), all other χ -parameters are chosen zero. For values of other parameters see text.

uncharged and a negatively charged surface. On an uncharged surface ($\sigma_0 = 0 \text{ C/m}^2$) the block copolymer adsorbs only because of the non-electrostatic attraction between the neutral block and the surface; the charged block, being repelled from the surface, forms buoys. The strong electrostatic repulsion between the buoys limits the adsorption so that adsorption occurs only at a relatively low charge contents. When the charged block becomes smaller, this repulsion diminishes and the adsorption increases. Addition of salt screens the repulsion and adsorption is promoted.

On an oppositely charged surface the conformation of the block copolymer on the surface is different. The charged segments are in close contact with the surface, compensating the surface charge; however, the neutral segments do also adsorb, to an extent depending on the amount of space left. When the length of the charged block is decreased, more molecules are needed to compensate the surface charge. At a certain point a maximum is reached: at even smaller charge content, the electrostatic attraction to the surface becomes too small to maintain the relatively high adsorption levels, and the adsorption drops to the value for the homopolymer ($n = 0$). Addition of salt weakens the electrostatic attraction and the adsorption decreases, causing the maximum to shift to a higher charge content on the block copolymer.

There is a somewhat unexpected effect of the surface charge on the adsorption of the neutral homopolymer ($n = 0$). When the surface charge increases, the adsorption becomes smaller. This is due to adsorbed ions that have to compensate the surface charge and displace the polymer, as discussed in reference (2).

Comparison of the experimental and theoretical results leads to the following observations:

- The maximum in the calculated curve is much sharper than in the experiments.
- The adsorbed amount of the homopolyelectrolyte seems to be higher in the experiments.
- The conformation of the block copolymer, having both blocks on the surface as deduced from the sequential adsorption experiments, agrees with theoretical profiles on oppositely charged surfaces (not shown).
- When the surface charge becomes more negative, the adsorption is enhanced, which was also found in the experiments when the pH was increased.

- In the theoretical model, addition of salt reduces the adsorption on a negatively charged surface, while experimentally a more complicated behaviour is found.

The main reason for the difference between theory and experiment is the existence of the induced electrostatic interaction, which is neglected in the present theoretical calculations. Since at high charge content compensation of the surface charge occurs, the adsorbed amount is inversely proportional to the charge content per molecule and, hence, to n : $\Gamma \propto \sigma_0 / n$.

The experimental surface charge can be thought of as a superposition of an intrinsic part σ_0 and an induced part. The induced surface charge depends on the charge in the adsorbed layer, and thus on the composition of the block copolymer. This charge regulation could possibly explain the difference in shape between the experimental and theoretical curves. A fully charged polymer will give rise to a high induced charge and the adsorption can be much higher than in the calculations. Also, because of this induction effect, the curves at pH = 4.5 on TiO₂ can probably be compared best with theoretical results for a negatively charged surface, even though pH = 4.5 is close to the i.e.p..

The effect of addition of salt alters the subtle balance between the repulsive and attractive interactions in the system. Since the experimental system is much more complex, the effect of ionic strength is not reproduced fully by the present theoretical calculations.

4.4 Conclusions

The adsorption of charged block copolymers is governed by the balance between repulsive and attractive interactions. In our system electrostatic interactions, including an induced interaction, play a key role. The induced interaction, equivalent to a local charge regulation mechanism, influences the dissociation of the surface groups, thereby reducing the build-up of the electrostatic potential on the surface.

When the composition of the block copolymer is varied, a maximum in the adsorbed amount is observed. This maximum is caused by the cross-over between two regimes: at high AMA content the strive for charge compensation is dominant, whereas at low AMA content the electrostatic attraction to the surface limits the adsorption. Such an effect was also found for the adsorption of homopolyelectrolytes with varying segment

charge.

The conformation of charged block copolymers with two adsorbing blocks on an oppositely charged surface differs from that of neutral block copolymers. Whereas in the latter case an anchor-buoy conformation is present, a charged block copolymer forms a mixed layer. In this conformation the charged block is in contact with the surface, whereas the conformation of the neutral block depends on the amount of space left. For low adsorbed amounts the neutral block can adopt a relatively flat conformation, whereas at high adsorbed amounts it will be forced into loops and tails.

A conformation with an anchoring neutral block and extending charged hairs is not easily formed. When the charged block can in principle adsorb on the surface, charged hairs will only be formed when the neutral block is able to displace the charged one. This will only happen at extremely high non-electrostatic affinities of the neutral block for the surface. If, however, the charged block does not adsorb on the surface despite the heterogeneity effect and the induced interaction, a conformation with charged hairs could be formed more easily. In such a case the density of such a charged buoy layer is expected to be rather low, since the lateral repulsion between the buoys is very strong.

Qualitative agreement is found between the experimental results and the theoretical calculations as to the effect of variation of surface charge and composition. The effect of the ionic strength can not be fully reproduced since the experimental system has some electrostatic features that are not covered in the present version of the theory.

4.5 References

- (1) D.H. Napper, *Polymeric stabilization of colloidal dispersions*, Academic Press, London, 1983.
- (2) G.J. Fleer, M.A. Cohen Stuart, J.M.H.M. Scheutjens, T. Cosgrove, and B. Vincent, *Polymers at interfaces*, Chapman & Hall, London, 1993.
- (3) C.M. Marques and J.F. Joanny, *Macromolecules*, 1969, **22**, 1454.
- (4) O.A. Evers, J.M.H.M. Scheutjens, and G.J. Fleer, *J. Chem. Soc. Faraday Trans.*, 1990, **86**, 1333.
- (5) D.T. Wu, A. Yokohama, and R.L. Setterquist, *Polymer J.*, 1991, **23**, 711.
- (6) O.A. Evers, G.J. Fleer, J.M.H.M. Scheutjens, and J. Lyklema, *J.*

Colloid Interface Sci., 1986, **111**, 446.

(7) H.G.M. van de Steeg, M.A. Cohen Stuart, A. de Keizer, and B.H. Bijsterbosch, *Langmuir*, 1992, **8**, 2538.

(8) T.K. Wang and R. Audebert, *J. Colloid Interface Sci.*, 1988, **121**, 32.

(9) J. Blaakmeer, M.R. Böhmer, M.A. Cohen Stuart, and G.J. Fleer, *Macromolecules*, 1990, **23**, 2301.

(10) H. Mori, A. Hirao, and S. Nakahama, *Macromolecules*, 1994, **27**, 35.

(11) M. Newman and M. Renoll, *J. Am. Chem. Soc. (B)*, 1945, **67**, 1621.

(12) J.C. Dijt, M.A. Cohen Stuart, and G.J. Fleer, *Adv. Colloid Interface Sci.*, 1994, **50**, 79.

(13) W.N. Hansen, *J. Optical Soc. Am.*, 1968, **58**, 380.

(14) R. Israëls, J.M.H.M. Scheutjens, and G.J. Fleer, *Macromolecules*, 1993, **26**, 5405.

(15) T. Hiemstra, W.H. van Riemsdijk, and G.H. Bolt, *J. Colloid Interface Sci.*, 1989, **133**, 91.

(16) M. Sidorova, T. Golub, and K. Musabekov, *Adv. Colloid Int. Sci.*, 1993, **43**, 1.

(17) B.C. Bonekamp and J. Lyklema, *J. Colloid Interface Sci.*, 1986, **113**, 67.

(18) J.E. Gebhardt and D.W. Fuerstenau, *Colloids Surfaces*, 1983, **7**, 221.

(19) S. Chibowski, *J. Colloid Interface Sci.*, 1990, **140**, 444.

(20) A. Foissy, A. El Attar, and J.M. Lamarche, *J. Colloid Interface Sci.*, 1983, **96**, 275.

(21) H.G.M. van de Steeg, A. de Keizer, M.A. Cohen Stuart, and B.H. Bijsterbosch, *Colloids Surfaces A*, 1993, **70**, 77.

(22) D. Andelman and J.F. Joanny, *Macromolecules*, 1991, **24**, 6040.

(23) T. Odijk, *Macromolecules*, 1990, **23**, 1875.

(24) C.C. van der Linden, B. van Lent, F.A.M. Leermakers, and G.J. Fleer, *Macromolecules*, 1994, **27**, 1915.

(25) G. Durand, F. Lafuma, and R. Audebert, *Progr. Colloid Polym. Sci.*, 1988, **266**, 278.

(26) J.C. Dijt, M.A. Cohen Stuart, and G.J. Fleer, *Macromolecules*, 1994, **27**, 3219.

(27) A.W.M. de Laat and G.L.T. van den Heuvel, *Colloids Surfaces A*, 1993, **70**, 179.

Chapter 5 Charged (block co)polymers as stabilisers and flocculants of oxides

We have examined the use of polyelectrolytes and charged block copolymers as flocculants and stabilisers. The adsorbed layer was characterised by adsorption data and ζ -potential measurements. Furthermore, the stability of ludox dispersions in the presence of these polymers was investigated.

We conclude that charged polymers can be used both as stabilisers and flocculants. The influence that the polymers have depends critically on the polymer charge, the dosage and the molar mass of the polymers. In order to optimise their performance we formulate a number of requirements for the polymers.

5.1 Introduction

Before, we reported on the adsorption properties of polyelectrolytes (Chs. 2 and 3) and of charged block copolymers (Ch. 4) on oxides. In this chapter we investigate the effect of these polymers on the colloidal stability of a dispersion. The wide-spread application of charged polymers in the industry, both as stabilisers (for example in the paint industry) and as flocculants of aqueous dispersions (for example in the paper industry and in water purification), illustrates the importance of this topic. As described in the literature¹, the main mechanisms for destabilisation of particles by charged polymers are:

- (i) Bridging flocculation, whereby one polymer chain adsorbs on two or more particles simultaneously.
- (ii) Mosaic flocculation. Upon adsorption of, *e.g.*, positively charged polymers on negatively charged particles, locally positive patches on the particles may be formed. The electrostatic attraction between the positive patches on one particle and negative patches on another may cause destabilisation.
- (iii) Charge neutralisation. When upon adsorption of charged polyelectrolytes on an oppositely charged surface the surface charge is nearly compensated, no electrostatic repulsion remains and the Van der Waals interaction may lead to coagulation of the particles.

Bridging flocculation and mosaic flocculation take place when the surface is not yet completely covered, *i.e.*, when the concentration of polymer is low, or in the initial stages of the adsorption process. Since these processes may already take place immediately after addition of the polymer, they depend very much on the mixing conditions¹. Charge neutralisation may take place both at low and high coverages, depending on the surface charge density and the polymer charge.

In the mechanisms described above a distinction is made between flocculation and coagulation processes. The process is termed *flocculation* when the polymer has an active role, *i.e.*, it forms a bridge or a charged patch, and thereby causes aggregation. When the polymer has a passive role, *i.e.*, it acts merely as a multivalent ion, then we term the aggregation process *coagulation*. Although this subdivision is to some extent arbitrary, we will use these terms throughout this paper.

Stabilisation of colloids by charged polymers occurs at higher coverages. Also in this case different mechanisms may be distinguished. The main ones² are

- (i) Electrostatic stabilisation, which occurs when upon adsorption the net charge increases.
- (ii) Steric stabilisation, when upon adsorption a steric layer is formed which prevents the particles from approaching each other too closely.
- (iii) Electrosteric stabilisation. In this case both the electrostatic and the steric component contribute to the stabilisation. This type of stabilisation was found by Einarson and Berg³ for latex dispersions covered by small polyethylene oxide/polypropylene oxide (PEO/PPO) block copolymers in the presence of salt.

The aim of this study is to find out which type of charged polymer is most suited for stabilisation and which type for flocculation. For this purpose we performed adsorption measurements, studied the electrokinetic properties (ζ -potential) of the adsorbed layers, and investigated the effect of the polymers on the colloidal stability. The ζ -potential is a measure for the net charge at the plane of shear and is a characteristic of the adsorbed layer. For example, Johnson and Matijevic⁴ showed that the electrophoretic mobility of particles with adsorbed protein layers could be correlated to the stability of the dispersion. When the mobility was high, and the particles thus highly charged, the dispersion proved to be most stable.

by thermal oxidation of the silicon wafers, whereas the TiO_2 -films were sputtered onto the wafers. Streaming potential measurements were performed on glass slides covered with sputtered TiO_2 -layers (≈ 25 nm). Stability measurements were carried out with Ludox (SiO_2) dispersions with a diameter of about 27 nm, as determined from dynamic light scattering. The concentration of Ludox in the stability experiments was 0.3 % (mass/mass) and the concentration of polymer about 1000 mg/kg.

In all experiments a barbitol-acetate buffer with an ionic strength of 0.005 mol/kg was used. Sometimes extra salt (NaCl) was added to obtain a higher ionic strength.

5.2.2 Methods

The adsorption measurements were done using reflectometry in a stagnation point-flow⁵. All relevant information about these measurements can be found in Ch. 2 (PVP+) and Ch. 4 (block copolymers).

The streaming potentials were measured in a set-up as described in ref. (6). The streaming potential V_s was recorded as a function of the applied pressure ΔP . The ζ -potential of a layer in contact with a solution of viscosity η , dielectric permittivity ϵ , and specific conductivity κ_{sp} is given by⁷

$$\zeta = \frac{\eta \kappa_{sp} V_s}{\epsilon \Delta P} \quad (5.1)$$

In this equation surface conductivity is not taken into account.

The ζ -potential of a bare TiO_2 layer is presented in Fig. 5.2 as a function of pH. The iso-electric point (i.e.p.) is located at $\text{pH} \approx 4$. This value is considerably lower than for colloidal rutile or anatase dispersions, which have an i.e.p. of about 6⁸. Probably, the structure of the sputtered layer is amorphous.

The colloidal stability of bare ludox particles upon addition of NaCl was determined from optical transmission measurements. The dispersion proved to be stable, i.e., no decrease of transmission was observed, both at $\text{pH} = 7$ and $\text{pH} = 4$, even for an ionic strength as high as 1 mol/kg. For the experiments with adsorbing polymer added, it was thus possible to first add salt to the dispersion of bare particles in the cuvet, after which the polymer solution was added. After rapid end-over-end mixing, the cuvet was placed in the spectrophotometer and the change of the transmission with time was recorded.

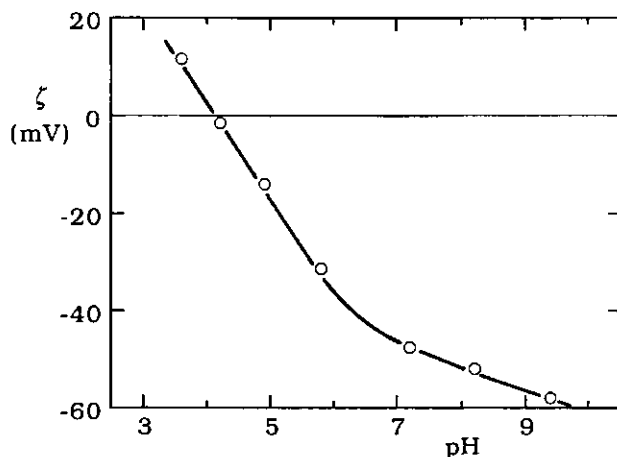


Figure 5.2 Electrokinetic potential of bare TiO_2 -layers on macroscopic glass surfaces at an ionic strength $I = 0.005$ mol/kg. The ζ -potential was calculated from Eq. 5.1.

5.3 Results

In this section the results of the adsorption experiments, the streaming potential experiments, and the stability measurements are presented. The section is split up in two parts. In the first part the results for the strong homopolyelectrolyte PVP^+ are given, and in the second those for the block copolymers.

I. Results for PVP^+

5.3.1 Adsorption experiments

In Fig. 5.3 we present the adsorption of PVP^+ with molar masses of 3 K (triangles) and 120 K (circles) on TiO_2 (open symbols) and on SiO_2 (filled symbols) at $\text{pH} = 8$ as a function of the ionic strength. This figure is reproduced from Ch. 2. As discussed before in Ch. 2, the most prominent features are the following: (i) upon increasing the ionic strength, the adsorbed mass at first increases slightly. (ii) On SiO_2 this increase continues over the entire investigated range of the ionic strength, whereas on TiO_2 a maximum is reached after which the adsorbed amount decreases strongly. (iii) The position of the maximum on TiO_2 depends on the molar mass of PVP^+ ; for 3 K it is situated around $I = 0.05$ mol/kg and for 120 K around $I = 0.2$ mol/kg. (iv) For the low-molar-mass PVP^+ the

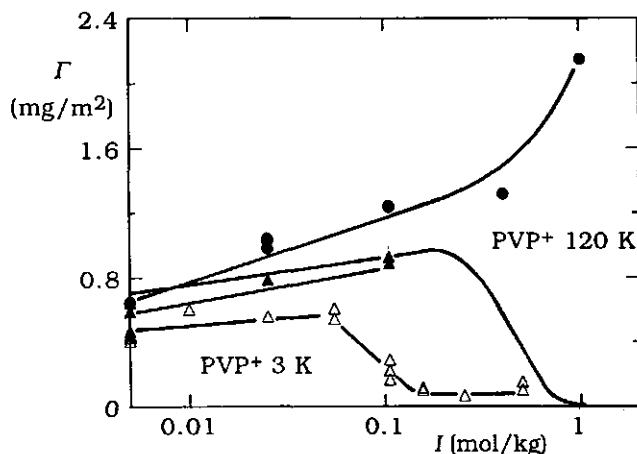


Figure 5.3 The adsorbed amounts of PVP⁺ with molar masses 3 K (triangles) and 120 K (circles) on TiO₂ (open symbols) and SiO₂ (filled symbols) as a function of the ionic strength of solutions containing monovalent ions only. Other parameters: polymer concentration = 10 mg/kg and pH = 8.

adsorbed amounts on both SiO₂ and TiO₂ are lower than for high M .

These trends can be explained by considering the balance between all interactions in the system and how this is affected by the ionic strength. The most important interactions are the repulsive electrostatic interaction between the polymer segments, the attractive electrostatic interaction of the positively charged polymer segments with the negatively charged surface groups, and a non-electrostatic interaction between PVP⁺ and SiO₂, which probably originates from hydrophobic bonding. The adsorption proceeds until the attraction to the surface is just balanced by the repulsion within the adsorbed layer. When salt is added, both electrostatic interactions are weakened. A weakening of the lateral repulsion would stimulate adsorption. At the same time, however, the electrostatic attraction between polymer and surface is also screened, which tends to reduce the adsorbed amount. For these highly charged polyelectrolytes it is apparent from Fig. 5.3 that at low ionic strength the repulsion is more strongly affected than the attraction; the net effect is that the adsorbed amount increases. For polyelectrolytes with a low polymer charge, this trend is opposite, i.e., at low I the adsorption already decreases, as shown in Ch. 2.

At high ionic strength, the adsorption on TiO₂ starts to decrease above $I = 0.05$ mol/kg for PVP⁺ 3 K and above $I = 0.2$ mol/kg for PVP⁺ 120 K.

At these ionic strengths the reduction of the electrostatic attraction becomes the dominant effect and the adsorption goes down. For PVP⁺ on SiO₂, where there is an additional non-electrostatic attraction with the surface, we find the opposite trend. This non-electrostatic interaction is not affected by the ionic strength, and the screening of the repulsion in the layer therefore leads to higher adsorbed amounts.

The differences found between PVP⁺ 3 K and 120 K (i.e., the lower adsorbed amount and the position of the maximum) originate from the fact that a longer molecule forms more bonds with the surface, and therefore is more strongly attached to it.

5.3.2 Streaming potential measurements

In Fig. 5.4 the ζ -potential of TiO₂ layers covered with PVP⁺ is compared to the adsorbed amount under the same circumstances. In the experiment the pH is cycled from 8 to 4 to 8 and from 4 to 8 to 4. The adsorbed amount and the ζ -potential were measured separately by reflectometry and streaming potential measurements, respectively.

In the first step of the experiment the adsorbed amount is lower at pH = 4 than at pH = 8. The corresponding ζ -potential, however, is identical within experimental error. When in the second step, after adsorption at pH = 4, the pH is raised to 8, almost the same adsorbed amount and ζ -

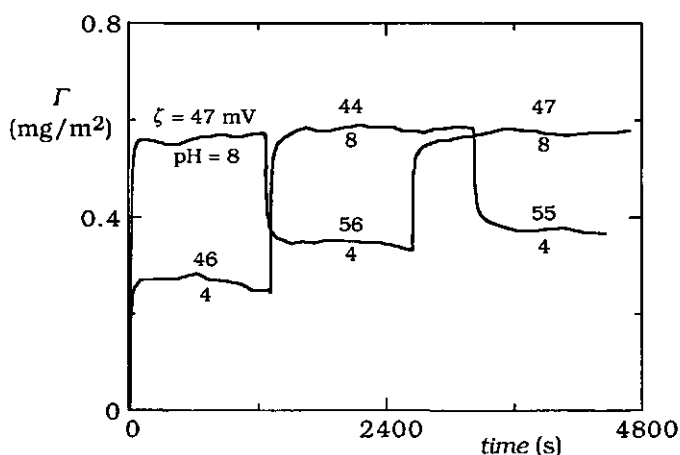


Figure 5.4 The adsorbed amount of PVP⁺ (120 K) as a function of time upon cycling the pH from 8 to 4 to 8 and from 4 to 8 to 4. The corresponding ζ -potentials and pH's are indicated in the figure. Other parameters: polymer concentration = 10 mg/kg and I = 0.005 mol/kg.

potential are found as for direct adsorption at $\text{pH} = 8$. When the pH is decreased, however, from 8 to 4, the adsorbed amount and the ζ -potential remain higher than for direct adsorption at $\text{pH} = 4$. These trends are also observed for the third step.

The dependence of the adsorbed amount on the pH is qualitatively as expected. At $\text{pH} = 8$ the surface is much more negatively charged than at $\text{pH} = 4$, where the net charge is almost zero (see Fig. 5.2). In both cases the surface charge is overcompensated as can be seen from the highly positive values for ζ . The fact that the ζ -potential in both cases is equal is surprising. It suggests that for direct adsorption of these highly charged polymers the maximum adsorbed amount is dictated by a maximum electrostatic potential of the adsorbed layer. Apparently, the adsorbed amount increases, at fixed pH , until a certain ζ -potential is reached. Adsorption then stops, even though a higher adsorbed amount and ζ -potential can be stable, as is seen from the result after a pH drop from 8 to 4.

This assumption is supported by an observation of Oertel *et al.*⁹. They studied the adsorption of a strong polyelectrolyte (polydiallyl dimethylammonium chloride, PDADMAC) on several oxidic substrates. Though the adsorbed amounts varied strongly for the different substrates they all had, at the maximum adsorbed amount, the same value of the ζ -potential.

These observations corroborate the theory put forward by De Laat *et al.*¹⁰ who suppose that the electrostatic potential of the adsorbed layer forms a kinetic barrier which slows down the attachment process. At the plateau adsorbed amount, more polymer could in principle adsorb (because polymer/surface contacts can lower the free energy), but the kinetic barrier is too high for the molecules to reach the surface so that these favourable contacts cannot form.

A way to circumvent this barrier is by adsorbing PVP⁺ at $\text{pH} = 8$ and then switching the pH to 4. Although some desorption occurs, the level remains higher than that for direct adsorption at $\text{pH} = 4$. The higher adsorbed charge results also in a higher electrostatic potential. Meadows *et al.*¹¹ showed that such an indirect route can lead to a much higher colloidal stability.

5.3.3 Effect on the colloidal stability

The effect of PVP⁺ on the colloidal stability of ludox particles at $\text{pH} = 7$ and

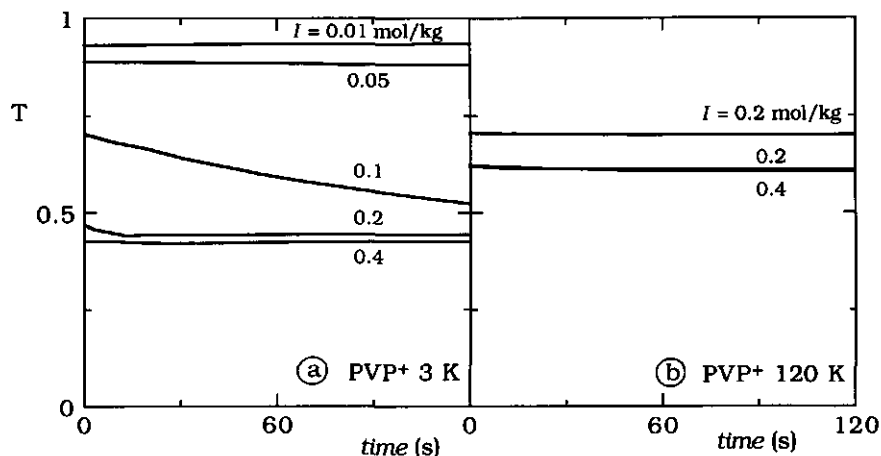


Figure 5.5 The transmission T as a function of time of ludox dispersions covered with PVP+ 3 K (a) and PVP+ 120 K (b) at various ionic strengths. The bare ludox dispersion was stable at all ionic strengths ($T \approx 0.96$). Polymer concentration = 1000 mg/kg and pH = 7.

for various ionic strength is presented in Fig. 5.5 for PVP+ 3 K (a) and PVP+ 120 K (b). We obtained these data by adding polymer to a mixture of ludox and salt, as described in the experimental section. Figure 5.5 shows the relative transmission T as a function of time, where $t = 0$ is the time at which the cuvet is placed into the spectrophotometer. The bare ludox has a transmission of 96% (not shown here), which is not affected by the ionic strength. All the curves for PVP+-covered ludox lie below the value for bare ludox, indicating that some flocculation (or coagulation) has occurred before $t = 0$. At $I = 0.01$ mol/kg (3 K) and at $I = 0.2$ mol/kg (120 K), however, the curve is perfectly horizontal. Apparently, the flocculation did only occur in the mixing stage and then came to a halt. At higher ionic strengths all the curves, except for the experiment at $I = 0.4$ mol/kg (3 K), show a decrease of T with time. In the latter case the initial flocculation is very fast and already at $t = 0$, the flocs have become so large that the transmission at $t > 0$ is no longer a function of the floc size. From the slopes of the curves we can conclude that, apart from the initial flocculation, ludox covered with PVP+ 3 K and 120 K becomes unstable at $I > 0.05$ mol/kg and at $I > 0.4$ mol/kg, respectively.

The extreme stability of the Ludox sols upon addition of NaCl probably originates from a low Van der Waals attraction between SiO_2 particles of that size. Also, when the silica interface is "gel-like" as sometimes claimed

in the literature¹², the charged gel-layer would provide an electrosteric barrier, which makes the sol even more stable.

When positively charged polymer is added to the negative sol at pH = 7, it will adsorb on the particle and produce an overcompensation of the particle charge. Hence, upon adsorption the net charge changes from negative to positive. During this process flocculation probably occurs via a bridging or a mosaic flocculation process, as mentioned in the introduction. The flocculation process depends strongly on the mixing conditions.

When the adsorption is more or less completed, the particles have attained a net positive charge. Since the particle is now completely covered, no mosaic flocculation can occur. At low ionic strength the particles are completely restabilised due to their net positive charge (electrostatic stabilisation). At higher ionic strength the electrostatic repulsion is small and the size of the flocs increases. A measure for the effectiveness of the stabilisation by PVP⁺ is the ionic strength at which the covered particles become unstable. For PVP⁺ 3 K and 120 K this occurs at $I > 0.05$ mol/kg and at $I > 0.4$ mol/kg, respectively. We conclude that the longer the molecule, the better the stabilisation. We ascribe this trend to the higher adsorbed amount for the longer polymer (see Fig. 5.3), and, hence, to a larger overcompensation of the surface charge.

II. Results for HMA-AMA block copolymers

5.3.4 Adsorption experiments

Figure 5.6 illustrates the effect of the composition on the amount of block copolymer adsorbed onto TiO₂ (a) and SiO₂ (b). This figure is reproduced from Ch. 4. The experiments were performed at pH = 4.5 (circles) and 7 (triangles) and at $I = 0.005$ (open symbols) and 0.1 mol/kg (filled symbols).

As discussed before in Ch. 4, the following trends are found. (i) At high AMA content ($v_{\text{AMA}} > 0.1$) the adsorbed amount increases when the charged block becomes smaller. At $v_{\text{AMA}} \approx 0.1$ a maximum in the adsorbed amount is found, and at even lower AMA content the adsorbed amount decreases again. (ii) In all cases, the adsorbed amount is higher at a higher pH. (iii) The addition of salt leads to a decrease in the adsorbed amount at pH = 7, and at pH = 4.5 for block copolymers with small AMA blocks. For block copolymers with a long AMA block, however, the amount

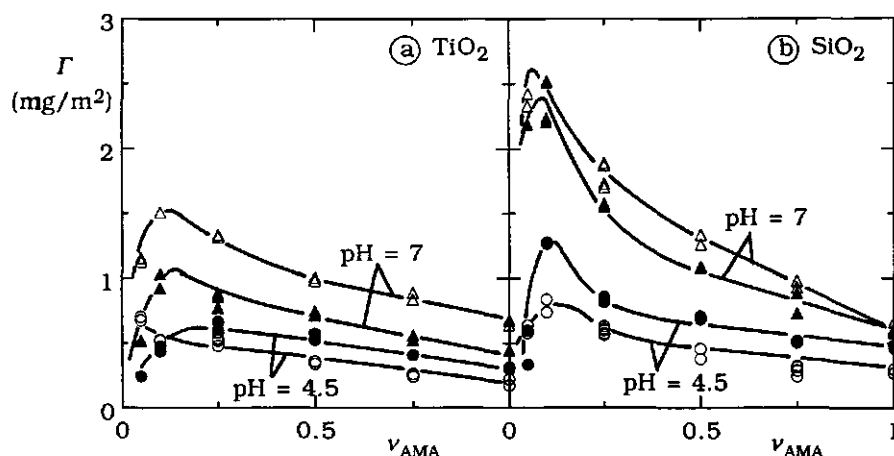


Figure 5.6 Adsorbed amounts of HMA-AMA block copolymers on TiO_2 (a) and on SiO_2 (b) as a function of the composition: the parameter v_{AMA} denotes the fraction of AMA segments. The measurements were performed at $\text{pH} = 4.5$ (circles) and at $\text{pH} = 7$ (triangles), and at two ionic strengths: $I = 0.005$ mol/kg (open symbols) and $I = 0.1$ mol/kg (filled symbols). The polymer concentration was 10 mg/kg and its molar mass about 20 K.

adsorbed at $\text{pH} = 4.5$ increases upon addition of salt. (iv) The curves on TiO_2 and on SiO_2 manifest the same general trends, although the absolute values are different.

These trends are all related to the electrostatic character of the adsorption of charged block copolymer and agree qualitatively with theoretical predictions for polyelectrolyte adsorption. Adsorption on oppositely charged surfaces in the absence of other non-electrostatic interactions can be viewed upon as an ion exchange process¹³. Since a highly charged polymer (polyion) screens the surface more effectively than small ions, it will displace the counterions in the electrical double layer. If there is a complete charge compensation by the polyelectrolyte, the adsorbed amount Γ is related to the surface charge σ_0 and the polymer charge τ according to

$$\Gamma \propto -\frac{\sigma_0}{\tau} \quad (5.2)$$

This simple equation illustrates that when the polymer charge is reduced the adsorbed amount has to increase. Also, when the surface is more negatively charged, i.e., at higher pH, the adsorbed amount is higher.

When v_{AMA} and thus the polymer charge becomes very low the

polymer molecule cannot compete as effectively with the counterions. Charge compensation only by the polyelectrolyte will then no longer be achieved, and the adsorbed amount decreases. This effect will be stronger at a higher ionic strength.

Even though this theory of ion exchange is capable of explaining most of the features found in Fig. 5.6, there are some findings which contradict the idea of charge compensation. In many cases, instead of charge compensation an overcompensation of the surface charge is observed. The occurrence of this overcompensation in the present case is clearly demonstrated by ζ -potential measurements (see Figs. 5.4 and 5.7). One could argue that these polymers not only interact through electrostatic but also through non-electrostatic interactions, which could stimulate the adsorption. However, for the homopolymer AMA adsorbing on TiO_2 , we showed in Ch. 2 that no non-electrostatic interaction with the surface exists.

The discrepancy between the experimental data and theoretical predictions probably results from the discreteness of the charges in the practical system. In most theoretical models the simplification is used that the substrate and polymer molecules are homogeneously charged, whereas in reality these charges are discrete. The discreteness of charges has important consequences, especially when the distance between the charges on the polymer chain is smaller than between the surface charges. In that case the polymer molecules do not "fit" and upon adsorption local overcompensation of the surface charge has to occur (see ref. (14) and Ch. 3).

Addition of salt reduces the lateral repulsion in the adsorbed layer, which may increase the adsorbed amount. On the other hand, however, small ions also affects the electrostatic attraction of the polymer with the surface, which might reduce the adsorbed amount. The net result depends on the relative importance of both effects. A reduction of the adsorbed amount is observed when the number of contacts with the surface is low. This is the case for polymers with a low charge (i.e., block copolymers with small AMA blocks), or when the ionic strength is high, so that already many bonds with the surface are screened. For PVP⁺ 3 K and 120 K on TiO_2 the system crosses over from repulsion-limited to attraction-limited behaviour upon addition of salt. At the cross-over a maximum in the adsorbed amount is found.

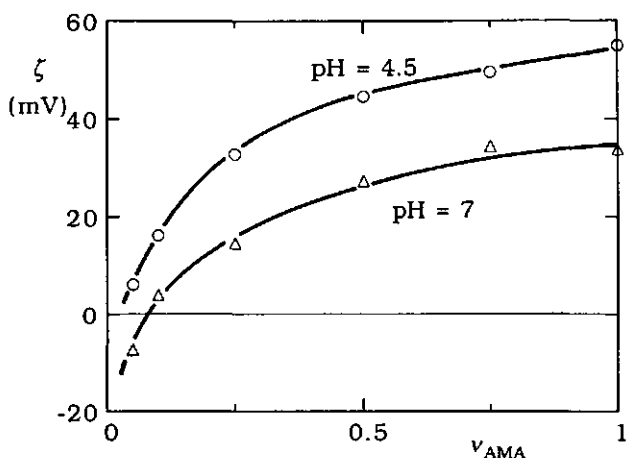


Figure 5.7 The ζ -potential of TiO_2 -layers covered with HMA-AMA block copolymers as a function of the composition v_{AMA} at pH = 4.5 (circles) and pH = 7 (triangles). The conditions are the same as for Fig. 5.6a at $I = 0.005$ mol/kg (open symbols).

5.3.5 Streaming potential measurements

In Fig. 5.7 the results of streaming potential measurements for adsorbed block copolymer layers on TiO_2 are presented as a function of the composition. The ionic strength I was 0.005 mol/kg, and the pH = 4.5 (circles) or 7 (triangles). The ζ -potential of bare TiO_2 at pH = 4.5 is -15 mV, and at pH = 7 it is -45 mV (see Fig. 5.2).

For TiO_2 covered by block copolymers almost exclusively positive values for ζ are found, as for PVP⁺. Only for $v_{AMA} = 0.05$ at pH = 7 does the net charge remain negative. There is a strong effect of pH, which was not the case for PVP⁺ (Fig. 5.4). This is presumably related to the deprotonation of the weakly charged groups in the AMA block at high pH. The degree of dissociation in the bulk solution decreases from 1 at pH = 4.5 to 0.5 at pH = 7. In the adsorbed state the degree of dissociation is lowered by the high positive electrostatic potential generated by the overcompensation of the surface charge (see Ch. 2); the degree of dissociation in the adsorbed layer was found to change from about 0.75 at pH = 4.5 to about 0.35 at pH = 7.

When we compare the values for ζ with the adsorbed amount (Fig. 5.6a) under the same conditions, we find completely different curves; the ζ -potential decreases monotonically with decreasing AMA content, whereas the adsorbed amount reaches a maximum around $v_{AMA} \approx 0.1$.

Since the ζ -potential is an indication for the net charge it should, however, not be compared to the adsorbed amount but to the adsorbed charge σ_{ads} . This charge is related to the adsorbed amount of AMA ($\Gamma_{\text{AMA}} = \Gamma v_{\text{AMA}}$) and to the degree of dissociation α of AMA:

$$\sigma_{\text{ads}} = \frac{\Gamma_{\text{AMA}} \alpha F}{M_s} \quad (5.3)$$

Here F is the Faraday constant and M_s the molar mass of the monomeric unit. In Fig. 5.8a we plot σ_{ads} at pH = 4.5 as a function of v_{AMA} , using $\alpha = 1$ and $M_s = 0.15$ K. In Fig. 5.8b we plot the electrokinetic charge σ_{ek} , which is the charge behind the plane of shear as seen from the bulk solution. Using the linear Hückel expression σ_{ek} is calculated from the ζ -potential via

$$\sigma_{\text{ek}} = \epsilon \kappa \zeta \quad (5.4)$$

where ϵ is the dielectric permittivity of the solution and κ the reciprocal Debye length. Figure 5.8 demonstrates that at pH = 4.5 σ_{ads} increases in a similar way with v_{AMA} as the ζ -potential and σ_{ek} . The same type of curves is found also at pH = 7 (not shown here). A remarkable observation, however, is that the electrokinetic charge σ_{ek} is less than one percent of the adsorbed charge. Apparently, most of the charge is compensated inside the plane of shear, as is found generally for bare

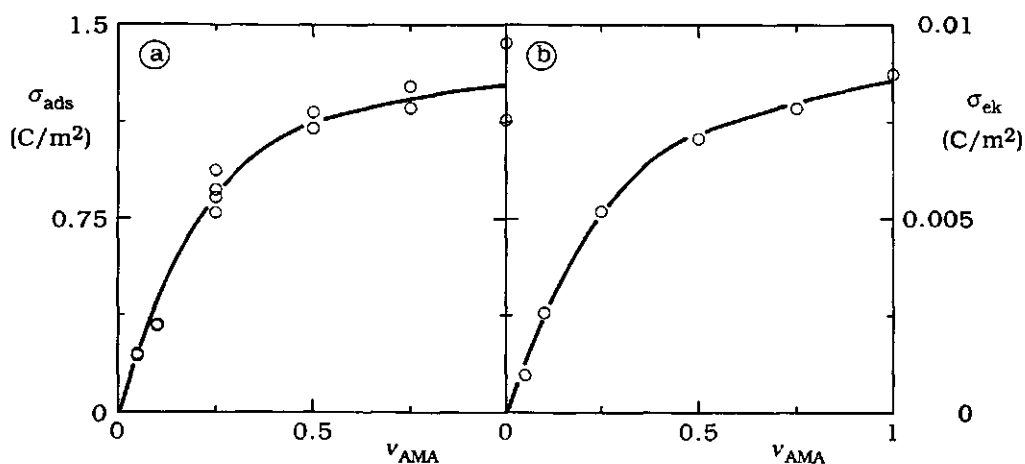


Figure 5.8 The adsorbed charge σ_{ads} (a) and the electrokinetic charge σ_{ek} (b) at pH = 4.5 as a function of the composition of the block copolymer. The adsorbed charge and the electrokinetic charge were calculated using Eqs. 5.3 and 5.4, respectively. Other parameters are identical as in Fig. 5.7.

oxides¹⁵. This also explains why oxidic dispersions are usually not very stable, despite their very high titratable surface charge.

Even more puzzling is the fact that σ_{ek} and σ_{ads} have the same dependence on v_{AMA} : there is a linear dependence between σ_{ek} and σ_{ads} . At present, the background of such a linear dependence (and of the proportionality factor, which is about $\sigma_{ads}/\sigma_{ek} = 150$) is unclear.

5.3.6 Stability measurements

First, we investigated the effect of the dosage of block copolymer on the colloidal stability to verify that the dosage used in the experiment (≈ 1000 mg/kg) was high enough to saturate the particles with polymer. In Fig. 5.9 the results of the experiments at pH = 4.5 for the homopolymer of AMA (circles) and for a 75/25 HMA-AMA block copolymer (crosses) are given. The ionic strength was 0.1 (open symbols) and 0.2 mol/kg (filled symbols), respectively, for the homopolymer, and 0.05 mol/kg for the block copolymer sample. The stability of the dispersion is characterised by the value of the transmission T_2 after 2 min.

Figure 5.9 shows that, both at low and high dosage of polymer the ludox dispersion is stable, except for AMA at $I = 0.2$ mol/kg. At intermediate dosages, however, rapid floc formation upon addition of

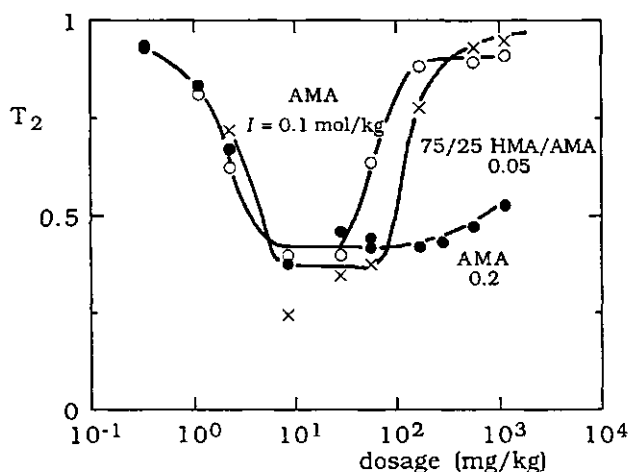


Figure 5.9 The stability of ludox dispersions at pH = 4.5 covered with the homopolymer AMA at $I = 0.1$ mol/kg (open circles) and at $I = 0.2$ mol/kg (filled circles), and with the 75/25 HMA-AMA block copolymer at $I = 0.05$ mol/kg (crosses) as a function of the concentration of polymer. The transmission after 2 min. T_2 was used as a measure of the stability of the sol.

polymer is observed. The point where restabilisation is found depends on the type of polymer and on the ionic strength. For AMA (at $I = 0.1$ mol/kg) and for the block copolymer restabilisation starts at dosages above 35 and 60 mg/kg, respectively. The dispersions are completely stable again above dosages of 170 and 500 mg/kg, respectively. For AMA at $I = 0.2$ mol/kg, no restabilisation takes place.

The destabilisation found at intermediate dosage is most likely due to mosaic flocculation. When the dosage is low, the surface is only partially covered. The particles then have positive (coated) and negative (bare) patches. The flocculation will be most successful when about half of the area of the particles is positively charged, as was also suggested by Gregory¹. When there are fewer positive patches (at low dosage) or fewer negative ones (at high dosage) the number of collisions that lead to aggregation is less and the flocculation rate decreases. If the particles are completely saturated with polymer no mosaic flocculation can occur. It then depends on the stability against coagulation, i.e., on the attained net surface charge and on the ionic strength, whether the dispersion is stable or not. From Fig. 5.9 we infer that dispersions covered with AMA at $I = 0.1$ mol/kg and with the 95/5 HMA-AMA block copolymer at $I = 0.05$ mol/kg are stable, whereas a dispersion with AMA at $I = 0.2$ mol/kg is unstable. In all cases, however, the dosage of 1000 mg/kg, which is used in all other stability measurements, is high enough to completely saturate

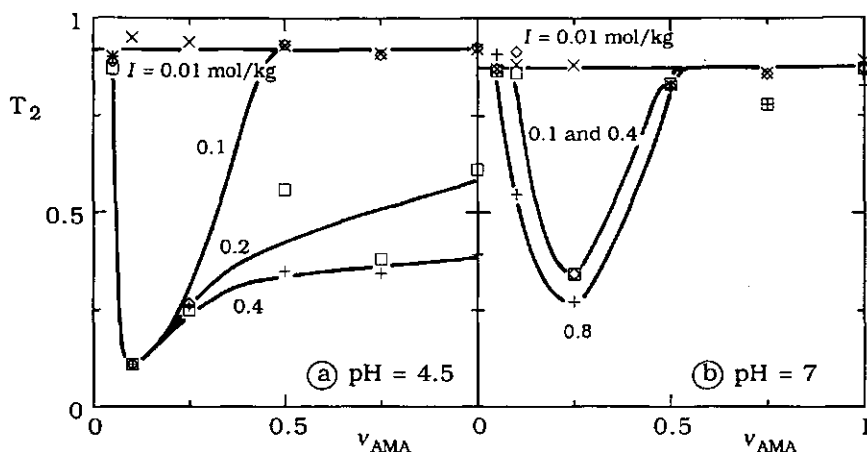


Figure 5.10 The stability of ludox dispersion at pH = 4.5 (a) and at pH = 7 (b) covered with HMA-AMA block copolymers as a function of the composition at various ionic strengths, as indicated. The polymer concentration was 1000 mg/kg.

the particles in the dispersion.

The effects of the ionic strength and the composition of the block copolymer on the colloidal stability are shown in more detail in Fig. 5.10. Again the transmission after 2 min. is used to characterise the colloidal stability. The results at pH = 4.5 (a) and 7 (b) indicate that at a certain composition the stability has a minimum; for pH = 4.5 this occurs around $v_{\text{AMA}} = 0.10$ and for pH = 7 around $v_{\text{AMA}} = 0.25$. Both for higher and lower v_{AMA} the dispersion becomes increasingly stable. The position of the minimum seems to be independent of the ionic strength. To the right of the minimum the stability of the system is, however, significantly lower at higher ionic strength.

In order to seek an explanation for these effects we compare these results with the ζ -potential measurements (Fig. 5.7) and the adsorbed amounts on SiO_2 (Fig. 5.6b). Unfortunately, we do not have ζ -potential data on ludox particles, but we assume that the general trend found in Fig. 5.7, which is a monotonous decrease of ζ with v_{AMA} still holds. From the comparison we find that the minimum in the stability occurs when the ζ -potential is low and the adsorbed amount high. This suggests that, even though there is a possibility of steric effects at these relatively high adsorbed amounts ($\Gamma = 1 - 2 \text{ mg/m}^2$), the electrostatics are more important and that the loss of stability is caused by charge neutralisation. Only at pH = 7 at an even lower v_{AMA} ($\approx 0.05 - 0.10$) and a still higher adsorbed amount ($\Gamma \approx 2.3 \text{ mg/m}^2$), does a steric component seem to influence the stability. In this case the loss of stability by charge neutralisation is compensated by the formation of a steric layer, which results in a high stability against addition of salt. At pH = 4.5 we find that also at $v_{\text{AMA}} = 0.05$ the dispersion is stable. In our opinion this is not due to formation of a steric layer since the adsorbed amount is now rather low ($\Gamma \approx 0.5 \text{ mg/m}^2$), and decreasing with ionic strength (Fig. 5.6b). The stability in this case is probably related to the high stability of the bare ludox particles, which is not affected much by the adsorbing polymer.

At high v_{AMA} the electrostatics determines the stability. At both pH's the charge overcompensation is so high that an electrostatic barrier against coagulation is present. This barrier is lowered by addition of NaCl, which is most clearly demonstrated in Fig. 5.10a at pH = 4.5. It is not clear yet why we do not observe a similar decrease in stability upon addition of salt at pH = 7.

5.4 Discussion

In this section we examine what kind of charged polymer is most suitable to act as a stabiliser or as a flocculant. In Table 5.1 an overview of the most important requirements for polymers for different stabilisation and flocculation mechanisms is given. Since the desired polymer properties are very different for the various cases, we discuss these requirements and some implications in more detail.

5.4.1 Electrostatic stabilisation

For electrostatic stabilisation the particles must be highly charged and the ionic strength should not be too high, since salt screens the electrostatic interactions. The polymer added can either enhance the charge or cause an overcompensation of the charge. For this purpose it is best to use highly charged, strong homopolyelectrolytes (like PVP⁺). In the discussion of Fig. 5.5 we have already noted that the longer the polymer, the higher the adsorbed charge and therefore the better the stabilisation.

When these polymers are added to a dispersion two complications can arise.

(i) In the initial stages it is possible that mosaic flocculation or bridging flocculation occurs. By applying a high shear these flocs can be broken up. Another way to reduce the amount of flocs is by stabilising particles in a dilute solutions before they are concentrated.

(ii) Since the charged layer forms a kinetic barrier which prevents the adsorption of more polyelectrolyte molecules, the adsorbed charge can be enhanced by using an indirect route, *i.e.*, adsorption under conditions (*I*, pH) where a high adsorbed amount is spontaneously achieved, after which the system can be taken to the desired conditions. In this way, the

Table 5.1 Requirements of charged polymers for stabilisation and flocculation purposes.

mechanism	polymer charge	dosage	M_w
electrostatic stabilisation	high	saturation	high
steric stabilisation	low (10 %)	saturation	high
electrosteric stabilisation	variable	saturation	high
bridging flocculation	any value	low	high
mosaic flocculation	high	low	high
charge neutralisation	low (10 %)	saturation	low

adsorbed amount can be made higher than by direct spontaneous adsorption (see Fig. 5.4).

5.4.2 Steric stabilisation

In this case the objective is to form a thick steric layer. Such thick layers are formed when the adsorbed amount is high. For neutral polymers this is usually not the case, since the non-electrostatic interaction of neutral polymers with oxidic surfaces is usually not very strong. When the polymers are charged, electrostatic interactions come into play, and these can be considerably stronger. We found that, even on net neutral oxidic surfaces, polyelectrolytes still attach by electrostatic interactions, because of the heterogeneous nature of the surface of oxides (see Chs. 2 and 4).

We can therefore use the charged groups on a polymer to increase its interaction to the surface. When, however, the number of charged groups is too high the adsorbed amount is lowered by the lateral repulsion between these groups in the adsorbed layer. In Fig. 5.6 we find a maximum adsorbed amount when about 10% of the groups is charged. The charge does not have to be located in one block, as was the case for our block copolymers, but might also be distributed randomly in the chain. Again, a high molecular weight polymer is preferable and yields thicker layers. Good examples of such stabilisers are natural or modified polysaccharides such as gum tragacanth¹⁶, gum xanthan and carboxy methyl cellulose¹⁷.

For these steric stabilisers the same complications upon adsorption exist, and these can be addressed in the same way, as described above for electrostatic stabilisers. Some flocculation can occur upon adsorption, either by bridging flocculation and/or by mosaic flocculation. The latter mechanism will, however, be less effective, since the polymer charge is relatively low.

5.4.3 Electrosteric stabilisation

Electrosteric stabilisation occurs when both electrostatic and steric factors influence the stability. This takes place when charged particles are coated with a neutral polymer³, or when particles are covered with a charged steric layer. Since we are interested in the stabilisation by charged polymers, we only consider the latter situation. In order to simultaneously provide electrostatic and steric protection one needs to have a thick, highly charged layer. We have seen, however, that highly charged layers

are usually not very thick and thick layers are usually not very highly charged, since the strong electrostatic repulsion in such a layer precludes its formation. Therefore, in our opinion, it is impossible to make these layers directly. Indirect ways can be used, however, like adsorption or grafting of a thick and lowly charged layer, after which the charge of the layer is increased by changing the conditions. An example of this would be the adsorption of a weak polyelectrolyte at a pH where the degree of dissociation is low, after which the pH is changed so that the layer becomes highly charged. Care has to be taken that the binding to the surface is strong enough, so that no significant desorption occurs.

5.4.4 Bridging flocculation

For bridging flocculation one needs to have molecules which adsorb simultaneously on two or more particles, thereby forming a "bridge". The requirements for such molecules are: (i) they have to adsorb on the particles, and (ii) they must be long enough to adsorb on different particles. The length needed to fulfil this latter requirement depends strongly on the ionic strength, since the polymer length must be at least twice the effective range of the electrostatic repulsion between two particles¹. When a polymer molecule adsorbs onto a particle its initial conformation is not much different from that in solution, and the initial layer thickness will be of the order of the radius of gyration. The layer thickness decreases with time, however, due to rearrangements in the adsorbed layer. Bridge formation will therefore be most effective when the particle collides with other particles just after a polymer molecule has adsorbed. Gregory¹⁸ termed this process non-equilibrium flocculation. Adachi *et al.*¹⁹ observed a tremendous increase in the rate of flocculation upon addition of a polymer, as compared to rapid salt-induced coagulation. This effect could be contributed to a strong increase of the effective collision radius of the particle due to freshly attached polymer coils. Particles with equilibrated polymer layers turned out to be much smaller.

The interaction by which the polymers adsorb on the particles can be electrostatic or non-electrostatic. Therefore a neutral polymer molecule could in principle be as successful in providing bridging flocculation as a charged one.

In contradistinction with stabilisers, which have to be added in high dosages to saturate the dispersion with polymer, one now has to use a low

dosage, since a bridge must be formed between bare particles. At higher dosage more bridges can be formed, but also the coverage of the particles becomes higher. Therefore an optimum dose exists. Addition of too high a dosage could cause restabilisation of the system.

The floc formation with bridging flocculation is very fast partly because the larger the aggregates, the more reactive they are, especially when the particle concentration is high. Large flocs with an open structure will then be formed.

5.4.5 Mosaic flocculation

Mosaic flocculation only works when charged polymers adsorb on oppositely charged surfaces and overcompensate the surface charge. The subsequent electrostatic attraction between covered patches on one particle and uncovered patches on another particles may lead to flocculation. Eriksson *et al.*¹⁴ suggested, from their results of the flocculation of negatively charged polystyrene latex by positively charged modified polyacrylamide polyelectrolytes, that at low charge density the flocculation occurred mainly by a bridging mechanism whereas for highly charged polymers mosaic flocculation was more important. Therefore long, strongly charged polymers, which invoke the highest local charge overcompensation, are preferably used to induce mosaic flocculation. The adsorption of small molecules will produce more homogeneous layers (see ref. (1) and Ch. 3) and therefore small molecules are more suited for coagulation by charge neutralisation. The dosage of the polymer must be below saturation. Bleier and Goddard²⁰ reported optimum flocculation well below 50 % surface coverage, and according to Gregory¹ the optimum flocculation occurs when the overall surface charge is reduced to near zero.

Again the flocculation will be fast and an open floc structure will be found.

5.4.6 Charge neutralisation

In this type of coagulation the role of the polymer is analogous to that of coagulating salt. Both screen the surface charge, but charged polymers can do so much more effectively. Care has to be taken though, that the charge is compensated and not overcompensated as is often found upon polyelectrolyte adsorption. In Fig. 5.7 we find that charge compensation occurs when about 10 % of the polymer groups are charged. Also, the

polymer molecules should not be too long to prevent formation of thick layers which provide additional steric stabilisation.

The floc structure resulting from this mechanism is much more dense, since the coagulation is slower and the rate is comparable to the one found for coagulation with salt.

5.5 Conclusions

In this paper the use of charged polymers both as stabilisers and as flocculants of oxidic dispersions was examined. For that purpose adsorption and ζ -potential data were combined with stability measurements of covered ludox dispersions. Two types of polymer were studied: strongly charged homopolyelectrolytes (quaternised polyvinyl pyridine, PVP⁺), and block copolymers consisting of one uncharged water-soluble block (dihydroxypropyl methacrylate, HMA) and one pH-dependently charged block (dimethylaminoethyl methacrylate, AMA).

The measurements suggest that charged polymers can indeed be used both for stabilising and destabilising purposes. The most important parameters that determine the influence of these polymers on the colloidal stability upon adsorption are the polymer charge, the dosage and the molar mass of the polymer. Since there are different ways in which flocculation (bridging flocculation, mosaic flocculation and charge neutralisation coagulation) and stabilisation (electrostatic, steric and electrosteric stabilisation) can be achieved, we propose a number of requirements to optimise the operation of each mechanism. These requirements are listed in Table 5.1. The table shows that the same polymer can be used both effectively as a flocculant (at low dosage) and as a stabiliser (at high dosage). Furthermore, due to the different mechanisms some polymers are most effective when they are highly charged, and others when they have only a low charge.

5.6 References

- (1) J. Gregory, *J. Colloid Interface Sci.*, 1973, **42**, 448.
- (2) D.H. Napper, *Polymeric stabilization of colloidal dispersions*, Academic Press, London, 1983.
- (3) M.B. Einarson and J.C. Berg, *J. Colloid Interface Sci.*, 1993, **155**, 165.

- (4) J.E. Johnson and E. Matijevic, *Colloid Polym. Sci.*, 1992, **270**, 364.
- (5) J.C. Dijt, M.A. Cohen Stuart, and G.J. Fleer, *Adv. Colloid Interface Sci.*, 1994, **50**, 79.
- (6) W. Norde and E. Rouwendal, *J. Colloid Interface Sci.*, 1990, **139**, 169.
- (7) S.S. Dukhin and B.V. Derjaguin in *Surface and Colloid Science*; E. Matijevic, Ed.; Wiley: New York, 1974; Vol. 7.
- (8) T. Hiemstra, J.C.M. de Wit, and W.H. van Riemsdijk, *J. Colloid Interface Sci.*, 1989, **133**, 105.
- (9) U. Oertel, S. Schwarz, H. Buchhammer, G. Petzold, H. Jacobasch, and M. Rätzsch, *Angew. Makromol. Chem.*, 1993, **207**, 203.
- (10) A.W.M. de Laat, G.L.T. van den Heuvel, and M.R. Böhmer, *Colloids Surfaces*, 1995, accepted.
- (11) J. Meadows, P.A. Williams, M.J. Garvey, and R. Harrop, *J. Colloid Interface Sci.*, 1992, **148**, 160.
- (12) J. Lyklema, *J. Electroanal. Chem.*, 1968, **18**, 341.
- (13) M.A. Cohen Stuart, G.J. Fleer, J. Lyklema, W. Norde, and J.M.H.M. Scheutjens, *Adv. Colloid Interface Sci.*, 1991, **34**, 477.
- (14) L. Eriksson, B. Alm, and P. Stenius, *Colloids Surfaces A*, 1993, **70**, 47.
- (15) R.J. Hunter and H.J.L. Wright, *J. Colloid Interface Sci.*, 1971, **37**, 564.
- (16) A. Yokoyama, K.R. Srinivasan, and H.S. Fogler, *J. Colloid Interface Sci.*, 1988, **126**, 141.
- (17) *Handbook of water-soluble gums and resins*; R.L. Davidson, Ed.; McGraw-Hill book company: New York, 1980.
- (18) J. Gregory, *Colloids Surfaces*, 1988, **31**, 231.
- (19) Y. Adachi, M.A. Cohen Stuart, and R. Fokkink, *J. Colloid Interface Sci.*, 1994, **167**, 346.
- (20) A. Bleier and E.D. Goddard, *Colloids Surfaces*, 1980, **1**, 407.

Chapter 6 The formation and stability of multilayers of polyelectrolytes

Subsequent addition of anionic and cationic polyelectrolytes may lead to the formation of multilayers at a solid surface. The build-up of such multilayers is characterised by a step-wise increase of the adsorbed amount and layer thickness, and by alternating highly positive and highly negative values for the ζ -potential.

The prime variables which determine the stability of these structures are the polymer charge and the ionic strength. Very stable multilayers are formed when both polymers are highly charged and when the ionic strength is low. For weakly stable multilayers complexation at the surface may first occur, followed by desorption of the complexes.

For strongly charged polyelectrolytes the charge stoichiometry, which is not always 1:1, seems to be unique for each pair of polyelectrolytes; no influence of the substrate, of the pH, and of the ionic strength could be observed.

6.1 Introduction

Pairs of oppositely charged polyelectrolytes in aqueous solution are well known to form complexes¹. The complexation is mainly due to the attractive electrostatic interaction between the chains. The stability of the complexes therefore depends on the strength of this attraction and, hence, on the polymer charge densities and the ionic strength.

Both stoichiometric and non-stoichiometric complexes can be formed^{2,3}. In stoichiometric complexes (coacervates⁴) the charges are nearly completely neutralised, so that these aggregates are usually insoluble. Non-stoichiometric complexes⁵, however, remain in solution, stabilised by the uncompensated polymer charge.

The tendency of pairs of oppositely charged polyelectrolytes to form complexes can be used to form multilayers. In the first step of the assembly process a polyelectrolyte (say, cationic) is adsorbed onto a suitable substrate. Then alternately anionic and cationic polymers are supplied. In every step the supplied polymer adsorbs on top of the previously adsorbed layer. Decher and Hong⁶⁻⁸ showed that all kinds of

strongly charged molecules can be combined into ordered multilayers and that this technique can be used to obtain well-defined layers with specific, *e.g.*, optical or electrical properties.

In most of the studies published so far, the conditions which determine the stability of the multilayers have not been studied systematically. Little is known about the conditions under which stable multilayers can be formed. The aim of this study is therefore to achieve a better understanding of the formation and the stability of multilayers. Central questions are:

- Under what conditions can multilayers be formed?
- How stable are the multilayers?
- What determines the stoichiometry between the layers?

In order to answer these questions we followed the total adsorbed amount, the ζ -potential, and the hydrodynamic layer thickness upon subsequent additions of anionic and cationic polymers.

6.2 Materials and methods

6.2.1 Materials

As the cationic polymers we used partially quaternised polyvinyl imidazole (PVI⁺), polydimethylaminoethyl methacrylate (AMA), and quaternised polyvinyl pyridine (PVP⁺), and as the anionic polymers polyacrylic acid (PAA), polymethacrylic acid (PMA), and polystyrene sulfonate (PSS⁻). Some of these polyelectrolyte carry a constant charge indicated by the superscript "+" or "-"; the others are pH-dependently charged. The structural formulas of these polymers are given in Fig. 6.1. Some

Table 6.1 Properties of the polyelectrolytes employed in the experiments

polymer	source	charge	M_w (kg/mol)	M_w/M_n
PVI ⁺	Deratani ⁹	constant	76	2.1
AMA	Arnold	variable	100	1.9
AMA	Arnold	variable	20	narrow
PVP ⁺	Rochrom, the Netherlands	constant	120	1.03
PAA	Allied Colloids	variable	10	broad
PMA	BDH Chemicals, England	variable	high	broad
PSS ⁻	Pressure Chemical Co.	constant	88	1.10

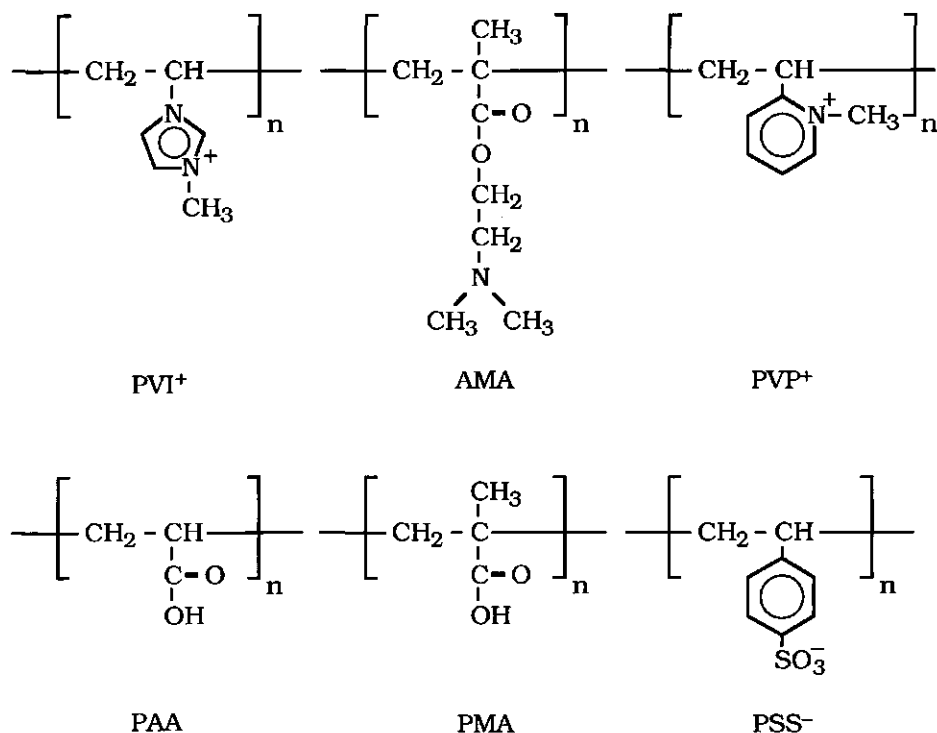


Figure 6.1 Structural formulas of the cationic polymers: partially quaternised polyvinyl imidazole (PVI⁺), polydimethylaminoethyl methacrylate (AMA), and quaternised polyvinyl pyridine (PVP⁺), and of the anionic polymers: polyacrylic acid (PAA), polymethacrylic acid (PMA), and polystyrene sulfonate (PSS⁻).

characteristics of the samples are summarised in Table 6.1. PVI was synthesised and subsequently quaternised by Deratani as described in ref. [9]. The number of charged groups is given by their degree of quaternisation d_q . AMA was synthesised by Dr. Arnold's group in Halle (Germany) by anionic polymerisation as described in Ch. 4.

The reflectometric measurements were performed on silicon wafers (Aurel GmbH, Germany) bearing a 100 nm thick SiO₂ or a 25 nm thick TiO₂ layer. The ζ -potential and the hydrodynamic layer thickness were measured on monodisperse silica particles with a radius of 100 nm (Monospher 200 of Merck). All other chemicals were of analytical grade.

6.2.2 Reflectometry

The adsorption measurements were performed using optical reflectometry combined with a stagnation-point flow-cell¹⁰. The relative change in the

reflectometer signal $\Delta S/S_0$ is proportional to the adsorbed amount Γ , provided Γ is not too high¹⁰

$$\Gamma = \frac{1}{A_s} \cdot \frac{\Delta S}{S_0} \quad (6.1)$$

Here, A_s is the sensitivity factor. It is proportional to the refractive index increment dn/dc of the polymer.

For adsorption of a single component, it is straightforward to convert $\Delta S/S_0$ to adsorbed amounts. However, when two or more components with different dn/dc participate, this cannot be done unambiguously, because one must know what part of the change in signal is due to each polymer. For these reasons such a conversion is only partaken for stable multilayers, for which the increase in the signal can be safely assigned to the adsorption of the supplied polymer. Another complication occurs when Γ becomes too high ($> 10 \text{ mg/m}^2$). Then the change of signal is no longer linear with the adsorbed amount.

6.2.3 Electrophoretic mobility

Electrophoretic mobilities of colloidal particles in contact alternately with PVI⁺ and PAA were measured using a Malvern zeta-sizer II. The mobility v was converted into a ζ -potential using the Smoluchowski relation ($\zeta = v\eta/E\varepsilon$, where η and ε are the viscosity and the permittivity of the solution, respectively, and E is the electric field strength). The samples were treated as follows. First, adsorption was allowed to take place overnight at a 200 mg/kg PVI⁺ concentration. Prior to the measurement the suspension was diluted, so that a very low ($< 3 \text{ mg/kg}$) concentration of free polymer remained. Subsequently, PAA was added up to a concentration of 10 mg/kg and the mobilities were measured half an hour later. After that PVI⁺ was added up to a concentration of 300 mg/kg. Such a high concentration is needed to complexate all the free PAA in solution, also at low degrees of PVI⁺ quaternisation. Half an hour later, the mobility was again measured. In the final step PAA was added up to a concentration of 500 mg/kg and a last mobility measurement was taken. During the experiment the solution was continuously stirred by means of a roller bench.

6.2.4 Hydrodynamic layer thickness measurements

Photon correlation spectroscopy (PCS) of colloidal dispersions was used to assess the development of the hydrodynamic layer thickness upon

addition of PVI^+ and, subsequently, PAA. Measurements with PCS are very sensitive to flocculation, so that stable dispersions are required.

The preparation of the samples for the PCS measurement was the same as for the measurement of the electrophoretic mobility. We were only successful in preparing stable suspensions of $\text{SiO}_2\text{-PVI}^+$ and $\text{SiO}_2\text{-PVI}^+\text{-PAA}$ systems. Subsequent additions of PVI^+ led to flocculation for the lowly quaternised ones. We therefore only report measurements for $\text{SiO}_2\text{-PVI}^+$ and $\text{SiO}_2\text{-PVI}^+\text{-PAA}$.

The results are an average of 8 measurements with a standard deviation of about 2 nm.

6.3 Results and discussion

6.3.1 Experimental information on multilayer formation

In order to obtain a more complete picture of multilayer formation, we compared adsorption data obtained from reflectometry (Fig. 6.2) with results for the ζ -potential and the hydrodynamic layer thickness d_h (Table 6.2). All these measurements were performed at $\text{pH} = 10$ and 0.01 mol/kg KNO_3 with two pairs of polyelectrolytes: PAA, which is fully charged at $\text{pH} = 10$, and two samples of PVI^+ with a degree of quaternisation d_q of 0 and 0.52, respectively. The substrate was either oxidised silicon (reflectometry) or colloidal silica (mobility and layer

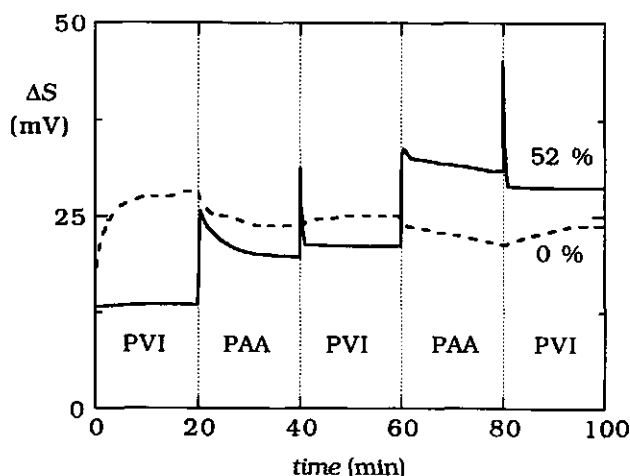


Figure 6.2 Multilayer formation of PVI^+ , with degrees of quaternisation d_q of 0 (dashed curve) and 0.52 (solid curve), with fully deprotonated PAA on SiO_2 . Other parameters: polymer concentrations 100 mg/kg, $I = 0.01$ mol/kg (KNO_3) and $\text{pH} = 10$.

thickness measurements).

In Fig. 6.2 the time evolution of the reflectometric signal ΔS upon alternated addition of lowly charged PVI⁺ ($d_q = 0$, dashed curve) and PAA, and of highly charged PVI⁺ ($d_q = 0.52$, solid curve) and PAA is presented. Every 20 min., as indicated by the vertical dotted lines, the solution was switched from PVI⁺ to PAA or vice versa. The reflectometric signal cannot be converted quantitatively into adsorbed amounts since we do not know the composition of the multilayer and both polymers have a different dn/dc . The trends found for ΔS are expected to correspond qualitatively with changes in the adsorbed amount.

From Fig. 6.2 we conclude that for the combination of PVI⁺ ($d_q = 0$) and PAA no multilayer formation takes place, whereas when with PVI⁺ ($d_q = 0.52$) higher adsorbed amounts are attained in the successive addition steps. For the latter system the response upon addition of a new polymer is unexpected: after an expected initial rise in the signal (adsorption), it decreases again (desorption). Such a decrease is only found in the second and higher layers. It is probably caused by desorption of PVI⁺/PAA complexes. We return to this point later.

The conclusion that multilayer formation only occurs for PAA and highly charged PVI⁺ is corroborated by the data for the ζ -potential and layer thickness d_h in Table 6.2. For PVI⁺ ($d_q = 0$) no change in the ζ -potential is found upon sequential addition of PVI⁺ and PAA. Also, the layer thickness d_h does not increase (it even seems to decrease somewhat). For highly charged PVI⁺ ($d_q = 0.52$) an increase in the layer thickness is observed after addition of PAA to SiO₂ with preadsorbed PVI⁺. The changes in the ζ -potential for this system are quite significant. Upon addition of PVI⁺ (layers 1 and 3) the ζ -potential is highly positive, and when PAA was added last (layers 2 and 4) it is highly negative. This result

Table 6.2 ζ -potential and hydrodynamic layer thickness d_h data of PAA/PVI⁺ multilayer systems on SiO₂. Experimental conditions: pH = 10 and $I = 0.01$ mol/kg.

$d_q = 0$	ζ (mV)	d_h (nm)	$d_q = 0.52$	ζ (mV)	d_h (nm)
1 PVI ⁺	-30	15	1 PVI ⁺	59	3
2 PAA	-28	12	2 PAA	-73	7
3 PVI ⁺	-28		3 PVI ⁺	50	
4 PAA	-33		4 PAA	-58	

clearly demonstrates that upon adsorption of PVI⁺ and PAA the surface charge is not more or less compensated, as predicted from theoretical (equilibrium) models¹¹, but strongly overcompensated. The occurrence of strong overcompensation is the principal reason for the existence of multilayers. Only in the case of such an overcompensation does adsorption of one layer lead to reversal of charge, so that the oppositely charged molecule is again attracted to it. Strong overcompensation was reported earlier in Chs. 2 and 5 for the adsorption of polyelectrolytes on oxides.

From the observations described above we infer that both the adsorbed amount and the layer thickness increase when a multilayer is formed. Furthermore, we find that the reflectometric signal gives detailed information about the kinetics of the adsorption and about the stability of the multilayer. The ζ -potential is an indication for the outer charge of the multilayer, which is alternately positive and negative. Since reflectometry provides direct information about the stability of the multilayers, we will now use this technique to examine the conditions for multilayer formation in detail.

6.3.2 Conditions for multilayer formation

Effect of polymer charge

Above we noted that the degree of quaternisation, and, hence, the charge on the polymer molecule plays a decisive role. It is probable that a certain (critical) polymer charge exists above which multilayer formation is possible. Since the driving force for complexation is mainly electrostatic, this critical polymer charge most likely depends on the ionic strength. In order to check this assumption we tried to produce multilayers of PAA and PVI⁺ on SiO₂ at pH 10 at two different ionic strengths: $I = 0.001$ and 0.01 mol/kg. In Fig. 6.3 the reflectometric signals after one adsorption step (open circles) and after four consecutive adsorption steps (filled circles) are given as a function of d_q .

First, we examine the adsorption of PVI⁺ onto the bare substrate (open circles in Fig. 6.3). The reflectometric signal and, hence, the adsorbed amount in the first step passes through a maximum value at low degree of quaternisation, in the range $d_q = 0.05 - 0.07^9$. Such a maximum in the adsorbed amount as a function of the polymer charge is often observed; examples can be found in Ch. 2 and ref. (9). It is due to the balance of the attractive electrostatic interaction between the polyelectrolyte and the

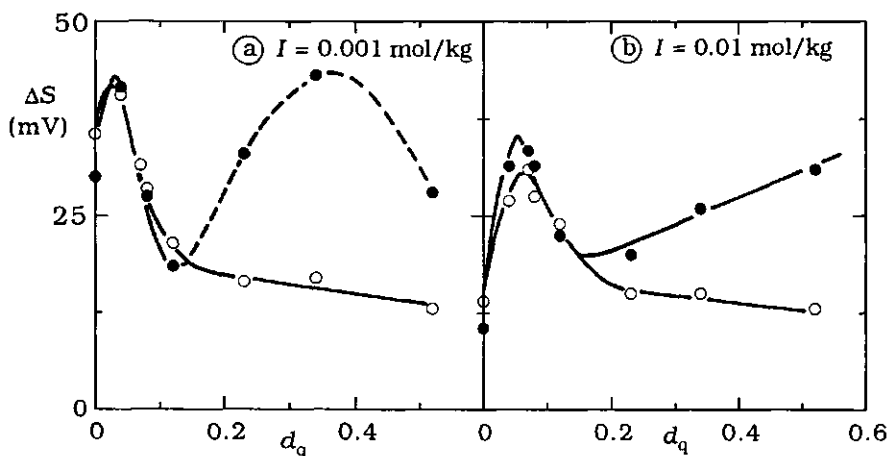


Figure 6.3 Multilayer formation of PAA and PVI^+ on SiO_2 at pH 10 at two ionic strengths: $I = 0.001$ and 0.01 mol/kg (KNO_3). The reflectometric signals after one adsorption step (open circles) and after four adsorption steps (filled circles) are plotted as a function of the degree of quaternisation of PVI^+ .

oppositely charged substrate and the repulsive lateral electrostatic interaction in the adsorbed layer. When the polyelectrolyte is highly charged the repulsion prohibits the accumulation of many polymer molecules. By decreasing the polymer charge the number of adsorbing molecules increases. When the polymer charge becomes too low, however, the attraction to the surface is weakened too much, so that less molecules adhere to the surface. The result of both trends is the observed maximum in the adsorbed amount.

Next, we compare the reflectometric signal after four steps with the one of the first layer. At low d_q (< 0.12 for $I = 0.001$ mol/kg (Fig. 6.3a) and < 0.18 for $I = 0.01$ mol/kg (Fig. 6.3b)) both values are almost the same; no multilayer formation occurs. When the degree of quaternisation is higher than the critical value the adsorption increases significantly over four steps, indicating that complexation at the surface takes place. The multilayer is not very stable though; overshoots in the adsorbed amount as shown in Fig. 6.2 ($d_q = 0.52$) take place in all experiments. These overshoots are smaller (especially the ones after addition of PAA) and, hence, the stability is better when PVI^+ has a higher charge and when the ionic strength is low (not shown here).

The exact shape of the curve at polymer charges higher than the critical charge is not clear yet. The datapoints at $I = 0.001$ mol/kg (Fig.

6.3a) suggest the existence of a second maximum at $d_q \approx 0.35$, but more research should be carried out to confirm this.

The critical polymer charge of PVI⁺ above which multilayer formation with PAA takes place is higher at high ionic strength (0.12 for $I = 0.001$ mol/kg (Fig. 6.3a) and 0.18 for $I = 0.01$ mol/kg (Fig. 6.3b)), as expected. Salt ions weaken the electrostatic interaction between the polymer molecules, so that a higher polymer charge is needed to keep the attraction between the molecules strong enough.

Effect of rinsing on the stability

In the experiments presented in Figs. 6.2 and 6.3 the polymer supply was switched directly from a PVI⁺ to a PAA solution and *vice versa*. In other studies⁶⁻⁸ usually a rinsing step was included. We therefore studied the effect of such a rinsing on the multilayer formation of PAA and PVI⁺ ($d_q = 0.23$) at pH = 10 and at $I = 0.01$ mol/kg. The rinsing (20 min. of buffer solution at pH 10) took place between switching from one polymer solution to another. During rinsing no major changes in the signal were seen.

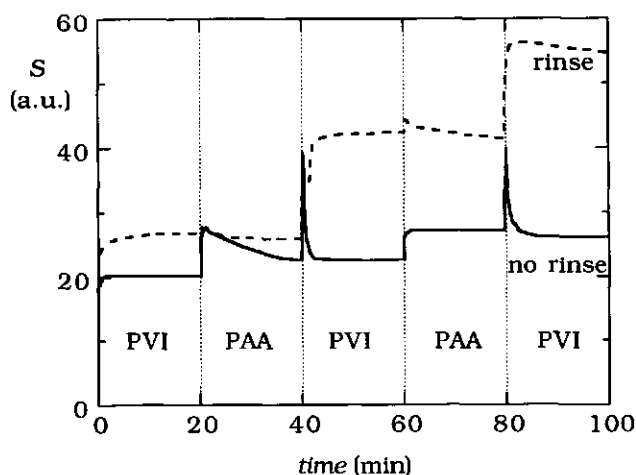


Figure 6.4 The effect of rinsing on the multilayer formation of PVI⁺ ($d_q = 0.23$) and PAA on SiO₂. The dashed curve represents the experiment in which a rinsing step (20 min. of buffer solution) is applied before switching from one polymer solution to another. The experiment without rinsing is represented by the solid curve. Since the signal underwent no significant changes during rinsing, this step is not shown in the graph to enable a better comparison. Parameters: pH = 10, $I = 0.01$ mol/kg (KNO₃), polymer concentrations 100 mg/kg.

In Fig. 6.4 we compare data taken with (dashed curve) and without (solid curve) rinsing. To enable a better comparison of the two curves only the adsorption steps are presented in Fig. 6.4. It is immediately seen that when rinsing is applied much higher adsorbed amounts are reached over a few steps. Also, the overshoots have nearly vanished. Apparently, rinsing has a major effect on the stability of the multilayer. Presumably, the rinsing removes the polymer molecules that are only loosely attached to the preadsorbed polymer layer. These are only few as can be inferred from the slight decrease in the signal during rinsing. Also, during the rinsing step some rearrangements in the adsorbed layer can occur, so that the layer becomes more stable.

Multilayers of weak polyelectrolytes

Before, we have shown that the formation and the stability of the multilayer structures of PAA and PVI⁺ depend on the polymer charge. For weak polyelectrolytes which have a pH-dependent charge this must mean that the pH is an important variable. In Fig. 6.5 the multilayer formation of AMA ($M_w = 100$ K) and PMA, which both have a pH-dependent degree of dissociation, on SiO₂ as a function of pH is given. The pH was

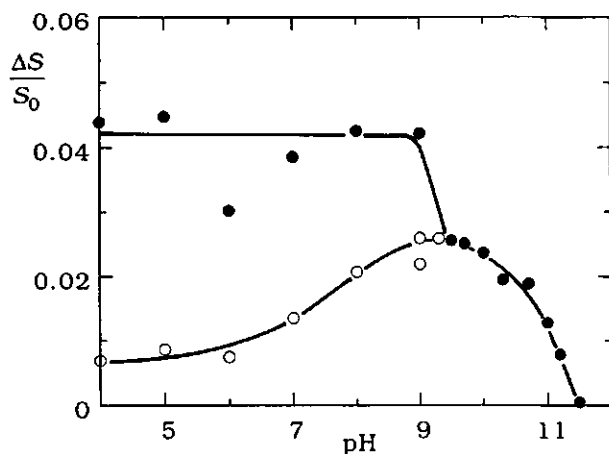


Figure 6.5 Multilayer formation of AMA ($M_w = 100$ K) and PMA on SiO₂ as a function of pH. The relative changes in the reflectometry signal $\Delta S/S_0$ after one adsorption step (AMA, open circles) and after three consecutive adsorption steps (AMA - PMA - AMA, filled circles) are given. Experimental parameters: $I = 0.02$ mol/kg (barbital-acetate buffer in the pH-range 4 - 9 and glycine buffer in the pH-range 9 - 12), polymer concentrations 10 mg/kg.

maintained by use of a barbital acetate buffer with an ionic strength of 0.02 mol/kg. The adsorption of the positively charged AMA in the first layer (open circles) is compared to the total adsorbed amount after three consecutive adsorption steps (filled circles). A rinsing step was applied before switching from one polymer solution to another.

As in Fig. 6.2, we find a maximum in the adsorbed amount in the first layer as a function of pH, and, thus, of the polymer charge. Such a maximum adsorbed amount was also reported for AMA ($M_w = 20$ K) on TiO_2 (see Ch. 2). On TiO_2 the maximum is positioned at pH = 8.5 for $I = 0.005$ mol/kg, and at pH = 7.5 for $I = 0.1$ mol/kg. On SiO_2 the maximum is located at a higher value of the pH (pH = 9.5) and, hence, at a lower polymer charge. Probably, an additional non-electrostatic interaction exists between AMA and SiO_2 , as is also present between quaternised polyvinyl pyridine (PVP^+) and SiO_2 (see Ch. 2) and between uncharged PVI and SiO_2 ⁹.

When we compare the adsorbed amount of AMA in the first layer with that after three adsorption steps (AMA - PMA - AMA) we find a strong increase in the adsorbed amount at pH < 9.5. At pH > 9.5 no increase in the signal can be observed upon addition of PMA. Apparently, at pH > 9.5 the polymer charge of AMA is too low to form complexes. From titration experiments of AMA ($M_w = 20$ K), reported in Ch. 2, we know that at pH = 9.5 the degree of proton association is less than 0.05. Hence, the polymer charge density is then quite small.

One would expect that at low pH another region exists where the polymer charge of PMA is too small to form multilayers. At pH = 4, the degree of dissociation is around 0.2, as estimated from titration experiments. Apparently, this value is still high enough to enable multilayer formation. Only at still lower values of the pH one would expect again an unstable region.

The stability of the multilayers (not shown here) formed in the experiments of Fig. 6.5 follows the same trends as observed before. At pH values close to the point where multilayer formation starts, the layers are rather unstable and considerable desorption occurs, especially at higher ionic strengths ($I > 0.02$ mol/kg, not shown). At pH = 4, however, the multilayer is quite stable; no desorption is detected even when the multilayer is grown at high ionic strength ($I = 0.1$ mol/kg).

Obviously, the multilayer formation of the PVI^+/PAA pair (Figs. 6.2, 6.3 and 6.4) and the AMA/PMA pair (Fig. 6.5) are similar. For both pairs a

critical polymer charge exists below which no multilayer formation is found. Also, in both cases the multilayers are rather unstable when the polymer charge is close to the critical point and the stability increases at higher polymer charges.

Clearly, both the charge density on the polymer where multilayer formation starts and the stability of the multilayers are determined by the electrostatic interactions. Presumably, these two characteristic variables are interrelated. When we examine the effect of the polymer charge on the multilayer formation, three situations might be distinguished, as illustrated in Fig. 6.6. (i) At a very low polymer charge the attraction between the polymer molecules is too weak to cause complexation at the surface (Fig. 6.6a). (ii) At a higher polymer charge complexation does occur. During complexation the conformation of the underlying polymer

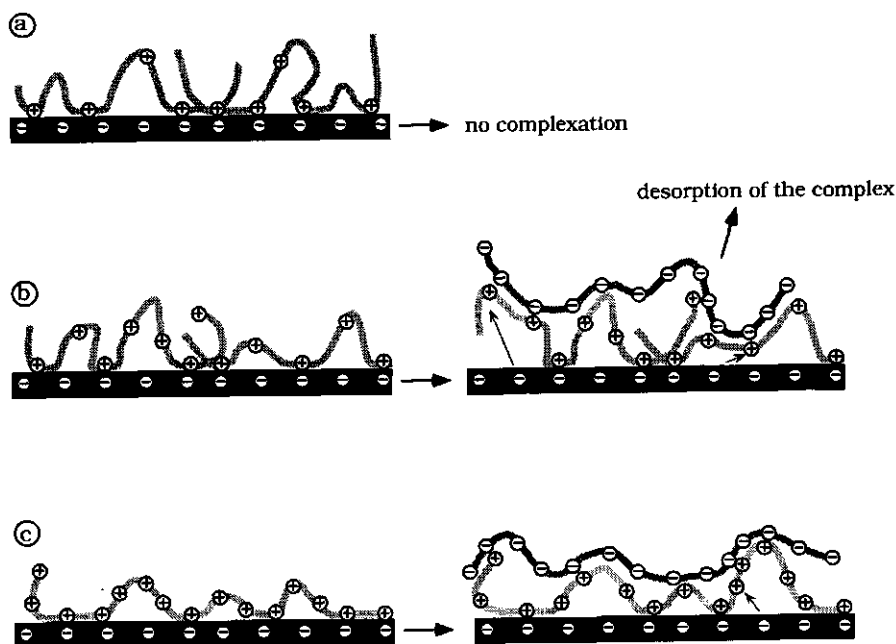


Figure 6.6 The complex formation of a highly charged anionic polymer to a substrate pre-covered with a cationic polymer. Three possible situations can arise depending on the charge density of the cationic polymer: (a) When this charge density is low no complexation occurs. (b) At a higher polymer charge density complexation at the surface occurs, followed by (partial) desorption of the complexes. (c) When both polymers are highly charged the complex remains strongly bound to the substrate; stable multilayers can be formed.

layer will adjust itself somewhat to the new outer layer. Because of this adjustment some bonds to the surface will be broken, as indicated by the arrows in the Fig. 6.6b and c. When the polymer charge is low too little bonds remain to keep the complex is attached to the substrate; desorption of the complex can take place (Fig. 6.6b). In this case no, or instable, multilayers are formed. (iii) At high polymer charge both the bond to the newly adsorbing molecule and to the underlying polymer layer is strong; stable multilayers are formed (Fig. 6.6c).

Effect of changes in the pH on the stability of multilayers

Multilayers of weak polyelectrolytes are potentially unstable, since a variation in the pH can influence the polymer charges. In order to check how multilayers with incorporated weak polyelectrolytes react to a change in the pH we performed the following experiment. First, we adsorbed AMA ($M_w = 20$ K) at pH = 8 onto TiO_2 after which the pH was decreased to 4. In a second experiment we made a bilayer of AMA (first layer) and PSS^- (second layer) at pH = 8 before we changed the pH to 4. Similarly, we also tested the stability of multilayers consisting of three (AMA - PSS^- - AMA), four, and eight layers. The results of the stability experiments up to four layers are shown in Fig. 6.7. The switches to a new polymer solution or to a buffer solution at pH = 4 are indicated by arrows.

As observed before, the signal increases stepwise upon addition of AMA or PSS^- . This indicates the formation of a multilayer. When the solution was switched to a buffer solution at pH = 4, however, the response depends on the number of underlying layers. If only one layer of AMA is adsorbed onto TiO_2 the signal decreases fast, indicating that desorption occurs. At pH = 4 AMA becomes more positively charged whereas the substrate TiO_2 becomes less negatively charged. Hence, the lateral repulsion between AMA molecules in the adsorbed layer increases. As a result some desorption occurs.

The response to the pH switch is more complicated for the multilayers. For multilayers with two, four or eight layers (the latter is not shown in Fig. 6.7) a slight *increase* in the signal is observed, whereas for a multilayer of three layers the signal first *increases* and then *decreases* again. One is inclined to think that the increase in the signal indicates extra adsorption, but this is highly unlikely since no polymer is supplied. Another reason for an increase in the signal could be an increase in dn/dc of the polymer (see Eq. 6.1). It was reported before in Ch. 2 that dn/dc of

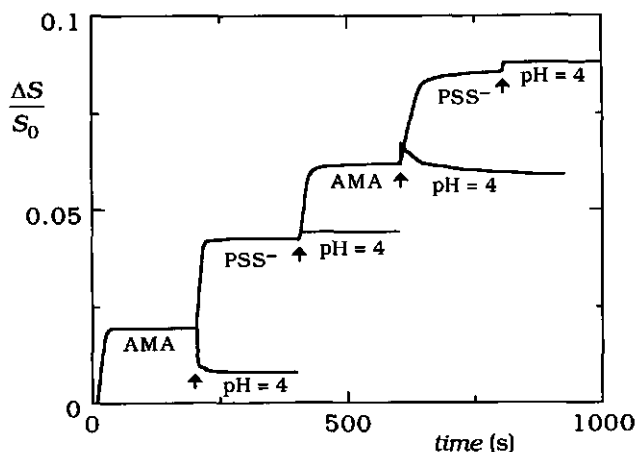


Figure 6.7 The stability of AMA (20 K)/PSS⁻ multilayers against changes in the pH. In this experiment multilayers of one, two, three or four layers were formed onto TiO₂ at pH = 8. After that the pH was decreased from 8 to 4. The switch to either a new polymer solution or to the buffer solution at pH = 4 is indicated by the arrows. The ionic strength in all solutions was 0.005 mol/kg (barbital-acetate buffer) and the polymer concentrations were 10 mg/kg.

AMA depends on its degree of protonation. Its value ranges from 0.14 cm³/g (uncharged, high pH) to 0.21 cm³/g (fully charged, low pH). Therefore, an increase in the signal upon changing the pH from 8 to 4 is more likely to be due to a higher dn/dc of AMA. The absence of a decrease in the signal (no desorption) when PSS⁻ is the outer layer (for an even number of layers) suggests that the multilayer is stable enough to overcome increases in the polymer charge of AMA.

When AMA forms the outermost layer some desorption is indeed observed as a decrease of the signal after an initial increase. The desorbed molecules are probably loosely attached AMA molecules in the outer layer.

6.3.3 Stable Multilayers

Above, we concluded that the stability of the multilayer is high when both polymers are highly charged. We therefore tried the combination of the strongly charged polyelectrolytes PVP⁺ and PSS⁻ on TiO₂ at $I = 0.005$ and 0.1 mol/kg and at pH = 8 to check this assumption. Indeed, very stable multilayers were obtained; no desorption was observed even for multilayers consisting of as much as 20 layers (not shown here) at both ionic strengths. The total adsorbed mass of these multilayers at $I = 0.005$

and 0.1 mol/kg is then 8.4 and 34 mg/m², respectively. Both values were calculated assuming Eq. 6.1 to be applicable. Data by Decher⁸ for PSS⁻ and polyallylamine corroborate the conclusion that highly charged polyelectrolytes form very stable multilayers.

Effect of the substrate

We can use these stable multilayers to study the effect of the substrate. It is well known that the substrate largely determines the amount of polyelectrolyte adsorbed onto it¹¹. It can influence the adsorbed amount through its interactions with the polymer (which may be electrostatic and non-electrostatic). The strength of the electrostatic interaction depends on the charge on the substrate, and, hence, on the pH. In Fig. 6.8 we present the increments in adsorbed amount for consecutive layers of PVP⁺ and PSS⁻ on SiO₂ (at pH = 4, crosses) and TiO₂ (at pH = 4, open circles and 8, filled circles). Since multilayers of PVP⁺ and PSS⁻ are stable we were in this case able to convert changes in the signal to adsorbed amounts through Eq. 6.1.

We notice in Fig. 6.8 that the adsorbed amount of PVP⁺ in the first layer varies strongly with pH and the type of substrate, as expected. Beyond the third layer (for TiO₂) or beyond the sixth layer (for SiO₂), however, no major differences in the adsorbed amount of each

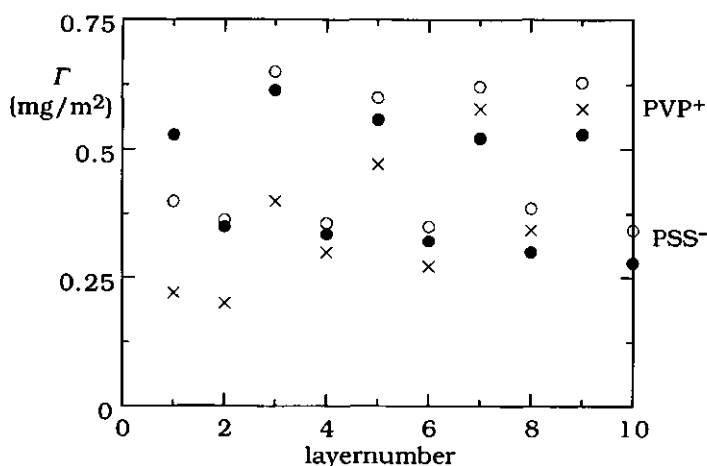


Figure 6.8 The adsorbed amounts in each step for stable multilayers of PVP⁺ and PSS⁻ on SiO₂ (pH = 4, crosses) and TiO₂ (pH = 4, open circles, or 8, filled circles). The ionic strength in all experiments was 0.005 mol/kg (barbital-acetate buffer) and the polymer concentrations were 10 mg/kg.

polyelectrolyte are found. Apparently, the influence of the substrate is restricted to the first few layers. In higher layers it is the interaction between both polymers which governs the adsorbed amount. This polymer/polymer interaction leads to a substantially higher adsorbed amount of PVP⁺ as compared to that of PSS⁻.

Stoichiometry of multilayers

In order to find out what factors determine the stoichiometry in polyelectrolyte multilayers we prepared multilayers from two different pairs: PVP⁺ ($M_w = 120$ K) with PSS⁻ ($M_w = 88$ K), and AMA ($M_w = 20$ K) with PSS⁻ ($M_w = 88$ K). The latter pair was studied at low pH (pH = 4) only to ensure that AMA is fully dissociated. The adsorbed amounts per layer (in the higher layers) and the stoichiometry between the polymers are summarised in Table 6.3 for various orders of addition, substrates, pH values, ionic strengths, and types of polymer. The stoichiometric factor f is defined as the ratio between the number of cationic and anionic charges on the polymers in the multilayer. It was calculated from the adsorbed amounts Γ_+ and Γ_- and the molar monomeric masses M_+ and M_- of the cationic and anionic polyelectrolyte, respectively, as

$$f = \frac{\Gamma_+ M_-}{\Gamma_- M_+} \quad (6.2)$$

Upon inspection of Table 6.3 we observe that neither the order of addition, nor the substrate or the pH have an effect on the adsorbed amounts and on the stoichiometry in the higher layers. As to the effect of ionic strength we find that the adsorbed amounts per layer are much higher when the ionic strength is increased to 0.1 mol/kg. Such an increase of the adsorbed amount with ionic strength, which is also found in Ch. 2 for monolayers of PVP⁺ adsorbing onto TiO₂, is due to a screening of the lateral repulsion within the layer, so that more polymer molecules adsorb per layer. In spite of this higher adsorbed amount in the higher layers no significant influence is seen on the stoichiometry.

The only factor that does affect the stoichiometry of multilayer formation is the types of polymers. It is not clear why the stoichiometry between PVP⁺/PSS⁻ differs from the one between AMA/PSS⁻. Possibly, this difference results from structural differences between the polymers (see Fig. 6.1). For both AMA and PSS⁻ the charge is located at the far end of the side chain, which is relatively flexible, whereas the charge in PVP⁺ is situated close to the relatively stiff backbone, where it is not so easily

Table 6.3 Stoichiometric factor f of stable multilayers of PVP⁺/PSS⁻ and AMA/PSS⁻ under several conditions.

order	substrate	pH	I (mol/kg)	PVP ⁺ (mg/m ²)	PSS ⁻ (mg/m ²)	f
PSS ⁻ ->PVP ⁺	SiO ₂	4	0.005	0.56	0.35	2.7
PSS ⁻ ->PVP ⁺	TiO ₂	4	0.005	0.59	0.35	2.8
PSS ⁻ ->PVP ⁺	TiO ₂	8	0.005	0.56	0.32	2.9
PVP ⁺ ->PSS ⁻	SiO ₂	4	0.005	0.59	0.34	2.9
PVP ⁺ ->PSS ⁻	SiO ₂	8	0.005	0.59	0.26	3.8
PVP ⁺ ->PSS ⁻	TiO ₂	4	0.005	0.63	0.36	2.9
PVP ⁺ ->PSS ⁻	TiO ₂	8	0.005	0.52	0.29	3.0
PVP ⁺ ->PSS ⁻	SiO ₂	4	0.1	2.18	1.13	3.2
PVP ⁺ ->PSS ⁻	SiO ₂	8	0.1	2.19	1.21	3.0
PVP ⁺ ->PSS ⁻	TiO ₂	4	0.1	2.02	1.05	3.2
PVP ⁺ ->PSS ⁻	TiO ₂	8	0.1	2.11	1.09	3.2
order	substrate	pH	I (mol/kg)	AMA (mg/m ²)	PSS ⁻ (mg/m ²)	f
AMA->PSS ⁻	TiO ₂	4	0.005	0.26	0.34	1.0
AMA->PSS ⁻	TiO ₂	4	0.1	0.80	0.94	1.1

accessible. Therefore the charged groups of AMA and PSS⁻ "fit" together rather well. For PVP⁺ and PSS⁻ the "fit" is not so good; only one third of the positive charge is compensated by the anionic polymer. Since the multilayer must be electroneutral the rest of the charge must be compensated by small ions; large amounts of small ions must therefore be incorporated in the multilayer.

6.4 Conclusions

In this chapter the formation and the stability of polyelectrolyte multilayers were examined. The complexation of anionic and cationic polyelectrolytes at the surface is accompanied by a regular increase in the adsorbed amount and in the layer thickness as more layers are deposited at the surface. The ζ -potential changes dramatically from highly positive values to highly negative ones upon addition of cationic and anionic polyelectrolytes, respectively.

The stability of the multilayer is largely determined by the electrostatic

interactions between the anionic/cationic polymer pair, and, hence, by the polymer charge densities and the ionic strength. Unstable multilayers could be stabilised by rinsing before switching to the other polymer solution. For weak polyelectrolytes, which have a pH-dependent charge, also the pH of the solution was shown to be an important variable.

For stable multilayers of strongly charged polyelectrolytes the influence of the substrate is restricted to the first few layers. The adsorbed amounts in the higher layers are the same regardless of the type of substrate, the pH and the order in which the multilayer was formed. The stoichiometry seems to be unique for a certain pair of polyelectrolytes; for PVP⁺/PSS⁻ it was 3:1, whereas for the combination of AMA (at pH = 4, where this polymer is completely charged) with PSS⁻ it was 1:1. When the complexation is not stoichiometric small ions must be incorporated in the multilayer.

6.5 References

- (1) K. Petrak in *Polyelectrolytes : Science and Technology*; M. Hara, Ed.; Marcel Dekker: New York, 1992; pp 265.
- (2) E. Tsuchida, Y. Osada, and K. Sanada, *J. Polym. Sci.*, 1972, **10**, 3397.
- (3) J. Koetz, K.J. Linow, B. Philipp, L.P. Hu, and O. Vogl, *Polymer*, 1986, **27**, 1574.
- (4) C.J. van Oss, *Polym. Prepr.*, 1991, **32**, 598.
- (5) V.A. Kabanov and A.B. Zezin, *Makromol. Chem., Suppl.*, 1984, **6**, 259.
- (6) G. Decher and J.D. Hong, *Makromol. Chem., Macromol. Symp.*, 1991, **46**, 321.
- (7) G. Decher and J.D. Hong, *Ber. Bundesges. Phys. Chem.*, 1991, **95**, 1430.
- (8) G. Decher, J.D. Hong, and J. Schmitt, *Thin Solid Films*, 1992, **210/211**, 831.
- (9) M.R. Böhmer, W.H.A. Heesterbeek, A. Deratani, and E. Renard, *Colloids Surfaces A*, 1995, **99**, 53.
- (10) J.C. Dijt, M.A. Cohen Stuart, and G.J. Fleer, *Adv. Colloid Interface Sci.*, 1994, **50**, 79.
- (11) M.A. Cohen Stuart, G.J. Fleer, J. Lyklema, W. Norde, and J.M.H.M. Scheutjens, *Adv. Colloid Interface Sci.*, 1991, **34**, 477.

Summary

The aim of the study described in this thesis was to examine the adsorption properties of polyelectrolytes and charged block copolymers on oxides, and the effect of these polymers on the colloidal stability of oxidic dispersions. For this purpose the interaction of some well-characterised polyelectrolytes and block copolymers with oxidic substrates has been systematically studied. A set of block copolymers with one charged block and one neutral water-soluble block had to be synthesised because this type of block copolymers was not commercially available. These block copolymers were prepared by anionic polymerisation by Dr. Arnold's group in Halle (Germany).

In order to measure the amount of polymer adsorbed as a function of several experimental parameters (pH, ionic strength, type of polymer, type of substrate) we used a reflectometer equipped with a stagnation-point flow-cell. With this optical technique the adsorbed amount on an (optically flat) solid substrate is measured. This technique is also suited to follow the kinetics of the adsorption process. Information about the amount of charge in the adsorbed layer was obtained from streaming potential measurements (on flat surfaces, Ch. 5) and electrophoresis (on particles, Ch. 6). The effect of polymer on the colloidal stability of oxidic dispersions was probed by measuring the changes in the optical transmission with time (Ch. 5).

In Chapter 1 it is explained that in many applications there is a need to control the colloidal stability of oxidic dispersions, and it is described how in general the stability can be affected by polymer addition. Also, the aim, scope and outline of this study are given.

In the following three chapters we present the adsorption properties of *homopolyelectrolytes* (Chs. 2 and 3) and of *charged block copolymers* (Ch. 4) on oxides. The homopolyelectrolytes used were two polymers with a constant charge (quaternised polyvinyl pyridine, PVP⁺, and quaternised polydimethylaminoethyl methacrylate, AMA⁺), and one with a pH-dependent charge (polydimethylaminoethyl methacrylate, AMA). The block copolymers consisted of a charged block (AMA) and a water-soluble neutral one (dihydroxypropyl methacrylate, HMA). As the substrates we used both silicon oxide (SiO₂), which is acidic in nature and the amphoteric titanium dioxide (TiO₂).

In Chapter 2 the rate of adsorption and the final adsorbed amount of

the homopolyelectrolytes are studied as a function of pH and ionic strength. The initial adsorption rate is found to be equal to the rate with which the polymer molecules arrive to the surface; hence, the transport of molecules from the bulk of the solution to the surface is rate-limiting. Above a certain coverage the adsorption rate goes down, indicating that the already adsorbed molecules form a kinetic barrier for further adsorption.

The adsorbed amount at saturation depends on pH and ionic strength. For both PVP⁺ and AMA⁺ a monotonic increase in the adsorbed amount is observed with increasing pH, since the surface gets more negatively charged. For AMA, which has a pH-dependent charge, a maximum in the adsorbed amount is found when the pH, and, thus the polymer charge, is varied.

When the adsorbed charge of polyelectrolyte is compared to the bare surface charge, as determined from titration experiments, it is found that the net adsorbed charge exceeds by far the net bare surface charge (overcompensation). Part of the surplus of charge is neutralised by adjustment of the pH-dependent charges on the surface and on the polymer.

In *Chapter 3* the reversibility of the adsorption of PVP⁺ and AMA is studied by taking the system out of equilibrium, *e.g.*, by a change of the pH or the free polymer concentration. Then, the subsequent relaxation is followed. In case of complete reversibility, the adsorbed amount of the relaxed system should be equal to that for direct adsorption on a bare surface under these conditions. Also, the reversibility was investigated by examining the exchange of adsorbed polyelectrolyte molecules by molecules from the solution.

The experiments indicate that the adsorbed layer was never fully relaxed. Therefore, we conclude that the experimental systems are only partly reversible on the timescale of the experiments (30 min.). Presumably, the reorganisation of molecules in the adsorbed layer is rather slow, because of the strong (electrostatic) bond between polyelectrolyte and surface. A model for the structure of the adsorbed layer of strongly charged polyelectrolytes, allowing little reconfiguration, is proposed. In this model the molecules adsorb as isolated chains on the surface. These islands repel mutually, thereby forming a heterogeneous layer. An indication for the existence of empty spaces between the molecules comes from the observation that after adsorption of the

polyelectrolyte neutral polymer molecules can attach to the surface.

In *Chapter 4* the synthesis and characterisation of the AMA-HMA block copolymers are described. Next, the adsorption properties of the block copolymers are studied as a function of pH, ionic strength and block length ratio. A maximum in the adsorbed amount is observed when the composition of the block copolymer is varied, similar to the maximum found for homopolyelectrolytes upon variation of the segment charge (see Ch. 2). Also, the adsorbed amount follows the same trends with pH and ionic strength as does the homopolyelectrolyte AMA; almost no effect of the presence of the neutral block on the adsorption data can be detected. From these facts we infer that the charged block in the block copolymer anchors on the surface. Probably, the neutral block can also adsorb, since charged molecules usually do not cover the surface completely, because they repel each other (see Ch. 3). Only at high adsorbed amounts the surface becomes so densely populated that the neutral block is forced into the solution, thereby forming an extended layer which may provide steric stabilisation.

In *Chapter 5* we discuss the effect of addition of charged (block co)polymers on the stability of oxidic dispersions. We note that the same type of polymer can both stabilise and destabilise a dispersion. For example, a low dosage of strongly charged (say, cationic) polymer molecules to a dispersion of oppositely charged (anionic) particles may cause mosaic flocculation, whereby bare (negatively charged) and covered (positively charged) parts on neighbouring particles attract each other. When the polymer is very long bridging flocculation could also occur whereby one polymer molecule adsorbs on two particles at the same time. When, however, the dosage is high enough to saturate the particles, the dispersion may be stabilised sterically or electrostatically, depending on the thickness of the steric layer and on the amount of charge on the particles.

As illustrated above, the effect of the polymers depends critically on the polymer charge, on the dosage and on the molar mass of the polymer. In Ch. 5 a set of requirements could be formulated to optimise the performance of the polymers for stabilisation or flocculation.

Finally, in *Chapter 6* we describe the formation and stability of multilayers of polyelectrolytes. Since charge reversal occurs upon adsorption of a strongly charged (say, cationic) polyelectrolyte (see Ch. 2), an oppositely charged (anionic) polymer molecule is attracted to such a

covered surface. Therefore, when cationic and anionic polymers are supplied in alternating order to a solid substrate, multilayers can be formed.

The multilayer build-up is characterised by a step-wise increase of the adsorbed amount and the layer thickness, and by alternatingly highly positive and highly negative values for the ζ -potential. The stability of the multilayer is shown to depend strongly on the polymer charges and the ionic strength and, hence, on the electrostatic interaction between the polymers involved. When this interaction is weak no stable multilayers form, but polycations and polyanions form complexes at the surface which then may desorb. For pairs of strongly interacting polymers, which formed very stable multilayers, the charge stoichiometry could be studied. This charge stoichiometry, which was not always 1 : 1, was found to be independent of the substrate, the pH or the ionic strength, but rather sensitive to the monomer structure.

Adsorptie van polyelectrolyten en geladen blokcopolymeren op oxiden: gevolgen voor de kolloïdale stabiliteit

Samenvatting

Het doel van het in dit proefschrift beschreven onderzoek is het bestuderen van de adsorptie van polyelectrolyten en geladen blokcopolymeren op oxiden, en het effect daarvan op de stabiliteit van oxidedispersies. Hiertoe is de interactie van een aantal goed gekarakteriseerde polyelectrolyten en geladen blokcopolymeren met oxidische oppervlakken systematisch onderzocht. Aangezien blokcopolymeren met een geladen blok en een ongeladen, wateroplosbaar blok niet beschikbaar waren, moesten deze eerst gesynthetiseerd worden. Dit werd uitgevoerd door de groep van Dr. Arnold in Halle (Duitsland).

De hoeveelheid geadsorbeerd polymeer is gemeten als functie van diverse experimentele parameters (pH, zoutconcentratie, type polymeer, type oppervlak) met een reflectometer. Met deze optische techniek kan de geadsorbeerde hoeveelheid op een optisch vlak oppervlak direct en continu gemeten worden. Hierdoor is de techniek ook geschikt om de kinetiek van het adsorptieproces te volgen. Informatie over de ladingstoestand van de geadsorbeerde laag werd verkregen uit stromingspotentiaalmetingen aan vlakke oppervlakken (hoofdstuk 5) en uit electroforese aan deeltjes (hoofdstuk 6). Het effect dat toevoeging van polymeer heeft op de stabiliteit van oxidedispersies werd gevolgd door de verandering in de doorgelaten hoeveelheid licht te meten.

In *hoofdstuk 1* wordt aangegeven dat voor vele toepassingen van oxidedispersies beheersing van de kolloïdale stabiliteit van groot belang is. Tevens wordt uitgelegd hoe in het algemeen de stabiliteit kan worden beïnvloed door toevoeging van polymeer. Daarna worden het doel en de opzet van het onderzoek uiteengezet.

In de volgende drie hoofdstukken wordt de adsorptie van *homopolyelectrolyten* (hoofdstukken 2 en 3) en van *geladen blokcopolymeren* (hoofdstuk 4) op oxiden behandeld. De gebruikte homopolyelectrolyten hadden ofwel een constante lading (gequaterniseerd polyvinylpyridine, PVP⁺, en gequaterniseerd polydimethylaminoethyl methacrylaat, AMA⁺) ofwel een pH-afhankelijke lading (polydimethylaminoethyl methacrylaat, AMA). De blokcopolymeren bestonden uit een geladen blok (AMA) en een ongeladen wateroplosbaar blok

(dihydroxypropyl methacrylaat, HMA). We gebruikten twee typen oxidische oppervlakken: het zure siliciumdioxide (SiO_2) en het amfotere titaniumdioxide (TiO_2).

In *hoofdstuk 2* worden de adsorptiesnelheid en de geadsorbeerde hoeveelheid van de homopolyelectrolyten bestudeerd als functie van de pH en de zoutconcentratie. De initiële adsorptiesnelheid bleek gelijk te zijn aan de snelheid waarmee moleculen naar het oppervlak aangevoerd worden; de snelheidsbepalende stap is dan dus de aanvoer van materiaal door de oplossing. Boven een bepaalde bedekkingsgraad wordt de adsorptiesnelheid lager; de al geadsorbeerde moleculen vormen een barrière voor de adsorptie van anderen.

De maximaal geadsorbeerde hoeveelheid hangt af van de experimentele omstandigheden (pH, zoutconcentratie). De geadsorbeerde hoeveelheid van beide constant geladen polymeren (PVP^+ en AMA^+) stijgt monotoon bij toenemende pH, doordat het oppervlak dan steeds negatiever geladen wordt. De geadsorbeerde hoeveelheid van het zwak geladen AMA gaat echter door een maximum als de pH, en dus de polymeerlading gevarieerd wordt.

Als de hoeveelheid lading van geadsorbeerd polyelectrolyt vergeleken wordt met de kale oppervlaktelading, zoals die uit protontitraties kan worden berekend, dan blijkt dat de netto geadsorbeerde lading de netto kale oppervlaktelading veruit overtreft (overcompensatie). Een gedeelte van het teveel aan lading wordt geneutraliseerd door een aanpassing van de ladingstoestand van de zwakke ladingen op oppervlak en polymeer.

In *hoofdstuk 3* wordt de reversibiliteit van de adsorptie van PVP^+ en AMA bekeken door het systeem uit evenwicht te brengen en de relaxatie te volgen, bijvoorbeeld door na adsorptie de pH of de polymeerconcentratie in de oplossing te veranderen. Bij volledige reversibiliteit is de geadsorbeerde hoeveelheid in de gerelaxeerde toestand gelijk aan die bij directe adsorptie onder de nieuwe omstandigheden op een onbedekt oppervlak. Ook werd de reversibiliteit getest door de uitwisseling van geadsorbeerde polymeermoleculen tegen polymeermoleculen uit de oplossing te bestuderen.

Uit de experimenten bleek dat de relaxatie van de geadsorbeerde laag nooit volledig was. Daaruit kunnen we concluderen dat de bestudeerde systemen slechts gedeeltelijk reversibel zijn op de tijdschaal van het experiment (30 min.). Waarschijnlijk is de reorganisatie van de moleculen in de geadsorbeerde laag erg langzaam door de sterke (electrostatische)

band tussen oppervlak en molecuul. Een model voor de structuur van de geadsorbeerde laag van sterk geladen polymeren, waarin slechts weinig reconformatie wordt toegestaan, wordt beschreven in hoofdstuk 3. In dit model vormen de op het oppervlak geadsorbeerde moleculen elkaar afstotende geïsoleerde eilandjes met daartussen open ruimtes. Een aanwijzing voor het bestaan van de open ruimtes is de waarneming dat na adsorptie van het polyelectrolyt ook ongeladen polymeren nog hechten aan het oppervlak.

In hoofdstuk 4 worden eerst de synthese en de karakterisering van de AMA-HMA blokcopolymeren beschreven. Vervolgens wordt de adsorptie van deze blokcopolymeren bestudeerd als functie van pH, zoutconcentratie en van de samenstelling van het blokcopolymeer. Als de samenstelling van het blokcopolymeer gevarieerd wordt, dan wordt er een maximum in de geadsorbeerde hoeveelheid gevonden, net als voor het homopolyelectrolyt AMA bij variatie van de polymeerlading (zie hoofdstuk 2). De geadsorbeerde hoeveelheid laat bovendien hetzelfde verloop met pH en zoutconcentratie zien als het homopolyelectrolyt AMA; het ongeladen blok lijkt vrijwel geen effect te hebben op de adsorptie. Uit deze gegevens concluderen we dat primair het blokcopolymeer adsorbeert met het geladen blok op het oppervlak. Omdat de geladen moleculen het oppervlak niet geheel bezetten (omdat deze elkaar afstoten) zal het ongeladen blok waarschijnlijk ook op het oppervlak adsorberen (zoals ook in hoofdstuk 3 beschreven wordt). Alleen bij relatief hoge geadsorbeerde hoeveelheden is de bezetting van het oppervlak zo groot, dat het neutrale blok van het oppervlak afgeduwd wordt. Op deze manier wordt er een harige laag gevormd die mogelijk een deeltje sterisch kan stabiliseren.

In hoofdstuk 5 wordt dan ook gekeken hoe de toevoeging van geladen (blok co)polymeren de stabiliteit van een oxidedispersie kan beïnvloeden. Eenzelfde polymeer blijkt een dispersie zowel te kunnen stabiliseren als te destabiliseren, afhankelijk van de experimentele omstandigheden. Bijvoorbeeld een lage dosis van een sterk (bv. positief) geladen polymeer kan een dispersie van (negatief) geladen deeltjes destabiliseren door zogenaamde mozaïekvlokkings, waarbij onbedekte (negatief geladen) en bedekte (positief geladen) gebieden op naburige deeltjes elkaar aantrekken. Bovendien kan, als het gebruikte polymeer erg lang is, dat polymeer ook vlokkings veroorzaken door op twee deeltjes tegelijk te adsorberen (brugvorming). Wordt nu echter een grote hoeveelheid van het polymeer toegevoegd, zodat de deeltjes verzadigd worden met polymeer,

dan kunnen de beide hiervoor genoemde destabiliserende mechanismen niet meer optreden. De dispersie kan nu sterisch of electrostatisch gestabiliseerd worden, afhankelijk van de dikte van de polymeerlaag en van de netto lading.

Zoals hierboven toegelicht, hangt het effect van toevoeging van polymeren sterk af van de polymeerlading, de dosis en het molecuulgewicht van het polymeer. In hoofdstuk 5 formuleren we een aantal voorwaarden om het effect van de polymeren voor stabilisatie of vlokking te optimaliseren.

Tenslotte worden in *hoofdstuk 6* de vorming en stabiliteit van multilagen van polyelectrolyten bekeken. Doordat er bij adsorptie van een sterk geladen polyelectrolyt overcompensatie van de oppervlaktelading plaats heeft, zal een geadsorbeerde (bv. positief geladen) laag een negatief geladen polymeer aantrekken. Door nu afwisselend positief en negatief geladen polymeren toe te voegen aan een geladen oppervlak kunnen multilagen gevormd worden.

Bij de vorming van elke nieuwe laag nemen de geadsorbeerde hoeveelheid en laagdikte stapsgewijs toe en verandert de waarde van de ζ -potentiaal van sterk negatief naar sterk positief of andersom. De stabiliteit van de multilaag blijkt sterk af te hangen van de hoeveelheid lading op beide polymeren en van de zoutconcentratie, en dus van de electrostatische interactie tussen de polymeren. Als deze interactie zwak is, kan, nadat het toegevoegde polymeer geadsorbeerd is op de onderlaag, het tesamen met een of meer moleculen uit de onderlaag loslaten en als complex de oplossing ingaan. Voor paren van polymeren die een sterke interactie met elkaar hebben en dus zeer stabiele multilagen vormen, kon de ladingsstoichiometrie bestudeerd worden. Deze ladingsverhouding, die niet altijd 1 : 1 is, blijkt onafhankelijk te zijn van de pH, de zoutconcentratie van het medium en van het gebruikte substraat, maar vrij gevoelig voor de structuur van de monomere eenheid.

Curriculum vitae

Nynke Geeske Hoogeveen werd op 27 januari 1967 geboren te Oss en verhuisde binnen 6 maanden naar Stiens. Na het behalen van het diploma gymnasium β aan het Stedelijk Gymnasium te Leeuwarden in 1985, begon zij de studie Moleculaire Wetenschappen aan de Landbouwhogeschool te Wageningen. Na afstudeervakken bij de vakgroepen Moleculaire Fysica en Fysische en Kolloïdchemie en een 5 maands stage bij het Pulp and Paper Research Institute Canada (PAPRICAN) te Montreal, studeerde zij in november 1990 af. Van december 1990 tot december 1994 werkte zij als assistent in opleiding (AIO) bij de vakgroep Fysische en Kolloïdchemie van de Landbouwuniversiteit te Wageningen. Gedurende die tijd werd het in dit proefschrift beschreven onderzoek uitgevoerd.

Nawoord

No dit wie it dan. (Vrij vertaald: Hoera, het is af.)

Voor U ligt het resultaat van 4 jaar promotieonderzoek bij de vakgroep Fysische en kolloïdchemie van de Landbouwniversiteit in Wageningen. Tijdens deze periode hebben vele mensen direct of indirect bijgedragen aan de totstandkoming van dit boekje. Enkelen wil ik hier met name noemen.

Allereerst mijn copromotor Martien Cohen Stuart, die mij met zijn grenzeloze optimisme steeds weer wist te motiveren, ook toen we na twee jaar nog steeds geen geschikte set blokcopolymeren hadden. Inderdaad, Martien, alles is op zijn pootjes terechtgekomen.

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Demon, Juliet van Veen, Judith van Unen, Mariska Rietveld en Henk van Ballegoyen heb ik heel Nederland afgereisd en vele mooie potten gespeeld.

Jaap Dijt heeft door de jaren heen een steeds grotere plaats ingenomen in mijn leven, eerst als collega, toen als vaste vriend en sinds kort zelfs als mijn echtgenoot.

Iedereen bedankt!

A handwritten signature in cursive script, likely belonging to Mariska Rietveld, positioned centrally on the page.