

# Depletion of Polyelectrolytes near Like-Charged Substrates Probed by Optical Reflectivity

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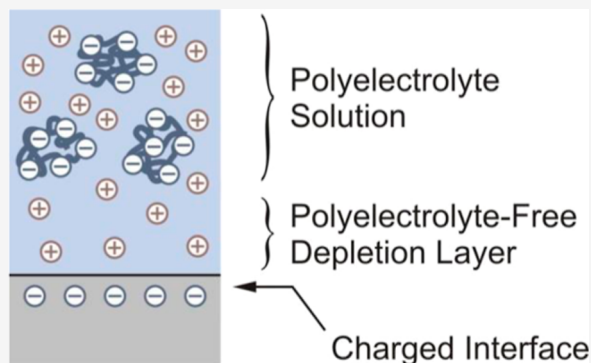
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**ABSTRACT:** Salt-free polyelectrolyte solutions form a polyelectrolyte-free depletion layer near like-charged solid interfaces. This evidence is provided by optical reflectivity measurements from planar silica substrates in contact with aqueous solutions of sodium poly(styrene sulfonate). Analysis of the observed reflectivity signal, which features unusual negative signals and optical matching points, with a two-slab model demonstrates the existence of such a polyelectrolyte-free depletion layer. Moreover, the applied model permits the extraction of the corresponding layer thickness, which typically is several tenths of nanometers. This thickness decreases as the inverse square root of the polyelectrolyte concentration, but the actual values exceed the expected Debye length substantially. These results clearly provide independent evidence for the existence of a polyelectrolyte-free depletion layer, as previously suggested on the basis of direct force measurements with the atomic force measurement.



## 1. INTRODUCTION

Adsorption of polyelectrolytes on solid substrates is relevant in various industrial applications, including papermaking, water treatment, and cement processing.<sup>1–4</sup> The relevance of these applications motivated various researchers to study the fundamental aspects of such adsorption processes. However, the vast majority of this work focused on the oppositely charged situation, meaning that the charge of polyelectrolytes is opposite to the one of the substrate.<sup>5–10</sup> In this situation, the adsorption of the polyelectrolytes is rapid and irreversible due to the attractive electrostatic interactions between the substrate and the monomeric units of the polyelectrolyte. Subsequently, the adsorption process saturates quickly due to the electrostatic repulsion between the adsorbing monomeric units, leading to thin and stable adsorbed films, which further induce a charge reversal of the substrate. The stability of these films together with the corresponding charge reversal represents the basis of the layer-by-layer self-assembly technique.<sup>11,12</sup> This technique can be used to fabricate multilayer films with an alternating sequence of oppositely charged polyelectrolytes by simple repetitive dipping,<sup>12–14</sup> spraying,<sup>15–17</sup> or electrochemical deposition.<sup>18–20</sup>

Interactions between charged substrates and like-charged polyelectrolytes have been investigated in much lesser detail, principally because many authors have concluded that adsorption will be prevented by the repulsive electrostatic interactions between the substrate and the monomeric units of the polyelectrolyte.<sup>21</sup> This conclusion appears mostly correct at low polyelectrolyte concentrations in the presence of

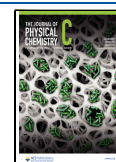
monovalent counterions. However, adsorption does occur at higher salt levels, in the presence of multivalent counterions, or for strongly hydrophobic polyelectrolytes and/or substrates.<sup>21–25</sup> Overall, however, polyelectrolyte adsorption in such a like-charged situation is poorly understood.

Another important, but largely overlooked feature of the like-charged situation is the depletion of polyelectrolytes from the substrate. It seems intuitively obvious that polyelectrolytes will be strongly repelled from a like-charged interface, and therefore, a depletion layer next to the interface should form. Direct force measurements carried out in concentrated polyelectrolyte solutions between like-charged surfaces reveal an oscillatory force profile, which suggests that the corresponding concentration profile is also oscillatory near interfaces.<sup>26–30</sup> However, some of these measurements further indicate the presence of strongly repulsive forces at shorter separation distances, which decay with distance slowly at first and then sharply.<sup>30</sup> This characteristic force profile occurring at shorter distances can be well described with the Poisson–Boltzmann theory for a highly asymmetric electrolyte. These observations and model calculations suggest the presence of a

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well-defined polyelectrolyte-free depletion layer near the interface.

The evidence from direct force measurements for the presence of this depletion layer is indirect at best, and an independent experimental confirmation for polyelectrolyte depletion near a like-charged interface would be most desirable. The present letter aims at this point. This study demonstrates the presence of a well-defined polyelectrolyte-free depletion layer by means of optical reflectivity. This technique allows one to measure the magnitude of the ellipsometric signal in a flow-through cell and has been previously used to probe the adsorption of polyelectrolytes, typically in an oppositely charged situation.<sup>5–8</sup> Here, we use this technique to study negatively charged silica substrates in aqueous solutions of anionic polyelectrolytes. We show that the reflectivity signal exhibits unusual, but characteristic features. These features can be quantitatively interpreted with an optical model that assumes the existence of a polyelectrolyte-free depletion layer. This model further allows extracting the corresponding layer thickness.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Sodium poly(styrene sulfonate) (NaPSS) of molecular mass 21, 64, 260, and 620 kg/mol was purchased from Polymer Standard Service (Mainz, Germany), and it was used as received. Sodium chloride was purchased from Sigma-Aldrich. Milli-Q (Millipore) water was used throughout.

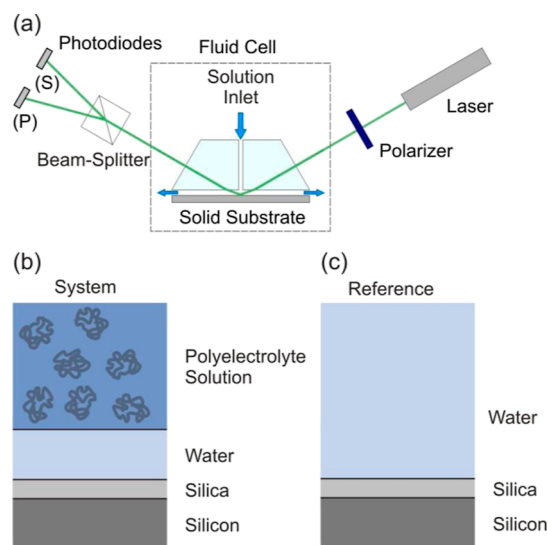
NaPSS solutions, in a range of 0.5–40 g/L, were prepared by dissolving in Milli-Q water. The concentration range was limited by the disappearance of the signal in the experimental noise at low polyelectrolyte concentrations, while at high concentrations, the solution viscosity limited the pumping speed and promoted the formation of air bubbles within the cell. The measurements were carried out at pH 4 and pH 10.0 adjusted with 0.1 M HCl and 0.1 M NaOH, respectively.

Silicon wafers (p-type) were obtained from Silchem and used as substrates in the optical reflectivity experiments. Approximate squares of 1 cm were cut out of these wafers and they were calcined at 1000 °C for 10–20 min. The calcination resulted in forming of a silica layer on its surface. The wafer was then treated in a piranha solution, which is a mixture of concentrated sulfuric acid (96%, Carlo Erba Reagents) and hydrogen peroxide (30%, Rectolab) in a volume ratio of 3:1, at a temperature of  $21 \pm 2$  °C for 20 min. Then it was rinsed in pure water, and dried in a flow of nitrogen gas. The final cleaning step was carried out in with a plasma cleaner (PDC-32 G, Harrick) for 30 min in air.

**2.2. Methods.** The refractive index increment of NaPSS in solution was measured by means of an automatic refractometer (Abbemat WR/MW, Anton Paar GmbH). The value was extracted from refractive index measurements of a concentration series. We find 0.171 mL/g independently of the molar mass.

Nulling ellipsometry (Multiskop, Optrel) was used to accurately measure the thickness of each wafer. The measurements were carried out in air at an angle of 69°. The instrument uses a He–Ne laser with a wavelength of 633 nm. The thickness was calculated from the ellipsometric angles by means of a slab model. This model uses the refractive indices equal to of  $3.85 + 0.02i$  for silicon and 1.457 for silica, respectively.<sup>31,32</sup> The measured layer thickness was typically in the range of 10–30 nm.

The reflectivity experiments were carried out with a home-built optical reflectometer, see Figure 1a.<sup>6,33</sup> The reflectometer



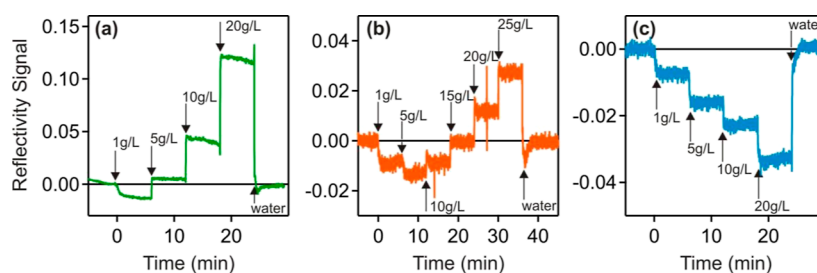
**Figure 1.** Scheme of the reflectivity experiment and the optical model used. (a) Illustration of the reflectivity instrument. (b) Two-slab optical model used to model the polyelectrolyte-free depletion layer. (c) One-slab reference used for the baseline.

consists of two goniometer arms and a sample cell. One goniometer arm carries the laser working at a wavelength of 532 nm, which serves as the light source. The laser beam is reflected from a well-cleaned planar silicon (Si) wafer, which is covered with a thermally grown silica (SiO<sub>2</sub>) coating. The wafer is mounted in the reflectometer with an impinging-jet flow-through cell. The impinging-jet cell is built of capped quartz prism with a vertical bore hole of 1.0 mm in diameter. The prism is separated from the wafer with a spacer of 0.85 mm. The bore hole serves as the inlet to the stagnation point flow cell, which is fed with a peristaltic pump with a flow rate of 1 mL/min. The reflected beam is focused into a polarizing beam-splitter, which is mounted on the second goniometer arm. From the reflected beam, one extracts the reflectivity signal, which is proportional to the ratio of the reflectivities in the perpendicular (S) and parallel (P) direction to the reflection plane. The baseline is then subtracted from the signal, and the resulting difference is normalized to the baseline. The baseline is obtained at the beginning of the experiment by flushing the cell at a constant flow rate with pure water with adjusted pH. A sequence of aqueous solutions of NaPSS with adjusted pH is then passed through the cell. To verify the reversibility of the process, the cell is finally flushed with the initial polyelectrolyte-free electrolyte solution of the same pH.

All experiments were carried out at a reflection angle of 60°, which was calibrated, at room temperature of  $21 \pm 2$  °C, according to the method presented by Porous et al.<sup>33</sup> More details on similar reflectivity experiments can be found elsewhere.<sup>33–35</sup>

## 3. RESULTS AND DISCUSSION

Typical traces of reflectivity experiments are shown in Figure 2. One observes that with increasing NaPSS concentration, the reflectivity signal decreases at first, becomes negative, and then increases again to attain positive values. For a particular



**Figure 2.** Typical traces of the reflectivity experiments. The cell was first flushed with water, then with solutions of NaPSS with a molecular mass of 260 g/mol of increasing concentration, and finally again with water. All experiments were carried out at pH 4.0. The subfigures refer to different thicknesses of the silica over layer, namely (a) 10, (b) 16, and (c) 28 nm.

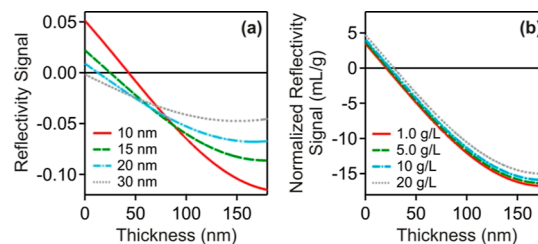
concentration, the reflectivity signal vanishes, and thus, one passes an optical matching point. The position of this match strongly depends on the thickness of the silica coating. For thin coatings, the matching point occurs at low concentrations and is hardly visible in Figure 2a. For intermediate coating thickness, this matching point occurs in the middle of the accessible concentration range as shown in Figure 2b. For thicker coatings, only a negative signal is observed, see Figure 2c.

One always observes full reversibility, meaning that the signal always returns to the baseline when the cell is flushed with the polyelectrolyte-free solution. Similar behavior is observed for other molecular masses, whereby the concentration at which the optical matching point occurs at a similar NaPSS concentration.

These features are most uncommon in polyelectrolyte adsorption experiments.<sup>5–8</sup> First, the reflectivity signal is normally positive and is proportional to the adsorbed amount of the polyelectrolyte. Second, polyelectrolyte adsorption is typically irreversible, whereby the baseline cannot be recovered after the adsorption experiment.<sup>6,33</sup>

These surprising observations can be quantitatively interpreted by assuming the existence of a polyelectrolyte-free depletion layer next to the interface. This situation was implemented by means of an optical model, which assumes that two homogeneous slabs are sandwiched between the silicon wafer and the NaPSS bulk solution, see Figure 1b. The first slab corresponds to the solid silica coating, which was thermally grown on the silicon wafer, and for which, the thickness is accurately known. The second slab corresponds to the fluid polyelectrolyte-free depletion layer and is assumed to consist of pure water with a well-defined but unknown thickness. The refractive index of the NaPSS bulk solution is calculated from the measured refractive index increment, while the refractive indices of water, silica, and silicon are known, and they are 1.335, 1.461, and  $4.132 + 0.033i$  at 532 nm, respectively.<sup>31,32</sup> The same wafer in contact with pure water is taken as reference, see Figure 1c. The refractive index of the bulk solution is used to correct for the refraction of the light inside the cell. This results in a change in the incidence angle. The optical reflectivity signal for this model is calculated in a standard fashion with the Abeles matrix method.<sup>36–38</sup>

Figure 3 shows the expected reflectivity signal versus the thickness of the polyelectrolyte-free depletion layer. One observes that the signal is strongly dependent on the silica coating thickness, see Figure 3a. Furthermore, the signal decreases with increasing layer thickness, and it is approximately proportional to the NaPSS concentration, see Figure 3b. Thus the presence of a depletion layer may indeed explain



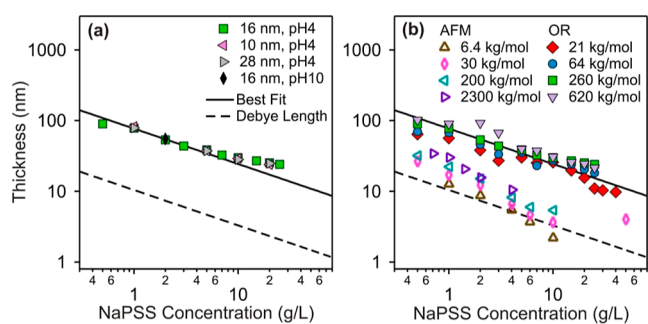
**Figure 3.** (a) Calculated reflectivity signal versus the thickness of the polyelectrolyte-free depletion layer for NaPSS concentration of 5 g/L and different thicknesses of the silica coating as indicated. (b) Normalized reflectivity signal by the NaPSS concentration for a silica coating of a thickness of 16 nm.

the unusual negative reflectivity signal. This assumption equally rationalizes the observed reversibility in these experiments. Because no polyelectrolyte adsorption occurs, no irreversibility is expected.

To demonstrate that the two-slab model is indeed able to explain the experimental data quantitatively, we have extracted the thickness of the depletion layer from the experiments shown in Figure 2 and some additional ones. This thickness is determined from the two-slab model by inverting the calculated relations shown in Figure 3, by taking the appropriate polyelectrolyte concentration and the thickness of the silica layer into account. From this analysis, we find that the depletion layer thickness is the same for the different substrates, see Figure 4a. This agreement strongly supports the present interpretation and the existence of a polyelectrolyte-free depletion layer next to the interface.

The depletion layer thickness decreases with concentration. This aspect is illustrated in Figure 4a, whereby, Figure 4b also shows the minor influence of the molecular mass. The thickness decreases as an inverse square root of the NaPSS concentration as illustrated by the best fit with this law. This thickness can be compared with the expected Debye length, which is calculated from the concentrations of the free  $\text{Na}^+$  ions. The fraction of free ions of 35% was calculated from the ion condensation theory proposed by Manning.<sup>30,39,40</sup> While the Debye length shows the same inverse square root law, the measured thickness is found to be larger by about a factor of seven. Moreover, the fitted fraction of free ions was found to be ca. 1% for optical reflectometry data. The observed discrepancies from the Manning theory are probably related to the high PSS concentrations used in this study.

One may further compare the present findings with previous direct force measurements between two symmetric silica surfaces in NaPSS solutions with the AFM. At larger separation distances, one observes weak oscillatory force profiles.<sup>26–30</sup> At



**Figure 4.** Thickness of the polyelectrolyte-free depletion layer vs the NaPSS concentration. The solid lines are the best fit of the present measurements with the inverse square root law, and the dashed line is the Debye length estimated from the concentration of free  $\text{Na}^+$  ions. (a) Resulting depletion layer thickness is determined from the data shown in Figure 2 for different thicknesses of the silica coating as indicated. (b) Comparison of the present data from optical reflectivity of different molecular mass with earlier results based on direct force measurements with the atomic force microscopy.<sup>30</sup>

shorter distances, very strong repulsion sets in.<sup>30</sup> The respective force profile decays slowly at first, then very rapidly, and subsequently, the force becomes negative, which signals the onset of the first oscillation. Moazzami-Gudarzi et al.<sup>30</sup> were able to quantify this characteristic profile with the Poisson-Boltzmann theory for a highly asymmetric electrolyte, whereby the multivalent co-ions mimicked the polyelectrolyte molecules. These calculations indeed confirmed that all multivalent co-ions were excluded from this region. Moreover, the characteristic shape of these force profiles suggests that the gap remains polyelectrolyte-free up to characteristic distances, where the polyelectrolytes enter the gap. This distance corresponds to the maximum thickness of the polyelectrolyte-free depletion gap and can be easily estimated from the first zero of the force curve. This distance reflects twice the depletion layer thickness for an isolated interface. These distances are also compared with the present reflectivity measurements, shown in Figure 4b.

The fitting of the AFM measurements gives the inverse 0.4 concentration dependence and the fraction of free ions equal to 2%. Additionally, the respective thicknesses are clearly smaller. The reason for this discrepancy could be related to the different nature of the silica substrates. While the present oxidized silicon block is very smooth, the silica substrate used for the force measurements is rougher, and the asperities could lead to a thinner layer. Another explanation for this difference could be that the box profile used to interpret the present reflectivity measurements is only approximate. However, in spite of these discrepancies, the depletion thickness obtained with the two entirely different techniques remains similar and shows a very similar concentration dependence. The combination of these techniques, thus, provides unambiguous evidence for the existence of the polyelectrolyte-free depletion layer.

Our findings might be even more interesting in the light of our previous study on the particle-free layer in suspensions of charged nanoparticles next to a like-charged solid substrate.<sup>41</sup> In that study, we used three different techniques (optical reflectivity, quartz crystal microbalance, and AFM) to measure the depletion of nanoparticles (silica and sulfate latex) near silica substrate. First, similar inverse square root dependence of the measured layer thickness on the particle volume fraction

was found. Second, results obtained from the three mentioned techniques differed even by 30%, showing similar discrepancies as observed in this study.

## 4. CONCLUSIONS

We have demonstrated that salt-free polyelectrolyte solutions next to like-charged interfaces form a polyelectrolyte-free depletion layer of several tenths of nanometers in thickness. The thickness of this depletion layer decreases as the inverse square root of the polyelectrolyte concentration, but the actual values exceed the expected Debye length substantially. The present measurements, which feature unusual negative signals and optical matching points, were carried out with optical reflectivity but can be consistently interpreted with an optical two-slab model. These results clearly provide independent evidence for the existence of a polyelectrolyte-free depletion layer, as previously suggested on the basis of direct force measurements with the AFM. The presence of such polyelectrolyte-free depletion layers is of substantial importance for adsorption studies of like-charged polyelectrolytes because such adsorption processes will be accompanied by the depletion effects described here.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- Bolto, B.; Gregory, J. Organic Polyelectrolytes in Water Treatment. *Water Res.* **2007**, *41*, 2301–2324.
- Chen, X.; Huang, R.; Pelton, R. The Reinforcement of Calcium Carbonate Filled Papers with Phosphorus-Containing Polymers. *Ind. Eng. Chem. Res.* **2005**, *44*, 2078–2085.
- Pochard, I.; Labbez, C.; Nonat, A.; Vija, H.; Jönsson, B. The Effect of Polycations on Early Cement Paste. *Cem. Concr. Res.* **2010**, *40*, 1488–1494.
- Szilagyi, I.; Trefalt, G.; Tiraferri, A.; Maroni, P.; Borkovec, M. Polyelectrolyte Adsorption, Interparticle Forces, and Colloidal Aggregation. *Soft Matter* **2014**, *10*, 2479–2502.
- van Duijvenbode, R. C.; Rietveld, I. B.; Koper, G. J. M. Light Reflectivity Study on the Adsorption Kinetics of Poly(Propylene Imine) Dendrimers on Glass. *Langmuir* **2000**, *16*, 7720–7725.

- (6) Popa, I.; Cahill, B. P.; Maroni, P.; Papastavrou, G.; Borkovec, M. Thin Adsorbed Films of a Strong Cationic Polyelectrolyte on Silica Substrates. *J. Colloid Interface Sci.* **2007**, *309*, 28–35.
- (7) Kosior, D.; Morga, M.; Maroni, P.; Cieřla, M.; Adamczyk, Z. Formation of Poly-L-Lysine Monolayers on Silica: Modeling and Experimental Studies. *J. Phys. Chem. C* **2020**, *124*, 4571–4581.
- (8) Hansupalak, N.; Santore, M. M. Sharp Polyelectrolyte Adsorption Cutoff Induced by a Monovalent Salt. *Langmuir* **2003**, *19*, 7423–7426.
- (9) Xie, F.; Nylander, T.; Piculell, L.; Utsel, S.; Wågberg, L.; Åkesson, T.; Forsman, J. Polyelectrolyte Adsorption on Solid Surfaces: Theoretical Predictions and Experimental Measurements. *Langmuir* **2013**, *29*, 12421–12431.
- (10) Morga, M.; Adamczyk, Z. Monolayers of cationic polyelectrolytes on mica - Electrokinetic studies. *J. Colloid Interface Sci.* **2013**, *407*, 196–204.
- (11) Decher, G.; Schlenoff, J. *Multilayer Thin Films*; WILEY-VCH GmbH & Co. KGaA: Weinheim, 2002.
- (12) Decher, G. Fuzzy Nanoassemblies: Toward Layered Polymeric Multicomposites. *Science* **1997**, *277*, 1232–1237.
- (13) Morga, M.; Adamczyk, Z.; Kosior, D.; Oćwieja, M. Hematite/Silica Nanoparticle Bilayers on Mica: AFM and Electrokinetic Characterization. *Phys. Chem. Chem. Phys.* **2018**, *20*, 15368–15379.
- (14) Ariga, K.; Lvov, Y.; Decher, G. There Is Still Plenty of Room for Layer-by-Layer Assembly for Constructing Nanoarchitectonics-Based Materials and Devices. *Phys. Chem. Chem. Phys.* **2022**, *24*, 4097–4115.
- (15) Schlenoff, J. B.; Dubas, S. T.; Farhat, T. Sprayed Polyelectrolyte Multilayers. *Langmuir* **2000**, *16*, 9968–9969.
- (16) Izquierdo, A.; Ono, S. S.; Voegel, J.-C.; Schaaf, P.; Decher, G. Dipping versus Spraying: Exploring the Deposition Conditions for Speeding Up Layer-by-Layer Assembly. *Langmuir* **2005**, *21*, 7558–7567.
- (17) Kolasinska, M.; Krastev, R.; Gutberlet, T.; Warszynski, P. Layer-by-Layer Deposition of Polyelectrolytes. Dipping versus Spraying. *Langmuir* **2009**, *25*, 1224–1232.
- (18) Li, M.; Ishihara, S.; Akada, M.; Liao, M.; Sang, L.; Hill, J. P.; Krishnan, V.; Ma, Y.; Ariga, K. Electrochemical-Coupling Layer-by-Layer (ECC-LbL) Assembly. *J. Am. Chem. Soc.* **2011**, *133*, 7348–7351.
- (19) Plausinaitis, D.; Sinkevicius, L.; Mikoliunaite, L.; Plausinaitiene, V.; Ramanaviciene, A.; Ramanavicius, A. Electrochemical polypyrrole formation from pyrrole “adlayer”. *Phys. Chem. Chem. Phys.* **2017**, *19*, 1029–1038.
- (20) Plausinaitis, D.; Balciunas, D.; Ramanavicius, A. Synthesis of Heterogeneously Conductive Polypyrrole Layer from Non-Aqueous Solution Using The Double-Step Potential Technique. *J. Electrochem. Soc.* **2020**, *167*, 086510.
- (21) Dobrynin, A. V.; Rubinstein, M. Effect of Short-Range Interactions on Polyelectrolyte Adsorption at Charged Surfaces. *J. Phys. Chem. B* **2003**, *107*, 8260–8269.
- (22) Pastré, D.; Hamon, L.; Landousy, F.; Sorel, I.; David, M.-O.; Zozime, A.; Le Cam, E.; Piétremont, O. Anionic Polyelectrolyte Adsorption on Mica Mediated by Multivalent Cations: A Solution to DNA Imaging by Atomic Force Microscopy under High Ionic Strengths. *Langmuir* **2006**, *22*, 6651–6660.
- (23) Tiraferri, A.; Maroni, P.; Borkovec, M. Adsorption of Polyelectrolytes to Like-Charged Substrates Induced by Multivalent Counterions as Exemplified by Poly(Styrene Sulfonate) and Silica. *Phys. Chem. Chem. Phys.* **2015**, *17*, 10348–10352.
- (24) Maroni, P.; Montes Ruiz-Cabello, F. J. M.; Tiraferri, A. Studying the role of surface chemistry on polyelectrolyte adsorption using gold-thiol self-assembled monolayer with optical reflectivity. *Soft Matter* **2014**, *10*, 9220–9225.
- (25) Luque-Caballero, G.; Martín-Molina, A.; Quesada-Pérez, M. Polyelectrolyte Adsorption onto Like-Charged Surfaces Mediated by Trivalent Counterions: A Monte Carlo Simulation Study. *J. Chem. Phys.* **2014**, *140*, 174701.
- (26) Milling, A. J. Depletion and Structuring of Sodium Poly(styrenesulfonate) at the Silica–Water Interface. *J. Phys. Chem.* **1996**, *100*, 8986–8993.
- (27) Biggs, S.; Prieve, D. C.; Dagastine, R. R. Direct Comparison of Atomic Force Microscopic and Total Internal Reflection Microscopic Measurements in the Presence of Nonadsorbing Polyelectrolytes. *Langmuir* **2005**, *21*, 5421–5428.
- (28) Théodoly, O.; Tan, J. S.; Ober, R.; Williams, C. E.; Bergeron, V. Oscillatory Forces from Polyelectrolyte Solutions Confined in Thin Liquid Films. *Langmuir* **2001**, *17*, 4910–4918.
- (29) Üzüüm, C.; Christau, S.; von Klitzing, R. Structuring of Polyelectrolyte (NaPSS) Solutions in Bulk and under Confinement as a Function of Concentration and Molecular Weight. *Macromolecules* **2011**, *44*, 7782–7791.
- (30) Moazzami-Gudarzi, M.; Kremer, T.; Valmacco, V.; Maroni, P.; Borkovec, M.; Trefalt, G. Interplay between Depletion and Double-Layer Forces Acting between Charged Particles in Solutions of Like-Charged Polyelectrolytes. *Phys. Rev. Lett.* **2016**, *117*, 088001.
- (31) Schinke, C.; Christian Peest, P.; Schmidt, J.; Brendel, R.; Bothe, K.; Vogt, M. R.; Kröger, I.; Winter, S.; Schirmacher, A.; Lim, S.; et al. Uncertainty Analysis for the Coefficient of Band-to-Band Absorption of Crystalline Silicon. *AIP Adv.* **2015**, *5*, 067168.
- (32) Malitson, I. H. Interspecimen Comparison of the Refractive Index of Fused Silica\*. *J. Opt. Soc. Am.* **1965**, *55*, 1205–1209.
- (33) Porus, M.; Maroni, P.; Borkovec, M. Highly-Sensitive Reflectometry Setup Capable of Probing the Electrical Double Layer on Silica. *Sens. Actuators, B* **2010**, *151*, 250–255.
- (34) Böhmer, M. R.; van der Zeeuw, E. A.; Koper, G. J. M. Kinetics of Particle Adsorption in Stagnation Point Flow Studied by Optical Reflectometry. *J. Colloid Interface Sci.* **1998**, *197*, 242–250.
- (35) Kleimann, J.; Lecoultré, G.; Papastavrou, G.; Jeanneret, S.; Galletto, P.; Koper, G. J. M.; Borkovec, M. Deposition of Nanosized Latex Particles onto Silica and Cellulose Surfaces Studied by Optical Reflectometry. *J. Colloid Interface Sci.* **2006**, *303*, 460–471.
- (36) Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; North Holland Publishing Company: Amsterdam, 1977.
- (37) Koper, G. J. M. Optical Properties of Colloidal Films. *Colloids Surf., A* **2000**, *165*, 39–57.
- (38) Kooij, E. S.; Wormeester, H.; Brouwer, E. A. M.; van Vroonhoven, E.; van Silfhout, A.; Poelsema, B. Optical Characterization of Thin Colloidal Gold Films by Spectroscopic Ellipsometry. *Langmuir* **2002**, *18*, 4401–4413.
- (39) Manning, G. S. Limiting Laws and Counterion Condensation in Polyelectrolyte Solutions I. Colligative Properties. *J. Chem. Phys.* **1969**, *51*, 924–933.
- (40) Trizac, E.; Téllez, G. Onsager-Manning-Oosawa Condensation Phenomenon and the Effect of Salt. *Phys. Rev. Lett.* **2006**, *96*, 038302.
- (41) Kosior, D.; Gvaramia, M.; Scarratt, L. R. J.; Maroni, P.; Trefalt, G.; Borkovec, M. Thickness of the Particle-Free Layer near Charged Interfaces in Suspensions of like-Charged Nanoparticles. *Soft Matter* **2021**, *17*, 6212–6224.