

Structure of an Adsorbed Polyelectrolyte Monolayer on Oppositely Charged Colloidal Particles

Andrea Vaccaro, José Hierrezuelo, Michal Skarba,[†] Paolo Galletto, Jörg Kleimann,[‡] and Michal Borkovec*

Department of Inorganic, Analytical, and Applied Chemistry, University of Geneva, 1211 Geneva 4, Switzerland.

[†] Current address: Department of Physical Chemistry, University of Bayreuth, Bayreuth, Germany. [‡] Current address: Metrohm AG, Herisau, Switzerland.

Received March 3, 2009. Revised Manuscript Received March 23, 2009

An adsorbed layer of a cationic polyelectrolyte, poly(diallyldimethyl-ammonium) chloride (PDADMAC) on negatively charged colloidal latex particles was investigated by small-angle neutron scattering (SANS) and dynamic light scattering (DLS). SANS gives a layer thickness of 8 ± 1 Å and a polymer volume fraction of 0.31 ± 0.05 within the film. DLS gives a somewhat larger thickness of 18 ± 2 Å, and the discrepancy is likely due to the inhomogeneous nature of the layer and the existence of polymer tails or loops protruding into solution. These results show that a highly charged polyelectrolyte adsorbs on an oppositely charged colloidal particle in a flat configuration due to the attractive forces acting between the polyelectrolyte and the substrate.

Surface properties of colloidal particles can be significantly altered by adsorption of neutral or charged polymers (i.e., polyelectrolytes).^{1–8} To design polymer coatings with known properties, the structure of the adsorbed layer in situ must be known. Scattering techniques have been frequently used to achieve this aim.^{8–22} Dynamic light scattering (DLS) gives access to the thickness of an adsorbed layer by comparing the hydrodynamic radius of colloidal particles in the presence of the polymer with that in its absence. While the technique works well

in the case of neutral polymers,^{11,19,23,24} conflicting results have been reported for polyelectrolytes, probably due to difficulties to properly differentiate between layer growth and colloidal aggregation.^{8,16} Small angle X-ray and neutron scattering provides additional information, as one can access the relevant wave vectors. While good time resolution can be obtained with small-angle X-ray scattering (SAXS),^{25,26} small-angle neutron scattering (SANS) offers the possibility of contrast variation.^{9,13,17,22} The latter technique was successfully used to probe adsorbed and grafted layers of neutral polymers on colloidal particles.^{14,15,17–21,27} In particular, adsorbed layers of neutral poly(oxyethylene) (PEO) were studied in substantial detail. Depending on the molecular mass, the layer thickness obtained from SANS varies between 30 and 300 Å, while the hydrodynamic layer thickness was often reported to be 2–3 times larger.^{17,24,27,28} The adsorbed layer is relatively tenuous with volume fractions below 0.1, and the concentration profile could be established to be approximately exponential.^{18,21}

On the other hand, few studies have focused on adsorbed polyelectrolytes.^{13,29} Estrela-Lopis et al.²⁹ studied polyelectrolyte multilayers, which were obtained by depositing cationic and anionic polyelectrolytes on colloidal particles in an alternating fashion. From SANS, they obtained a thickness of about 200 Å. Likos et al.¹³ established that an adsorbed gelatin layer has a thickness of about 100 Å near its isoelectric point (IEP). However, studies focusing on the important case of monolayers of polyelectrolytes adsorbed on oppositely charged particles are lacking,

*Corresponding author. E-mail: Michal.borkovec@unige.ch.

- (1) Howe, A. M.; Wesley, R. D.; Bertrand, M.; Cote, M.; Leroy, J. *Langmuir* **2006**, *22*, 4518–4525.
- (2) Claesson, P. M.; Poptoshev, E.; Blomberg, E.; Dedinaite, A. *Adv. Colloid Interface Sci.* **2005**, *114*, 173–187.
- (3) Biggs, S.; Healy, T. W. *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 3415–3421.
- (4) Ballauff, M. *Prog. Polym. Sci.* **2007**, *32*, 1135–1151.
- (5) Kenausis, G. L.; Voros, J.; Elbert, D. L.; Huang, N.; Hofer, R.; Ruiz-Taylor, L.; Textor, M.; Hubbell, J. A.; Spencer, N. D. *J. Phys. Chem. B* **2000**, *104*, 3298–3309.
- (6) Borkovec, M.; Papastavrou, G. *Curr. Opin. Colloid Interface Sci.* **2008**, *13*, 429–437.
- (7) Bouyer, F.; Robben, A.; Yu, W. L.; Borkovec, M. *Langmuir* **2001**, *17*, 5225–5231.
- (8) Gillies, G.; Lin, W.; Borkovec, M. *J. Phys. Chem. B* **2007**, *111*, 8626–8633.
- (9) Oberdisse, J. *Curr. Opin. Colloid Interface Sci.* **2007**, *12*, 3–8.
- (10) Guo, X.; Ballauff, M. *Langmuir* **2000**, *16*, 8719–8726.
- (11) Min, G. K.; Bevan, M. A.; Prieve, D. C.; Patterson, G. D. *Colloids Surf. A* **2002**, *202*, 9–21.
- (12) Vaynberg, K. A.; Wagner, N. J.; Sharma, R. *Biomacromolecules* **2000**, *1*, 466–472.
- (13) Likos, C. N.; Vaynberg, K. A.; Lowen, H.; Wagner, N. J. *Langmuir* **2000**, *16*, 4100–4108.
- (14) Auroy, P.; Auvray, L.; Leger, L. *Macromolecules* **1991**, *24*, 2523–2528.
- (15) Auroy, P.; Mir, Y.; Auvray, L. *Phys. Rev. Lett.* **1992**, *69*, 93–95.
- (16) Cosgrove, T.; Obey, T.; Vincent, B. *J. Colloid Interface Sci.* **1986**, *111*, 409–418.
- (17) Hone, J. H. E.; Cosgrove, T.; Saphiannikova, M.; Obey, T. M.; Marshall, J. C.; Crowley, T. L. *Langmuir* **2002**, *18*, 855–864.
- (18) Marshall, J. C.; Cosgrove, T.; Leermakers, F.; Obey, T. M.; Dreiss, C. A. *Langmuir* **2004**, *20*, 4480–4488.
- (19) Flood, C.; Cosgrove, T.; Howell, I.; Revell, P. *Langmuir* **2006**, *22*, 6923–6930.
- (20) Flood, C.; Cosgrove, T.; Qiu, D.; Espidel, Y.; Howell, I.; Revell, P. *Langmuir* **2007**, *23*, 2408–2413.
- (21) Qiu, D.; Flood, C.; Cosgrove, T. *Langmuir* **2008**, *24*, 2983–2986.
- (22) Zackrisson, M.; Stradner, A.; Schurtenberger, P.; Bergenholtz, J. *Langmuir* **2005**, *21*, 10835–10845.

- (23) Baker, J. A.; Berg, J. C. *Langmuir* **1988**, *4*, 1055–1061.
- (24) Mears, S. J.; Cosgrove, T.; Obey, T.; Thompson, L.; Howell, I. *Langmuir* **1998**, *14*, 4997–5003.
- (25) Chibowski, S.; Wisniewska, M.; Marczewski, A. W.; Pikus, S. *J. Colloid Interface Sci.* **2003**, *267*, 1–8.
- (26) Bolze, J.; Pontoni, D.; Ballauff, M.; Narayanan, T.; Colfen, H. *J. Colloid Interface Sci.* **2004**, *277*, 84–94.
- (27) Barnett, K. G.; Cosgrove, T.; Vincent, B.; Burgess, A. N.; Crowley, T. L.; King, T.; Turner, J. D.; Tadros, T. F. *Polymer* **1981**, *22*, 283–285.
- (28) Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces*; Chapman and Hall: London, 1993.
- (29) Estrela-Lopis, I.; Leporatti, S.; Moya, S.; Brandt, A.; Donath, E.; Mohwald, H. *Langmuir* **2002**, *18*, 7861–7866.

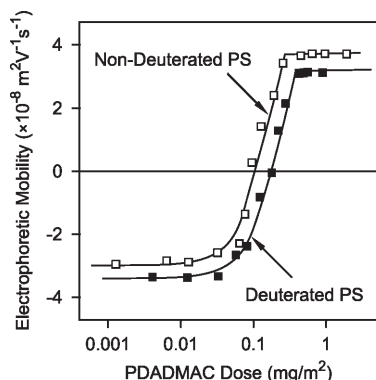


Figure 1. Electrophoretic mobility of deuterated and nondeuterated latex particles as a function of PDADMAC added. The ionic strength is 10 mM and pH 4. For the deuterated particles, the saturation plateau sets in at 0.38 ± 0.06 mg/m², while this value is somewhat lower for the nondeuterated ones. The solid lines serve to guide the eye only.

probably because, in such systems, the adsorbed layers are extremely thin and difficult to detect.

This letter aims to fill this gap, and shows for the first time how the structure of a polyelectrolyte layer adsorbed on oppositely charged colloidal particles can be elucidated by scattering techniques. SANS and DLS are used to measure the layer thickness of a strongly charged cationic polyelectrolyte adsorbed on negatively charged sulfate latex particles. Both methods confirm that the adsorbed layer is very thin.

This study focuses on cationic polyelectrolyte poly(diallyldimethyl ammonium) chloride (PDADMAC) with a molar mass of 450 kg/mol. PDADMAC is a strong cationic polyelectrolyte, which carries one positive charge per monomer unit, resulting in a line charge density of about 0.11 \AA^{-1} . For the SANS experiments, PDADMAC was adsorbed to nanosized sulfate-terminated deuterated polystyrene (PS) latex particles. The fact that this polyelectrolyte adsorbs strongly to these particles was demonstrated by electrophoresis. Figure 1 shows the electrophoretic mobility to increase with increasing dose of the positively charged PDADMAC due to the adsorption to the particle surface. With increasing doses, it first passes through the IEP, and later indicates a charge reversal of the particles (i.e., overcharging). At higher PDADMAC doses, the mobility remains unchanged as a result of a saturated polyelectrolyte layer with an adsorbed mass of 0.38 ± 0.06 mg/m². This behavior is generic for strongly charged polyelectrolytes adsorbing to oppositely charged particles.^{2,3,6–8}

Figure 2a shows the scattering intensity of the bare latex particles for different water contents in 1.5 mM KCl. By increasing the amount of water, the scattering from the particles increases because of a stronger contrast between particles and surrounding medium. Since the profiles are not simply displaced along the ordinate, the particles must have an internal structure. A simple core-shell model assuming a core consisting of fully deuterated PS and a nondeuterated shell with the known scattering length densities³⁰ turns out to be fully consistent with the data. We obtained an average particle radius of 120 Å and a polydispersity with a coefficient of variation (CV) of 0.18, in good agreement with the values obtained by transmission electron microscopy. The resulting shell thickness was 3.7 Å. Figure 2 also shows the effect of the structure factor, which was kept constant for the

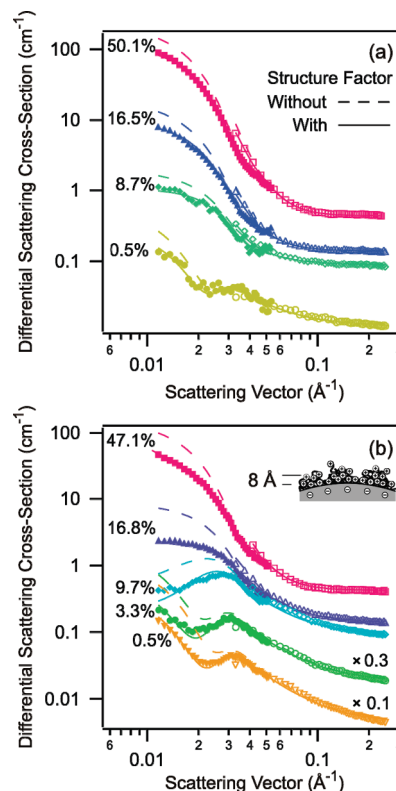


Figure 2. SANS profiles from deuterated sulfate latex particles in mixtures of D₂O and H₂O at pH 4. The volume fraction of H₂O is indicated. Closed symbols correspond to large detector distance, while the open symbols correspond to small distance. Best fits to core-shell models including a common structure factor are shown as solid lines, while dashed lines indicate the model predictions without the structure factor. Curves scaled for clarity are indicated by the respective multiplicative factors. (a) Bare deuterated latex particles in 1.5 mM KCl fitted to a core-shell model. (b) Same deuterated latex particles in the presence of PDADMAC fitted to the same model with one additional layer representing the polyelectrolyte.

different contrasts considered. This contribution is only important in the low- q region. We suspect that the nondeuterated shell is formed by isotopic fractionation during the synthesis of the particles or by isotopic exchange with the water during storage. However, we cannot exclude that the thin low-contrast shell is of different origin, for example, as a result of the presence of a hairy-layer or surface impurities.^{31,32}

Figure 2b shows the scattering profiles from particles with adsorbed PDADMAC. Clearly, the experiment is sensitive to the adsorbed polyelectrolyte layer at low contrasts only. Experiments were performed at a PDADMAC dose, where the electrophoretic mobility saturates and the adsorption is complete. During the fitting procedure of the particles with adsorbed PDADMAC, the values obtained from the fits of the scattering profiles of the bare particles were used and kept constant. The structure factor was derived from the high- q limit of the structure factor for particle aggregates proposed recently.³³ Both parameters describing the adsorbed layer can be determined from the global fit of the data with confidence, and the resulting layer thickness is $L = 8 \pm 1 \text{ \AA}$, while the volume fraction is $\phi_p = 0.31 \pm 0.05$. Both values must be interpreted as

(30) Wallace, W. E.; Tan, N. C. B.; Wu, W. L.; Satija, S. *J. Chem. Phys.* **1998**, *108*, 3798–3804.

(31) Seo, Y. S.; Satija, S. *Langmuir* **2006**, *22*, 7113–7116.

(32) Seebergh, J. E.; Berg, J. C. *Colloids Surf., A* **1995**, *100*, 139–153.

(33) Lattuada, M.; Wu, H.; Morbidelli, M. *J. Colloid Interface Sci.* **2003**, *268*, 106–120.

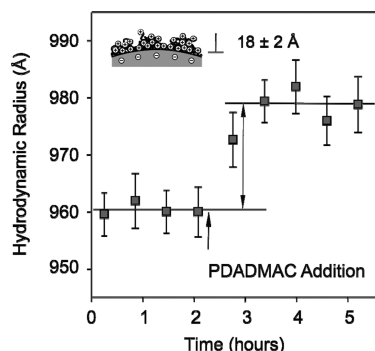


Figure 3. Determination of the hydrodynamic layer thickness by dynamic DLS with nondeuterated sulfate latex particles. The hydrodynamic radius of the bare particles was first monitored in 10 mM KCl and pH 4, and the change in radius was measured upon PDADMAC addition (arrow). The points correspond to averages of 100 data points and the bars indicate the error of the mean.

average quantities in the normal as well as in the lateral direction. In particular, the existence of island-like structure of the adsorbed films will tend to lower these values.

The consistency of the present data analysis can be verified by calculating the adsorbed mass per unit area with the expression $\Gamma = L\phi_p d$, where d is the PDADMAC density. With the known³⁴ value of $d = 1.2 \text{ g cm}^{-3}$, the adsorbed mass Γ was estimated from SANS as $0.30 \pm 0.03 \text{ mg/m}^2$. This value should be compared with $0.38 \pm 0.06 \text{ mg/m}^2$ obtained from the onset of the mobility plateau. The excellent agreement between the two independently measured values of the adsorbed mass represents a strong indication of the validity of the present experimental protocol.

The used box profile with uniform density yields a good description of the data. One might be tempted to use alternative models accounting for a radial variation of the shell profile. However, given the small thickness of the layer, the limited q -range probed, and the substantial instrumental smearing, further information on the profile is impossible to extract. Such profiles were successfully extracted from SANS data for neutral polymers,¹⁸ but in the latter case, the layers are substantially thicker than the present ones.

The present findings agree with similar SANS data on larger particles coated with a much thicker polyelectrolyte multilayer films and neutron reflectivity measurements on similar flat substrates.²⁹ When dividing the observed layer thickness by the number of deposited layers, the average thickness of a single layer turns out to be $16 \pm 2 \text{ Å}$, and the polymer volume fraction is $\phi_p = 0.58$. While these values are well comparable to the ones reported here, an isolated single adsorbed layer appears somewhat thinner and more porous than an individual layer in the multilayer. This observation can be explained by the fact that a single layer is probably laterally inhomogeneous. These inhomogeneities lead to a smaller average thickness and to larger porosity. Within a multilayer, the subsequent layers will smooth out the lateral inhomogeneities, and an individual layer will appear thinner and less porous. On the other hand, adsorbed layers of neutral polymers are usually substantially thicker and more tenuous.^{18,21}

We have further compared the present results with layer thickness measurements by DLS. While DLS represents a classical technique for the measurements of the thickness of adsorbed

polymer layers, its application in the present case is tricky. The problem is that one cannot easily distinguish particle aggregation and layer formation in a DLS experiment. We have resolved this problem by diluting the suspension to the point that particle aggregation becomes negligible in the experimental window. Since the scattering signal of the small particles used in the SANS experiment is extremely low under these conditions, it was necessary to carry out this experiment with larger, but otherwise similar particles. We have used nondeuterated sulfate-terminated latex of a comparable surface charge density. Their radius measured by DLS was about 960 Å. The similarity of both types of particles is illustrated by the congruent electrophoresis data shown in Figure 1. The small discrepancies could be related to the differences in the surface curvatures or small differences in their surface properties. The relevant time-resolved DLS results are shown in Figure 3. PDADMAC was added after a certain time resulting in the same dose as in the SANS experiments corresponding to the onset of the electrophoretic mobility plateau. Upon addition of PDADMAC, one could clearly detect an increase in the hydrodynamic radius by a $18 \pm 2 \text{ Å}$. The experiment shown was performed at ionic strength of 10 mM in KCl, which is similar to one in the SANS experiments. The ionic strength in the latter samples was estimated by assuming the full dissociation of the PDADMAC and latex particle counterions. The layer thickness measured by DLS is about a factor of 2 larger than the value measured by SANS. Similar ratios were reported for adsorbed layers of neutral polymers.^{17,24,27,28} The discrepancy is most likely related to the lateral inhomogeneity of the adsorbed layer. The hydrodynamic thickness will be dictated by the thicker parts of the layers, while an average layer thickness will be measured by SANS. Tails or loops protruding into the solution will create an additional drag on the particle. Finally, the smaller curvature of the larger particles may lead to a somewhat thicker layer.^{35,36} All these effects will lead to a larger hydrodynamic layer thickness than the one observed by SANS.

We conclude that the adsorbed monolayer of a strong cationic polyelectrolyte (PDADMAC) on negatively charged colloidal particles was successfully characterized with SANS and DLS for the first time. SANS gives a layer thickness of $8 \pm 1 \text{ Å}$, while DLS gives a larger value of $18 \pm 2 \text{ Å}$. The discrepancy is probably due to the lateral inhomogeneity of the adsorbed layer and the existence of protruding polymer tails or loops into the solution. These results suggest that the polyelectrolyte layer is rather thin, but still substantially thicker than the typical size of a monomer. Therefore, the polyelectrolyte chains do not lie completely flat on the surface, but a certain degree of coiling persists within the adsorbed chains. From SANS one further concludes that the polyelectrolyte occupies a volume fraction of 0.30 ± 0.03 . Since the adsorbed layer is likely to be laterally inhomogeneous, this number suggests that the adsorbed polyelectrolyte is adsorbed in a moderately compact configuration. The validity of the present analysis is confirmed by the fact that SANS and electrophoretic mobility measurements lead both to consistent adsorbed amounts of $0.31 \pm 0.05 \text{ mg/m}^2$ and $0.38 \pm 0.06 \text{ mg/m}^2$, respectively. The experiments thus clearly demonstrate that highly charged polyelectrolytes flatten substantially during adsorption on oppositely charged colloidal particles, but in spite of the strong attractive interactions acting between the polyelectrolyte and the substrate, some coiling of the polyelectrolyte prevails. This

(34) Dautzenberg, H.; Gornitz, E.; Jaeger, W. *Macromol. Chem. Phys.* **1998**, *199*, 1561–1571.

(35) Cosgrove, T.; Griffiths, P. C.; Lloyd, P. M. *Langmuir* **1995**, *11*, 1457–1463.

(36) Lin, E. K.; Gast, A. P. *Macromolecules* **1996**, *29*, 390–397.

behavior is in contrast to neutral polymers, which adsorb in thicker and less dense layers.

Acknowledgment. We thank Pavel Strunz and Thomas Geue for valuable coaching during the SANS sessions spent at the Paul Scherrer Institute (PSI), Stéphane Torelli and Claude Piguet for NMR analysis and data interpretation, and Jan S. Pedersen for useful discussions. The research was

supported by the Swiss National Science Foundation and the University of Geneva. The neutron beam time was provided by the PSI.

Supporting Information Available: Detailed information on the materials, experimental protocols, and data analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.