Permeation of a cationic polyelectrolyte into mesoporous silica
Part 3. Using adsorption isotherms to elucidate streaming potential results

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ABSTRACT

Parts 1 and 2 of this series showed that the streaming potential of silica gel particles in aqueous media can be profoundly affected by their exposure to solutions of a cationic polyelectrolyte. The extent of the change in streaming potential depended on such variables as pH, salt concentration, polyelectrolyte molecular mass and concentration, pore size, and time. However, questions arose concerning the relationship between the observed changes in streaming potential and the net amount of adsorbed polyelectrolyte. Some preliminary experiments suggested that, compared to adsorption tests, the streaming potential method may be much more sensitive to the permeation of minor amounts of oligomeric impurities into the network of mesopores in the substrate. The present article follows up on these findings, evaluating adsorption isotherms for the same systems that earlier had been examined by the streaming potential method. In contrast to the earlier work, it was possible to interpret the isotherms based on a model in which adsorbate interacts with a set of equivalent, non-interacting adsorption sites. The kinetics of adsorption were time-dependent and diffusion limited. The polymer adsorbed amount 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 polyelectrolyte. The results could be fit well to a Langmuir model of the adsorption process.

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1. Introduction

Silica gel having pore sizes in the range 2–50 nm (i.e. mesoporous silica) has been used in applications that demand solid substrates with high specific surface area and pore volume. Wang et al. [1], and references therein, reported on the use of mesoporous particles in biosensing [2], biocatalysts [3], drug delivery [4], and protein separation [5]. 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 have reflected a broad interest, with numerous applications in papermaking [6,7], enhanced oil recovery [8], water treatment [9], and other fields [10]. Silica gel particles also can be used to model the behavior of polyelectrolytes interacting with cellulosic fibers, a type of interaction that has drawn considerable interest [11–16]. Cellulosic fibers’ pore structure is complex and subject to change in dimension significantly with changes in the surrounding aqueous solution. Compared to cellulosic fibers, silica gel with narrowly distributed pore size can be an ideal model of mesoporous material [17].

Part 1 of this series of articles [18] revealed unexpected behavior when silica gel suspensions were treated with cationic polyelectrolytes and then evaluated with streaming potential tests in the presence of a background electrolyte. Changes in streaming potential were promoted by decreasing pH and, to a minor extent, by increasing electrical conductivity – both factors tending to decrease the strength of electrostatic interactions between the cationic polyelectrolyte (poly-diallyldimethyl ammonium chloride, poly-DADMAC) and the substrate. These findings appeared to be consistent with a greater ease with which polyelectrolyte molecules would be able to permeate into the mesoporous particles. However, some preliminary tests carried out in Part 2 of this series did not find any corresponding increase in the net amount of adsorbed materials under selected conditions where the streaming potential had been changed. These apparent contradictory results were attributed to the effect of diffusion of a minor amount of oligomeric impurity into the mesopore structure of the silica gel. Therefore, a motivation for the present work was to clarify these issues and to test a hypothesis that the net adsorption of the silica gel can be described by a Langmuirian model that considers readily accessible sites of adsorption, i.e. it is dominated by the outermost surfaces.

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Polyelectrolyte adsorption measurements can be carried out using a streaming current titration method. In paper industry applications such tests are often used to study the charge demand of aqueous solutions or suspensions. At or near zero charge demand, the fiber furnish often shows its best drainage and retention of fine matter during the formation of the paper [19]. In the present investigation a similar method was used to measure the aqueous solution concentration of poly-DADMAC. In other words, the concentration of poly-DADMAC in the solution phase was measured before and after adsorption to calculate the amount that adsorbed within silica gel particles. A series of such experiments was carried out at different levels of the variables of interest with the goal to explore their influence on the adsorption behaviors. Different levels of factors were considered, such as substrate (pore size), polymer characteristics (molecular weight and dosage), and aqueous solution pH (see Table 1).

### 2. Experimental

#### 2.1. Materials

Water used in the experiments was deionized with a Pureflow system. The “default buffer” solution of 1000 μS/cm conductivity was prepared by addition of sodium sulfate 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 5–20 kDa and 400–500 kDa ranges, respectively. Radius of gyration data for these two kinds of polymer were obtained earlier by Burkhardt et al., 1987, as reported by Wågberg [20].

The very low mass poly-DADMAC has a radius of gyration in the range 8.9–13.4 nm, whereas the high mass sample is in the range 44.8–49.6 nm.

The anionic polyelectrolyte used for titrations was NaAl product 460-S5434 Soln. P.V.S.K. (polyvinylsulfate, potassium salt), 0.0025 N (Chicago, IL, USA).

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 Granulars 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 S0, S6, S15, and S30, respectively. See detailed information in Table 2.

The relatively low value of surface area in the case of sample S0 is consistent with the absence of internal pores. Mechanically it is reasonable to expect that the primary particles that were fused together during the formation of samples S0 were smaller than those of the other silica gel samples considered, and it is reasonable to expect the surface area to be approximately proportional to the inverse of primary particle size. In fact, the surface area in similar systems has been found to be inversely proportional to the 2.2 power of the pore radius [17]. In agreement with these expectations S0 had the highest surface area with pore volume 0.75 cm³/g, which is consistent with the smallest pore size, and sample S30, having the largest pore size, showed the lowest surface area with pore volume 1.1–1.2 cm³/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 more difficult it will be for the polymer to diffuse in. Some differences were observed between the nominal surface area (as stated by the supplier) and the measured surface area of silica gel, especially for sample S0. The measured silica gel surface area characterization results were consistent with those of Mishael et al. [17], who studied the correlation between surface area and wider range of controlled pore size of porous glass.

#### 2.2. Adsorption experiments

Poly-DADMAC adsorption kinetics and adsorption isotherms were investigated. For kinetic tests, poly-DADMAC having a concentration of ~1.0% (10 mg/ml) was prepared in default pH 7 buffer solution with conductivity 1000 μS/cm (see Materials section). Adsorption experiments were conducted by mixing 30 ml poly-DADMAC with 0.3 g silica gel particles (poly-DADMAC/silica gel weight ratio of 1:1) in rotating bottles at room temperature for 1, 2, 4, 8, 12, or 24 h. Thereafter the mixture was allowed to settle for about 1 min, and then 0.45 μm nylon filters were used to remove any residual silica gel particles from the supernatant solution. Finally, an aliquot of the filtrate solution was titrated to determine the concentration of poly-DADMAC, using a Mütek PCD-

### Table 1

<table>
<thead>
<tr>
<th>Variables</th>
<th>Additive(s)</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Silica gel</td>
<td>poly-DADMAC</td>
</tr>
<tr>
<td></td>
<td>pore size (nm)</td>
<td>6, 15, 30</td>
</tr>
<tr>
<td>Polyelectrolyte</td>
<td>Mol. mass</td>
<td>poly-DADMAC</td>
</tr>
<tr>
<td></td>
<td>Dosage (% on dry mass of silica gel)</td>
<td>poly-DADMAC</td>
</tr>
<tr>
<td>Medium conditions</td>
<td>pH</td>
<td>HCl, NaOH</td>
</tr>
<tr>
<td>Kinetics factor</td>
<td>Time (h)</td>
<td>poly-DADMAC</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Silica type</th>
<th>Pore size (nm)</th>
<th>Pore volume (cm³/g)</th>
<th>Particle and mesh sizes</th>
<th>Nominal surface area (m²/g)</th>
<th>Measured surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0</td>
<td>Fisher chemical silica</td>
<td>6</td>
<td>0.75</td>
<td>60–100 mesh</td>
<td>150–250 μm</td>
</tr>
<tr>
<td>S6</td>
<td>Davisil®, grade 615</td>
<td>15</td>
<td>1.15</td>
<td>60–100 mesh</td>
<td>150–250 μm</td>
</tr>
<tr>
<td>S15</td>
<td>Davisil®, grade 645</td>
<td>30</td>
<td>1.1–1.2</td>
<td>230–400 mesh</td>
<td>50 μm</td>
</tr>
<tr>
<td>S30</td>
<td>Davisil® sorbent, grade 653 XWP</td>
<td>30</td>
<td>1.1–1.2</td>
<td>230–400 mesh</td>
<td>50 μm</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 h.
03 streaming current device. Poly-DADMAC adsorption amounts at different concentrations were determined by the same procedure as used in the kinetics experiments, except that the samples were equilibrated for 4 h with a concentration range from 0.02 to 1.0% poly-DADMAC based on dry mass of silica gel. Issues affecting the precision and accuracy of such titrations were considered in a previous study [19,21].

2.3. Streaming current measurements

The same streaming current device was used to titrate with 0.0010 N potassium polyvinyl sulfate (PVSK). Poly-DADMAC samples were diluted 1–50 times, as needed, in order to consume the same approximate volume of 0.0010 N PVSK titrant. An aliquot of 5 ml diluted poly-DADMAC sample was added to the titration cell, followed by 10 ml salt buffer, and then PVSK was added gradually to reach the titration endpoint.

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 in the polyelectrolyte of opposite charge via complexation interactions, i.e., 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 [19,21]. In principle, higher salt concentration compresses the electrical double layer and decreases the electrostatic interactions between charged groups, resulting in unbalanced ionic pairing between oppositely charged polyelectrolytes. Polyelectrolyte molecules tend to become more compact with increasing salt concentration. Also, 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 [21].

During the implementation of the titrations it was observed that the titration endpoint depended to a moderate extent on the rate of titrant addition. For instance, addition of PVSK at a higher rate during titration of very low mass poly-DADMAC (Mw 5–20 kDa) made it appear that a somewhat lower amount of poly-DADMAC adsorption had occurred. By contrast, a slow titration process always resulted in an apparent higher adsorbed amount. One explanation is based on the fact that the PVSK with nominal molecular weight 170 kDa likely had a much larger molecular chain length than that of very low mass poly-DADMAC. When PVSK was freshly added to the mixture, one can expect that it was initially coiled up due to the salt condition, but given sufficient time it changed its conformation and reacted with more of the very low mass poly-DADMAC. 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

3.1.1. High mass polymer with S15 and S30 silica samples

As shown in Fig. 1, a direct relationship was found between the adsorbed amount of high mass poly-DADMAC and the logarithm of adsorption time for both 15 and 30 nm silica gel. Mathematical models for the kinetics of adsorption of polymers are widely used in the literature; they predominantly stress the fact that adsorption proceeds on the internal surfaces and therefore adsorption is diffusion-controlled, where the mass transport is limited by diffusion but not by adsorption or desorption of macromolecules at the adsorbing sites. Typically, the experimental situations are complex and a phenomenological description would require the use of many simplifying assumptions. Complicating factors include the polydisperse nature of the adsorbing polymers and the size of the pores as well as pore size distribution. Issues related to capillarity and tortuosity and the local details of polymer chain are not known. Therefore, in order to understand the underlying phenomena, it would be necessary to consider well-characterize systems. Overall, the data in Fig. 1 show semilog relations between x and y, which is the same kind of relationship reported recently by Horvath et al. [11]. Notably, this type of fit to the data differs from that derived by Kiselko et al. [22], based on a diffusion model incorporating forward and reverse interactions, and it is distinct from what has been predicted based on the dynamics of polymer reptation [23,24]. Factors contributing to hindrance of polyelectrolyte permeation into porous media have been reviewed [8], but to the authors’ knowledge no log-time dependency of polyelectrolyte adsorption onto and into porous media has been derived. Clearly this is an important area for development of mechanistic models.

In the case of high-mass polyelectrolyte it is worth noting that after 12 h, there was no major change in the adsorbed amount. In the case of 15-nm silica gel about 63% of the adsorption of high mass poly-DADMAC had already been achieved at 4 h, compared to the amount at 24 h. In the case of 30-nm silica gel the corresponding percentage was 90%.

3.1.2. Very low mass

As shown in Fig. 2, a straight-line relationship also was found in adsorption amounts of very low mass poly-DADMAC equilibrated with various pore size silica gels, when the results were plotted as a function of the log of time. Compared with high mass poly-DADMAC mentioned above (see Fig. 1), the adsorbed amount of very low mass poly-DADMAC increased considerably with time, 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 6 nm silica gel at 4 h (log t/s = 4.16), was nearly 79% of its value at 24 h. This

Fig. 1. Adsorption dynamics for high mass poly-DADMAC on S15 and S30. The lines are best fit and the size of the symbols is larger than the experimental standard deviation.
percentage rose to around 89% for 15-nm silica gel, and 90% for 30-nm silica gel.

It is notable that the log-time dependency shown in Figs. 1 and 2 is consistent with results shown in Part 2 of this work [25], except that the dependent variable was streaming potential in the cited study. This apparent agreement must be placed into context, however. Whereas the present results show a log-time dependency for the net amount of poly-DADMAC adsorption, the streaming potential results would not necessarily be expected to correspond to the net amount of adsorption. However, it is tentatively proposed that within sufficiently narrow ranges of the variables, a change in the adsorbed amount could produce a linearly related change in the observed streaming potential. Further research in this area is recommended.

When looking at the same time point, it can be seen that the 15-nm silica gel achieved the highest adsorbed amount of very-low-mass poly-DADMAC, followed by 30 nm, and then 6 nm. Although 6-nm silica gel had the highest surface area, the results suggest that the poly-DADMAC molecules of very low mass were still too large to diffuse efficiently into the 6 nm pores. For 15-nm silica gel with the medium surface area, the pore size was large enough for poly-DADMAC of very low mass to permeate to a detectable extent, and in the case of 30-nm silica gel diffusion would be even much easier, but its relatively low surface area resulted in lower adsorption compared with the 15-nm silica gel. 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. As noted in section 2.1, the radius of gyration was either 8.9–13.4 nm or 44.8–49.6 nm, respectively, for the very low mass and the high mass poly-DADMAC.

To summarize findings for different molecular mass poly-DADMAC adsorption, it is proposed that as long as the poly-DADMAC molecule is small enough or the pores in the silica gel are large enough to allow passage of poly-DADMAC, then surface area dominates the adsorption amount. The larger the surface area of the silica gel, 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, then even with high surface area, the adsorbed amount is very low. Similar findings have been reported by Wang et al. [1]. In order to compare pore size and other variable effects, 4 h was chosen as the equilibrium time for all subsequent tests.

In an effort to estimate how much poly-DADMAC would adsorb onto the outer surfaces, parallel tests with non-porous silica were carried out. Within the repeatability of the methods, no significant adsorption was observed for nonporous silica (200 mesh and finer particle size). This result, in combination with the observed effects related to pore size, make it possible to reject at least part of the hypothesis described earlier. It is clear that the internal surfaces, within the pore structure, were largely responsible for the observed adsorption of poly-DADMAC throughout the range of molecular mass considered.

3.2. Poly-DADMAC adsorption isotherms

Adsorption isotherms of poly-DADMAC on silica gel substrates having different pore sizes (S6, S15, and S30) are shown in Fig. 3 (a) and (b). The Langmuir equation $I = I_{\text{max}} \times KC/(1 + K \times C)$ was well fitted in each case, where $K$ is the Langmuir equilibrium constant (with units of reciprocal concentration), $C$ is the aqueous concentration, $I$ the adsorbed amount of poly-DADMAC molecules, and $I_{\text{max}}$ the maximum amount adsorbed. Letting $I_{\text{max}} \times K = a$, and $K = b$, the Langmuir equation can be also expressed as $I = a \times C/(1 + b \times C)$, where $I_{\text{max}} = a/b$.

The plotted results show the dependence of the adsorbed amount on the poly-DADMAC concentration in the range of 0–0.5%...
Comparison of silica gel particles $\Gamma_{\text{max}}$ of very low mass poly-DADMAC.

<table>
<thead>
<tr>
<th>Silica gel type</th>
<th>$\Gamma_{\text{max}}$ based on mass (mg/g-substrate)</th>
<th>$\Gamma_{\text{max}}$ based on area (mg/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{10}$</td>
<td>74</td>
<td>0.4</td>
</tr>
<tr>
<td>$S_{15}$</td>
<td>62</td>
<td>0.2</td>
</tr>
<tr>
<td>$S_{30}$</td>
<td>32</td>
<td>0.1</td>
</tr>
</tbody>
</table>

(on dry mass of silica gel). Poly-DADMAC adsorbed amounts were calculated based on the mass and the surface area of the silica gel particles, as shown in Fig. 3(a) and (b), respectively. The slope at a relatively lower concentration indicates high affinity of poly-DADMAC to the surfaces in the porous structure. $S_{30}$, having the biggest pore size, showed the highest initial slope, which is consistent with an expectation that the very low mass poly-DADMAC macromolecules should have the easiest access into the silica gel having the largest pores. Based on values of $\Gamma_{\text{max}}$, which were calculated from the term $a/b$, the maximum adsorption for the three types of silica gel in the case of very low mass poly-DADMAC are compared in Table 3.

As shown, the 30-nm pore size of silica gel achieved a higher maximum adsorbed amount of very low mass poly-DADMAC based on either mass or surface area of silica gels. These results provide further evidence that the bigger the pore size of silica gel, the greater was the access to the poly-DADMAC molecules. The fact that the adsorbed amount was inversely related to the surface area provides evidence that, at least in the cases of the two samples with smaller pore size, a majority of the internal surfaces within the silica gel remained inaccessible by most of the polyelectrolyte molecules in the sample. In Fig. 4 the adsorption isotherms for high mass and very low mass poly-DADMAC are compared. A very high slope at a relatively low concentration demonstrates a high affinity of the very low mass poly-DADMAC to the accessible surfaces. The fact that the isotherm reached a plateau of adsorption with increasing bulk concentration is typical for polyelectrolyte adsorption onto surfaces that are readily accessible. Similar adsorption isotherms have been reported for quaternized poly(vinylpyridine) onto the interior surfaces of controlled porous glass (0–20 g/L in 0.5 M NaCl, pH 9.5) with a series of pore sizes, 7.5, 8, 49, and 285 nm [17]. In the case of high mass poly-DADMAC, the adsorption results did not follow a Langmuir isotherm. This can be explained by the limited accessibility of high-mass poly-DADMAC into 30-nm pore size silica gel. Consistent with the analysis in Part 2 of this series of articles [25], increased adsorption with increasing polymer solution concentration can be explained by an increased presence of very-low-mass (oligomeric) polyelectrolyte material.

3.3. Effects of pH

As shown in Fig. 5, the adsorption of very-low-mass poly-DADMAC onto silica gel (pore size 15 nm) increased with increasing pH in the range of 3–8. 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 [26]. Thus, the results in Fig. 5 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; possibly it is due to the characteristics of the hydration layer around silica at high pH, preventing adsorption.

There is an apparent contradiction between the effect of pH on adsorption, as shown in Fig. 5, and the corresponding effects on streaming potential, as reported earlier [18]. 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 3–4 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 if one makes two assumptions. 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 adsorbed. 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 relaxation of the adsorbed 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 [14,27–30]. Secondly, it can be 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.

The results described in the present article also help to provide context to the effects of a cationic polyelectrolyte on streaming potential results, as was reported in Parts 1 and 2 of this series [18,25]. The present results pertain to the net amounts of adsorption, whereas the streaming potential test results presented in the foregoing articles appeared to be very sensitive to effects of permeation of oligomers, which were not the main component of the polyelectrolytes under study. The contrast between the net amounts adsorbed vs. the degree of change of streaming potential has potential to provide a means of obtaining information about polyelectrolyte coverage of interior surfaces. The authors hope that the present series of work will encourage further progress both on the theoretical and experimental side in order to take fuller advantage of this combination of methods.

4. Conclusions

1. 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 (15 nm).

2. The adsorption 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.

3. Adsorption of very low mass poly-DADMAC was pH-dependent. This is consistent with the fact that the surface charge of silica gel becomes more negative when pH increases. Thus, adsorption would be enhanced as long as sufficient very low mass poly-DADMAC is present.

Appendix A. Supplementary data


References


