



## Permeation of a cationic polyelectrolyte into mesoporous silica. Part 2. Effects of time and pore size on streaming potential

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### ABSTRACT

Streaming potential tests were carried out to determine effects of time and pore size in the adsorption and desorption from aqueous suspensions of cationic polyelectrolytes on silica gel particles. Results in Part 1 of this series showed that the adsorption of cationic polyelectrolytes exposed to mesoporous silica gels can be highly dependent on pH, the polyelectrolyte's molecular mass, and the solution's electrical conductivity. Also, the observed changes in streaming potential indicated that the adsorption tended to be relatively slow and incomplete under the conditions of analysis. The present results indicate that the rate of change of streaming potential is proportional to the logarithm of exposure time. The related changes in adsorbed amounts of polyelectrolyte were below the detection limits of typical polyelectrolyte titration procedures. Contrasting charge 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 the effect of adsorption of high-mass cationic polymers on the outer surfaces, but produced only a relatively small effect on streaming potential related to their permeation into silica gel (nominal pore sizes of 6 nm or 30 nm). Adsorption of very-low-mass cationic polymer onto the outer surfaces and inside the 6 nm pore size silica gel appeared to be maximized at an intermediate salt level. Finally, electrokinetic tests were used for the first time in a protocol designed to provide evidence of polyelectrolyte desorption from the interiors of mesoporous materials.

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### 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. Many unit operations in these applications depend on the ability and rate for the polyelectrolytes to diffuse from solution into the sub-micron interior spaces of the adsorbate material. For instance, in papermaking applications it is often preferred that polyelectrolytes remain on the outer surfaces of cellulosic fibers, where they can participate in such useful functions as retention of fine particles during the formation of a sheet. Though those polyelectrolyte molecules that are able to permeate into the cell wall of the fibers, before the fiber web is consolidated, have little influence on retention and inter-fiber bonding, other effects are expected, such as reinforcement of fiber wall strength and dimensional stability under different relative humidities.

Part 1 of this series of articles considered electrokinetic tests to demonstrate how the adsorption of linear, highly cationic

poly-(diallyldimethylammonium chloride) (poly-DADMAC) was affected by molecular mass, electrical conductivity, and pH [1]. By measuring the streaming potential of silica gel particles held within a packed bed and by comparing the results in the presence or absence of salt it has been possible to gain information concerning the location (outside or inside the porous network) of the adsorbed cationic polymers [2–4].

The present set of experiments was carried out to investigate the effects of time and pore size, together with molecular mass of the cationic polymer used in pretreatment, and the concentration of background electrolyte, on the streaming potential of silica gel particles. As summarized in a recent review article [5], it is reasonable to expect that considerable time is required for a polyelectrolyte to reach adsorption equilibrium in porous material, especially if the molecular mass is relatively high and the adsorbate material is mesoporous, *i.e.*, pore size of ca. 2–50  $\mu\text{m}$  [6]. This pore size range generally coincides with the range associated with the characteristic dimensions of cell walls of cellulosic fibers after various preparation procedures [3–4,7–12]. In various papermaking applications it can be important for polymeric additives to remain on the outer surfaces of cellulosic fibers for long enough so that they can efficiently affect flocculation behaviors, as well as for junctions of hydrogen-bonds to be formed between adjacent fibers [13–15]. On

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the other hand, some applications, such as cell-wall filling, demand effective penetration of nanomaterials in the interior of porous systems [16,17].

Key questions to be considered in this article are: (1) Can streaming potential be used as a highly sensitive method to evaluate rates of permeation of a cationic linear polyelectrolyte into the interior spaces of a negatively charged mesoporous material from aqueous solution? (2) What is the mathematic form of the time dependencies of adsorption and desorption of the cationic polymer? and (3) How do changes in pore size, in combination with ionic strength and polymer molecular mass, affect the streaming potential as a consequence of permeation and adsorption of the cationic polymers on the silica gel?

Based on transport mechanisms, including diffusion, it is expected that the changes in streaming potential associated with adsorption or desorption of polyelectrolyte from a mesoporous material should be related to the extent of adsorption. However, to our knowledge, no model is available to permit calculation of streaming potential for an arbitrary distribution of polyelectrolyte adsorbed within a mesopore structure. Therefore, as a first approximation, a direct relation between the change in streaming potential and the corresponding adsorbed amounts will be assumed within suitably narrow intervals of potential. Under such an assumption, different mathematical relations can be drawn, depending on whether the transport is governed by simple diffusion or other mechanisms.

For example, an expected dependency of adsorbed amount on the square-root time of exposure of a solution to a porous material can follow from Fick's second law, which can be expressed in integrated form as [18,19],

$$C(x, t) = S[(\pi Dt)^{1/2}] \exp \left[ \frac{-x^2}{4Dt} \right] \quad (1)$$

where  $S$  is the amount of diffusing substance added at the initial time,  $D$  is the diffusion rate constant,  $t$  is the elapsed time, and  $x$  is the distance of the sampling point from the surface. As an approximation, Eq. (1) can be linearized as follows:

$$C(x, t) \approx C_0 \left[ 1 - \frac{x}{(\pi Dt)^{1/2}} \right] \quad (2)$$

where  $C_0$  is the initial concentration at the sampling location. Thus, a diffusion-controlled mechanism implies that the adsorbed amount is approximately proportional the square-root of elapsed time following a change in bulk solution concentration.

Alternatively, from diffusion experiments with fluorescently tagged dextran molecules in porous silica, similar to those used in the present work [20], a logarithmic dependency of adsorbed amount within a mesoporous substrate with elapsed time was found. Specifically, the time-dependent concentration at a specified location within the porous material was described by an equation

of the form:

$$C(x, t) = C_0 - \frac{1}{B} \ln \left[ \frac{t}{t_0} \right] \quad (3)$$

where  $B$  is a constant and  $t_0$  is the starting time of observation. Landsberg [21] attributed such a relationship to a time-dependent chemical interaction with the substrate, in addition to diffusion. Thus, if this mechanism governs the interaction of cationic polyelectrolytes adsorbing from aqueous solution within an acidic, mesoporous material, the attraction between the polyelectrolyte and the substrate would be expected to yield a dependency of the adsorbed amount as that shown in Eq. (3). Interestingly, a similar dependency of dissolved polymer transport distance on the logarithm of exposure time was found in simulation work by Wolterink et al. [22], who considered the reptation of non-interacting polymers in solution through a membrane.

By performing direct measurements of changes in streaming potential, our experimental work was aimed to elucidate the effects of pore size and polymer molecular mass on the dynamics and adsorption/desorption behaviors in suspensions of mesoporous silica gel particles.

## 2. Experimental

### 2.1. Materials

Some materials used in this work were described in Part 1 of this series of articles [1]. Water used in the experiments was deionized with a Pureflow system. The "default buffer" solution was 1000  $\mu\text{S}/\text{cm}$  conductivity sodium sulfate solution that also contained  $10^{-4}$  M  $\text{NaHCO}_3$ . An alternative "salt-free buffer" solution had the same  $\text{NaHCO}_3$  concentration, but no  $\text{Na}_2\text{SO}_4$ . 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 range of nominal molecular masses of the polyelectrolytes are given as 5–20 kDa and 400–500 kDa, respectively. Polyvinylsulfate potassium salt (PVSK) used in polymer titrations was from Nalco Chemical Co., having product code 460-S5434.

Three types of mesoporous silica gels, having different nominal pore sizes, were used in the experiments. The default substrate was catalogue S745-1 from Fisher Scientific, also known as Davisil Silica Gel 150, labeled as "S<sub>15</sub>" in this article. It was reported to have 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, labeled as "S<sub>15'</sub>" and a larger nominal pore size of 30 nm (Fisher S814-1), also known as Davisil Silica Gel 300, labeled as "S<sub>30'</sub>" (see Table 1).

**Table 1**  
Characteristics of silica gel particles.

|                 | Silica type                                 | Pore size (nm) | Pore volume (cm <sup>3</sup> /g) | Particle size ( $\mu\text{m}$ and mesh sizes)             | Nominal Surface area (m <sup>2</sup> /g) | Experimental surface area (m <sup>2</sup> /g) <sup>*</sup> |
|-----------------|---|----------------|----------------------------------|---|--|--|
| S <sub>6</sub>  | Davisil <sup>®</sup> , Grade 635            | 6              | 0.75                             | 60–100 mesh   | 480                                      | 345  |
| S <sub>15</sub> | Davisil <sup>®</sup> , Grade 645            | 15             | 1.15                             | 150–250 $\mu\text{m}$<br>60–100 mesh                      | 300                                      | 282  |
| S <sub>30</sub> | Davisil <sup>®</sup> Sorbent, Grade 653 XWP | 30             | 1.1–1.2                          | 150–250 $\mu\text{m}$<br>Mesh 230–400<br>50 $\mu\text{m}$ | 150–170                                  | 179  |

<sup>\*</sup> 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 h before surface area was tested.

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