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Adsorption of water-soluble polymers onto barium titanate and its effect on colloidal stability

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Adsorption of water-soluble polymers onto barium titanate and its effect on colloidal stability

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STELLINGEN

-1-

Blokcopolymeren met twee wateroplosbare blokken kunnen uitstekende sterische stabilisatoren zijn.

Dit proefschrift - Hoofdstuk 6.

-2-

Het overbrengen van arbeidsintensieve produktie naar landen met lage loonkosten kan gezien worden als een vorm van ontwikkelingssamenwerking.

-3-

Elke vorm van volledige subsidiëring of verzekering houdt het gevaar in van grenzeloos en zorgeloos gebruik.

-4-

De fractionering in moleculairgewicht bij adsorptie van polyelektrolyten hangt van hun moleculairgewichtsverdeling af.

Dit proefschrift - Hoofdstuk 4.

-5-

Lastenverlaging bij laagbetaalde arbeid is een eerste stap naar het legaliseren van zwart werk.

-6-

Muziek met een hoog geluidsniveau werkt eerder sfeerverlagend dan -verhogend.

-7-

Het opvoeden van kinderen heeft ook een corrigerende werking op het gedrag van de ouders.

(P.N. Kuin)

-8-

Het zoeken naar een pure vloeistof als dispersiemiddel voor keramische poeders heeft geen praktische betekenis.

S. Mizuta, M. Parish and H.K. Bowen, Ceram. Internat. 10 (1984) 43

-9-

De bewering van Esumi c.s. dat de adsorptie van polyvinylpyrrolidon op Al_2O_3 en TiO_2 de dispersiestabiliteit verbetert is niet in overeenstemming met hun experimentele resultaten.

K. Esumi, K. Takamine, M. Ono, T. Osada and S. Ichikawa,
J. Colloid Interface Sci., 161 (1993) 321

-10-

Gedetineerden zouden niet automatisch strafkorting moeten krijgen, maar zouden die moeten verdienen door sociale of maatschappelijke taken te verrichten.

-11-

De verkeersveiligheid kan verder vergroot worden als het nog in te voeren derde remlicht van auto's automatisch gaat knipperen boven een bepaalde remvertraging.

Stellingen behorende bij het proefschrift:

"Adsorption of water-soluble polymers onto barium titanate
and its effect on colloidal stability"

A.W.M. de Laat

Wageningen, 25 oktober 1995.

Aan Hanny
Aan Esther en Ingrid

Contents

CHAPTER 1

Introduction

1.1 CERAMICS

Ceramic products are common in everyday life. Ceramic vases and tableware are probably the best-known examples, having existed for many centuries. Technological applications of ceramics began to appear only in the last century. Electrical ceramics like steatite porcelains were among the first applications [1]. In the period after World War 2 many new ceramic materials were developed. At present the electronics industry uses large quantities of ceramic insulators, capacitors, piezoelectric and magnetic products [2].

The production of a ceramic product often starts with a dry powder. This dry powder must be processed into a so-called green product, which is a powder compact whose shape is dictated by the final product. Organic binders are frequently used to bind the powder particles in the green product in order to obtain sufficient strength [3]. Subsequently, the organic materials are burned out and a sintering process at high temperature is executed. The actual temperature needed for sintering depends on the type of ceramic. The driving force for sintering is the decrease in the total surface energy of the particles by reduction of the solid-gas surface area [4].

High-quality electronic ceramics require a high density and purity, and a uniform microstructure. Therefore, the products are manufactured by the so-called solid-state sintering process, without the presence of a liquid phase. In this sintering process, solid material is transported to the areas of contact between the particles by grain-boundary diffusion, solid-state diffusion and creep. As the necks between the particles grow, a significant shrinkage occurs. The smaller the particles are, the higher their surface energy is and the faster the sintering process proceeds. Due to residual pores, the final density is often slightly below the theoretical value for the crystalline material. Pores with a diameter smaller than half the particle size can usually be removed during sintering [5]. However, large pores will remain, while intermediate ones may even grow in size due to pore coalescence. Large pores have a highly negative effect on the performance of the ceramic product [6]. For example, fracture often starts at a hole, and electrical properties, such as insulation, are also strongly affected by the presence of voids. In some cases sintering is performed under high pressure in order to remove the voids and increase the density [7]. Such methods are very expensive, and therefore not very attractive for large-scale manufacturing.

The manufacturing of high-quality ceramic products requires powders with a sufficiently small size, with a controlled particle size distribution, and with a controlled, preferably spherical, shape [8]. If such particles, with a uniform and high curvature, are shaped into a homogeneously packed green body, the sintering process proceeds quickly and without local differences. Homogeneous shrinkage without defects is possible. The presence of hard agglomerates (very stable, often highly porous particle structures) is highly detrimental. Unfortunately, ceramic powders often contain such hard agglomerates, which cause large pores in the final product.

1.2 COLLOID CHEMISTRY

Colloid chemistry studies the behaviour of materials which are distributed as very small entities in another material [9]. Typically, the size of these entities is between 0.01 mm and 0.00001 mm. Such a distribution of small entities in a continuous phase is called a dispersion; the small entities are denoted as the dispersed phase, and the continuous phase is known as the dispersion medium.

Familiar examples are paints, in which the colour pigments are present as small particles in a liquid; smokes, consisting of small solid particles in air; foams, which have finely divided gas bubbles in a liquid; and milk, which has small fat globules distributed in an aqueous protein solution. Blood could also be considered as a colloidal system with the red blood cells (typical size 7 μm) acting as the colloidal particles dispersed in the plasm.

For the present purpose, we shall restrict the discussion to colloidal systems in which the dispersed phase is a solid and the continuous phase a liquid. Particles of equal composition dispersed in a liquid always attract each other due to the universal Van der Waals force [10]. If the Van der Waals force is the only force present between the particles, a dispersion initially containing only single particles will eventually contain only large clumps of particles [11].

The terminology related to this process of particles sticking together is somewhat confusing. According to the IUPAC definitions [12], the terms aggregation, flocculation and coagulation can be used interchangeably. In ceramic technology the term agglomeration is often used. As this thesis deals with the application of colloid chemistry in ceramic technology, the term agglomeration will be used in conjunction with the IUPAC list. The clumps of particles may then be called flocs, aggregates or agglomerates.

The agglomerates usually have an open, porous structure. Upon settling, such a flocculating dispersion forms a loose, open sediment. In order to prevent the flocculation it is necessary that repulsive forces act between the particles in the liquid. If these repulsive forces are strong enough, the particles remain as separate entities in the liquid. If, for large particles, sedimentation of such a stable dispersion occurs, the repulsive particles in the sediment roll over each other until the lowest available position is reached, resulting in a compact sediment.

Roughly speaking, the colloid chemist has two possibilities for introducing repulsive forces between particles. If all the particles are provided with a sufficiently high electrical charge of the same sign, they will repel each other [13]. Such electrical charging can be realised by the adsorption of ions, ionic surfactants or charged polymers from the liquid phase onto the surface of the particles. The second possibility is the adsorption of (uncharged) polymers on the particles, which may lead to so-called steric stabilisation [14].

Polymer adsorption and the mechanism of steric stabilisation will be discussed in some more detail in the next section.

1.3 POLYMERS AND THEIR EFFECTS ON COLLOIDAL STABILITY

1.3.1 Polymers

Polymers are very long molecules with a repetitive structure. Life produces a wide variety of bio-polymers with very complex compositions and structures. Familiar examples are: gelatin, starch, cellulose and DNA. Synthetic linear polymers have a simpler composition which can be visualised easily [15]. The polymer chains may consist of identical units called segments. Sometimes, a limited number of segment types with a different chemical composition is present. The simplest example of a polymer is polyethylene,

$$\cdots\cdots\cdots\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\cdots\cdots\cdots$$

or alternatively, in the segment notation:
$(\text{-}CH_2\text{-})_n$, where n is the number of segments present in the chain. Polymer chains usually do not have a uniform length. Often a wide distribution in chain lengths (i.e., in n) is found.

A polymer consisting of only one type of segment is called a *homopolymer.* If segments of different chemical composition are used, the polymer is denoted as a *copolymer.* A further classification of copolymers may be made according to the distribution of the different segments within the chain. In the simplest case with two segment types, A and B, at least three copolymer types can be distinguished. In a *random copolymer* the A and B segments are distributed randomly over the chain:

··········AABABBAAAB··········

Individual polymer molecules of a random copolymer will then differ in the sequence of the A and B segments along the polymer chain.

Block copolymers have the segments of each type clustered:

```
··········AAAAAAABBBBBB··········
```

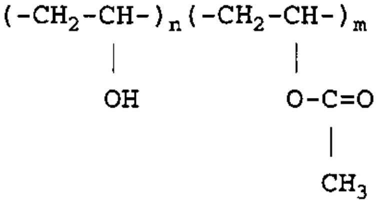
Such block copolymers may be denoted as: A_n-b-B_m.

Finally, so-called *graft copolymers* have a backbone of one segment type and side chains of the other type:

```
··········AAAAAAAAAAAAAA··········
                 B
                 B
                 B
                 B
                 B
                 B
                 B
                 B
```

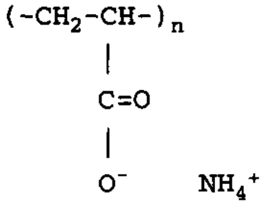
A separate class of polymers are *polyelectrolytes*, in which the segments carry an electrical charge in solution. *Strong* and *weak* polyelectrolytes can be distinguished, similar to salts. In strong polyelectrolytes the dissociation of the segments is independent of the pH. Examples are sulphate ($-SO_4^-$) and quaternised amine ($-N(CH_3)_3^+$) groups attached to the polymer chain. Weak polyelectrolytes, however, carry an electrical charge which depends on the pH. Polymers with carboxylic acid groups (-COOH) and amine groups ($-NH_2$) are familiar examples. In polymers with carboxylic acid groups, the fraction of these groups which is dissociated, increases with pH. Above a certain pH, all the groups are dissociated and the polymer behaves as a strong polyelectrolyte in that pH range.

Several polymers are used in the experiments described in this thesis. Polyvinyl alcohol (PVA) is a copolymer which consists of vinyl alcohol and vinyl acetate segments [16]:



$$(-CH_2-\underset{\displaystyle OH}{CH}-)_n(-CH_2-\underset{\displaystyle O-\underset{\displaystyle CH_3}{C}=O}{CH}-)_m$$

Although PVA is basically a random copolymer, there is a degree of blockiness, as many of the vinyl acetate segments occur in short blocks [16]. Polyacrylic acid (PAA) or its salt (PAAS), where S stands for a salt ion like Na^+ or NH_4^+, is a polyelectrolyte with a relatively simple composition [17], which for a PAAS with NH_4^+ as the counterion is:



$$\begin{array}{lll} (-CH_2- & CH & -)_n \\ & | & \\ & C{=}O & \\ & | & \\ & O^- & \quad NH_4^+ \end{array}$$

Block copolymers of PAAS and PVA and, in addition, PVA based copolymers with randomly distributed COO- groups were also used in our experiments.

In solution, the chains of an uncharged, flexible, linear polymer adopt a random coil conformation, according to the random flight statistics. For a sequence of a certain number of segments (often below 10) the correlation in orientation is lost. The size of a random coil depends not only on the chain length, but also on the chain flexibility and on the degree of swelling by the interaction between segments and solvent molecules.

The charged chains of a polyelectrolyte adopt a much more extended conformation in solution than an uncharged chain, due to the electrostatic repulsion between the segments. This repulsion also causes the chains to be locally stiffer. As the salt concentration of the solution is raised, the charges on the chain are increasingly screened and the chains gradually adopt conformations which are more comparable to those of uncharged polymers.

1.3.2 Adsorption of polymers

Adsorption of polymers from solution will occur if the adsorption energy is high enough to compensate for the loss of entropy [18,19]. An isolated, uncharged homopolymer chain adsorbed on a surface will adopt a flat conformation. This situation only occurs at extremely low solution concentrations, however. In a realistic situation many chains adsorb and compete for the available surface sites. The adsorbed layer thickness increases as loops and tails develop (Fig. 1).

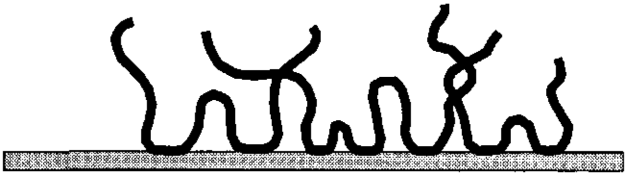


Figure 1 The conformation of adsorbed polymer chains in a crowded layer.

A sequence of polymer segments in contact with the surface is called a *train*. A *loop* is a part of the chain which protrudes into the solution, but ends on both sides in a train. *Tails* have only one end adsorbed on the surface. The extension of the tails determines the hydrodynamic adsorbed layer thickness, a parameter which is very important for steric stabilisation as will be discussed in the next section. The maximum tail length is related to the chain length of the adsorbed polymer.

In adsorption from a polydisperse polymer solution a fractionation effect is found; from dilute solutions the longest chains adsorb preferentially. This is due to the difference in the loss of translational entropy, which is smaller for the longer chains per unit of of mass.

Absorbed polymers can be displaced from the surface by other polymers or by small molecules with a higher surface affinity than the displaced polymer [20-22]. If the adsorption is done from a mixture of polymers, competition between chemically different chains for the surface sites occurs. Often, only one type adsorbs. Such studies may lead to the design of block copolymers with only one adsorbing block. A completely different adsorbed layer conformation is found with such block copolymers (Fig. 2).

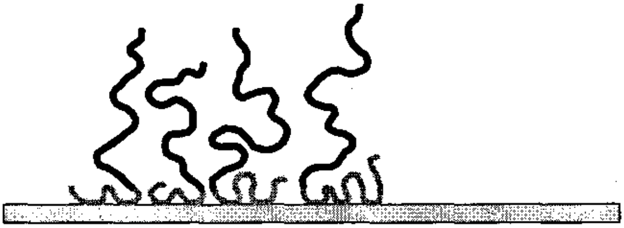


Figure 2 The conformation of adsorbed block copolymers in a crowded layer; grey, adsorbing block; black, non-adsorbing block.

The conformation of the adsorbed block is similar to the situation with homopolymers. However, the non-adsorbing block protrudes far from the surface as a tail which can be highly stretched, depending on the ratio in length between the adsorbing and non-adsorbing blocks and the surface coverage. Very thick adsorbed layers are possible.

In the adsorption of polyelectrolytes, charge effects are very important. The situation is rather complicated as the solid surface often carries an electrical charge too. In case of adsorption of a strong polyelectrolyte on an oppositely charged surface, the adsorbed amount is related to the value of the surface charge in most cases. If a non-electrostatic surface affinity is present, a slight overcompensation of the surface charge is found. Due to the repulsion between the chains, the polyelectrolyte chains adopt a rather flat conformation, unless the salt concentration is very high. Adsorption on a surface of the same charge sign is only possible if the non-electrostatic adsorption energy is high enough.

We continue the discussion on polymer adsorption by considering the kinetics of the adsorption process. Three steps are usually distinguished. The first step is the transport of the chains in solution towards the surface. In the next step, the chains must attach to the surface. Finally, the attached chains change their conformation to allow more segments to adsorb on the surface. Several stages can be distinguished in the adsorption process. In the initial stage, starting from a bare surface, the adsorbed amount increases fast. The transport of the chains towards the surface is then usually the rate-limiting step. As the surface becomes increasingly covered by chains, the rate of adsorption slows down because attachment of arriving chains to the surface becomes rate limiting. Although reconformation of the adsorbed chains starts immediately, it may take quite some time before the final conformation is reached, especially if the adsorbed amount is high.

Again, additional charge effects have to be considered with polyelectrolytes. If the surface and the polyelectrolyte have opposite charges, faster adsorption can be expected because of the electrostatic attraction. On the other hand, with equal charges, an electrostatic repulsion is present which will slow down the adsorption process. Chains already adsorbed on the surface will repel newly arriving ones.

1.3.3 Colloidal stabilisation

Several effects may occur upon mixing a polymer solution with a dispersion. Flocculation due to bridging (adsorption of a polymer chain on more particles) may occur, but this is not considered for the present purpose. Often an enhanced colloidal stability is found which is due to the loops and trains of an uncharged polymer which protrude into the solvent surrounding the particles (Fig. 1). Napper [14] distinguishes two effects if two particles with such adsorbed polymer layers approach and hit. The first contact is between the outer parts of the adsorbed layers which, in the case of a homopolymer, have a relatively low segment density. In the contact area, the local segment density increases, causing a higher free energy. The osmotic pressure difference between this contact area and the surrounding liquid will suck in liquid, causing the particles to move apart. This contribution to the repulsion is the so-called mixing or osmotic free energy.

An additional effect occurs when the particles approach to distances smaller than the thickness of the adsorbed polymer layer. Then, the adsorbed polymer layer will be compressed. This is the elastic or volume restriction free energy contribution which is due to loss of configurational entropy of the adsorbed chains.

Block copolymers often have a higher segment density in the outer region of the adsorbed layer due to crowding and stretching of the chains. In such a situation the elastic contribution already becomes significant at a low degree of overlap.

In all cases the repulsion starts at the particle separation where the first contact between the adsorbed layers occurs. Accordingly, the hydrodynamic adsorbed layer thickness is the main parameter in steric stabilisation. If the adsorbed layer is too thin, the repulsion starts at a distance where the Van der Waals attraction is already significant (Fig. 3, curve d).

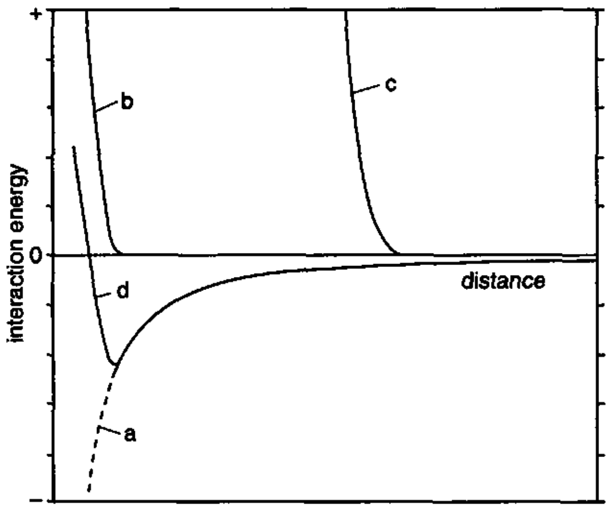


Figure 3 *The effect of the adsorbed layer thickness on the particle interaction; a, van der Waals attraction; b, steric repulsion from thin adsorbed layer; c, steric repulsion from thick adsorbed layer; d, sum of a and b.*

In such a situation there is a net attraction and the particles will flocculate into the minimum in the interaction curve. Steric stabilisation can only be achieved with thick enough adsorbed layers. As explained in section 1.3.2, thick layers can be obtained with high molecular weight homopolymers or, more easily, with block copolymers.

Once again, polyelectrolytes deviate in their effects on colloidal stability. If the salt concentration is not too high, the adsorbed layer is thin and a strong steric effect is not expected. Usually, an electrostatic effect is present because the surface charge of the particles is slightly overcompensated upon adsorption. If the adsorbed layer is thicker (e.g. at high salt concentration), combined effects may occur, which sometimes lead to the so-called electrosteric stabilisation.

1.3.4 Depletion flocculation

In many practical formulations a certain amount of non-adsorbed polymer is required. In ceramic technology, the strength of the green product is directly related to the amount of non-adsorbed polymer in the dispersion. Unfortunately, the concentration of free polymer influences the dispersion stability [14,19]. Often, flocculation occurs over a certain polymer concentration range.

Depletion flocculation is related to the concentration fluctuations which occur in polymer solutions. Therefore, these will be discussed first. At a sufficiently low polymer concentration, single coils occur in the solution. The concentration fluctuates in space; it has a finite value in a coil, but is zero between coils. This is the so-called dilute concentration regime. Polymer coils start to overlap at a concentration where the total volume of the coils equals the volume of the solution. At this concentration the semi-dilute regime is entered. The polymer concentration is still very low in the region where the coils touch and reaches a maximum inside the coils. If the concentration is increased further, the coils are forced to overlap more and more. The volume (ξ^3) in which only segments of one chain are found (often denoted as a "blob") decreases gradually. The parameter ξ is called the correlation length. Note that ξ equals the radius of the coil in the dilute regime. The concentration fluctuations decrease in magnitude and size with increasing concentration. Above a certain concentration the strong concentration fluctuations typical for the semi-dilute regime have disappeared and the so-called marginal regime is entered.

To discuss depletion flocculation, particles in a solution of non-adsorbing polymer are considered. Generally, polymer coils resist deformation because of entropic reasons. Therefore, the centre of mass of a coil cannot come closer to the surface of a particle than a distance comparable to the correlation length. A depletion layer with a lower polymer concentration exists close to the surface of a particle.

If two particles in a dilute solution have approached closer than the size of a coil, a polymer-free zone between the particles will be present. Due to the osmotic pressure difference between the overlap region and the surrounding polymer solution, the liquid between the particles is sucked into the surrounding solution. This is tantamount to an attraction between the particles. Note that this effect is the reverse of the steric stabilisation mechanism. The magnitude of the flocculation effect is related to the size of the overlap area of the depletion layers and the osmotic pressure difference. With increasing polymer concentration the osmotic pressure increases but the thickness of the depletion layer decreases. The attraction free energy goes through a maximum and the effect vanishes at higher polymer concentration [23].

If the particles have an adsorbed polymer layer, the depletion zone is different and the attraction is weaker [24].

1.4 COLLOIDAL PROCESSING IN CERAMIC TECHNOLOGY

In the discussion on ceramics (Section 1.1) it was explained that the quality of the ceramic products is often decreased by the presence of inhomogeneities such as large holes or pores in the product. As the sintering process cannot remove large inhomogeneities present in the green phase [25], the quality of the ceramic powder and the processing to shape the green body are crucial. Defects are caused by the presence of hard agglomerates in the starting powder or by inadequate processing of the powder. Intensive milling, often in a liquid, is employed to break down hard agglomerates. By dispersing the particles in a liquid, control over the particle interactions in the green processing stage is obtained [26].

Ceramicists and colloid chemists have discovered each other in the last few decades [27]. This cooperation resulted in a more controlled processing of ceramic powder dispersions [28]. With methods known in colloid chemistry, ceramic particles can be packed in a dense structure free of large voids.

Traditionally, ceramicists used dispersants for stabilising ceramic dispersions and used binders for obtaining sufficient green strength. In many cases, however, the compatibility between these additives is not sufficient, which results in some degree of flocculation or in a relatively low green strength. By designing compatible systems of dispersants and binders, or by using additives which act as both dispersant and binder, improved properties can be achieved [29].

By optimising the experimental conditions, the repulsive forces between the ceramic particles can be maximised [30]. Highly concentrated (up to 60 vol%) dispersions of ceramic particles can be made which, nevertheless, have a relatively low viscosity. Such a high particle concentration has proven to be beneficial for making a homogeneous green structure.

Initially it was thought that the use of monodisperse particles would result in a very homogeneous green structure, which can then be sintered to give high-density and high-quality ceramics. Synthetic methods to make such monodisperse particles have become available and colloidal processing methods could pack them into highly structured green bodies with a nearly crystalline packing. Unfortunately, the ever-present defects between the different domains of cubic closed-packed regions remained intact in the sintered product [31]. By using a narrow distribution of particles sizes instead and with sterically stabilised dispersions, dense green bodies with random packing can be made [32]. The overall packing density is then slightly below that corresponding to cubic close-packing, but the material is much more homogeneous and without defects. At present this packing method is believed to be the best one to produce ceramic products with a high degree of homogeneity in the structure.

Over the last decade there has been a growing interest in the use of very small, nanometer-sized, particles [33]. Low sintering temperatures and improved properties of the ceramic product can be obtained with such particles. This interest by the ceramicists will certainly stimulate colloid chemists to develop new stabilisers and processing methods suitable for these particles.

1.5 OUTLINE OF THE THESIS

$BaTiO_3$ is an important material for electronic ceramic components such as ceramic capacitors and ceramic resistors with a positive temperature coefficient (the resistance increases decades over a small temperature range) [34]. This is the reason that we chose this material for the present investigation.

$BaTiO_3$ particles can be colloidally stabilised in aqueous systems by adsorption of polyelectrolytes comparable to PAAS [35]. Probably, the particles are electrostatically stabilised. We experienced that flocculation of such dispersions occurs upon addition of PVA, a polymer which is frequently used as a binder in ceramic processing technology [36]. Steric stabilisation may offer an alternative way to prepare stable $BaTiO_3$ dispersions. Compatibility problems in the formulation can be avoided if the polymer used for steric stabilisation can also be used as a binder.

The main subject of this thesis is the investigation of the possibilities of making sterically stabilised dispersions of $BaTiO_3$ with PVA-based copolymers. Adsorption experiments with PVA and PAAS are included. The amounts adsorbed and the molecular weight fractionation upon adsorption of both PVA and PAAS are evaluated with Size Exclusion Chromatography (SEC). SEC is based on a size-dependent retention relative to the mobile phase, due to diffusion of the polymer molecules into pores of various sizes in the stationary phase. Huisman et al. [37] used SEC for the quantitative analysis of adsorption phenomena in their organic solvent-based magnetic tape formulations. Although the development of the SEC method for our water-based systems is not a principal subject of the present investigations, SEC became increasingly more important during the course of the experiments. Important results were obtained by its application. Therefore, the principles of SEC and the development of this analytical tool for and during this study are summarised in Chapter 2.

Block copolymers can be suitable for steric stabilisation if only one block adsorbs. The composition of potentially suitable block copolymers can be derived from adsorption experiments with the separate homopolymers making up the block copolymer of interest. As polyelectrolytes similar to PAAS [35] adsorb on $BaTiO_3$ and PVA is a well-known binder in ceramic technology, these polymers are chosen for the present investigations. The amounts adsorbed and the molecular weight fractionation upon adsorption onto $BaTiO_3$ are determined not only for the separate polymers, but also for adsorption from mixtures and for sequential addition of the polymers. Results are given in Chapter 3.

In the adsorption experiments with PAAS we were confronted with a very peculiar molecular weight fractionation; preferential adsorption was found for an intermediate molecular weight fraction. We decided to study this fascinating effect in more detail, even though it is not of direct relevance to the steric stabilisation of $BaTiO_3$. This is the topic of Chapters 4 and 5. To exclude the possibility of an artifact, PAAS with different molecular weights are included in the study of the fractionation upon adsorption. The effect of the salt concentration on the fractionation is also evaluated in Chapter 4. We arrived at the conclusion that the fractionation can be explained from kinetic arguments. Therefore, it was decided to study the kinetics in more detail for two of the PAAS samples. In Chapter 5 results are given for changes with time in the amount adsorbed and the molecular weight fractionation over a period of several weeks.

In Chapter 6 experiments to obtain sterically stabilised $BaTiO_3$ dispersions are described. One of the results obtained in Chapter 3 is that PVA does not adsorb from mixtures with a sufficient amount of PAAS to cover the surface of the $BaTiO_3$. Therefore, block copolymers of PAAS and PVA are potentially suitable steric stabilisers for $BaTiO_3$. In addition to such block copolymers, random copolymers of PVA with acrylic acid are also included in the evaluation of the colloidal stability. All the block copolymers proved to be effective stabilisers, whereas only some of the random copolymers are suitable. The stabilising mechanism of both block and random copolymers is evaluated. Flocculation effects, occurring with an excess of polymer added as a binder, were also investigated.

The reason for the differences in behaviour of the random copolymers are studied in Chapter 7. One of the block copolymers is included for comparison. The chemical compositions are determined by IR spectroscopy. SEC is used to compare the molecular weights of the polymers and to compare the adsorption behaviour on $BaTiO_3$. The most probable reason for the ineffectiveness of the random copolymers studied is their low molecular weight.

In thesis it is shown that the design of powerful steric stabilisers can be based successfully on adsorption experiments.

REFERENCES

[1] F.H. Norton, Cycles in Ceramic History, in: Ceramic Processing Before Firing, G.Y. Onoda Jr. and L.L. Hench (Eds), Wiley, New York, 1978.
[2] Ceramic Materials for Electronics, R.C. Buchanan (Ed.), Dekker, New York, 1986.
[3] R. Moreno, Am. Ceram. Soc. Bull., 71 (1992) 1521-1531.
[4] W.D. Kingery, H.K. Bowen and D.R. Uhlmann, Introduction to Ceramics, Wiley, New York, 2nd Ed., 1976.
[5] J. Zheng and J.S. Reed, Am. Ceram. Soc. Bull., 71 (1992) 1410-1416.
[6] F.F. Lange, Influence of Agglomerates on Sintered Ceramics, in: Microstructure and Properties of Ceramic Materials, T.S. Yen and J.A. Pask (Eds), North-Holland Physics Publishing, Amsterdam, 1984.
[7] P.J. James, Application of Hot Isostatic Pressing to the Removal of Internal Defects, in: Isostatic Pressing Technology, P.J. James (Ed.), Applied Science Publishers, London, 1983.
[8] K. Kendall, Powder Techn., 58 (1989) 151-161.
[9] P.C. Hiemenz, Principles of Colloid and Surface Chemistry, Dekker, New York, 1977.
[10] J. Mahanty and B.W. Ninham, Dispersion Forces, Academic Press, London, 1976.
[11] Th.F. Tadros, Colloids Surfaces, 18 (1986) 137-173.
[12] IUPAC, Definitions, Terminology and Symbols in Colloid and Surface Chemistry, Pure and Applied Chem., 31 (1972) 579-638.
[13] J.Th.G. Overbeek, Adv. Coll. Int. Sci., 16 (1982) 17-30.
[14] D.H. Napper, Polymeric Stabilization of Colloidal Dispersions, Academic Press, London, 1983.

[15] F.A. Bovey and F.H. Winslow, An introduction to Polymer Science, Academic Press, London, 1979.
[16] Polyvinyl alcohol - Properties and Applications, C.A. Finch (Ed.), Wiley, New York, 1973.
[17] H.L. Greenwald and L.S. Luskin, Poly(acrylic acid) and its homologs, in: Handbook of water-soluble gums and resins, R.L. Davidson (Ed.), McGraw-Hill, London, 1980.
[18] G.J. Fleer, J.M.H.M. Scheutjens and M.A. Cohen Stuart, Colloids Surfaces, 31 (1988) 1-29.
[19] G.J. Fleer, M.A. Cohen Stuart, J.M.H.M. Scheutjens, T. Cosgrove and B. Vincent, Polymers at interfaces, Chapman & Hall, London, 1993.
[20] M.A. Cohen Stuart, G.J. Fleer and J.M.H.M. Scheutjens, J. Colloid Interface Sci., 97 (1984) 515.
[21] M.A. Cohen Stuart, G.J. Fleer and J.M.H.M. Scheutjens, J. Colloid Interface Sci., 97 (1984) 526.
[22] M. Kawaguchi, Adv. Colloid Interface Sci., 32 (1990) 1-41.
[23] B. Vincent, Colloids Surfaces, 50 (1990) 241-249.
[24] A. Milling, B. Vincent, S. Emmett and A. Jones, Colloids Surfaces, 57 (1991) 185-195.
[25] W.D. Kingery, Firing - The Proof Test for Ceramic Processing, in: Ceramic Processing before firing, G.Y. Onoda Jr. and L.L. Hench (Eds), Wiley, New York, 1978.
[26] B.V. Velamakanni, J.C. Chang, F.F. Lange and D.S. Pearson, Langmuir, 6 (1990) 1323-1325.
[27] Emergent Process Methods for High-Technology Ceramics, R.F. Davis (Ed.), Plenum, New York, 1984.
[28] Surface and Colloid Chemistry in Advanced Ceramic Processing, Surfactant Science Series Vol. 51, R.J. Pugh and L. Bergström (Eds), Dekker, New York, 1994.
[29] J. Rives and B.I. Lee, Ceramic Industry, May (1990) 62.
[30] J. Cesarano III and I.A. Aksay, J. Am. Ceram. Soc., 71 (1988) 1062-1067.
[31] S.J. Milner, M. Patel and E. Dickinson, J. Eur. Ceram. Soc., 11 (1993) 1-7.
[32] M. Persson, Surface and Colloid Chemistry in Ceramic Casting Operations, in: Surface and Colloid Chemistry in Advanced Ceramic Processing, Surfactant Science Series Vol. 51, R.J. Pugh and L. Bergström (Eds), Dekker, New York, 1994.
[33] A.J. Burggraaf, G.S.A.M. Theunissen and A.J.A. Winnubst, Synthesis and Properties of Nanophase Ceramics and Composites, in: Euroceramics, Vol 1, Processing of Ceramics, G. de With, R.A. Terpstra and R. Metselaar (Eds), Elsevier, London, 1989.
[34] A.J. Moulson and J.M. Herbert, Electroceramics: Materials-Properties-Applications, Chapman and Hall, London, 1990.
[35] H. Itoh, M.V. Parish and H.K. Bowen, Mater. Sci. Eng., 96 (1987) 303-310.
[36] C.W. Nies and G.L. Messing, J. Am. Ceram. Soc., 67 (1984) 301-304.
[37] H.F. Huisman, H.J.M. Pigmans, A.J.P. Roegies and W.J.J.M. Sprangers, Progr. Org. Coatings, 13 (1986) 377-420.

CHAPTER 2

Size exclusion chromatography

2.1 INTRODUCTION

In the research described in this thesis, Size Exclusion Chromatography (SEC) was used extensively for evaluating polymer adsorption phenomena. In this chapter an overview will be given of the principles of SEC, and of its possibilities and limitations. The modifications introduced in our method and equipment in the course of the investigation will be mentioned.

Fractionation of polymers upon adsorption was studied qualitatively with SEC for both uncharged polymers [1] and polyelectrolytes [2]. The amount of adsorbed polymer can also be measured with SEC, as demonstrated by Huisman et al. [3] in their study of organic solvent-based lacquers for magnetic recording media.

2.2 PRINCIPLE OF OPERATION

In any chromatographic technique, the separation of a mixture of components is achieved by differences in the partitioning between a mobile and a stagnant (stationary) phase. Several properties can be used to realise the separation. In SEC the differences in the size of the solutes are used [4].

The mobile phase is pumped through a packed column of porous particles. The pore size distribution of the particles is chosen in relation to the size distribution of the dissolved molecules to be separated. The scanning electron micrograph in Fig. 1 shows the nature of the PW3000 material used in our experiments. Further details will be given in Chapter 2.3.

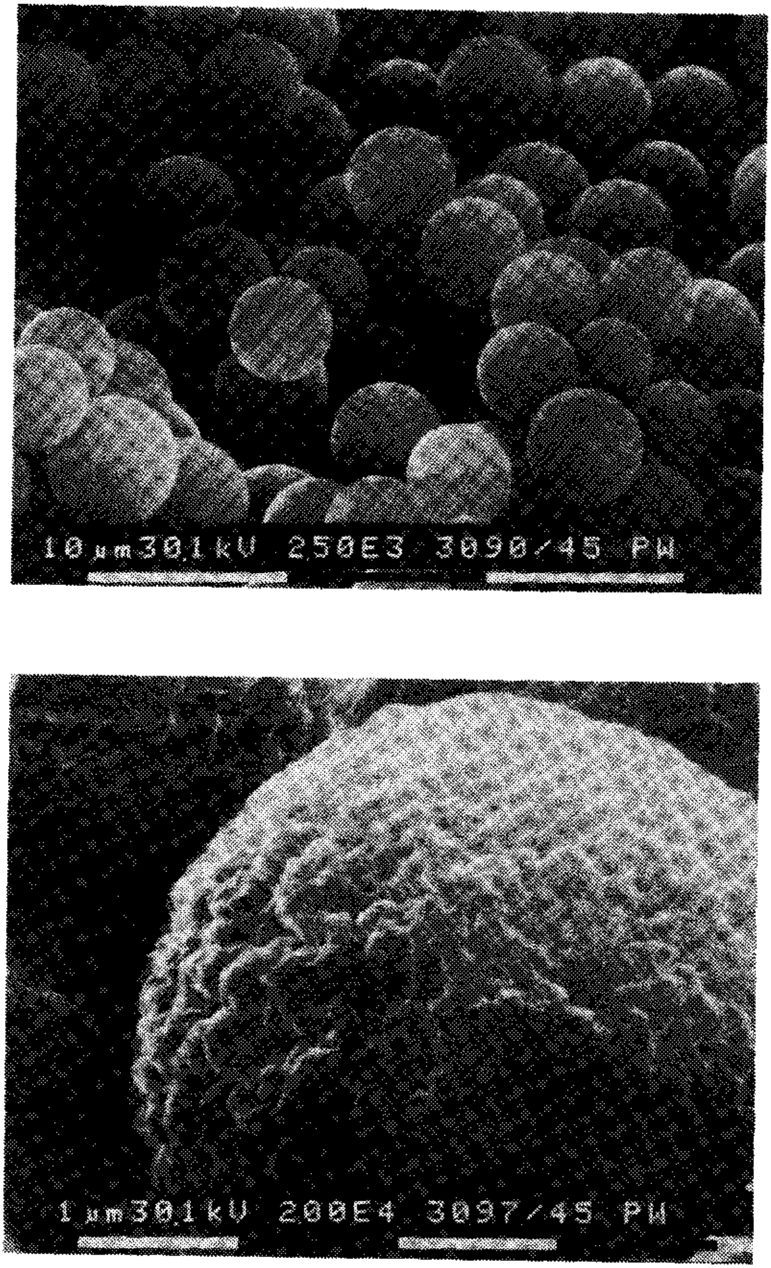


Figure 2 *Scanning electron micrographs of PW3000 material at two magnifications; top, particles; bottom, porous surface structure.*

The sample is injected as a narrow band in the mobile phase which transports the mixture through the column.

A molecule of a certain size can diffuse into the fraction of pores which are wide enough. The larger the molecule is, the less pores can be penetrated. If a molecule diffuses into a pore, it is not transported in the length direction of the column and, accordingly delayed with respect to the mobile phase. Large molecules, which can enter only a small fraction of the total pore volume, are eluted first. The smaller molecules leave the column at a higher elution volume. Molecules that cannot enter any pores are eluted at the so-called 'total exclusion limit', whereas small ones which can enter all the pores are eluted at the 'total permeation limit'.

The quality of the separation for a certain combination of column material and sample depends on parameters related to diffusion and transport such as the column length, the solvent velocity and the temperature. The sample injection volume and concentration also have an influence. At large injection volumes, the sample is spread out over a certain length of the column, which results in peak broadening. At a high concentration, the diffusion of the solutes into the pores is affected. Pores large enough in size can be unavailable for a certain solute molecule because they are already occupied by another one. These experimental conditions need to be optimised carefully for each sample.

2.3 COLUMN MATERIALS AND MOBILE PHASES

Originally, 'soft' polysaccharide gels were used for protein separation in biochemical investigations [5]. Columns with these gels had a low efficiency and were not very suitable for Molecular Weight Distribution (MWD) evaluations. Moreover, these gels were very sensitive to the applied liquid pressure. In the mid-sixties, semi-rigid porous styrene-divinylbenzene resins were introduced which appeared to be very suitable for solvent-based SEC separations. Around 1980, high-efficiency columns for aqueous SEC were commercialised. At present a variety of column materials is available such as crosslinked synthetic hydrophilic polymer gels and porous silica materials with a choice of chemical surface modifications [6].

The porous particles in the columns must be packed as densely as possible to reduce the interstitial volume. The best columns which are commercially available have an interstitial volume fraction of 0.30 to 0.35. High-efficiency columns contain small particles, typically 5 - 10 μm in diameter. Often, columns with particles of different pore size distributions are combined to obtain a suitable size range for the analysis.

Ideally, the separation is purely a geometrical effect. All other effects, such as adsorption, must be avoided. Therefore, the column material and the mobile phase must be carefully selected with respect to the chemical composition of the polymer to be analysed. Due to this subtle balance, porous silica-based columns with a variety of surface modifications have been developed and commercialised. The proper selection for a given type of polymer may take a lot of effort.

Compared with non-aqueous solvents, charge effects are much more pronounced in an aqueous environment and such charge effects may interfere in aqueous SEC [5,7]. Both the particles in the column packing and the dissolved polymer may carry an electrical charge. Crosslinked polymer gels may show a salt-concentration dependent swelling, resulting in variations in pore sizes. Polyelectrolytes with a charge opposite to the column packing will adsorb on the column. Clearly, this must be avoided. In the case of charges of the same sign, the electrostatic repulsion between the polyelectrolyte and the column particles may prevent the diffusion of the polyelectrolyte into the pores, which would inhibit separation. Therefore, salt is added to the mobile phase to screen the charges. In many cases a buffer solution is used to fix the pH. This buffer serves to avoid changes in the charge on weak polyelectrolytes, and possibly also on the column packing, upon a drift in pH. Too high salt concentrations, however, may stimulate adsorption. A suitable balance between screening and adsorption must be found. Sometimes organic modifiers such as acrylonitrile, methanol or dimethylsulfoxide are added to prevent adsorption.

The porous particles of the PW type synthetic polymer gel columns (Toyo Soda Manufacturing Co, Tokyo, Japan) have only a low number of charged surface groups [8], which is beneficial for polyelectrolyte separations. Separations with uncharged polymers at different salt concentrations proved that the porosity of the PW material is independent of the salt concentration [9]. These columns proved to be suitable for the analysis of both polyvinyl alcohol (PVA) and polyacrylic acid salts (PAAS) (see Chapter 3). No adsorption of PVA or PAAS was found under our experimental conditions. In the experiments described in chapter 7 we used 0.05 M $NaNO_3$ as the eluent for the PVA samples. In all the other experiments a 0.06 M potassium phosphate buffer with a pH of 6.8 was employed.

2.4 MOLECULAR WEIGHT DETERMINATION

With SEC, the polydisperse polymer solution is separated according to the size of the molecules. In order to obtain the molecular weight M of the fraction eluted at a certain moment (or volume), several methods are available. Calibration of the columns under the chosen experimental conditions can be done with a set of monodisperse polymer standards. A linear relation between log(M) and the elution volume is obtained in the working range of the column. The example given in Fig. 2 is the calibration of a set of PW columns with polyethylene oxide standards as determined in our experiments. The retention time (at constant flow rate) is used instead of the elution volume.

Deviations from linearity are found at the extremes of the separation range. At the total exclusion limit, the curve turns upwards almost vertically because all molecules above the corresponding size collect there. A more gradual deviation is found at the total permeation limit. By this calibration method, an absolute molecular weight value for the sample fractions is obtained only if the calibration standard has the same chemical composition as the sample to be analysed.

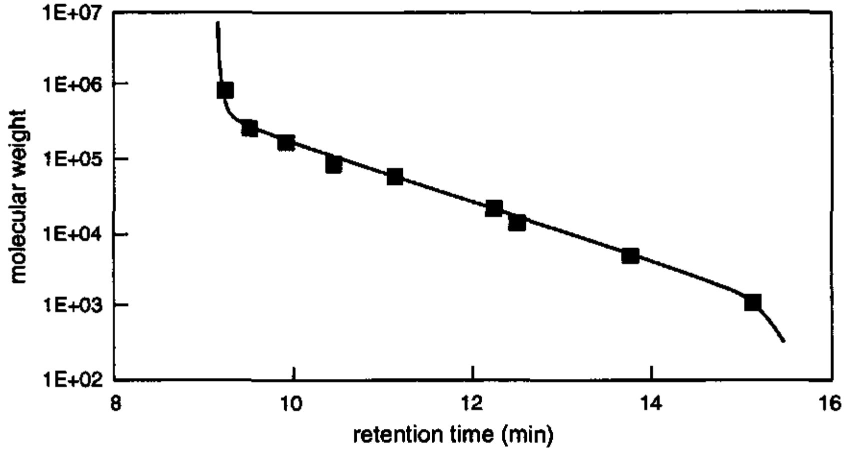


Figure 2 *Calibration of a set of two PW columns (PW3000 + PW4000) with polyethylene oxide standards.*

The swelling of polymer coils in solution depends on their interaction with the solvent molecules. Accordingly, polymers with a different chemical composition but with the same molecular weight, may have a different size in a certain solvent. Therefore, if the standard used for calibration differs in chemical composition from the sample studied, this calibration results only in a relative value.

Absolute calibrations are possible if the size of the polymer molecules with different chemical compositions is taken into account. Benoit et al. [10] used the intrinsic viscosities [η] of polymer solutions to make a 'universal calibration curve'. The intrinsic viscosity is defined as:

$$[\eta]=\lim_{c\to 0}(\eta/\eta_0-1)/c$$

where η is the viscosity of the polymer solution, η_0 that of the solvent and c is the polymer concentration.

According to the Einstein viscosity law:

$$[\eta] = \alpha * N * V_h / M$$

where α is a shape factor (α=2.5 for spheres), N is Avogadro's number and V_h is the hydrodynamic volume of the polymer chain in solution. Hence, the product of $[\eta]$ and M is related to the hydrodynamic volume which, as discussed above, is the separation parameter for SEC. A universal calibration curve for all polymer - mobile phase combinations is then obtained by plotting $\log([\eta]*M)$ against the elution volume. The relation between M and $[\eta]$ of a polymer in solution is given by the Mark-Houwink relation $[\eta] = K*M^a$. If the constants K and a are known, the $\log([\eta]*M)$ axis can be directly converted to $\log(K*M^{a+1})$ for a certain polymer - mobile phase combination, from which M values for each fraction are easily calculated.

Alternatively, the intrinsic viscosity $[\eta]$ can be measured for each fraction eluted with an on-line differential viscometer detector in combination with a refractive index detector [11]. The differential viscometer detector determines the value of (η/η_0), and the polymer concentration is obtained from the refractive index detector. The quotient of these values approaches $[\eta]$ at the low polymer concentrations used in SEC.

Absolute molecular weights can also be determined with detectors based on light scattering, such as low angle laser light scattering (LALLS) [12] and multiangle laser light scattering (MALLS) [13]. With these methods the molecular weights are measured directly and calibration of the column is not necessary. In addition, the multiangle analysis with MALLS provides conformational information.

In this thesis, relative calibration with polyethylene oxide standards for both PVA and PAAS was used. A refractive index and a ultraviolet detector were used to monitor the amount of polymer eluted.

2.5 QUANTITATIVE MEASUREMENTS

To obtain quantitative information from SEC, care must be taken to keep the experimental conditions, such as temperature and mobile phase velocity, constant. The detector sensitivity and linearity in the concentration range studied must be determined. The shape of the peak should be independent of the amount of polymer injected. According to our experience, an automatic injector is a prerequisite to obtain a sufficiently constant and accurate injection volume of the sample. Two different approaches for the injected amount can be employed. By estimating the concentration in the sample and by adjusting the injection volume, the load on the column can be kept constant. This procedure is used for the experiments described in Chapter 7. At low concentrations the injection volume becomes too high, which causes a shift of the chromatogram over the retention volume axes leading to erroneous molecular weights (Chapter 7).

Alternatively, the injection volume can be kept constant so that the peak area becomes variable. This set-up can be employed if the peak shape is independent of the concentration in the sample. The latter, more practical method, is used in the experiments presented in the other chapters.

For all the measurements, the samples were injected in triplicate. After each injection the column was carefully reconditioned by eluent flow. Between samples, a reference solution was injected to check the system and the detector sensitivity. A reproducibility of 3% could be obtained in this way.

Mixtures of two different polymers can also be analysed, even if incomplete separation occurs. The use of two detectors with different sensitivities for the polymers in the mixture allows the calculation of the separate chromatograms [14,15]. At a certain elution volume the signal of each detector is the sum of the contributions of both polymers, resulting in two equations with the two concentrations as the unknowns. Applying the method on incremental elution volumes (slicing) reveals the chromatograms of each of the polymers. Of course, the polymers in the mixture should be compatible. As our old software system did not allow slicing of the chromatograms, we could only obtain total amounts of each polymer by analysing the total peak area (chapter 3). An accuracy of about 4 % was obtained.

The experimental setup for analysis (including mixtures) is displayed in Fig. 3.

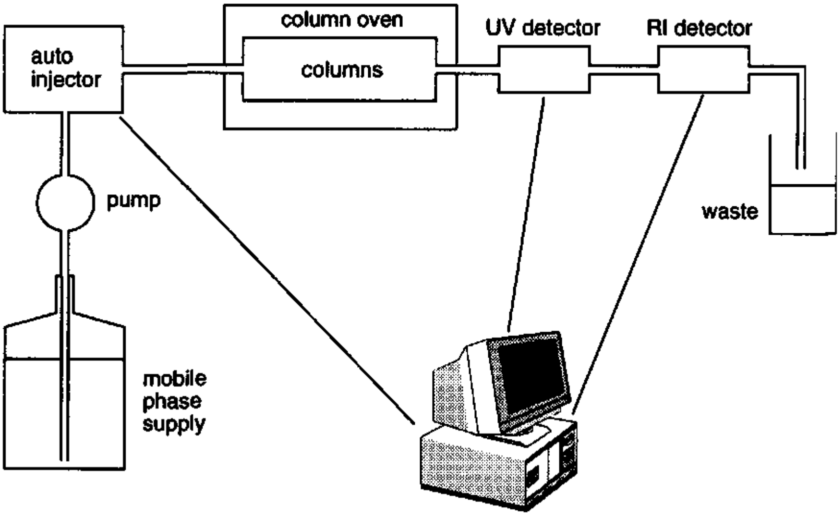


Figure 3 *Experimental SEC setup.*

In the experiments described in chapters 3 and 7 the SEC system was controlled by Nelson (Perkin Elmer, USA) software running on a HP 8916 computer. Detection was done with an Optilab 5902 interferometric refractive index (RI) detector (Tecator, Sweden) and a PU4020 ultraviolet (UV) detector (Pye Unicam, Cambridge UK) in series. The UV detection was carried out at a wavelength of 200 nm. Columns were kept at ambient temperature in a thermostatted room.

For the later experiments with PAAS (Chapters 4 and 5) we modernised the computer system and software and installed new detectors. Detection was now performed with a Waters 410 Refractive Index detector (Millipore Corp, Waters Chromatography Div., Milford, MA, USA) placed in series with a Waters 484 Ultraviolet detector set at 200 nm. System control and data analysis were done with Waters Baseline and Waters GPC software. The

Wisp 712B Autoinjector (Waters) was used throughout. The columns were at 30 °C in a column oven. With the new setup an improved temperature stability and data analysis were achieved.

The molecular weight fractionation upon adsorption was evaluated by comparing the chromatograms of the solution before and after adsorption. The adsorbed amounts were calculated from the difference in the total peak areas.

2.6 CONCLUSIONS

A reliable SEC analysis is possible, but several conditions must be fulfilled. In some cases the selection of a suitable column and mobile phase composition for the polymer to be analysed requires a considerable effort. Adsorption of the polymer on the column particles is often a serious problem. During analysis a careful control of the experimental conditions is needed to obtain reliable data.

If these requirements are fulfilled a powerful tool is obtained for the analysis of polymer adsorption experiments. Both the adsorbed amounts and the molecular weight fractionation can be evaluated. Moreover, the MWDs of the separate compounds in a binary polymer mixture can be calculated from the readings of two different detectors, even if the chromatograms overlap.

REFERENCES

[1] R.E. Felter, E.S. Moyer and L.N. Ray, J. Pol. Sci., part B, Polymer Letters, 7 (1969) 529-533.
[2] R. Ramachandran and P. Somasundaran, J. Colloid Interface Sci., 120 (1987) 184-188.
[3] H.F. Huisman, H.J.M. Pigmans, A.J.P. Roegies and W.J.J.M. Sprangers, Progr. Org. Coat., 13 (1986) 377-420.
[4] B.G. Belenkii and L.Z. Vilenchik, Modern Liquid Chromatography of Macromolecules, J. Chromatogr. Library, Vol. 25, Elsevier, Amsterdam, 1983.
[5] P. Dubin, Aqueous Size Exclusion Chromatography, J. Chromatogr. Library, Vol. 40, Elsevier, Amsterdam, 1988.

[6] K. Makino and H. Hatano, Rigid polymer gels for SEC and their application to biopolymers, in P.L. Dubin (Ed.), Aqueous Size Exclusion Chromatography, J. Chromatogr. Library, Vol. 40, Elsevier, Amsterdam, 1988.
[7] M. Rinaudo, J. Desbrières and C. Rochas, J. Liq. Chromatogr., 4 (1981) 1297-1309.
[8] M. Potschka, J. Chromatogr., 441 (1988) 239-260.
[9] M. Potschka, Macromolec., 24 (1991) 5023-5039.
[10] H. Benoit, Z. Grubisic, P. Rempp, D. Decker and J.G. Zilliox, J. Chim. Phys. Physicochim. Biol., 63 (1966) 1507.
[11] D.J. Nagy, J. Liq. Chromatogr., 13 (1990) 677-691.
[12] K. Konishi, Application of SEC/LALLS to biopolymer assemblies, in: P.L. Dubin (Ed.), Aqueous Size Exclusion Chromatography, J. Chromatogr. Library, Vol. 40, Elsevier, Amsterdam, 1988.
[13] P.J. Wyatt, J. Liq. Chromatogr., 14 (1991) 2351-2372.
[14] B. Trathnigg, J. Liq. Chromatogr., 13 (1990) 1731-1743.
[15] G.J. Verhoeckx and W.J.L. van Tilburg, private communication.

CHAPTER 3

Competitive and displacement adsorption of polyvinyl alcohol and the NH_4-salt of a polyacrylic acid on $BaTiO_3$*

Abstract

Adsorption isotherms for polyvinyl alcohol (PVA) and the ammonium salt of a polyacrylic acid (NH_4-PAA) on $BaTiO_3$ have been measured with separate solutions, with mixtures and after sequential addition. Size-exclusion chromatography was used to measure the amounts adsorbed from the depleted supernatants. The amounts adsorbed from separate solutions reach plateaux at 0.19 mg m^{-2} for PVA and 0.40 mg m^{-2} for the NH_4-PAA. Both polymers adsorb from mixtures as long as the amount of the NH_4-PAA is not enough to reach the plateau adsorption. Above this level no adsorption of PVA is found. If PVA is adsorbed first and the NH_4-PAA added afterwards, both polymers are adsorbed at amounts almost equal to the separate plateau values. After long contact times the adsorbed amount of PVA decreases slightly to 0.17 mg m^{-2}.

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*A.W.M. de Laat and G.L.T. van den Heuvel, Colloids Surfaces A: Physicochem. Eng. Aspects, 70 (1993) 179-187.

3.1 INTRODUCTION

Aqueous suspensions with $BaTiO_3$ particles are used in ceramic technology. The formulation studied in this report contains, in addition to the particles, the ammonium salt of a polyacrylic acid (NH_4-PAA) as polymeric dispersant and polyvinyl alcohol (PVA) as binder. Knowledge of the adsorption behaviour assists optimisation of the formulation.

A theoretical model to describe polymer adsorption has been developed by Scheutjens and Fleer [1,2]. Extensions and results of the Scheutjens and Fleer model have been reviewed by Fleer [3]. The adsorption of polydisperse polymers has been modelled by Cohen Stuart et al. [4], Roe [5] and Scheutjens and Fleer [6]. Theory predicts high affinity adsorption isotherms for monodisperse polymers and more rounded curves for polydisperse polymers. The high molecular weight fraction of the polymer is expected to adsorb preferentially unless the solution concentration is very high.

The adsorption of PVA on latexes [7-9], AgI [10-11] and inorganic oxides [9] has been studied. The acetate groups control the adsorption on the hydrophobic latex surface [8] and the adsorbed amount at the plateau is in the range of a few milligrams per square metres. A similar adsorbed amount has been found on AgI [10]. The hydrodynamic layer thickness of the adsorbed PVA layer on latex is much higher than on silica [9]. This may be due to different adsorption mechanisms on hydrophobic and hydrophilic surfaces.

Böhmer et al. [12] extended the Scheutjens and Fleer theory to polyelectrolyte adsorption. The theoretical predictions from this model have been confirmed with experiments by Blaakmeer et al. [13]. The adsorbed amount and conformation strongly depend on the charge on the polymer chain and on the surface. Highly charged polyelectrolytes adsorb on oppositely charged surfaces in a flat conformation and with a low amount adsorbed.

Polyacrylic acid derivatives are widely used as dispersants in ceramic technology [14]. Adsorption studies on inorganic oxides [15,16] reveal low and surface-charge-dependent amounts adsorbed, in agreement with theoretical predictions.

To our knowledge no adsorption studies of PVA and polyacrylic acid derivatives on $BaTiO_3$ have been reported.

Adsorbed polymers can be desorbed by suitable displacers, either small molecules or other polymers. Kawaguchi [17] has recently reviewed the subject of competitive adsorption and displacement. Cohen Stuart et al. [18] and van der Beek [19] have studied displacement with low molecular weight displacers for a number of adsorbed polymers on different surfaces. Desorption of polymers with small molecules (solvents) usually is fast [19]. Displacement of adsorbed polymers by other polymers can be fast also [17], but in some cases it may take weeks [19]. With polyelectrolytes thermodynamic equilibrium is often not attained and the final amounts adsorbed are determined kinetically [17]. Displacement of adsorbed polymers by small molecules has been described theoretically by Cohen Stuart et al. [20]. Displacement by polymers of a different chemical composition has not yet been covered theoretically.

In the present study adsorption isotherms on $BaTiO_3$ in water have been measured for PVA and NH_4-PAA separately, for the case of sequential addition and from mixtures of both polymers. A method based on size-exclusion chromatography (SEC) has been developed to measure the adsorbed amounts and the molecular weight fractionation upon adsorption.

3.2 EXPERIMENTAL

3.2.1 Materials

$BaTiO_3$ powder used in this study has a number average particle size of 1.1 μm with a standard deviation of 0.55 μm as measured by the CIS-1 particle sizer (Galai Production Ltd, Migdal Ha-Emek, Israel). The specific surface area is 3 $m^2\ g^{-1}$ according to the BET method. The isoelectric point (IEP) is located at pH=9.9, determined by measuring the dynamic electrokinetic mobility as a function of the pH with the ESA-8050 system (Matec Instruments, Hopkinton, MA, USA).

NH_4-PAA is used as an aqueous solution with a concentration of 43.8 wt%. The weight average molecular weight M_w, the number average molecular weight M_n and the polydispersity index M_w/M_n have been determined by SEC and are, respectively, 13000, 8550 and 1.5.

PVA contains approximately 12 mol% of acetate groups. SEC results indicate a M_w of 126000 and M_w/M_n= 2.3. Master solutions of about 6 wt% have been prepared by stirring for 4 hours at 95 °C.

All materials have been used as received.

3.2.2 Adsorption experiments

Six grams of $BaTiO_3$ are weighed into a 25 ml centrifuge tube, then 10.00 ml of a polymer solution with a variable concentration are added. A few glass balls are added to assist homogeneous mixing. The tubes are capped and tumbled head over head for 24 h at room temperature. In experiments with sequential polymer addition the first polymer is added in a volume of 8.00 ml and the second one in a volume of 2.00 ml, 15 hours later. In one experiment the tumbling time was varied. The area to volume ratio which influences the shape of the adsorption isotherm [4] is kept constant in all experiments. The pH of the suspensions is between 8.2 and 8.8 which is well below the IEP of $BaTiO_3$.

The particles are removed by centrifugation in a Heraeus Labofuge GL (Heraeus-Christ GmbH, Osterode am Harz, Germany) at 4000 rev min^{-1} for 20 min. The amount adsorbed is determined by the amount depleted from the liquid as measured by SEC.

3.2.3 Size exclusion chromatography

In all experiments four columns have been used in series: TSK guard PW, TSK 4000PWXL and two TSK 3000PWXL (Toyo Soda Manufacturing Co, Tokyo, Japan). The length and width of the PWXL columns are 300 and 7.5 mm respectively. The eluent was 0.06 M potassium phosphate buffer (pH=6.9) with a flow rate of 1 ml min^{-1}. Samples with a volume of 100 μl are injected with the Wisp 712B Autoinjector (Waters-Millipore Corp, MA, USA). The system is controlled by Nelson (Perkin Elmer, USA) software running on an HP 8916 computer.

Detection was done with an Optilab 5902 interferometric refractive index (RI) detector (Tecator, Sweden) and a PU4020 ultraviolet (UV) detector (Pye Unicam, Cambridge, UK) set at 200 nm, mounted in series. Relative molecular weights have been calculated from the chromatograms after calibration with polyethylene oxide standards (Polymer Laboratories, Shrewsbury, UK) using the Nelson SEC software. The polymer concentrations are determined from three separate injections.

3.3 RESULTS AND DISCUSSION

3.3.1 Size-exclusion chromatography

With SEC not only can the amount adsorbed be measured but also the molecular weight fractionation can be monitored. In our laboratory the method used by Huisman et al. [21] has been extended to mixtures of polymers in aqueous solution. The selection of TSK columns for aqueous SEC with PVA was based on the work reported by Nagy [22] and library information [23,24]. No adsorption of the polymers on these columns has been detected (Figs 1 and 2).

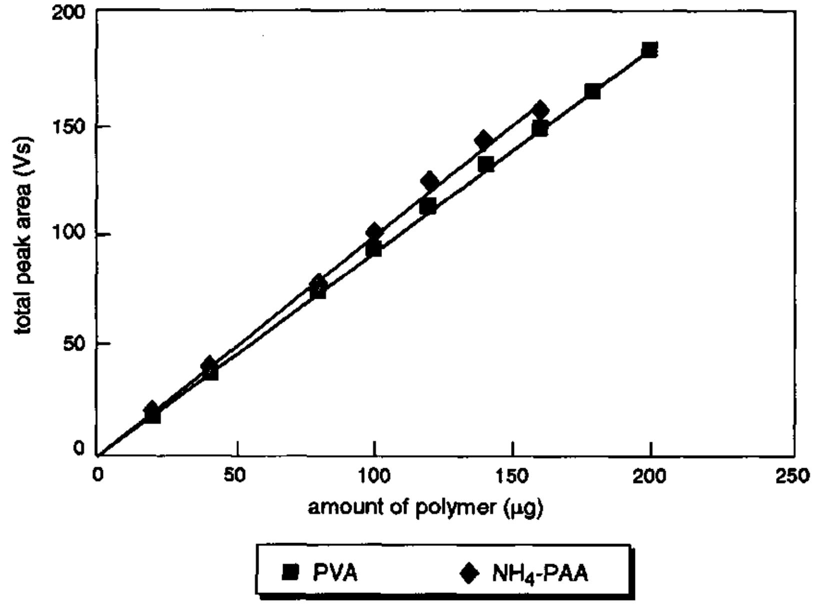

Figure 1 *Total peak area from the RI detector with increasing amount of polymer.*

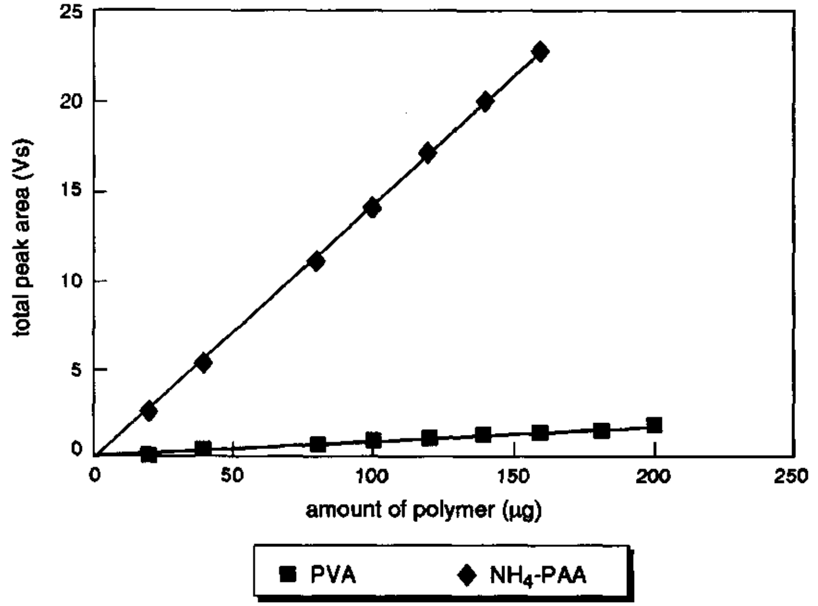

Figure 2 *Total peak area from the UV detector with increasing amount of polymer.*

In a calibration run samples of the separate polymers at increasing concentration have been injected. The total peak areas (TPA) have been measured and plotted against the amount of polymer injected which is equal to the concentration C multiplied by the injection volume I. Both the RI and UV detector responses are linear over the concentration range up to 2000 ppm as can be seen in Figs 1 and 2. The slope of these lines gives the detector sensitivities S for both polymers according to: TPA = S*C*I. The resulting sensitivities are reported in Table 1.

Table 1: Sensitivities for NH_4-PAA and PVA in the RI and UV detectors.

Sensitivity	Value (Vs μg^{-1})
$S_{pva\text{-}ri}$	0.91661
$S_{pva\text{-}uv}$	0.00757
$S_{paa\text{-}ri}$	0.98724
$S_{paa\text{-}uv}$	0.14050

The polymer concentrations after adsorption are calculated with the above equation. The detector sensitivities are checked in each series of experiments.

The amount adsorbed is calculated from the difference in concentration between the initial solution C_0 and after adsorption C_e. C_e has been calculated directly from the RI peak area for experiments with only one polymer.

Because the chromatograms of both polymers partly overlap, as can be seen in Figs 3 and 4, the analysis of the results of polymer mixtures requires both detectors:

$$\begin{aligned} TPA_{ri} &= S_{pva\text{-}ri}*I*C_{pva} + S_{paa\text{-}ri}*I*C_{paa} \\ TPA_{uv} &= S_{pva\text{-}uv}*I*C_{pva} + S_{paa\text{-}uv}*I*C_{paa} \end{aligned}$$

The concentration of each polymer follows after simple algebraic manipulation from these equations.

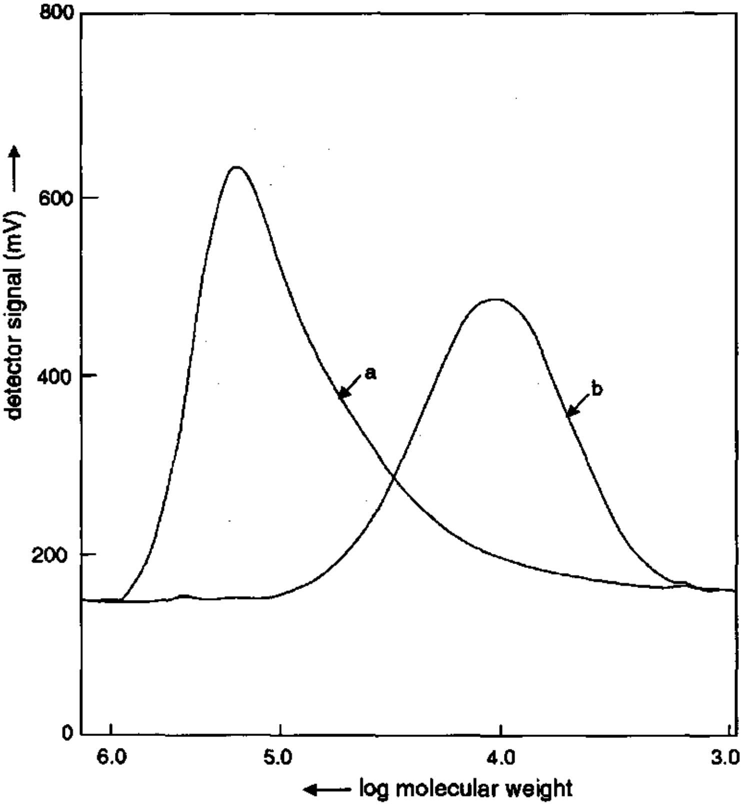

Figure 3 *Chromatogram with RI detection: curve a, 1000 ppm PVA; curve b, 600 ppm* NH_4*-PAA.*

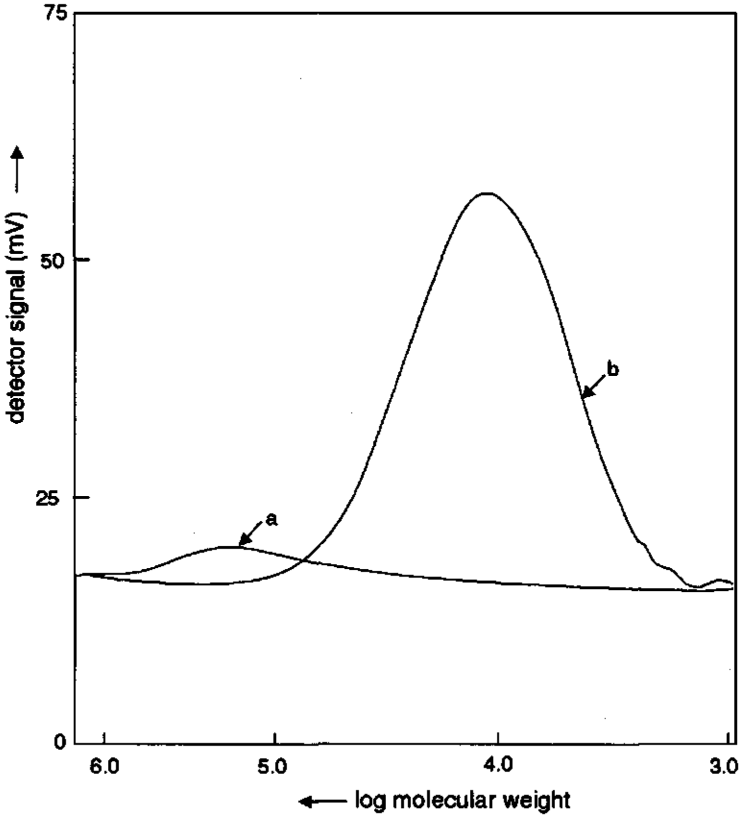

Figure 4 Chromatogram with UV detection: curve a, 1000 ppm PVA; curve b, 600 ppm NH_4-PAA.

In experiments with mixtures the sensitivities are recalculated regularly from injections of a known polymer mixture. With the assumption that the ratios $S_{pva\text{-}ri}/S_{paa\text{-}ri}$ and $S_{pva\text{-}uv}/S_{paa\text{-}uv}$ are both constant, the S values follow from the above equations.

The method is checked by injection of mixtures of PVA and NH_4-PAA with known concentrations. Results collected in Table 2 show that the accuracy of the method is around 4%.

Table 2: Determination of the accuracy of the calculation method with mixtures of known concentration.

Injected mixture		Calculated values	
C_{pva} (ppm)	C_{paa} (ppm)	C_{pva} (ppm)	C_{paa} (ppm)
800	800	802	792
400	800	393	793
1000	200	959	202
1000	400	985	382

The above method is suitable for obtaining the separate polymer concentrations. Separate chromatograms can be calculated by applying the method at sufficiently small intervals as has been shown by Trathnigg [25]. With our equipment this is not possible because of limitations in the Nelson software.

3.3.2 Adsorption of PVA

The molecular weight distributions before and after adsorption (Fig. 5) show that adsorption takes place over the whole molecular weight range. There is no preference for the high molecular weight fraction in the adsorption. Such a preference is predicted theoretically by Cohen Stuart et al. [4] and has also been found experimentally [17,21]. However, the adsorption isotherm (Fig. 6) has a rounded shape which is an indication of competition between chains and preferential adsorption of the longest chains in the case of a polydisperse homopolymer. The two results (Figs 5 and 6) seem to be contradictory. This behaviour is probably due to the nature of PVA. PVA is not a regular polymer but contains short polyvinyl acetate blocks and branches [26]. Moreover, Van den Boomgaard et al. [27] found that the degree of hydrolysis depends on the chain length. The short chains have a higher acetate content than the longer ones. The chains of a PVA type with a degree of hydrolysis of 88% have a broad distribution of the acetate content in contrast with the very homogeneous acetate content of the chains in a 98% hydrolysed material [8]. PVA with a low degree of hydrolysis is not a polydisperse homopolymer but in fact is a mixture of several polymers with a slightly different chemical compositions.

We have checked the influence of the degree of hydrolysis on the SEC chromatogram. The average degree of hydrolysis of the PVA was increased in steps from 88% to 91, 92 and 94% by controlled addition of KOH. The chromatograms of these samples show a shift towards higher molecular weight with an increasing degree of hydrolysis. Since it is unlikely that the molecular weight distribution has been changed, the shift can be attributed to the decreasing amount of acetate groups in the chains. If we combine this result with the dependence of the acetate content on the chain length we can conclude that the chromatogram is broadened.

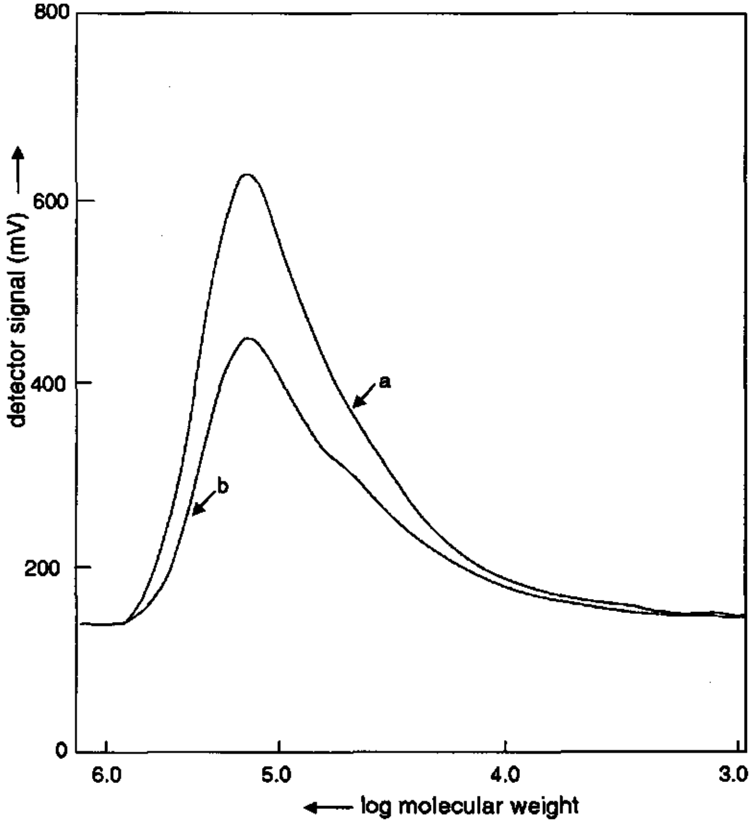

Figure 5 Chromatogram before (curve a) and after (curve b) adsorption from 1000 ppm PVA solution (RI detector).

In the adsorption of a polydisperse homopolymer there would be no adsorption of the short chains. In our experiments with PVA the short chains do adsorb (Fig. 5).

This indicates that there is a preference in the adsorption for the chains with a higher acetate content. The apparent contradiction in the results is expected to be caused by two competing effects; the polydispersity effect for homopolymers which stimulates the adsorption of the longest chains and the effect of the acetate groups which stimulates the adsorption of the short chains. A similar situation has been found by Croot et al. [8] for the adsorption of PVA with a degree of hydrolysis of 88% on polystyrene latex. Koopal [10] used a PVA with a degree of hydrolysis of 98% and found a preference for the long chains in the adsorption on AgI. Since the chains in this type of PVA all have the same acetate content [8], only the polydispersity effect remains and preference for the long chains is the expected behaviour.

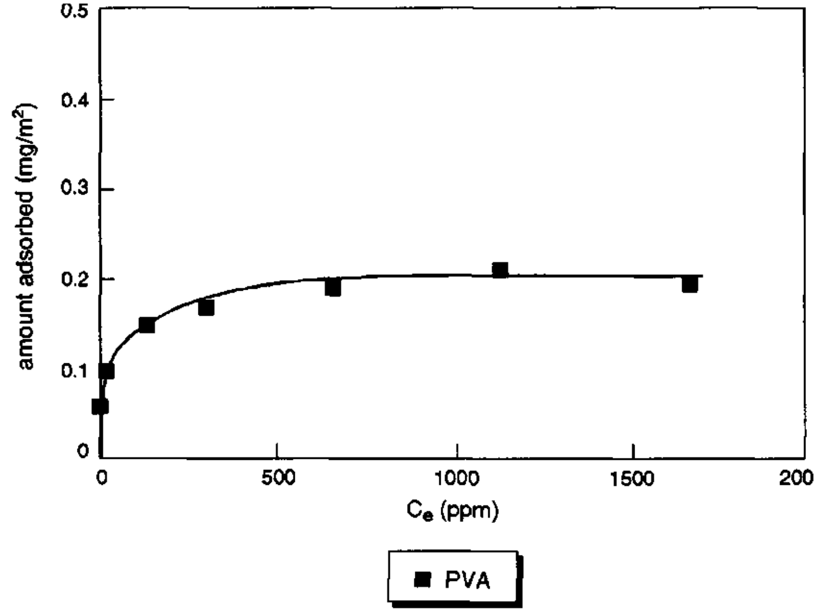

Figure 6 Adsorption isotherm for PVA.

The adsorption isotherm (Fig. 6) shows that the amount adsorbed at the plateau is 0.19 mg m^{-2}. Even lower values have been found by Bonekamp et al. [28] for the adsorption of PVA on alumina.

3.3.3 Adsorption of NH_4-PAA

At low concentrations there is a clear preference for the higher molecular weight fractions (Fig. 7), all NH_4-PAA molecules adsorb except the smallest ones.

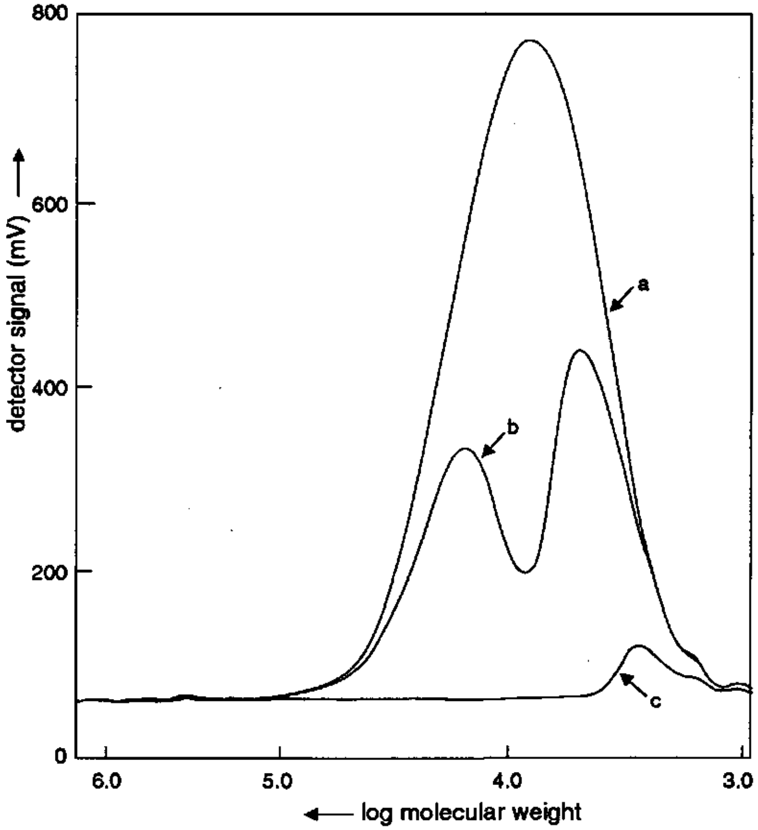

Figure 7 Chromatograms for the adsorption of NH_4-PAA (RI detector): curve a, 1500 ppm before adsorption; curve b, after adsorption from 1500 ppm solution; curve c, after adsorption from 600 ppm solution.

At higher concentrations (above 800 ppm) a peculiar molecular weight fractionation is found; the intermediate molecular weight fraction adsorbs preferentially over both the low and high molecular weight fractions. The smallest molecules do not adsorb at all, while only a part of the highest molecular weight fraction adsorbs.

It is reasonable to expect that initially the smallest molecules adsorb also as they have the highest diffusion rate. Obviously they are displaced from the surface by larger molecules afterwards. Since not all of the highest molecular weight fraction is adsorbed, these are not the chains that displace the smaller ones. So an intermediate chain length is responsible for the displacement of the short chains. The small amount of adsorbed high molecular weight fraction is expected to be due to the initial contact.

Displacement between charged molecules of different molecular weights is hindered by the charge on the surface and on the chain. Ramachandran et al. [29] showed that displacement of adsorbed low molecular weight polystyrene sulfonate by high molecular weight chains does not occur unless salt is added to screen the charges. The exchange is expected to begin at a certain reduction of the charge. From our results we expect that chains up to a certain total charge (or molecular weight) are able to displace smaller molecules. With increasing chain length the total charge hinders more and more the approach to the surface until exchange is no longer possible.

Another explanation of the stronger adsorption of the intermediate molecular weight fraction can be based on the assumption that the chemical composition depends on the chain length in such a way that the intermediate chain length has a higher affinity for the surface. In our point of view this is, however, unlikely since the polymerisation of acrylic acid is expected not to introduce such variations.

The plateau level in the adsorption isotherm (Fig. 8) has a value of 0.40 mg m^{-2}.

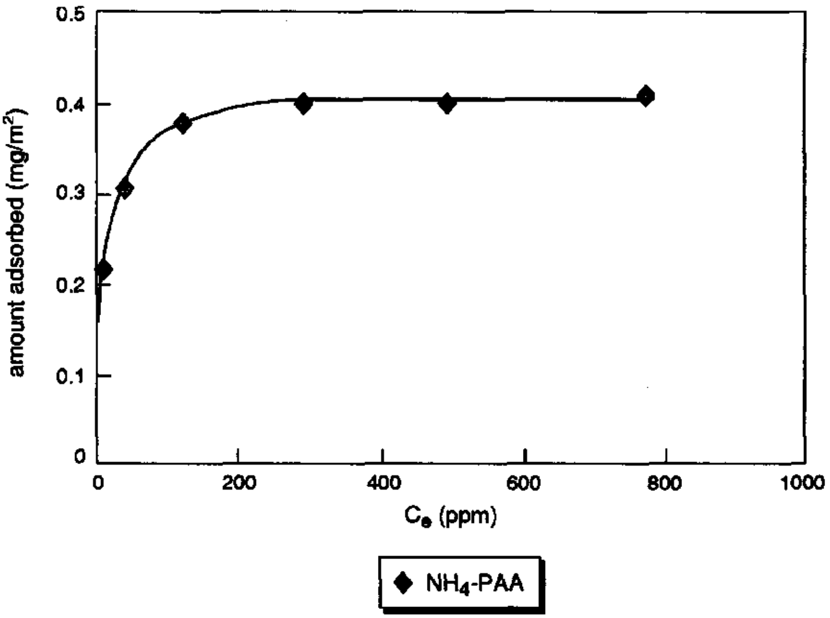

Figure 8 Adsorption isotherm for NH_4-PAA.

3.3.4 Adsorption from mixtures of PVA and NH_4-PAA

The initial concentration of PVA is 1000 ppm in these experiments which is enough to reach the plateau value in the adsorption isotherm of PVA. The C_0 values in this series have been recalculated to the final volume of 10 ml. The concentration of NH_4-PAA is varied. The final concentrations of NH_4-PAA and PVA and the amount of each polymer adsorbed have been calculated from the total peak areas of the RI and UV detectors. Results have been collected in Fig. 9 and Table 3, the latter of which contains additional C_0 data.

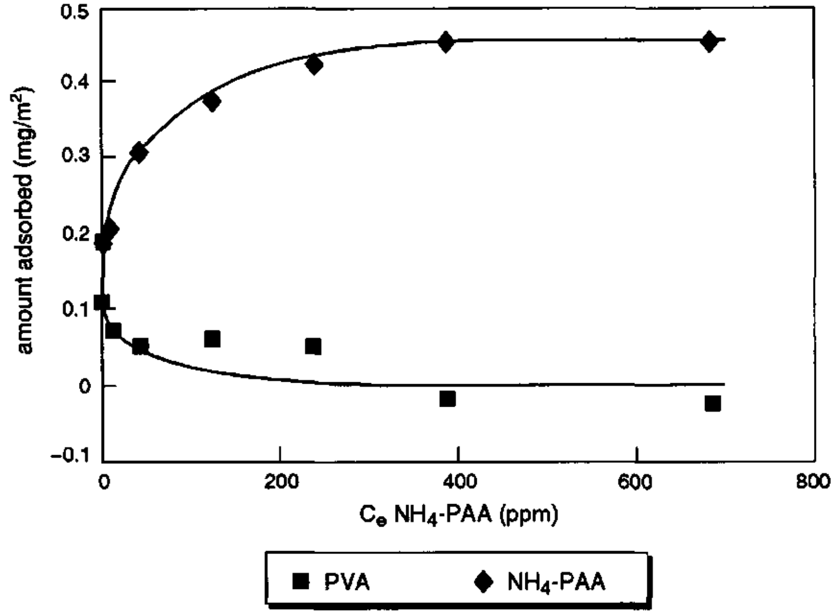

Figure 9 Amounts adsorbed from mixtures of PVA and NH_4-PAA.

Table 3: The adsorption of PVA and NH_4-PAA from mixtures.

C_0 (ppm)	C_e (ppm)		Amounts adsorbed (mg m^{-2})	
NH_4-PAA	PVA	NH_4-PAA	PVA	NH_4-PAA
0	650	0	0.19	0
200	661	0	0.11	0.19
400	877	13	0.07	0.21
600	914	45	0.05	0.31
800	897	125	0.06	0.37
1000	912	239	0.05	0.42
1200	1031	387	−0.02	0.45
1500	1054	686	−0.03	0.45

The C_0 of PVA is 1000 ppm in all experiments.

At a NH_4-PAA concentration of 200 ppm the surface of the particles cannot be covered completely with NH_4-PAA. In this case adsorption of PVA is found. With increasing NH_4-PAA concentration, the surface of the particles is covered more completely with NH_4-PAA and the adsorption of PVA decreases. At 1200 ppm NH_4-PAA a plateau value in the NH_4-PAA adsorption is reached and no adsorption of PVA is found. In the experiments with the highest concentration of NH_4-PAA the final concentration of PVA is higher than the initial concentration and because of this the adsorbed amount is negative. This is due to the limited accuracy of the calculation method. The adsorption of NH_4-PAA from this mixture closely resembles the separate adsorption isotherm. The only difference is the slightly higher plateau value which may be due to a different conformation of the adsorbed molecules.

3.3.5 Addition of NH_4-PAA to $BaTiO_3$ with adsorbed PVA

The particles are mixed with a PVA solution of 1000 ppm (recalculated to a final volume of 10 ml) which is enough to reach the plateau value in the adsorption. After 15 h the NH_4-PAA solutions with a variable concentration are added. After a total mixing time of 24 h the particles are removed and the supernatant is analysed. The results have been collected in Fig. 10 and Table 4 with additional C_0 data.

Table 4: The amounts adsorbed after preadsorption of PVA and sequential addition of NH_4-PAA.

C_0 (ppm)	C_e (ppm)		Amounts adsorbed (mg m^{-2})	
NH_4-PAA	PVA	NH_4-PAA	PVA	NH_4-PAA
50	664	3	0.19	0.03
100	664	1	0.19	0.06
200	676	3	0.18	0.11
400	673	16	0.18	0.21
600	661	60	0.19	0.30
800	643	205	0.20	0.33

The C_0 of PVA is 1000 ppm in all experiments.

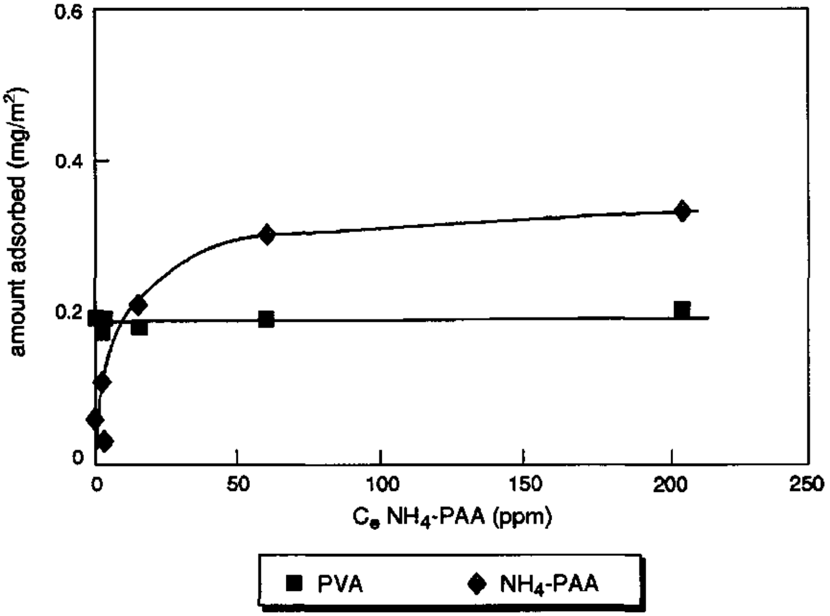

Figure 10 Amounts adsorbed after addition of NH_4-PAA to $BaTiO_3$ with adsorbed PVA.

The amount of NH_4-PAA adsorbed increases with the C_0 value. The amount of PVA adsorbed remains unchanged and equal to the plateau value, regardless of the amount of NH_4-PAA adsorbed. Although NH_4-PAA adsorbs onto the surface of the particles, displacement of PVA does not occur. The final situation is a mixed adsorbed layer with an amount of PVA adsorbed equal to the value obtained in a separate adsorption experiment and an amount of NH_4-PAA which is slightly lower than in the separate adsorption isotherm.

Since it may take a long time before equilibrium is attained, we followed the amounts adsorbed from a mixture for a period of 2 weeks. The results in Table 5 reveal that there is a slight decrease in the first 7 days in the amount of PVA adsorbed while the adsorption of NH_4-PAA has increased somewhat. In the next period of 7 days there is no further change. The amount of PVA adsorbed remains much higher than in an adsorption experiment with mixtures of both polymers.

Table 5: The variation of the amounts adsorbed with time (addition of 800 ppm NH_4-PAA after preadsorbing from 1000 ppm PVA solution).

Time (days)	C_e (ppm)		Amounts adsorbed (mg m^{-2})	
	PVA	NH_4-PAA	PVA	NH_4-PAA
1/3	643	205	0.20	0.33
7	702	122	0.17	0.38
14	699	93	0.17	0.39

In experiments with mixtures we expect that both polymers adsorb initially and NH_4-PAA displaces PVA shortly afterwards. However, if the PVA is allowed to reach a more favorable adsorbed conformation in a period of 15 h, NH_4-PAA can displace only a small proportion of the PVA molecules. The amount of NH_4-PAA adsorbed is lower since some of the available surface sites remain occupied by PVA. Probably the adsorption sites on the $BaTiO_3$ surface have a distribution of affinities. If the adsorption energy is above a certain critical value, desorption of the adsorbed PVA segments requires stronger displacers. We shall call this fraction of sites above the critical value for displacement with NH_4-PAA the 'high energy sites'. We expect to have a small amount of these high energy sites on the $BaTiO_3$ surface. PVA adsorbs initially on the main sites and needs some time to reach a conformation in which the high energy sites are included. Some of the PVA molecules have not included high energy sites after 15 hours of equilibrium time and these are displaced by NH_4-PAA.

3.4 CONCLUSIONS

The SEC method is suitable for the measurement of the amounts adsorbed from mixtures. PVA adsorbs on $BaTiO_3$ up to 0.19 mg m^{-2} without preference for the longest chains. The NH_4-PAA adsorption in the plateau region is 0.40 mg m^{-2} with a preference for the intermediate molecular weight fraction which can be explained if adsorbed small chains can be displaced by longer ones up to a certain total charge on the chain (or molecular weight). No PVA adsorbs from mixtures if enough NH_4-PAA is present to cover the surface of the particles completely. Some PVA adsorption is found if a shortage of NH_4-PAA exists. If NH_4-PAA is added 15 h after adsorbing PVA, it cannot displace the adsorbed PVA from the surface. In this case of sequential addition, both polymers adsorb with amounts almost equal to the plateau values of their individual adsorption isotherms, resulting in a mixed adsorbed layer.

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REFERENCES

[1] J.M.H.M. Scheutjens and G.J. Fleer, J. Phys. Chem., 83 (1979) 1619-1635.
[2] J.M.H.M. Scheutjens and G.J. Fleer, J. Phys. Chem., 84 (1980) 178-190.
[3] G.J. Fleer, Colloids Surfaces, 35 (1989) 151-167.
[4] M.A. Cohen Stuart, J.M.H.M. Scheutjens and G.J. Fleer, J. Polym. Sci. Polym. Phys. Edition, 18 (1980) 559.
[5] R.-J. Roe, Polym. Sci. Technol., 12B (1980) 629
[6] J.M.H.M. Scheutjens and G.J. Fleer in Th.F. Tadros (Ed.), The effect of polymers on dispersion properties, Academic Press, New York, 1982.
[7] M.A. Cohen Stuart, T. Cosgrove and B. Vincent, Adv. Colloid Interface Sci., 24 (1986) 143-239.
[8] R.A. Croot, A.R. Goodall and S.B. Lubetkin, Colloids Surfaces, 49 (1990) 351.
[9] E. Killmann, H. Maier and J.A. Baker, Colloids Surfaces, 31 (1988) 51-71.
[10] L.K. Koopal, J. Colloid Interface Sci., 83 (1981) 116.
[11] L.K. Koopal, V. Hlady and J. Lyklema, J. Colloid Interface Sci., 121 (1988) 49.
[12] M.R. Böhmer, O.A. Evers and J.M.H.M. Scheutjens, Macromolecules, 23 (1990) 2288-2301.
[13] J. Blaakmeer, M.R. Böhmer, M.A. Cohen Stuart and G.J. Fleer, Macromolecules, 23 (1990) 2301-2309.
[14] J. Cesarano III and I.A. Aksay, J. Am. Ceram. Soc., 71 (1988) 1062.
[15] J.E. Gebhardt and D.W. Fuerstenau, Colloids Surfaces, 7 (1983) 221.
[16] R.R. Vedula and H.G. Spencer, Colloids Surfaces, 58 (1991) 99-110.
[17] M. Kawaguchi, Adv. Colloid Interface Sci., 32 (1990) 1-41.
[18] M.A. Cohen Stuart, G.J. Fleer and J.M.H.M. Scheutjens, J. Colloid Interface Sci., 97 (1984) 526-535.
[19] G.P. van der Beek, Ph.D. Thesis, Agricultural University, Wageningen, The Netherlands, 1991.

[20] M.A. Cohen Stuart, G.J. Fleer and J.M.H.M. Scheutjens, J. Colloid Interface Sci., 97 (1984) 515.
[21] H.F. Huisman, H.J.M. Pigmans, A.J.P. Roegies and W.J.J.M. Sprangers, Progr. Organic Coatings, 13 (1986) 377-420.
[22] D.J. Nagy, J. Liquid Chromatogr., 14 (1990) 677-691.
[23] B.G. Belenkii and L.Z. Vilenchik, Modern Liquid Chromatography of Macromolecules, Journal of Chromatography Library, Vol 25, Elsevier, Amsterdam, 1983.
[24] K. Makino and H. Hatano in P.L. Dubin (Ed.), Aqueous Size Exclusion Chromatography, Journal of Chromatography Library, Vol 40, Elsevier, Amsterdam, 1988.
[25] B. Trathnigg, J. Liquid Chromatogr., 13 (1990) 1731-1743.
[26] C.A. Finch in C.A. Finch (Ed.), Polyvinyl alcohol, John Wiley & Sons, London, 1973.
[27] Th. van den Boomgaard, T.A. King, Th.F. Tadros, H. Tang and B. Vincent, J. Colloid Interface Sci., 66 (1978) 68-74.
[28] B.C. Bonekamp, W.H. van 't Veen, M.J. Schoute and H.J. Veringa, in G. de With, R.A. Terpstra and R. Metselaar (Eds), Euroceramics, Vol. 1, Elsevier, London, 1989.
[29] R. Ramachandran and P. Somasundaran, J. Colloid Interface Sci., 120 (1987) 184-188.

CHAPTER 4

Molecular weight fractionation in the adsorption of polyacrylic acid salts onto $BaTiO_3$*

Abstract

The molecular weight fractionation resulting from the adsorption of a polyacrylic acid salt (PAAS) onto $BaTiO_3$ depends on the molecular weight distribution (MWD) of the PAAS. Preferential adsorption of the longest chains is found if the entire MWD is below a certain chain length. If the MWD extends to over this limit while still including a sufficient amount of smaller chains, a preferential adsorption of an intermediate molecular weight fraction occurs. The effect is quite pronounced for PAASs of relatively low molecular weight (<20 000). Adsorption over a wide molecular weight range but with a higher proportion of short chains is observed if the MWD of the PAAS is mainly above the aforementioned limit.

The molecular weight fractionation can be understood using a sequential adsorption process in which mainly the smallest chains of the PAAS adsorb first. These initially adsorbed chains overcompensate the positive surface charge and thereby generate an electrostatic barrier for the PAAS chains in the solution. The height of this barrier depends (at a constant charge of the PAAS covered surface) on the total charge on the polyelectrolyte chain in solution, which is directly related to the chain length at high pH. The length of the chains that displace the shorter ones is limited by the electrostatic barrier. With an increased salt concentration the barrier is lower, allowing longer chains to reach the surface and displace shorter ones. Consequently, the preferential adsorption from solutions with higher salt concentration is shifted to higher molecular weights.

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*A.W.M. de Laat and G.L.T. van den Heuvel, Colloids Surfaces A: Physicochem. Eng. Aspects, 98 (1995) 53-59

4.1 INTRODUCTION

Preferential adsorption of the high molecular weight fraction of polydisperse uncharged homopolymers was found from the theoretical calculations by Cohen Stuart et al. [1], Roe [2] and Scheutjens and Fleer [3]. Experimental evidence has been collected by several authors [1,4-7]. The effect is caused by the difference in translational entropy of chains of different lengths in the solution [3]. To our knowledge there are no theoretical predictions for the molecular weight fractionation in the adsorption of polyelectrolytes. A similar preference can be expected as will be shown in Chapter 5 of this thesis.

Experimental results, however, show a different preference in many situations. We previously reported the preferential adsorption of an intermediate molecular weight fraction in the adsorption of the ammonium salt of a polyacrylic acid onto $BaTiO_3$ [8]. Ramachandran and Somasundaran [9,10] found preferential adsorption of low molecular weight sodium-polystyrene sulphonate from a salt-free solution onto Fe_2O_3 but a preference for the long chains in the presence of 0.1 M NaCl. Wright et al. [11] reported no displacement of preadsorbed low molecular weight polyacrylic acid on $BaSO_4$ by high molecular weight polyacrylic acid in a salt-free solution. However, significant displacement was found in 0.5 M NaCl. Bain et al. [12] reported the preferential adsorption of the low molecular weight fraction of both sodium polyacrylate and sodium carboxymethyl cellulose onto $BaSO_4$ from solutions without added salt. Tanaka et al. [13] adsorbed fluorescence labelled cationic polyacrylamide onto polystyrene latex, and studied the exchange with unlabelled polymer of the same molecular weight which was added after equilibration. A significant exchange was found with low ($4*10^5$) molecular weight polymer, while no exchange over a 40-day period with high molecular weight ($8*10^6$) polymer was reported.

A preference for the low molecular weight fraction in the adsorption of polyelectrolytes onto a variety of substrates is often found at low salt concentrations. At high salt concentrations the expected preference for the high molecular weight fraction is found in some studies.

In the present study we extend our previous results [8] with a series of polyacrylic acid salts (PAASs) of different molecular weights. The influence of salt concentration is also included.

4.2 EXPERIMENTAL

4.2.1 Materials

The $BaTiO_3$ powder used in this study has slightly different properties compared with the previously used batch [8]. The present number average particle size is 0.92 μm with a standard deviation of 0.33 μm, as was measured by a CIS-1 particle sizer, Galai Production Ltd, Migdal Ha-Emek, Israel. The specific surface area is 2.4 $m^2\ g^{-1}$ according to the BET method. The isoelectric point (IEP) is located at pH=10.2, which was determined by measuring the dynamic electrokinetic mobility as a function of the pH with an ESA-8050 system, Matec Instruments, Hopkinton, MA, USA.

The PAAS labelled as PAAS-10 was obtained from Allied Colloids Ltd, Bradford, Yorkshire, UK, while the other five samples are products of Polysciences Inc., Warrington, PA, USA. All PAASs were obtained as aqueous solutions.

All materials were used as received.

4.2.2 Size exclusion chromatography

Details of the size exclusion chromatography (SEC) method have been published previously [8]. Changes introduced since then are mentioned below, along with some relevant points.

The SEC chromatograms of the PAASs were determined with a set of four columns in series: TSK guard PW, TSK 4000PWXL and 2* TSK 3000PWXL (Toyo Soda Manufacturing Co, Tokyo, Japan). This set was chosen after optimisation for PAAS-10. It is a suitable combination over a wide molecular weight range but the resolution for very short chains is low. The eluent was 0.06 M potassium phosphate buffer at pH=6.8 at a flow rate of 1 ml min^{-1}. Detection was performed with a Waters 410 Refractive Index (RI) detector (Millipore Corp, Waters Chromatography Div, Milford, MA, USA) placed in series with a Waters 484 Ultraviolet (UV) detector set at 200 nm. At a high salt concentration in the sample, washing out the excess salt from the column takes quite some time after the total permeation. The RI detector is very sensitive for small changes in the KNO_3 concentration, accordingly, the base line goes back to its initial level very slowly. Peak integration of a new sample is hampered by a base line change. As the UV detector is less sensitive for this effect, a new sample can be injected sooner without having integration problems. Thereore, the UV detector is more practical with samples with a high salt concentration.

System control and data analysis were done with Waters Baseline and Waters GPC software.

Both detectors have linear response in the tested concentration range of 0-1800 ppm PAAS with an injected volume of 100 µl. The chromatograms obtained with both detectors are similar. An accuracy better than 3% in the adsorbed amount is obtained by recalibration of the detector sensitivities with a reference sample of known PAAS concentration just before each sample is injected. The difference between the peak areas before and after adsorption must be at least 10%.

Table 1 presents the calibration of the retention time of the RI detector with polyethylene oxide (PEO) standards which allows the conversion to (relative) molecular weights (Chapter 2). All retention times for the UV detector are 0.13 minutes shorter.

Table 1: Calibration of the retention time of the RI detector with PEO standards.

PEO molecular weight ($g\ mol^{-1}$)	Retention time (min)
900 000	14.86
770 000	14.95
325 000	15.94
160 000	16.72
83 000	18.26
23 000	20.21
12 600	21.42
7 100	22.69
4 250	23.82
1 470	25.57
960	25.98

4.2.3 Adsorption experiments

10.00 ml of a PAAS solution with the chosen polymer and KNO_3 concentrations were mixed with 6.00 grams of $BaTiO_3$ in a 25 ml centrifuge tube. A few glass balls were added to assist homogeneous mixing. The pH of the suspensions was usually slightly below the IEP of $BaTiO_3$; data will be given for each experiment.

After tumbling the tubes head-over-head for the chosen time at room temperature, the powder was removed by centrifugation in a Heraeus Labofuge GL (Heraeus-Christ GmbH, Osterode am Harz, Germany) for 20 min at 4000 rev min^{-1}.

The adsorbed amount and the change in molecular weight distribution were determined from the chromatograms as measured by SEC of the polymer solutions before and after adsorption.

4.3 RESULTS AND DISCUSSION

4.3.1 PAAS characterisation

The SEC chromatograms which reflect the molecular weight distributions (MWDs) of the PAAS samples are given in Fig. 1.

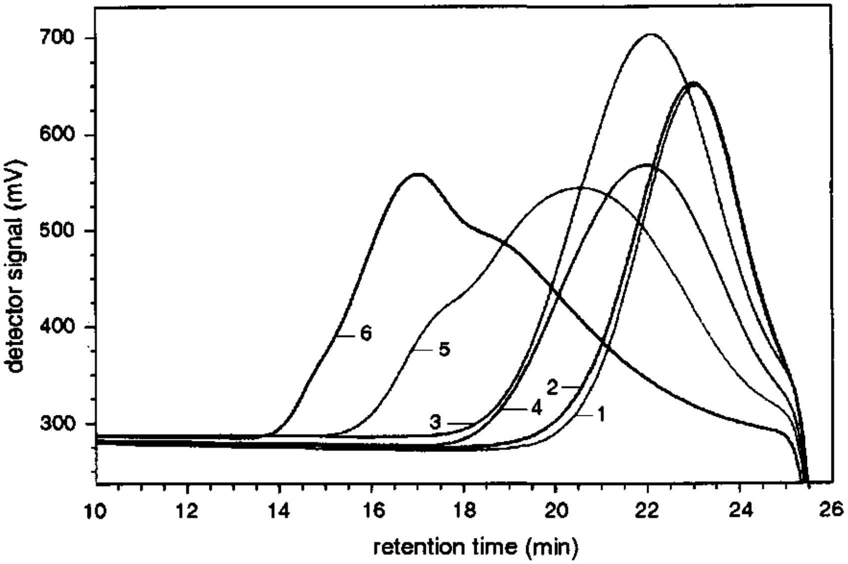

Figure 1 *SEC chromatograms (RI detector) of all PAASs; 1, PAAS-7; 2, PAAS-8; 3, PAAS-10; 4, PAAS-13; 5, PAAS-48; 6, PAAS-151.*

The steep decrease at the end of the chromatogram indicates the total permeation limit. Not all of the PAAS elutes before this limit, owing to the low resolution in the short chain length range. Note that the total amounts of PAAS are similar, but not precisely the same for each sample. This is due to deviations in the PAAS concentration data as provided by the suppliers. To obtain good data in further experiments the solids content of PAAS-10 was determined by evaporation of the water; the PAAS content was 40.6 wt%. This value was used to calibrate the UV and RI detector sensitivities. The adsorbed amounts of the other PAASs are calculated from SEC data assuming the same detector sensitivity. A small difference in sensitivity is possible due to the different counter ions.

The MWDs of PAAS-7 and PAAS-8 are almost the same. PAAS-10 and PAAS-13 have higher but mutually similar MWDs. The symmetry of the SEC chromatograms depends not only on the sample but also on the choice of the columns. The chromatograms of PAAS-7 to PAAS-13 are symmetrical because they fall in the range of the 3000PWXL columns. If one of the 3000PWXL columns from the present set is replaced by a 5000PWXL column, the chromatogram of PAAS-48 is symmetrical but the PAAS-151 chromatogram still has an asymmetry. Hence, PAAS-151 is probably a mixture of more than one separate polymerization; it also has the lowest amount of short chains. Conversion to relative molecular weights is possible with the calibration in Table 1. The weight-averaged molecular weight (M_w) and the polydispersity index, which is the ratio of M_w to the number-averaged molecular weight (M_n), calculated from these chromatograms are given in Table 2. The broad MWDs of samples PAAS-48 and PAAS-151 are reflected in the high M_w/M_n values.

Table 2: Molecular weights of the PAASs.

Sample	Counter ion	M_w (10^3 g mol^{-1})	M_w/M_n
PAAS-7	Na^+	7.1	1.3
PAAS-8	Na^+	8.0	1.5
PAAS-10	NH_4^+	10.4	1.6
PAAS-13	Na^+	13.2	1.9
PAAS-48	Na^+	47.6	4.2
PAAS-151	Na^+	150.9	6.9

4.3.2 Adsorption isotherms

Adsorption isotherms (Fig. 2) were measured after a mixing time of 24 h for PAAS-7 at pH=9.0±0.2 and for PAAS-10 at pH=9.5±0.5.

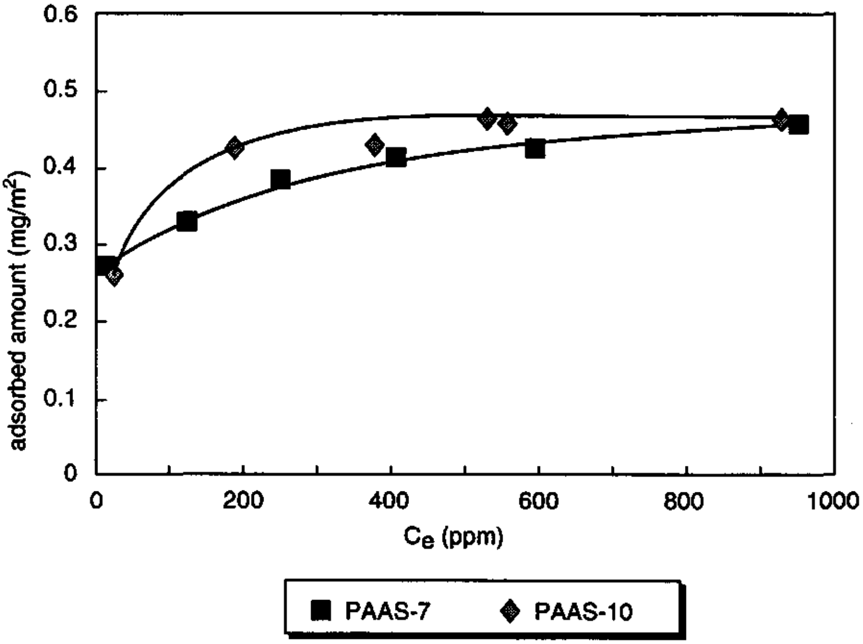

Figure 2 Adsorption isotherms for PAAS-7 and PAAS-10.

Salt was not added in these experiments. A high adsorbed amount at low equilibrium concentration (C_e) is found for both PAASs. After this initial steep region, the adsorbed amount of PAAS-7 increases more gradually than that of PAAS-10. The adsorbed amount of both PAASs reaches a plateau at 0.45 mg m^{-2}. This value is slightly higher than the value of 0.40 mg m^{-2} found previously for the old batch of $BaTiO_3$ [8]. Theory [14] predicts plateau adsorbed amounts which are roughly independent of the molecular weight of the polyelectrolyte at low salt concentrations.

4.3.3 Fractionation without added salt

The fractionation effect can be evaluated most clearly at an equilibrium concentration just in the plateau of the adsorption isotherm. At low concentrations all polymer adsorbs, while at a large excess the adsorbed fraction can hardly be determined as the chromatograms before and after adsorption are almost the same.

Assuming that the adsorption isotherms for all PAASs are roughly the same, the initial concentration is chosen at 1200 ppm, on the basis of the adsorption experiments of PAAS-7 and PAAS-10.

After mixing for 48 h the powder was removed and the supernatant analysed. The equilibrium pH values were not all the same but were in the range of 9.6±0.7. The chromatograms of the polymers in solution before and after adsorption are compared in Figs 3-8 for all the PAASs.

Adsorption over the whole molecular weight range is found with all PAASs.

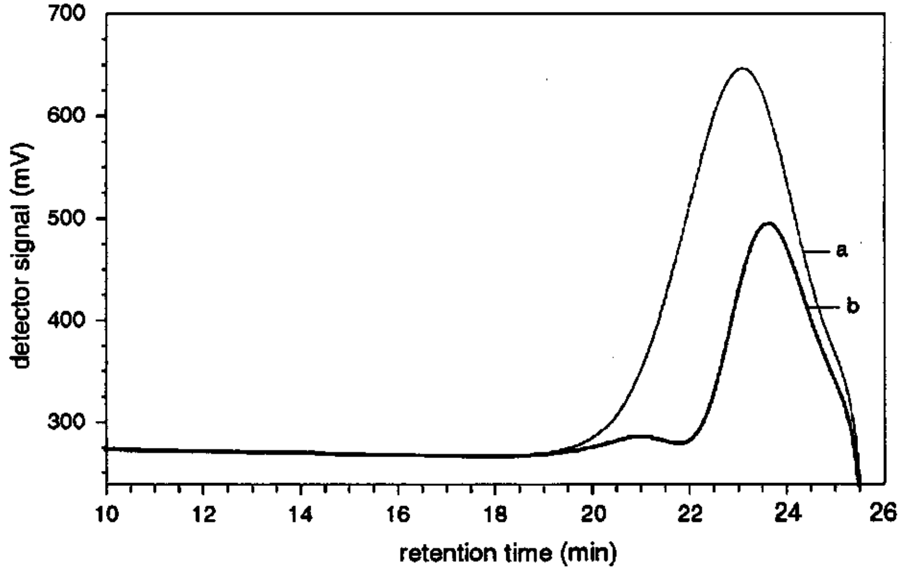

Figure 3 SEC chromatograms (RI detector) for PAAS-7: a, before adsorption; b, after adsorption; pH=9.5.

With PAAS-7 (Fig. 3) a large amount of unadsorbed low molecular weight chains is found, while the high molecular weight fraction is adsorbed. A shallow minimum in the curve after adsorption at a retention time of around 22 min can be observed. Remarkably, some of the low molecular weight chains also remain adsorbed. The chromatograms of the other PAASs gradually extend into the higher molecular weight range. From PAAS-8 to PAAS-13 (Figs 4-6) a gradual increase in a non-adsorbed high molecular weight fraction is found, while at the same time more short chains adsorb. The fraction with the highest adsorbed amount has a retention time of about 22 min in all cases. The chromatogram after adsorption of PAAS-48 (Fig. 7) does not have a minimum.

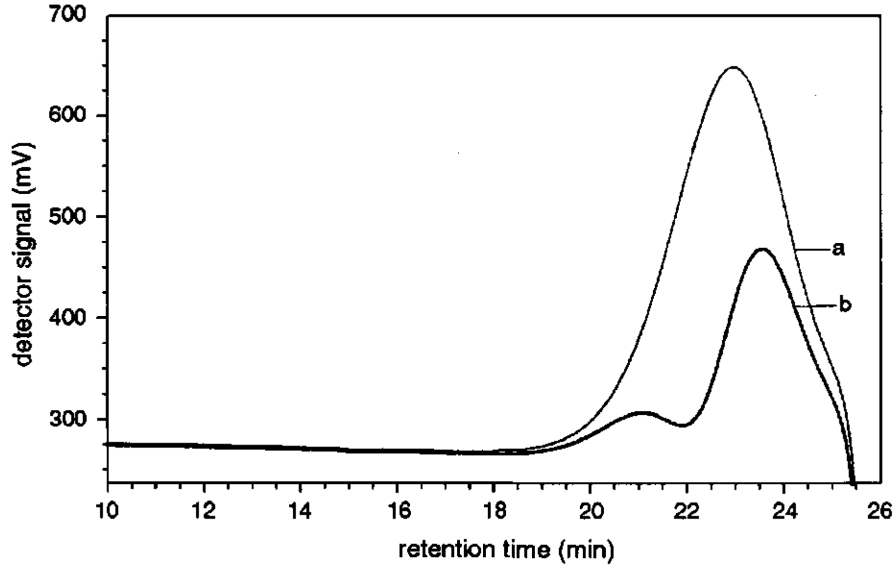

Figure 4 *SEC chromatograms (RI detector) for PAAS–8: a, before adsorption; b, after adsorption; pH=9.6.*

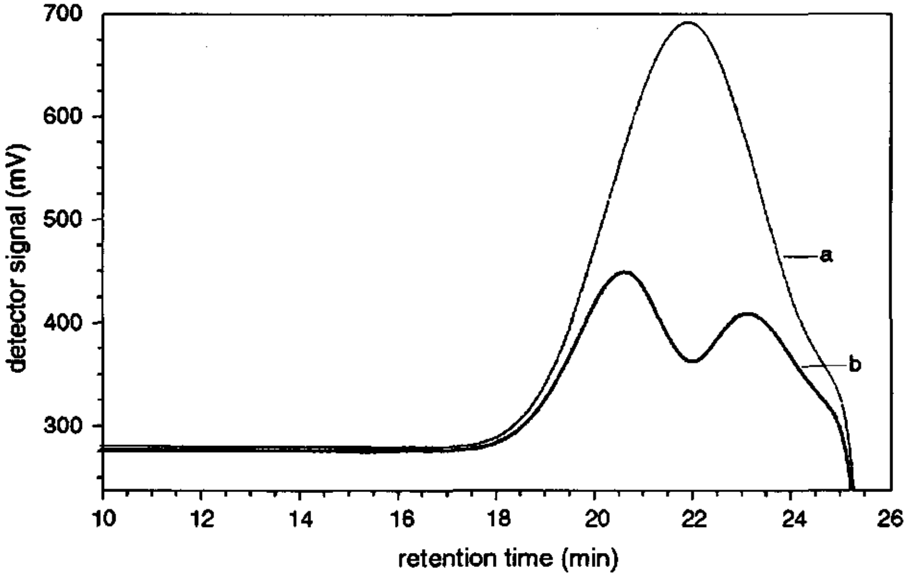

Figure 5 *SEC chromatograms (RI detector) for PAAS–10: a, before adsorption; b, after adsorption; pH=8.9.*

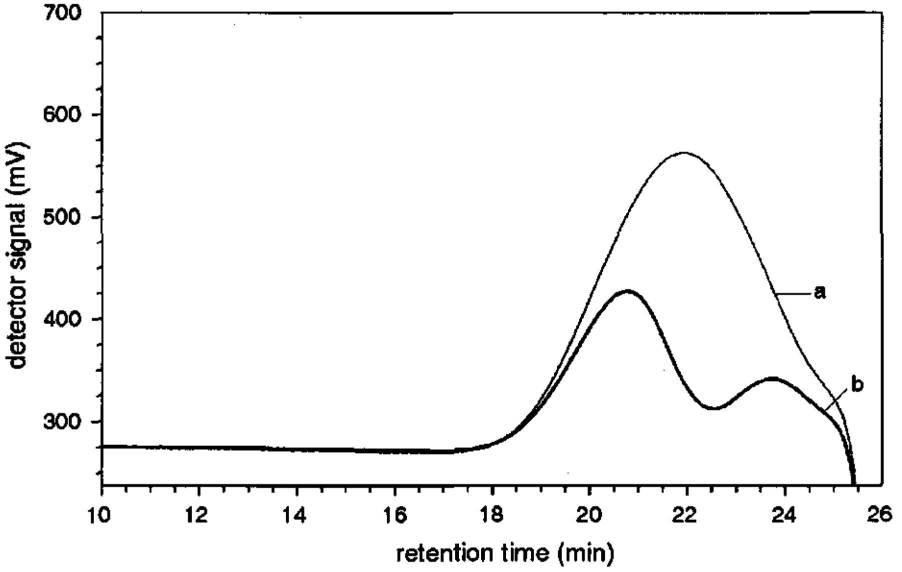

Figure 6 *SEC chromatograms (RI detector) for PAAS–13: a, before adsorption; b, after adsorption; pH=10.0.*

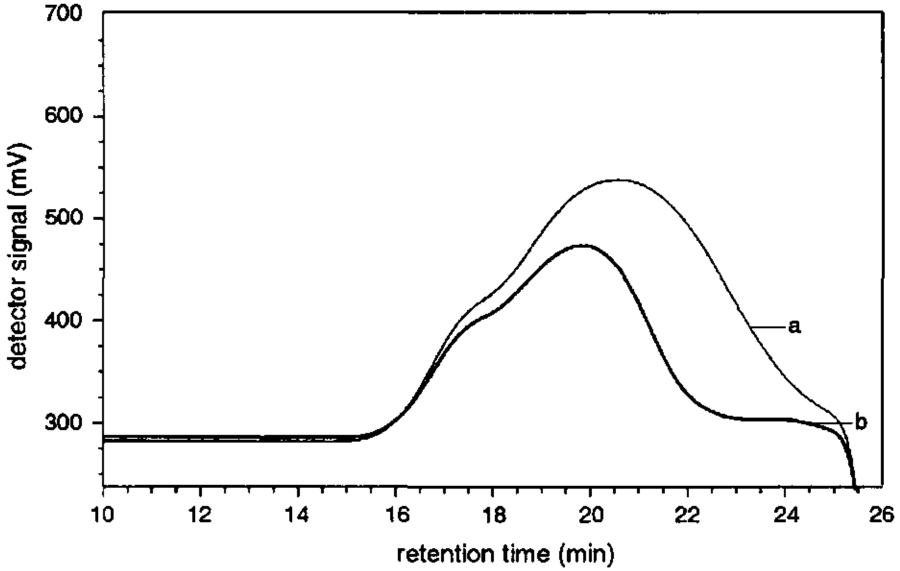

Figure 7 *SEC chromatograms (RI detector) for PAAS–48: a, before adsorption; b, after adsorption; pH=10.4.*

The adsorbed amount of the short chains is much higher than of the longer ones, with almost no adsorption of the longest chains at all. The maximum adsorbed amount is again at a retention time of around 22 min. The fractionation on adsorption with PAAS-48 is similar to the situation described by Bain et al. [12] for the adsorption of sodium polyacrylate onto $BaSO_4$ where adsorption occurs over the whole molecular weight range except for the longest chains.

PAAS-151 (Fig. 8) has a deviating behaviour because significant adsorption up to fairly high molecular weights occurs. The highest relative adsorption, however, is again in the lower molecular weight range.

Preferential adsorption of an intermediate molecular weight fraction with a retention time of about 22 min is found in the experiments with the first four PAASs. The PAASs with higher molecular weights labelled as PAAS-48 and PAAS-151 do not have a minimum in the chromatogram after adsorption.

The preference in adsorption with these two PAASs is clearly still in the low molecular weight range.

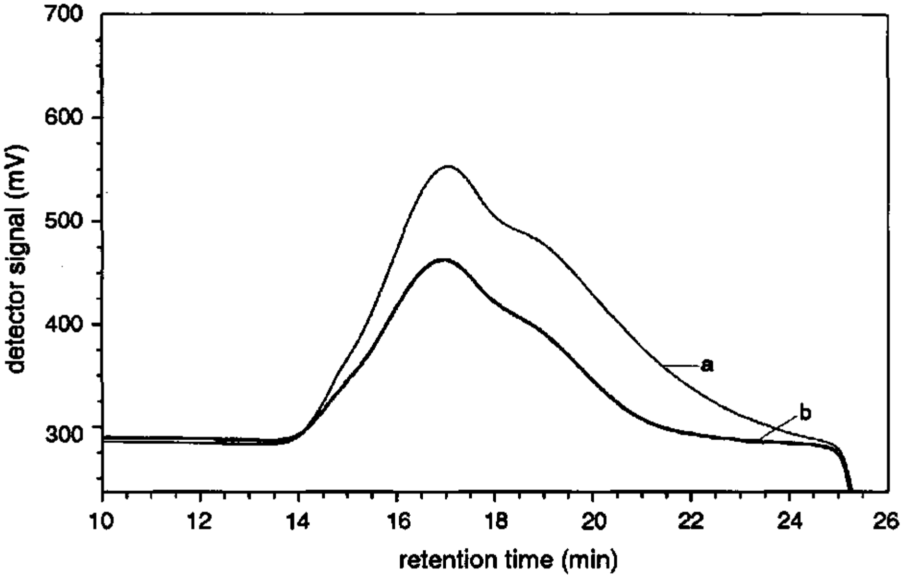

Figure 8 *SEC chromatograms (RI detector) for PAAS–151: a, before adsorption; b, after adsorption; pH=10.3.*

These experimental results can be understood by considering the several stages in the adsorption process and by recognising the development of an electrostatic barrier as proposed previously [8,12]. At first, the adsorption process will be dominated by diffusion of the chains towards the positively charged surface. The surface will be covered initially by mainly short chains because of their higher diffusion rates, but a few long chains can also reach the surface in this phase. This explains the adsorption of some long chains in all experiments. Note that the chromatograms as measured with the RI detector display a mass distribution. Conversion to a chain number distribution would show the presence of a large amount of very short chains.

As more of the surface becomes covered, an electrostatic barrier develops due to overcompensation of the positive surface charge by the negatively charged chains. The height of the electrostatic barrier is related to the total charge of the PAAS covered surface of the particles (constant at first approximation) and the total charge on the chain in solution, which is directly related to the chain length of the PAAS at the pH values employed in this study.

Assuming preferential adsorption of the longest chains in thermodynamic equilibrium, an exchange process will start directly after adsorption at initial contact in which the longer chains displace short ones from the surface. When there are no electrical charges the diffusion and concentration of the chains of various lengths in the solution are expected to cause an exchange process, in which the adsorbed chains are displaced by increasingly longer ones. For polyelectrolytes the electrostatic barrier, however, strongly affects the diffusion towards the surface. The longer the chains, the higher the barrier and the less chance they have of reaching the surface. Above a certain chain length the barrier will be too high and adsorption will not be possible. Accordingly, such long chains cannot participate in the exchange process.

The adsorption process of a PAAS with all chains below this limit (e.g. PAAS-7) is not affected by the electrostatic barrier, and preferential adsorption of the longest chains present occurs. If the chain length limit is exceeded (PAAS-10 and PAAS-13) the exchange will stop at this limit, leaving an intermediate chain length fraction adsorbed on the surface. A different situation arises for a PAAS with a chain length distribution which is mainly above the limit and without many short chains (PAAS-151). In this case there are not enough small, fast-adsorbing chains to generate an electrostatic barrier shortly after initial contact. The supply of chains towards the surface and adsorption are controlled by diffusion and concentration of the various chain lengths over longer periods of time, resulting in a significant adsorption over a wide molecular weight range. The electrostatic barrier gradually increases with increasing adsorption. It is doubtful if an exchange process develops when mainly long chains are present in solution.

Obviously, the preferential adsorption of an intermediate molecular weight fraction observed in our previous experiments [8] is not a peculiar effect of the system studied, but occurs quite generally in the adsorption of a range of PAASs onto $BaTiO_3$, provided the molecular weight distribution is suitable with enough short and long chains present.

Although experimental evidence is not yet available, similar fractionation behaviour can be expected in the adsorption of relatively low molecular weight polyelectrolytes onto a variety of substrates, provided that an electrostatic barrier develops.

4.3.4 The effect of salt on the fractionation

Screening of the electrostatic repulsion between the PAAS covered surface of the particles and the chains in solution by increased salt levels is expected to have an effect on the preference in the adsorption.

In a series of experiments PAAS-10 is adsorbed onto $BaTiO_3$ at different KNO_3 concentrations. The initial PAAS concentration was 1000 ppm and the mixing time was chosen to be 48 h. The pH values were between 8.6 and 8.9.

The results displayed in Fig. 9 show a gradual change in the molecular weight fractionation. Without added salt the intermediate molecular weight fraction adsorbs preferentially.

At increasing salt levels more and more high molecular weight chains adsorb while the adsorbed amount of the low molecular weight fraction gradually decreases. The molecular weight with the highest preference shifts to higher values with increasing salt concentration. Above $3*10^{-2}$ M KNO_3 the adsorbed amount of the long chains is so high that the minimum in the chromatogram disappears.

These results clearly show that by reducing the electrostatic barrier longer chains can reach the surface and adsorb, shifting the preferential adsorption to higher chain lengths.

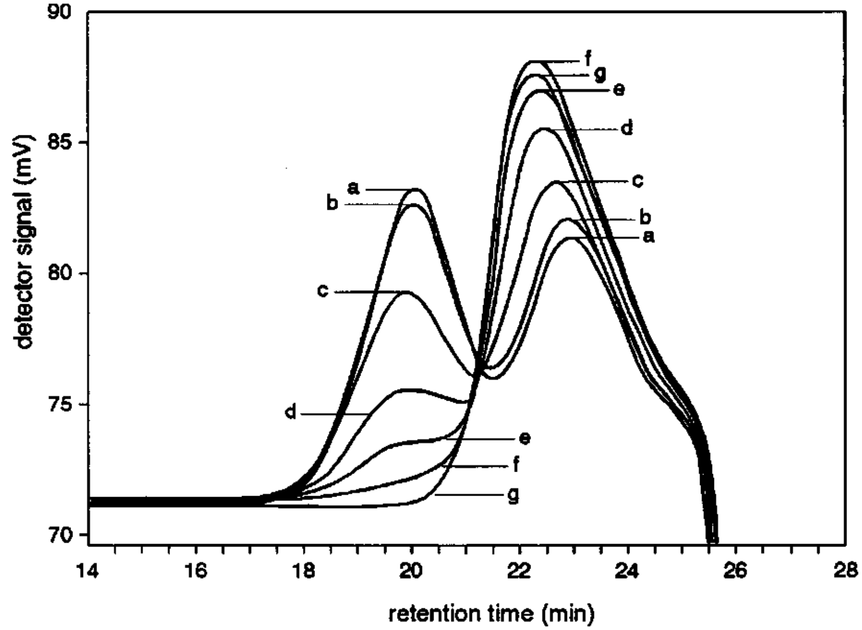

Figure 9 *The effect of salt on the fractionation of PAAS–10. SEC chromatograms with UV detector: a, no added salt; b, 10^{-1} M KNO_3; c, 10^{-2} M KNO_3; d, $3*10^{-2}$ M KNO_3; e, $6*10^{-2}$ M KNO_3; f, 10^{-1} M KNO_3; g, $2*10^{-1}$ M KNO_3.*

4.4 CONCLUSIONS

The adsorption isotherms without added salt were measured for two PAASs with low but different molecular weights, giving similar results. At low salt concentrations preferential adsorption of an intermediate molecular weight fraction is found for a range of PAASs with a molecular weight distribution including sufficiently short chains and chains above a certain limit in length. PAASs with chains only below this limit exhibit preferential adsorption of the longest chains present. PAASs with a molecular weight distribution above the limit and with few shorter chains display adsorption over a wide molecular weight range, including a relatively high adsorbed amount of the shortest chains present.

As the salt concentration is increased, more and more short chains are displaced by longer ones.

The experimental results can be understood using a sequential adsorption process in which mainly short chains adsorb first. The electrostatic barrier which develops due to overcompensation of the surface charge strongly affects the diffusion of the chains towards the PAAS covered surface. The electrostatic barrier limits the length of the chains which are able to reach the surface and displace shorter ones from the surface. At increasing salt concentrations the barrier is lower and increasingly longer chains can reach the surface and adsorb. The preference shifts to higher molecular weight values.

REFERENCES

[1] M.A. Cohen Stuart, J.M.H.M. Scheutjens and G.J. Fleer, J. Polym. Sci. Polym. Phys. Ed., 18 (1980) 559.
[2] R.-J. Roe, Polym. Sci. Techn., 12B (1980) 629.
[3] J.M.H.M. Scheutjens and G.J. Fleer, in Th.F. Tadros (Ed.), The effect of polymers on dispersion properties, Academic Press, New York, 1982.
[4] H.F. Huisman, H.J.M. Pigmans, A.J.P. Roegies and W.J.J.M. Sprangers, Progr. Org. Coatings, 13 (1986) 377-420.
[5] R.E. Felter, E.S. Moyer and L.N. Ray, J. Polym. Sci. part B, 7 (1969) 529.
[6] R.E. Felter and L.N. Ray, J. Colloid Interface Sci., 32 (1970) 349.
[7] C. van der Linden and R. van Leemput, J. Colloid Interface Sci., 67 (1978) 63.
[8] A.W.M. de Laat and G.L.T. van den Heuvel, Colloids Surfaces A: Physicochem. Eng. Aspects, 70 (1993) 179-187.
[9] R. Ramachandran and P. Somasundaran, J. Colloid Interface Sci., 120 (1987) 184-188.
[10] R. Ramachandran and P. Somasundaran, Colloids Surfaces, 32 (1988) 307-317.
[11] J.A. Wright, R. Harrop and P.A. Williams, Colloids Surfaces, 24 (1987) 249-258.
[12] D.R. Bain, M.C. Cafe, I.D. Robb and P.A. Williams, J. Colloid Interface Sci., 88 (1982) 467-470.
[13] H. Tanaka, L. Ödberg, L. Wågberg and T. Lindström, J. Colloid Interface Sci., 134 (1990) 229-234.
[14] M.R. Böhmer, O.A. Evers and J.M.H.M. Scheutjens, Macromolecules, 23 (1990) 2288-2301.

CHAPTER 5

Kinetic aspects in the adsorption of polyacrylic acid salts onto $BaTiO_3$*

Abstract

The adsorption kinetics of two polyacrylic acid salts (PAASs), with different molecular weights, on $BaTiO_3$ were studied from aqueous solutions. The pH values of the solutions were between 8.5 and 10.2, which is below the iso-electric point of $BaTiO_3$. The adsorbed amount and the molecular weight fractionation were determined with size exclusion chromatography after mixing times varying from 15 min to 24 days. They initially changed rapidly (within 2 days) and then more gradually over longer periods of time. Changes occured up to 24 days at low KNO_3 concentrations. The kinetics of the fractionation were highly dependent on the chain length, and the salt concentration. The chain-length effects were much more pronounced than could be expected on the basis of differences in diffusion rates. Theoretical calculations predict an electrostatic barrier between the negatively charged PAAS-covered surface and the PAAS chains in the solution. This barrier strongly increases with the length of the PAAS chains in the solution. Accordingly, the probability of reaching the surface decreases and the kinetics slows down. At higher salt concentrations the barrier is lower, and a faster adsorption of the long chains is found. Owing to the presence of the barrier, the length of the chains that displace the initially adsorbed short chains is limited. An adsorption model, in which the packing on the surface and the rearrangement of the adsorbed chains depends on the salt concentration, is introduced. This model is used to discuss further results.

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*A.W.M. de Laat, G.L.T. van den Heuvel and M.R. Böhmer, Colloids Surfaces A: Physicochem. Eng. Aspects, 98 (1995) 61-71.

5.1 INTRODUCTION

Preferential adsorption of the longest chains of a polydisperse, uncharged homopolymer has been reported by several authors [1-5] and is also predicted theoretically for thermodynamic equilibrium [1,6,7]. After mixing a polydisperse polymer solution with particles, the surface is initially covered by the smallest chains because of their higher diffusion rate. These adsorbed small chains are subsequently displaced by the longer ones. Equilibrium is usually assumed to be attained after a period of 1-2 days, when a constant adsorbed amount has been reached.

The adsorption of uncharged polymers is dominated by entropic effects and by polymer-surface and polymer-solvent interactions [8]. With polyelectrolytes the situation is complicated by the charge on the polymer chains and, in many cases, also on the surface of the particles. Fleer et al. [8] gave a systematic evaluation of the various situations which can occur with charged chains and surfaces. Mean-field lattice theories have been developed [9-12] to predict the adsorption behaviour of polyelectrolytes. Results are given for thermodynamic equilibrium which may or may not be achieved with polyelectrolytes. Fleer et al. [8] found good agreement between a range of experimental results and theoretical predictions. Therefore, they conclude that thermodynamic equilibrium can be achieved with polyelectrolytes in many cases. However, they also mention experiments in which thermodynamic equilibrium is not achieved. In a number of cases the final adsorbed amount [13,14] and the conformation of the adsorbed chains [14-17] depend on the experimental route towards the final conditions. Changes in pH and salt concentration often have a large influence. Some authors have reported on molecular weight fractionation and displacement effects [18-23] which depend on the salt concentration in the system. These effects can be explained from non-equilibrium arguments in which an electrostatic barrier hinders the approach of the charged chains in solution to the surface of the particles [8,18,19,24,25].

We have previously reported on the adsorption of polyacrylic acid salts (PAASs) on $BaTiO_3$ at low salt concentrations [18,24]. These studies revealed that the electrostatic barrier, which arises between the polyelectrolyte chains in the solution and the PAAS covered surface, prevents the adsorption of chains of length above a certain limit. The molecular weight fractionation on adsorption depends on the value of this limit relative to the molecular weight distribution (MWD) of the PAAS. If the entire MWD of the PAAS is below the limit, the longest chains adsorb; if the limit is located within the MWD, an apparent preferential adsorption of an intermediate molecular weight fraction is observed; finally, if the MWD is above the limit, adsorption over a wide molecular weight range is observed.

With increasing KNO_3 concentration, the preference for adsorption shifts to higher molecular weights owing to a reduction in the height of the barrier.

In the present study we focus on the adsorption kinetics at several salt concentrations. The adsorbed amount and the molecular weight fractionation in the adsorption of PAAS onto $BaTiO_3$ are measured over periods of time varying from 15 min to several weeks. The theoretical model developed by Böhmer et al. [12] is used to predict the preference in the adsorption with respect to the chain length. Moreover, the effect of the chain length on the height of the electrostatic barrier between a negatively charged surface and negatively charged chains in solution is calculated. Salt effects are also considered. Theoretical predictions are compared with the experimental results.

5.2 EXPERIMENTAL

Two PAASs from the previously used set [18] with different molecular weights were selected for the evaluation of the adsorption kinetics on $BaTiO_3$. The weight-averaged molecular weights of PAAS-10 and PAAS-48 are 10 400 and 47 600, respectively.

The $BaTiO_3$ particles were mixed at room temperature with the PAAS solution at the chosen salt (KNO_3) concentration. After the chosen period of time the particles are removed by centrifugation. Subsequently, the end concentration (C_e) and the MWD of the polyelectrolyte remaining in the supernatant are determined by size exclusion chromatography (SEC) using a refractive index (RI) detector. With SEC the longest chains elute first and are found, consequently, on the left in the chromatograms. The adsorbed amount is determined from the difference between C_e and the initial concentration (C_0), also measured by SEC. Short mixing times suffer from a relatively large uncertainty owing to the time needed for centrifugation. At longer mixing times these deviations become insignificant.

Further characteristics of the products used, and details of the experimental procedures, are available from earlier publications [18,24].

5.3 RESULTS

5.3.1 Adsorption isotherms

The adsorption isotherm of PAAS-10 on $BaTiO_3$ was determined from solutions without added salt, and from 0.1 M KNO_3. The mixing time was 48 h. The pH values in the experiments without added salt and at 0.1 M salt concentration were 8.6-8.9 and 8.9-9.0, respectively. The adsorption isotherm of PAAS-10 without added salt (Fig. 1) shows a high affinity character and reaches a plateau value of 0.46 mg m^{-2} at an equilibrium concentration of about 200 ppm.

The previously measured adsorption isotherm after 24 h of mixing, and at a slightly lower pH [18], showed a more gradual increase in the adsorbed amount but reached the same plateau value.

The adsorption isotherm of PAAS-10 at 0.1 M KNO_3 reaches a higher adsorbed amount: 0.54 mg m^{-2}. This difference is in qualitative agreement with the predicted small effect of salt on the adsorbed amount below a concentration of 0.3 M, where the conformation is not influenced [8].

A few points of the adsorption isotherm of PAAS-48 without added salt were also determined (Fig. 1). The mixing time was 48 h and the pH was 10. The adsorbed amount increases over the entire concentration range studied, but remains lower than the PAAS-10 plateau.

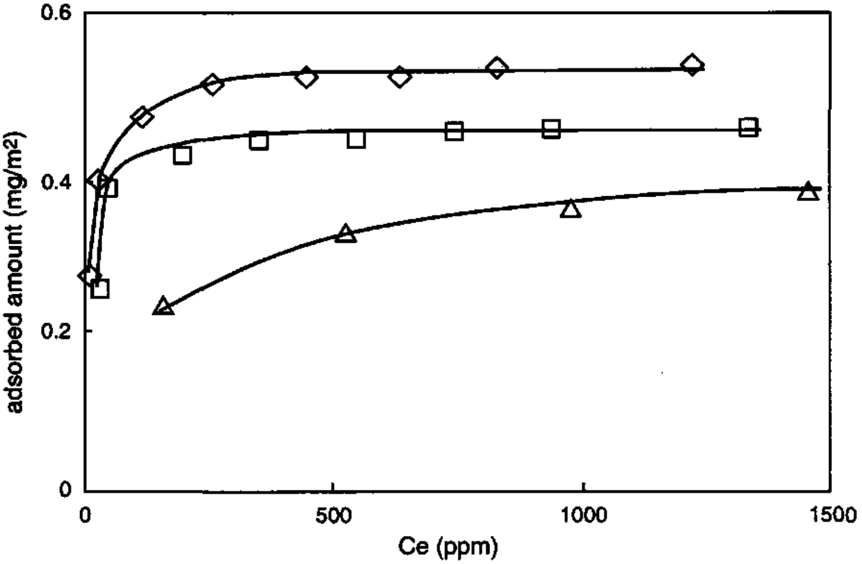

Figure 1 *Adsorption isotherms for PAAS-10 and PAAS-48 on $BaTiO_3$:*
□, *PAAS-10 without added salt;* ◊, *PAAS-10 in 0.1 M KNO_3;*
△, *PAAS-48 without added salt.*

5.3.2 Adsorption kinetics of PAAS-10

The adsorption of PAAS-10 onto $BaTiO_3$ from solutions without added salt, and from solutions at 0.03 M KNO_3, were determined over a period of 24 days. The pH values were between 9.0 and 9.4 in all experiments. Each point in Fig. 2 was obtained from a separate mixture with a C_0 of 1000 ppm PAAS-10. This concentration was chosen to obtain C_e values just in the plateau region after adsorption.

The adsorbed amount from a 0.03 M KNO_3 solution increases significantly over the first 2 days and reaches a value of about 0.51 mg m^{-2} after about 8 days. The adsorbed amount from a solution without added salt also increases significantly over the first 2–3 days. It is somewhat lower than from the 0.03 M salt solution, but continues to increase over a long period of time. Different results were obtained by Chen et al. [26] who reported equilibrium adsorbed amounts of PAAS on $BaTiO_3$ after 1 day at low salt concentration and pH=10.5. Small differences in the experimental conditions or in the polyelectrolytes and particles probably have a large influence.

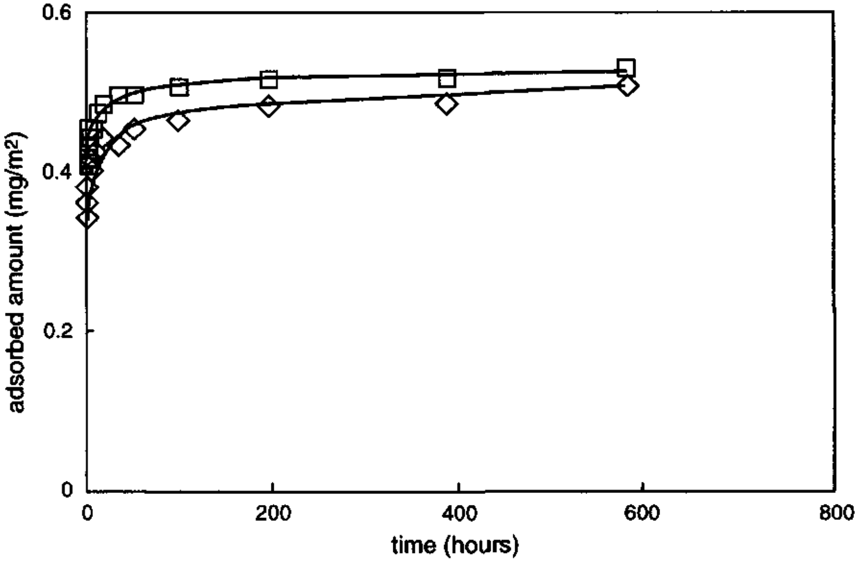

Figure 2 Adsorption of PAAS-10 with time from 1000 ppm solution: ◊, without added salt; □, with 0.03 M KNO$_3$.

First, we present the results for the changes in the molecular weight fractionation with time from a salt-free solution. After a mixing time of 15 min, adsorption has taken place over the entire molecular weight range, but the adsorption from the lower part of the MWD (right of the centre in the chromatogram) is much higher than that from the longer chains (Fig. 3).

The preferential adsorption of an intermediate fraction is already apparent after 15 min. Over longer periods of time the MWD in the adsorbed layer gradually changes. An increase in the adsorption of chains of intermediate length occurs, while the adsorption of the longest chains remains unchanged. Some desorption of the chains with a retention time (R_t) of about 24 min occurs, but the amount (on weight basis) is far below the increased adsorption of the longer chains. Remarkably, the shortest chains, R_t=25.5 min, show a small increase in adsorption. Despite the small differences, we believe that these changes with time in the low molecular weight range are real because of their systematic nature. Note the common intersection point at $R_t \approx 24.5$ min. The adsorption of the longer chains even increases between 16 and 24 days, which is reflected by the adsorbed amount (Fig. 2).

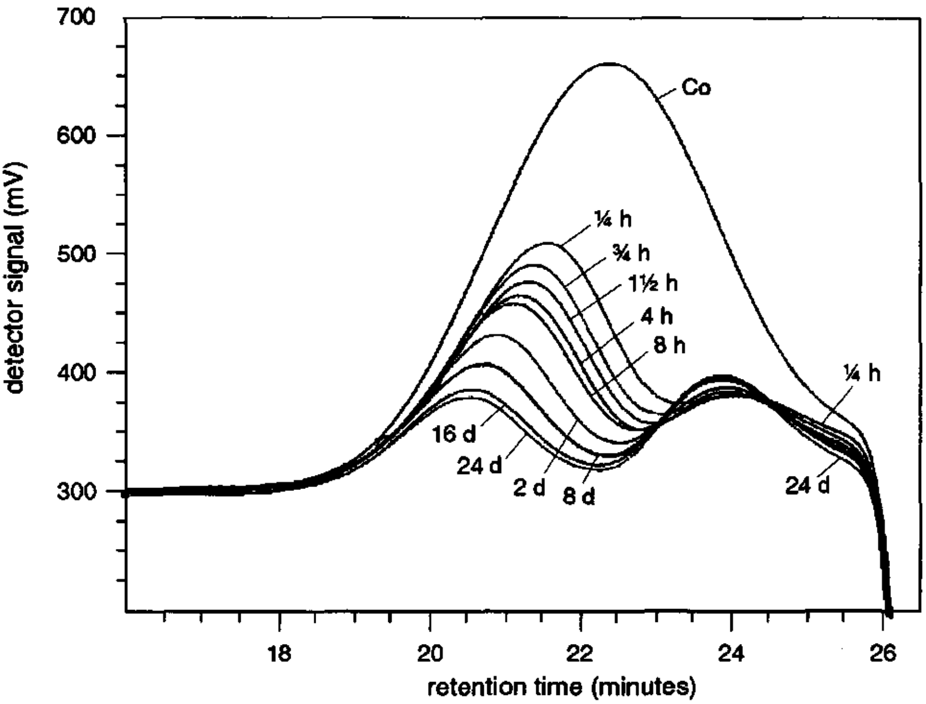

Figure 3 *Change in molecular weight fractionation with time in the adsorption of PAAS-10 onto* $BaTiO_3$ *without added salt: chromatogram before adsorption* (C_0)*; chromatograms after adsorption for the indicated time in hours (h) or days (d).*

Owing to the gradually increasing adsorption of the long chains, and the desorption of the smaller ones, the MWD at the surface completely changes. The molecular weight of the fraction with the highest preference (the minimum in the C_e chromatogram) shifts to higher values with time.

In the adsorption of PAAS-10 from 0.03 M KNO_3, the molecular weight fractionation is different from the first point at 15 min (Fig. 4).

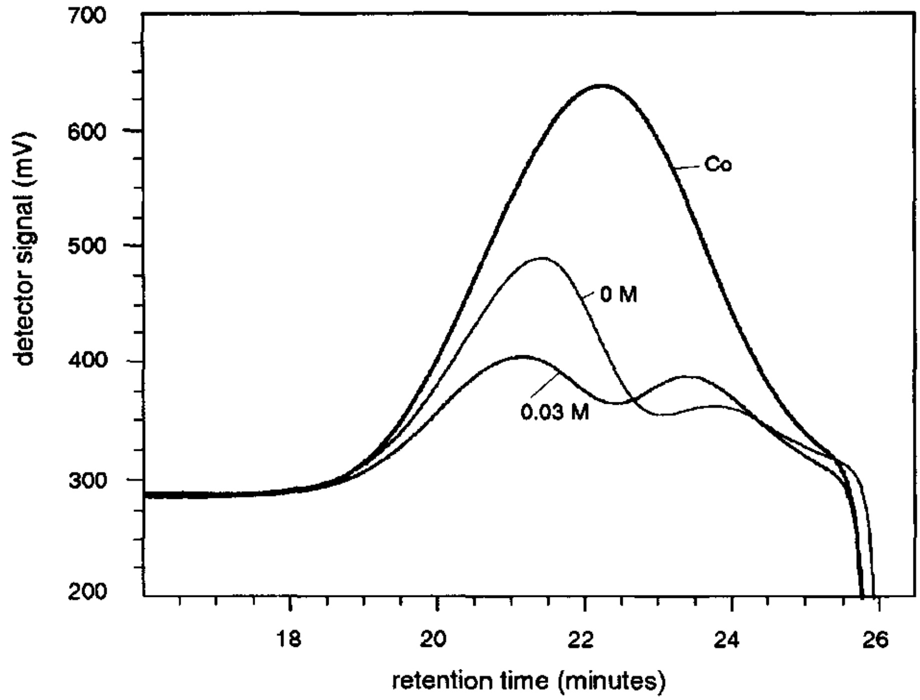

Figure 4 *Effect of salt on the fractionation after 15 min: chromatogram before adsorption (C_0) compared with the chromatograms after adsorption from KNO_3 solutions with concentrations as indicated.*

A larger part of the high molecular weight fraction has adsorbed, along with fewer small chains. With added salt, the minimum is situated at a higher molecular weight. Again, adsorption takes place over the entire molecular weight range.

Over longer periods of time (Fig. 5) the change in the molecular weight fractionation is similar, but not the same as in the experiment without added salt.

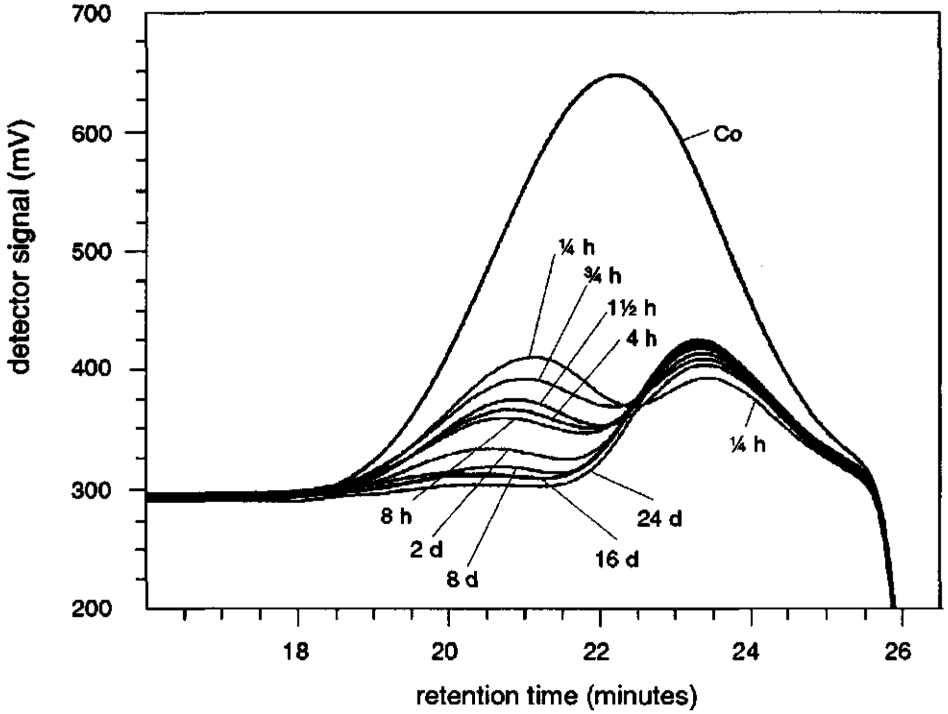

Figure 5 *Change of the molecular weight fractionation with time in the adsorption of PAAS-10 onto $BaTiO_3$ from 0.03 M KNO_3: chromatogram before adsorption (C_0); chromatograms after adsorption for the indicated time in hours (h) or days (d).*

At 0.03 M KNO_3 even the longest chains contribute to the increased adsorption with time. The desorption of the smaller chains is much more pronounced and now also occurs for the smallest chains. The major part of the long chains has adsorbed after about 8 days.

Comparing the adsorption from salt-free solutions and from 0.03 M KNO_3 after 24 days of mixing shows that the adsorbed amounts are almost the same (Fig. 2), but the molecular weight fractionation is different (Figs 3 and 5). There are many more long chains on the surface of the particles in 0.03 M KNO_3 solution.

5.3.3 Adsorption kinetics of PAAS-48

The adsorption kinetics of the higher molecular weight PAAS-48 are studied from solutions without added salt and from 0.01 and 0.03 M KNO_3. The initial PAAS concentration was 1500 ppm and the pH values were between 9.8 and 10.2 for all experiments. The results (Fig. 6) show somewhat higher adsorbed amounts at higher salt concentrations.

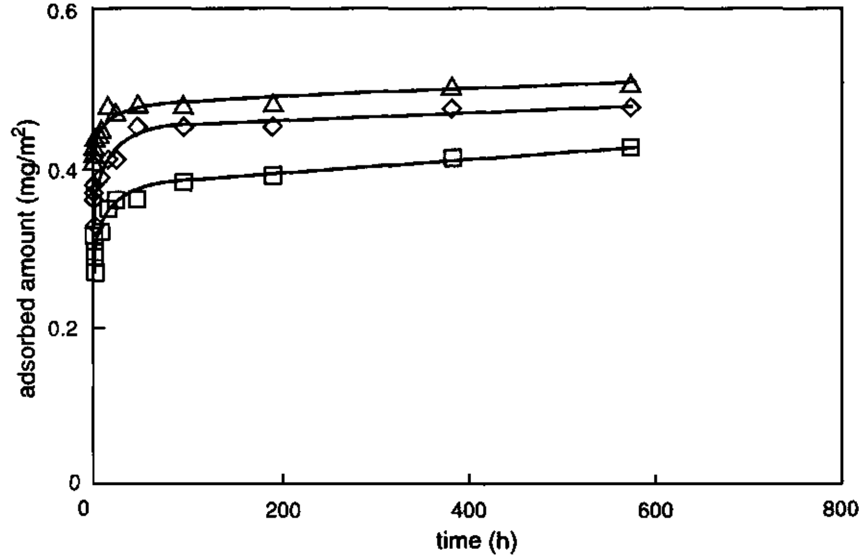

Figure 6 Adsorption of PAAS-48 with time from 1500 ppm solution:
□, without added salt; ◊, in 0.01 M *KNO_3; △, in 0.03 M* *KNO_3.*

There is a significant increase in the adsorbed amounts for all three experiments in the first 48 h. The adsorbed amounts from 0.01 and 0.03 M KNO_3 solutions remain fairly constant after about 100 h, while from salt-free solutions the adsorbed amount increases for at least 24 days.

The changes in the molecular weight fractionation with time are given in Figs 7-9 for the adsorption from 0, 0.01 and 0.03 M KNO_3 solutions, respectively. The difference between the C_0 and the C_e chromatograms after 15 min reveal that, initially, adsorption takes place over the entire molecular weight range at all salt concentrations with a preference for the short chains.

In the experiment without added salt (Fig. 7), it is found that over long periods of time an increased adsorption of intermediate molecular weight chains occurs.

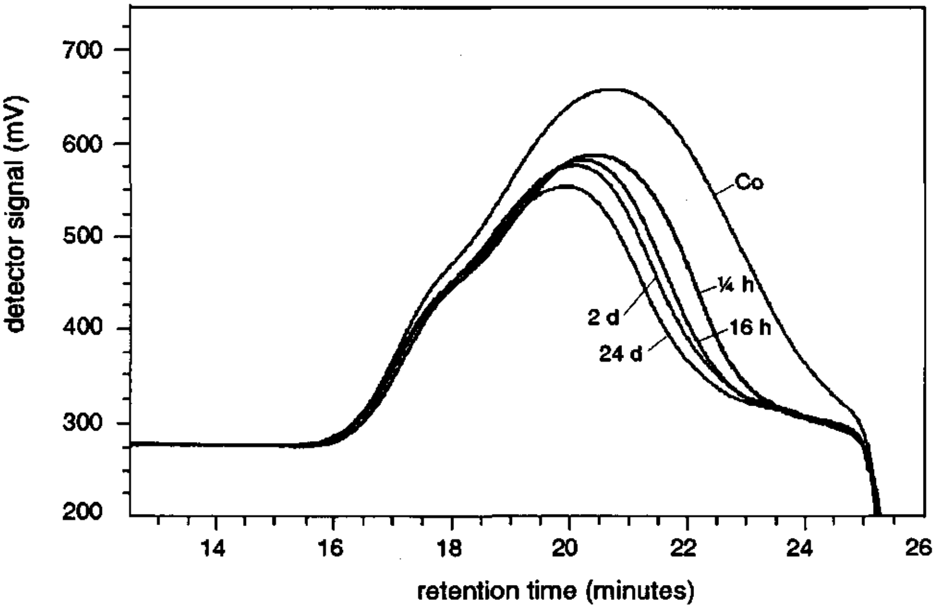

Figure 7 *Change in the molecular weight fractionation with time in the adsorption of PAAS-48 onto* BaTiO$_3$ *without added salt: chromatogram before adsorption* (C_0)*; chromatograms after adsorption for the indicated time in hours (h) or days (d).*

Apart from some variation in the chromatograms below R_t=19 min there is no systematic change. Therefore it is concluded that the adsorbed amount of the longest chains does not change over the 24-day period. Another remarkable feature is the lack of desorption of short chains.

The adsorption from 0.01 M KNO$_3$ solutions (Fig. 8) shows the same trend, but now chains with a higher length, up to R_t=17.5 min, participate in the increasing adsorption with time.

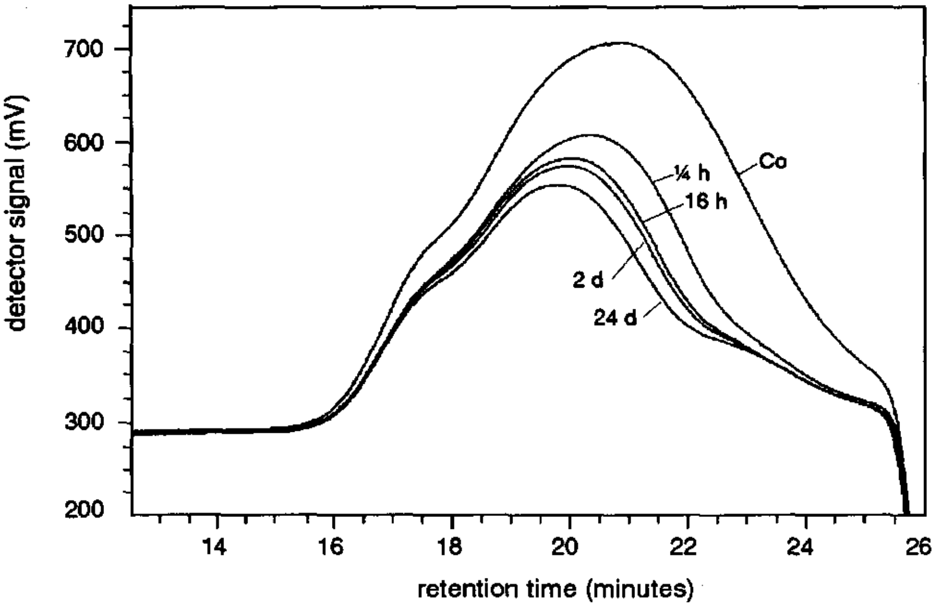

Figure 8 *Change in the molecular weight fractionation with time in the adsorption of PAAS-48 onto BaTiO$_3$ from 0.01 M KNO$_3$; chromatogram before adsorption (C$_0$); chromatograms after adsorption for the indicated time in hours (h) or days (d).*

In the low molecular weight range the chromatograms are practically the same. Again, there seems to be no desorption of small chains with time.

In 0.03 M KNO$_3$ solutions (Fig. 9) even the longest chains contribute to the increasing adsorption with time, although the relative partitioning decreases with increasing molecular weight.

In the low molecular weight range there is a sudden change in the chromatograms after 16 h. However, as no gradual systematic change is found, this is considered as an artefact. Once again it can be concluded that there is hardly any desorption of small chains.

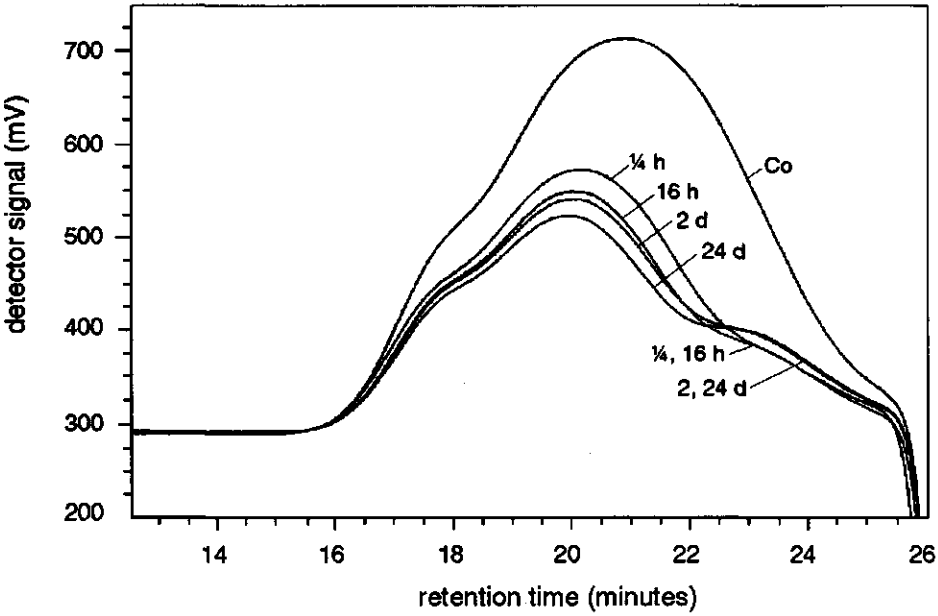

Figure 9 *Change in the molecular weight fractionation with time in the adsorption of PAAS-48 onto $BaTiO_3$ from 0.03 M KNO_3: chromatogram before adsorption (C_0); chromatograms after adsorption for the indicated time in hours (h) or days (d).*

In Fig. 10 the molecular weight fractionation after 24 days is compared for the three salt concentrations chosen.

At higher salt concentration a greater number of long chains are adsorbed, while the adsorption of short chains decreased. As virtually no changes with time are found in the adsorption of the small chains, this difference must have taken place within the first 15 min after contact.

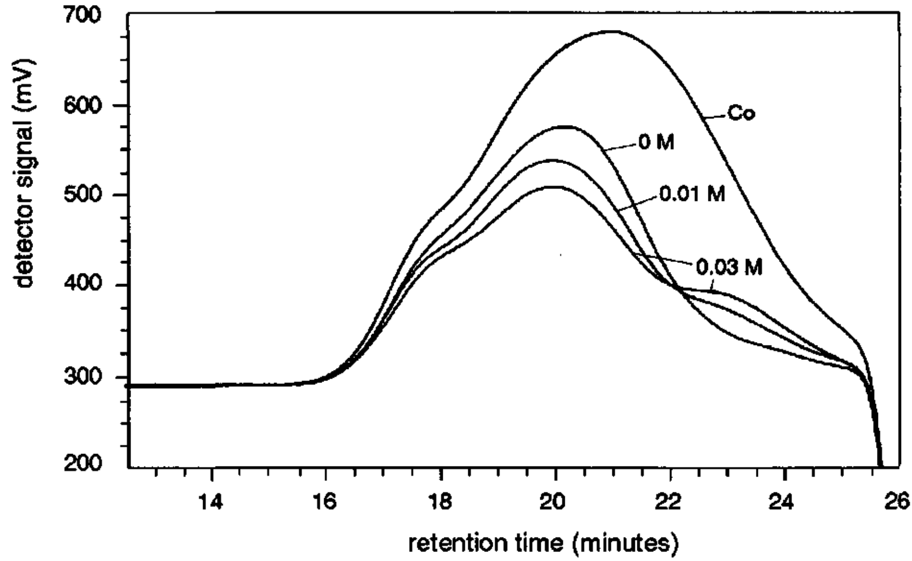

Figure 10 Molecular weight fractionation of PAAS-48 after 24 days of adsorption onto $BaTiO_3$: chromatogram before adsorption (C_0) compared with the chromatograms after adsorption from KNO_3 solutions with concentrations as indicated.

5.4 THEORETICAL PREDICTIONS

5.4.1 Outline of theory

The electrostatic repulsion between charged chains in solution and a surface of the same charge sign will result in a zone close to the surface containing a lower concentration of chains, the depletion layer. The expressions 'depletion layer' and 'electrostatic barrier' (between the chains in solution and the surface) are closely connected. The characteristics of the depletion layer are therefore expected to be important for the adsorption kinetics of the charged chains.

Van der Schee and Lyklema [9] showed some examples of depletion layers calculated using a mean-field lattice theory. Here, we will present some results obtained with the multilayer Stern model [12]. This is based on the self-consistent lattice theory, originally developed for homopolymer adsorption by Scheutjens and Fleer [8]. Using this theory, the equilibrium distributions perpendicular to the surface of polymer segments, solvent, and salt ions are calculated by minimizing the free energy of the system. A volume fraction profile is obtained from which, for example, the adsorbed amount can be calculated. The contact interactions, e.g. those between a polymer segment (p) and the solvent (o), are accounted for by using Flory-Huggins interactions parameters, χ_{po}. Flory-Huggins type interaction parameters between a segment and the surface (s) are also used. The conformational statistics on the lattice are evaluated using a matrix multiplication method. The electrostatic potential profile is calculated by dividing the space adjacent to the surface into charged planes and charge-free zones. The charged planes are located in the centres of the lattice layers. The space between these midplanes is free of charge, and therefore the potential decay between two midplanes is linear provided that the dielectric constant does not vary between lattice layers. Recently, Israëls et al. [27] suggested corrections in the multilayer Stern model to account for dissociation equilibria close to the surface more precisely than in the original model. As these changes only apply to the adsorption of weak polyelectrolytes, they can be omitted in the present calculations for strong polyelectrolytes. At high pH, a PAAS behaves as a strong polyelectrolyte.

5.4.2 Choice of parameters

The calculations were performed using a hexagonal lattice with lattice parameter λ_1, and the fraction of neighbouring lattice sites in the adjacent layer equal to 3/12. Because electrostatic forces are considered, the thickness (d) of a lattice layer is required for the calculation of potential differences; we used d = 0.6 nm. All calculations were done for a system of 40 layers adjacent to an adsorbing surface. The interaction parameter between an adsorbing polyelectrolyte segment and the surface (χ_{ps}) was set at −10 kT, which corresponds to $\chi_s = 2.5$ in the often-used Silberberg notation [8]. The other components in the system, salt ions, water and, in some calculations, non-adsorbing polyelectrolyte, do not have a specific interaction with the surface. The interaction parameter between polyelectrolyte and solvent was set at 0.5; the same value was used for polyelectrolyte-salt ion interactions. Salt ion-solvent interactions were assumed to be 0. The polyelectrolyte had a valency of –1 per segment and a bulk volume fraction of 10^{-4}. The relative dielectric constant was assigned a value of 80.

5.4.3 Preferential adsorption

First, the equilibrium volume fraction profile was calculated for a system containing three polymers A_{10}, A_{20} and A_{50}, with a different number of segments per chain, r = 10, 20 and 50 respectively, from a 10^{-3} M univalent salt solution. The surface charge ($\sigma(0)$) was fixed at +100 mC m^{-2}, which is equivalent to 0.225 charges per site. The results in Fig. 11 show that adsorption of the longest chains is preferential, similar to the results for uncharged chains [1,6,7].

There is some adsorption of the shorter chains, but the adsorbed amount in the first layer is about two orders of magnitude lower than that of the longest chains. Somewhat further away from the surface a depletion layer appears, as anticipated. This is a common feature of polyelectrolyte adsorption if overcompensation of the surface charge occurs [9].

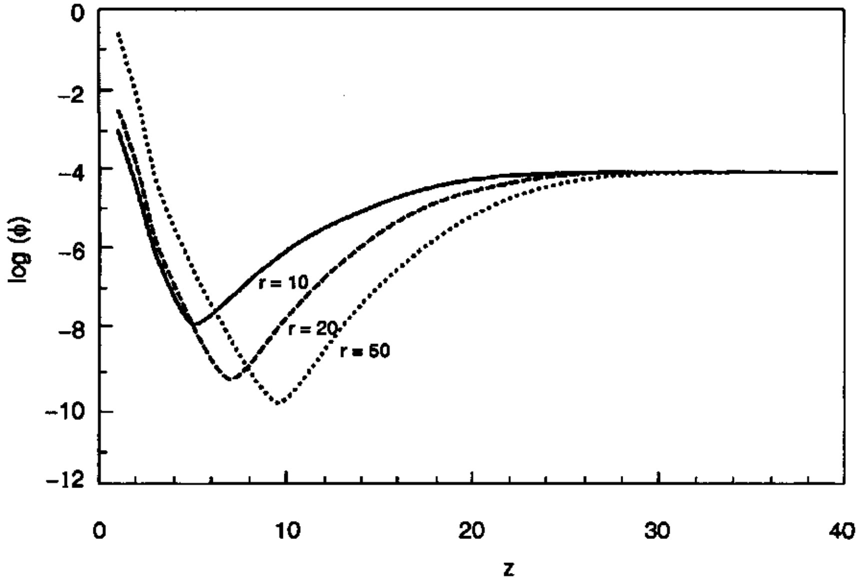

Figure 11 *Volume fraction profiles after adsorption from a mixture of three polyelectrolytes with different chain lengths at a positively charged wall: valency per segment = –1; bulk volume fraction = 10^{-4}; $\sigma(0)$ = 100 mC m^{-2}; χ_{ps} = –10 kT; Φ, volume fraction; z, lattice layer; number of segments per chain as indicated.*

5.4.4 Depletion layers

The volume fraction profiles in Fig. 11 have contributions from both adsorbed and free polyelectrolyte chains.

To get an impression of the volume fraction profiles of the non-adsorbed chains only, some additional calculations were carried out. The system was modified by modelling the surface and the adsorbed layer together as a non-adsorbing wall. We used $\chi_{ps} = 0$ and a $\sigma(0)$ value of –5 mC m^{-2}. The $\sigma(0)$ value represents the net charge of the system in the previous calculation of the surface and the two adjacent layers where more than 90% of the adsorbed chains are present. The results (Fig. 12) show that the depth of the depletion layer increases strongly with chain length, while only a small effect on the thickness of the depletion layer is apparent.

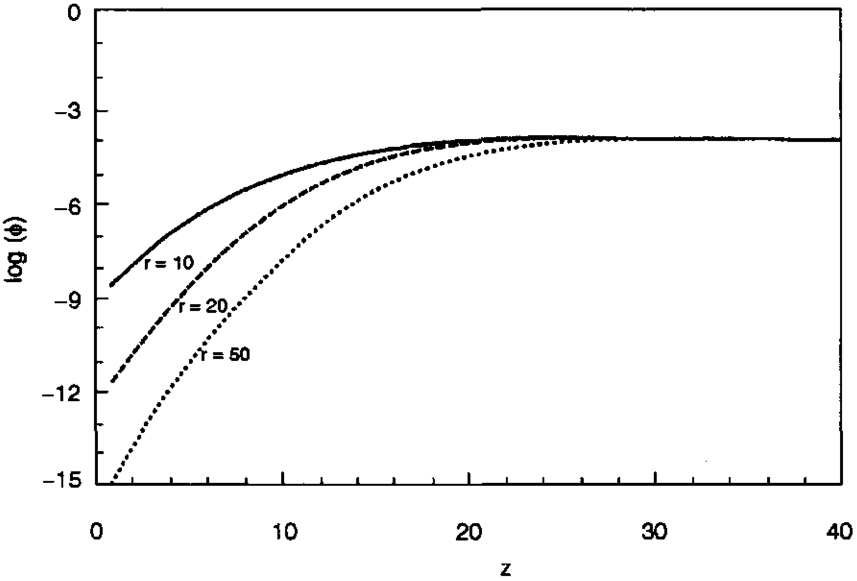

Figure 12 Volume fraction profiles of a mixture of three polyelectrolytes with different chain lengths adjacent to a negatively charged wall; valency per segment = −1; bulk volume fraction = 10^{-4}; $\sigma(0)$ = −5 mC m^{-2}; χ_{ps} = 0 kT; Φ, volume fraction; z, lattice layer; number of segments per chain as indicated.

The effect of the salt concentration (c_s) on the depletion layer thickness is demonstrated for one chain length, r = 50, in Fig. 13. The surface charge is again assumed to be −5 mC m^{-2}.

Both the thickness and the depth of the depletion layer shrink with increasing salt concentration but, even at a salt concentration of 0.1 M, the volume fraction in layer 1 is still two orders of magnitude lower than in the bulk. At c_s = 1 M, the volume fraction profile for A_{50} is very similar to that for an uncharged polymer of the same length, which is included in Fig. 13. The electrostatic charges are effectively screened at this salt concentration. A comparison of Figs 12 and 13 shows that the profile of the depletion layer is mainly determined by the total charge on the chains, while the length itself has only a minor effect. The difference in volume fraction profiles for A_{10}, A_{20} and A_{50} (Fig. 12) is mainly due to the difference in total charge for these three polymers.

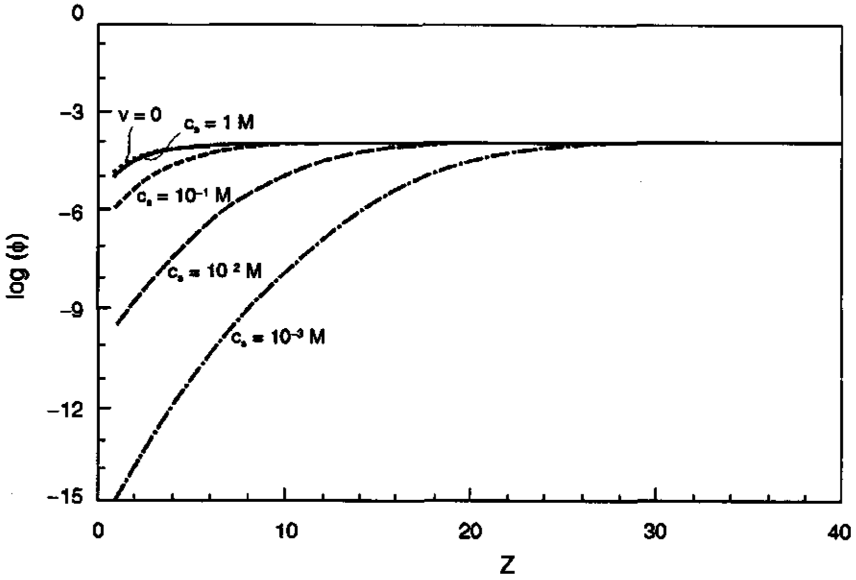

Figure 13 *Volume fraction profiles for A_{50} at different salt levels adjacent to a negatively charged wall: salt concentration as indicated; V=0, uncharged polymer of the same length; valency per segment = −1; bulk volume fraction = 10^{-4}; $\sigma(0) = -5$ mC m^{-2}; $\chi_{ps} = 0$ kT; Φ, volume fraction; z, lattice layer.*

5.5 DISCUSSION

The experimental results clearly show that equilibrium is not easily attained in the adsorption of PAASs onto $BaTiO_3$. The adsorbed amount and the molecular weight fractionation change over long periods of time, especially at low salt concentrations. The chain-length dependent kinetics, and the change with salt concentration, can be understood using the theoretical predictions presented.

Depletion layers are modelled by calculating the volume fraction profiles of the non-adsorbing charged chains close to a charged surface. In the multilayer Stern model, the segment weighting factors (the relative probability of finding a free segment in a certain layer with respect to the bulk solution) contain a Boltzman factor to take into account electrostatic forces. For chain molecules, these segment weighting factors have to be multiplied for each segment. Therefore, the electrostatic contribution depends strongly on the chain length, and can easily become very significant. This effect causes the strong increase in the depth of the depletion layer as the length (total charge) of the chains increases. With increasing salt concentration, the charge effects reduce, and the depletion layer gradually shrinks.

With these results for thermodynamic equilibrium, it can be stated that in a dynamic situation the approach of charged chains to a similarly charged surface is hindered by the electrostatic repulsion. Because the concentration of the polymer chains close to the surface will determine the adsorption kinetics, the depth of the depletion layer seems to be more important than the width. The hindering is expected to increase strongly with chain length, as the segmental concentration of charged chains close to the charged surface strongly decreases with the chain length. A chain-length dependent kinetic behaviour, much too strong to be caused solely by the differences in diffusion rate, is to be expected. At increased salt levels, partial screening of the electrostatic repulsion occurs. Accordingly, the depth of the depletion layer will be less, and a higher adsorption rate is to be expected for a given chain length.

A comparable adsorption process has previously been postulated in a more qualitative way [18,24].

Many of the experimental results match the theoretical predictions. In all experiments an increasing adsorption with time of longer chains is found, supporting the predicted preferential adsorption of long chains. The increasing adsorption with time depends on the chain length for both PAASs (Figs 3 and 7). Chains of intermediate length continue to adsorb over long periods of time, while no changes occur with chains above a certain length (Figs 3 and 7). This experimental result matches the predicted chain-length dependent kinetic behaviour. At higher salt levels in the experiments with both PAAS-10 and PAAS-48 (Figs 5,8,9), longer chains are involved in the increased adsorption with time. These experiments support the predicted effect of salt on the chain-length dependent adsorption kinetics.

More of the present results are included in the discussion, in a more qualitative way, by recalling the proposed adsorption process from initial contact [18], at which all chains close to the positively charged surface will adsorb. As small chains have higher rates of diffusion, many of these are expected to adsorb, but some longer chains will also be involved. This explains the adsorption of a small part of the high molecular weight range at the first point, measured after 15 min. As soon as the surface charge is overcompensated, the electrostatic barrier develops, slowing down the approach of the chains to the surface relative to their length. Chains above a certain length will be unable to reach the surface. Smaller chains can still can get to the surface and will continue to adsorb. Above a certain surface coverage, displacement of the smallest chains by larger ones begins. Owing to the chain-length dependent kinetics, the exchange is expected to start with chains slightly larger than the adsorbed ones, and gradually proceed over the available chain length range until the limit is reached. This explains the preferential adsorption of an intermediate molecular weight fraction and the gradual shift in the preference to higher molecular weights with time for PAAS-10 (Figs 3,5) and PAAS-48 (Figs 7-9).

A remarkable result in all experiments is the incomplete desorption of the short chains. For PAAS-10 in the absence of salt, the adsorption of the shortest chains ($R_t \approx 25.5$ min) even increases with time, while desorption of slightly longer chains ($R_t \approx 24$ min) is found to occur. The salt concentration clearly has an effect. Increasing it stimulates the desorption of the short chains of PAAS-10 (Figs 3,5). Moreover, all short chains participate in the desorption. With PAAS-48 the salt concentration determines the amount of short chains desorbed after 15 min, while at longer periods of time no increase in desorption is found.

An explanation of these effects is possible by the postulation of a different coverage of the surface by the adsorbed chains under various conditions. Polyelectrolytes are expected to adsorb in a flat conformation at low salt concentration [8]. Coiling of the chains is not expected at 0.03 M KNO_3.

Significant differences in the conformation of the adsorbed chains for various salt concentrations used are therefore not expected. The rigid chains will not come close to each other due to mutual electrostatic repulsion. This repulsion limits the adsorbed amount. At a higher salt concentration the repulsion between the adsorbed chains is reduced, allowing a closer approach and a higher adsorbed amount. Indeed, slightly higher adsorbed amounts are found at higher salt concentrations for both PAAS-10 (Fig. 2) and PAAS-48 (Fig. 6).

A homogeneous, high coverage of the surface of the particles will be difficult to attain with long chains at low salt concentrations. The electrostatic repulsion between the chains is expected to interfere with the rearrangements of the chains, especially the long ones. The gaps between the long chains may, however, be occupied by smaller ones. Displacement of these small chains is not necessary, because the large chains cannot approach each other more closely. This effect may serve as an explanation for the experimental result, which shows that a fraction of the small chains remains adsorbed in all experiments even after long periods of time. In the experiment with PAAS-10 in the absence of salt (Fig. 3), the increased adsorption of the smallest chains (R_t>24.5 min) with time while long chains (R_t<23 min) adsorb and intermediate chains (R_t≈23.5 min) desorb, may also be explained in this way. The presence of increasingly larger chains on the surface causes larger gaps which can be filled with the smallest chains, while the chains of intermediate length do not fit. At higher salt concentrations the chains on the surface will be able to approach each other more closely and the gaps will be smaller. This is consistent with the increased desorption of the smaller chains in the experiment with PAAS-10 at 0.03 M KNO_3 (Fig. 5). Obviously, at this salt concentration even the smallest chains do not fit into the gaps between the larger ones, as no increased adsorption of the smallest chains is found (Fig. 5).

Also, in the experiments with PAAS-48, fewer short chains remain adsorbed at higher salt concentrations (Fig. 10). With PAAS-48 the number of short chains adsorbed does not change after the first 15 min, contrary to the PAAS-10 results. As the adsorbed amounts are comparable, the effect of the barrier on the adsorption kinetics is expected to be the same. Indeed, the increased adsorption with time takes place from the same molecular weight range for both PAASs. The main difference is the chain-length distribution of the adsorbed chains. In the experiment with PAAS-48, longer chains have adsorbed, probably at initial contact before the barrier was effective. Obviously, this fraction of long chains on the surface has a large influence on the rearrangement and the desorption process.

The surface rearrangement rate of the adsorbed chains can be expected to depend on the electrostatic interaction between the surface and the polymer segments. Moreover, the chain length is also expected to have an effect. Long chains will be hindered by other adsorbed chains at lower coverages than short chains. The surface rearrangement rate can be expected to influence the increase of the adsorbed amount with time. Chains arriving at the surface can adhere more easily if currently adsorbed chains can move aside faster. At 15 min the adsorbed amounts of PAAS-10 and PAAS-48 in the experiment without added salt are 0.34 and 0.29 mg m^{-2}, respectively, i.e. almost the same. At longer periods of time the increase in the adsorbed amount is much slower for PAAS-48. As noted above, the main difference is the presence of a larger number of longer chains on the surface with PAAS-48, which obviously slows down the adsorption kinetics. We expect this to be caused by a lower rearrangement rate of the longer chains on the surface.

The increase in the adsorbed amount is faster at a higher salt concentration for both PAAS-10 (Fig. 2) and PAAS-48 (Fig. 6). Moreover, the results at 0.03 M KNO_3 are practically the same for both PAASs. A faster rearrangement rate is expected at a higher salt concentration owing to a reduction in the electrostatic attraction between the polymer segments and the surface, which allows a faster increase in the adsorbed amount. Obviously, the chain-length effect has vanished at 0.03 M KNO_3.

5.6 CONCLUSIONS

The adsorbed amount and molecular weight fractionation of PAAS in the adsorption onto $BaTiO_3$ change over long periods of time, up to 24 days at low salt concentration. The preferential adsorption of an intermediate molecular weight fraction of PAAS-10 and PAAS-48, and the influence of salt on the fractionation, can be understood on the basis of theoretical calculations. Theory predicts the preferential adsorption of the longest chains at thermodynamic equilibrium, but the presence of a depletion layer points to a kinetic barrier which hinders the approach of charged chains to an equally charged surface. A strong dependence of the chain length on the depth of the depletion layer is predicted. The significant decrease in the segmental probability close to the surface with increasing chain length predicts a chain-length dependent kinetic behaviour. At increased salt concentrations the depletion layer shrinks, and less effect on the adsorption kinetics is expected.

The experimentally determined adsorption over the entire molecular weight range at first contact can be understood by considering the initial phase of the adsorption process.

With the introduction of a chain-length and salt-concentration dependent packing and rearrangement rate of the adsorbed chains, further experimental results can be explained, including the incomplete desorption of the small chains, the increased desorption of the small chains at higher salt concentration, the slightly higher adsorbed amount at higher salt concentration, and, finally, the faster increase in the adsorbed amount with time at higher salt concentrations.

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REFERENCES

[1] M.A. Cohen Stuart, J.M.H.M. Scheutjens and G.J Fleer, J. Polym. Sci. Polym. Phys. Ed., 18 (1980) 559.

[2] H.F. Huisman, H.J.M. Pigmans, A.J.P. Roegies and W.J.J.M. Sprangers, Progr. Org. Coatings, 13 (1986) 377-420.

[3] R.E. Felter, E.S. Moyer and L.N. Ray, J. Polym. Sci. part B, 7 (1969) 529.

[4] R.E. Felter and L.N. Ray, J. Colloid Interface Sci., 32 (1970) 349.

[5] C. van der Linden and R. van Leemput, J. Colloid Interface Sci., 67 (1978) 63.

[6] R.-J. Roe, Polym. Sci. Technol., 12B (1980) 629.

[7] J.M.H.M. Scheutjens and G.J. Fleer, in Th.F. Tadros (Ed.), The effect of polymers on dispersion properties, Academic Press, New York, 1982.

[8] G.J. Fleer, M.A. Cohen Stuart, J.M.H.M. Scheutjens, T. Cosgrove and B. Vincent, Polymers at interfaces, Chapman & Hall, London, 1993.

[9] H.A. van der Schee and J. Lyklema, J. Phys. Chem., 88 (1984) 6661-6667.

[10] J. Papenhuijzen, H.A. van der Schee and G.J. Fleer, J. Colloid Interface Sci., 104 (1985) 540.

[11] O.A. Evers, G.J. Fleer, J.M.H.M. Scheutjens and J. Lyklema, J. Colloid Interface Sci., 111 (1986) 446.

[12] M.R. Böhmer, O.A. Evers and J.M.H.M. Scheutjens, Macromolecules, 23 (1990) 2288-2301.

[13] J. Meadows, P.A. Williams, M.J. Garvey, R.A. Harrop, G.O. Phillips, Colloids Surfaces, 32 (1988) 275-288.

[14] J. Meadows, P.A. Williams, M.J. Garvey, R.A. Harrop, J. Colloid Interface Sci., 148 (1992) 160-166.

[15] K.F. Tjipangandjara, Y-B. Huang, P. Somasundaran and N.J. Turro, Colloids Surfaces, 44 (1990) 229-236.

[16] K.F. Tjipangandjara, P. Somasundaran, Colloids Surfaces, 55 (1991) 245-255.

[17] P.F. Luckham and J. Klein, J. Chem. Soc. Faraday Trans. 1, 80 (1984) 865-878.

[18] A.W.M. de Laat and G.L.T. van den Heuvel, Colloids Surfaces A: Physicochem. Eng. Aspects, 98 (1995) 53-59.

[19] U.S. Adam and I.D. Robb, J. Chem. Soc. Faraday Trans. 1, 79 (1983) 2745-2753.

[20] R. Ramachandran and P. Somasundaran, J. Colloid Interface Sci., 120 (1987) 184-188.

[21] R. Ramachandran and P. Somasundaran, Colloids Surfaces, 32 (1988) 307-317.

[22] R. Ramachandran and P. Somasundaran, Colloids and Surfaces, 32 (1988) 319-329.

[23] J.A. Wright, R. Harrop and P.A. Williams, Colloids Surfaces, 24 (1987) 249-258.

[24] A.W.M. de Laat and G.L.T. van den Heuvel, Colloids Surfaces A: Physicochem. Eng. Aspects, 70 (1993) 179-187.

[25] D.R. Bain, M.C. Cafe, I.D. Robb and P.A. Williams, J. Colloid Interface Sci., 88 (1982) 467-470.

[26] Z.-C. Chen, T.A. Ring and J. Lemaître, J. Am. Ceram. Soc., 75 (1992) 3201-3208.

[27] R. Israëls, F.A.M. Leermakers and G.J. Fleer, Macromolecules, 27 (1994) 3087-3093.

CHAPTER 6

Colloidal stabilization of BaTiO3 with polyvinyl alcohol in water*

Abstract

Several polyvinyl alcohol (PVA) based copolymers were tested with respect to their ability to provide sterically stabilized $BaTiO_3$ dispersions. Regular PVA types, regardless of the degree of hydrolysis and the vinylacetate block character, cannot stabilize $BaTiO_3$. Block copolymers of PVA with a carboxylic acid-containing block proved to be successful. Random copolymers based on PVA with a few per cent of carboxylic-acid containing monomers were also studied. Some of these products can stabilize $BaTiO_3$ while others cannot. Depletion flocculation is not found with the block copolymers but does occur with dispersions stabilized with a random copolymer. The stabilizing mechanism is purely steric in the case of the block copolymers, while a combination of steric and electrostatic repulsion is found with the stabilizing random copolymer.

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*A.W.M. de Laat and W.P.T. Derks, Colloids Surfaces A: Physicochem. Eng. Aspects, 71 (1993) 147-153.

6.1 INTRODUCTION

Homogeneous green products are needed to prevent defects in the sintered product [1]. Itoh et al. [2] have studied the relation between the quality of the aqueous dispersion and the homogeneity of settled and compacted $BaTiO_3$ layers. Dense and homogeneous layers have been obtained with suitable dispersants. The formulations, however, contain no binder and are therefore unsuitable for the preparation of green products with sufficient strength. Formulations with binders have been reported by Hui et al. [3], however, no information on the homogeneity has been given. In our experience, flocculation of the particles occurs upon the addition of a polyvinyl alcohol (PVA) binder to a dispersion of $BaTiO_3$ stabilized with a polyelectrolyte.

The present study is focussed on the stabilization of $BaTiO_3$ without the use of separately added dispersants but directly with PVA, employing the principle of steric stabilization [4]. Steric stabilization requires a sufficiently thick adsorbed polymer layer. Stabilization of latexes and emulsions with PVA is well known [5,6]. An increased block character of the vinyl acetate units in the PVA is beneficial [6]. The adsorption mechanism of PVA on hydrophilic inorganic oxides is different [7] and also the ability to obtain steric stabilization can be different. Although literature is available on the adsorption of PVA on inorganic hydrophilic surfaces [7] and repulsion measurements between macroscopic bodies [8,9], we have found no studies concerning the steric stabilization of $BaTiO_3$ with PVA.

In the present study, several types of PVA and PVA-based copolymers were tested with respect to their ability to stabilize $BaTiO_3$. The PVA types include those differing in their degree of hydrolysis and the block character of the acetate units. From previous experiments [10] it was concluded that PVA does not adsorb from a mixture of PVA and the NH_4-salt of a polyacrylic acid. This result leads us to the definition of potentially suitable copolymers. A block copolymer with one block having carboxylic acid groups followed by one PVA block is expected to adsorb by means of the acid-containing block, leaving the PVA block in solution; this will make up the steric barrier. Unfortunately the commercial availability of such block copolymers is very limited. An alternative possibility could be a PVA-based copolymer with some randomly distributed carboxylic acid groups. If these acid groups can prevent the PVA from adsorbing on the particle surface there is a chance of obtaining a sufficiently thick steric barrier.

6.2 EXPERIMENTAL

6.2.1 Materials

The $BaTiO_3$ powder used in this study has a number-average particle size of 1.1 μm and a specific surface area of 3 $m^2\ g^{-1}$ according to the BET method. The isoelectric point is at pH=9.9 [10].

The PVA-based copolymers can be subdivided into three groups. The first group contains the regular PVA's without carboxylic acid groups. We have used Mowiol 18/88 and 20/98 (Hoechst, Frankfurt am Main, Germany) with weight-average molecular weights of 84 000 and 70 000, respectively. The second number in the product code is the degree of hydrolysis in mole per cent. In addition, we have used Poval PVA-217C, PVA-217E and PVA-217EE (Kuraray, Osaka, Japan), all with a degree of hydrolysis of about 88%. The C type is the usual one while the E and EE types have an increased vinyl acetate block character.

The second group contains the carboxylic acid-PVA block copolymers (PVA-b-COOH). We asked all major PVA manufacturers for such a product but Kuraray had the only one suitable, which was called Kurastomer AP-22. This product contained about 20 wt% of acid. On request, Kuraray synthesized two products having a lower amount of acid groups: X-0074, with about 1.5% and X-0075, with about 5% of acid groups.

The PVAs with a few per cent of randomly distributed carboxylic acid groups (PVA-r-COOH) make up the third group. These products are commercially available from several manufacturers. We have used Gohsenal T330 (Nippon Gohsei, Osaka, Japan), PVA-KL118, PVA-KL318, PVA-KL506, SK-5102 (Kuraray), Elvanol T-25G and T-66 (Dupont, Wilmington, DE, USA).

All PVA data were obtained from the manufacturers. The products were used as received. Master solutions of 10 wt% were prepared by stirring at 95°C for 4 h.

6.2.2 Methods

$BaTiO_3$ dispersions with a volume fraction ϕ of 0.15 were prepared in a Vibratom vibrating energy mill (VEM). Polyethylene vessels (volume 225 ml) were loaded with 140 g of 3 mm glass balls, 45 g of $BaTiO_3$ and 40 g water. After a 30 min pretreatment on the VEM to obtain completely wetted particles, the appropriate amounts of PVA solution and additional water were added to obtain a volume fraction of 0.15. After treatment for 4 h in the VEM, the dispersion was separated from the balls and subjected to ultrasonic treatment for 2 min with a Sonifier 250 (Branson, Danbury, CT, USA) equipped with a high gain horn. The pH in all experiments was between 8.2 and 8.8.

In the depletion flocculation experiments, dispersions at ϕ=0.25 with a low dosage of polymer were prepared by changing the amounts in the method described above. Afterwards the dispersion was dilute ϕ=0.15 with the appropriate amounts of water and PVA solution to obtain the desired polymer concentration. The dilution and mixing were completed by the ultrasonic treatment. These dispersions were used to cast a film with a wet thickness of 50 μm with a Doctor Blade. Directly after casting, the films were dried in a circulated hot air oven at 50°C.

A scanning electron microscope (Philips SEM 525M) was used to evaluate the homogeneity of the particle packing in the surface of the films.

Flow curves were measured with a LS30 apparatus (Contraves, Zurich, Switzerland) in the high (1 to 120 s^{-1}) shear rate mode. The viscosity η was calculated from the straight part of the curve obtained with a decreasing shear rate, and the Bingham yield value τ_b was obtained after extrapolation of this straight part to the force axes.

Microscopic observation of the particles in the dispersion is possible with transmitted light at a magnification of 400 after dilution of the dispersion to $\phi=0.05$. With stable dispersions, the single particles are in vigorous Brownian motion.

Microelectrophoresis experiments were carried out with a Zetasizer 2c (Malvern Instruments, Malvern, UK) after dilution of the dispersions with 0.001 M KNO_3. Mobilities were converted to zeta potentials with the use of the Smoluchowski equation.

6.3 RESULTS AND DISCUSSION

6.3.1 Stability tests

In the dispersion experiments, the amount of PVA relative to $BaTiO_3$ was varied in small steps from 0.9 to 9.1 mg m^{-2}. If the polymer can stabilize $BaTiO_3$ it is expected to occur within this range. The stability is judged in the microscope. The smallest amount of PVA required to obtain stable dispersions with all particles in Brownian motion is given in Table 1.

All regular types, regardless of the degree of hydrolysis or vinyl acetate block character, are unable to stabilize the $BaTiO_3$ particles. Although the types with a degree of hydrolysis of about 88% have been recommended by the manufacturers as stabilizers for emulsions, they cannot stabilize these inorganic particles. Killmann et al. [7] found a different adsorption behaviour on organic (hydrophobic) and inorganic (hydrophilic) surfaces with a significantly lower hydrodynamic layer thickness on the inorganic surface. Probably the adsorbed layer on the $BaTiO_3$ surface is not thick enough so that steric stability cannot be obtained.

Table 1: Amount of PVA required to obtain stable dispersions

PVA type	Product	Doseage required for stability (mg PVA m^{-2} $BaTiO_3$)
Regular PVA	18/88	–[a]
	20/98	–[a]
	217C	–[a]
	217E	–[a]
	217EE	–[a]
PVA-b-COOH	AP-22	5.4
	X-0074	3.1
	X-0075	3.1
PVA-r-COOH	KL118	–[a]
	KL318	–[a]
	KL505	–[a]
	SK-5102	6.3
	T-25G	–[a]
	T-66	–[a]
	T330	3.1

[a] : No stability obtained

Stable $BaTiO_3$ dispersions can be obtained with the block copolymers. The carboxylic acid units are expected to prevent the adsorption of the PVA block [10]. With such block copolymers the adsorbed layer can be very thick [11,12] due to the stretching of the unadsorbed block.

The random copolymers demonstrate a varying degree of effectiveness. Only two of the products are able to provide stability to the dispersion. Since we have no data on the amount of carboxylic acid, hydroxylic and acetate groups in contact with the surface, we can only speculate about the adsorbed layer conformation. Several situations may exist with the random copolymers. As discussed above, the adsorbed layer thickness with the regular PVA types is expected to be low. If the carboxylic acid groups in the PVA-r-COOH copolymers can prevent the PVA segments from adsorbing, the layer thickness is expected to increase, resulting in a better steric stabilization. If all the carboxylic acid groups adsorb, the loop size will depend on the length of the sub chain between the subsequent acid groups.

The distribution of the carboxylic acid groups along the chain will then determine the adsorbed layer thickness.

It is also quite possible that the acid groups cannot completely prevent the adsorption of the PVA segments. In this case, the adsorbed conformation will be comparable to the one without acid groups in the chain. The stability will then be more comparable to that with the regular PVA types.

6.3.2 Depletion flocculation

Green products with a sufficient mechanical strength require an additional amount of polymer. Therefore we have studied the effects of higher polymer concentrations on the stability of the dispersions for some of the polymers with which stable dispersions were obtained. The dilution of the concentrated dispersions with water and polymer solution is followed by an ultrasonic treatment. Without this treatment we find an increased flocculation with much higher yield values, especially with the T330-stabilized dispersions. This may be due to a strong osmotic effect when the concentrated polymer solution is mixed with the dispersion which has a very low polymer concentration. The liquid between the particles is sucked away towards the highly concentrated polymer solution droplets by the osmotic pressure difference. Due to this, the particles are pushed together. An additional dispersing treatment assures a homogeneous distribution of the polymer and the particles.

Bingham yield values obtained from the flow curves and the particle packing in the dried layers were compared. Examples of flow curves are given in Fig. 1 for a stable dispersion and in Fig. 2 for a flocculated dispersion.

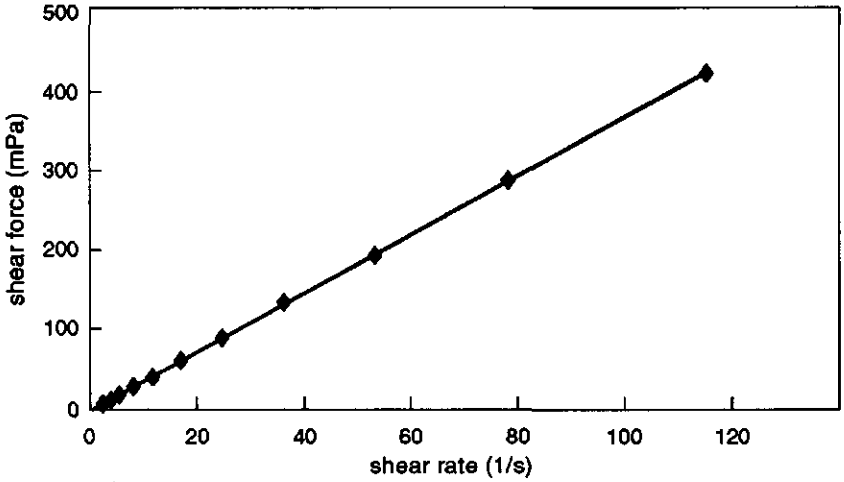

Figure 1 Flow curve for a stable dispersion (experiment 1)

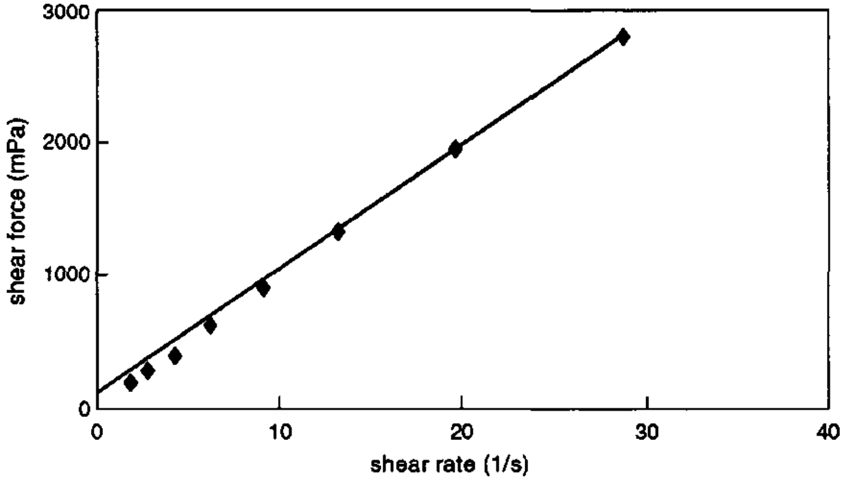

Figure 2 Flow curve for a flocculated dispersion (experiment 8)

The polymer concentration data in milligrams of PVA per gram of water were not corrected for the adsorbed amount. In all cases the error is less than 3 mg PVA g^{-1} water, which is the amount used to stabilize the particles. The results for dispersions stabilized with T330 in Table 2 show that depletion flocculation starts at about 16 mg PVA g^{-1} water and increases to about 42 mg PVA g^{-1} water. At higher concentrations the yield value decreases, indicating a lower degree of flocculation; this is often found with depletion flocculation [4]. Complete restabilization may occur at still higher concentrations, but this region was not accessible due to practical limitations.

Table 2: Depletion flocculation in the T330 stabilized dispersions.

Exp. no.	T330 conc. (mg g^{-1} water)	η (mpa s)	τ_b (mPa)
1	5.2	3.6	0
2	11.3	7.3	0
3	16.2	10.7	11
4	21.2	17.8	15
5	26.4	26.0	12
6	31.8	44.6	53
7	37.3	60.8	62
8	41.7	97.1	77
9	47.5	123.0	59
10	53.0	181.4	47

The scanning electron micrograph in Fig. 3 of the dried layer of experiment 1 shows a homogeneous particle packing. Decreasing homogeneity from experiment 2 to experiment 8 (Fig. 4) is found in the dried layers. This roughly agrees with the rheological data.

The homogeneity already starts to decrease in experiment 2 which still has a zero yield value. During drying, the polymer concentration increases and the dispersion enters the flocculation region. Although drying of the layers is complete within 2 min, obviously the flocculation is still noticeable. The homogeneity hardly improves at polymer concentrations above 42 mg T330 g^{-1} water where the yield value decreases.

Although the disturbing effect of the depletion flocculation on the layer homogeneity is clear, the layer structure is not very inhomogeneous, demonstrating the weak nature of depletion flocculation [13].

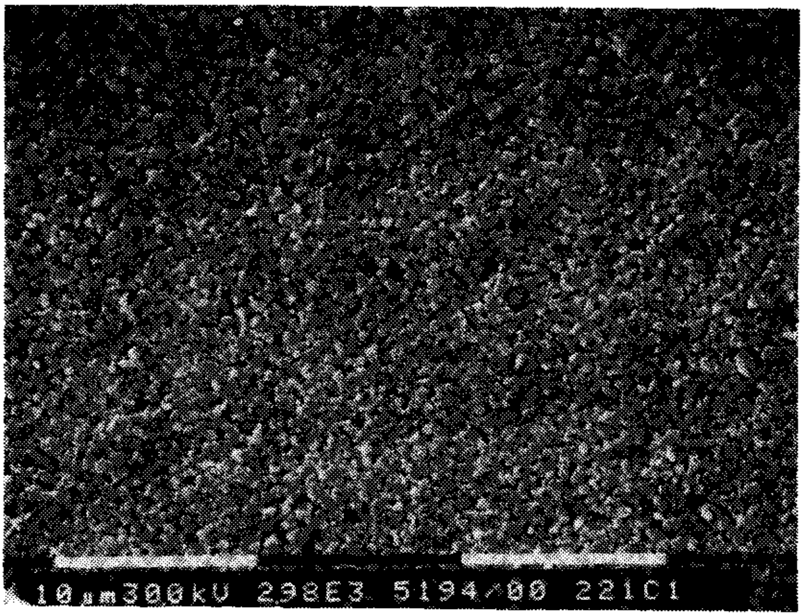

Figure 3 *Structure of a layer prepared with a stable dispersion (experiment 1)*

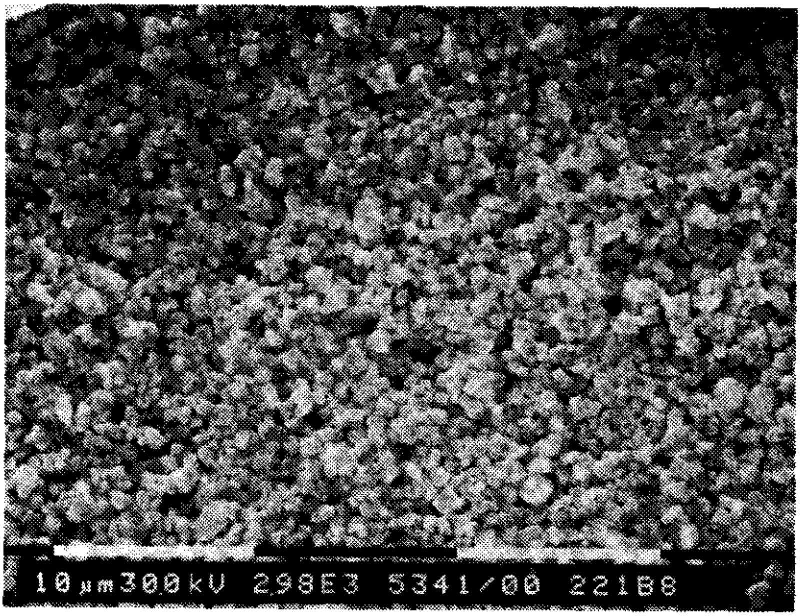

Figure 4 *Structure of a layer prepared with a flocculated dispersion (experiment 8)*

In experiments with X-0074 and X-0075 over the same concentration range, no indication of flocculation was found. The dried layer homogeneity (Fig. 5) is better than with the T330 formulation. In this case there is no risk of entering a flocculation region during drying.

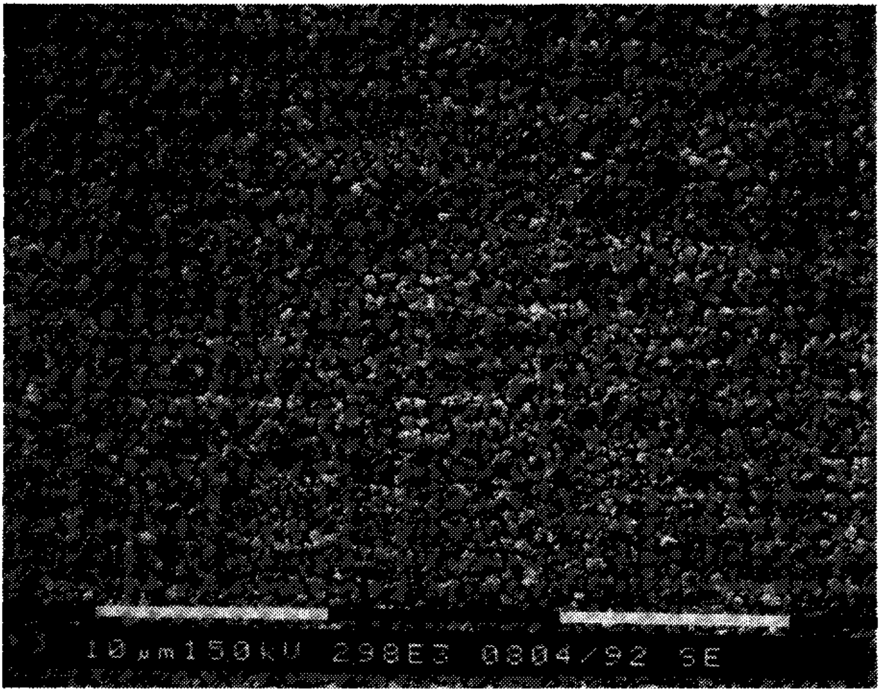

Figure 5 Structure of a layer prepared with a dispersion stabilized with X-0074

The difference in depletion flocculation behaviour between T330 and block copolymer-stabilized dispersions may be due to differences in the adsorbed layer conformation and thickness [14,15]. The block copolymers are expected to have a more extended conformation.

6.3.3 The stabilizing mechanism

Concentrated dispersions were diluted to ϕ=0.05 with water and a KCl solution to tehe stability against an increasing salt level. The stability is evaluated with use of the microscope and by rheological measurements. The results for the dispersions stabilized with T330 are presented in Table 3.

Table 3: Stability against salt with the T330-stabilized dispersion.

[KCl] (M)	η (mPa s)	τ_b (mPa)	Particles in Brownian motion[a]
0.012	1.40	0	all
0.032	1.40	0	many
0.10	1.50	0	several
0.20	1.58	0	some
0.40	1.87	2.9	few
0.49	1.79	2.1	less
0.58	1.91	5.6	less
1.0			none

[a] Microscopic evaluation

There seems to be some discrepancy between the yield value data and microscopic evaluation in which the onset of flocculation occurs at a lower salt concentration. The volume fraction, however, is fairly low so that the sensitivity in the rheological measurement for flocculation is not very high. The microscopic observation is considered to be more reliable for the starting point of the flocculation. Flocculation starts at 0.03 M KCl and slowly increases with the salt concentration. Even at 0.58 M KCl a part of the particles is still in Brownian motion. The smaller particles, especially, resist flocculation. At such high salt levels no charge stabilization is expected. So we may conclude that steric hindrance does play a role, but it is not effective enough to eliminate the effect of the salt concentration completely. Flocculation before the thermodynamic limit is reached occurs if the steric layer is relatively thin [4]. In such a situation the Van der Waals attraction between the particles becomes important, causing the larger particles to flocculate first. Indeed we find that the smaller particles remain in Brownian motion up to higher salt levels.

In dispersions stabilized with X-0074 and X-0075 all particles remain in Brownian motion even at 1 M KCl. Obviously the steric barrier is thick enough to provide full steric stabilization.

The particles are below their isoelectric point at the chosen pH in the dispersions. Upon polymer adsorption the hydrodynamic slipping plane is shifted from the particle surface further into the liquid [16]. This causes a decrease in the value for the zeta potential which is equal to the potential at the slipping plane. Charge compensation at the surfaces upon adsorption of oppositely charged polymers also lowers the zeta potential.

Microelectrophoresis experiments (Table 4) reveal a low but positive value for the zeta potential with both X-0074 and X-0075. All acid groups of the block copolymers will be located at or very close to the surface. But obviously the surface charge is not completely compensated. The surface coverage with carboxylic acid groups will be incomplete due to the mutual hindrance of the PVA chains. The very low values indicate that electrostatic repulsion is of no importance in these dispersions.

Table 4: Zeta potentials from microelectrophoresis.

Stabilizing polymer	Zeta potential (mV)
T330	−15.4
X-0074	2.3
X-0075	2.3

The zeta potential of the T330-stabilized dispersion has a negative value which can be explained by assuming an overcompensation of the positive charge on the surface by the carboxylic acid groups. The relative high absolute value in spite of the low amount of acid groups in the polymer is expected to be due to the distribution of the carboxylic acid groups in the adsorbed layer. The excess of the carboxylic acid groups may be located further away from the surface, partly in the outer regions of the adsorbed polymer layer. These groups are located much closer to the slipping plane and are therefore far less screened. The zeta potential value of −15.4 is high enough to expect some contribution in the stabilization.

Although there is no clear evidence, the flocculation experiments indicate that the steric layer thickness obtained with the T330 random copolymer is relatively thin and provides a marginal steric stabilization to the $BaTiO_3$ particles. The combination of both effects seems to be enough to provide stability to the dispersions.

6.4 CONCLUSIONS

Stable $BaTiO_3$ dispersions cannot be achieved with usual PVA polymers. Block copolymers of PVA with a carboxylic acid-containing unit are very powerful stabilizers. Some of the PVA copolymers with randomly distributed carboxylic acid groups can stabilize $BaTiO_3$ while others cannot. Depletion flocculation was found with the random copolymer tested but not with the block copolymers. If depletion flocculation occurs, the homogeneity of a dried layer made with these dispersions decreases. Pure steric stabilization was found with the block copolymers while the stabilizing random copolymer shows features of both steric and electrostatic stabilization.

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REFERENCES

[1] K. Kendall, Powder Technol., 58 (1989) 151.
[2] H. Itoh, M.V. Parish and H.K. Bowen, Mater. Sci. Eng., 96 (1987) 303-310.
[3] A. Hui, D. Bloomfield, A. Bell and M. Chu, Proc. 3rd European Capacitor Resistor Technol. Symp., CARTS-EUROPE '89, Component Technology Institute, Christchurch, UK, 1989 pp 78-85.
[4] D.H. Napper, Polymeric Stabilization of Colloidal Dispersions, Academic Press, London, 1983.
[5] R.A. Croot, A.R. Goodall and S.B. Lubetkin, Colloids Surfaces, 49 (1990) 351.
[6] C.A. Finch, Polyvinyl alcohol, John Wiley, London, 1973.
[7] E. Killmann, H. Maier and J.A. Baker, Colloids Surfaces, 31 (1988) 51-71.

[8] Th. Goetze and H. Sonntag, Colloids Surfaces, 31 (1988) 181.
[9] S. Lubetkin, Colloids Surfaces, 31 (1988) 203.
[10] A.W.M. de Laat and G.L.T. van den Heuvel, Colloids Surfaces A: Physicochem. Eng. Aspects, 70 (1993) 179.
[11] G.J. Fleer and J.M.H.M. Scheutjens, Colloids Surfaces, 51 (1990) 281.
[12] G.P.H.L. de Silva, P.F. Luckham and Th.F. Tadros, Colloids Surfaces, 50 (1990) 251.
[13] C. Prestidge and Th.F. Tadros, Colloids Surfaces, 31 (1989) 325.
[14] A. Jones and B. Vincent, Colloids Surfaces, 41 (1989) 113.
[15] A. Milling, B. Vincent, S. Emmett and A. Jones, Colloids Surfaces, 57 (1991) 185.
[16] L.K. Koopal, V. Hlady and J. Lyklema, J. Colloid Interface Sci., 121 (1988) 49.

CHAPTER 7

The adsorption of polyvinyl alcohols with carboxylate groups onto $BaTiO_3$*

Abstract

Adsorption isotherms and the molecular weight fractionation of polyvinyl alcohols (PVA) with carboxylate groups upon adsorption on $BaTiO_3$ were determined. One of the polyvinyl alcohols with carboxylate groups is a block copolymer, while the others have carboxylate groups randomly distributed along the polymer chain. The copolymers were characterised by infrared spectroscopy (IR) and size exclusion chromatography (SEC). Lactone formation was found in one of the PVAs while the others contain only free carboxylate groups. The carboxylate content varies from 0.7 to 3.4 mol% and the ester content from almost zero to 22 mol%. An interesting detail is the difference in the wavelength at which the carboxylate groups absorb in the IR spectra. This difference is probably related to the distribution of the carboxylate groups in the chain. The molecular weights, as determined by SEC relative to polyethylene oxide, vary from 33 000 to 110 000 for the copolymers studied. An amount adsorbed of 1.5 mg m^{-2} for the block copolymer was found. The random copolymers all have amounts adsorbed in the plateau region close to 0.41 mg m^{-2} in spite of the differences in chemical composition. There is, however, a significant difference in the shape of the adsorption isotherms at low equilibrium concentration and also in the molecular weight fractionation upon adsorption. The random copolymer with the highest molecular weight in the adsorbed fraction is the only one suitable for making stable $BaTiO_3$ dispersions. The amount

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*A.W.M. de Laat, A.W. de Bruijn and G.L.T. van den Heuvel, Colloids Surfaces A: Physicochem. Eng. Aspects, 82 (1994) 99-110.

adsorbed of the block copolymer increases above a certain equilibrium concentration without further exchange of short adsorbed molecules for longer ones. This behaviour can be explained by assuming an increasing stretching of the adsorbed chains in order to allow new chains to adsorb.

7.1 INTRODUCTION

Regular polyvinyl alcohol (PVA) is not a suitable polymer for the colloidal stabilisation of $BaTiO_3$ [1]. Block copolymers of polyvinyl alcohol and polyacrylic acid can be used to obtain sterically stabilised dispersions of $BaTiO_3$ [1]. A number of random copolymers of polyvinyl alcohol with carboxylic acid containing monomers were also studied with respect to their ability to provide stability to $BaTiO_3$ dispersions. Only a few of these random copolymers proved to be successful [1].

The present study is focussed on finding the reason for the difference in effectiveness of the random copolymers. One of the block copolymers and a selection of the random copolymers were characterised by infrared spectroscopy (IR) and size exclusion chromatography (SEC). Furthermore, the adsorption behaviour of the polymers on $BaTiO_3$ was studied by SEC.

7.2 EXPERIMENTAL

7.2.1 Materials

The $BaTiO_3$ powder used in this study has a number-averaged particle size of 1.1 μm and a specific surface area of 3 $m^2\ g^{-1}$ according to the BET method. The isoelectric point is at pH=9.9 [2].

Mowiol 18/88 and 20/98, both PVAs without carboxylic acid groups, were obtained from Hoechst (Frankfurt am Main, Germany). The block copolymer X-0075 was made by Kuraray (Osaka, Japan) and is reported to contain 2.5 mol% of acrylic acid. The random copolymers studied are Gohsenal T330 (Nippon Gohsei, Osaka, Japan), PVA-KL506 (Kuraray) and Elvanol

T66 (Dupont, Wilmington, DE, USA). According to the manufacturers, the degree of hydrolysis of these products is 74-80% for KL506, 95-98% for T330 and 98-99.8% for T66. Stock solutions of 10 wt% were prepared from the polymers (as received) by stirring at 95 °C for 4 h.

A polyacrylic acid (PAA) called Versicol E11 (Allied Colloids Ltd, Bradford, UK) was used as a reference material in the IR experiments.

7.2.2 IR spectroscopy

The IR spectra were recorded on a Nicolet 5-DX Fourier Transform Infrared Spectrophotometer (Nicolet Instrument Corp, Madison, WI, USA). The resolution is 4 cm^{-1}. PVA films were cast from a 5 wt% solution with a pH of 9 directly onto ZnSe windows. The IR spectra were recorded after drying at 120 °C for 1 h. The selected films have an absorbance between 0.4 and 0.8 for the 2941 cm^{-1} peak and are free of defects such as pinholes and dust. Calculated amounts were averaged from two separately determined spectra.

7.2.3 Size exclusion chromatography

Details of the equipment and the method used have been published elsewhere [2]. Here, only the main items and the differences are mentioned. Three columns in series: TSK guard PW, TSK 4000PWXL and TSK 3000PWXL (Toyo Soda Manufacturing Co., Tokyo, Japan) were used for the experiments with KL506, T66 and X-0075. In the experiments with T330, a 5000PWXL column was used instead of the 4000PWXL and 3000PWXL columns. The eluent was 0.05 M $NaNO_3$ at a flow rate of 1 ml min^{-1}. The sample volume was varied between 10 and 200 μl in order keep the total peak areas roughly the same. A refractive index detector was used to record the molecular weight fractionation. The reported molecular weights are relative to polyethylene oxide standards.

7.2.4 Adsorption experiments

The area to volume ratio, which is known to influence the shape of the adsorption isotherm [3], was kept constant in all experiments. In the chosen pH range (8.2 - 8.8), the surface of the $BaTiO_3$ particles is positively charged while the degree of dissociation of the carboxylic acid groups in the PVA is high. The adsorbed amount is calculated from the difference in concentration between the initial solution C_0 and the suspension medium after adsorption C_e as determined by SEC. By subtracting both chromatograms, information on the molecular weight distribution of the adsorbed fraction can be obtained. Further details have been given elsewhere [2].

7.3 RESULTS AND DISCUSSION

7.3.1 IR spectroscopy

As well as the qualitative analysis of the chemical composition of the PVAs, the spectra were used to obtain an estimate of the ester and carboxylate contents. The method of measuring the integral peak area (IPA) appeared to give results with a better reproducibility than the absorbance method [4]; 10% vs. 15-20%. Therefore the IPA method was used for estimating the ester and carboxylate contents.

The C-H stretching vibrations absorb at 2941 cm^{-1} (asymmetrical $C\text{-}H_2$ stretching), at 2913 cm^{-1} (symmetrical $C\text{-}H_2$ stretching) and at 2840 cm^{-1} (C-H stretching). These peaks (integrated between 2786 and 3003 cm^{-1}) were used as an internal reference for the estimation of the amounts of ester and carboxylate in each polymer. This integrated value will be referred to subsequently as IPA_{2941}. The $\text{-}CH_2\text{-}CH\text{-}$ backbone units of the alcohol, ester and acid groups in the polymer all contribute to the same extent to the C-H stretching peaks. The CH_3 group from the ester can introduce some deviation, especially at high ester contents.

The position at which the carbonyl of the ester group absorbs depends on its neighbours in the polymer chain. Ester groups in blocks absorb at

1736 cm^{-1}, while randomly distributed ester groups with OH neighbours absorb at 1715 cm^{-1} [5]. The amount of ester groups was determined by integration from 1660 to 1805 cm^{-1}. Calibration is performed with Mowiol 18/88 and 20/98, which have an ester content of 12.8 mol% and 1.7 mol% respectively, values which were measured with a titration method [6].

The ester content can now be calculated from:

$$\text{mol\% ester} = 20.1 * IPA_{1715\text{-}1736}/IPA_{2941}$$

The absorption of the carboxylic acid group is at 1710 cm^{-1} (Fig. 1a) which overlaps with the ester absorption at 1715 cm^{-1}.

Therefore the carboxylic acid groups were converted to carboxylate groups by increasing the pH of the solutions to about 9 with NaOH. The absorption of the carboxylate groups is at 1570 cm^{-1} (Fig. 1b), a region without PVA absorption bands. The amount was determined by integration from 1640 to 1510 cm^{-1}. The calibration of this integral value was performed with mixtures of Mowiol 20/98 and the sodium salt of PAA (Na-PAA).

Films with 1.5, 2.5 and 5.0 wt% Na-PAA in PVA gave results in agreement with the Lambert-Beer law for the carboxylate content.

Assuming that acrylic acid was used as a comonomer in the polymerisation, the carboxylate content after this calibration can be calculated from:

$$\text{mol\% carboxylate} = 10.5 *(IPA_{1570}/IPA_{2941})$$

Commercial PVAs always contain a certain amount of sodium acetate which remains in the product after the hydrolysis of the polyvinyl acetate. The amount is, however, fairly low as can be seen from the 1570 cm^{-1} absorbance in the spectrum of Mowiol 18/88 (Fig. 2). Corrections to account for this were not made.

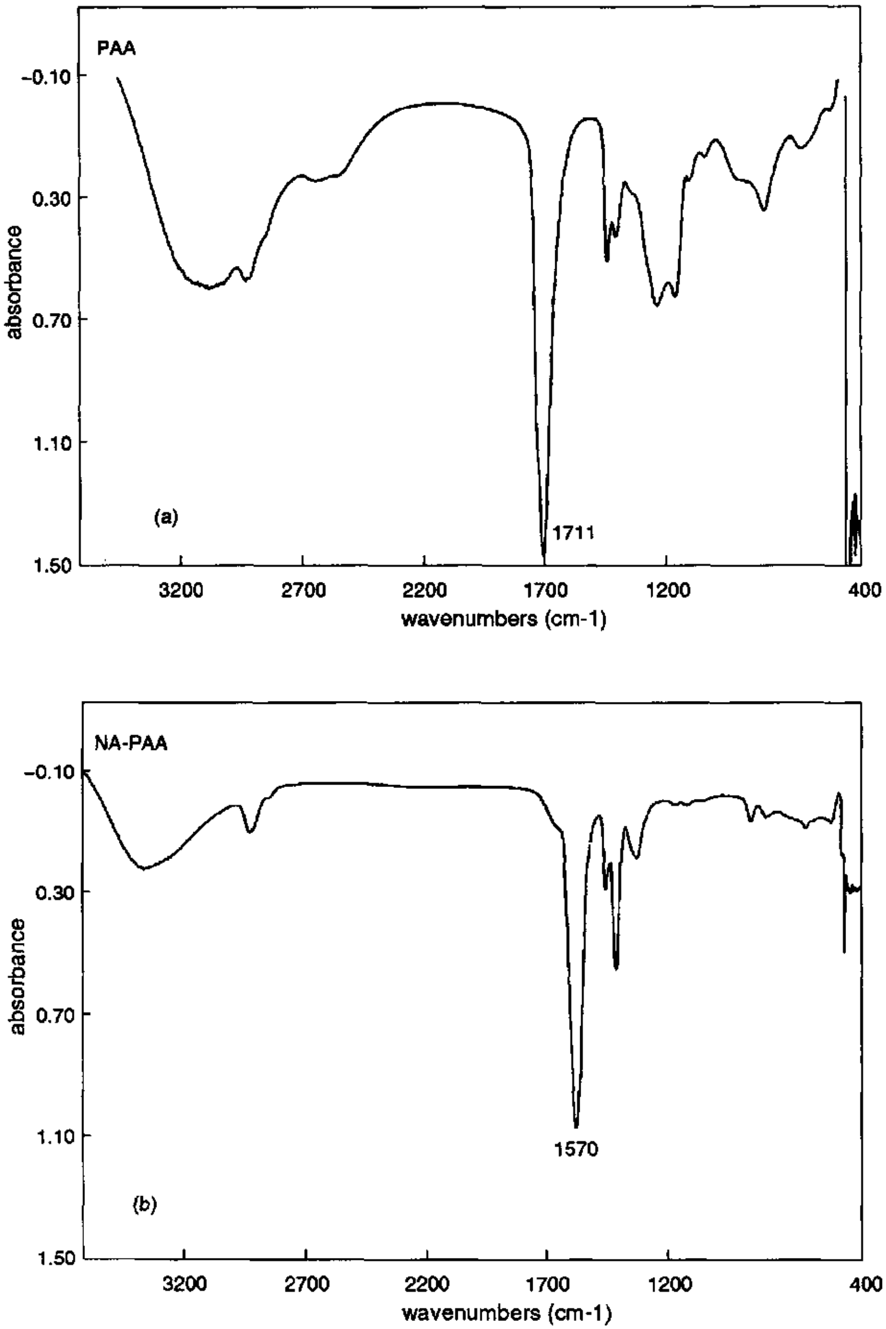

Figure 1 *The IR spectra of: (a) polyacrylic acid; (b) the sodium salt of polyacrylic acid*

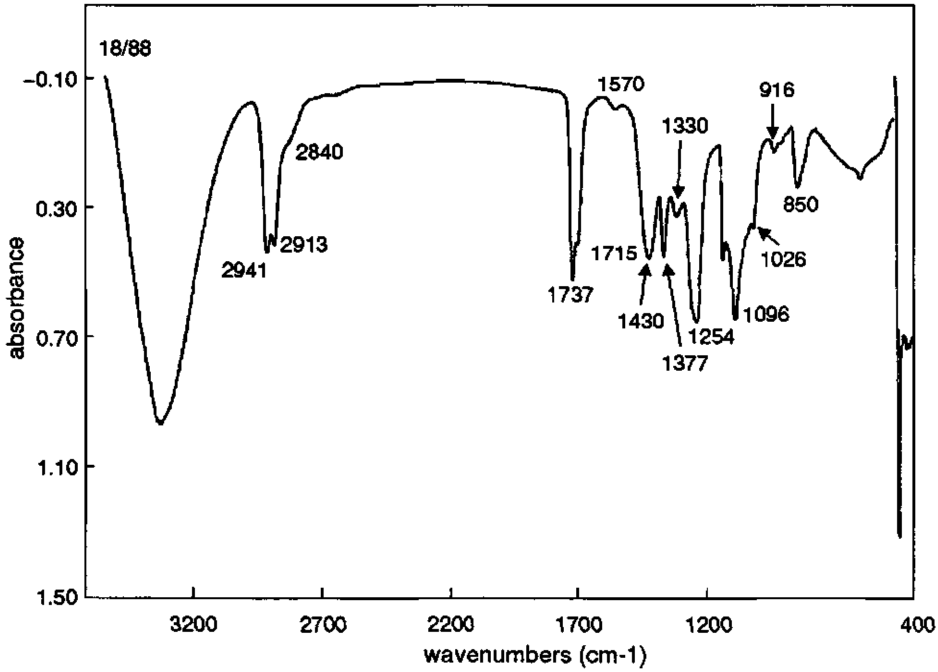

Figure 2 IR spectrum of Mowiol 18/88

The peaks in the Mowiol spectra compare well with those reported by Dunn [7]. In the spectra of X-0075 (Fig. 3) and T330 (Fig. 4) all peaks can be attributed to PVA or carboxylate.

The spectra of both T66 (Fig. 5) and KL506 (Fig. 6) contain additional peaks.

According to Tubbs [8], T66 is a copolymer which contains methyl methacrylate and a lactone ring due to reaction of neighbouring OH and COOH groups. The lactone carbonyl absorbs at 1746 cm^{-1} and the methacrylate carbonyl at 1204 cm^{-1}; both peaks can be identified in the spectrum. In the spectrum of KL506, an additional peak appears at 947 cm^{-1}. This peak can be assigned to backbone vibrations of the polyvinyl acetate parts of the molecule [4] which are expected to be present due to the high ester content.

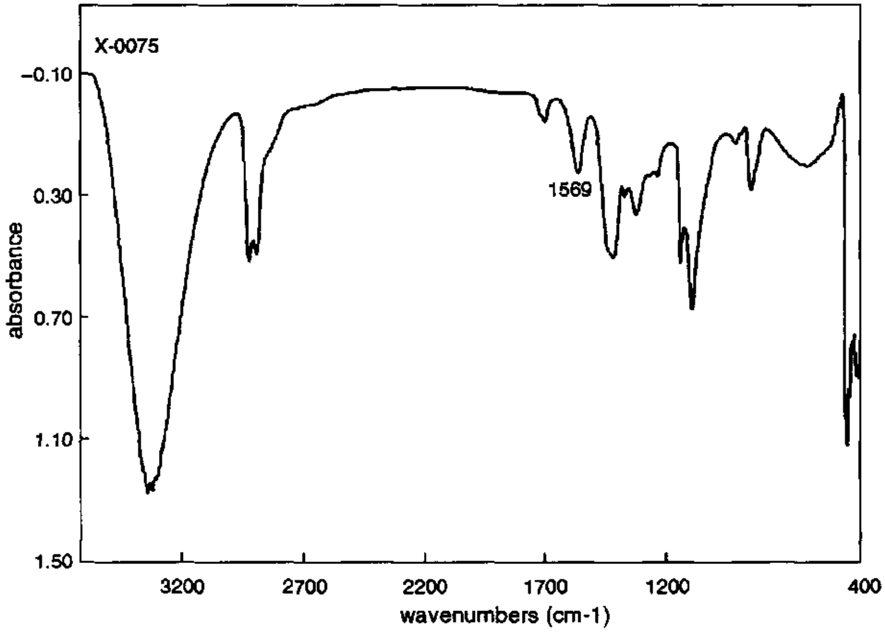

Figure 3 *IR spectrum of X-0075*

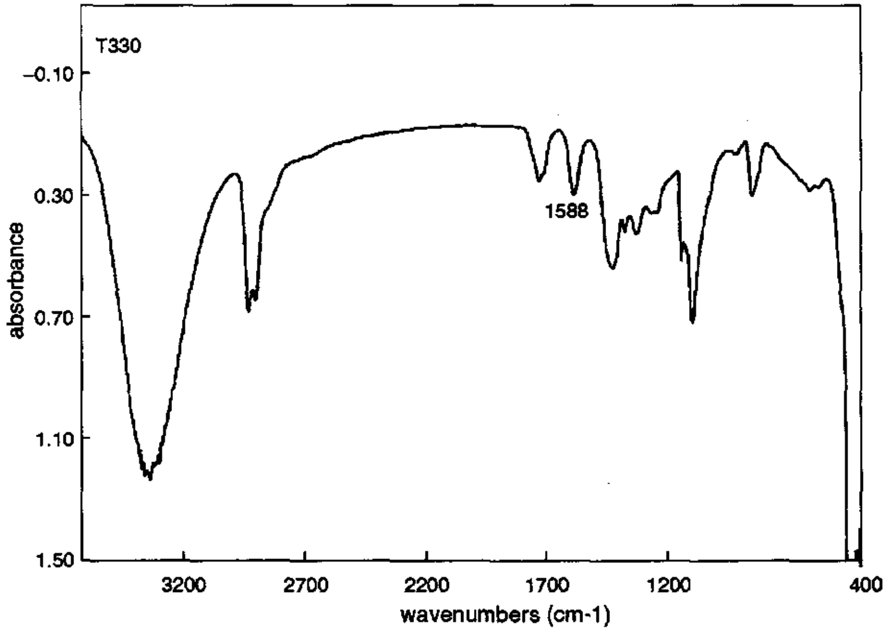

Figure 4 *IR spectrum of T330*

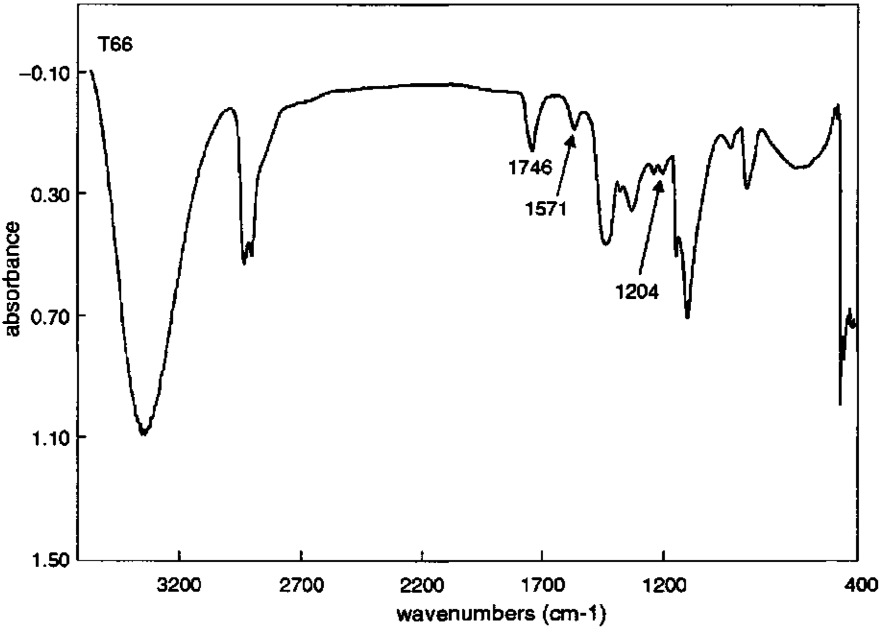

Figure 5 *IR spectrum of T66*

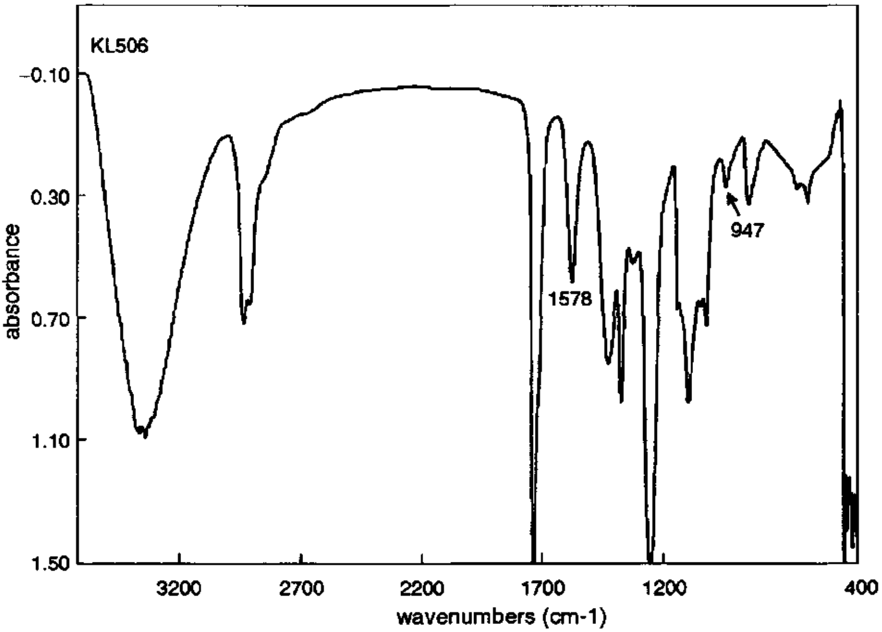

Figure 6 *IR spectrum of KL506*

The estimates of the amounts of carboxylate and ester groups (Table 1) are close to those reported by the manufacturers, as far as they are available.

Table 1: Estimates for the chemical composition from the IR spectra

Polymer	Carboxylate (mol%)	Ester (mol%)
X-0075	2.9	1.7
KL506	3.4	22
T66	0.7	–
T330	2.2	5.5

T66 contains a significant amount of additional carboxylic acid groups which have been reacted to the lactone. The amount of ester in T66 is expected to be low; no data could be obtained as the lactone peak is very close to the ester peak position.

A remarkable difference occurs in the position of the carboxylate absorption in the spectra (Table 2).

Table 2: Position of the carboxylate absorption in the IR spectra

Polymer	Carboxylate absorption (cm^{-1})
X-0075	1569
KL506	1578
T66	1571
T33	1588

The carboxylate groups in X-0075 and T66 absorb at the same position as in the sodium salt of polyacrylic acid (Fig. 1). This points to a block conformation of the carboxylate groups in these PVA copolymers just like in the polyacrylate. Since X-0075 is a block copolymer, this is what could be expected. Lactone groups are present in T66 which are the result of a reaction between neighbouring carboxylic acid and hydroxyl groups. The remaining carboxylate groups (after conversion from the carboxylic acid) appear to absorb at 1571 cm^{-1}, indicating an environment similar to that in Na-PAA. The occurrence of the remaining carboxylate groups of T66 in blocks explains why these groups were not converted to lactone; there were no OH neighbours.

The carboxylate absorption positions in KL506 and T330 deviate to higher values. This may be caused by an increasing amount of H-bridging by neighbouring OH groups in these polymers. Unfortunately, reference spectra to support this were not found.

7.3.2 Size exclusion chromatography

The weight-average molecular weight M_w and the ratio of the weight and number average molecular weight M_w/M_n, which is an indication of the polydispersity, were determined by SEC. The results are recorded in Table 3.

Table 3: The molecular weights and polydispersity of the copolymers

Polymer	M_w (10^3 g mol^{-1})	M_w/M_n
X-0075	106	2.8
KL506	33	2.5
T66	55	2.5
T330	109	3.2

T330 and X-0075 have the highest molecular weights, while those of T66 and KL506 are significantly lower. The high values for the polydispersity are not unusual for commercial polymers. The degree of polymerisation of T330 has been reported by Maruhashi [9] to be 1800, while Tubbs [8] reported a value of 1000 for T66. The present results show a molecular weight ratio of 2 for T330 compared with T66, which is in reasonable agreement.

7.3.3 Adsorption experiments

The results for the random copolymers will be discussed first. The adsorption isotherms for the three random copolymers are compiled in Fig. 7.

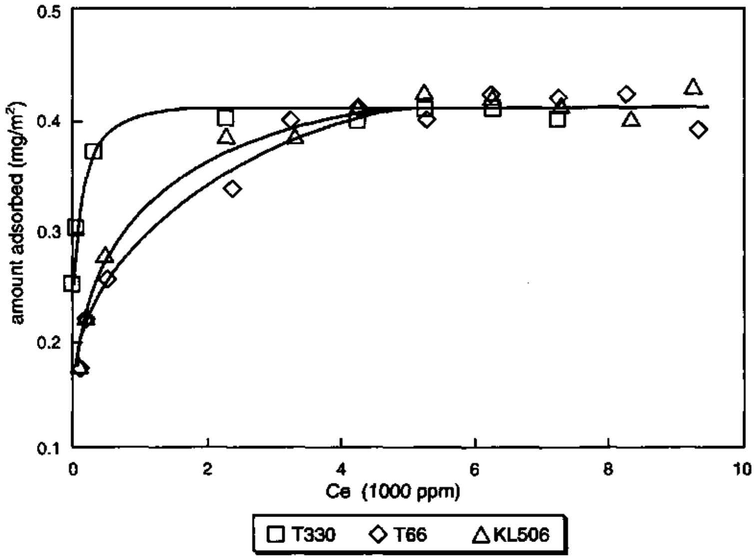

Figure 7 Adsorption isotherms for the random copolymers

The chromatograms before and after adsorption for T330 reveal that a fraction of the low molecular weight chains adsorbs over the whole concentration range studied. A typical example is displayed in Fig. 8.

Chains with a higher than average content of adsorbing groups are expected to have a strong preference for adsorption [10]. Such chains interfere with the usual preference for the high molecular weight chains in a polydisperse homopolymer [11]. As the carboxylate groups adsorb preferentially over alcohol and ester groups [2] it is expected that a part of the short chains has a higher carboxylate content.

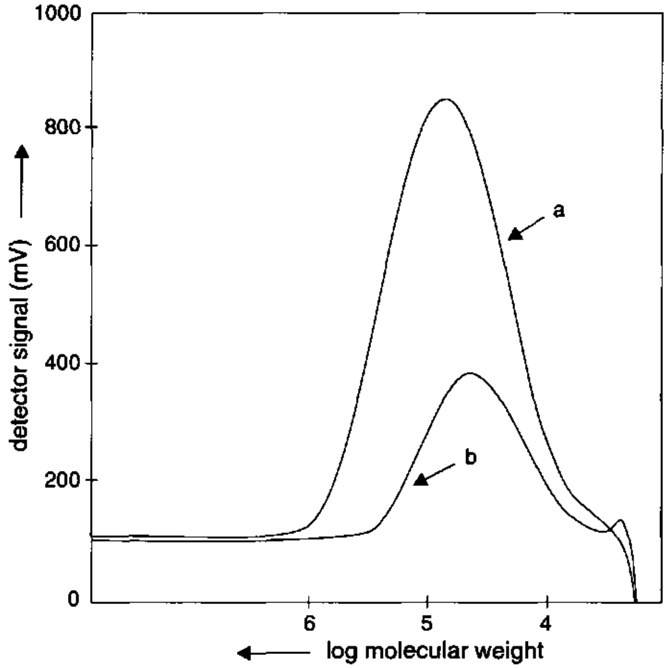

Figure 8 *Chromatograms: (a) before; (b) after adsorption from 1000 ppm T330 solution*

The calculated molecular weights of the adsorbed fraction are compared with those of the polymer solution before adsorption in Table 4.

The M_w values of the initial solutions should all be the same. The deviations at low C_0 are caused by the high injection volumes used. In these cases the M_w values for the adsorbed fraction are also too low. At high concentrations two almost equal chromatograms have to be subtracted. Because the molecular weight calculations are inaccurate in this concentration range, the results are not included in the Table. Similar deviations at low and high concentrations occur with the other copolymers.

In spite of the fraction of short chains which adsorbs, the data in Table 4 reveal a significant preference for the high molecular weight chains in the adsorption. The M_w of the adsorbed fraction increases with the equilibrium concentration roughly until the plateau in the amount adsorbed is reached.

Table 4: The molecular weight fractionation upon adsorption for T330

C_0 (ppm)	C_e (ppm)	Amount adsorbed (mg m^{-2})	M_w (10^3 g mol^{-1}) Initial solution	M_w (10^3 g mol^{-1}) Adsorbed fraction
400	1	0.25	94	95
600	55	0.30	99	108
1000	329	0.37	103	127
3000	2275	0.40	108	149
5000	4277	0.40	108	159
6000	5266	0.41	108	166
7000	6263	0.41	111	161
8000	7275	0.40	110	159

The plateau in the amount of T330 adsorbed is reached at an equilibrium concentration comparable with the one found with PVA without carboxylate groups [2].

The adsorption isotherms of both KL506 and T66 have an extremely low affinity character. A comparable situation was found by Cosgrove et al. [12] for the adsorption of ethylene-vinyl acetate random copolymers on modified silica surfaces. Generally, the low affinity character is caused by the exchange of short adsorbed chains for longer ones at increasing polymer dosages [11]. The extremely low affinity character of KL506 may be caused by the content of 22 mol% of ester groups. At high ester contents, the short chains are expected to have a significantly higher than average amount of ester groups [13,14]. Such short chains have a certain preference for the adsorption in PVA without carboxylate groups [2]. Previous results have shown that the carboxylate groups have the highest affinity for the surface [2]. The extremely low affinity character with KL506 may possibly be explained by a competition between the long chains (with a sufficient amount of carboxylate groups) and the shorter chains with a higher ester content. Information on the amount of carboxylate groups as a function of the chain length is not available.

A fraction of the short chains in KL506 remains adsorbed over the whole concentration range. In Fig. 9 a typical example is displayed.

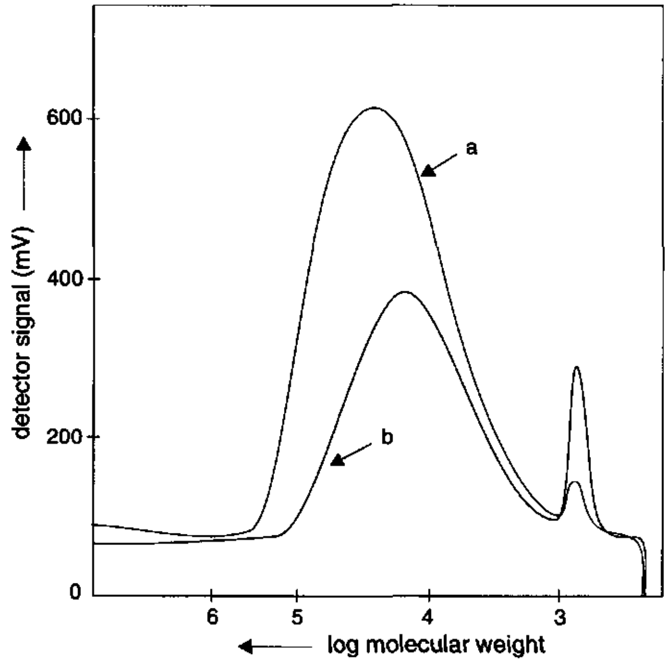

Figure 9 Chromatograms: (a) before; (b) after adsorption from 1000 ppm KL506 solution

This may be caused by a higher than average content of carboxylate groups in the short chains or by the distribution of the ester groups discussed above. Although some of the short chains adsorb, the data in Table 5 reveal that there is a preference for the long chains.

The M_w of the adsorbed fraction increases until the plateau value in the adsorption is reached. The calculated M_w values for KL506 cannot be compared directly with the other copolymers because the high ester content may affect the retention in the SEC analysis [2].

Table 5: The molecular weight fractionation upon adsorption for KL506

C_0 (ppm)	C_e (ppm)	Amount adsorbed (mg m^{-2})	M_w (10^3 g mol^{-1}) Initial solution	M_w (10^3 g mol^{-1}) Adsorbed fraction
400	77	0.18	29	34
600	195	0.22	30	37
1000	494	0.28	32	44
3000	2305	0.39	33	50
4000	3315	0.39	34	53
5000	4246	0.41	34	51
6000	5232	0.43	34	58
7000	6248	0.42	33	57

The adsorption isotherm of T66 has a similarly low affinity character as found for KL506. The chemical composition of T66 is, however, different. The polymer chains of T66 have lactone groups but hardly any ester groups and far fewer carboxylate groups are present. The adsorption behaviour of T66 is much more complex. The results of the adsorption experiments compiled in Table 6 show a slight preference for long chains at low equilibrium concentrations.

Table 6: The molecular weight fractionation upon adsorption for T66

C_0 (ppm)	C_e (ppm)	Amount adsorbed (mg m^{-2})	M_w (10^3 g mol^{-1}) Initial solution	M_w (10^3 g mol^{-1}) Adsorbed fraction
400	82	0.18	47	55
600	202	0.22	48	55
1000	539	0.26	51	59
3000	2393	0.34	53	50
4000	3278	0.40	55	59
5000	4267	0.41	54	45
6000	5278	0.40	56	54

This preference disappears before the plateau value in the amount adsorbed is reached. In this range the M_w values of the initial solution and the adsorbed fraction are the same within experimental error. Obviously, chain length and compositional effects compensate. Fig. 10 shows a typical chromatogram.

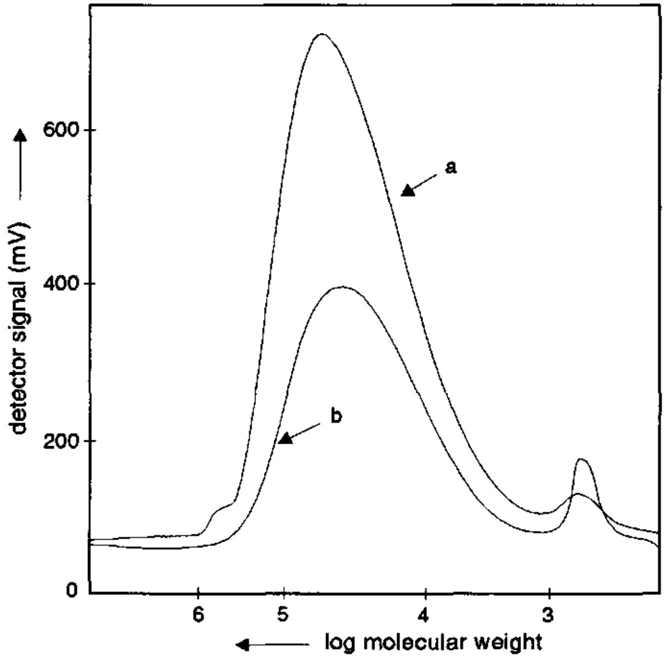

Figure 10 Chromatograms: (a) before; (b) after adsorption from 1000 ppm T66 solution

The gradual increase in the amount adsorbed cannot be explained by an exchange of short adsorbed chains for longer ones. Although no data are available, this behaviour can be explained by assuming a change towards a more extended conformation of the adsorbed chains as the amount adsorbed increases.

According to van Lent and Scheutjens [10] both the amount adsorbed and the hydrodynamic layer thickness are expected to increase with the fraction of adsorbing groups in a random copolymer with adsorbing and non-adsorbing groups. In PVA with carboxylate groups the situation is much more complicated since not only the carboxylate groups adsorb, but other segments also have a certain affinity for the surface. Remarkably, all three random copolymers reach the same amount adsorbed in the plateau in spite of the fairly large differences in chemical composition and in adsorption behaviour discussed above. The amount adsorbed of about 0.41 mg m^{-2} is significantly higher than the value of 0.19 mg m^{-2} found for PVA without carboxylate groups. Obviously, the amount adsorbed is increased due to the presence of the carboxylate groups and therefore the conformation is expected to be more extended. Stable dispersions of $BaTiO_3$ cannot be prepared with regular PVA [1], which also indicates a thin hydrodynamic layer thickness of the adsorbed layer. The hydrodynamic layer thickness of homopolymers increases strongly with the molecular weight, although the amount adsorbed remains almost constant [11]. T330, the only random copolymer suitable to make stable $BaTiO_3$ dispersions, has the highest molecular weight in the adsorbed fraction. The hydrodynamic layer thickness with KL506 and T66 is probably too low due to the lower molecular weight in the adsorbed layer.

Finally, the adsorption behaviour of the block copolymer X-0075 will be discussed. The amount adsorbed increases over a wide range of equilibrium concentrations (Fig. 11). The amount adsorbed of 1.5 mg m^{-2} is much higher than the value found for the random copolymers. High amounts adsorbed with block copolymers are expected theoretically [15]. The value found for X-0075 is still fairly low. The chromatograms in Fig. 12 reveal that even with this block copolymer there is a fraction of short chains which adsorb.

In relation to the low ester content of 1.7%, a homogeneous distribution of these ester groups over the chain lengths is expected [13,14]. The adsorption behaviour will not be affected. The strong adsorption of a fraction of the short chains can be attributed to a higher content of carboxylate groups. The data in Table 7 reveal that the M_w of the adsorbed fraction is always higher than the value in the initial solution.

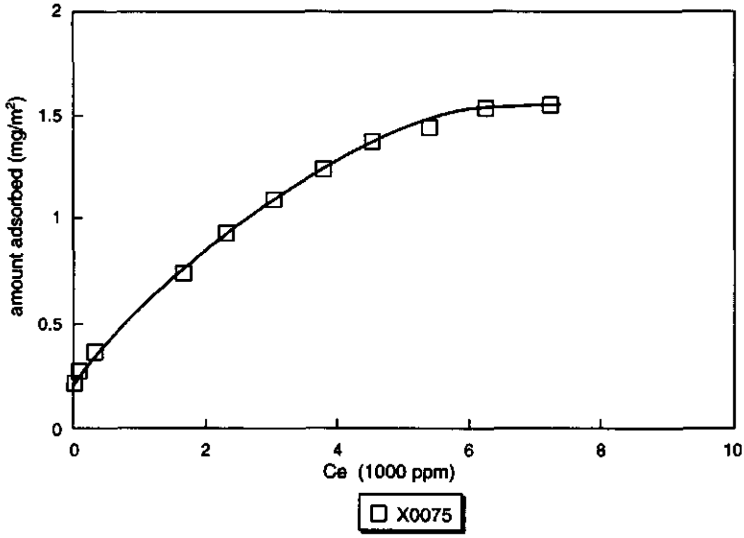

Figure 11 The adsorption isotherm for the block copolymer X-0075

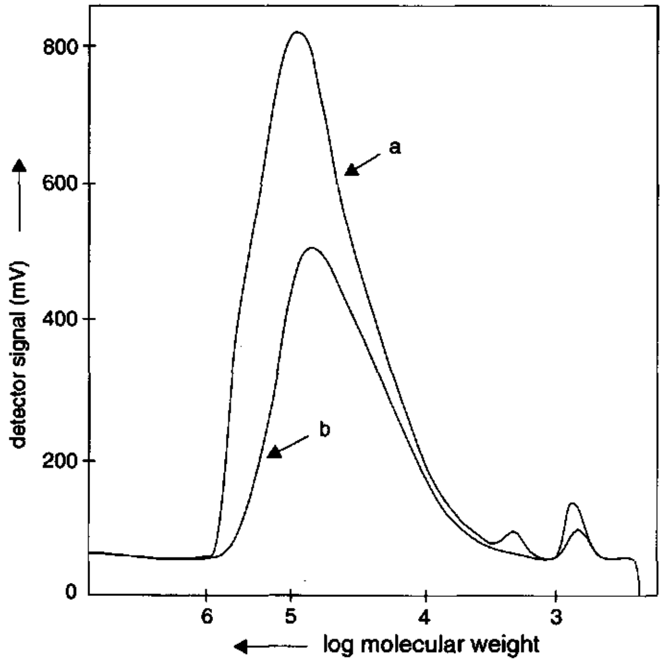

Figure 12 Chromatograms: (a) before; (b) after adsorption from 3000 ppm X-0075 solution

Table 7 The molecular weight fractionation upon adsorption for X-0075

C_0 (ppm)	C_e (ppm)	Amount adsorbed (mg m^{-2})	M_w (10^3 g mol^{-1}) Initial solution	M_w (10^3 g mol^{-1}) Adsorbed fraction
400	30	0.21	93	107
600	128	0.22	94	107
1000	365	0.36	97	120
3000	1670	0.74	108	161
4000	2334	0.93	107	164
5000	3040	1.09	105	162
6000	3781	1.23	106	163
7000	4558	1.36	107	163

The M_w value of the adsorbed fraction increases initially with the amount adsorbed due to the exchange of short adsorbed chains for longer ones. From a certain point on, the molecular weight of the adsorbed fraction remains constant while the amount adsorbed continuous to increase by more than a factor of two. In this range of the adsorption isotherm, stretching of the adsorbed chains probably increases, allowing more chains to adsorb while the molecular weight distribution of the adsorbed chains remains the same. A comparable situation is found with the random copolymer T66 while both other random copolymers have increasing M_w values of the adsorbed fraction until the plateau is reached.

The adsorbed molecular weight with X-0075 is comparable to the one found with T330, while the hydrodynamic layer thickness is expected to be much higher with block copolymers [16,17]. Therefore, it is not surprising that very stable $BaTiO_3$ dispersions can be made with the X-0075 block copolymer.

7.4 CONCLUSIONS

The amounts of ester and carboxylate groups in the copolymers were estimated by IR spectroscopy. The ester content varies from almost zero to 22% and the carboxylate content from 0.7 to 3.4%. T66 contains lactone groups while the other copolymers just have free carboxylate groups. The position at which the carboxylate peak absorbs varies, which indicates structural differences in the polymer chains. There is an indication that the free carboxylate groups in T66 are in blocks. The molecular weights vary from 33 000 to 110 000 g mol^{-1}. The differences in the chemical composition of the random copolymers has an influence on the adsorption behaviour at low equilibrium concentrations but not on the amount adsorbed in the plateau which is about 0.41 mg m^{-2}. Although there is no absolute preference for the longest chains in the adsorption, there is a certain molecular weight fractionation, except for T66. The presence of the carboxylate groups increases the amount adsorbed from 0.19 mg m^{-2} for regular PVA to 0.41 mg m^{-2} for PVA with randomly distributed carboxylate groups. Regular PVA cannot provide stability to $BaTiO_3$ dispersions while T330, the random copolymer with the highest molecular weight in the adsorbed fraction, is suitable. Both other random copolymers, T66 and KL506, have significantly lower molecular weights in the adsorbed fraction. Therefore, the hydrodynamic layer thickness is expected to be lower and accordingly these copolymers cannot stabilise $BaTiO_3$.

As the amount of the block copolymer X-0075 adsorbed increases, the molecular weight of the adsorbed fraction also increases initially. Above a certain equilibrium concentration, the molecular weight of the adsorbed fraction remains constant while the amount adsorbed continues to increase by more than a factor of two. Probably, the chains are stretched to allow more chains to adsorb on the surface.

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REFERENCES

[1] A.W.M. de Laat and W.P.T. Derks, Colloids Surfaces A: Physicochem. Eng. Aspects, 71 (1993) 147-153.

[2] A.W.M. de Laat and G.L.T. van den Heuvel, Colloids Surfaces A: Physicochem. Eng. Aspects, 70 (1993) 179-187.

[3] M.A. Cohen Stuart, J.M.H.M. Scheutjens and G.J. Fleer, J. Polym. Sci. Polym. Phys. Ed., 18 (1980) 559.

[4] J.T. Vandeberg, D.G. Anderson, J.K. Duffer, J.M. Julian, R.W. Scott, T.M. Sutliff and M.J. Vaickus, An Infrared Spectroscopy Atlas for the Coatings Industry, Federation of Societies for Coatings Technology, Philadelphia, PA, USA, 1980.

[5] E.V. Gulbekian and G.E.J. Reynolds, Polyvinyl alcohol in emulsion polymerization, in C.A. Finch (Ed.), Polyvinyl alcohol - Properties and Applications, Wiley, New York, 1973, chapter 17.

[6] Brochure: 'Mowiol Polyvinyl Alkohol', Hoechst, Frankfurt am Main, Germany, 1984.

[7] A.S. Dunn, Spectroscopic Properties of Polyvinyl alcohol, in C.A. Finch (Ed.), Polyvinyl Alcohol - Developments, Wiley, New York, 1992, Chapter 10.

[8] R.K. Tubbs, Polyvinyl alcohol acrylate and methacrylate copolymers and their applications in textile sizing and films, in C.A. Finch (Ed.), Polyvinyl Alcohol - Developments, Wiley, New York, 1992, Chapter 11.

[9] M. Maruhashi, Modified Polyvinyl Alcohols 1: preparation, properties, and applications of polyvinyl alcohols containing carboxylic groups, in C.A. Finch (Ed.), Polyvinyl Alcohol - Developments, Wiley, New York, 1992, Chapter 6.

[10] B. van Lent and J.M.H.M. Scheutjens, J. Phys. Chem., 94 (1990) 5033-5040.

[11] M.A. Cohen Stuart, T. Cosgrove and B. Vincent, Adv. Colloid Interface Sci., 24 (1986) 143-239.

[12] T. Cosgrove, N. Finch and J. Webster, Colloids Surfaces, 45 (1990) 377-389.

[13] Th. van den Boomgaard, T.A. King, Th.F. Tadros, H. Tang and B. Vincent, J. Colloid Interface Sci., 66 (1978) 68-74.

[14] R.A. Croot, A.R. Goodall and S.B. Lubetkin, Colloids Surfaces, 49 (1990) 351.

[15] M.R. Munch and A.P. Gast, J. Chem. Soc., Faraday Trans., 86 (1990) 1341-1348.

[16] G.J. Fleer and J.M.H.M. Scheutjens, Colloids Surfaces, 51 (1990) 281-298.

[17] O.A. Evers, J.M.H.M. Scheutjens and G.J. Fleer, J. Chem. Soc., Faraday Trans., 86 (1990) 1333-1340.

Summary

Ceramic products are usually made from powders which are processed into a green body, with a shape dictated by the final product. Organic binders are used to give the green product sufficient mechanical strength. A sintering process at high temperature converts the green body into the final ceramic product. In electronic ceramics, a high density and a homogeneous microstructure are required to obtain high quality products. For that purpose solid state sintering, in which no liquid phase is present, is applied. The result of the sintering process is highly dependent on the structure of the green body. Small pores will disappear during sintering but large ones will remain, resulting in a lower quality.

The ideal ceramic powder has small (submicron) particles with a narrow size distribution and no hard agglomerates. Unfortunately, hard agglomerates often occur in ceramic powders. Milling of the ceramic powder in a liquid is often used to break down hard agglomerates. Voids or holes in the ceramic product can be due to these hard agglomerates or due to inadequate processing of the powder, which leads to a green body with many large pores.

The study of the properties of powders dispersed in liquids is a branch of colloid chemistry. By using colloid chemical methods, control over the particle interactions can be achieved, which then allows the production of dense and homogeneous green bodies.

Van der Waals attraction between particles of the same composition may cause flocculation. A dispersion with such a flocculated material will give a highly porous, low density green body. Roughly speaking, two methods are available to make the particles repulsive, allowing the production of high-density homogeneous green bodies. The first is the adsorption of ionic species onto the surface of the particles. The particles will then repel each other electrostatically. The second method is to adsorb polymers onto the surface of the particles. If two particles with adsorbed polymer layers approach each other, the polymer concentration in the contact region between the particles is increased. The higher osmotic pressure in that region leads to repulsion. This so-called steric stabilisation can be quite effective if the adsorbed polymer layer has a sufficient thickness. The repulsion should start at a particle separation where the Van der Waals attraction still is weak.

Adsorbed layers with sufficient thickness can be made by adsorption of homopolymers, provided the molecular weight and the coverage are high enough. Long tails then develop due to crowding on the surface. However, block copolymers with only one adsorbing block can be much more effective. Very thick adsorbed layers occur if the non-adsorbing block is highly stretched, a situation that occurs at a suitable ratio in length between the adsorbing and non-adsorbing blocks.

Clearly, the adsorption of polymers and their conformation in the adsorbed layer are crucial in steric stabilisation. In this thesis the adsorption of polyvinyl alcohol (PVA) and polyacrylic acids salt (PAAS) onto $BaTiO_3$ are studied, with the objective to make sterically stabilised dispersions in an aqueous environment. $BaTiO_3$ is an important material for electronic ceramics; it is used in the manufacture of capacitors and in resistors with a positive temperature coefficient.

All adsorption experiments are analysed by Size Exclusion Chromatography (SEC). Using SEC, not only can the adsorbed amount of polymer be determined but also the fractionation in chain length upon adsorption. Even the separate adsorbed amounts from mixtures of polymers can be analysed. The principles of SEC, its possibilities, and the methods and equipment used, are presented in Chapter 2.

In Chapter 3, the adsorption of PVA and PAAS on $BaTiO_3$ is studied. Adsorption of PVA occurs over the whole molecular weight range including short chains. The rounded shape of the adsorption isotherm indicates competition between chains of different length, pointing to preferential adsorption of the longer chains. This contradiction is probably due to the nature of PVA, which can be considered as a copolymer with short polyvinyl acetate blocks and branches distributed over the chain. Moreover, the fraction of acetate groups depends on the chain length. Accordingly, PVA must be considered as a mixture of several polymers with slightly different chemical compositions. Pure homopolymer adsorption behaviour cannot be expected with such a polymer. The adsorption of PAAS results in a rather peculiar fractionation behaviour: an intermediate molecular weight fraction adsorbs preferentially. This phenomenon is analysed in more detail in Chapters 4 and 5. In the adsorption onto $BaTiO_3$ from mixtures of PAAS and PVA, no adsorption of PVA occurs if enough PAAS is present to cover the surface of the particles completely. On the other hand, pre-adsorbed PVA cannot be displaced from the surface by addition of PAAS afterwards. Mixed adsorbed layers are found in this situation.

The typical molecular weight fractionation with PAAS is studied in more detail in Chapter 4. Several PAAS samples with different molecular weights are used. It is shown that the molecular weight distribution (MWD) of the polymer has a significant influence on the result. The electrostatic repulsion between adsorbed chains on the surface and chains in solution prevents polymer chains above a certain length from reaching the surface. If the whole MWD is below this critical value, the longest chains adsorb preferentially, which is the expected behaviour for homopolymer adsorption. If the critical value lies within the MWD of the PAAS, the longer chains cannot participate in the exchange process, leaving an intermediate fraction adsorbed on the surface. PAAS samples with a MWD above the critical value and with only a few short chains show adsorption over a wide molecular weight range. Increasing the salt concentration of the solution decreases the electrostatic barrier, allowing longer chains to reach the surface. The preference in adsorption is then shifted to higher chain lengths.

In Chapter 5 we report on the kinetics of the adsorption of two PAAS samples. The adsorbed amount and molecular weight fractionation change relatively quickly over the first two days and more gradually over a longer period. At low salt concentrations changes occur for up to 24 days. Theoretical calculations predict a depletion layer with a minimum in polymer concentration that strongly depends on the chain length of the PAAS. This theoretical result is in line with the chain-length dependence of the adsorption kinetics and qualitatively explains the fractionation effects. The experiments show that part of the adsorbed short chains is not exchanged by larger ones, but remains on the surface. At low salt concentration, the amount of adsorbed short chains even increases with time. An adsorption model is postulated in which the packing and the rearrangement of the adsorbed chains on the surface depend on the chain length and the salt concentration. The short chains are expected to fill the gaps between the larger ones.

In Chapter 6 several PVA-based copolymers are tested for their ability to sterically stabilise $BaTiO_3$. Regular PVA is shown to be ineffective. The results obtained in Chapter 3 make it possible to define potentially suitable steric stabilisers for $BaTiO_3$ based on PAAS and PVA. The first choice is a block copolymer with PAAS as the anchor block and a PVA block as the stabilising moiety. Three types, with different ratios in block length, were evaluated. Each of these proved to be suitable for stabilisation. Random copolymers of PVA containing a small fraction of carboxylic acid are a possible alternative. Seven of these types were tested; only two were successful. An evaluation of the stabilising mechanism showed pure steric stabilisation with a block copolymer and combined steric and electrostatic stabilisation with one of the random copolymers. Green bodies with an improved homogeneity could be made with both the block and random copolymers, provided steric or electrosteric stabilisation is realised.

Finally, in Chapter 7, two of the ineffective random copolymers are compared with one of the successful types. In addition, one of the block copolymers was included for comparison. The chemical compositions were studied with IR spectroscopy, and SEC was used for comparing the MWDs and for studying the adsorption behaviour. The IR analysis showed deviating chemical compositions for the ineffective random copolymers. One of these has lactone groups in the chain while the other one has a very high acetate content. SEC analysis showed a significantly lower chain length for both ineffective PVA random copolymers in comparison with the one suitable for steric stabilisation. This is the most probable reason for the ineffectiveness of these random copolymers. With short chains the steric layer thickness is too low for steric stabilisation. The block copolymer has an average molecular weight comparable to the stabilising random copolymer. Moreover, the longest chains of the block copolymer adsorb preferentially, probably resulting in a thick adsorbed layer. In the fractionation upon adsorption of the block copolymer there is no further increase in the relative amount of adsorbed long chains above a certain surface coverage. Further increase in adsorption above this coverage is possible if an increased stretching of the adsorbed chains occurs at equal relative amounts of the various chain lengths.

In this thesis it is shown that the design of suitable block copolymers for steric stabilisation of particles can be based on adsorption experiments with the separate homopolymers. The chemical composition of stabilising random copolymers can be derived from the same experimental results. Moreover, it is shown that the adsorption kinetics of polyelectrolytes is highly influenced by the electrostatic barrier between the chains in solution and the surface of the particles.

Adsorptie van wateroplosbare polymeren op bariumtitanaat en het effect op de colloïdale stabiliteit

Samenvatting

In ons dagelijks leven worden veel keramische produkten gebruikt. Bekende voorbeelden zijn aardewerk vazen, potten en borden. Deze produkten worden al eeuwen gemaakt als gebruiksvoorwerp maar ook als kunstobject. Chinees porselein neemt hierbij een bijzondere plaats in door de veel hogere dichtheid. Keramiek voor technische toepassingen is echter pas in deze eeuw ontwikkeld. Het witte porselein dat gebruikt wordt om bovengrondse elektriciteitsdraden te leiden en te isoleren van de palen is een bekend voorbeeld. Later zijn talloze nieuwe soorten keramische materialen ontwikkeld die nu op grote schaal toegepast worden, zoals bijvoorbeeld hittebestendige produkten en slijtvaste lagen op snijgereedschappen.

Ook in de elektronische industrie worden veel keramische produkten toegepast. De meeste voorbeelden worden gevonden in elektrische schakelingen in TV's, radio's, CD spelers, computers, etc. Keramische weerstanden en condensatoren zijn hierbij de bekendste produkten. Daarnaast zijn er nog vele andere toepassingen. Een TV beeld wordt gemaakt met behulp van een keramische magneet die de elektronen afbuigt naar de juiste plaats op het TV scherm waardoor de gewenste kleur op die plaats ontstaat. Een keramische piëzoelectrische sensor zorgt voor het tijdig opblazen van een airbag in een auto.

Anders dan bij huishoudelijke toepassingen worden aan technische keramische produkten vaak hoge eisen gesteld met betrekking tot de homogeniteit en de dichtheid. Zo wordt de breeksterkte van een keramisch produkt veel lager indien er poriën in aanwezig zijn. Ook functionele eigenschappen (b.v. de weerstand) worden daardoor vaak nadelig beïnvloed.

Keramische produkten worden meestal gemaakt vanuit een keramisch poeder dat verwerkt wordt tot de gewenste vorm. Deze zogenaamde groene (nog niet gesinterde) vorm is bij voorkeur een compacte poederstapeling die dan echter altijd nog een porositeit van 40 tot 50 % heeft. Vaak worden additieven (binders) gebruikt om de poederstapeling voldoende sterkte te geven. Het groene produkt wordt vervolgens bij hoge temperatuur gebakken (gesinterd), waarbij de porositeit dient te verdwijnen. De organische binders verbranden bij het opwarmen naar de sintertemperatuur. Poriën boven een bepaalde grootte blijven echter achter in het produkt. Het zal duidelijk zijn dat de homogeniteit van het groene produkt bepalend is voor de kwaliteit van het uiteindelijke, gesinterde, keramische produkt. De kwaliteit van het keramische poeder en de verwerkings- en vormgevingstechnologie bepalen op hun beurt de homogeniteit en porositeit van het groene produkt. Vaak komen in keramische poeders poreuze klontjes (agglomeraten) voor met een sterke samenhang. Deze kunnen poriën in het eindprodukt veroorzaken. Door het poeder intensief te malen in een vloeistof wordt getracht deze agglomeraten af te breken. Verder moet bij de verwerking van het poeder voorkomen worden dat opnieuw klontering (agglomeratie of vlokking) van de deeltjes optreedt. In het laatste geval zal door de ijle agglomeraten een poreus groen produkt ontstaan.

De bestudering van het gedrag van kolloidale deeltjes in vloeistoffen is het vakgebied van de kolloidchemie. Met behulp van technieken uit deze tak van wetenschap is het mogelijk om dichte, homogene, groene produkten te maken die gesinterd kunnen worden tot keramische produkten met een hoge kwaliteit.

De kolloidchemicus kan gebruik maken van de adsorptie van polymeren uit een oplossing om het agglomeratiegedrag van deeltjes te beïnvloeden. Polymeren zijn lange, ketenvormige moleculen met een zich herhalende eenheidsstructuur (segment). Polymeren waarin verschillende soorten segmenten voorkomen worden copolymeren genoemd. Als deze segmenten willekeurig verdeeld over de polymeerketen aanwezig zijn, hebben we te maken met een random-copolymeer, terwijl we van een blokcopolymeer spreken als de segmenten soort-bij-soort gerangschikt langs de keten voorkomen. Een blokcopolymeer kan beschouwd worden als twee verschillende homopolymeren die aan de uiteinden met elkaar verbonden zijn.

In dit proefschrift wordt het adsorptiegedrag van enkele wateroplosbare polymeren op bariumtitanaat ($BaTiO_3$) bestudeerd. $BaTiO_3$ is een keramisch poeder dat als uitgangsstof voor een aantal elektronische componenten wordt gebruikt. Bovendien wordt het effect van deze adsorptie op het vlokkingsgedrag van de deeltjes onderzocht.

De adsorptie van polymeren kan bestudeerd worden met behulp van een techniek die als "Size Exclusion Chromatography" (SEC) bekend staat. Het voordeel van deze analytische techniek is dat niet alleen bepaald worden hoeveel polymeer adsorbeert, maar dat tegelijkertijd vastgesteld kan worden of er een voorkeur is voor ketens van een bepaalde lengte bij de adsorptie. In hoofdstuk 2 wordt het principe van deze meettechniek uitgelegd en worden de gebruikte opstelling en methoden beschreven.

In hoofdstuk 3 wordt het onderzoek naar het adsorptiegedrag op $BaTiO_3$ van twee polymeren, polyvinylalcohol (PVA) en polyacrylzuur zout (PAAS), beschreven. PAAS is een zogenaamd polyelektrolyt, een polymeer dat door dissociatie van groepen in waterige oplossingen een elektrische lading op de keten krijgt.

Uit oplossingen van elk van de polymeren afzonderlijk wordt adsorptie gevonden. Uit een mengsel van beide polymeren blijkt echter alleen PAAS te adsorberen. Wordt eerst PVA geadsorbeerd en pas na enige tijd PAAS toegevoegd, dan wordt het PVA niet verdrongen, maar wordt er adsorptie van beide polymeren gevonden. Bij adsorptie van alleen PAAS is een merkwaardige fractionering gevonden. Een middenfractie uit de moleculairgewichtsverdeling blijkt preferentieel te adsorberen, terwijl normaal gesproken de langste ketens deze preferentie vertonen.

Dit merkwaardige verschijnsel is verder uitgediept in de twee volgende hoofdstukken. De invloed van de moleculairgewichtsverdeling van het PAAS en van de zoutconcentratie in de polymeeroplossing worden nader bekeken in hoofdstuk 4. Tijdseffecten worden in hoofdstuk 5 beschreven. De resultaten wijzen op een mechanisme waarbij een electrostatische barrière ontstaat tussen de ketens in de oplossing en het oppervlak van de deeltjes. De hoogte van deze barrière hangt af van de elektrische potentiaal van het oppervlak en van de totale lading op de keten. Hierdoor wordt de hoogte van de barrière afhankelijk van de ketenlengte, immers: elk volgend polymeersegment draagt één extra lading bij. Zo worden de ketens sterker geremd tijdens hun nadering tot het oppervlak naarmate ze langer zijn. Door hun hogere diffusiesnelheid adsorberen de kortste ketens het eerst, waarna geleidelijk de iets langere ketens het oppervlak bereiken en adsorberen. Vaak worden de korte ketens dan weer verdrongen. Deze uitwisseling door lange moleculen dooft uit doordat ketens boven een bepaalde lengte het oppervlak niet meer kunnen bereiken. Hierdoor blijft een middenfractie achter op het oppervlak. Berekeningen ondersteunen deze hypothese.

Met de resultaten van hoofdstuk 3 kunnen blokcopolymeren ontworpen worden die in principe in staat moeten zijn om $BaTiO_3$-dispersies te stabiliseren tegen vlokking. Ook kan verwacht worden dat PVA's met willekeurig over de keten verdeelde geladen segmenten van dezelfde samenstelling als in PAAS, een stabiliserende werking zullen hebben. In hoofdstuk 6 worden verschillende van deze copolymeren getest op hun stabiliserende eigenschappen. De blokcopolymeren blijken inderdaad uitstekende stabilisatoren te zijn. Uit een reeks van random-copolymeren blijken er echter slechts enkele te werken. Met de stabiliserende polymeren kan de groene structuur van keramische produkten aanzienlijk verbeterd worden.

In hoofdstuk 7 wordt nagegaan waarom slechts enkele van de beproefde random-copolymeren een stabiliserende werking op $BaTiO_3$-dispersies hebben. Zowel de chemische samenstelling als de moleculairgewichtsverdeling van de polymeren worden bepaald. Bovendien wordt het adsorptiegedrag bestudeerd. Het random-copolymeer met de hoogste ketenlengte blijkt het meest efficiënt te zijn in stabilisatie.

In dit proefschrift is aangetoond dat het ontwerp van effectief kolloidaal stabiliserende blokcopolymeren gebaseerd kan worden uit adsorptie-experimenten met de afzonderlijke homopolymeren.
Bovendien is de adsorptie van polyelektrolyten bestudeerd. De electrostatische barrière tussen de ketens in oplossing en het oppervlak van de deeltjes blijkt het adsorptiegedrag sterk te beïnvloeden. Een bijzondere fractionering is het gevolg.

Levensloop

Ton de Laat werd geboren op 24 april 1952 te Sint Michielsgestel. Aldaar haalde hij in 1968 het Mulo-B diploma aan het Instituut 'Huize Ruwenberg'. Vervolgens werd via het 'Voorbereidend Jaar voor de Hogere Technische School' toegang tot het Hoger Beroeps Onderwijs verkregen. In 1969 werd begonnen met een studie aan de afdeling Chemie van de HTS in Eindhoven, die in 1973 met een diploma werd afgesloten.

Na zijn Militaire Dienstverplichting kwam hij op 1 maart 1975 in dienst van de NV Philips bij het Natuurkundig Laboratorium te Eindhoven in de groep Grensvlakchemie. In zijn eerste baan deed hij vooral onderzoek aan dispersies van magnetische deeltjes in water en organische vloeistoffen. In 1981 werd hij betrokken bij het opstarten van de Compact Disc plaatproduktie. In zijn laatste twee jaren op het Natuurkundig Laboratorium werkte hij aan de formulering van fosforsuspensies voor TL lampen.

Op 1 april 1984 verwisselde hij binnen Philips van afdeling en trad hij in dienst van het Centre for Manufacturing Technology (CFT). Elektrisch geleidende pasta's en lijmen was hier zijn eerste onderwerp. Enkele jaren later, bij het begin van de Pasta- en Poedertechnologie activiteit op het CFT, ging hij zich vooral bezig houden met de bijzondere aspecten van waterige formuleringen. In de loop der jaren zijn vele onderzoeken verricht met een zeer wisselend karakter, variërend van directe probleemoplossing voor de fabricage tot toegepast wetenschappelijk onderzoek. Uit één van de onderzoeken uit de laatste categorie is dit proefschrift ontstaan.

Dankwoord

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Derks heeft een groot deel van de stabiliteitsexperimenten uitgevoerd. Gerard van den Heuvel heeft de chromatografische methode ontwikkeld waarmee een groot deel van de experimenten geanalyseerd is, bovendien zijn vrijwel alle adsorptie-experimenten door hem uitgevoerd. Beste Gerard, zonder jouw inzet en nauwkeurige experimenten zou dit werk er nooit gekomen zijn. Ook Fred Verhoeckx en Wilko van Tilburg hebben bijgedragen aan de ontwikkeling van de chromatografische methode. André de Bruijn heeft de polymeren gekarakteriseerd met IR-spectroscopie. Marcel Böhmer, een van mijn Nat Lab collega's, heeft het rekenwerk verzorgd waarmee een groot deel van de polyelektroliet adsorptie-experimenten verklaard kon worden. Verder wil ik alle collega's danken die bijgedragen hebben door het lezen van mijn manuscripten. Valerie Mott heeft de figuren gemaakt en bovendien heeft zij de lay-out van dit proefschrift verzorgd.
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