ABSTRACT

WU, NING. Adsorption and Diffusion of Highly Charged Cationic Polyelectrolyte into Silica Gel Particles. (Under the direction of Martin A. Hubbe and Orlando J. Rojas.)

An understanding and ability to predict permeation behavior is important when applying polyelectrolyte treatments in enhanced oil recovery, papermaking, biomass hydrolysis, catalytic process, chromatographic separation, water treatment etc. In this research, polydiallyldimethylammonium chloride (poly-DADMAC) was used as a probe molecule to investigate major factors affecting penetration of polyelectrolyte into small pores, including time, polyelectrolyte concentration, substrate consistency, molecular mass, pH, conductivity, etc. Streaming potential tests were used innovatively to understand polyelectrolyte diffusion and adsorption on external surface and in nanopore networks. The magnitude change in streaming potential, which was taken as evidence of permeation, increased with increasing polyelectrolyte dosage, with decreasing molecular mass. Increasing ionic strength tended to enhance adsorption of high-mass cationic polymers on the outer surfaces, but only a relatively small effect on permeation of high-mass cationic polymer into silica gel (nominal pore sizes of 6 nm or 30 nm) was observed. Adsorption of very-low-mass cationic polymer onto the outer surfaces and inside the 6 nm pore size silica gel was maximized at an intermediate salt level (1000 μS/cm conductivity). Electrokinetic tests also were used to provide evidence of polyelectrolyte desorption from mesoporous material. Another technique, a streaming current titration with a particle charge detector (PCD) was used to quantitatively determine polyelectrolyte adsorption on the external and internal surfaces of silica gel.
particles at levels of the above factors. The diffusion slowed down as the extension of the time for adsorption experiment. The adsorbed amount of poly-DADMAC was controlled by both the pore size and the surface area. The highest adsorption amount, based on mass of the substrate, was achieved when using silica gel having an intermediate pore size (15 nm) at a relatively high solution concentration of very-low-mass poly-DADMAC. The results were fit well to an assumed Langmuir model of the adsorption process. Streaming potential tests and streaming current tests may produce different result due to the difference in measurement principles. Further investigation may be needed for confirmation. Several techniques, such as BET tests and gel permeation chromatography were used to characterize the substrates and poly-DADMAC.
Adsorption and Diffusion of Highly Charged Cationic Polyelectrolyte into Silica Gel Particles

by
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Chapter 1  Permeation of Polyelectrolytes and Other Solutes into the Pore Spaces of Water-Swollen Cellulose: A Review

Abstract

The rate and extent of transport of macromolecules and other solutes into cellulosic materials and fibers have important applications in such fields as papermaking, textiles, medicine, and chromatography. This review considers how diffusion and flow affect permeation into wood, paper, and other lignocellulosic materials. Because pore sizes within such materials can range from nanometers to millimeters, a broad perspective will be used, also considering some publications related to other porous materials. Factors that limit the rate or extent of polymer or other solute transport into pores can involve thermodynamics (affecting the driving motivation for permeation), kinetics (if there is insufficient time for the system to come to equilibrium), and physical barriers. Molecular flow is also affected by the attributes of the solute, such as molecular mass and charge, as well as those of the substrate, such as the pore size, interconnectedness, restricted areas, and surface characteristics. Published articles have helped to clarify which of these factors may have a controlling influence on molecular transport in different situations.

Keywords: Diffusion; Flow; Permeation; Porous materials; Cellulose; Polyelectrolytes; Solutes; Enablers
1. Introduction

Permeation of macromolecules and other dissolved or suspended matter from aqueous solution into cellulosic material is important in the manufacture of paper, in the sizing of textile fibers, in filtration, in various types of absorption processes, and in the manufacture of cellulosic composites or nanocomposites. In each of these domains it is important to understand factors that affect the degree to which molecules, ions, surfactants, polyelectrolytes, or colloids penetrate into the interior pores of lignocellulosic matter. Polyelectrolytes are of particular interest. In papermaking, often it is considered advantageous for polyelectrolytes to remain at or near to the outer surface of cellulosic fibers, thereby maximizing their contributions to various processes, such as fine-particle retention, dewatering, or the development of inter-fiber bonding. In the textile industry surface-finishing with polymers and other additives is important for fiber processing and use. In bioethanol production the diffusion of enzymes determines the efficiency with which cellulose hydrolysis can take place. In the wood industry it is important to understand the permeation of preservatives, components of surface finishes, and even of rot-related enzymes.

In many applications there is an advantage if one can achieve faster penetration of polymeric materials into the pores of cellulosic materials. This is certainly true in the case of glue penetration for wood-based construction (Kamke and Lee 2007). Material transport by convection and diffusion, as well as by fluid penetration are essential steps for chemicals to interact with wood chips during production cellulosic pulps (Gustafson
et al. 1997). The interior part of the wood chips is not easily reached by chemicals. Thus, short contact times of wood chips with reactive liquor may result in non-uniform cooking of cellulose pulp. Polymer permeation phenomena also are important in fields such as enhanced oil recovery; polymers may be used to influence the channeling of flow through oil-containing strata (Babadagli 2007).

Publications considered in this review article provide evidence of factors and mechanisms that affect the rate or extent to which solute transport occurs into the fine pores of cellulosic materials. The review takes advantage of the fact that relevant work also has been carried out with such materials as silica gel, mineral beds, and plastic materials. Emphasis will be placed on charged polymers, especially in cases where opposite charges contribute to a driving force favoring permeation. For completeness, such situations will be contrasted with cases where adsorption may be favored by changes in entropy accompanying permeation and adsorption. Both bulk transport by convection and molecular diffusion will be considered. Aspects of the fine-scale porosity, pore sizes, and interconnectedness of pores within cellulosic materials (tortuosity) also will be considered.

At the outset it is important to acknowledge several prior review articles, many of which go deeper than the present article in different areas that may be of interest to particular readers (Stamm 1953; Stone and Green 1958; Siau 1984; Robertson and Lönnberg 1991a,b; Lönnberg et al. 1992; Muralidhar and Ramkrishna 1993; Sahimi 1993; Starov 2004; Dechadilok and Deen 2006; Delgado 2006; Babadagli 2007; Johnson
et al. 2007; Kamke and Lee 2007; Chavez-Rojo et al. 2008). Also it is worth noting several articles dealing with nonuniformities in transport rates through packed columns, which can result in “tails” in eluted solutes (Newman and Walker 1992; Kosakowski 2004; Obi and Blunt 2004; Delgado 2006).

2. Organization of this Article

This article is organized into three main sections, the first of which deals with factors that can affect permeation. Emphasis is placed on publications reporting practical observations. Factors affecting permeation, relating to the nature of the pores, the fluids, and interactions at interfaces, tend to apply for a broad range of applications; therefore citations will be considered from diverse fields.

The next main section considers mechanisms of permeation, with emphasis on flow and diffusion. Flow can be defined as movement of a fluid phase relative to its surroundings. Diffusion can be defined as a mechanism by which transport is driven by a gradient in concentration. In many practical situations transport of solutes will result from a combination of diffusion and fluid motion. Flow is important in cases where liquid moves either into or through a porous material; in such cases the moving fluid may or may not be able to carry along various dissolved or entrained substances. As will be discussed, barriers related to entropy, charge, or physical inaccessibility may tend to exclude the polymeric material in some instances.

Realizing that certain readers may have an interest in promoting access of polyelectrolytes, enzymes, or other solutes into the interior spaces of cellulosic materials,
A third section of this article will be devoted to “enablers” of permeation. An enabler is defined here as anything that promotes either more rapid or more complete penetration, either by flow or by diffusion through aqueous solution.

3. Overview of Factors Affecting Diffusion and Flow in Pores

Various factors can affect the progress of dissolved or very finely suspended substances into porous media. These factors generally can be grouped into the pore attributes, the nature of the fluid (carrier), and the interactions between the fluid medium and the solids, including any dispersed substances (soluble, colloidal, or particulate) (Lönnberg et al. 1992; Lebon et al. 2006). The complexity of diffusion and flow in pores involves many branches of science, of which thermodynamics deserves special attention. Variables of interest for diffusion and flow in pores include the set of classical variables, e.g. mass, momentum, and heat, as well as the corresponding fluxes of these quantities.

3.1 Pore Attributes: Case of Cellulosic Materials

Cellulose is a porous material, especially when it is wet with water. Many applications of cellulose involve its interaction with fluids that flow or diffuse into its porous structure. Knowing the physical-chemical structures and attributes of these pores helps to understand associated interactions of cellulose’ surface with fluids and provides guidance for related applications. For instance, Kamke and Lee (2007) have considered many such factors in their review of adhesive penetration into wood.

Pore size and size distribution (morphology)
Permeability of cellulosic materials can be expected to increase with increasing pore size or with the removal of obstructions from pores. For instance, alkaline conditions tend to promote more rapid penetration into cellulosic materials (Scallan 1983); this has been attributed to increased swelling, an effect that can increase the sizes of pores.

There are at least two classes of pores within different types of cellulosic materials. Relatively large pores, often in the range of 0.1 to 100 µm, may exist either between the fibers (as in the case of paper products) or inside the fibers (i.e. the uncollapsed lumens of fibers in wood). Relatively small pores will be present within the cell walls of the fibers. The sizes of the latter pores have been the subject of considerable interest and discussion. Elegant work by means of the solute exclusion principle was used as evidence for pores in the cell walls of never-dried sulfite fibers having widths generally in the range of 2 to 20 nm (Stone and Scallan 1968). However, these estimates were later disputed as being too low, since the analysis was said not to take into account various entropic factors (Alince and van de Ven 1997). Based on adsorption of polyelectrolytes, the latter authors concluded that the pores in never-dried chemical pulps should mostly be larger, possibly 40 to 100 nm. Analyses of penetration into cellulosic materials also need to take into account the effects that the diffusing solution may have on the swelling, and thus the pore sizes within the material.

Senden et al. (2000) studied the effects of pore morphology on penetration rates for ink vehicles. In printing operations the setting of inks often involves the passing of a
vehicle though a surface of a paper. In such cases a higher amount of micro-pores near the surface of paper may allow more ink pigments to be held near the paper surface, and this would be expected to result in a higher density of the printed image. It was noted that different micro-pore systems imbibe liquids at different rates, depending on their geometries. For instance, converging pore features can promote more rapid permeation, whereas sharply diverging features, as one passes toward the interior of a porous material, can act as blocks to capillary penetration.

Pore Volume

The fractional porosity can be defined as the ratio of the voids volume to the total volume of that material. In other words, porosity represents the storage capacity. However, a high porosity doesn’t necessarily mean that the material has a high permeability, since the void spaces may be either interconnected or isolated. To give an example from geology, shales tend to have high porosity but very low permeability due to the poorly interconnected voids. By contrast, sandstones generally can have both high porosity and high permeability.

In the case of cellulosic materials, the pores may be between fibers, within the fiber walls, or consisting of the fiber lumens and their connections at pit openings (Stamm 1953). During wood’s growth, pores can serve as a medium for transport of water and other nutrients. Pits can become narrowed due to drying, and they also can become choked to various degrees by wood resins. They also enable chemical diffusion and penetration during pulping. In the case of hardwood pulps flow through vessels is
expected to be more important than flow through fiber lumens and pits (Stone and Green 1958).

Flow also can occur through the cell walls of cellulosic materials, especially when the material is water-saturated. The mesopores within cellulosic material tend to become somewhat enlarged during pulping operations due to the combined influences of swelling of the material and removal of lignin-rich domains, leaving behind the spaces once occupied by these domains (Berthold and Salmén 1997). The shapes and connections within the pore structure can be expected to change also as a result of mechanical refining of cellulosic pulps. When the pulp has been dried, some of pores will be irreversibly closed (Stone and Scallan 1966).

*Dimensions of the substrate*

Much can be learned about the porosity of wood by considering the dimensions of a typical wood chip used in pulping operations (Gustafson *et al.* 1997; Maattanen and Tikka 2008) or in a dilute acid pretreatment step in the production of cellulosic biofuels (Kim and Lee 2002). A wood chip for use in pulping often has a thickness in the range of 2-10 mm, whereas the length and breadth will be much larger (Schultz *et al.* 1999). The thinness of chips is intended so that pulping reagents can more-or-less completely penetrate the wood material before the onset of rapid chemical reaction. The thickness of chips has to be small enough so that diffusion in not the rate-limiting factor. Over-thick chips can be rechipped in order to overcome such problems (Maattanen and Tikka 2008).

*Tortuosity*
Tortuosity can be loosely defined as the ratio between the average distance that fluid has to travel to get through a material, compared to an imaginary straight-line distance. One way to quantify tortuosity of a non-conductive porous solid is by measuring the net conductivity when it is saturated with a salt solution of known bulk conductivity (Barrande et al. 2007). There also have been attempts at numerical simulation of tortuous pathways through a compact bed of particles (Ito et al. 2003). High tortuosity generally means that there are many twists and turns within the pore spaces.

In the case of pine and aspen wood, Jacobson and Banerjee (2006) estimated a tortuosity of 1.6, relative to the diffusion of the same aqueous solution in the absence of wood. A somewhat higher value for aspen, relative to pine was attributed to a finer fiber structure. Leyvaramos and Geankoplis (1994) obtained a tortuosity value of 3.5 for activated carbon, a material that can retain various structural features related to its origin as wood.

The effective tortuosity of a material can be strongly dependent on what one chooses as a probe to measure tortuosity. For instance, in one case Olson et al. (2005) observed that the tortuosity of a packed bed was about 40 times greater for bacteria, in comparison with the suspending medium. Though these observations might have other contributing explanations, it is reasonable to expect that relatively large particles or cells in a fluid medium might not be able to take advantage of the most direct routes through a porous material, depending on the dimensions of the most constricted passageways.
Törnqvist *et al.* (2001, 2004) measured the progress of HS ions through individual wood chips, when pulping liquor was placed on one side of the chip and deionized water was placed on the other. Though the movement of the front of ions (the drift speed) was similar to what was predicted by ion diffusions rates, there also was evidence that the nature of the pulping chemicals changed to degree of swelling of the pores in the chip.

*Pore orientation*

Liquid diffusion through porous material may also be related to the orientation of pores. This is particularly true for wood materials. Thus, Ra *et al.* (2001) studied the unsteady-state diffusion of boron through southern pine (*Pinus* spp.) at various moisture contents, temperatures, and treatment conditions. The fastest rates of diffusion were observed in the longitudinal direction, followed by the radial and the tangential directions. They reported longitudinal diffusion coefficients 10 to 20 times larger than the radial diffusion coefficients, and radial diffusion coefficients two to four times larger than the tangential diffusion coefficients. The diffusion rate increased with time in all directions. The longitudinal diffusion rate increased rapidly with moisture content (MC), while a slow increase in the radial diffusion rate was observed at MCs above 90%. Temperature was found to have a more pronounced effect than MC. In later work by the same authors Ra *et al.* (2002) investigated constant radial diffusion coefficients of boron through southern pine (*Pinus* spp.). The concentration profile (the total amount of boron diffusing through wood and the amount of boron remaining on the wood surface after
different diffusion periods) of the treated samples was measured using a slicing technique.

Directional dependencies have been observed also in the case of pressure-induced flows through wood material. Stamm (1953) cited studies showing that flow in the direction of fibers can be 50 to 200 times greater than flow perpendicular to the fiber orientation under matched conditions. Sernek et al. (1999) studied the penetration of a liquid urea-formaldehyde adhesive (UF) into beech (*Fagus sylvatica* L.) wood. They found that penetration in the tangential direction was greater than in the radial direction. They also concluded that external pressure can expedite penetration.

Another factor that can affect permeability of a porous material in different directions is the presence of channels, cracks, or fractures (Wallstrom and Lindberg 1999; Zvikelksy and Weisbrod 2006; Maatinen and Tikka 2008). It has been shown that a disproportionate amount of fluid may pass through such favorable routes, especially when one is concerned with colloidal matter (Kjaergaard et al. 2004a).

*Interconnectedness*

Pores can exist individually, or they may be interconnected to various extents. Interconnectedness makes it more difficult to interpret or simulate various consequences of porosity. Researchers often begin their analysis of diffusion or penetration within pores by making various simplifying assumptions, which may involve selecting an arbitrary degree of interconnectedness. As noted by Stamm (1953) a bubble of air in a pore sometimes can be just as effective in impeding flow as a physical blockage.
To predict effects of interconnectedness on diffusion of polymers in solution, Gauthier and Slater (2008) proposed a new one-dimensional lattice Monte Carlo algorithm that considered the polymer as single Brownian diffusing particle. They integrated various effects such as the entropic forces acting on the polymer segments that are outside the channel, the external forces that are pulling the polymer through the pore, and the frictional effects (inside and outside the pores) involving the polymer chains and their environment.

*Pinch-points*

The velocity of an incompressible Newtonian fluid passing through a smooth cylindrical pore under a specified pressure, assuming laminar flow, is proportional to the square of the radius. It follows that if a channel contains portions in which the radius is smaller, such restricted areas will have a disproportionate effect on the overall resistance to flow. For permeation in solid wood, one of the best examples of a pinch-point consists of the pit junctions that join fiber lumens (Meyer 1974). It has been shown that pretreatment with cellulase enzymes can break down the pit membranes that obstruct flow through the lumen network within wood (Jacobs-Young et al. 1998); such treatment was found to greatly increase the penetration rates of pulping liquors, especially in the direction of the fibers within a chip.

The relative permeability is even more affected in cases where the fluid contains dispersed or macromolecular substances with dimensions similar to those of the pores. For example, if a polyelectrolyte molecule needs to adopt a compromised conformation
(e.g. elongated or stretched) in order to pass through the pore, then one can expect an additional contribution to flow resistance (Andrews et al. 1998; Odell and Haward 2008). If a pinch-point is small enough to effectively prevent a polyelectrolyte molecular from passing through, then the molecule may have to take a more circuitous path, effectively increasing the tortuosity in terms of that substance (Olson et al. 2005).

*Wettability*

Wettability is the tendency for a liquid to spread on a solid surface. Relative to permeation into porous materials, such considerations can be important when there are two or more fluid phases present, e.g., polar (water), non polar (oil), or gaseous (air). For example, wettability of paper plays an important role relative to the penetration of coatings and inks (Bousfield and Karles 2004). The wettability of paper can be influenced by the fluid properties, surface forces, and complex pore geometry. Iveson et al. (2001) showed that wetting can be successfully included in a model of permeation of a liquid into initially dry porous particles that are submerged in a fluid. Factors affecting such permeation include capillary forces, viscous resistance of the liquid as it passes through narrow channels, and the pressure of any air that may be trapped within the particles. Because it may take a long time for such trapped air to dissolve into the adjacent fluid and eventually diffuse away, there can be a significant delay in achieving complete wetting. Cellulose pulp manufacturers often attempt to overcome such problems by pre-steaming of wood chips, so that the interior spaces are filled with water vapor rather than air before introduction of cooking liquors (Stamm 1953; Paranyi and
Rabinovitch 1958; Malkov et al. 2003; Törnvist et al. 2004). In principle, the same effect could be achieved by applying vacuum to wood before addition of a penetrating liquid (Stamm 1953).

The surface free energy of cellulosic surfaces can be expected to have a major impact on permeability of liquids into initially dry material. Dourado et al. (1998) showed that rates of wicking can be used as a sensitive means of determining the free energy of microcrystalline cellulose. The system’s capillary force can be basically described in terms of two variables, the radius (or an equivalent radius) of the capillary, and the interfacial surface energies of the solid-liquid-gas interfaces. When the interfacial surface energies change, the contact angle (meniscus shape) and consequently the pressure difference across a liquid-gas interface will change to reestablish equilibrium.

Papermakers employ internal sizing chemicals, *e.g.* alkylketene dimer and rosin products, to hydrophobize many paper products, an effect that reduces water wettability of cellulosic surfaces (see Hubbe 2007). Sarmadi et al. (1993) studied the effects of fluorochemical repellant finishes on the wettability of nonwoven fabrics. Capillary flow rates were estimated from analysis of the water contact angles in combination with the fabric pore radius. These predictions were then compared with experimental results obtained from demand wettability and static absorption tests. The highest rate of water penetration was found in a fabric type that exhibited the lowest contact angle and the largest pore radius. Water repellency was found to be influenced more by the structure of
a fabric than by the finish applied. Lin and Jorge (2005) modeled the wicking of liquid through paperboard, taking into account various properties of both the liquid and the solid surfaces.

Ershov et al. (2003) showed that polyelectrolytes can have a subtle effect on wettability when their solutions are allowed to flow into quartz capillaries. The polyelectrolytes did not affect the surface tension at the air-liquid interface. However, large hysteresis effects were observed when comparing advancing vs. receding contact angles; these effects were attributed to the formation of a polyelectrolyte film on the quartz surfaces.

3.2 Fluid Attributes

Properties of the fluid phase also can be expected to affect the diffusion and flow in pores. Important variables include fluid rheological behavior, fluid chemical composition, solute component dimensions, interfacial tension, wettability, and diffusion coefficients. If a fluid solution or suspension is sufficiently dilute, often one can neglect the interactions among the solute molecules or suspended particles. As the concentration becomes higher, the apparent viscosity may become a function of the shear rate and shear history. Increases in a dissolved polymer’s molecular mass or concentration generally increase the apparent viscosity of the solution. The Mark-Houwink equation (Hiemenz and Lodge 2007) provides a means of predicting how these factors influence the intrinsic polymer solution viscosity and can help to elucidate their contributions to fluid diffusion in porous structure.
Flow fields can affect the conformation of an adsorbed polyelectrolyte, depending on the flow and shear rate relative to the wall of a pore (Fleer et al. 1993). Adsorbed chains can be either deformed by the fluid field (compressed against the substrate, or stretched in the flow direction) or desorbed from the substrate. This is especially important if the flow rate is sufficiently high and the polymer used has high molecular mass or is strongly swollen. Under some conditions in which adsorption is relatively weak, it is expected that polymer chains that first are stretched by a flow field would subsequently become adsorbed in higher amounts and adhere the substrate more tenaciously. Experiments have shown that hydrodynamic thickness can depend on flow-rate. Similarly, it is reasonable to expect that flow-induced changes to conformation may have an effect on pore penetration.

Viscosity

One way that polyelectrolytes affect fluid flow is by raising the viscosity of a solution. Thus, Andersson and Jarnström (2006) studied the controlled penetration of starch during the surface-sizing of paper and board. The colloidal stability of surface size dispersions affected the location of components in the final sized substrate. Results showed that salt-induced flocculation lowered the penetration of amphoteric starch into the porous substrate, while the opposite effect was observed in the case of the anionic starch, probably due to screening-reduced adsorption. Viscosity was shown to affect the diffusion of sizing agents. It was found that the location of surface sizing components could be controlled by tuning of colloidal interactions in the dispersion.
Dissolved polymer attributes that can affect permeation

The adsorbed amount of polyelectrolytes within cellulosic fibers or other porous media depends on the molecular mass of the polyelectrolyte. A decrease in molecular mass tends to increase the adsorbed amount. This rule holds true for many cationic watersoluble polyelectrolytes, such as polyethyleneimine, cationic dextran, and polydiallyldimethylammonium chloride (Wågberg 2000). By contrast, earlier work by Tatsumi and Yamauchi (1997) showed that a high-mass cationic copolymer of acrylamide remained mostly on the outer surfaces of cellulose fibers in solution. A distribution of molecular mass of the polyelectrolyte implies that some of the material can reach different sites within the fine-scale porous structure of a cellulosic substrate. However, because polyelectrolyte diffusion into porous media involves conformational changes, in addition to the strength of interaction with substrate surfaces, it is possibly misleading to attribute such effects to size considerations alone.

Important new information relative to cationic polyelectrolyte diffusion into cellulosic fibers has been provided by Horvath et al. (2008). Using fluorescent-labeled polyelectrolytes and confocal microscopy, they showed dependencies of the rate and extent of permeation on polyelectrolyte charge density and salt concentration. High-charge-density polyelectrolytes, such as poly-diallyldimethylammonium chloride, required months to fully diffuse into the cellulose, whereas lower-charge cationic dextran molecules diffused into the cell walls in a matter of hours. Diffusion from salt-free solution did not proceed very far, appearing to be mainly restricted to the surface regions.
By contrast, increased diffusion into cellulose fiber cell walls was observed with increasing salt content of the solution. The adsorbed amount increased roughly in proportion to the logarithm of elapsed time in contact with the polyelectrolyte solution.

One of the most intriguing findings of the cited work was that cationic polyelectrolytes adsorbing near to the surface of the cellulosic fibers did not appear to progress further into the cellulose with the passage of time (Horvath et al. 2008). Rather, the initial adsorbing macromolecules became more or less fixed in location, and later-arriving macromolecules had to diffuse past the already-adsorbed molecules.

Another event that can arrest the flow of polyelectrolyte-containing solution through the channels of a packed bed is the formation of polyelectrolyte complexes (De et al. 1997). The cited authors found that because the complexes required sufficient space in which to form, they tended to precipitate within relatively large pores of a packed bed, leaving the smaller channels in the bed relatively free of obstructions to flow. In this way, the formation of polyelectrolyte complexes could be used as a means of directing more of the flow towards smaller channels.

3.3 Interactions that Affect Flow and Diffusion into Pores

Three kinds of interactions between the penetrating solution and the cellulosic substrate are of prime interest. First, various interactions can affect the angle of contact between the solid and liquid phases, thus affecting the capillary pressure that often provides the main driving force for wetting to take place. Such changes in contact angle can be critical during flow into initially dry cellulose. Second, the aqueous solution may
affect the swelling of the material, thus affecting pores size. And third, the solute may either be attracted or repelled from the surfaces; the strength of adsorption of solute molecules onto the pore walls can be expected to affect surface charge, and in some cases adsorption can have a significant effect on the remaining open area for solution and solutes to pass through constricted areas of the pore network.

The work of Sekine and Nakatani (2002) provides a good example of how the charged nature of a solute can promote its permeation into porous material. The role of electrostatic attractions between a cationic dye and the negatively charged internal surfaces of silica gel were demonstrated by varying the pH and ionic strength. Greater dye permeation and sorption occurred at higher pH, conditions that favor a stronger negative charge at the silica surface. Less permeation occurred at higher ionic strength, consistent with a weakening of electrostatic effects. Permeation was also strongly affected by the pore size of the silica gel (Sekine and Nakatani 2004). An apparently increasing diffusion constant of dye molecules was observed for increasing pore size of the substrate.

*Interactions that may affect pore size*

Simple ions in water can affect diffusion within cellulosic materials by affecting the swelling, and hence by changing the effective size of the pore spaces. Past studies have shown that more swollen pulps tend to be more accessible to tracer substances (Bendzalova *et al.* 1996). In general, relatively high levels of salt ions can be expected to decrease swelling, due to the suppression of electrostatic and osmotic forces (Lindström
and Carlsson 1982; Scallan 1993). By shortening the range over which electrostatic forces of repulsion can act, the carboxyl groups that are found in many cellulosic materials become less effective in swelling the material. What is less often noted is that such salt effects can have an opposite trend at the limit of very low levels of ions in solution. Thus, relatively low levels of swelling have been observed in cases where deionized water has been used to suspend ion-free cellulosic fibers (Fält and Wågberg 2003; Li and Dai 2004). The latter observations have been attributed to a mismatch between the size of the available pore spaces and the space required for the existence of counter-ions in a diffuse double layer (Hubbe 2006).

The pH of the solution can be critically important to the wetting of cellulosic materials due to the fact that the water-loving character of the surfaces will be affected by the state of association of carboxylic acid groups. Thus, if the pH is higher than about 5, a majority of carboxyl groups associated with the outer cellulosic surfaces can be expected to be in their negatively charged carboxylate form (Herrington and Petzold 1992). As noted in an earlier review article (Hubbe 2006), the situation can be more complicated in the case of carboxyl groups on the surfaces of very small pores within the cell walls of fibers. In such cases dissociation may be suppressed due to the lack of sufficient space for the formation of ionic double layers adjacent to a charged surface. Such effects may be equivalently viewed as a difference in pH between the bulk phase and within the gel structure of the cellulose (Wågberg et al. 1989; Bygrave and Enlezos 1998). Such differences can be expected to become less important with increasing
electrolyte concentration, since double-layer thickness becomes very small in the presence of salt ions (Hiemenz and Rajagopalan 1997).

*Interaction effects of polyelectrolytes*

The degree to which a polyelectrolyte is either attracted or repelled from a substrate can have manifold consequences relative to its permeation. Before considering other, more subtle effects related to permeation, it can be useful to review how charge characteristics of a polymer and substrate are likely to affect adsorption. There often is a mechanistic relationship between a polymer’s adsorption characteristics and its rate or extent of permeation.

In the case of a charged polymer one can expect mutual repulsion between the like-charged segments. This repulsion can oppose accumulation in a surface region. A surface can carry a charge as well, and it is expected that changing the environmental conditions such as pH, salt concentration, *etc.*, would change the number of active surface sites. In particular, an increase in salt can decrease the energy penalty resulting from charge accumulation at a surface. But at the same time, increasing salt will tend to weaken electrostatic interactions between a charged polymer segment and an oppositely charged site on a substrate.

The main effects of charge interactions within and between a polymer and a surface, including both like-charge interactions and opposite-charge interactions, are summarized in Table 1.1, which is adapted from Fleer *et al.* (1993). The table shows in a general sense how the charged nature of both a dissolved polymer and a substrate can be
expected to affect adsorption, with special attention paid to the effects of salt addition. The quantity $\chi_s$ in Table 1.1 is the adsorption energy parameter, given by the difference in adsorption energy of the solvent vs. that of the polymer, all divided by the thermal energy $kT$. Spontaneous adsorption from the solvent onto the substrate occurs if $\chi_s$ has a positive value (Fleer et al. 1993).

Table 1.1 Polyelectrolyte Adsorption as a Factor Related to Permeation

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Surface</th>
<th>Main factor(s)</th>
<th>Salt effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Uncharged</td>
<td>Uncharged</td>
<td>Competition between ions and polymer segments</td>
</tr>
<tr>
<td>B</td>
<td>Charged</td>
<td>Uncharged</td>
<td>Mutual repulsion between polymer segments</td>
</tr>
<tr>
<td>C</td>
<td>Same charge signs</td>
<td>Segment-segment and segment-surface repulsion (high $\chi_s$)</td>
<td>+</td>
</tr>
<tr>
<td>D1</td>
<td>Opposite charge signs</td>
<td>D1 pure electrosorption ($\chi_s \leq 0$)</td>
<td>-</td>
</tr>
<tr>
<td>D2</td>
<td>Opposite charge signs</td>
<td>D2 electrosorption enhanced by surface affinity ($\chi_s &gt; 0$)</td>
<td>- or +</td>
</tr>
</tbody>
</table>

+ salt promotes the adsorption  - Hinder the adsorption

One of the most fascinating aspects related to Table 1.1 is the concept that ionic charge can affect adsorption even in cases where the water-soluble polymer is uncharged. For example, adsorption of polyethylene oxide (PEO) on silica will decrease with increasing pH, holding other conditions constant. A more general effect has to be considered, namely, the fact that the surface charge has to be compensated by counter-ions in the double layer, competing for space with the uncharged segments. The competition is enhanced when counter-ions have a non-electrostatic affinity for the surface. Segment-surface interaction involving electrostatic forces can either promote or
hinder the adsorption. As this kind of electrostatic forces can be screened by salt ions, it is reasonable to expect results to be affected by the type of ions, their concentrations, as well as the pH.

4. Mechanisms of Diffusion and Flow into a Porous Substrate

The previous section highlighted examples showing the effects of different factors on the permeation of polyelectrolytes and other substances from solution into porous materials. A number of mechanisms were mentioned to account for these effects. The present section considers some of these mechanisms in greater detail. By applying such concepts, permeation phenomena can be understood as an overlapping set of thermodynamic, kinetic, substrate morphological, and mechanical considerations that together govern the location of a polyelectrolyte as a function of time.

The fluid phase will be considered first. The fluid system may be a single phase, such as pure water, an aqueous solution, or multi-phase (such as water with air or oil, or others). In the case of multiple phases, the fluids might be immiscible or miscible. Solutes can significantly affect flow behavior. The discussion below will start with simple cases and works toward more complicated cases.

4.1 Pure Water

The movement of pure water into porous solids, including cellulosic materials, can serve as a kind of introduction to the mechanisms controlling permeation. Water’s
permeation into porous solids can be expected to occur by means of diffusion and/or flow.

**Diffusion (ordinary and anomalous)**

Though many details of diffusion theory are beyond the scope of this article, some general concepts can be summarized. Diffusion phenomena generally obey Fick’s first law (1855), which for the flux of a selected substance in an isotropic material can be written as,

\[ J_x = -D \left( \frac{\partial C}{\partial x} \right) \tag{1} \]

where \( D \) is the diffusivity constant, \( C \) is the concentration or number density, and \( x \) is the distance in the direction perpendicular to the gradient of concentration. This relationship follows from a “random walk” analysis of motions at the level of individual particles or molecules undergoing the diffusion process. The diffusion constant is generally related to the thermal energy of the system (i.e., the temperature), the viscosity of the fluid, and the size of the particle. In the case that a diffusing particle can be described as a sphere, its diffusivity is given by the Stokes–Einstein relation,

\[ D = \frac{k T}{6 \pi \eta r} \tag{2} \]

where \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, \( \eta \) is the solution viscosity, and \( r \) is the particle’s radius.

One of the most immediate consequences of Equation (2) is that the rate of diffusion increases with increasing temperature. This is a consequence not only of the higher kinetic energy within the system, but also due to a decreasing fluid viscosity with
increasing temperature. Robertson and Lönnberg (1991) observed, however, that rates of diffusion of solutes in wood increased with temperature according to an Arrhenius relationship, suggesting that the rate-limiting step involved overcoming of an energy barrier (see also Stamm 1959).

Li et al. (1992) considered the self-diffusion of water molecules within never-dried bleached softwood kraft pulp fibers. Using a pulsed echo spin gradient (PGSE) nuclear magnetic resonance (NMR) method, they detected two echo attenuation profiles associated with water in the pores. One of these was attributed to water between the fibers, and the other was associated with water within the cell walls. The self-diffusion coefficient of water was reduced slightly even in the relatively large spaces between the fibers. This effect was attributed to the obstructing effect of cellulosic material. Vargas-Florenca et al. (2007) came to a similar conclusion in their study of water within nanostructured TiO₂ films, and Veith et al. (2004) found restricted diffusion in the case of water within silica gel. Within the cell walls Li et al. (1992) observed that the self-diffusion of water was reduced by approximately one-third, in comparison to bulk water. Greater diffusion was detected in the length-wise direction of fibers, an observation that is consistent with the expected orientation of pores. It was concluded that pores within the walls of the fibers had lengths in the range of about 2-20 μm, but that they were quite narrow in other dimensions. Ek et al. (1994) used a similar approach to characterize the pore sizes within cellulose beads of differing porosity.
The term “anomalous diffusion” has been used to describe the mobility of water that is very close to a solid surface. Mitra et al. (2001) employed quasi-elastic neutron scattering to distinguish between different types of water within porous alumina having a mean pore size of 5 nm. Some of the water appeared to be essentially bound to the solid surfaces. Other water displayed restricted diffusion. Ironically, the results showed higher self-diffusion rates of the non-attached water within small pores at temperatures near of below the freezing point of bulk water, suggesting that freezing did not occur within the pores of alumina under the conditions of testing. In other words, the water within the tiny pores appeared to be super-cooled liquid below the freezing point of bulk water. These ideas are consistent with the findings of Weise et al. (1996) and Maloney et al. (1998), who used differential scanning calorimetry to quantify the amounts of bulk-like water, freezing bound water, and non-freezing bound water within the small pores of fiber cell walls. Nakashima (2003), who used a spin-echo type NMR method, reported similar observations in the case of clay suspensions of the type that delaminate to a great extent in suspension. Topgaard and Soderman (2001), who used a similar approach to study wetted paper, obtained information about the pore structure within fibers. Tovbin (2005) carried out numerical simulations that helped to support the interpretation of data from these types of observations. Likewise Kim et al. (2005) concluded, based on numerical simulations, that simple fluids would experience restricted diffusion when the pore size was less than twice the diameter of the diffusing molecules.

*Viscous flow*
In the simplest case of an incompressible Newtonian liquid entering a smooth, cylindrical pore under laminar flow conditions, the average fluid velocity can be estimated by considering the contributing effects of viscous resistance to flow, capillary pressure, and any externally applied pressure. For a cylindrical capillary the viscous resistance to flow can be expressed in terms of a pressure as,

\[
\Delta P_{\text{viscous}} = 8 \eta v L / R^2
\]  

(3)

where \( \eta \) is the viscosity of the fluid, \( v \) is the average velocity in the pore, \( L \) is the wetted length of pore, and \( R \) is the pore’s radius. The capillary pressure is given by

\[
\Delta P_{\text{capillary}} = 2 \gamma \cos \theta / R,
\]  

(4)

where \( \gamma \) is the tension at the air-liquid interface and \( \theta \) is the angle of contact between the liquid and the solid (measured through the liquid phase). In cases where only capillary and viscous forces are opposing each other, these two expressions can be set equal to each other, yielding the following expression,

\[
dL / dt = \gamma R \cos \theta / \left[ 4 \eta L \right]
\]  

(5)

where \( L \) is the distance that the liquid already has penetrated into the pore and \( t \) is time. Equation 5 then can be integrated to give the well-known Lucas-Washburn equation,

\[
L = \left\{ (2r \gamma_{LV} \cos \theta t / (4 \eta)) \right\}^{1/3}
\]  

(6)

Flow also can be influenced by a pressure differential between the inside and the outside of a porous material. The following equation can be used to estimate the extent of fluid penetration as a function of time under the combined influences of capillary wetting and applied pressure (see Eklund and Salminen 1987),
\[ L = \left\{ \left[ (2r \gamma_{LV} \cos \theta + \Delta P_{\text{appl.}} r^2) t / (4\eta) \right] \right\}^{1/2} \] 

where \( \Delta P_{\text{appl}} \) is the applied pressure difference between the liquid phase and the interior of a porous material.

Because the foregoing equations were based on simple, cylindrical pores, one would not necessarily expect that they could be applied to real cellulosic materials. Nevertheless, the square-root dependency of penetration depth vs. time, as predicted by Eq. 6, has been observed in the case of low-surface-energy fluids penetrating into paper (Bristow 1967; Lyne and Huang 1993). Deviations from that relationship have been attributed to surface roughness of paper and to delayed wetting of cellulosic surfaces due to gradual rehydration (Lyne and Aspler 1982). In addition, it has been shown that the liquid-gas interfacial tension term \( \gamma_{LV} \) can be strongly time-dependent; thus, values of \( \gamma_{LV} \) determined under quasi-static conditions, as with a Denouy tensometer, are not necessarily expected to give accurate predictions for rapid wetting phenomena, as occur during lithographic printing (Aspler et al. 1987). The discrepancy was attributed to the fact that surfactant molecules may require time to migrate to an interface, especially if the interfacial area is being created at a relatively rapid rate.

In the preceding equations it is implicitly assumed that the liquid cannot slip at the fluid-solid interfaces. However, it can be worth examining this assumption in specific instances, such as cases involving very small pores (Dimitrov et al. 2007). Thus Saugey et al. (2005) carried out a numerical study of liquid confined between two planes, and they varied the boundary conditions. Substantially higher apparent diffusion constants
can be expected if the conventional boundary assumptions are replaced by a “partial slip”
condition. It was proposed that their calculated results could be used to establish whether
such boundary conditions provide a useful description of any real systems.

*Capillary forces (and geometrical effects)*

Interfacial tension is the amount of work per unit area that has to be done in order
to separate one phase, say a liquid, from another phase, say, a solid, gas, or another
immiscible liquid. Interfacial tension comes from the inward attraction of the molecules
towards the interior of a substance upon those on the surface. The work required to
separate a unit area of a solid from a liquid is related to the corresponding surface and
interfacial tensions $\gamma$ by,

$$W_{SL} = \gamma_S + \gamma_L - \gamma_{SL}$$ (8)

where the subscripts refer to the solid-gas, liquid-gas, and solid-liquid interfaces.

Capillary forces resulting from interfacial tensions may cause a fluid to penetrate
into small spaces that are filled with another liquid or air. As discussed by Senden *et al.*
(2000), significant research in this area started in the 1950s. Calderwood and Mardles
(1955) studied the rate of flow of liquids into capillaries. Tollenaar (1954) investigated
the rise of liquids into a wedge-shaped crevice.

The geometries of pores can profoundly affect the capillary wetting of pores.
Wetting tests even can be used to evaluate the geometries of pores. Thus, Everett *et al.*
(1977), who used a simple gravimetric technique to determine the rate of capillary
imbibition into glass-fiber filter papers, were able to use the Lucas-Washburn equation
(Eq. 6) to obtain an “imbibition-equivalent” pore size. Although it is difficult to relate pore sizes measured in this way to the real geometry of a fiber mat, it would nevertheless be valuable to seek empirical correlations to such variables as fiber diameter and packing density. Pre-wetting of the porous substrate was found to decrease the rate constant for subsequent imbibition. Bousfield and Karles (2004) likewise were able to use simplifying assumptions to model the capillary penetration of printing ink vehicle and related fluids into porous coatings on the paper surface.

*Thermal transport of water through cellulosic material*

Temperature gradients within wood or other porous material can be expected to result in gradients of moisture content. The mechanism appears to involve preferential evaporation from hotter locations and preferential recondensation in cooler locations (Skaar and Siau 1981). This kind of effect can be a nuisance in various practical applications, such as in the storage of paper, where the outside of a paper roll or stack tends to cool first, resulting in a higher moisture content toward the outside. A baggy or puckered appearance of the outside can result due to the greater swelling in locations having higher moisture content. A related mechanism can cause migration of wood extractives towards the outer surfaces of paper rolls or stacks as they cool; this situation can result in greater hydrophobicity (“self-sizing”) in those locations (Swanson and Cordingly 1959).
4.2 Molecules in Solution

Another layer of complexity needs to be considered when the liquid phase contains a solute, even in cases where the solute molecules are very small relative to the size of pores. For instance, many researchers have studied the diffusion of metal ions in cellulosic (Cooper 1998; Ra et al. 2001, 2002; Davis and Van Hise 2006; Srivastava et al. 2006) and other porous materials (Osaki et al. 1993; Kunetz and Hench 1998; Tantemsapya and Meegoda 2004; Fisher and Eizenberg 2008). In bulk solution the diffusion of ions in aqueous solution can be expected to be proportional to a concentration gradient; in other words, rates of diffusion ought to obey Eq. (1). Diffusion generally can be explained in terms of a “random walk” process, which over the passage of time would be expected to yield a more uniform concentration.

Ion exchange

Though it would make logical sense to assume that equations (1) and (2) could be used to predict rates of metal ion diffusion, relative to a concentration gradient into cellulosic material, various studies have shown instead that the rates of diffusion and uptake in such cases may be controlled by ion exchange effects (Osaki et al. 1993; Cooper 1998; Kunetz and Hench 1998; Srivastava et al. 2006; Sud et al. 2008). In other words, the metal ions are at any moment partitioned between the liquid phase and an adsorbed state. In the case of cellulosic materials it would be expected that metal ions would associate themselves with bound carboxylate groups. The ion exchange capacities
of cellulosic materials have been found to vary within wide limits, depending on conditions of preparation and purification (Herrington and Petzold 1992).

Osaki et al. (1993) found that the diffusion coefficients of Sr and Co in silica gel layers decreased with the second power of porosity. If the porosity was kept constant, the diffusion coefficients depended on the distribution coefficients ($K$) of Sr and Co between silica gel and water in pores as a function of $1/(1 + K)$ at various pHs. Kanungo and Collinson (2003) observed that the diffusion rates of some ions were the same in silica gel medium, compared to the bulk solution, whereas other ions displayed sharply reduced diffusion rates in the gel. The latter effect was attributed to relatively strong molecular interactions.

Cooper (1998) found that the diffusion coefficients of copper in wood samples were about 1/10 to 1/10,000 times those of water molecules, depending on pH and temperature conditions. Durr et al. (2005) studied the adsorption of ruthenium-dye molecules out of ethanol solution onto and through nanoporous TiO$_2$ films. They found these diffusion constants through the fine porous network were up to three orders of magnitude lower than in bulk ethanol; the results were discussed with respect to the material properties and pore structure.

Suppressed diffusion of solute molecules within very small capillaries also can be predicted based on molecular dynamics simulations. Thus, Lai et al. (2004) predicted that electrolytes would have a slower diffusion rate by as much as two orders of magnitude within a fine porous material.
### 4.3 Surfactant Solutions

Surfactants can be expected to have an especially large effect on transport into or through porous materials in cases involving more than one fluid phase, *e.g.* water and air or water and oil. However, it is not always legitimate to expect well-established laws governing macroscopic aspects of capillarity to remain true for interactions at the submicroscopic level. Thus Starov *et al.* (2004) considered spreading of small liquid drops over thin dry porous layers. They proposed that drop motion over a porous layer is caused by interplay between the two processes of spreading (expanding of the drop base) and imbibition (drop shrinkage during expansion of a wetted region inside the porous layer). If the mean pore size was below a critical value, then the permeability of the porous medium was not influenced by the presence of surfactants, whatever the value of the concentration. If the mean pore size was larger than the critical value, then the permeability increased with increasing surfactant concentration. Such results suggest that surface-active agents require a certain minimum of space in order to exhibit the kinds of effects that can be observed as a macroscopic scale.

Permeation of the surfactants themselves also can be expected to be profoundly affected by their adsorption onto the walls of porous materials. Petel'skii and Abramzon (1999) studied the process of dialysis of solutions of surfactants through porous membranes. They found a dependency of surfactant molecule size vs. permeation rate. Physical adsorption of surfactants on the pore walls during the dialysis decreased the
membrane permeability. It was proposed that the sorption of the diffusing substances largely depends on van der Waals interactions instead of electrostatic forces.

*Surface diffusion*

In cases where solute molecules are attracted to pore wall surfaces it is reasonable to consider whether such solute material can migrate while in contact with the surface (Alanissila and Ying 1992; Ho *et al.* 2000; Choi *et al.* 2001). As a prime example, it is reasonable to expect cellulase molecules to diffuse along cellulosic surfaces (Jervis *et al.* 1997). Such “surface diffusion” also has been proposed to explain rates of permeation of direct dyes into water-swollen cellulose membranes (Gutsche and Yoshida 1994; Maekawa *et al.* 1995).

*Emulsification*

Surfactants can be expected to dramatically affect the transport of various other solute molecules in cases where the latter can be emulsified or stabilized. This is one of the underlying mechanisms of detergency (Ang and Abdul 1991). Thus, Weigenand *et al.* (2007) found that surfactant was beneficial for the permeation of silicone into wood. Microemulsions were much more effective penetrants, in comparison to emulsions having a typical droplet size. Surfactants also have been found effective for enhanced oil recovery (El-Batanoney *et al.* 1999; Summ and Soboleva 2003; Standnes 2004). Ang and Abdul (1991) used an alcohol ethoxylate surfactant to wash automatic transmission fluid from sandy soil. Water washed little of the oily matter from a column of the soil, while dilute surfactant solutions washed the soil much more effectively. Displacement of
oil was proposed as the main washing mechanism. Supplementary mechanisms of oil removal were dispersion of oil (due to reduced surface tension), and the solubilization of oil by surfactant micelles.

Vesicles, which can be described as droplets defined by surfactant bilayers, can serve as models for biological cells. Linke et al. (2006) carried out a theoretical study of their passage through fine pores. Rates of passage were predicted based on the thermodynamic fluctuations of the membrane shape, and also the requirement of water to pass through the bilayer in order for the vesicle to be small enough to get past narrow points in the pore.

*Multiphase flow in porous media*

Complex interactions take place if an immiscible mixture is forced through an array of capillaries. As a general rule, a given channel can be expected to contain a single fluid phase, and other components of an immiscible mixture will generally be found in other channels. The mixing of miscible liquids in capillary networks also has been considered (Levenspiel and Smith 1957; Levenspiel 1958); though the details of mixing present computational challenges even in that case, diffusion processes ensure that the system tends toward a uniform mixture with the passage of time.

**4.4 Polyelectrolytes in Solution**

In comparison to the simple ions and surfactants just considered, polyelectrolytes can be described as relatively large, deformable, and possessing a multiplicity of charged
groups. All of these factors can be expected to influence their diffusion, as well as their flow behavior in pores.

Wettability effects

It is reasonable to expect that the presence of polyelectrolyte in a fluid ought to affect wetting and capillary imbibition phenomena. Ershov et al. (2003) found such evidence when they measured the flow rates and the dynamic contact angles of aqueous solutions of a cationic polyelectrolyte in quartz capillaries. Their results showed that the macromolecules adsorbed on the negatively charged quartz surface, resulting in a change of contact angle. As the solution concentration increased, the advancing contact angles were reduced, favoring wetting.

Though dissolved polyelectrolytes can be expected to increase the viscosity of a solution, it can be misleading to employ shear viscosity information to predict resistance to flow through porous media. That is because the presence of high-mass dissolved polymers can greatly increase the extensional viscosity of the solution, leading to substantial resistance to flow at the entrances and exits of pores, as well as anywhere in a network of pores where a flow channel narrows or widens (Andrews et al. 1998; Odell and Haward 2008). As noted by Shaqfeh and Kock (1992), dissolved polymers can be expected to become stretched if they are present in a solution that is forced through a packed bed. Such flow conditions also can lead to the break-down of high-mass polymers in solution (Nguyen and Kausch 1992). In related research, Carrington et al.
(1996) used extensional flow measurements to find evidence of intermolecular effects affecting the flow behavior of xanthan gum solutions.

Molecular mass

Effects of molecular mass on the adsorption of polyelectrolytes onto cellulose and other porous materials have been shown in various studies. In contrast to what would be expected in the case of non-porous surfaces, many studies have shown increasing adsorbed amount with deceasing molecular mass of the polyelectrolyte (Hostetler and Swanson 1974; Petlicki and van de Ven 1994; Gruber et al. 1996; Alince and van de Ven 1997; Hubbe et al. 2007b; Wang et al. 2007). Petlicki and van de Ven (1994) investigated the adsorption of a low and a high molecular weight polyethylenimine (PEI) onto pulp fibers. They found that low molecular weight PEI could penetrate into the porous wall of the fibers, while for high molecular weight PEI, adsorption in pores was negligible. Evidence of much slower penetration of polyelectrolytes, with increasing mass, has been found in studies that employed electrokinetic measurements (Koethe and Scott 1993; Farley 1997; Wang and Hubbe 2002; Hubbe et al. 2007b; Wu et al. 2008). By contrast, Jeremic et al. (2007) observed that poly(ethylene glycol) penetrated the cell walls of red pine wood without any obvious effects of molecular mass in the relatively low range of 1000 to 20,000 Daltons.

Charge density

There are several reasons to expect the charge density of a polyelectrolyte to affect its transport within fine pores of wet cellulosic material. First, as already
discussed, ionic charges on a dissolved polymer cause it to adopt a more expanded molecular conformation. But in addition, one can expect interactions with charged groups on and within pores of the substrate should become stronger with increasing charge density of the polyelectrolyte. The adsorption of polyelectrolyte on an oppositely charged substrate can be considered to be a form of polyelectrolyte complexation, and such interactions become stronger with increasing charge densities (Fleer et al. 1993). Such an effect may at least partly explain why Horvath et al. (2008) observed very slow adsorption of high-charge-density cationic polymers into cellulose, in comparison to lower-charge-density polyelectrolytes. If a polyelectrolyte molecule becomes strongly adsorbed and essentially immobilized in the entrance region of a porous system, then it is reasonable to expect that like-charged polyelectrolytes will experience electrostatic forces of repulsion and be less likely to diffuse into such pores. However, as was actually observed in the cited study, diffusion past or through the obstructing polyelectrolytes would be expected to be facilitated by the presence of salt ions, which would tend to screen the electrostatic effects. Kim and Anderson (1991) and Linden et al. (1999) earlier considered the degree to which adsorbed polyelectrolyte may hinder the diffusion and flow of solvents and solutes, including macromolecules; Idol and Anderson (1986) showed already that adsorbed polyelectrolytes can hinder solvent convection and diffusion.

Because adsorption phenomena are often controlled by a pairing of charges on the substrate with those on an oppositely charged absorbing species, it is usual to expect
increasing adsorbed amounts with decreasing charge density of the polyelectrolyte (Fleer et al. 1993; Wågberg 2000). Results of work by Wang et al. 2007 showed that the same trends remain true in the case of highly porous material. They used changes in pH to adjust the effective charge density of poly(acrylic acid) adsorbing from NaCl solution onto cationized nanoporous silica particles. The amount of polyelectrolyte adsorbed fell with increasing pH (and charge density) in the range 3 to 7, consistent with increasing dissociation of the carboxyl groups. In the case of the highest-mass polyelectrolyte tested, highest adsorbed amounts were obtained at an intermediate salt concentration; such results are consistent with a balance between (a) increasing salt tending to make the conformation of the polyelectrolyte less extended, allowing more to pack within a given space, and (b) increasing salt tending to weaken the charge interaction that favors adsorption (Fleer et al. 1993).

Flexibility and conformation of macromolecules

The deformability, in conjunction with thermal energy and the associated collisions of polymer segments with solvent molecules, will give rise to ceaseless changes in macromolecular conformation. To a first approximation, the “size” of a dissolved polymer can be equated to the average radius of gyration, or some other suitable measure of its most frequent dimensions that arise from the random motions. Thus it is possible to use polyelectrolytes of well-defined degree of polymerization as probes to evaluate pore sizes. Notably, Stone and Scallan (1968) used such an approach in their evaluation of pore sizes within cellulosic fibers; they chose to use uncharged,
highly water-soluble dextran macromolecules in their work. It was assumed that the macromolecules were neither attracted nor repelled from the cellulosic surfaces.

Polyelectrolytes, due to their ionized groups, can be expected to have more expanded macromolecular conformations, compared to their uncharged counterparts. As noted by Horvath et al. (2008), increasing charge density of a polyelectrolyte can be expected to increase its stiffness. This expansion tends to be reduced with increasing electrolyte concentrations (Beer et al. 1997; Lin and Cheng 2000); the effect is consistent with a decrease in the Debye-Hückel length with increasing ionic strength. What is less certain is whether such considerations will still apply when a polyelectrolyte is interacting with pore walls that have charged groups of the opposite sign. In that case it may be more reasonable to expect counter-ions to diffuse away from the site of adsorption. A possible alternative contributing explanation for why Horvath et al. (2008) observed extremely slow permeation of a high-charge cationic polymer into cellulose is that they employed poly-diallyldimethylammonium chloride, which is known to have a relatively stiff molecular structure (Brand et al. 1997).

The average or characteristic size of a polyelectrolyte in solution also is a key factor in determining the distribution of molecular mass, using gel permeation chromatography (GPC). As noted by Potchka (1993) one can assume that convection is the main mechanism by which polyelectrolytes progress through a GPC column, whereas diffusion will be the main mechanism by which they enter or leave a generally “stagnant zone” within the porous packing material. Reeder et al. (2000) considered an analogous system
in which the porous material contains interconnected pores having a wide range of sizes; possibly this kind of modeling would also be appropriate for wood-based porous materials, including carbon black. Neuman and Walker (1992), whose analysis was not limited to polymeric solutes, showed that a mathematical model combining both mass transfer and pore diffusion gave the best predictions for packed columns of relatively large cellulosic particles, whereas simpler models were adequate in some other cases.

*Excluded volume*

Excluded volume is a term that is used to account for the fact that the average concentration of polymer segments at a specific location can be less than what would be calculated based on a completely random distribution of matter within a fluid phase. One type of excluded volume is due to the fact that one part of a long chain molecule cannot occupy space that is already occupied by another part of the same molecule. Such excluded volume causes the ends of a polymer chain in a solution to be further apart (on average) than they would be were there no excluded volume. This is an important factor in analyzing rates of polymer molecule penetration in porous media.

A more important kind of exclusion volume, in terms of the present discussion, involves a depletion of polyelectrolyte segments in the close neighborhood of a non-interacting surface (Fleer *et al.* 1993). As illustrated in Fig. 1.1, the origin of such excluded volume can be understood by considering the shape of a polyelectrolyte in solution as a round ball, consistent with its time-averaged segment density in space relative to its center. The substrate surface is modeled as a smooth, flat wall.
Figure 1. 1. Illustration of the concept of excluded volume. Left: Dissolved polymers modeled as spheres, the centers of which cannot approach closer than one radial length from a smooth wall, but which otherwise are uniformly distributed in the solution. Right: Example of an expected concentration distribution of polymer segments (for instance, if the spheres are taken as being of uniform density of polymer segments).

The concentration of polymer segments in the bulk of solution then can be estimated in a simple way, based on the volume fraction occupied by the spheres, relative to the solution as a whole. But locations very close to the wall can be occupied only by polyelectrolyte segments that are near to the outer extremities of polyelectrolyte macromolecules, since, according to the model, the centers of the molecules are held away from the wall. It follows that there will be a reduced concentration of macromolecule segments at locations less than one radial length of the macromolecule from the wall. As noted by Alince and van de Ven (1997), this kind of effect implies that the concentration of non-interacting polymer within a sufficiently small pore is likely to be lower in comparison to the bulk concentration of the polymer.
Significant implications of excluded volumes can arise in cases where entrance of a polyelectrolyte into a fine pore changes the entropy of the system (Miklavic 1993; Kumar and Muthukumar 2008). Stone and Scallan (1968) assumed that the size of the pores can be equated to the size of non-interacting macromolecules that can fit into them. However, a polymer in a small pore, even if it has no significant interaction with the wall material, has less degrees of freedom of motion. Any macromolecular conformation that requires polymer segments to pierce the wall material has to be excluded from the physically possible set. In a real system one cannot usually expect to have enough information to accurately estimate the ratio of concentrations in the pores versus an adjacent bulk solution. The assumption of true non-interactivity also may be subject to doubt in a given case. To avoid problems related to excluded volumes and questions about affinity, Alince and van de Ven (1997) advocated the use of cationic macromolecules of different size in their analysis of pore sizes within water-swollen cellulose, which has negatively charged surfaces.
Reptation

Reptation is a term sometimes used to describe the manner in which a flexible polymer can pass through a pore space that might be too narrow to allow passage of the polymer in its average bulk-phase conformation (de Gennes 1971). As described by Teraoka et al. (1992), if a macromolecule’s persistence length is greater than the characteristic size of the pores, then the macromolecule still might be expected to progress through the porous material by means of wiggling motions. The effect is illustrated in Fig. 1.2. Cule and Hwa (1998) predicted that rates of reptational migration can be critically dependent on polymer structure; in the cases that they considered, a copolymer was predicted to migrate much more slowly through narrow pores in comparison to a homopolymer of similar mass. Wolterink et al. (2006) used Monte Carlo simulations to study the effects of polymer length, radius of gyration, and pore diameter on rates of translocation. Wang and Luo (2007) simulated the movement of polymer chains through a small hole with the dynamic Monte Carlo method. They studied the dependence of the relaxation time and escaping time on the chain concentration. Inter-chain interactions appeared to play an important role in the translocation process.
Figure 1. 2. Schematic illustration of reptation, a mechanism by which a solubilized polymer chain can crawl through tortuous pore passages, even if the pore size is smaller than the polymer’s persistence length.

Guo et al. (1990) used quasi-elastic light scattering and observed two time scales associated with the permeation of polystyrene into porous glass saturated with toluene solution. The faster time scale was attributed to initial diffusion into the entrances of pores under conditions governed mainly by hydrodynamic interactions. The slower time scale was attributed to diffusion within the tortuous passages of the material. In general, as shown by the research group’s earlier work (Bishop et al. 1986), the diffusion rate was significantly reduced relative to bulk diffusion. Lua and Grosberg (2005) modeled the migration of dissolved polymers within pores having a “sawtooth” distribution of potential energies and on this basis predicted that the time of passage may depend on the direction of diffusion.

Kabanov et al. (1989) suggested a mechanism in which polyelectrolyte molecules may follow each other in single file as they progress down especially narrow pores in a
substrate. Horvath et al. (2008) did not think that such a model applied to their systems, since they observed that polyelectrolytes adsorbing near to the surface of cellulosic fibers remained pretty much fixed in location; polyelectrolyte molecules penetrating further into the fibers had to diffuse past the initially adsorbed molecules. The expected repulsion between an adsorbed cationic polyelectrolyte and another such molecule trying to squeeze past it may well explain the effect of salt concentration in the cited work (Horvath et al. 2008). In the absence of salt the effective distance over which electrostatic forces can be effective may be several nanometers, and as a consequence the initially adsorbed polyelectrolyte molecules could block further permeation. In the case of lower-charge polyelectrolytes it is reasonable to expect that such blocking effects would be less effective. Miller and Bruening (2005) considered effects of more drastic treatment of a system with alternating layers of cationic and anionic polyelectrolytes, forming a multilayer film on a porous support; in that case it was possible to control permeability of the film by adjustments in the film components. Results were well correlated to the degree of swelling in the polyelectrolyte multilayer films.

4.5 Colloidal Particles in Suspension

Many of the same factors that affect ionic solutes, surfactants, and polyelectrolytes in solution are also expected to affect the permeation of colloidal particles. This section will highlight some special circumstances that are likely to be important for colloidal particle permeation.

Sieving
Compared to molecular substances in water, colloidal particles are much more likely to become mechanically entrapped of “sieved.” A recent review article (Hubbe et al. 2009) cited evidence that sieving is a leading cause of permeability reduction in porous media. Various publications have reported that sieving mechanisms may slow down the permeation of colloidal matter into porous materials (Inglezakis et al. 1999; Oswald and Ibaraki 2001; Yamamoto et al. 2004; Auset et al. 2005; Grznarova et al. 2005; Mays and Hunt 2005; Bauer and Nadler 2006; Shin 2006; Alvarez et al. 2007; Johnson et al. 2007; Bauer et al. 2008; Shen et al. 2008).

Brownian motion of particles

The same effect of thermal energy underlying the previously mentioned diffusion of ions and polyelectrolytes also causes very small suspended particles to undergo ceaseless semi-random motion (Einstein 1905). In the case of colloidal particles, however, such motions often can be seen through the microscope (Brown 1828). Various researchers have used calculations to predict effects of Brownian motion as a colloidal suspension passes through a porous medium (James and Chrysikopoulos 1999, 2000; Dudko et al. 2005; Chavez-Rojo et al. 2008). Nitsche and Balgi (1994) predicted that Brownian diffusion within small pores should be significantly decreased by boundary effects. In essence, the viscous resistance to particle motion becomes greater when it is very close to a wall, and such locations become dominant as pore size becomes smaller. Wei et al. (2000) and Nelissen et al. (2007) considered the special circumstance in which the pores are not large enough for two suspended particles to pass each other; kinetic
relationships were therefore derived under the assumption of single-file diffusion. Ten Bosch (2001) carried out detailed Brownian dynamics calculations leading to the conclusion that colloidal particles will tend to be more concentrated near the centers of pores, assuming that there are no significant forces of attraction with the pore walls. Chaplain and Mills (1992) carried out Brownian simulations to predict the movement of colloidal particles in groundwater; their results showed that two widely different outcomes are likely. On the one hand, the rate of diffusion of an individual particle in a porous medium can be more rapid in comparison to its diffusion in the bulk solution. On the other hand, some particles may spend an extremely long time in the porous medium before they diffuse out.

*Electrostatic and van der Waals forces*
A more complete analysis based on Brownian motion needs to take into account electrostatic, dispersion, and hydrodynamic forces acting upon a diffusing particle. Revil (1999) and Chavez-Rojo et al. (2008) constructed models to consider all of these influences. Their calculations were found to agree with published data. Chen (1998) predicted that attractive interactive forces with pore walls will tend to slow down the diffusion of Brownian particles in comparison to their bulk diffusion, whereas the opposite should be true in the case of repulsion from the wall. These tendencies were consistent with an expected enhancement of viscous resistance to motion in the case of particles near to a wall (Pawar and Anderson 1993; Dechadilok and Deen 2006).

Observations by Kluijtmans et al. (1998) provide corroboration for this work, since they observed higher diffusion rates in the case of like-charged particles, compared to uncharged particles diffusing in the same-charged porous media. In both cases the diffusion rates were much lower than in the bulk solution. The principle underlying this effect is illustrated in Fig. 1.3. The reason that the particle concentration profile marked “d” in the figure shows depletion very near to the wall is due to the hydrodynamic effect described by Saffman (1965). In all cases Brownian motion can be expected to make the distribution of particles somewhat more uniform, so that the particles are not all focused at the position of minimum interactive energy.
Figure 1. 3. Principle underlying faster migration of particles that are repelled by pore walls during flow of a suspension. Left: The expected parabolic flow velocity profile favors faster movement of particles near the center of flow (a) relative to near the pore walls (c). Right: Particles that are repelled from the walls tend to be enriched near the center of flow (d). Particles that are neither attracted nor repelled from the walls are still influenced by Brownian motion and a hydrodynamic effect that favors movement away from the pore wall (e).

Chun (2005) predicted a partitioning effect, with particles having higher attraction to pore walls eluting later in comparison to particles that are less attracted to the walls. Johnson et al. (2007) considered mechanical filtering effects to explain hindered elution of colloidal particles in the presence of repulsive colloidal forces between the surfaces.

Substantial delay in permeation can be expected in cases where colloidal particles are deposited onto the pore walls for at least part of the time that they are migrating within porous media (James and Chrysikopoulos 1999, 2000; Bauer and Nadler 2006; Simunek et al. 2006). Qian and Sen (2006) considered the case in which the particles
spend part of the time in an attached state and derived predictive equations for net diffusion rates.

Although, as mentioned above, there are many reasons to expect that colloidal particles may become stuck or delayed in their transport through porous media, elution of particles through a packed bed can be substantially more rapid in comparison with smaller solute materials. As noted by McKay et al. (2000) and Zvikelsky and Weisbrod (2006), colloidal tracer particles can tend to elute as a “pulse,” since they will tend to be excluded from smaller pores and remain in relatively large channels. Such channels, such as the fractures in a mineral formation, can be expected to carry a disproportionately large proportion of the net flow. This mechanism is in many respects identical to that of gel permeation chromatography, as mentioned earlier (Potchka 1993).

5. Enablers for Diffusion and Flow

There are many situations in which one would like to speed up the penetration of solutes or colloidal-dispersed substances into cellulosic material. Such issues have occupied the attention of technologists in the wood, paper, and biofuels industries for many years. The goal of this section is to highlight relevant published work in this area, as well as to bring together some of the points already mentioned earlier in this article.

Heating

Raising the temperature can make sense both in terms of flow and in terms of solute diffusion rates. Fluid viscosities generally fall with increasing temperature. For example, if one raises the temperature of water from 25 °C to 60 °C, the viscosity falls by
a factor of two. The consequences can be judged, to a first approximation, by applying Eq. (3). Though the same trend does not necessarily hold true for a given solution of polyelectrolyte, raising the temperature is still a reasonable strategy to consider if one wants to increase flow rates at a given applied pressure.

Raising the temperature also can be expected to increase rates of diffusion. The fact that the viscosity coefficient appears in the denominator of Eq. (2), and also the absolute temperature appears in the numerator, means that the effect can be quite important.

A third way in which increased temperatures might increase permeation rates can be important in cases where the rate-limiting step in the process involves an energy of activation. For example, a polyelectrolyte or colloidal particle may have to pass through a zone of electrostatic repulsion in order to enter a pore. Such repulsion implies that the free energy of interaction is unfavorable, and diffusing entities will have to overcome a barrier of free energy to pass. The Arrhenius equation predicts, in analogous cases, that reaction rates tend to double with each 10-degree rise in temperature on the Celsius scale.

**Pressure**

Increased applied pressure is another almost self-evident strategy to increase permeation. As shown by Jeong and Corapcioğlu (2005), increased pressure can be especially important if the viscous drag forces of the fluid are being used to displace blobs of a second phase, as in the case of soil remediation or enhanced oil recovery. However, sometimes excessive pressure can have the opposite effect by dislodging fine
particulate matter that is present within porous media; such particles then may clog pores further downstream, often decreasing permeability to a drastic extent (Khilar and Fogler 1987; Hubbe et al. 2009).

5.1 Strategies to Widen Cellulosic Pores

During the current push to develop cellulosic biofuels technology there has been considerable emphasis on finding ways to increase the accessibility of cellulosic biomass to enzymes, as well as to various reagents (see, for example, Kim and Lee 2002; Hu et al. 2008). Some strategies to accomplish this objective can be summarized by the terms delignification, refining, swelling, and enzymatic treatment.

Delignification

Removal of lignin is currently practiced as a highly mature, large-scale industry. The annual world production of kraft pulp is over 100 million tons (Anon. 2000). As shown by Stone and Scallan (1968), delignified fibers tend to be considerably more porous in comparison to mechanically separated wood fibers. Though chemical pulping often removes about half of the solid material from wood, the result can be quite favorable from the standpoint of producing ethanol and related products; in principle the cellulose can be hydrolysed to sugars, which then can be fermented with ordinary yeast into ethanol (Taherdazeh and Karimi 2007a,b). One of the slow steps in this process can be due to the limited accessibility of the cellulose matrix to cellulase enzymes. These protein structures may be 5-20 nm in size; this means in theory that the enzymes can enter many of the pores in cellulosic materials, especially after kraft pulping. Of course
the degree to which enzymes actually permeate cellulose may depend on binding affinity and other factors.

Refining

In the manufacture of paper often the next key operation after pulp production involves passing a fiber slurry between rotating plates with raised rectangular bars, \textit{i.e.} refining (Laine \textit{et al.} 2004). During refining, groups of wetted fibers are repeatedly compressed and sheared. This mechanical treatment causes progressive delamination of the cell walls, and the outer layers of the fiber partially unravel, resulting in a fibrillated surface. As shown by Strazdins (1980), refining increases both the hydrodynamic surface area of the pulp, as well as the adsorption capacity of the pulp for cationic polymers. Conditions that favor greater swelling of fibers often can make refining somewhat more efficient, decreasing the amount of energy that is required to achieve a given level of fibrillation (Lindström and Kolman 1982).

Swelling

The subject of fiber swelling was already mentioned in the context of salt ions, which tend to shrink the pores within cellulosic fibers. If one wants to go the other direction and widen those pores, then one of the basic approaches involves raising the pH. Cellulose fibers tend to have increased water-holding capacity with increased pH, especially over the pH range between about 4 and 8 (Jayme and Büttel 1964). Such effects tend to become more important with increasing carboxyl group content of the fibers (Lindström and Carlsson 1982).
**Enzymatic treatments**

Though enzymes may be hindered from entering the finest pores within the cell walls of fibers, fiber lumens are much larger. Thus, as was mentioned earlier, cellulase has been used to open up the bordered pit areas that connect the lumen space of one fiber with its nearest neighbors (Meyer 1974; Jacobs-Young et al. 1998). Analogously, in the field of enhanced oil recovery Lazar et al. (2007) introduced the use of enzymes to selectively break down some components of crude petroleum to improve its flow characteristics.

**Lowering of interfacial tension**

Surfactants can be used to accelerate penetration of certain other chemicals into cellulosic materials. Petrova et al. (1979) studied the effect of a nonionic surfactant on the impregnation of NaOH into birch and larch chips. The nonionic surfactant favored the penetration of alkali into the wood particles, as well as a partial dispersion and dissolution of wood components, resulting in loosening of wood structure and hence in better impregnation. Weignand et al. (2007) found that micro-emulsification of an amino-silicone greatly increased the efficiency of wood impregnation.

Brown and Jaffe (2001) found that certain nonionic surfactants facilitated the transport of bacterial cells through a sand filter. Though an explanation was offered, based on electrokinetic effects, it seems more likely that the effect was due to steric stabilization of the suspended matter (Fleer et al. 1993).
For cases involving displacement of oil from water-saturated porous media, various researchers have proposed that conditions for oil mobilization could be optimized based on the principles of interfacial tensions (Novozhilova et al. 1991; El-Batanoney et al. 1999; Abdel-Moghny 2004; Babadagli 2006). For instance, in a study aimed at removing residual oil from contaminated soil, Ang and Abdul (1991) found that the addition of surfactant had beneficial effects on displacement of the oil through the pores, dispersion of the oil into droplets due to the reduced interfacial tension, and solubilization of some of the oil in the water phase as micelles. In many of the cited studies favorable results have been obtained when the surfactants or pairs of surfactants were adjusted to obtain the lowest feasible interfacial tension. Summ and Soboleva (2003) found that injected emulsions were much more effective than simple surfactant solutions for the purpose of displacing dodecane from pores within a bed of quartz sand.

Colloids and piggy-backing

For purposes of enhancing the permeation of small but highly absorbing species, one strategy is to adsorb those materials onto colloidal particles. Researchers have identified this mechanism in connection with the movement of heavy metals and other contaminants in groundwater (Li et al. 2004; Simunek et al. 2006; Johnson et al. 2007). The approach was studied mathematically and in the lab by Grolimund and Borkovec (2005). It was found that results were influenced by adsorbed divalent ions, which can be expected to affect the colloidal stability of the particles.

Anti-fouling polyelectrolyte layer
An innovative way to maintain the permeability of certain porous substrates in contact with potential contaminants can involve treatment with a water-loving polyelectrolyte. Thus Dainiak et al. (2002) employed a shielding layer of high-mass poly(acrylic acid) to minimize deposition of yeast cells on an ion exchange resin, while allowing binding of protein. A similar strategy might be used to minimize clogging of other porous systems.

**Electro-osmosis**

As noted by Park (1995), application of an electric field to a porous system that contains a diffusing polyelectrolyte will tend to orient the macromolecules in the field’s direction. The convective velocity of the polyelectrolyte in a porous gel can be accelerated by this effect. Though the cited work was aimed at separation and analysis of DNA, it is possible that a similar approach could find applications in the treatment of cellulosic materials.

**Salt optimization / affinity optimization**

In the special case where the diffusing species is attracted to the pore walls, several studies have pointed to the need to optimize the aqueous conditions to favor permeation. On the one hand the attraction to the pore walls can provide a driving force for permeation to occur. But if the attraction is too strong, then, as was found by Horvath et al. (2008), the solute species may merely attach themselves near to the outer surfaces of the porous material and then remain fixed. Kluijtmans et al. (1998) found evidence that tracer particles may become trapped at pore junctions under condition of very low
ionic strength, due to electrostatic forces. These effects were not observed at a higher salt level.

6. Concluding Remarks

Published sources cited in this article indicate that a number of different factors and mechanisms can affect permeation of simple ions, surfactants, polyelectrolytes, and colloids into the pores of cellulosic material immersed in water. It is evident that much progress has been made, using a broad range of experimental and theoretical approaches.

Despite the progress that has been made with respect to permeation into water-swollen wood and cellulosic fibers, one has to express some admiration for the somewhat recalcitrant nature of the material. Under ordinary conditions of pulping, refining, and swelling, the pores within the cell walls of cellulosic fibers still tend to remain small enough to discourage rapid enzymatic hydrolysis (Taherzadeh 2007b). Maybe this is a good thing. If cellulose were much more accessible, then one could expect much too rapid decay of standing trees and standing houses. We can expect that cellulosic materials will provide many challenges in the years ahead to technologists who choose to enter this field.

References


Chapter 2  Permeation of a Cationic Polyelectrolyte into Meso-porous Silica.

Part 1. Factors Affecting Changes in Streaming Potential

Abstract

A recently developed streaming potential (SP) strategy was used for the first time to investigate factors affecting permeation of the cationic polyelectrolyte poly-(diallyldimethylammonium chloride) from aqueous solution into silica gel particles. Four factors affecting cationic polyelectrolyte permeation were considered, including polyelectrolyte dosage, molecular mass, solution pH, and electrical conductivity. Samples were equilibrated for approximately 20 hours before testing. The magnitude of change in streaming potential, which was taken as evidence of permeation, increased with increasing polyelectrolyte dosage, with decreasing molecular mass, and with decreasing pH in the range 11 to 3. The pH effect supports a mechanism in which excessively strong electrostatic attraction between the polyelectrolyte and the substrate immobilizes macromolecules at or near the entrances to the pore network, thus inhibiting permeation of like-charged macromolecules. The same mechanism is consistent with observations that permeation increased with increasing electrical conductivity, though the latter observation also could be explained in terms of conformational changes.

1. Introduction

Our interest in the permeation of polyelectrolytes into very small spaces has been motivated by both practical and theoretical interests. An understanding and ability to
predict permeation behavior is important when applying polyelectrolyte treatments during enhanced oil recovery (Zhang, 2001; Kjøniksen et al., 2008; Wang and Dong, 2009), papermaking (Koethe, 1993; Farley, 1997; Wågberg, 2000; Horvath et al., 2008a; Wu et al., 2009b), and biomass hydrolysis (Mansfield et al., 1999; Himmel et al., 2007; Hu et al., 2008). Theoretically it has been proposed that kinetic and thermodynamic factors dominate the permeation of macromolecules in confined spaces (de Gennes, 1971; Bishop et al., 1986; Fleer et al., 1993; Cule and Hwa, 1998; Wu et al., 2009b). From a colloidal and interfacial perspective, permeation may depend on factors which our research focused on, such as electrostatic forces and the effective size of macromolecules in solution, etc.

Experimentally, it has been relatively difficult to obtain direct evidence of polyelectrolyte adsorption within mesoporous substrates (pore size 2 - 50 nm according to IUPAC). Definitive work related to permeation into pores within this size range has been based on adsorption isotherms (Alince and Ven, 1997; Alince, 2002). For instance, Alince and van de Ven (Alince and Ven, 1997) presented some work obtained by J. Day, who measured adsorption isotherms for cationic polyelectrolytes of different molecular mass interacting with silica gel in suspension. Discontinuities in the functions of adsorbed amount vs. the polymer radius (based on solution viscosity) were explained based on geometrical considerations, comparing the sizes of the pores versus the effective size of the polyelectrolytes. Recently, Horvath et al. (Horvath et al., 2008a) used a more direct approach based on fluorescently labeled polyelectrolytes and confocal microscopy.
to study factors affecting the permeation of cationic polyelectrolytes into cellulosic fibers.
By using batches of polyelectrolyte labeled with contrasting colors, they demonstrated for
the first time that the initial layer polyelectrolytes adsorbing onto the cellulosic fibers
tended to remain near to the outer surface of those fibers, rather than diffusing further
into the pore structure. Later-arriving polyelectrolyte molecules had to squeeze past
already-adsorbed molecules at given long-term exposure to diffuse further into the fibers.
It was proposed that the initially-adsorbed polyelectrolyte layers tended to inhibit further
permeation due to charge-charge repulsion.

Research by the present authors has focused on effects of ionic strength and
dosage of commercial high mass cationic polyelectrolyte on the streaming potential of
either silica gel or cellulosic fibers in aqueous suspensions (Lee et al., 2006; Hubbe et al.,
2007a; Hubbe et al., 2007b; Wu et al., 2008). It was found that the sign of streaming
potential could be changed in a reversible manner from positive to negative and back
again, just by changing the ionic strength and electrical conductivity of the solution. The
effects were explainable in terms of double layer theory, since the full development of
ionic double layers at charged surfaces is predicted to be strongly suppressed within pore
spaces that are small relative to the Debye-Hückel reciprocal length parameter (Rice and
Whitehead, 1965; Wan, 1997; Alkafeef et al., 2001). However, it was still unclear that
whether the effect was due to the high concentration per se, or mainly due to a sufficient
concentration of very-low-mass oligomers (impurities), which were capable of
permeating into small spaces at high polyelectrolyte concentrations. These results led us
to choose the present experimental conditions, which were designed to answer the above questions, and to look at the factors affecting polyelectrolyte penetration into mesoporous silica gel particles more comprehensively, as shown in Table 2. 1. When considering each of the factors, default variable levels (marked in bold font) were used.

Table 2. 1 Levels of independent variables and default conditions

<table>
<thead>
<tr>
<th>Factors</th>
<th>Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-DADMAC dosage (on dry mass of silica gel)</td>
<td>0.1%, 1%, 3%, 10%, 30%</td>
</tr>
<tr>
<td>Molecular mass of poly-DADMAC</td>
<td>High mass as received, dialyzed high mass</td>
</tr>
<tr>
<td>Solution pH</td>
<td>3, 7, 10</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>10, 100, 1000, 10000 µS/cm</td>
</tr>
</tbody>
</table>

*Bold was the default condition

A packed bed cell was used in which the silica gel sample was contained between a pair of 200-mesh stainless steel screens. This was a modification to the streaming potential equipment used in the group’s past research (Wang and Hubbe, 2001; 2002), as described in an earlier conference article (Wu et al., 2008). In the original one-screen system, silica gel particles (or, alternatively, fibers of various types) were periodically collected on a screen through which the suspending medium (water) passed when high pressure was applied, and a magnetic stirrer was used to keep the silica gel particles suspended when the pressure was released. However, it was found that the magnetic stirring tended to grind the silica gel particles, and this effect eventually would result in a markedly decreased flow rate through a mat of particles forming on the screen. The grinding effect resulted in a loss in accuracy of the method. In addition, the particles’ tendency to fall away from the screen surface after cessation of the pressure application
could be expected to contribute to a sedimentation potential effect, whose magnitude would be difficult to determine. Those problems were overcome by the modified approach.

2. Experimental

2.1 Materials

The water used in the experiments was deionized with a Pureflow system. Inorganic chemicals were of reagent grade. The cationic polyelectrolytes were linear poly-(diallyldimethylammonium chloride) (poly-DADMAC) from the Aldrich, catalogue numbers 52,237-6 (very low mass) and 40,903-0 (high mass). The nominal molecular masses of the products are given as 5k-20k and 400k-500k ranges, respectively.

The mesoporous silica gel used in the experiments was obtained as catalogue S745-1 from Fisher Scientific (also known as Davisil Silica Gel 150), which was 60-100mesh with a nominal pore size of 15 nm. Certain control experiments were also carried out with a non-porous silica powder, having a mesh size of “200 and finer” (Fisher Scientific product cat. no. S153-3). See Table 2.2 for properties of these silica gel particles.
Table 2. 2 Characteristics of silica gel particles

<table>
<thead>
<tr>
<th>Silica type</th>
<th>Pore size (nm)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Particle size (μm and mesh sizes)</th>
<th>Surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fisher Chemical Silica</td>
<td>nonporous</td>
<td>0</td>
<td>Floated (200 Mesh and Finer)</td>
<td>0.737</td>
</tr>
<tr>
<td>Davisil®, Grade 645</td>
<td>150 Å</td>
<td>1.15 cm$^3$/g</td>
<td>60-100 mesh 150-250 μm</td>
<td>282</td>
</tr>
<tr>
<td>Grind Davisil®, Grade 645</td>
<td>150 Å</td>
<td>1.15 cm$^3$/g</td>
<td>Not measured</td>
<td>292</td>
</tr>
</tbody>
</table>

2.2 Dialysis and Gel Permeation Chromatography (GPC)

A Spectra/Por® Biotech cellulose ester (CE) dialysis membrane was used for separating the high-mass poly-DADMAC solutions into fractions, of which the retained fraction was saved. The molecular mass cut-off value was 100,000 Daltons, and the tube diameter was 10 mm. Dialysis was carried out with initial poly-DADMAC concentrations in the range 40 to 85 g/L, and the external solution consisted of 0.158% sodium chloride (Fisher). The external solution was replaced at approximately 3, 8.5, and 13 hours after the start, and the retained solution was collected after about 24 hours.

A Waters 2695 GPC system with a Waters 2996 Photodiode Array refractive index detector was equipped with 3000Å-porosity and 300Å-porosity (particle size 10μm) columns connected in series. The packing material consisted of OH-functionalized methacrylate-copolymer-network. The flow rate was 1.0 ml/min, and the column temperature was maintained at 35°C. The system was calibrated with four broad molecular mass poly-DADMAC standards obtained from the supplier of the columns.
Results of GPC showed that most of the low-mass component of the poly-DADMAC was removed by the dialysis.

2.3 Equilibrium of Adsorbate and Adsorbent

In our research, aqueous solutions were prepared with solutions containing $10^{-4}$ M sodium bicarbonate (for purposes of buffering the pH near neutral), plus sufficient sodium sulfate to reach the electrical conductivity values (at about 24 °C) as specified later in this report. Silica gel was added to each of 6 beakers (see Fig. 2), which were stirred vigorously by impeller to keep the particles suspended (approx. 100 rpm). Poly-DADMAC treatment was based on the dry mass percentage relative to silica gel. After approximately 18 to 24 hours, the streaming potential was tested.

Figure 2. 1. System for stirring 6 SiO$_2$ gel samples in parallel for comparative testing of changes in streaming potential due to permeation of cationic polyelectrolyte under closely matched conditions of equilibration.
2.4 Packed Bed Used in Steaming Potential Tests

Before the streaming potential test, one screen at the lower end of the packed bed fitting (see Fig. 1) was unscrewed, leaving the part with the other screen held in a clamp with a beaker below. Silica gel suspension having a mesh size of 60 to 100 was poured through the opened packed bed fitting and retained on a 200mesh screen after allowing the particles in the beaker to sediment for at least 5 minutes. Filtrate was collected in the waiting beaker. A syringe was used to ensure nearly quantitative transfer of the filterable solids into the packed bed. Finally, the unscrewed part was assembled again.

The screens were of 316L stainless steel, having a 200 mesh size. The metal probes, for detection of the electrical potential differences, were composed of silver alloy wires (45% Ag, 30% Cu, 25% Zn) (Wang and Hubbe, 2001).

Immediately before the streaming potential tests, the silica gel in the packed bed was rinsed by passing fresh buffer solution through it.

2.5 Streaming Potential Tests

Electrokinetic tests were carried out with “Streaming Potential Jar” (SPJ) apparatus (Wang and Hubbe, 2001)fitted with the packed bed fitting described above(Wu et al., 2008), as illustrated in Fig. 1. The streaming potential test was performed by carrying out several repeated measurement cycles involving successive application of high pressure, low pressure, and then sufficient vacuum to return the filtrate to the jar at the end of the measurement cycle. The difference of potential detected by the two electrodes on either side of the screen between high pressure and low
pressure is defined as the streaming potential. Vacuum was used to return the filtrate to its starting point for the next cycle measurement. A “high pressure” applied was 207 kPa for at least 8 seconds (default), except that a 16 second was used to obtain more stable results in the absence of sodium sulfate and also for the finer grade of non-porous silica suspension. These tests were carried out with the treated silica gel particles freshly resuspended in the default buffer solution (pH 7, 1000 µS/cm).

Figure 2. 2. Sample cell for the Streaming Potential Jar (SPJ) apparatus to allow for a “packed bed” format during semi-automated streaming potential tests.
3. Results and Discussion

3.1 Repeatability of Streaming Potential Measurements

An individual streaming potential test involved 5 or more cycles of measurement. In each cycle, the SPJ’s software automatically recorded one streaming potential value (potential difference sensed by the two electrode on either side of the screen between high pressure and low pressure), as described in more detail elsewhere (Wu et al., 2008). Results from the first cycle were routinely discarded, since the electrical signals were generally not as stable as for the subsequent tests. The relative error among the remaining four or more cyclical measurements was typically less than 10% of the mean recorded potential. It is possible that the error was related to how well the electrical potential signal was stabilized near the end of the high pressure application and during the period between 6 and 8 s after the pressure had been released to ambient pressure (Wang and Hubbe, 2001).

Five independent replicate experiments (each based on five or more cycles of pressure and vacuum) were carried out at the center point of the experimental conditions, i.e. testing with an electrical conductivity of 1000 µS/cm, pH=7, and an addition level of 1% of very-low-mass poly-DADMAC based on silica gel solids. The mean streaming potential obtained under those conditions was -1.30 mV, which was markedly less negative than -13.4 mV, the results obtained under in the same conditions in the absence of polyelectrolyte. The standard deviation among the independent replications of the
default treated condition was 0.29 mV, which implies a 95% confidence interval for the mean value between -1.66 and -0.94 mV.

3.2 Tests with Dialyzed Poly-DADMAC

Figure 2.3 shows results of initial tests to compare streaming potential values at various levels of treatment of the silica gel with dialyzed vs. as-received high-mass poly-DADMAC. Our GPC results showed that dialysis process removed smaller portion of commercial poly-DADMAC, making its polydispersity decrease considerably. Addition of relatively small amounts of the polyelectrolyte (both undialyzed and dialyzed) was sufficient to increase the measured streaming potential from the initial value of -8 mV up to the range -4 to -2 mV, which is in agreement with earlier test results of this type [18]. This change has been attributed to progressive build-up an adsorbed layer of macromolecules on the outer surfaces of the silica gel particles. It was proposed that at relatively small amounts of the polyelectrolyte, there would be relatively little permeation into silica gel particles nanopore network (nominal pore size 15 nm) due to the relatively high molecular mass of the poly-DADMAC samples (nominally 400-500 kilo Daltons). Thus, it is possible to explain a net negative electrokinetic effect, resulting from the balance of the two opposing effects, on the other hand the effect of liquid passing through the particles (giving a negative contribution). In agreement with this interpretation, follow-up tests with non-porous silica under the same conditions yielded strongly positive streaming potential values of
+31.3 mV, compared to -70.1 mV for the non-porous silica in the absence of the polyelectrolyte.

Figure 2.3. Results of streaming potential tests at increasing levels of either undialyzed (top curves) or dialyzed (bottom curves) high-mass poly-DADMAC to silica gel suspensions under the default conditions.

Figure 2.3 shows streaming potential as a function of high mass poly-DADMAC treatment in salt buffer with 1000µs/cm conductivity. Due to the shape of the function of streaming potential vs. treatment level, as implied by the data, non-polynomial regression models were used to obtain fitted lines. A fourth-order model of the type $y = \beta_0 + \beta_1x + \beta_2x^2 + \beta_3x^3 + \beta_4x^4 + \varepsilon$ was found to give suitable fits with adjusted R-square values of approximately 0.93 for each of the plotted lines.
When comparing the two plotted lines in Fig. 3, the most distinguishing differences corresponding to undialyzed vs. dialyzed samples were at the highest levels of poly-DADMAC treatment. In the case of the systems treated with dialyzed poly-DADMAC, the measured streaming potential remained negative throughout the range of dosages considered. By contrast, positive values of streaming potential were obtained at highest levels of as-received poly-DADMAC. For example, at an addition level of 0.1 polymer to SiO$_2$ solids, the regression lines gave values of 2.9 and -1.4, respectively for the undialyzed vs. dialyzed poly-DADMAC, respectively. This difference was significant at the 95% confidence level. These results support a hypothesis proposed earlier (Lee et al., 2006; Hubbe et al., 2007a; Hubbe et al., 2007b), namely that low-mass material in the as-received poly-DADMAC (Swerin and Wågberg, 1994) could permeate into the silica gel, and that such effects would have a significant effect on steaming potential tests carried out at very high concentrations in the bulk solution.

3.3 Effects of Polyelectrolyte Dosage and Molecular Mass

Figure 2.4 shows the results of streaming potential tests carried out within a broader range of poly-DADMAC treatment levels. Streaming potential was evaluated with fresh buffer solution (p-DADMAC free buffer with 1000 $\mu$S/cm conductivity), instead of with the original liquid with which the silica gel had been equilibrated. By this approach it was possible to observe changes associated just with poly-DADMAC adsorption and permeation during a defined period of equilibration. As shown, the
degree of permeation tended to increase with increasing cationic p-DADMAC treatment during the equilibration period.

Figure 2.4. Effect of dosage of high-mass cationic polymer in the bulk solution during equilibration (relative to the dry mass of silica gel) on the streaming potential measured in the presence of fresh default buffer. Note that the error limits are small relative to the size of the plotted symbols.

Figure 2.5 shows the results of similar tests with both very-low-mass and high-mass poly-DADMAC. In the case of the very-low-mass cationic polymer (upper curve), the observed streaming potential rose almost in direct proportion with the logarithm of polymer dosage. Interestingly, the results for high-mass poly-DADMAC showed a somewhat different trend, with a less apparent effect of dosage. These results are tentatively attributed to (a) a relatively strong adsorption of high-mass polyelectrolyte
onto the outer surfaces of the gel particles, reaching near-saturation at relatively low treatment levels, and (b) a substantially less tendency to permeate into the mesoporous structure, compared with the very-low-mass poly-DADMAC.

![Graph showing streaming potential vs. polymer dosage.](image)

**Figure 2.** Effect of cationic polymer dosage (very low vs. high mass) on the streaming potential of silica gel particles, with tests carried out in the presence of fresh default buffer.

### 3.4 Effects of pH

As shown in Fig. 6, the pH at which the system was equilibrated had a large effect on the streaming potential measured. In these tests, again the streaming potential was measured with p-DADMAC free buffer with 1000 µS/cm conductivity, in order to observe changes associated with poly-DADMAC adsorption and permeation, not those
due to the direct effect of pH on the streaming potential of the substrate itself. As shown, the least change in streaming potential, relative to the -13 mV measured for untreated silica gel under the same electrolyte conditions, was observed at the highest pH of equilibration. The greatest change in streaming potential, even achieving positive SP values, was observed when the equilibration was at pH values below 5.

Figure 2. 6. Effect of pH on the streaming potential of silica gel particles treated with very-low-mass poly-DADMAC and evaluated with fresh default buffer solution. The limit bars shown 95% confidence intervals for the observations.

The trends shown in Fig. 6 directly contradict a possible hypothesis that permeation might be favored by increasing strength of electrostatic attraction between the polyelectrolyte and the substrate. It is well known that SiO₂ surfaces become more negative with increasing pH (Heston et al., 1960; Wiese et al., 1971; Scales et al., 2002)
and that the charge characteristics of positively charged poly-DADMAC are essentially pH-independent (Nicke et al., 1992). Thus, a stronger electrostatic interaction is expected at high pH, presumably providing a greater driving force favoring eventual permeation into the negatively charged pores.

A more successful way to explain the effect of pH is based on the principle of trapped, non-equilibrium states (Fleer et al., 1993; Beer et al., 1997; Claesson et al., 2005). Accordingly, it is reasonable to expect that a relatively strong electrostatic interaction might result in polyelectrolyte molecules becoming essentially immobilized at their positions of first contact with the strongly negative substrate, i.e. on the outer surfaces and at or near the entrances into the porous network within the silica gel. Subsequent movement of the polyelectrolytes, either by transient desorption or by reptation [14], would be greatly suppressed due to multiple simultaneous points of attachment. By contrast, at relatively low pH, where the negative charge density of the silica surface is expected to be much weaker (Heston et al., 1960; Wiese et al., 1971; Scales et al., 1992), one would expect polyelectrolytes to be more able to continue their permeation into the pore network, thus allowing additional macromolecules to occupy their recently vacated positions, and so on. This same mechanism also was found to explain many of the effects recently observed by Horvath et al. (Horvath et al., 2008a) in their study of cationic polyelectrolyte adsorption into cellulosic fibers.

Figure 2.7 shows corresponding results obtained for systems treated with high-mass poly-DADMAC at the 0.2% level and compared with a control experiment (in the
absence of poly-DADMAC). Again, the testing was done with fresh buffer solution having a conductivity of 1000 µS/cm. It is clear from these results that although the cationic polymer had a large effect on the streaming potential at each of the pH values considered, the sign of potential was not reversed. These results, which agree with previous findings (Hubbe et al., 2007b), are attributed to the fact that the interior surfaces within mesopores were not covered by cationic polymer, and such surfaces can be expected to contribute a negative component to the overall electrokinetic effect.

![Graph showing streaming potential vs pH](image)

Figure 2.7. Effect of pH on the streaming potential of silica gel particles treated with high-mass poly-DADMAC (0.2% level) and evaluated with fresh default buffer. The control tests were without the presence of poly-DADMAC.
3.5 Effects of Salt Concentration

Reasons to expect that the concentration of a monomeric electrolyte in the solution might affect permeation of a cationic polyelectrolyte into silica gel include (a) the more condensed conformation of polyelectrolytes (Beer et al., 1997), and (b) a weakening of the electrostatic interactions between the polyelectrolyte and substrate surfaces with increasing salt levels (Fleer et al., 1993). As shown in Fig. 8, there was only a very modest increase in the positive value of streaming potential with increasing conductivity during the over-night equilibration in the presence of very-low-mass poly-DADMAC. Though this finding is consistent with the mechanism described in the previous subsection, i.e. an expected weakening of the electrostatic attraction between the macromolecules and the substrate with increasing salt, the results suggest that such a mechanism did not have a large effect. An alternative explanation for an effect of electrical conductivity can be based on changes in the radii of gyration of the polyelectrolytes in solution; indeed the tests related to molecular mass (see Figs. 3 and 5) already had established that “smaller” molecules are more able to permeate into the silica gel. These issues related to geometrical constraints and effects of salt ions will be further considered in part 2 of this series of articles.
Figure 2. Effect of electrical conductivity during equilibration (adjusted by sodium sulfate addition) on the streaming potential of silica gel treated with very-low-mass versus high-mass poly-DADMAC at the 1% level on SiO$_2$ solids with evaluation carried out with default buffer.

4. Conclusions

1. A streaming potential protocol was used for the first time to obtain evidence of different factors affecting cationic polyelectrolyte penetration into silica gel particles from aqueous solutions during a fixed period of equilibration.

2. The tendency for poly-(diallyldimethylammonium chloride) to permeate into silica gel particles increased with increasing bulk concentration and with decreasing
molecular mass of the polyelectrolyte. Salt concentration did not have a marked effect on permeation within the range considered.

3. The tendency of the cationic polyelectrolyte to permeate into the silica gel also increased markedly with decreasing pH. These results were attributed to strong immobilization of the polyelectrolyte under conditions favoring strong electrostatic attraction between the polyelectrolyte and the substrate. By contrast, conditions of low pH are expected to weaken the interaction forces, thus favoring easier migration adjacent to oppositely charged surfaces.

References


Chapter 3 Permeation of a Cationic Polyelectrolyte into Meso-porous Silica. Part 2. Effects of Time and Pore Size on Streaming Potential

Abstract

As indicated by results shown in Part 1 of this series, the adsorption of cationic polyelectrolyte exposed to mesoporous silica gel can be highly dependent on pH, and it also may be affected by its molecular mass and solution electrical conductivity. Much greater sorption was found under acidic conditions, which was taken as evidence that at higher pH values some of the cationic polyelectrolyte molecules underwent essentially irreversible adsorption near to the entrances of the pore system, thus inhibiting later-arriving macromolecules from diffusing into the mesopore system. The present results quantify aspects of the kinetics and pore-size dependency of adsorption and desorption, showing in particular that desorption tended to be relatively slow and incomplete under the conditions of analysis. Contrasting adsorption behaviors were observed on the exterior vs. interior surfaces of silica gel particles as a function of pore size, electrical conductivity, and polyelectrolyte molecular mass. Increasing ionic strength tended to enhance adsorption of high-mass cationic polymers on the outer surfaces, but only a relatively small effect on permeation of high-mass cationic polymer into silica gel (nominal pore sizes of 6 nm or 30 nm) was observed. Adsorption of very-low-mass cationic polymer onto the outer surfaces and inside the 6 nm pore size silica gel was maximized at an intermediate salt level (1000 µS/cm conductivity). Electrokinetic tests also were used for the first time to provide evidence of polyelectrolyte desorption from mesoporous material.
1. Introduction

The interactions of cationic polyelectrolytes with porous materials have current and potential applications in a wide range of fields, including paper manufacture, pollution abatement, textiles, and the preparation of nanomaterials. Part 1 of this series of articles considered electrokinetic tests to demonstrate how the adsorption of linear, highly cationic polyelectrolyte poly-diallyldimethylammonium chloride (poly-DADMAC) was affected by molecular mass, electrical conductivity, and pH (Wu et al., 2009a). By measuring the streaming potential of silica gel particles held within a packed bed and comparing the results in the presence or absence of salt it was possible to gain information concerning the location (outside or inside the porous network) of adsorbed cationic polymer in silica gel particles (Lee et al., 2006; Hubbe et al., 2007a; Hubbe et al., 2007b).

The present set of tests was carried out to investigate the effects of time, pore size, molecular mass of the cationic polymer used in pretreatment, and the concentration of background electrolyte on the streaming potential of the silica gel particles. As summarized in a recent review article (Wu et al., 2009b), it is reasonable to expect that considerable time is required for a polyelectrolyte to reach equilibrium states in porous material, especially if the molecular mass is relatively high and the pores are in the mesopore range, i.e. about 2 to 50 µm (Rouquerol et al., 1994). This pore size range generally coincides with the range associated with the cell walls of cellulosic fibers after various preparation procedures (Stone et al., 1968; Li et al., 1993; Alince and Ven, 1997;
Berthold and Salmen, 1997; Alince, 2002; Andreasson et al., 2003; Lee et al., 2006; Hubbe et al., 2007a). In various papermaking applications it can be important for polymeric additives to remain on the outer surfaces of cellulosic fibers at least long enough so that they can efficiently affect flocculation behaviors, as well as the formation of a hydrogen-bonded junction between adjacent fibers during paper manufacture (Koethe, 1993; Gruber et al., 1996; Farley, 1997). On the other hand, some applications demand effective macromolecular penetration in the interior of porous systems (Allan et al., 1992; Klungness et al., 2000).

2. Experimental

2.1 Materials

Some materials used in this work were the same as in Part 1 of this series of articles (Wu et al., 2009a). Water used in the experiments was deionized with a Pureflow system. The “default buffer” solution was 1000 µS/cm conductivity sodium sulfate solution that also contained $10^{-4}$ M NaHCO$_3$. An alternative “salt-free buffer” solution had the same NaHCO$_3$ concentration, but no Na$_2$SO$_4$. Inorganic chemicals were of reagent grade. The cationic polyelectrolytes were linear poly-(diallyldimethylammonium chloride) (poly-DADMAC) from Aldrich, catalogue numbers 52,237-6 (very low mass) and 40,903-0 (high mass). The nominal molecular masses of the polyelectrolytes are given as 5k-20k and 400k-500k ranges, respectively. Polyvinylsulfate potassium salt (PVSK), product code 460-S5434 from Nalco Chemical Co.
Three types of mesoporous silica gels, having different nominal pore sizes, were used in the experiments (see Table 3.1). The default substrate was catalogue S745-1 from Fisher Scientific (also known as Davisil Silica Gel 150), which has a nominal pore size of 15 nm and a mesh size range of 60-100. Tests also were carried out with silica gel having a smaller nominal pore size of 6 nm (Fisher S735-1, also known as Davisil Silica Gel 60) and a larger nominal pore size of 30 nm (Fisher S814-1, also known as Davisil Silica Gel 300).

Table 3.1 Characteristics of silica gel particles

<table>
<thead>
<tr>
<th>Silica type</th>
<th>Pore size (nm)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Particle size (μm and mesh sizes)</th>
<th>Nominal Surface area (m$^2$/g)</th>
<th>Tested Surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S6</td>
<td>Davisil®, Grade 635</td>
<td>6</td>
<td>60-100 mesh 150-250 μm</td>
<td>480</td>
<td>345</td>
</tr>
<tr>
<td>S15</td>
<td>Davisil®, Grade 645</td>
<td>15</td>
<td>60-100 mesh 150-250 μm</td>
<td>300</td>
<td>282</td>
</tr>
<tr>
<td>S30</td>
<td>Davisil®, Sorbent, Grade 653 XWP</td>
<td>30</td>
<td>Mesh 230-400 50 μm</td>
<td>150-170</td>
<td>179</td>
</tr>
</tbody>
</table>

*BET Surface area was determined by 3-point analysis in a HORIBA SA-9601-MP surface area analyzer. The samples were dried at 150°C under nitrogen atmosphere for 2 hours.

2.2 Adsorption Tests by Streaming Potential

Modified streaming potential procedures were used to observe certain electrokinetic effects using the same equipment and general procedures as described in Part 1 (Wu et al., 2009a). In that research, we obtained preliminary results for the effect of poly-DADMAC concentration, molecular mass of poly-DADMAC, pH, and
conductivity. In this paper, we designed our experimental conditions to investigate factors affecting polyelectrolyte penetration into mesoporous silica gel particles more comprehensively, as shown in Table 3.2. When considering each of the factors, default variable levels (marked in bold font) were used.

Table 3.2 Levels of independent variables and default conditions

<table>
<thead>
<tr>
<th>Factors</th>
<th>Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-DADMAC dosage, % (on dry mass of silica gel)</td>
<td>0.1, 1, 3, 15, 30</td>
</tr>
<tr>
<td>Time, h</td>
<td>0.5, 1, 2, 4, 12, 24</td>
</tr>
<tr>
<td>Electrical conductivity, µS/cm</td>
<td>10, 100, 1000, 10000</td>
</tr>
<tr>
<td>Pore size, nm</td>
<td>6, 15, 30</td>
</tr>
</tbody>
</table>

*Bold was the default condition

The following procedure was used to compare the effects of different conditions on the degree to which adsorbed poly-DADMAC shifted the streaming potential:

Silica gel having a specified mean pore size was added to one liter of the aqueous solution and equilibrated with a dilute solution of poly-DADMAC of specified mass in the presence of the default or salt-free buffer solution. Poly-DADMAC treatment was based on the dry mass percentage relative to silica gel. For the adsorption tests done at different electrical conductivity, the equilibration time was approximately 20 hours. At the start of this equilibration time a low vacuum was applied to the mixture in a hermetic vessel for approximately 60 seconds to deaerate the dispersion and promote release of internally-held air; this procedure ensured that the silica gel particles were substantially saturated with aqueous solution. However, our later results showed there was no significant difference in the streaming potential results, depending on vacuum application. The mixture was stirred using a multiple stirrer device during different
equilibration time to keep the particles suspended (approx. 100 rpm). (see details in Part 1 (Wu et al., 2009a)). Then the solids were collected as a packed bed of the streaming potential jar. When considering the time variable, the silica gel held in the packed bed was rinsed by flowing fresh default buffer solution through the packed bed once. When considering conductivity variable, the silica gel trapped in the packed bed was rinsed by flowing buffer solution corresponding to the conductivity of testing, rather than the equilibrium condition. The streaming potential was measured by continuously recording the potential between the two electrodes placed adjacent to the two sides of the packed bed.

2.3 Desorption Tests by Streaming Potential

Modified streaming potential analyses was also used to detect evidence of the desorption of high mass poly-DADMAC. The following procedure was used to compare time effect on the degree to which desorption of poly-DADMAC shifted the streaming potential: The selected dry silica gel (Fisher S735-1) was added to poly-DADMAC aqueous solution (15% on dry mass of silica gel). The mixture was shaken within a given time period (between 1h and 27 hours) in a thermostated shaker. Then the solids were collected in a packed bed of the streaming potential jar and rinsed by flowing fresh default buffer solution through the packed bed once.

In principle, a streaming potential requires the evaluation of electrical potential difference between two sides of a porous material, through which liquid is flowing at a determined pressure. The method used in the present work employed a second
measurement at zero applied pressure as a means of calibration (Wang and Hubbe, 2001). Each measurement cycle was completed by applying a slight negative pressure to allow ample time for gently returning the filtrate to the reservoir of the streaming potential device. A complete cycle, involving pressure application (8 to 16 s), then zero applied pressure (20 s), then gentle vacuum (150 s) required about 180 s. The streaming potential tests were started promptly after preparing the packed bed, using polyelectrolyte-free buffer solution.

2.4 Desorption Tests by Streaming Current

A polyelectrolyte titration method was used in order to evaluate whether significant amounts of poly-DADMAC would desorb from silica gel within a given time period (between ca. one minute and 48 hours). In order to fully understand whether or not the desorption behavior happens, two procedures were used. In the first procedure the initial step was to prepare 30 mL of 1% poly-DADMAC solution relative to silica solids in 40ml vials, to which 0.3 g of dry silica gel was added. The mixtures, confined within screw-capped cylindrical glass vial (40 mL volume), were kept in suspension with a holder rotating at 18 rpm. (a) After 24h, the silica gel particles were allowed to settle for 60 seconds, (b) the vial openings were covered with a 500mesh screen, inverting the vial, and applying vacuum to the aqueous solution, so that the silica gel was retained on the 500mesh screen and kept within the vial, (c) the vials were carefully filled with 25ml default buffer by pipette, (d) the mixture was rotated for a selected period of time: 60s, 4h, 24h, and 48h, (e) the silica gel particles were allowed to settle, and (f) the
concentration of cationic polyelectrolytes in the supernatant solution was determined by titration with PVSK. (An aliquot of 5 mL of supernatant solution was titrated with 10 to 1000 µN PVSK).

In the second procedure, the polyelectrolyte titration method was again used to evaluate the amounts of poly-DADMAC that would desorb from silica gel within a given time period (between ca. one minute and 48 hours). But this time, we prepared 120 mL of 1% poly-DADMAC solution relative to silica solids in bottles, to which 20 g of dry silica gel was added. The mixtures, confined within screw-capped glass bottle (120 mL volume), were kept in suspension with a holder rotating at 18 rpm. (a) After 24h, the silica gel particles were allowed to settle for 60 seconds, (b) the bottle openings were covered with a 500mesh screen, inverting the bottle, and applying vacuum to the aqueous solution, so that the silica gel was retained on the 500mesh screen and kept within the bottle, (c) the bottle was carefully filled with 80ml default buffer by syringe, (d) the mixture was rotated for a selected period of time, and (e) samples of cationic polyelectrolytes in the supernatant solution were periodically taken out from the bottle at 60s, 15min, 4h, 24h, and 48h, (f) 0.45µm nylon filters were used to further exclude any silica gel fragments from the supernatant poly-DADMAC solutions, and (g) the concentration of cationic polyelectrolytes in the supernatant solution was determined by titration with PVSK. (An aliquot of 5 mL of supernatant solution was titrated with 10 to 1000 µN PVSK). The endpoint of the polyelectrolyte titration was determined by means of a Mütek PDC-03pH streaming current detector. It is worth noting that the initial poly-
DADMAC concentration of samples was always high enough to provide a positive signal of the streaming current detector at the start of the titration. Thus, the amounts of poly-DADMAC adsorbed onto and into silica gel later desorb from silica gel under specified conditions were quantified by means of polyelectrolyte titrations (Chen et al., 2003; Hubbe and Chen, 2004).

3. Results and Discussion

3.1 Effect of Equilibration Time on Polymer Permeation

As shown in Fig. 1, the time of equilibration of the default silica gel sample (pore size 15 nm) with a dilute solution of high-mass poly-DADMAC had a significant effect on the streaming potential measured at the end of the equilibration period. Since both the equilibration and the testing were done at an electrical conductivity level of 1000 µS/cm (default buffer), the results imply that the amount of cationic polymer within the fine pores of the silica gel increased with increasing time of equilibration. As shown in previous work (Lee et al., 2006; Hubbe et al., 2007a; Hubbe et al., 2007b), when streaming potential tests of this class of silica gel are carried out in solution having an electrical conductivity of 1000 µm, the results mainly indicate the charged nature of the interior surfaces. The fact that even after about 3 x 10^5 seconds (4 days) the signal was still negative implies that coverage of the internal surface area was far from complete. The logarithmic scale used in plotting Figure 3.1 helps to emphasize the fact that adsorption still continued to some extent even after 24 hours of equilibration. The rather slow approach to equilibrium is consistent with predictions of slow diffusion through
confined zones in porous media (Teraoka et al., 1992; Cule and Hwa, 1998; Chao Wang, 2007; Wu et al., 2009b).

![Diagram showing streaming potential over time.](image)

Figure 3.1. Effect of equilibration time on the streaming potential of silica gel particles measured in fresh default buffer.

### 3.2 Evidence of Desorption, and Extrapolation to Zero Time of Desorption

Figure 3.2 shows results from a series of streaming potential measurements carried out with default buffer solution after the silica gel had been equilibrated for different lengths of time with high-mass poly-DADMAC solution (15% treatment level on SiO₂ solids). The horizontal axis corresponds to the cumulative time during which a continuous series of streaming potential measurements was conducted with polyelectrolyte-free buffer solution. The negative slopes of the linear regression lines through the data give evidence of progressive desorption of the cationic polymer from the
silica surfaces. Reasons for using linear regression, rather than a non-linear regression for fitting these data included simplicity and a desire to avoid excessive emphasis on data collected during the earliest cycles of testing; the baseline for the voltage measurements typically becomes more stable during later cycles.

By extrapolating the results in Figure 3.2 back to zero seconds, one can obtain an estimate of what the streaming potentials would have been if they could have been measured at the moment of replacement of the supernatant solution with fresh buffer. This procedure was followed, and the results are presented in Figure 3.3 as streaming potential values vs. the logarithm of time following the replacement of the supernatant solution. As shown, a regression of streaming potential vs. the log of time gave a straight line with an $R^2$ value of 0.978. This semi-logarithmic relationship implies that the change of streaming potential was a decelerating function of time. A plausible reason for such behavior is that each successive increment of adsorbed polyelectrolyte near to the outer entrances of the network of internal pores would be expected to increase the barrier to further diffusion of like-charge polyelectrolytes.
Figure 3. 2. Fall-off of streaming potential with time when in fresh default buffer during streaming potential analyses. Note that the initial streaming potential increased with increasing time of the initial equilibration, before the solids were exposed to polymer-free solution.

Figure 3. 3. Streaming potential as a function of equilibration time. The streaming potential value was obtained by extrapolating the data in Fig. 2 to time equal to zero, using the regression results.
3.3 Desorption Tests Following Different Concentration and Molecular Mass Exposure

Figure 3.4 and Figure 3.5 compare the decay of streaming potential following different levels of poly-DADMAC treatment. In the case of very-low-mass poly-DADMAC, Figure 3.4 shows that at the highest level of poly-DADMAC treatment (3% based on silica) there was a steady, positive value of streaming potential. At the lowest level of treatment there was tentative evidence of desorption (the streaming potential was reduced from -2 to ca. -7 mV with rinsing time or number of cycles). For reference, a streaming potential of -13 mV was observed for the default silica gel with the same buffer solution and no polymer treatment. A reason for believing that the observed decay of streaming potential values toward more negative values was due to desorption is that the systems had been already equilibrated for 20-24 hours, providing time for the adsorbed conformation of the polymers to approach a steady state.
Figure 3.4. Fall-off of streaming potential with time when in the fresh default buffer during streaming potential analyses after equilibration of the silica gel with different dosages of very-low-mass poly-DADMAC (based on SiO$_2$ dry mass for about 20 hours.

A tentative explanation for the results in Figure 3.4 follows from preceding studies in which it was proposed (Hubbe et al., 2007b) and then demonstrated (Wu et al., 2009a) that the positive values of streaming potential observed under the conditions represented by Fig. 3A were attributable to very-low-mass oligomers present in the poly-DADMAC samples. The cited studies together demonstrated that very-low-mass cationic oligomers were able to permeate into the silica gel to an extent that was sufficient to reverse the streaming potential to a positive value, even in the presence of background electrolyte (1000 $\mu$S/cm conductivity). The results in Figure 3.4 imply that after such permeation, the rate of desorption of cationic oligomers from the pore structure must
have been slow relative to the time of observation. The fact that a significant decrease in
streaming potential with time was observed in the case where the silica gel had been
exposed to the lowest concentration of cationic polymer is consistent with there being at
least a factor of ten less very-low-mass material present in the system (due to a lower
concentration used during the equilibration step), hence less material capable of
permeating to a significant extent into the 15-nm pores of the silica gel.

A unique effect was observed during the collection of the data in Figure 3.4. It
was found that the streaming potential returned to slightly more positive or less negative
values each time that the system was allowed to “rest” for extended periods between
rinsing cycles during measurement of streaming potential. These shifts can be seen in
Figure 3.4 corresponding to cycle’s number 5, 3, and 26 for exposure levels of 3%, 1%,
and 0.1%, respectively. The cause of this effect is not known. It is possible that flow
causes the adsorbed polyelectrolytes to adopt a less extended confirmation, and a rest
period between applications of pressure or vacuum allows the adsorbed polymer to revert
to a more extended adsorbed conformation. Another possibility is that some time may be
required, between cycles, in order for the packing density of the adsorbed polyelectrolyte
to relax toward a previous state prior to the imposition of flow. (The same effect is
evident in Figure 3.5 for the 10% level of exposure with high-mass poly-DADMAC, see
cycle 12.)
Figure 3.5. Fall-off of streaming potential with time when in the fresh default buffer during streaming potential analyses after equilibration of the silica gel with different dosages of high-mass poly-DADMAC (based on SiO₂ dry mass) for about 20 hours.

Figure 3.5 shows corresponding results for high-mass poly-DADMAC. In this case there was consistent, clear evidence of desorption of poly-DADMAC with rinsing, as judged from the increasingly negative streaming potential values measured with time for all levels of polymer concentration during the equilibration (adsorption) with the silica gel. From higher initial streaming potential value at corresponding poly-DADMAC concentration in Figure 3.7 and 3.8 compared to Figure 3.4, it can be expected that the large molecules are less able to permeate into the entrances of the internal pores of the silica gel during the equilibration period, and that significant time is required in order to
reverse this process when the supporting medium is replaced by fresh default buffer. In addition, results of gel permeation chromatography are consistent with a lesser proportion of very-low-mass oligomers present in the “high mass” sample of poly-DADMAC.

Two mechanisms are likely to account for the general shape of the curves appearing in Figure 3.5. First, it is likely that some of the greater persistence of relatively high values of streaming potential following the highest level of treatment was due to the same effects mentioned in the context of Figure 3.4. The lesser proportion of very-low-mass oligomers in the high-mass polymer sample explains why no streaming potential values above zero were observed. The observed decay of streaming potential values is consistent with desorption of polyelectrolyte molecules from the outer surfaces of the silica gel. The reason to expect significant desorption even in the case of a very-high-mass cationic polyelectrolyte is due to the expected crowded condition of the adsorbed layer. Upon re-suspension of the silica gel in polyelectrolyte-free medium, the adsorbed macromolecules can be expected to gradually adopt flatter adsorbed conformation, a process that tends to evict some of the macromolecules from the surface (Odberg et al., 1993; Wågberg, 2000). Past studies have suggested that higher-mass macromolecules tend to out-compete lower-mass macromolecules, and the expected result is (a) a lower net adsorbed amount and (b) less extension of loops and tails of polyelectrolyte outward form the surface. Both of these effects can be expected to account for a drift in streaming potential signals to more negative values, as shown in Figures 3.4 and 3.5.
3.4 Streaming Current Titrations to Evaluate Desorbed Amounts

Figure 3.6 shows results of tests that were designed to detect desorption of very-low-mass poly-DADMAC from silica gel particles, following their treatment, removal of most of the suspending medium, and then their prompt resuspension in polyelectrolyte-free buffer solution. As shown, there was no significant change in the amount of poly-DADMAC in the solution. Thus, the results of the streaming current (SC) titrations were in contrast to those from the streaming potential (SP) tests. In the SC tests, mixing of silica gel and poly-DADMAC was achieved by rotating the sample containers, and the tests of the concentrations of the residual poly-DADMAC remaining in solution were determined in the absence of solids. By contrast, in the SP tests, part of the flow induced by pressure went through silica gel particles, giving rise to the streaming potential signals. It is proposed that pressure-induced flow might be the reason for poly-DADMAC desorbing from the silica gel particles.

As the regression results showed, with 95% confidence that the desorbed amount of poly-DADMAC, was no higher than 1.53mg for small vials and was no higher than 0.55mg for big batches.

Another possibility is that the amount of desorption giving rise to the observed changes in streaming potential was below the detection limit of the streaming current titrations.
Figure 3.6. Desorption amount of very low mass poly-DADMAC from SiO$_2$ with 15nm pore size detected by streaming current titration

3.5 Effects of Large Pore Size, Molecular Mass, and Salt Content

Figures 3.7 and 3.8 show results obtained with silica gel having a characteristic pore size twice as large as those reported so far in this work (including in Part 1 of this series (Wu et al., 2009a)). It is reasonable to expect that larger pores (30 nm, compared to a default value of 15 nm) would permit more rapid and complete permeation, though the results also could be expected to depend on molecular mass and other factors. The conductivity values plotted in Figures 3.7 and 3.8 and Figures 3.9 and 3.10 correspond to the conditions used during overnight equilibration of the cationic polyelectrolyte and the silica gel. The electrolyte conditions during the cyclic streaming potential runs are
specified in the legends and captions. Following the strategy developed in previous work (Hubbe et al., 2007a; Hubbe et al., 2007b), tests were conducted under highly contrasting concentration of background electrolyte in order to be able to distinguish between effects due to cationic polymer either on the outer surface of the silica gel (mainly observed by streaming potential tests in the absence of electrolyte) versus effects due to permeation of cationic polymer into the mesopores (mainly observed by streaming potential tests carried out in the presence of salt).

Figure 3. Effect of electrical conductivity during equilibration with poly-DADMAC of very low vs. high mass on the streaming potential of the outer surfaces, later measured with fresh salt-free buffer solution on silica gel having 30 nm a pore size.
Figure 3.8. Effect of electrical conductivity during equilibration with poly-DADMAC of very low vs. high mass on the streaming potential (with the major contribution to effect coming from pre surfaces) the later measured with fresh 1000 µS/cm buffer solution on silica gel having 30 nm a pore size.

As shown in Figure 3.7, streaming potential measurements carried out in the absence of salt (with just $10^{-4}$ M NaHCO$_3$ to buffer the pH) revealed evidence of increasing poly-DADMAC adsorption with increasing background salt during equilibration. The trend was especially evident in the case of the high-mass cationic polymer. These results are consistent with an expectation of very high-affinity adsorption of the large cationic macromolecules; thus it is reasonable to expect suitably strong adsorption even at the very high conductivity level of 10,000 µS/cm. High affinity
adsorption is attributable to the large change in free energy when a multiplicity of the polyelectrolyte’s ionic groups replace counter-ions at a substrate surface during the adsorption event. In addition, increased salt content favors polyelectrolyte to adopt a more condensed, coiled conformation, allowing more of it to adsorb on a given amount of accessible surface area. The situation is expected to be somewhat different in the case of the very-low-mass poly-DADMAC, since the free energy change associated with adsorption of one macromolecule is much lower. As the salt concentration is increased, it is reasonable to expect to reach a balance between the effects of weakening of the adsorption affinity and increased packing ability. This balance between a more condensed macromolecular conformation and decreased adsorption affinity with increasing salt may explain why the effect of very-low-mass poly-DADMAC on streaming potential appeared to go through a maximum with respect to salt content of the solution during equilibration.

As shown in Figure 3.8, streaming potential measurements carried out with polymer-free default buffer solution (larger salt concentration compared to reported experiments in Figure 3.7) revealed a strong dependency of the resulting streaming potential on molecular mass of the poly-DADMAC used in the equilibration step. As described earlier (Lee et al., 2006; Hubbe et al., 2007a; Hubbe et al., 2007b), results of streaming potential tests of mesoporous material carried out in the presence of salt can be interpreted as mainly revealing the charged condition of internal surfaces – i.e. the surfaces of the pores. Thus, the results in Figure 3.8 reveal a substantial effect of salt on
the permeation of the very-low-mass cationic polyelectrolyte. No such effect was observed in the case of the high-mass cationic polymer. This difference is tentatively attributed to space hindrance in the permeation of a very large polymer into small pores — even in cases where electrostatic effects have been weakened by the presence of salts. Further evidence in support of this explanation is the fact that Figure 3.8 shows negative values of streaming potential, whereas Figure 3.7 shows positive values for samples that were equilibrated under identical conditions. The difference is attributed to an inability of the high-mass polyelectrolyte to reach the interior surfaces of the mesoporous material, allowing those surfaces to negative in charge, a condition that is observable only when the streaming potential tests are carried out in the presence of salt (Lee et al., 2006; Hubbe et al., 2007a; Hubbe et al., 2007b).

3.6 Effects of Small Pore Size, Molecular Mass, and Salt Content

Results shown in Figures 3.9~3.11 correspond to tests carried out in silica gel having nominal pore sizes of 6 nm, about half the size of the default silica gel (noting that some corresponding results for the default silica gel already were given in Part 1 (Wu et al., 2009a)). Results in Figure 3.9, which involve streaming potential tests in the absence of salt, show some of the same trends as in Figure 3.7 (for which the treatment and testing conditions were the same, but the pore size was 30 nm). Thus, the effect of the high-mass poly-DADMAC on increasing the streaming potential became more evident at higher salt concentrations during the equilibration phase. By contrast, the effect of the very-low-mass poly-DADMAC achieved a maximum when the equilibration took place
at the intermediate electrical conductivity value of 1000 µS/cm. The explanations for these two observations presumably are just the same as those that were given in the discussion of Figure 3.7.

![Figure 3.9](image)

Figure 3.9. Results for salt-free system with smaller pores: Effect of electrical conductivity during equilibration with poly-DADMAC of very low vs. high mass on the streaming potential of the outer surfaces, later measured with fresh salt-free buffer solution on silica gel having 6 nm a pore size.

Closer comparison of the results in Figure 3.7 and Figure 3.9 shows that in the case of the high-mass poly-DADMAC approximately twice as high values of streaming potential were achieved throughout the range of electrical conductivities tested when the polyelectrolyte was adsorbing onto the substrate having the larger pore size. One
possible explanation (to be tested in future work) can be offered that is related to the expected slow interaction of a high-mass polyelectrolyte in the entrance of a suitably-sized mesopore network. If the pores are large enough, one can consider a mechanism in which the ends of a high-mass polymer can function like the roots of the plant; reptation of the polymer ends even a short distance into the mesopore structure can be expected to achieve hard-to-reverse adsorption. Though such a mechanism could account for results in Figure 3.7 (with the 30 nm pores), the 6 nm pores (Figure 3.9) can be expected to be too small for the high-mass poly-DADMAC to have an appreciable tendency to interact with the pores.

The experiments represented in Figure 3.10 were essentially the same as those in Figure 3.8, except that there was a very large difference in pore size. Even though earlier work had shown that sodium sulfate solution having a conductivity of 1000 µS/cm was enough to overcome the suppression of double layer effects in the mesopore structure, the same assumption would not necessarily be true in the case of smaller pores. So the large contrast between the results in Figure 3.8 and Figure 3.10 may be due to the fact that the 1000 µS/cm conductivity level was not sufficiently high in order for the mesopore surfaces to make a dominant contribution to the observed streaming potential. Thus, it is notable that Figure 3.10 shows positive values of streaming potential in most cases. To help evaluate this hypothesis, Table 3.3 compares the factors by which electrokinetic effects are predicted to be suppressed (Alkafeef et al., 2001), when comparing the three types of silica gel and the levels of salt concentration used in the present work.
Figure 3. Same system as the previous (6 nm pore size), but with streaming potential evaluation in the presence of 1000 µS/cm buffer solution.

Table 3. Suppression factors giving relative magnitude of electrokinetic effects within pores, compared to outer exposed surfaces, for various electrolyte conditions and pore sizes.*

<table>
<thead>
<tr>
<th>Conductivity (µS/cm)</th>
<th>Na₂SO₄ Conc. (mM)</th>
<th>Debye-Hückel length (nm)</th>
<th>Suppression Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pore Size (nm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>10</td>
<td>0.025</td>
<td>35.0</td>
<td>0.010</td>
</tr>
<tr>
<td>60</td>
<td>0.14</td>
<td>14.8</td>
<td>0.051</td>
</tr>
<tr>
<td>1,000</td>
<td>2.51</td>
<td>3.50</td>
<td>0.453</td>
</tr>
<tr>
<td>8,000</td>
<td>25.1</td>
<td>1.11</td>
<td>0.815</td>
</tr>
<tr>
<td>10,000</td>
<td>31.6</td>
<td>0.98</td>
<td>0.835</td>
</tr>
</tbody>
</table>

* Based on sodium sulfate as main electrolyte; conditions match those used in this study.
To confirm the explanation just given, similar tests were carried out at a yet higher level of sodium sulfate addition, sufficient to give an electrical conductivity of 8000 µS/cm. As shown in Figure 3.11, this high level of salt during the analyses yielded more negative values of streaming potential, thus supporting the hypothesis. The longer error bars in Figure 3.11 are attributed to the decreasing resolution of streaming potential measurements at very high conductivity. However, it is notable that the trends shown in Figure 3.11 generally match those in Figure 3.9, suggesting that permeation as well as adsorption and of very-low-mass poly-DADMAC went through a maximum with respect to conductivity of the equilibration solution, whereas permeation and adsorption of the high-mass poly-DADMAC increased monotonically with increasing conductivity within the range considered.
Figure 3. Same system as the previous (6 nm pore size), but with streaming potential evaluation in the presence of 8000 µS/cm buffer solution.

4. Conclusions

Evidence of progressive, though limited permeation of high-charge linear cationic polymer was obtained by measuring streaming potential of polymer-treated silica gel particles in the presence of polymer-free buffer solution, following 18 to 24 hours of equilibration with a poly-DADMAC solution. Changes in streaming potential observed in the presence of salt suggested that oligomers in the poly-DADMAC solutions permeated into the silica gel to a much greater extent than higher-mass macromolecules.
5. Desorption of poly-DADMAC from silica gel was monitored by recording the changes in streaming potential during series of automated cycles of pressure (high, ambient, and negative pressures). Desorption effects were especially apparent when high-mass cationic polymer was used during the equilibration part of the experiment. These results were attributed to mainly desorption from the outer surfaces of silica gel particles.

6. Tests with different nominal pore size samples of silica gel carried out with different levels of background electrolyte were consistent with only limited permeation of either the high-mass or the very-low-mass cationic polymer. Streaming potential tests carried out at very low electrolyte levels gave evidence, however, that adsorption of the high-mass cationic polymer on the outer surfaces of the silica gel increased with increasing salt throughout the range of experimentation. Permeation of very-low-mass poly-DADMAC into silica gel having a small pore size was favored by an intermediate level of electrical conductivity.

References


Chapter 4  Permeation of a Cationic Polyelectrolyte into Meso-porous Silica.

Part 3. Adsorption Isotherms

Abstract
Adsorption of cationic polyelectrolytes onto and into porous media has applications in papermaking, the petroleum industry, and separation processes, etc. In this research, polydiallyldimethylammonium chloride (poly-DADMAC) was used as a probe molecule to investigate major factors affecting penetration of polyelectrolyte into silica gel with various pore sizes. Key variables, such as time, polyelectrolyte concentration, molecular mass, pH, etc. were investigated by means of adsorption isotherms and compared at different levels of variables. Streaming current titrations were used to detect the net amount of polyelectrolyte adsorption on the external and internal surfaces. The adsorption kinetics were time dependent and diffusion limited. The adsorbed amount of poly-DADMAC was controlled by both the pore size and the surface area. The highest adsorption amount, based on mass of the substrate, was achieved when using silica gel having an intermediate pore size (15 nm) at a relatively high solution concentration of very-low-mass poly-DADMAC. The results could be fit well to an assumed Langmuir model of the adsorption process.
1. Introduction

The discovery of how to prepare silica gel with pore size in the range 2-50nm (i.e. mesoporous) has created applications in many areas due to its high specific surface area and pore volume. Applications such as those reported by Wang, et al. (Wang et al., 2007), and references therein, include biosensing (Xu et al., 2003), biocatalysts (Diaz and Balkus, 1996), drug delivery (Radu et al., 2004), and protein separation (Han et al., 1999). In the case of catalytic materials, for example, it is desirable to have small pores to increase surface area, but not too small, so that the reactants can flow easily. Studies concerning the adsorption within porous media has reflected a broad interest, with numerous applications in papermaking (Hubbe et al., 2007b; Martin et al., 2009), enhanced oil recovery (Wu et al., 2009b), water treatment (Bratby, 2006), and other fields (Dave et al., 2008). For instance, in the paper industry, dissolved polyelectrolytes associated with the fiber suspensions can include lignin byproducts, hemicelluloses, and wood extractives; cationic polyelectrolytes are often added to neutralize such dissolved polymeric and colloidal matter, i.e. the “anionic trash,” before removing the water during the formation of a paper sheet. Better knowledge of the interactions between cationic polyelectrolytes and oppositely charged substrates, such as cellulose and colloid particles has the potential to promote increased productivity in papermaking processes.

The mechanism of polymer adsorption into cellulosic fibers is drawing increased attention in recent years (Petlicki and van de Ven, 1994; Wågberg, 2000; Shirazi et al., 2003; Horvath et al., 2008a; b; c). However, studies of adsorption of polyelectrolytes
onto and into cellulosic substrates can present a challenge to quantitative techniques. Cellulosic fibers’ pore structure is complex and subject to change in dimension significantly with changes in the surrounding aqueous solution. Compared to cellulosic fibers, which have complex pores and structure, silica gel with narrowly distributed pore size can be an ideal model of nanoporous material. By use of a good model substrate it is our hope to shed light on the complex subject of the mechanisms affecting polyelectrolyte diffusion into porous matter (Mishael et al., 2007).

Polyelectrolyte adsorption measurements can be carried out using a streaming current titration method. In paper industry applications this kind of analysis is often used to measure charge demand of an aqueous solution or suspension. It is well known that at near zero charge demand, the fiber furnish often shows its best drainage and retention (Chen, 2004). In the present investigation the same method was used to measure the residual poly-DADMAC concentration. In other words, the amount of poly-DADMAC in the solution phase was measured before and after adsorption test to calculate the amount of poly-DADMAC adsorbed within silica gel particles. A series of experiments was performed to investigate the adsorption of poly-DADMAC in silica gels at different levels of the variables of interest. The goal of the work was to explore the influence of several key variables on the adsorption of polyelectrolyte onto silica gel particles. Different levels of factors were concerned, such as substrate polymer characterization (pore size, polyelectrolyte molecular weight) and aqueous solution conditions (pH) (see Table 4.1).
Table 4. 1 Independent variables & ranges

<table>
<thead>
<tr>
<th>Variables</th>
<th>Additative(s)</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Silica gel</td>
<td>P- DADMAC</td>
</tr>
<tr>
<td>pore size</td>
<td>P-DADMAC</td>
<td>6, 15, 30 nm</td>
</tr>
<tr>
<td>Polyelectrolyte</td>
<td>Mol. mass</td>
<td>P- DADMAC</td>
</tr>
<tr>
<td></td>
<td>Dosage</td>
<td>P-DADMAC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.01%, 0.02%, 0.05%, 0.1%,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5% 1.0% on dry mass of silica gel</td>
</tr>
<tr>
<td>Medium conditions</td>
<td>pH</td>
<td>HCl, NaOH</td>
</tr>
<tr>
<td></td>
<td>Time</td>
<td>P-DADMAC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1, 2, 4, 8, 12, 24 h</td>
</tr>
</tbody>
</table>

2. Experimental

2.1 Materials

Water used in the experiments was deionized with a Pureflow system. The “default buffer” solution was prepared with 1000 µS/cm conductivity by addition of sodium sulfate solution to a $10^{-4}$ M solution of sodium bicarbonate. The cationic polyelectrolytes were linear poly-(diallyldimethylammonium chloride) (poly-DADMAC) from Aldrich, catalogue numbers 52,237-6 (very low mass) and 40,903-0 (high mass). The nominal molecular masses of the polyelectrolytes are given as 5k-20k and 400k-500k ranges, respectively.

One nonporous silica and three types of mesoporous silica gels, having different nominal pore sizes, were used in the experiments. The following samples were obtained from Fisher Scientific: Fine Granuals 40-100 Mesh Chemical Silica; Davisil Silica Gel 60 with pore size of 6 nm and mesh size range of 60-100 (Fisher S735-1); Davisil Silica Gel
150 with nominal pore size of 15 nm and a mesh size range of 60-100 (Fisher S745-1); and Davisil Silica Gel 300 with nominal pore size of 30 nm and mesh size of 50 micron (Fisher S814-1). These samples were denoted as \( S_0 \), \( S_6 \), \( S_{15} \), and \( S_{30} \). See detailed information in Table 4.2.

Table 4.2 Characteristics of silica gel particles

<table>
<thead>
<tr>
<th>Silica type</th>
<th>Pore size (nm)</th>
<th>Pore volume (cm(^3)/g)</th>
<th>Particle and mesh sizes</th>
<th>Nominal surface area (m(^2)/g)</th>
<th>Tested surface area (m(^2)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_0 ) Fisher Chemical Silica</td>
<td>Nonporous</td>
<td>/</td>
<td>Floated (200 Mesh and Finer)</td>
<td>/</td>
<td>0.737</td>
</tr>
<tr>
<td>( S_6 ) Davisil®, Grade 635</td>
<td>6</td>
<td>0.75</td>
<td>60-100 mesh 150-250 μm</td>
<td>480</td>
<td>345</td>
</tr>
<tr>
<td>( S_{15} ) Davisil®, Grade 645</td>
<td>15</td>
<td>1.15</td>
<td>60-100 mesh 150-250 μm</td>
<td>300</td>
<td>282</td>
</tr>
<tr>
<td>( S_{30} ) Davisil® Sorbent, Grade 653 XWP</td>
<td>30</td>
<td>1.1-1.2</td>
<td>Mesh 230-400 50 μm</td>
<td>150-170</td>
<td>179</td>
</tr>
</tbody>
</table>

*BET Surface area was determined by 3-point analysis in a HORIBA SA-9601-MP surface area analyzer. The samples were dried at 150 C under nitrogen atmosphere for 2 hours.

The relatively low value of surface area in the case of sample \( S_0 \) is consistent with the absence of internal pores. \( S_6 \) had the highest surface area with pore volume 0.75 cm\(^3\)/g, which is consistent with the smallest pore size, and \( S_{15} \), having medium size, showed an intermediate surface area, with pore volume 1.15 cm\(^3\)/g. \( S_{30} \), having the largest pore size, showed the lowest surface area with pore volume 1.1-1.2 cm\(^3\)/g. Pore size and surface area are closely related competing factors that control how the rate and
extent to which the poly-DADMAC can access these pores. The smaller the pores, the harder it would be for the poly-DADMAC diffuse in. Some differences were observed between the nominal surface area (as stated by the supplier) and tested surface area of silica gel after performing substrate characterization, especially for sample S6. However, an inverse relationship was observed between pore size and surface area, regardless of which set of surface area information was used. Our silica gel surface area characterization results were consistent with those of Mishael et al. (Mishael et al., 2007), who studied the correlation between surface area and wider range of controlled pore size of porous glass. Their fitting curve shows that the area is inversely proportional to the 2.2 power of the pore radius.

2.2 Adsorption Tests

Poly-DADMAC adsorption kinetics and adsorption isotherms at different concentration of poly-DADMAC were investigated. For tests involving kinetics, poly-DADMAC having a concentration of ~1.0% (10mg/ml) was prepared in default buffer solution with conductivity 1000µs/cm (see earlier), and with the pH adjusted to 7 using 0.05-1M HCl or NaOH. Adsorption experiments were conducted by mixing 30ml poly-DADMAC with 0.3g silica gel particles (Poly-DADMAC/silica gel weight ration 1:1), followed by rotating the bottles containing the mixture at room temperature for 1, 2, 4, 8, 12, and 24h. Thereafter the mixture was allowed to settle for about 1min, and then 0.45µm nylon filters were used to remove any residual silica gel particles from the supernatant solution. Side experiments showed that the filtration did not result in
observed differences of the supernatant solution concentration. Finally, an aliquot of the filtrate solution was titrated to determine the concentration of poly-DADMAC, using a M"uket PCD-03 streaming current device. Poly-DADMAC adsorption determinations at different concentrations were done by the same procedure as kinetics experiments, except equilibrated for 4h with concentration range from 0.02%-1.0% based on dry mass of silica gel.

2.3 Streaming Current Measurements

A M"uket PCD-03(Particle Charged Detector) device was used. The titrant used in such tests was NALCO 0.0010N potassium polyvinyl sulfate (PVSK). Poly-DADMAC samples were diluted 1-50 times, as needed, in order to consume the same approximate volume of 0.0010N PVSK titrant. An aliquot of 5ml diluted poly-DADMAC sample was added to the titration cell, followed by adding 10ml salt buffer, then PVSK was added gradually to reach an endpoint of zero.

2.4 Titration Stoichiometry

When performing polyelectrolyte titrations, commonly it has been assumed that each anionic group of a polyelectrolyte associates with one cationic group during a complexation interaction with a polyelectrolyte of opposite charge. In other words, one assumes a one-to-one charge complex formation. However, it has been observed that with increasing conductivity there is some deviation from 1:1 stoichiometry in the endpoint detection (Chen, 2004). In principle, higher salt concentration compresses the electrical double layer and decreases the repulsion force between charged groups, resulting in non-
equal ionic interaction of two polyelectrolyte (not perfect 1:1 zipper shape). These
effects would tend to be favored by shielding the electrostatic attraction between charged
sites. Moreover, polyelectrolyte conformation tends to become more compact with
increasing salt concentration. The cited work also showed that non-stoichiometric effects
can be due to an excess of one of the polyelectrolytes at the surfaces of charge-stabilized
complexes, which remain suspended in the solution phase (Chen, 2004).

During the implementation of the titrations it was observed that the titration
endpoint depended to a moderate extent on the rate of titration. For instance, addition of
PVSK at a higher rate during titration of very low mass poly-DADMAC (Mw 5-20K)
made it appear that a somewhat lower amount of poly-DADMAC adsorption had
occurred. By contrast, a slow titration process always resulted in the calculation of a
higher adsorbed amount. One likely explanation is based on the fact that the PVSK with
nominal molecular weight 170K had a much larger molecular chain length than that of
very low mass poly-DADMAC. When PVSK is freshly added to the mixture, it may
initially coil up due to the salt condition, but given sufficient time it may change its
conformation and react with more of the very low mass poly-DADMAC. The idea is that
with the passage of time the polyelectrolytes can partly unfold, exposing more active sites
to interact with a polyelectrolyte of opposite charge. As a consequence, the apparent
adsorption of poly-DADMAC increased when more time was allowed for the titration.
3. Results and Discussion

3.1 Effect of Equilibration Time on Polyelectrolyte Adsorption

1) High mass 15 & 30 nm

As shown in Figure 4.1, a straight-line relationship was found between the adsorbed amount of high mass poly-DADMAC and the logarithm of adsorption time for both 15nm and 30nm silica gel. The observed logarithmic relationship means that with increasing time of exposure, the incremental increase per unit of time in the adsorption and penetration amount became less. The straight-line relationship also indicates that the adsorption of high mass poly-DADMAC was diffusion limited, so it would be easy to understand why at the same time point, high mass poly-DADMAC adsorbed and diffused more into 30nm silica gel in comparison to 15nm gel. It is worth noting that after 12h (log t/s = 4.64), there was no big change in adsorbed amount. In the case of 15nm silica gel about 63% adsorption of high mass poly-DADMAC had already been achieved at 4h, compared to the amount at 24h. In the case of 30nm silica gel the corresponding percentage was 90%.
Figure 4. 1. Adsorption kinetics curve for high mass poly-DADMAC on \( S_{15} \) and \( S_{30} \)

2) Very Low Mass

As shown in Figure 4.2, a linear relationship also was found in adsorption amounts of very low mass poly-DADMAC equilibrated with various pore size silica gels. Compared with high mass poly-DADMAC mentioned above (see Figure 4.1), the adsorbed amount of very low mass poly-DADMAC increased considerably, as would be expected due to its greater accessibility. Based on results of linear regression fitting, it is easy to note that the slope decreased with increasing pore size. This observation provides evidence that the bigger the pore size, the faster the very low mass poly-DADMAC can absorb and diffuse in, so that much of the process becomes completed even before the minimum time of measurement. The adsorbed amount of very low mass poly-DADMAC into 6nm silica gel at 4h (log \( t/s = 4.16 \)), was nearly 78.7% of its value at 24 hours. This percentage rose to around 89.1% for 15nm silica gel, and 90.1% for 30nm silica gel.
When looking at the same time point, it can be seen that the 15nm silica gel achieved the highest adsorbed amount of very-low-mass poly-DADMAC, followed by 30nm, and then 6nm. Although 6nm silica gel had the highest surface area, the results suggest that the poly-DADMAC molecules denoted as very low mass were still too large to diffuse efficiently into the 6nm pores. For 15nm silica gel with the medium surface area, the pore size was large enough for poly-DADMAC of very low mass to diffuse in, and in the case of 30nm silica gel diffusion would be even much easier, but its relatively low surface area resulted in lower adsorption compared with 15nm.

When interpreting effects related to molecular mass, it can be beneficial to consider the radius of gyration of poly-DADMAC corresponding to the conditions used in our research. Table 4.3 provides some information about radius of gyration of poly-DADMAC of the types used in our research, based on tests in 1M NaCl.
Table 4. 3 Poly-DADMAC characteristics including the radius of gyration according to (Burkhardt et. Al. 1987) reviewed by Lars Wågberg (Wågberg).

<table>
<thead>
<tr>
<th>Type of polymer</th>
<th>Molecular mass (weight range)</th>
<th>Radius of gyration (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very low mass</td>
<td>5-20K</td>
<td>8.94-13.45</td>
</tr>
<tr>
<td>High mass</td>
<td>400-500K</td>
<td>44.81-49.58</td>
</tr>
</tbody>
</table>

To summarize findings for different molecular mass poly-DADMAC adsorption kinetics, it is proposed that as long as the poly-DADMAC molecule is small enough or the pores in the silica gel are large enough for poly-DADMAC to allow passage, then surface area dominates the adsorption amount. The more the surface area, the larger the adsorbed amount. If poly-DADMAC is too large to permeate to a significant extent, or if the pore size of silica gel is too small, even with high surface area, the adsorbed amount is very low. Wang, et al. reported similar results (Wang et al., 2007).

In order to compare pore size and other variable effects, we choose 4h as our equilibrium time for all later tests.

In an effort to estimate how much poly-DADMAC would adsorb onto the outer surfaces, we carried out parallel tests with non-porous silica. Within the repeatability of the methods, no significant adsorption was observed for nonporous silica (200 mesh and finer particle size).

3.2 Effects of Concentration of Poly-DADMAC

Adsorption isotherms of poly-DADMAC on silica gel substrates having different pore size ($S_6$, $S_{15}$, and $S_{30}$) are shown in Figures 4.3(a) and 4.3(b). The Langmuir equation
\( \Gamma = a^{\ast}C/(1+b^{\ast}C) \) was well fitted in each case, and the plotted results show the dependence of poly-DADMAC adsorbed amount on the poly-DADMAC concentration in range of 0-0.5% (on dry mass of silica gel). In Figure 4.3, the poly-DADMAC adsorbed amounts were calculated based on the dry mass of the silica gel particles, while in Figure 4.4, poly-DADMAC adsorbed amounts were calculated based on the surface area of the silica gel particles. The adsorption isotherm curves showed a linear relationship at relatively lower concentration of poly-DADMAC, and a plateau of adsorbed amount was reached at relatively high concentration.

Figure 4.3. Very low mass poly-DADMAC adsorption isotherm on S\(_6\), S\(_{15}\), and S\(_{30}\).
In Figure 4.4 the poly-DADMAC adsorbed amount was calculated based on the surface area of the silica gel particles. The slope at a relatively lower concentration indicates high affinity of poly-DADMAC to the surfaces in the porous structure. S30, having the biggest pore size, showed the highest initial slope, which that the very low mass poly-DADMAC macromolecules had the easiest access into S30.

Figure 4. 4. Very low mass poly-DADMAC adsorption isotherm on S_6, S_{15}, and S_{30}.

In Figure 4.5 the adsorption isotherms for high mass and very low mass poly-DADMAC are compared. It is interesting to note that high mass poly-DADMAC
followed a linear curve instead of following a Langmuir adsorption isotherm. This can be explained by the limited accessibility of high-mass poly-DADMAC into 30nm pore size silica gel. As we just discussed above, the higher slope at a relatively lower concentration indicates high affinity of very low mass poly-DADMAC to the surfaces. Similar adsorption isotherms have been reported for quaternized poly(vinylpyridine) onto the interior surfaces of controlled porous glass (0-20 g/L in 0.5MNaCl, pH 9.5) with a series of pore sizes, 7.5, 8, 49, and 285 nm (Mishael et al., 2007).

Figure 4.5. Adsorption isotherm of high mass and very low mass poly-DADMAC on silica gel (pH 7, 1000μs/cm) with pore size of 30 nm.
3.3 Effects of pH

As shown in Figure 4.6, the adsorption of very-low-mass poly-DADMAC onto silica gel (pore size 15 nm) increased with increasing pH in the range of 3 to 8. This trend is generally consistent with the effect of pH on the relative charge density of the substrate; the silica gel surface becomes more negative when pH increased in the range of 3-10 (Iler, 1979). Thus, the results in Figure 4.6 generally agree with what would be expected based on a charge-driven adsorption mechanism. The reason for an apparent decrease in adsorption with increasing pH above 7 is unknown, but it is possible that the accessible surface had become saturated with polyelectrolyte.

![Figure 4.6. Adsorption curve of very low mass poly-DADMAC on 15 nm silica gel at different pH](image-url)
There is an apparent contradiction between the effect of pH on adsorption, as shown in Figure 4.6, and the corresponding effects on streaming potential, as reported earlier (Wu et al., 2009a). In those earlier reported tests the silica gel was exposed to very-low-mass poly-DADMAC under matching conditions of conductivity, pore size, and mixing time; then the supporting electrolyte was replaced with polymer-free neutral buffer so that all of the streaming potential tests could be carried out at the same pH. The results showed a much greater effect on streaming potential in cases where the equilibration had occurred at low pH. When the streaming potential was measured in the presence of salt, making it possible to observe effects due to the charged nature of a mesoporous network, the exposure to poly-DADMAC in the pH range 3 to 4 was sufficient to raise the observed streaming potential from -13 mV, in the case of untreated silica gel, to about +2 mV for the treated systems. Much lesser changes in streaming potential were observed when the equilibration with poly-DADMAC solution was carried out at higher pHs.

The apparent contradiction can be resolved by the same mechanism that was used in explaining the earlier reported results (Wu et al., 2009a). The explanation rests on two hypotheses. First it is assumed that at the higher pH values the interaction between the polyelectrolyte and the highly negative substrate is sufficiently strong that the macromolecules remained fixed in the positions where they first adsorb. Depending on the relative rates at which macromolecules arrive at the surface and the rate at which they adopt a flattened conformation, it is likely that the presence of adjacent adsorbed
polyelectrolyte molecules limits the amount of spreading and flattening of the adsorbed conformation of each molecule. As a consequence, the adsorbed amount on the most readily accessible surfaces will exceed the amount needed to neutralize the surface charges of the substrate (Fleer et al., 1993; Semenov and Joanny, 1995; Swerin et al., 1997; Wågberg, 2000; Hubbe et al., 2003). Secondly, it is assumed that at the lower pH values, due to the lesser negative charge of the silica surfaces, the strength of interaction between the polymers and the substrate is sufficiently weakened so that the macromolecules are able to permeate into the interior parts of the mesopore network. It is reasonable also to expect that a weaker free energy of interaction will allow the macromolecules to spread out on the interior substrate surfaces, achieving a more efficient coverage of the negatively charged groups on the silica.

4. Conclusions

1. The adsorption and penetration of the poly-DADMAC molecules into the silica gel particles slowed down with time.

2. Both pore size and surface area affected poly-DADMAC adsorption. The maximum adsorption amount of very low mass poly-DADMAC at the 1% level was achieved with an intermediate pore size silica gel (15nm).

3. The adsorption behavior followed a Langmuir model, except for the high mass poly-DADMAC on 30 nm silica gel, which showed evidence of being controlled by kinetics of permeation, rather than surface area alone.
4. Adsorption of very low mass poly-DADMAC was pH-dependent. This is consistent with the fact that the surface charge of silica gel become more negative when pH increased. Thus, adsorption would be enhanced as long as sufficient very low mass poly-DADAMAC is present.

References


Wågberg, L. "Kinetics of polyelectrolyte adsorption on cellulosic fibres," (Mid-Sweden University).


