

Penetration of High-Charge Cationic Polymers into Silica Gel Particles and Cellulosic Fibers

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ABSTRACT

The gradual penetration of positively charged polymeric additives below the outer surfaces of cellulosic fibers can play an important role in the selection of addition points and optimization of chemical dosages on a paper machine. The present work was undertaken to help understand the role of high and low-molecular-mass fractions of a cationic polyelectrolyte, in determining the charge behavior of the outer surfaces of fibers. Commercial polyelectrolyte samples typically contain a broad range of molecular masses. A dialysis procedure was used to selectively remove the low-mass fraction of poly-diallyldimethylammonium chloride (poly-DADMAC) from aqueous solutions of the polymer. Only cationic polymer samples having a very-low-mass component exhibited penetration into the interior spaces of silica gel, which has a well-defined, narrow pore size distribution. The presence of low-mass components of the polymer also affected the electrical potential associated with the outer surfaces of solids treated with high-mass poly-DADMAC. Preliminary observations showed related behavior in the case of cellulosic fibers. The wide range of time required for measured streaming potential values to decrease to zero, depending on the amount of poly-DADMAC added at time zero, was consistent with a gradual diffusion of the macromolecules below the outer surfaces of the fibers.

Keywords: cationic polyelectrolytes; sorption; nanopores; streaming potential; penetration; cellulose; silica gel

INTRODUCTION

Procedures have been developed recently that make it possible to differentiate between the state of electrical charge at the outer surface versus the internal surfaces within the porous structure of materials such as kraft fibers and silica gel [1-3]. The present article describes the first preliminary work to apply these procedures using well-characterized cationic polyelectrolytes.

Papermakers rely on a variety of highly charged cationic polyelectrolytes for such purposes as promoting more rapid release of water during the formation of paper [4-5], the control of the charge balance on paper machines [6], and the optimization of retention aid systems [7], among other uses. Polyelectrolytes of various molecular mass require different amounts of time to change their molecular conformation, changing from a semi-random, three-dimensional conformation to a relatively flat adsorbed structure after having been adsorbed for some time [8]. It also has been suggested that the polyelectrolytes gradually diffuse beneath the outer layer of fibrils at the fiber surface or that they even penetrate into nanopore spaces within the cell wall [1, 3].

Certain earlier studies attempted to study aspects related to the adsorption and penetration of high-charge cationic polyelectrolytes onto and into cellulosic fibers by means of electrokinetic tests. For example, studies [9-12] showed evidence of "charge decay." In other words, immediately after addition of a sufficient amount of cationic polymer, the electrokinetic tests indicated a

positive charge of the cellulosic material. Then, within minutes, the charge had steadily decreased to a negative value, even approaching the initial negative potential of the surfaces in the starting, untreated suspension.

Although the general results described above were confirmed more recently [1], the cited work raised concerns about the methodology by which some of the earlier results had been obtained. In particular it was shown that streaming potential tests carried out at ordinary electrical conductivity values, i.e. values higher than about 100 $\mu\text{S}/\text{cm}$, are responsive to two different factors operating simultaneously. Not only do such tests respond to the electrical potential near to the outer surface of the fibers, but they also are influenced by the net ionic charge at the surfaces of nanometer-sized pores within the fiber cell walls. In order to obtain information exclusively about the outermost surfaces of kraft fibers it is necessary to replace the suspending aqueous solution with distilled water just before the measurement [1, 3].

Another issue of concern in the cited earlier work has been the lack of characterization of the molecular mass distribution of the polyelectrolytes. Relatively broad molecular mass distributions can be expected in various high-charge cationic polymer additives [13].

The present article presents the first experimental work to address the issues just described. Samples of poly-diallyldimethylammonium chloride (poly-DADMAC) were fractionated, using dialysis membranes, and the retentate was subsequently characterized by gel permeation chromatography (GPC). These polymers were

then used as “probe molecules” in studies with solid, nanoporous substrates. Because the porous nature of kraft fibers is likely to be complex, and also it is affected by aqueous conditions, supplementary tests were carried out with silica gel, a material with a relatively well characterized pore diameters near to 7.5 nm.

EXPERIMENTAL

Chemicals

The water used in the experiments was deionized water prepared with an ion-exchange system from Pureflow Inc.

Sodium bicarbonate, which was used as a buffering electrolyte in some cases, was certified ACS (Fisher). The default concentration was 10^{-4} M. Sodium sulfate, which was used as a background electrolyte in some experiments, was reagent grade (Fisher), used without further purification. In cases where sodium sulfate was added to the supporting electrolyte, its concentration was adjusted such that the electrical conductivity at a laboratory temperature of approximately 23 °C was 1000 μ S/cm.

The samples of poly-diallyldimethylammonium chloride (poly-DADMAC) were Aldrich catalogue number items 40,903-0 (“high molecular mass”, nominally 400,000 to 500,000 Daltons), and 52,237-6 (“very low molecular mass,” nominally 5000 to 20,000 Daltons).

Materials

The cellulosic fibers were bleached hardwood kraft fibers obtained from a local southern US pulp and paper mill.

The silica gel was catalogue item S745-1 from Fisher Scientific, also known as Davisil Silica Gel 150. The particles of this product are generally large enough to be retained on a 200-mesh screen filter, and the nanopores within this product have a nominal size of 15 nm. Earlier work showed that the stated pore size agreed well with estimates based on differential scanning calorimetry [2].

Procedures

Dialysis of polyelectrolyte

Spectra/Por® Biotech cellulose ester (CE) dialysis membranes were used for separating the poly-DADMAC solutions into fractions, of which the retained fraction was saved. Molecular mass cut-off values were 100,000 and 8000 Daltons, and the tube diameters were 10 and 18.5 mm, respectively. 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. 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.

Gel permeation chromatography (GPC)

A Waters 2695 GPC system with a Waters 2996 Photodiode Array refractive index detector was equipped with the following columns in series: porosity 3000Å first and then 300Å with particle size 10 μ m. The supporting electrolyte 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.

Streaming current analysis

A Mutek PCD-03 device was used in carrying out streaming current tests, as a means of evaluating the concentration of poly-DADMAC fractions after dialysis experiments. The titrant used in such tests was NALCO 0.0025N potassium polyvinyl sulfate (PVSK).

Streaming potential analyses

Tests made use of the Streaming Potential Jar (SPJ) equipment and general procedure, as described previously [14] (see Fig. 1). In each case a differential pressure of 207 kPa was applied by raising the applied pressure on one side of the sample and measuring the voltage change sensed with alloy metal probes on either side of the porous mat of material. The suspended matter was introduced to the apparatus as a suspension (0.5% solids in the case of cellulosic fibers and 1% solids in the case of silica gel). During each of the automatically actuated tests the mixture was forced toward a screen having a mesh size of 100 (in the case of cellulosic fibers) or 200 (in the case of silica gel). Each such measurement was concluded by application of vacuum, returning the entire mixture to the stirred beaker, ready for the next cycled of testing.

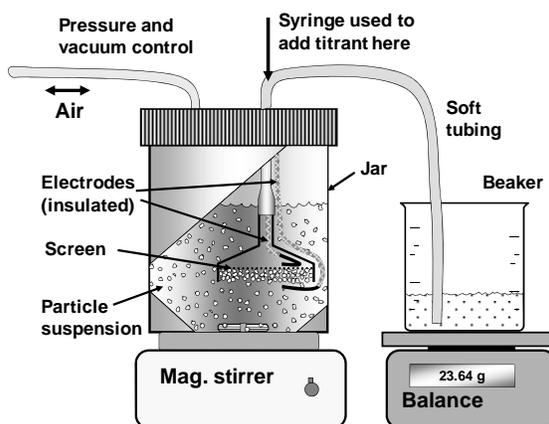
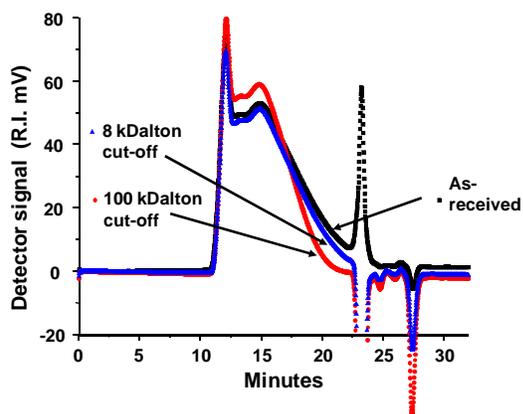


Fig. 1. Schematic view of cell for streaming potential measurements with packed beds of nanoporous materials.

RESULTS AND DISCUSSION

Fig. 2 shows a gel permeation chromatogram obtained with undialyzed vs. dialyzed “high mass” poly-DADMAC, when using dialysis membranes having two molecular mass cut-off values. The sharp peak at approx. 12 seconds is attributed to a relatively high injected amount. Results at 18-22 minutes indicate substantial removal of lower-mass poly-DADMAC when using the 100 kDalton membrane. Maxima and minima after 22 minutes can be attributed to sodium chloride and sodium azide in the background electrolyte and samples.

Fig. 2. Gel permeation chromatograms of undialyzed and



dialyzed “high mass” poly-DADMAC (retained fraction) with membranes of two molecular mass cut-off values.

Streaming Potential of Silica Gel

Fig. 3 shows that in the presence of salt it was possible to achieve reversal of the sign of streaming potential by adding a sufficiently large amount of very low-mass poly-DADMAC. These findings are attributed to the ability of the lowest-mass polymer fraction to penetrate into the nanoporous spaces. Only negative streaming potentials would be expected if the polymer stayed on the outside.

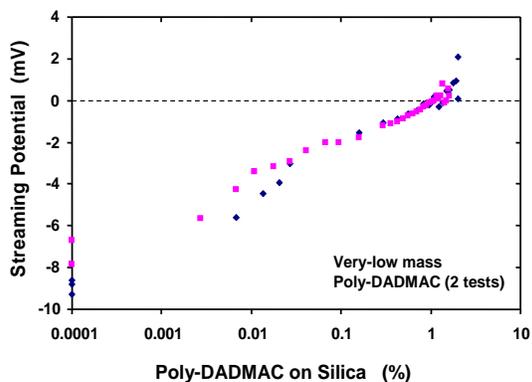


Fig. 3. Streaming potential as a function of addition of very low-mass poly-DADMAC at the levels shown (dry mass basis on silica gel) at a conductivity of 980 $\mu\text{S}/\text{cm}$

In Fig. 4, one can see that both dialyzed and undialyzed high-mass poly-DADMAC addition resulted in negative streaming potential throughout each experiment, even at extremely high levels of addition. These findings are attributed to the inability of high-mass poly-DADMAC to penetrate into the nanopores. Regardless of whether the poly-DADMAC had been dialyzed, the streaming potential increased at relatively low addition of polymer, reached a plateau at intermediate addition levels, and decreased at relatively high dosage. Remarkably, the dialyzed poly-DADMAC achieved less negative streaming potential than the undialyzed as-received material at moderate to high dosage of poly-DADMAC.

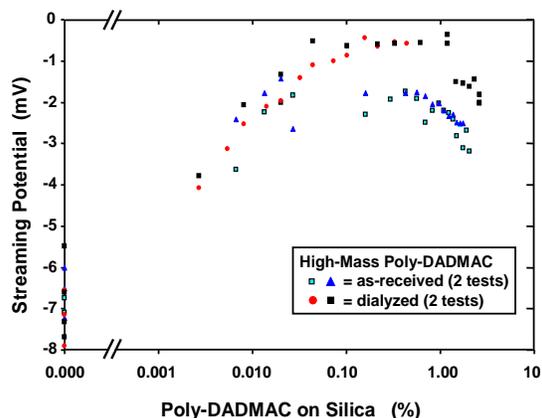


Fig. 4. Streaming potential as a function of addition of undialyzed and dialyzed high-mass poly-DADMAC at the levels shown (dry mass basis on silica gel) at a conductivity of 980 $\mu\text{S}/\text{cm}$

It is notable that at relatively high dosage of addition, the streaming potential became more negative, both in the case of undialyzed and dialyzed poly-DADMAC. To explain these observations, it was hypothesized that the effect was due to increased electrical conductivity of the solution at the high polymer addition levels. Tests were carried out with gradual addition of Na_2SO_4 after the addition of 0.45% high-mass poly-DADMAC to silica. Consistent with the hypothesis, the measured streaming potential became more negative and reached a maximum absolute value at a conductivity of about 1100 $\mu\text{S}/\text{cm}$. The conductivity effect is attributed to more complete development of electrical double layers, which are thinner due to the presence of salt, within the narrow pores.

Streaming Potential of Cellulosic Fibers

Figs. 5 and 6 show the streaming potential of suspensions of either unrefined, bleached hardwood kraft pulp or the fiber fraction after refining the same kind of pulp, respectively. In each case the suspensions were treated at time equal to zero with different amounts of high-mass poly-DADMAC. As shown, the streaming potential gradually tended to become negative. The time required to reach zero streaming potential was increased with increasing addition of the poly-DADMAC.

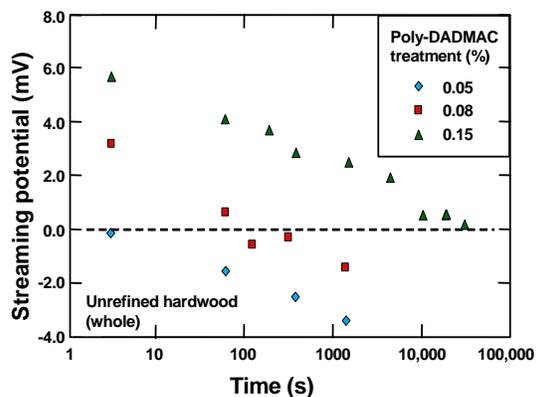


Fig. 5. Streaming potential unrefined hardwood pulp (whole furnish) as a function of the time following addition of high-mass poly-DADMAC at the levels shown (dry mass basis on fibers) at a conductivity of 1000 $\mu\text{S}/\text{cm}$

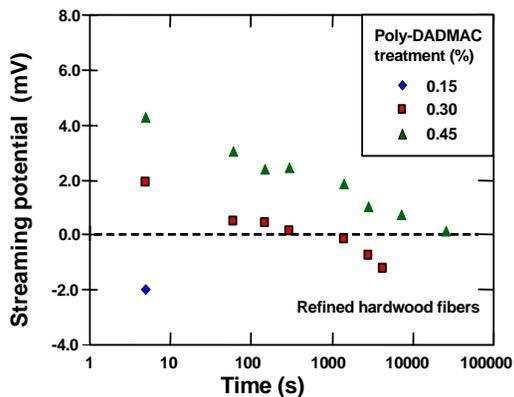


Fig. 6. Streaming potential of refined hardwood fibers (fines removed) as a function of the time following addition of high-mass poly-DADMAC at the levels shown (dry mass basis on fibers) at a conductivity of 1000 $\mu\text{S}/\text{cm}$

Because the streaming potential of cellulosic fibers at intermediate to high levels of electrical conductivity depends both on surface charges and charges within nanopores in the cell walls [1], it is not yet possible to account quantitatively for the data in Figs. 5 and 6. However, in a qualitative sense, it is shown that rather large polymer molecules are able to diffuse inside of the outer surface of the fibers, given sufficient time.

CONCLUSIONS

1. Gel permeation chromatography revealed broad molecular mass distributions of the high-charge-density probe molecules used in this study. By dialysis it was possible to remove the lowest-mass molecules of poly-DADMAC.

2. The present results provided the first confirmatory

evidence to explain why treatment of suspensions of silica gel with high-mass poly-DADMAC can result in a net positive electrokinetic potential, even in the presence of salt [2]. It was found that such effects were obtained only when using poly-DADMAC solutions containing very-low-molecular mass material. Treatment with high molecular mass poly-DADMAC solutions did not show such charge reversal at high treatment dosages. It follows that the earlier observations were attributable to migration of a very low-mass component of poly-DADMAC into nano-pore spaces in the silica gel.

3. Time-dependent decreases in electrokinetic potential were observed following treatment of bleached kraft fibers, in suspension, with the high-charge cationic polyelectrolyte poly-DADMAC. The molecular mass of the polymer affected the time required for decay of the potential, back towards its initial negative value before treatment. The relatively long times required to reach zero streaming potential are consistent with a process of gradual diffusion of the polymers below the outer surfaces of the fibers.

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