Distinctive electrokinetic behavior of nanoporous silica particles treated with cationic polyelectrolyte

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Abstract

In this study we show, for the first time, that the streaming potential of aqueous suspensions of nanoporous silica gel, after treatment with the cationic polyelectrolyte poly-diallyldimethylammonium chloride (poly-DADMAC), can depend very strongly on the concentration of background electrolyte. An increase in the electrical conductivity from 60 to 1000 $\mu\text{S}/\text{cm}$ resulted in an approximately 1000-fold increase in the amount of poly-DADMAC that was required to reach an endpoint of zero streaming potential. Results were explained by two contributions to the overall electrokinetic behavior – one due to the outer surfaces and another due to the interior surfaces of nanopore spaces that were inaccessible to the polyelectrolytes. Experiments with cyclical changes in salt content revealed a high degree of reversibility; such observations help to rule out explanations based on salt-induced desorption or enhancement of pore penetration. Supplementary tests with non-porous glass fibers showed no evidence of the distinctive electrokinetic behavior observed in the case of nanoporous particles. Effects of polymer molecular mass and pH, evaluated under similar experimental conditions, agreed with well-established trends.

Key words: Streaming potential, pores, nanopores, polyelectrolytes

I. Introduction

1.1. Distinctive electrokinetic behavior

Intriguing and potentially important phenomena were observed, involving the streaming potential cellulosic fiber suspensions treated with cationic polyelectrolytes of high charge density [1]. It was possible to reverse the sign of apparent charge of the fiber surfaces multiple times, just by cycling between salt-free and salt-containing aqueous solution.

Our interest in electrokinetic measurements of nanoporous fibers in the presence of cationic polyelectrolytes was motivated by the very widespread use of such polymers in the paper industry, mainly to improve paper machine operating efficiencies and rates of production [2-5]. Paper technologists have placed increasing reliance on streaming potential measurements as a tool to optimize and control the addition rates of highly cationic additives that are used during the formation of paper [6-15]. However, the unexpected electrokinetic behavior that we have observed in the case of cellulosic fibers [1] suggests a need for further analysis, possibly leading to new measurement procedures, as well as new and more reliable strategies for data interpretation. To gain more insight, the present work involves aqueous suspensions of silica gel as a model nanoporous material. Compared to cellulosic fibers, the pores within silica gel are more narrowly distributed, and they are not expected to change in dimension as significantly with changes in the surrounding aqueous solution.

1.2. Conceptual models

Two concepts may help to account for the electrokinetic behavior of nanoporous particles or fibers in the presence of oppositely charged polyelectrolytes. The first concept, as illustrated in Fig. 1, considers discontinuous pores that are accessible to the bulk aqueous solution. As shown in Fig. 1A, if the most typical dimensions of the macromolecules in solution are large relative to the pores, then it is expected that the polymers mainly remain on the outer surface of the nanoporous substrate [16-18]. A moderate excess of adsorbed cationic charge on such a surface is expected to give rise to a positive streaming potential, due to the fact that flow past the surface will induce a net flow of negative counter-ions.

Figure 1B shows a contrasting circumstance in which the hydrodynamic radii of the macromolecules are small in comparison to the statistical average pore size. Let's assume that the pores sizes, the molecular masses, and the amounts of macromolecules are identical to those considered in part A of the figure, but a contraction of the macromolecules has been brought about by an increase in ionic strength [19-21]. Under

such circumstances, macromolecular penetration into pore spaces is facilitated. The degree to which such penetration takes place is expected to depend, in complex ways, on the adsorption enthalpy, as well as on the entropic penalty for confining a macromolecule within the restricted spaces [19]. Evidence that macromolecular penetration actually takes place has been shown, for instance, by the decay of streaming potential values following the treatment of cellulosic fibers with a high-charge density cationic polyelectrolyte [6,22-24]. As suggested by the figure, penetration of cationic polyelectrolyte into discontinuous nanopores within a substrate may deplete the concentration of those molecules at the surface, leading to a reduced positive streaming potential, or even a reversion towards the initial, negative streaming potential of the substrate prior to the addition of the polyelectrolyte.

Figure 2 considers a contrasting concept that may be used to anticipate effects of continuous nanopores or networks of pores within suspended materials exposed to polyelectrolytes of opposite charge. The figure is drawn to illustrate a case in which the polyelectrolytes are too large to penetrate, to a significant degree, into the pores. If one considers an individual nanoporous particle within a packed bed, as shown, one can expect two contributions to the overall electrokinetic effect. First, as in the case considered in Fig. 1, flow past the outer surfaces of the nanoporous particles would be expected to produce a positive sign of the measured streaming potential. But another contribution to the electrokinetic effect can be expected to arise if the fluid is able to flow through the (continuous) pore channels. We are especially interested in conditions where the nanopore surfaces remain negatively charged, consistent with the inability of high-mass cationic polyelectrolyte molecules to penetrate into those spaces.

1.3. Salt vs. streaming potential of nanoporous substrates

Some complexities of the situation depicted in Fig. 2 can be expected if one considers consequences of a constant applied pressure, inducing a constant flow of dilute aqueous solution, as shown. If the packing material and structure of packing within the column is uniform, then it is reasonable to assume that both the pressure and electrical potential will vary in an approximately linear way as a function of distance through the packing material (Fig. 2). The Helmholtz-Smoluchowski equation [25-30], as follows, is often cited as a convenient way to estimate the streaming potential, under the neglect of surface conduction effects, which tend to be most significant in the absence of salt [31].

$$\zeta = 4 r \pi \eta \Omega E / (\varepsilon P) \quad (1)$$

In eq. (1) ζ is the zeta potential (usually expressed in millivolts), η is the viscosity of the solution, Ω is the electrical conductivity, E is the measured change in electrical potential resulting from the application of pressure, ε is the dielectric constant of the solution, and

P is the differential pressure applied across the sample. The coefficient r , which will be defined later, ordinarily has a value of one, except that it may be considerably lower within a narrow pore, especially at very low electrolyte concentrations.

Applying eq. (1) directly to the situation shown in Fig. 2 leads to the following apparent dilemma: If one were to begin by assuming that flow proceeds from left to right *around* the nanoporous particles, a positive streaming potential difference is expected, whereas flow *through* the nanopores in the same direction would yield the opposite effect on potential. At least one of these predictions would appear to violate the statement given earlier, that the potential varies linearly with distance through the material. Factors that help to resolve this apparent conflict include (a) the generation of an electro-osmotic back-pressure within the nanopores [28,32], (b) the fact that velocities of laminar flow generally vary as a function of distance from solid surfaces, and (c) some suppression of electrokinetic effects within nanopores at the limit of small pore size and low salt concentrations [33-35]. In short, the facile assumption that flow merely proceeds from left to right within the nanopores illustrated in Fig. 2 is not an adequate description. An example demonstrating this fact is inherent in the determination of zeta potential by classical micro-electrophoresis, using a capillary cell. Despite the fact that there is a zero net flow of solution in the capillary, the sign of local solution velocity can be either positive or negative, depending on the local distance from the capillary walls. Similar phenomena can be expected in porous spaces between and within a bed of porous particles in the presence of flow.

Though the details of flow velocities within and around an individual nanoporous particle are beyond the scope of the present work, it is important to review the manner in

which electrokinetic effects become suppressed at the limit of small pore diameters and low electrolyte concentrations. As a working hypothesis it is proposed that such effects are responsible for the odd electrokinetic behavior that has been observed in the case of cellulosic fibers exposed to high-mass cationic polymers [1]. An estimate of the relative suppression of streaming current within a tiny, continuous pore is given by the following equation [35],

$$r = 1 - \tan(\kappa h) / (\kappa h), \quad (2)$$

where r is the ratio of streaming current in a narrow pore of width h in comparison to the streaming current in a pore many times larger than the Debye length κ^{-1} corresponding to the ionic strength of the flowing aqueous solution [36]. The Debye length is calculated from the following expression,

$$\kappa^2 = 4\pi e^2 \sum [z_i^2 n_{i0}] / \varepsilon kT \quad (3)$$

where e is a unit of charge, z_i is the valence of the “ i^{th} ” ionic species in the solution, n_{i0} is the average molar concentration of that species far from any surface, ε is the dielectric constant of the medium, k is Boltzmann’s constant, and T is absolute temperature.

Because streaming current and potential quantities are proportionally related, assuming fixed geometries [35-36], it is justified to use Eq. (2) as a basis for obtaining the value of r for Eq. (1). Due to the fact that surface conductance is not considered in making this substitution, the results need to be viewed as being an approximation.

To illustrate how eq. (2) affects electrokinetic effects, as a function of pore diameter and salt concentrations, Table 1 gives values of r calculated for three electrical conductivities of sodium sulfate solutions, assuming slit-like capillaries, each having a width of 15 nm.

Table 1. Streaming current ratio r calculated for 15 nm slit-like pores in the presence of sodium sulfate solutions			
Na ₂ SO ₄ Conc. (mmol/L)	Electrical Conductivity (μ S/cm)	Debye Length κ^{-1} (nm)	r
0.13	60	30	0.076
2.6	1000	4	0.73
14	4800	1	0.93

The fact that the value of r within nanopores is predicted to be so strongly dependent on salt concentration is a starting point for explaining the experimentally observed effects. Polyelectrolytes can be used to reveal the separate influences of pressure-induced flow *around* or *through* nanoporous particles, as illustrated in Fig. 2. By judiciously varying polyelectrolyte attributes, and by varying the salt concentration, it should be possible to unveil or control issues related (a) the relative ability of polyelectrolytes of certain sizes or structures to penetrate into nanopores, and (b) the degree to which the nanopores surfaces contribute to observed streaming potentials. The expected salt-dependence of streaming potentials of nanoporous materials also implies that new strategies need to be used to more accurately predict charge-dependent coagulation, deposition, and adhesion phenomena that have important applications in industry and in natural aqueous environments.

2. Experimental

2.1. Materials

The experiments to be described were carried out with deionized water, to which reagent-grade inorganic chemicals were added. The water was prepared with an ion-exchange system from Pureflow, Inc. Many of the experiments were conducted in either of two “default” conditions of background electrolyte. The “no-salt” default condition

consisted of a 10^{-4} M sodium bicarbonate solution. The buffering ability of the solution ensured that the pH remained close to 7 throughout the experiments. The “salt-containing” conditions involved the same concentration of sodium bicarbonate, but with the addition of sufficient sodium sulfate so that the resulting electrical conductivity was 1000 $\mu\text{S}/\text{cm}$.

The high-charge, linear polyelectrolytes used in this study were polydiallyldimethylammonium chloride (poly-DADMAC) from the Aldrich, catalogue numbers 52,237-6 (very low mass), 40,901-4 (low mass) and 40,903-0 (high mass). The nominal molecular masses of the products are given as 5k-20k, 100k-200k, and 400k-500k ranges, respectively. In addition to these research samples, an industrial product Alcofix® 109 from Ciba Specialty Chemicals, was also used. This product has a mass-average molecular weight of approximately one million grams per mole, so it will be labeled as “very high mass” in subsequent discussions.

The nanoporous substrates used in the experiments were silica gel particles, catalogue S745-1 from Fisher Scientific. These particles were selected due to their mesh size range of 60-100, which is (a) large enough so that the particles are efficiently excluded by the 200-mesh screen used during the streaming potential tests (see next), and (b) small enough and with sufficiently low density so that they can be easily stabilized in suspension with moderate magnetic stirring. The nominal pore size of the silica gel was given as 15 nm. Scanning electron micrographs (SEMs) of the silica gel particles were obtained by field emission, as well as by environmental SEM methods.

Non-porous glass micro-fibers used in some of the tests were product C-50-R from Lauscha Fibre International of Sommerville, SC. The nominal size of the fibers is

about 4 μm in thickness and about 4 mm in length. Though such fibers have a negative surface charge, as do cellulosic fibers [37], the surfaces are not fibrillated and the generation of fines when immersed in aqueous solution is expected to be negligible. Previous work showed advantages of using such fibers in a model system to understand the functions of dual-polymer dry-strength systems [38]. The average fiber length was decreased by passing the fibers four times through a paper shredder (Novitech Model PS 026/B1), having a 4mm distance between adjacent cutting elements. The device was modified with a “hopper” to accommodate approximately 50 ml of dry fiber at one time, and the fibers were fed safely into the cutting zone with a specially designed plastic tool. Before use, the cutting elements were extensively rinsed with acetone to remove any oils.

2.2. Pore size evaluation

Pore size distributions within the silica gel particles were characterized by differential scanning calorimetry (DSC) [39-44]. The wet silica gel was cooled to -30°C in the DSC apparatus and held for 5 min. The temperature then was raised to -25°C at $1^{\circ}\text{C}/\text{min}$. This first segment ($-30 \sim -25^{\circ}\text{C}$) was used to determine the sensible heat of the wet silica, assuming that there was no melting. Subsequent heating steps to slightly higher temperatures ($-20, -15, -10, -6, -4, -2, -1.5, -1.1, -0.8, -0.5^{\circ}\text{C}$) were then performed in succession. In each step the temperature was raised at $1^{\circ}\text{C}/\text{min}$ to the target temperature and then the sample was maintained isothermally until the heat flow returned to the baseline. The detailed procedure can be found elsewhere [40,42,44].

The amount of water that has its melting temperature depression at each isothermal procedure was calculated by integrating the endotherm. Each endotherm represents a specific pore diameter based on the Gibbs-Thomson equation, Eq. (4). The

relationship between a pore diameter (D) and the depressed melting temperature (T_m) has been described previously [41]. The use of this equation is based on the assumption that the silica is not soluble in the water and its pores can be treated as cylinders,

$$\Delta T = T_0 - T_m = \frac{-4T_0\gamma_{ls}}{D\rho H_f} \quad (4)$$

where T_0 is the melting temperature of water (273.15 K), γ_{ls} is the surface energy at the ice-water interface as a function of temperature [39], ρ is the density of water as a function of temperature [39], H_f is the specific heat of fusion of freezing bound water assuming the same as that of unbound water (334 J/g) [40,45], D is the diameter of pore, and ΔT is the depression of the melting temperature (K). Thus, water held in a smaller pore has a larger melting temperature depression. The average pore size was also calculated based on the pore size distribution that was measured using DSC.

2.3. Streaming potential evaluation

Streaming potential tests were carried out with the SPJ device described elsewhere [46]. In the case of tests with silica gel, 7.5g of the dry material was added to 750ml supporting electrolyte. In the case of glass microfibers, 4g of solid was added to 800ml of electrolyte. The pH was adjusted with dilute solutions of HCl or NaOH. The default supporting electrolyte, except where noted otherwise, contained 10^{-4} molar sodium bicarbonate (to stabilize the pH near to the neutral point) and sufficient sodium sulfate to achieve an electrical conductivity of 1000 $\mu\text{S}/\text{cm}$ at about 23 °C (laboratory temperature). “Salt-free” conditions were similarly prepared, but without the sodium sulfate. Streaming potentials were evaluated with an applied pressure of 207 kPa.

3. Results and Discussion

3.1. Particle morphology and porosity

Figure 3 is an environmental scanning electron micrograph of one of the silica gel particles. Aside from showing the shape of a typical silica gel particle, Fig. 3 (including the enlarged area obtained by field emission SEM) confirms an important point; the size of the pores in this material is very small. The smallest surface undulations revealed in Fig. 3 are of the order of 10-20 nm, consistent with the nominal 15 nm pore size of the gel.

Figure 4 shows the pore size distribution as obtained by differential scanning calorimetry (DSC) for the same silica gel. The analysis is based on the concept of freezing and non-freezing bound water, vs. water that is far enough away from the surfaces so that it freezes at the “bulk” freezing point [39-45]. Two determinations yielded mean pore diameters (based on a cylindrical model) of 15.6 nm (for 100-200 mesh silica gel) and 16.0 nm (for 60-100 mesh gel), which are in good agreement with the nominal pore size of 15 nm, listed by the supplier of the silica gel particles (Aldrich).

Fig. 3. Scanning electron micrographs of silica gel particles showing whole particle and surface detail. White, horizontal bars show scale of each figure.

Fig. 4. Cumulative pore size distribution as revealed by bound water, according to DSC analysis

3.2 Streaming potentials at constant salt concentration

The amount of cationic polyelectrolyte (titrant) required to reach a zero streaming potential endpoint was found to be very sensitive to salt concentration. Figures 5A and 5B show results obtained, respectively, in the absence of salt and with a sufficient sodium sulfate added to reach an electrical conductivity of 1000 $\mu\text{S}/\text{cm}$. The pH was equal to seven in both cases (10^{-4} M sodium bicarbonate as buffer). Note that the endpoints shown in Fig. 5A are in the range of 0.0005 to 0.001% poly-DADMAC, based on solids, whereas the endpoints in the presence of a moderate salt concentration (Fig. 5B) were about 0.3 to 1%, roughly three factors of ten higher.

Fig. 5A. Streaming potential for titration of silica gel with cationic polyelectrolytes of various molecular masses in salt-free solution.

Fig. 5B. Results of tests as in Fig. 5A, with salt (sodium sulfate) added (total conductivity of 1000 $\mu\text{S}/\text{cm}$)

Though it is possible to rationalize a moderate salt-dependency of electrokinetic [24,27] and adsorption phenomena [18,47-48] based on conventional colloid-chemical principles (including changes in Debye length and the respective long range interaction forces, effects related to ion exchange, *etc.*), there is no precedent for an effect large enough to reconcile Figs. 5A and 5B. The mean molecular masses of the poly-

DADMAC samples ranged from about 20k (very low), 100k-200k (low), 400k-500k (high), and 2 million (very high) Daltons.

An additional puzzling observation was that separate determinations of the amount of poly-DADMAC adsorbed onto the same silica gel, under the same electrolytic conditions (by back titrations of the supernatant polymer suspension) showed only a weak dependence of the adsorbed amount on the salt concentration, within the range considered. Furthermore, the plateau level of adsorption was approximately 0.03%, on a mass basis, far lower than the measured endpoints of the titrations carried out in the presence of salt (Fig. 5B).

If one focuses on Fig. 5A, it is apparent that molecular mass had a significant effect on the results. In general, poly-electrolyte samples having low mean molecular mass tended to be less efficient in achieving neutral streaming potential in the absence of salt. The fact that the “very-high-mass” poly-DADMAC appears to be somewhat out of place, relative to the other results in Fig. 5A suggests that this technical sample is rather polydisperse and contains large amount of low-mass macromolecules (see Experimental). The higher efficiency of the high-mass cationic polyelectrolytes, for purposes of achieving zero streaming potential in the absence of salt, is attributed to their relative inability to diffuse into the porous spaces and to remain outside of the silica gel particles [17-18].

Turning next to the details of Fig 5B, one can see an interesting reversal of the effect of molecular mass on the efficiency of the poly-DADMAC samples for achieving zero streaming potential (circled area). SP results at low polyelectrolyte concentrations look remarkably similar to those in Fig. 5A, except that all of the streaming potentials are

shifted downward relative to zero on each vertical axis. To interpret these results it can help to separately consider contributions to the net electrokinetic signal, *i.e.* the outside surfaces and the surfaces within nanopores. The initially greater efficiency of the high-mass cationic polymers in changing the streaming potential values, as shown in Fig. 5B, is consistent with their greater ability to remain at the outer surfaces of the gel particles. However, with respect to bringing about charge neutralization, there was a crossover, and higher molecular mass polyelectrolytes were less effective. The latter observation is consistent with the fact that the interior surface area is expected to be many times higher than the external area of silica gel particles [49]. The observed greater effectiveness of the lowest-mass cationic polymer in bringing about neutralization of the silica gel, in the presence of electrolytes, is consistent with some diffusion of polyelectrolytes into nanopores. At low salt concentration no such cross over was observed, and the streaming potential measurements appeared to indicate only the fact that the external surface area is neutralized (as opposed to giving information about the surface area within nanopores).

3.3 Streaming potentials with varying salt concentrations

The unusual nature of the results shown in Fig. 5 prompted us to carry out experiments in which the salt content of the solution was varied repeatedly. Results are shown in Fig. 6. At the start of the experiment (left-hand side of Fig. 6A), the streaming potential of untreated silica gel was evaluated in the absence of salt. Then, poly-DADMAC was added at a dosage of 0.133% based on solids, which is intermediate between the conditions yielding zero streaming potential in the absence or presence of salt (see Fig.

5). Next, the salt concentration was increased and decreased several times by adding concentrated sodium sulfate solution or by replacing a portion of the filtrate with salt-free bicarbonate buffer solution during each successive streaming potential test. In Fig. 6A the lower curve (filled diamonds) represents the total conductivity (note semilog scale), while the upper curve (squares) represents streaming potential. Cycles of automatic measurement each lasted 100 s.

As shown in Fig. 6A, it was possible to shift the sign of streaming potential of poly-DADMAC-treated silica gel from positive to negative back and forth, several times, just by changing the salt content of the aqueous solution. Each time that sufficient salt was added to the system, the sign of streaming potential changed from positive to negative. Each time that the salt concentration (and conductivity) of the solution was sufficiently reduced, the signal headed towards a positive streaming potential. The final upward portion of the streaming potential curve, coincident with the addition of enough salt to raise the conductivity within the range of 1 to 10 mS/cm, is tentatively attributed to an expected decrease in the absolute value of zeta potentials with such increases in salt.

To evaluate whether such effects were reversible, Fig. 6B shows streaming potential as a function of electrical conductivity. As shown, the streaming potential was almost uniquely determined by the conductivity under the conditions of testing. A moderate shift in time with the value obtained at about 1000 $\mu\text{S}/\text{cm}$ is tentatively attributed to conformational changes and/or some gradual diffusion of the polyelectrolyte molecules into pores. The observed reversibility of the streaming potential results, when the system was subjected to varying salt environments, helps to rule out the possibility

that the main effects of salt resulted from either desorption of polyelectrolytes or from a major enhancement in their penetration into the nanopores.

3.4. Comparative tests with non-porous glass

To further demonstrate that the observed effects were due to nanoporosity, supplementary experiments were carried out with non-porous glass micro-fibers. As shown in Fig. 7, the non-porous glass had a negative streaming potential at pH values greater than about 3 (evaluated at 207 kPa applied pressure difference and *ca.* 60 μS/cm electrical conductivity). This observation is consistent with the expected deprotonation of silanol groups with increasing pH [27,50-53]. Interestingly, though the silica gel showed a related trend, the absolute magnitudes of streaming potential were approximately one-fourth of those for the glass at any given pH. Though it is tempting to relate such results to theories of electrokinetics of nanoporous materials [54-56], it is essential that such work be repeated with sets of porous and non-porous materials that are closely matched in composition.

Results in Fig. 8 provide a further demonstration of the effect of pH in the case of low-mass poly-DADMAC addition to a silica gel suspension at an electrical conductivity of 60 $\mu\text{S}/\text{cm}$. The fact that less poly-DADMAC was needed to achieve neutral streaming potential at the lower pH is consistent with the expected lower density of negative surface charge [27,50-53].

Fig. 7. Contrast between SP results for silica gel and glass fibers vs. pH, in the absence of polymer.

Fig. 8. SP titrations of silica gel suspensions at two pH values

Figure 9 compares results of streaming potential titrations of non-porous glass with poly-DADMAC of differing molecular mass under two contrasting salt contents of aqueous solution at pH=7. Notably, all of the zero streaming potential end-points shown in Fig. 9 are within about a factor of two of each other, despite major variations in both molecular mass and electrical conductivity. As shown in Fig. 9A, high-mass poly-DADMAC was somewhat more efficient in achieving zero streaming potential in the absence of salt. Such an effect is consistent with the expected greater extension of very-high-mass polyelectrolytes from surfaces to which they become adsorbed [57-59]. No significant effect of molecular mass was apparent in the data obtained in the presence of salt (Fig. 9B). The main point, however, is that the effects of salt addition on the end-point were within a factor of two, a result that is in sharp contrast to the factor of about

1,000 difference when one compares results for the nanoporous silica gel in the presence or absence of salt (Fig. 5).

4. Conclusions

1. Streaming potential tests of nanoporous silica gel particles in the presence of high-mass cationic polyelectrolyte at neutral pH revealed unprecedented effects resulting from changes in salt concentration. The amount of poly-DADMAC required to achieve zero streaming potential increased by a factor of about 1000 when the electrical conductivity was increased from 60 to 1000 $\mu\text{S}/\text{cm}$.
2. The experimental results were consistent with a model in which separate contributions to the overall electrokinetic effect arise due to features of the outer surface of nanoporous particles, which can become coated by oppositely charged polyelectrolyte molecules, and interior nanopore surfaces, which may be too narrow to allow efficient access by the macromolecules. The present results support a theory that the contribution of the nanopores to the measured streaming

- potential is strongly suppressed in the absence of salt in case where the pores are small relative to the Debye length κ^{-1} . Such a model accounts for the main effects of salt and other observations in the present report.
3. The reversible nature of the streaming potential of polyelectrolyte-coated silica gel particles was demonstrated by tests in which the salt concentration was repeatedly cycled between high and low values. The fact that streaming potential of such a system depended almost uniquely on electrical conductivity made it possible to rule out such processes as desorption of the polyelectrolyte molecules or enhanced penetration of polyelectrolytes into the pore spaces as having dominant influences on the observed phenomena.
 4. Supplementary tests involving non-porous glass micro-fibers in the presence of the same polyelectrolytes and background electrolyte showed only moderate dependencies of streaming potential endpoints on salt concentration. Results were consistent with expected effects of pH and molecular mass on electrokinetic potentials.

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