

Article

Insights into $\text{Na}^+/\text{Ca}^{2+}$ Ion Exchange on Poly(4-styrenesulfonate) Anion in Bulk Solution and Adsorbed on TiO_2 Nanoparticles

Ivor Vavra Plavšić ¹, Filip Margetić ¹, Juraj Nikolić ^{1,†} , Klemen Bohinc ² , Tin Klaić ^{1,*}  and Tajana Begović ^{1,*}
¹ Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102A, 10000 Zagreb, Croatia

² Faculty of Health Sciences, University of Ljubljana, 1000 Ljubljana, Slovenia

* Correspondence: tin.klagic@chem.pmf.unizg.hr (T.K.); tajana@chem.pmf.unizg.hr (T.B.)

† Current address: Department for Materials Synthesis, Jožef Stefan Institute, Jamova Cesta 39, 1000 Ljubljana, Slovenia.

Abstract

This study investigates $\text{Na}^+/\text{Ca}^{2+}$ ion exchange on poly(4-styrene sulfonate) anion (PSS) chains both in solution and PSS adsorbed onto TiO_2 nanoparticles to gain deeper insights into the behavior of surface-bound polyelectrolytes and evaluate their potential as ion exchangers. Nanoparticle characterization was performed using electrokinetic light scattering (ELS) and a particle charge detector. PSS adsorption on TiO_2 nanoparticles was evaluated by spectrophotometry and ELS. Subsequent ion exchange was investigated *via* isothermal titration calorimetry, ion-selective electrode potentiometry, and dynamic light scattering (DLS). The $\text{Na}^+/\text{Ca}^{2+}$ exchange on PSS chains was found to be an endothermic process, indicating that the favorable binding and rehydration effects are insufficient to compensate for the strongly unfavorable Ca^{2+} ion dehydration. In solution, the $\text{Na}^+/\text{Ca}^{2+}$ exchange on PSS is more pronounced than in the TiO_2 /PSS system. Conformational changes in the PSS polymer and surface modifications of the nanoparticles as a function of Ca^{2+} ion concentration were indirectly investigated using DLS. The calculated $\text{Na}^+/\text{Ca}^{2+}$ ion-exchange capacity was 2.99 mmol/g for PSS in solution and 0.26 mmol/g for the TiO_2 /PSS system. These findings suggest that adsorbing PSS onto TiO_2 nanoparticles substantially decreases the ion-exchange capacity, probably due to the conformational constraints imposed by surface immobilization. However, potential practical implementation will require a comprehensive evaluation of the ion selectivity and regeneration efficiency of these PSS-based materials.

Keywords: ion exchange; poly(4-styrenesulfonate) anion; TiO_2 ; adsorption; surface properties



Academic Editor: Spencer E. Taylor

Received: 27 July 2026

Revised: 17 September 2026

Accepted: 21 September 2026

Published: 23 September 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

Polyelectrolytes are polymers whose constitutional units bear ionic or ionizable groups that dissociate in polar solvents such as water. According to the sign of charge produced on the constitutional units after dissociation, polyelectrolytes are traditionally classified as polycations or polyanions. In addition, polyelectrolytes may be either strong or weak. The ionization of the charges on constitutional units of strong polyelectrolytes in water is most often presumed to be complete and independent of composition of the solution. On the other hand, the degree of ionization of weak polyelectrolytes depends on the pH of a solution. Well-known examples of polyelectrolytes include biopolymers (e.g., chitosan, pectin, heparin, hyaluronic acid, xanthan gum, etc.) and synthetic polymers such as poly(diallyldimethylammonium chloride), poly(allyamine hydrochloride),

poly(ethyleneimine), poly(acrylic acid) and poly(methacrylic acid). These macromolecules are used or have the potential to be used as flocculants [1], detergents [2], superabsorbents [3], corrosion inhibitors [4], membranes [5], anti-fouling coatings [6], etc. The wide application potential of polyelectrolytes lies in the fact that they possess unique physicochemical properties that combine the properties of polymers and those of electrolytes. Therefore, they are the subject of intensive theoretical and experimental investigations. Despite the progress in this field of research, several authors of review papers have indicated that further fundamental studies are needed for a deeper understanding of polyelectrolyte behaviour in solutions and at surfaces [7–9]. This additional understanding could greatly improve their application possibilities.

As mentioned before, the electrolyte groups on polyelectrolyte chain molecules can dissociate in water, leaving charges on the polymer backbone through the release of counterions. The dissociation of a polyelectrolyte molecule is accompanied by the presence of oppositely charged counterions that compensate for the charge on the constitutional unit. The extent of the counterion binding to polyelectrolyte units in solution was generally found to depend on the nature and charge of the polyelectrolyte constitutional unit, as well as on the nature and charge of counterions, and the solvent used [10–12]. Among these parameters, the ion charge plays an important role in the application of polyelectrolytes as water softeners. Commonly, polyelectrolytes are used in the process of water softening in the form of ion-exchange resins. The basic mechanism of action of polyelectrolyte ion-exchange resins is the substitution of monovalent ions condensed to polyelectrolyte units with divalent ions present in tap water (primarily Ca^{2+} and Mg^{2+}) [13]. The replacement of monovalent cations with divalent ones in polyelectrolyte aqueous solution is known to have a strong influence on the conformation of polyelectrolytes, and thus on the properties of the polyelectrolyte solutions. In the case of divalent ions, monomer units of polyelectrolytes are well-screened with ions, and polymer molecules adopt a coiled conformation. On the contrary, in the case of monovalent ions, polyelectrolytes are present in solution in a more extended rod-like form because charge screening is less pronounced [14–16].

While the effect of divalent ions on the behaviour of polyelectrolytes in solution has been extensively studied from experimental [14,17–19], computational [20–23], and theoretical [24–26] points of view, there is a lack of data concerning the influence of divalent ions on the behaviour of polyelectrolytes adsorbed at the solid–liquid interface. When present on the surface, the segments of the polyelectrolyte chain typically adopt train, loop, or tail conformation. The segments in train conformation are electrostatically bound to the surface and therefore not available for ion exchange. On the other hand, polymer segments in loop and tail conformation protrude from the surface and are accessible to ions [27]. The question arises whether ion substitution is as effective for free polyelectrolytes in solution as for polyelectrolytes adsorbed on the surface. The answer to this question is of significant importance both from a fundamental and applied point of view. In particular, understanding the influence of the surface on polyelectrolyte ion exchange reactions can help in developing strategies to increase the efficiency of water softeners based on polyelectrolytes.

This study aims to investigate and compare the substitution of Na^+ ions with Ca^{2+} ions on poly(4-styrenesulfonate) anions (PSS) when the polymer chains are free in solution and adsorbed to the surface of TiO_2 nanoparticles. The PSS (Figure 1) was selected for this study because it is a rigorously studied strong polyanion that is a common component of many cation-exchange resins used for water softening [28]. The ion-exchange resins of this kind are typically prepared by introducing sulfonic groups to the surface of water-insoluble polystyrene microspheres through a sulfonation reaction [29,30]. However, we did not find any study that specifically investigates the possibility of using PSS adsorbed to the surface of nanoparticles as a water softener. Also, there have been no reported efforts to compare

the ion-exchange capabilities of PSS ions dissolved in water with those attached to the surface of nanoparticles.

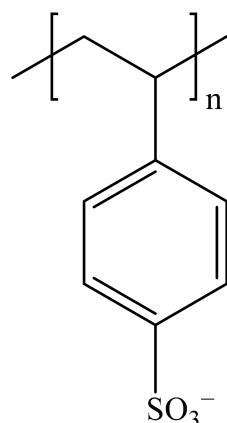


Figure 1. Chemical structure of poly(4-styrenesulfonate) anion.

While several types of nanoparticles were considered as potential carriers for PSS, titanium dioxide (TiO_2) was ultimately selected. TiO_2 nanoparticles feature a well-established research background and hold strong potential for water treatment applications due to their biocompatibility, low cost, and high availability. Because the surface charge density of TiO_2 nanoparticles strongly depends on the solution pH, ionic strength, as well as nanoparticle morphology and size [31–33], we conducted particle charge detector (PCD) and electrophoretic light scattering (ELS) measurements prior to investigating ion exchange reactions. To study these reactions, we employed isothermal titration calorimetry (ITC), potentiometry, and dynamic light scattering (DLS). This multi-method approach allowed us to observe the $\text{Na}^+/\text{Ca}^{2+}$ exchange reaction on PSS in the solution and adsorbed to TiO_2 surface from different analytical perspectives, providing comprehensive insights into the studied systems.

2. Materials and Methods

2.1. Materials

Sodium poly(4-styrene sulfonate) (NaPSS , $M_w = 70,000 \text{ g mol}^{-1}$) was obtained from Sigma Aldrich, Merck (Darmstadt, Germany). Poly(*N*-ethyl-4-vinylpyridinium) bromide (PE4VPBr) was synthesized by ethylating the commercially available poly(4-vinylpyridine) ($M_w \approx 60,000 \text{ g mol}^{-1}$), obtained from Sigma Aldrich (Darmstadt, Germany), as described by Jukić et al. [34] NaCl and CaCl_2 used as background electrolytes were obtained from GramMol (Zagreb, Croatia) and Fluka (Seelze, Germany), respectively. HCl and NaOH aqueous solutions (1 mol dm^{-3} and 0.1 mol dm^{-3}) used for pH adjustments and titrations were obtained from Merck (Darmstadt, Germany).

TiO_2 nanoparticles (99.9% purity) were obtained from GetNanoMaterials (Saint-Cannat, France). As reported by Jukić et al. [35], the nanoparticles consist of pure anatase phase (confirmed by XRPD analysis) and have a specific surface area of $s = 72.1 \text{ m}^2/\text{g}$ (measured via BET analysis). The nanoparticles were purified by dispersing 1.0 g of the powder in 1.0 dm^3 of Milli-Q water. The suspension pH was adjusted to $\text{pH} \approx 6.5$, which is the previously determined isoelectric point of TiO_2 [35], under vigorous magnetic stirring. The suspension was allowed to sediment for 24 h, after which the supernatant was decanted, and its electrical conductivity was measured. This rinsing process was repeated with water until the supernatant conductivity dropped below $10 \mu\text{S cm}^{-1}$.

All experiments were performed using Milli-Q water (total carbon < 3 ppb and conductivity < 0.055 $\mu\text{S cm}^{-1}$) that was produced by Advantage A10 Water Purification System (Merck Millipore, Darmstadt, Germany).

2.2. Characterization of TiO_2 Nanoparticles

2.2.1. Particle Charge Detector Measurements

PCD is a valuable instrument for obtaining the surface charge density of colloidal particles. Nowadays, the PCD is widely used in the water treatment, ceramic and paper-making industry. Unlike measuring zeta potential by ELS, the PCD technique is relatively simple and requires no additional electrokinetic model assumptions. In principle, the PCD technique measures surface charge density by combining a streaming potential measuring cell with polyelectrolyte titration. Polyelectrolytes used in the PCD technique should have functional groups with strong basic or acidic character to ensure that nearly all counterions are dissociated. In the PCD setup (BTG Instruments, GmbH, Hessling, Germany), the oscillation of a polytetrafluoroethylene (PTFE) piston drives the flow of fluid and mobile counterions, generating a streaming potential across two electrodes. Titrating the suspension with an oppositely charged polyelectrolyte leads to its adsorption onto particles, thereby neutralizing the particle charge. This charge compensation alters the mobility of nearby counterions, shifting the measured PCD potential toward zero. By monitoring the PCD potential, several parameters can be determined, including the surface charge density (σ_0) and the point of zero charge (pH_{pzc}). Specifically, the volume of polyelectrolyte titrant (V) required to reach the zero point of the PCD titration curve corresponds to surface charge neutralization, allowing the calculation of the surface charge density via Equation (1)

$$\sigma_0 = \frac{n_m F}{A} = \frac{c_m V F}{ms} \quad (1)$$

where n_m and c_m are the amount and the molar concentration of polyelectrolyte monomer units, V is the volume of polyelectrolyte solution required to reach the zero point, F is the Faraday constant, and A is the total surface area of the particles calculated from the mass of the particles (m) and the specific surface area (s) [36].

For the purpose of PCD measurements, TiO_2 nanoparticles were dispersed in an aqueous NaCl solution ($c = 10^{-3} \text{ mol dm}^{-3}$) to yield a final particle mass concentration of 2.0 g dm^{-3} . The suspension pH was adjusted using HCl or NaOH to prepare ten distinct samples spanning a pH range from 3 to 11. For each measurement, the suspension was transferred into the PTFE cell of the PCD and titrated with either NaPSS ($c_m = 2 \text{ mmol dm}^{-3}$) or PE4VPBr ($c_m = 1 \text{ mmol dm}^{-3}$) solutions, while monitoring the potential difference between the electrodes.

To assess whether particle concentration influences surface charge density, additional measurements were performed by varying the nanoparticle mass concentration under constant pH and ionic strength. Four TiO_2 suspensions were prepared with mass concentrations ranging from 0.5 to 2.0 g dm^{-3} at a fixed pH of 7.0 and a background electrolyte (NaCl) concentration of $10^{-3} \text{ mol dm}^{-3}$. These suspensions were sequentially transferred to the PCD cell and titrated with a PE4VPBr solution ($c_m = 1 \text{ mmol dm}^{-3}$).

2.2.2. Hydrodynamic Diameter and Zeta Potential of TiO_2 Nanoparticles

To investigate the effect of CaCl_2 on the pH_{iep} of the TiO_2 nanoparticles, the suspensions containing 0.1 g dm^{-3} of TiO_2 nanoparticles in CaCl_2 background electrolyte were titrated with NaOH solution ($c = 0.1 \text{ mol dm}^{-3}$). The nanoparticle size and ζ -potential were determined at predetermined pH values via dynamic and electrophoretic light scattering in Nano Series Disposable folded capillary cells (code: DTS1070) using Zetasizer Ultra

(Malvern Panalytical, Malvern, UK). These measurements were conducted across three distinct background electrolyte concentrations at 25 °C.

2.3. Adsorption Experiments

For adsorption experiments, the required amount of NaPSS was dissolved in water to prepare solutions with monomer concentration ranging from 5×10^{-3} to 100 mmol dm^{-3} . The solution pH was adjusted to pH = 3.0 prior to adding TiO_2 nanoparticles using HCl ($c = 1 \text{ mol dm}^{-3}$), and the ionic strength was maintained at $10^{-3} \text{ mol dm}^{-3}$ by adding NaCl. Adsorption was carried out in centrifuge tubes by mixing 12 mg of TiO_2 nanoparticles with 12 mL of the respective NaPSS solution ($\gamma(\text{TiO}_2) = 1.0 \text{ g dm}^{-3}$). Based on prior mass titration studies for TiO_2 particles with similar specific surface areas (Ref. [37]), an addition of 1 g dm^{-3} does not noticeably alter the solution pH, particularly in polyelectrolyte media, thereby maintaining a pH of approximately 3.0 throughout mixing. The suspensions were agitated on a rotational mixer for 18 h. Subsequently, a 4 mL aliquot of each suspension was centrifuged at $10,976 \times g$ for 60 min in a Centric 400 R centrifuge (Domel, Železniki, Slovenia). The supernatant was removed, and the equilibrium PSS concentration in the supernatant was determined by measuring its absorbance at 225 nm and 25 °C in a 1 cm cuvette using an Cary 5000 spectrophotometer (Agilent Technologies, Santa Clara, CA, USA). The surface concentrations of the polyelectrolyte were calculated from the determined amount of adsorbed monomers, n_m , and the available surface area of the TiO_2 nanoparticles A calculated from the mass of the particles, m , and the specific surface area, s

$$\Gamma = \frac{n_m}{A} = \frac{n_m}{ms}. \quad (2)$$

The sedimented nanoparticles were resuspended in a NaCl solution ($c = 10^{-3} \text{ mol dm}^{-3}$, pH = 3.0) so that the particle concentration was 0.1 g dm^{-3} and their size and ζ -potential were determined using Zetasizer Ultra (Malvern Panalytical, Malvern, UK).

2.4. Ion Exchange Experiments

2.4.1. Isothermal Titration Calorimetry

Isothermal titration calorimetry measurements were performed using a MicroCal VP-ITC (Malvern Panalytical, Malvern, UK). CaCl_2 solution ($c = 0.2 \text{ mol dm}^{-3}$) was injected stepwise into the reaction cell containing 1.4 mL of NaPSS solution ($c_m = 5 \text{ mmol dm}^{-3}$) every 8 min (11 additions of 8 μL , followed by 3 additions of 15 μL , followed by 6 additions of 20 μL). The temperature was 25 °C and the rate of stirring was 307 rpm. The raw enthalpy changes were corrected for the heat of dilution of CaCl_2 , which was determined in an analogous blank titration by injecting a CaCl_2 solution ($c = 0.2 \text{ mol dm}^{-3}$) into pure water. The dilution of the NaPSS solution due to the addition of the titrant was disregarded given that the total NaPSS monomer concentration decreases by only 15% by the end of the ITC experiment relative to the initial concentration. Each calorimetric experiment was repeated three times.

2.4.2. Potentiometric Titrations

A reaction cell was thermostated at 25 °C and filled with 30 mL of NaPSS solution ($c_m = 10 \text{ mmol dm}^{-3}$). The system was equipped with a sodium ion-selective electrode (Na-ISE, 6.0501.100, Metrohm, Herisau, Switzerland), a combined calcium ion-selective electrode (Ca-ISE, 6.0510.100, Metrohm, Herisau, Switzerland), and a combined pH electrode (6.0234.100, Metrohm, Herisau, Switzerland) whose internal $\text{Ag} | \text{AgCl}$ reference electrode served also as the reference electrode for the Na-ISE. Before titration experiments, the Na-ISE and Ca-ISE were calibrated using NaCl and CaCl_2 solutions by standard analytical procedures. More details about the calibration of Na-ISE and Ca-ISE, as well as

examples of the calibration diagrams (Figures S7 and S8), are given in the Supplementary Information. During titrations, a 0.1 mol dm^{-3} CaCl_2 solution was added stepwise to the reaction cell. After each addition, the NaPSS solution was briefly stirred using a magnetic stirrer, and then the electromotive forces (open circuit potentials) of the cells comprising the aforementioned electrodes were measured using 913 pH meters (Metrohm, Herisau, Switzerland). The relative activities of Na^+ , Ca^{2+} , and H^+ (pH) ions were determined from the measured electromotive forces and obtained calibration curves. Afterwards, the analogous titrations were performed using a suspension of PSS-coated TiO_2 nanoparticles ($\gamma = 1.0 \text{ g dm}^{-3}$).

2.4.3. Dynamic Light Scattering Measurements

Solutions containing NaPSS ($c_m = 10 \text{ mmol dm}^{-3}$) and varying concentrations of CaCl_2 ($c = 0$ to 1 mol dm^{-3}) were prepared and thoroughly mixed on a vortex mixer (VORTEX 1 S000, IKA, Staufen, Germany). The hydrodynamic diameter (D_h) of PSS chains was determined via dynamic light scattering in Nano Series Disposable folded capillary cells (code: DTS1070) using Zetasizer Ultra (Malvern Panalytical, Malvern, UK). Measurements were performed in triplicate with 30 runs in each repetition. The detector angle was 173° , the dispersant viscosity was set at 0.8872 cP , the dispersant refractive index at 1.33 , and the material refractive index at 1.37 . The general purpose model was used for data analysis. Analogous experiments were performed by substituting the NaPSS solution with a suspension of PSS-coated TiO_2 nanoparticles ($\gamma = 1.0 \text{ g dm}^{-3}$). The experiments were designed so that the concentration of monomer units adsorbed on TiO_2 particles ($c_{m,ads}(\text{PSS}) = 10 \text{ mmol dm}^{-3}$) was equal to that in the solution. The reported D_h values correspond to the maxima of the number-based particle distribution.

3. Results

3.1. Surface Charge of TiO_2 Nanoparticles

The titration curves obtained by measuring the streaming potential difference via the PCD technique are shown in Figures S1–S4 (Supplementary Information). The surface charge densities (σ_0) for TiO_2 , calculated using Equation (1), at the boundary between the solid particle surface and the aqueous phase are presented in Figure 2. The effect of the mass concentration of TiO_2 nanoparticles on the surface charge density determined by the PCD method was investigated in separate experiments, and it was found that the particle mass concentration does not significantly affect the obtained values (Figure S5 in the Supplementary Information).

The surface charge densities of TiO_2 particles are consistent in order of magnitude with previously reported data obtained using the potentiometric mass titration [37–39]. The TiO_2 surface charge density changes from positive to negative values with increasing pH. This charge reversal occurs at around $\text{pH} \approx 5$, as can be seen from Figure 2, which corresponds to the point of zero charge, pH_{pzc} . This value is slightly lower than the isoelectric point ($\text{pH}_{\text{iep}} = 6.5$) previously reported for these particles by Jukić et al. [35] It should be noted that determining surface charge density at the 0-plane by PCD titration, potentiometric mass titration, and acid–base titration relies on surface charge compensation by counterions. In contrast, determining electrokinetic potential involves measuring the electrophoretic mobility of moving colloid particles along with their bounded ions in an external electric field.

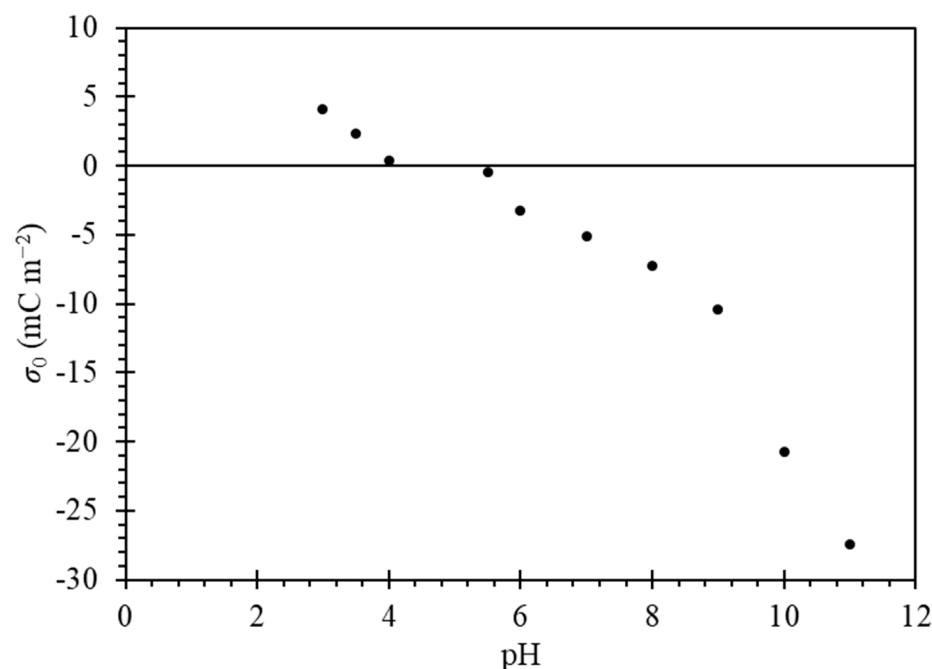


Figure 2. Effect of pH on surface charge density of TiO₂ nanoparticles ($\gamma = 2.0 \text{ g dm}^{-3}$) obtained using the PCD; $c(\text{NaCl}) = 10^{-3} \text{ mol dm}^{-3}$; $\theta = 25^\circ \text{C}$.

3.2. Effect of Ca²⁺ Ion Adsorption on Properties of TiO₂ Nanoparticles

The electrokinetic potential and hydrodynamic diameter of TiO₂ nanoparticles were measured over a broad pH range using CaCl₂ as a background electrolyte at several different concentrations. The results are presented in Figure 3. Note that analogous measurements were previously published [35] for the same TiO₂ nanoparticles using NaCl as the background electrolyte.

Across all CaCl₂ concentrations, the isoelectric point occurs at a pH between 6.5 and 7.0 (Figure 3a), shifting slightly with increasing electrolyte concentration. The result at lower CaCl₂ concentration is consistent with reported literature values for TiO₂/NaCl suspension [33,35,40]. At pH values below the pH_{iep} , the electrokinetic potential follows a nearly identical pH-dependent profile, regardless of the electrolyte concentration. Above the isoelectric point, a similar trend is initially observed across all CaCl₂ concentrations: as the pH increases, the electrokinetic ζ -potential reaches a minimum value between pH 7.5 and 8.0, after which it begins to slightly increase. At lower CaCl₂ concentrations ($3.3 \times 10^{-4} \text{ mol dm}^{-3}$), the electrokinetic potential reaches more negative values, whereas at the highest concentration, it remains weakly negative ($> -3 \text{ mV}$). Interestingly, at CaCl₂ concentration of $3.3 \times 10^{-3} \text{ mol dm}^{-3}$, the electrokinetic potential undergoes a second sign reversal back to positive values at $\text{pH} = 8.4$.

Figure 3b illustrates that the hydrodynamic diameter of the TiO₂ nanoparticles exhibits a similar pH dependence across all three CaCl₂ concentrations. Overall, the particle size increases slightly with rising pH, closely reflecting the trends observed in the measured zeta potential values.

3.3. Adsorption of Poly(4-styrene Sulfonate) Anion onto TiO₂ Nanoparticles

To verify that the PSS anion adsorbs onto the surface of TiO₂ nanoparticles and to determine the optimal conditions for PSS adsorption onto TiO₂ nanoparticles, adsorption experiments of PSS onto TiO₂ nanoparticles were performed across a PSS monomer concentration range of $5 \times 10^{-3} \text{ mmol dm}^{-3}$ to 100 mmol dm^{-3} at a constant background electrolyte concentration of NaCl ($c = 10^{-3} \text{ mol dm}^{-3}$). Figure 4 presents the resulting adsorption

isotherm, which correlates the residual polyelectrolyte concentration in the bulk solution ($c_{\text{fin,PSS}}$) with the surface concentration of polyelectrolyte derived from Equation (2).

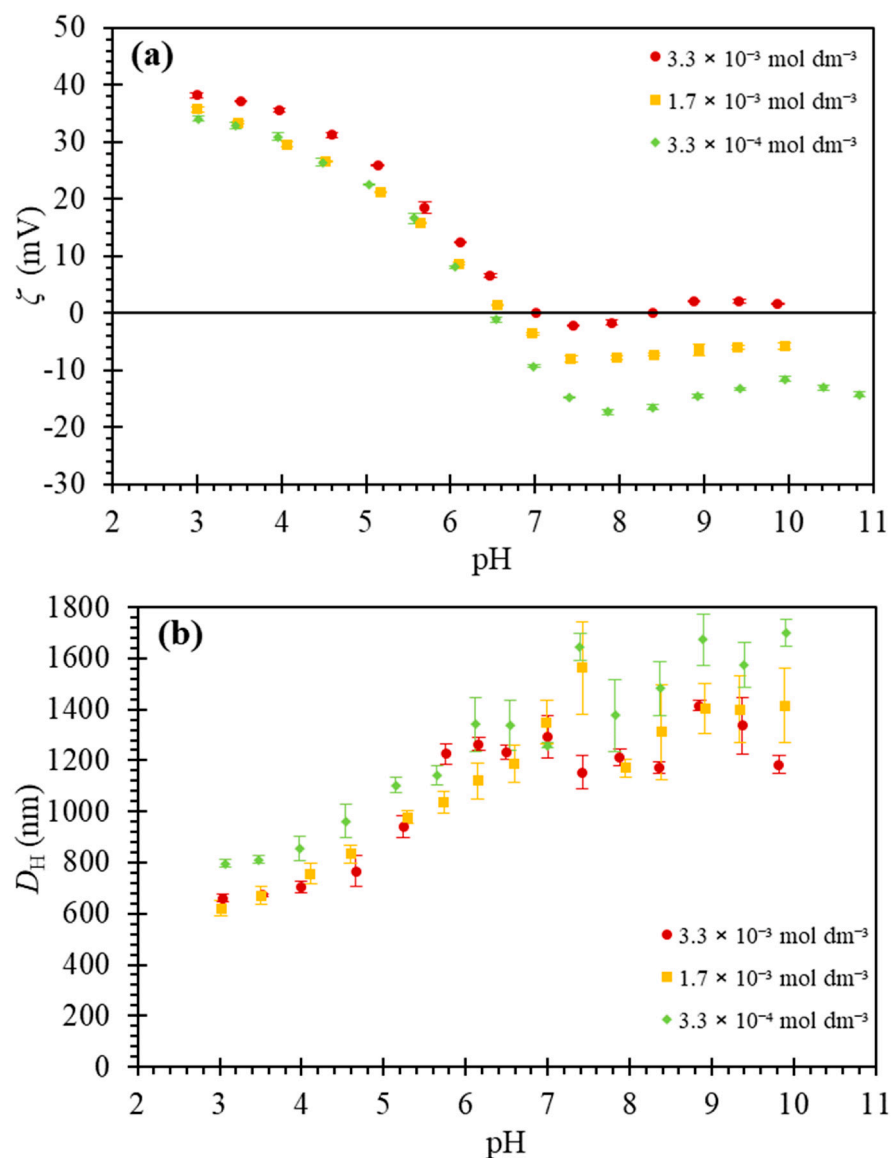


Figure 3. (a) ζ -potential and (b) hydrodynamic diameter of TiO_2 nanoparticles ($\gamma = 0.1 \text{ g dm}^{-3}$) over a broad pH range at three different CaCl_2 concentrations as a background electrolyte; $\theta = 25^\circ \text{C}$. Error bars represent the standard deviation of three independent measurements.

As shown in Figure 4, the surface concentration of PSS increases continuously with its concentration in solution, without reaching a plateau or surface saturation within the investigated range of PSS concentrations. This lack of a well-defined plateau is typical of the cooperative adsorption which can be observed in some other systems containing polyelectrolytes [41–43]. In addition, such an adsorption curve is also possible for explaining the cooperative adsorption of gases onto solid surfaces [44]. In this study, this behaviour may be explained by the polyelectrolytes adopting a non-flat conformation (loops or tails) or forming multilayer structures [45,46]. Conversely, other possible explanations may include aggregation of the polyelectrolytes on the nanoparticle surface or heterogeneous adsorption. Additionally, as the concentration of the polyelectrolyte is quite high ($>10 \text{ mmol dm}^{-3}$) and accounting for the duration of the adsorption process (18 h), a degree

of concentration dependent rearrangement could occur during the adsorption process which would result with a lack of an adsorption plateau.

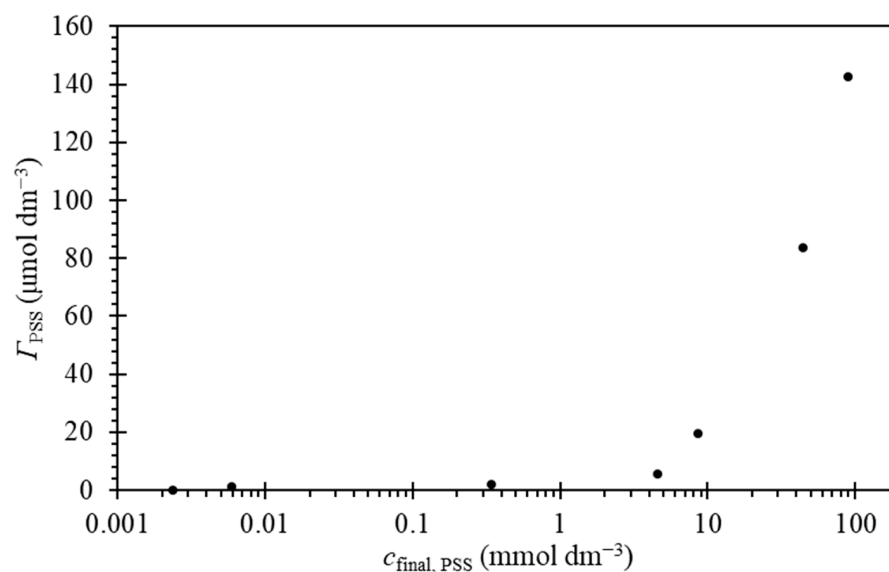


Figure 4. Adsorption isotherm of poly(4-styrene sulfonate) anion onto TiO_2 nanoparticles ($\gamma = 1.0 \text{ g dm}^{-3}$, $s = 72.1 \text{ m}^2/\text{g}$) at $\text{pH} = 3.0$ and $\theta = 25^\circ\text{C}$ in a NaCl background solution ($c = 10^{-3} \text{ mol dm}^{-3}$).

To evaluate the effect of macromolecular binding on particle properties, the TiO_2 nanoparticles were characterized after each adsorption experiment using ELS and DLS. The resulting electrokinetic potentials and hydrodynamic diameters are presented in Figures 5 and S6.

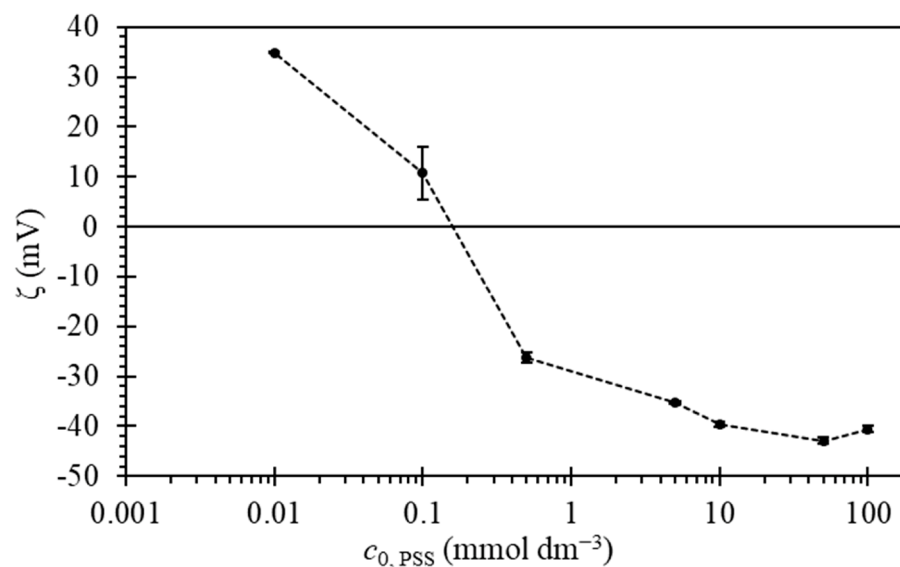


Figure 5. ζ -potential of PSS-coated TiO_2 nanoparticles ($\gamma = 0.1 \text{ g dm}^{-3}$) at $\text{pH} = 3.0$ and NaCl ($c = 10^{-3} \text{ mol dm}^{-3}$) as a function of initial concentrations of NaPSS. Dashed line has no physical meaning and was added as a guide to the eye.

In Figure 5 one can see a clear and sharp transition of the ζ -potential from positive (around +40 mV) to negative values (−40 mV) in the PSS concentration range from 0.1 mmol dm^{-3} to 0.5 mmol dm^{-3} .

The data in Figure S6 show that the hydrodynamic diameter remains relatively constant without significant changes as the initial concentration of PSS changes. The only significant deviation of the hydrodynamic diameter occurs at a PSS concentration of

0.1 mmol dm^{−3}. According to the results of ELS measurements, at that concentration of polyelectrolyte PSS-coated TiO₂ nanoparticles have ζ -potential around 0 which could promote aggregation.

3.4. Na⁺/Ca²⁺ Ion Exchange Experiments

The highest surface coverage of TiO₂ nanoparticles with PSS molecules was found to be at 100 mmol dm^{−3} PSS monomer concentration (Figure 4). Therefore, all PSS-coated TiO₂ nanoparticles used in subsequent ion-exchange experiments were prepared at that PSS concentration, only scaled up by a factor of 4.2 (50 mg of nanoparticles in 50 mL of solution). To compare the amount of exchanged Na⁺/Ca²⁺ ions, the concentration of PSS monomers in the solution was normalized so that the amount of free PSS monomers in the solution was equal to the amount of PSS monomers adsorbed onto the TiO₂ particles.

The stability of the system is the main condition for conducting Na⁺/Ca²⁺ ion exchange experiments on the TiO₂/PSS surface. It is important to prepare a system of PSS-coated TiO₂ particles where the desorption of PSS from the surface is minimal and, ideally, does not occur at all. The stability of the system, i.e., the desorption of PSS from the TiO₂/PSS particles, was investigated by analyzing the supernatants after subsequent rinsing cycles of the particles. Following the adsorption, the supernatant was separated from the precipitated particles, and the PSS-coated particles were resuspended in 100 mL of deionized water. After 24 h, the supernatant of the resuspended particles was analyzed again using UV-Vis spectrophotometry to determine the amount of desorbed PSS. The same procedure was repeated after 7 days. It was found that 6.9% of the adsorbed PSS was desorbed after the first rinsing cycle, whereas after the second rinsing cycle, only an additional 0.1% of PSS was desorbed. Therefore, it was concluded that a single rinse cycle is sufficient to remove most of the weakly bound polyelectrolyte molecules, and such a system was found to be suitable for subsequent experiments in which ion exchange on free PSS chains was compared with that on PSS adsorbed onto particles.

3.4.1. Enthalpy Changes

The ion exchange of Na⁺ ions for Ca²⁺ ions on PSS chains dissolved in water was investigated calorimetrically using ITC. The resulting cumulative enthalpy changes are presented in Figure 6.

The curve shown in Figure 6 clearly indicates that the exchange of Na⁺ with Ca²⁺ ions on the PSS chains is an endothermic process. Notably, a distinct inflection point characterized by a change in slope is observed at an added volume of approximately 80 μ L of 0.1 mol dm^{−3} CaCl₂ solution.

3.4.2. Release of Na⁺ and Binding of Ca²⁺ Ions on PSS

In addition to calorimetry, the titration of dissolved NaPSS and the PSS-coated TiO₂ nanoparticles with CaCl₂ solution was investigated by potentiometric titrations. These measurements were performed by titrating a NaPSS solution and a suspension of PSS-modified TiO₂ nanoparticles with CaCl₂ solution utilizing Na-ISE and Ca-ISE (Figures 7 and 8).

As shown in Figure 7, the initial Na⁺ activity in the NaPSS solution is approximately 4×10^{-3} , indicating that a portion of the Na⁺ ions has already dissociated from the PSS chain in the initial solution. Conversely, in the suspension of PSS-coated TiO₂ nanoparticles, the initial Na⁺ ion activity is significantly lower (approximately 2×10^{-4}), indicating enhanced binding of Na⁺ counterions to the adsorbed polyelectrolyte chains. The activity of free Na⁺ ions increases steadily at the beginning of the titration. After adding approximately 5 mL of the 0.1 mol dm^{−3} CaCl₂ solution, the Na⁺ ion activity plateaus, remaining constant at around 10^{-2} for the NaPSS solution, and significantly lower, at approximately

1.5×10^{-3} , for the PSS-coated TiO_2 suspension. For the polyelectrolyte solution, this plateau activity matches the initial monomer concentration of the starting NaPSS solution ($c_m = 10 \text{ mmol dm}^{-3}$).

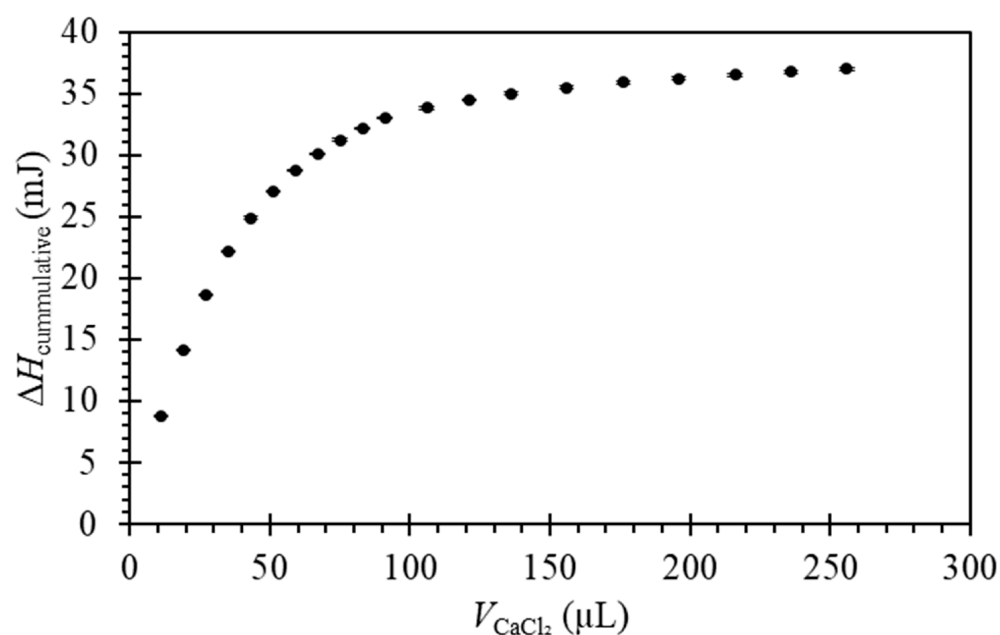


Figure 6. Cumulative enthalpy changes (corrected for titrant dilution) during the titration of a NaPSS solution ($c_m = 5 \text{ mmol dm}^{-3}$) with CaCl_2 solution ($c = 0.2 \text{ mol dm}^{-3}$) at $\theta = 25^\circ \text{C}$. The volume of the reaction cell was 1.4 cm^3 .

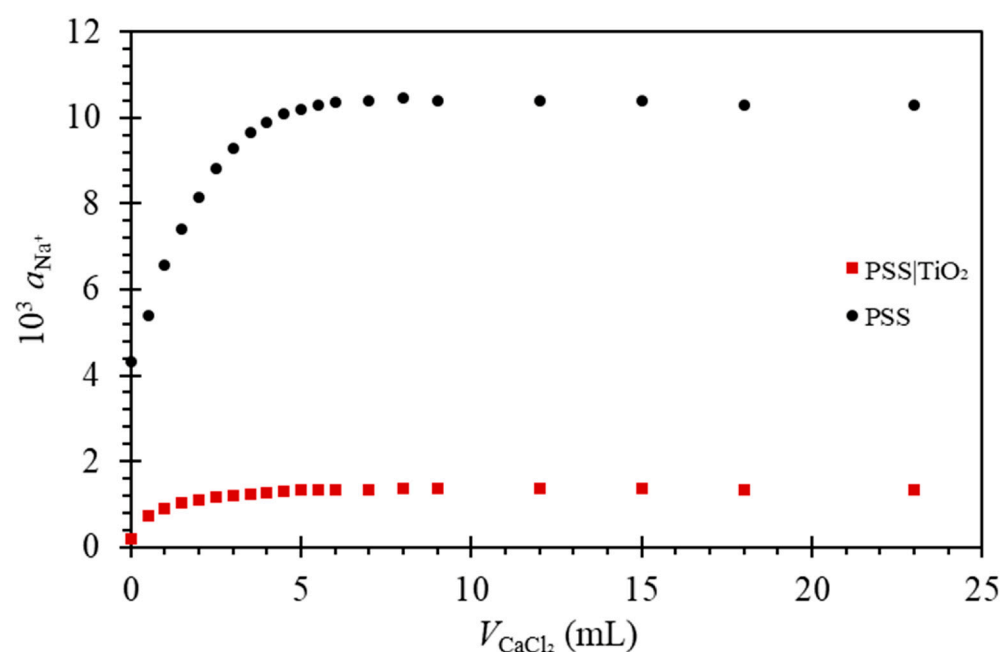


Figure 7. Na^+ ion activity measured using a Na-ISE during the titration of a 10 mmol dm^{-3} NaPSS solution (●) and a suspension of PSS-coated TiO_2 nanoparticles ($\gamma = 1 \text{ g dm}^{-3}$, $c_{\text{m,ads}}(\text{PSS}) = 10 \text{ mmol dm}^{-3}$) (■) with 0.1 mol dm^{-3} CaCl_2 solution at 25°C . The initial volume of the titrant was 100 cm^3 .

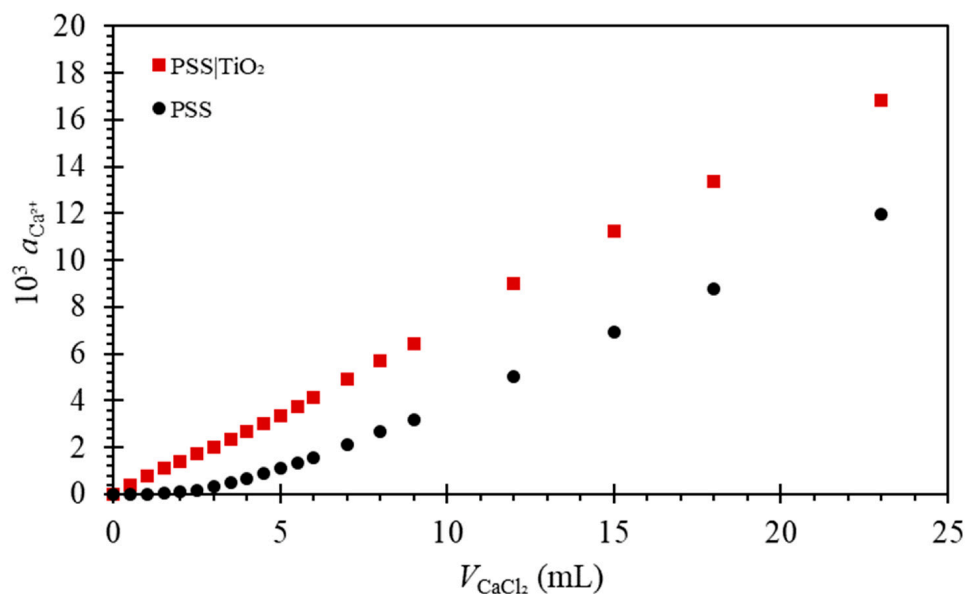


Figure 8. Ca^{2+} ion activities measured using Ca-ISE during the titration of a 10 mmol dm^{-3} NaPSS solution and a suspension of PSS-coated TiO_2 nanoparticles ($\gamma = 1 \text{ g dm}^{-3}$, $c_{\text{m,ads}}(\text{PSS}) = 10 \text{ mmol dm}^{-3}$) with 0.1 mol dm^{-3} CaCl_2 solution at 25°C . The initial volume of the titrant was 100 cm^3 .

Figure 8 demonstrates that generally the activity of Ca^{2+} ions increases with the increase in Ca^{2+} ion concentration. However, for the NaPSS solution, the Ca^{2+} ion activity is negligible when the volume of added 0.1 mol dm^{-3} CaCl_2 solution is below 2.5 cm^3 . In contrast, this threshold behavior is absent during the titration of PSS-coated TiO_2 nanoparticles. Overall, the Ca^{2+} ion activity is systematically lower when titrating PSS in solution than when titrating the PSS-coated particles, which could mean that more Ca^{2+} ions are bound to PSS chains when they are present in the solution than on the surface of TiO_2 nanoparticles.

It is also worth mentioning that the pH changed from 6.2 to 5.9 during titration of the PSS solution. However, the pH change during the titration of the PSS-coated nanoparticles was greater. Before the titration, the particle suspension had a pH of 5.2, and after the titration, the pH was 4.5. The change in the pH value of the suspension suggests that the concentration of H^+ ions increased during titration with CaCl_2 solution. This effect could be due to the release of H^+ ions from the surface of TiO_2 nanoparticles or the dissolution of CO_2 from the air.

3.4.3. Hydrodynamic Diameter of NaPSS(aq) and PSS-Coated TiO_2 Nanoparticles

The hydrodynamic diameter of PSS chains in solution (Figures 9 and 10) and PSS-coated TiO_2 nanoparticles (Figure 10) was examined via DLS across a wide range of CaCl_2 concentrations, at pH approximately 6.

At low CaCl_2 concentrations (below approximately 20 mmol dm^{-3}), the apparent hydrodynamic diameter of PSS chains in solution increases from 3 nm to 6 nm with increasing CaCl_2 concentration (Figure 9). On the contrary, at high CaCl_2 concentrations (above 0.5 mol dm^{-3}) hydrodynamic diameter is approximately 10 nm and independent on CaCl_2 concentration (Figure 10).

The suspended PSS-coated TiO_2 nanoparticles have a hydrodynamic diameter around 200 nm when CaCl_2 is not present in the solution. By increasing the CaCl_2 concentration, the hydrodynamic diameter of PSS-coated TiO_2 nanoparticles increases until it reaches a constant value of approximately 1100 nm at $c(\text{CaCl}_2) > 0.6 \text{ mol dm}^{-3}$.

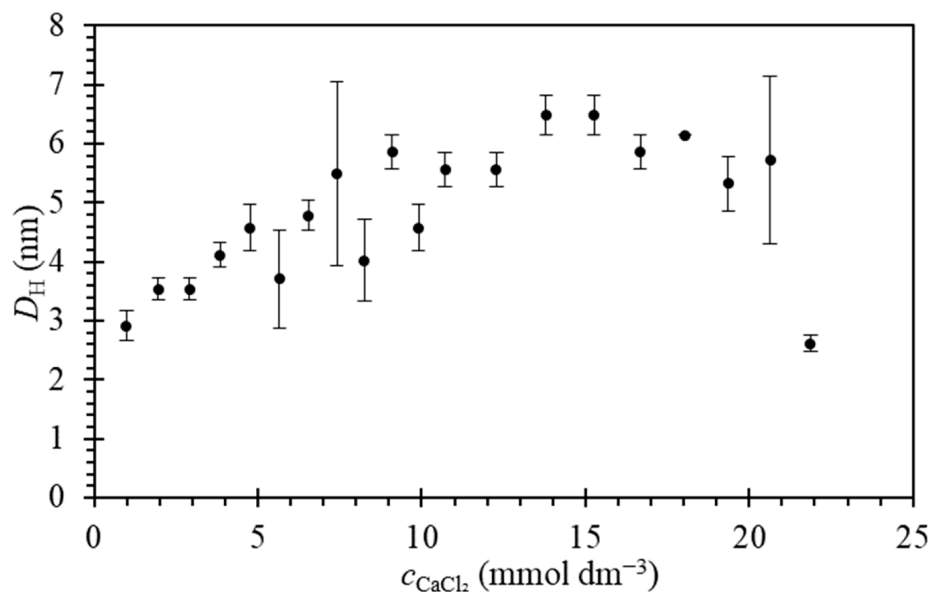


Figure 9. Influence of CaCl_2 concentration on hydrodynamic diameter of free PSS chains in solution ($c(\text{NaPSS}) = 10 \text{ mmol dm}^{-3}$) measured by DLS at 25°C .

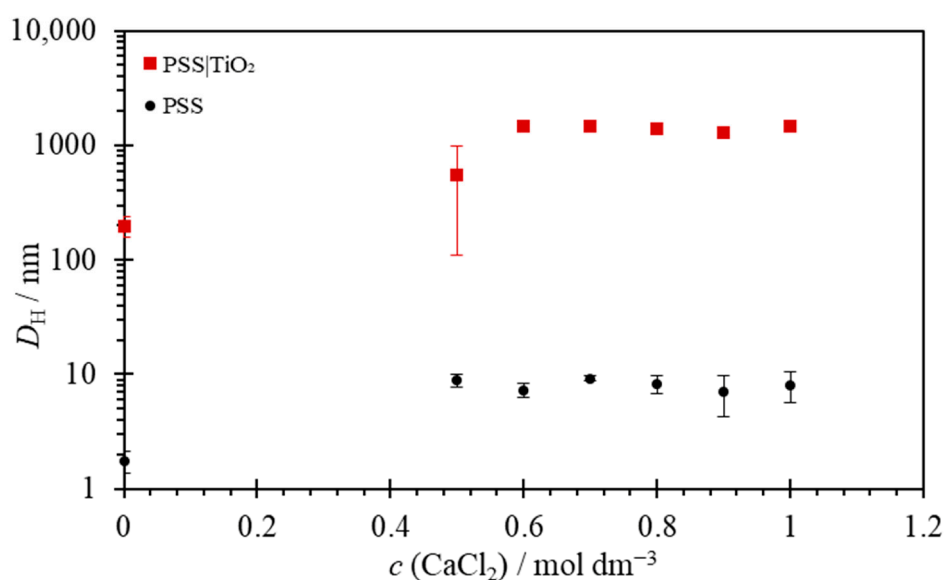


Figure 10. Hydrodynamic diameter of PSS chains in solution ($c(\text{NaPSS}) = 10 \text{ mmol dm}^{-3}$) and PSS-coated TiO_2 nanoparticles ($\gamma = 1 \text{ g dm}^{-3}$, $c_{\text{m,ads}}(\text{PSS}) = 10 \text{ mmol dm}^{-3}$) at higher CaCl_2 concentration, measured by DLS.

4. Discussion

In this study, we investigated the substitution of Na^+ ions by Ca^{2+} ions on the PSS chains, both free in solution and adsorbed onto the surface of TiO_2 nanoparticles. For this purpose, the TiO_2 nanoparticles were coated with PSS at $\text{pH} = 3.0$ (Figure 4). At this pH , both the surface charge density (Figure 2) and ζ -potential (Figure 3a) of TiO_2 nanoparticles are positive values, driving the electrostatic adsorption of the negatively charged polyelectrolyte chains. A sign reversal of ζ -potential of TiO_2 nanoparticles at PSS concentration of $10^{-1} \text{ mmol dm}^{-3}$ (Figure 5) suggests that at lower polyelectrolyte concentrations the particles are only partially covered and retain a net positive surface charge. As the PSS concentration increases beyond this threshold, the ζ -potential of the TiO_2 nanoparticles transitions from positive to negative, confirming successful overcharging and successful adsorption of the polymer onto the nanoparticle surface.

In a first set of ion-exchange experiments, we investigated the enthalpic effects of substituting Na^+ with Ca^{2+} ions on the free PSS chains in solution. This reaction was found to be endothermic (Figure 6), which aligns well with isothermal titration calorimetry results reported by other research groups. For instance, Požar and coworkers [47] conducted microcalorimetric titrations of NaPSS solutions with aqueous solutions of $\text{Mg}(\text{ClO}_4)_2$, $\text{Sr}(\text{ClO}_4)_2$, and $\text{Ba}(\text{ClO}_4)_2$, demonstrating that all these substitution reactions are endothermic. A similar endothermic effect was observed by Sinn et al. [48] for the binding of Ca^{2+} ions to poly(sodium acrylate) and by Ospennikov et al. [49] for the binding of Ca^{2+} ions to cellulose nanofibrils. Therefore, regarding the heat of the reaction, it can be concluded that the replacement of a monovalent cation with a divalent cation on a polyelectrolyte chain in solution is independent of the specific ion or polyelectrolyte type. Generally, counterion exchange reactions of this type are endothermic.

To explain the endothermic nature of $\text{Na}^+/\text{Ca}^{2+}$ exchange on PSS(aq), all contributing thermodynamic processes need to be considered. Specifically, the net enthalpy change is a balance between the dehydration of incoming Ca^{2+} ions, the release of bound Na^+ ions from the PSS chains, the subsequent binding of Ca^{2+} ions to the PSS polymer backbone, and the rehydration of the released Na^+ ions. The stripping of the hydration shell from highly hydrophilic Ca^{2+} ions is a strongly endothermic (unfavorable) process. Conversely, the electrostatics of ion binding to the negative PSS chain should be enthalpically more favorable for Ca^{2+} than for Na^+ due to the higher charge density of the divalent cation. Furthermore, the rehydration of the released Na^+ ions contributes an additional exothermic (favorable) component. Ultimately, this ion-exchange reaction comprises two enthalpically favorable steps and one highly unfavorable step. Given that the overall measured enthalpy change remains positive, it can be concluded that the favorable binding and rehydration effects are insufficient to compensate for the strongly unfavorable effect of Ca^{2+} ion dehydration.

The spontaneous substitution of Na^+ with Ca^{2+} ions on PSS chains in solution therefore could be explained by the increase in entropy. A molecular interpretation that supports this assumption includes two possible contributions to the entropy change. One possible contribution is the release of structured water molecules from the hydration shells of the interacting species involved in the exchange of Na^+ with Ca^{2+} ions on the PSS. The total amount of released water molecules during this process is governed by the dehydration of the sulfonate groups ($-\text{SO}_3^-$) and incoming Ca^{2+} ions, offset by the partial rehydration of the displaced Na^+ ions. According to Marcus [50], the hydration shell of a Ca^{2+} ion contains approximately 7 water molecules, whereas that of Na^+ ion contains only 3. Therefore, the displacement of Na^+ by Ca^{2+} ions on the polymer backbone is expected to liberate a significant amount of free water into the bulk solution, drastically increasing the configurational entropy of the solvent. Another possible reason for the positive entropic effect lies in the stoichiometry of the counterion exchange. For every divalent Ca^{2+} ion bound to PSS chain, two monovalent Na^+ ions are released into the bulk solution. This net increase in the number of free ions should significantly enhance the entropy of the system. In conclusion, the $\text{Na}^+/\text{Ca}^{2+}$ exchange on PSS chains is expected to be entropically driven process, favored probably by the desolvation of the reacting species and the stoichiometric release of a greater number of counterions into the solution.

As shown in Figure 7, the amount of Na^+ ions released from the PSS chains adsorbed onto the TiO_2 nanoparticles is significantly smaller than that released from the free polymer in solution. This result is expected, as a large fraction of the PSS monomer units is directly anchored to the TiO_2 surface through electrostatic interactions, rendering these specific groups unavailable for counterion exchange. Furthermore, the crowded conformation of the adsorbed polymer layer induces steric hindrance, which drastically limits the accessibility of the remaining sulfonate groups compared to the completely uncoiled, fully accessible

free chains in bulk solution. Additionally, Figure 7 demonstrates that beyond a specific threshold of CaCl_2 addition, the Na^+ ion activity reaches a constant plateau in both systems. This indicates that a complete and stoichiometric exchange of all accessible Na^+ ions with Ca^{2+} ions has been successfully achieved in both environments.

The results obtained with the Ca-ISE (Figure 8) are highly complementary to those from the Na-ISE measurements (Figure 7). Consistently, fewer Ca^{2+} ions bind to PSS when the polymer is adsorbed to the surface of the TiO_2 nanoparticles than when it is free in solution. For the free PSS(aq) system, the concentration of free Ca^{2+} ions in solution remains negligibly small upon the initial additions of titrant (Ca^{2+} ions), this confirms that at the beginning of the titration, nearly every introduced Ca^{2+} ion exchanges with bound Na^+ ions. In contrast, for the PSS-coated TiO_2 nanoparticles, free Ca^{2+} ions are detectable in the bulk phase even at very low titrant (Ca^{2+} ions) volumes. This distinct behavior suggests that the apparent binding affinity (binding constant) of Ca^{2+} ions to the PSS is significantly weaker when the polyelectrolyte is attached to the nanoparticle surface compared to when it is free in bulk solution.

To clarify these findings, it is instructive to examine the potential configurations through which Ca^{2+} ions can coordinate with the sulfonate repeating units of PSS. Generally, two distinct modes of Ca^{2+} binding can be distinguished: chelate binding and bridging coordination (Figure 11) [51]. Chelate binding involves the positioning of a Ca^{2+} ion between two adjacent monomers on the same PSS chain. In contrast, bridging refers to the cross-linking of two distant monomer units located either on separate, neighboring polymer chains (intermolecular bridging) or within separate segments of the same chain (intramolecular bridging). The observed reduction in the apparent binding affinity when PSS is adsorbed to the TiO_2 surface could be attributed to the severe loss of conformational freedom, which drastically limits these binding pathways. Specifically, because the polyelectrolyte chains are structurally constrained by their attachment to the solid surface, they cannot easily loop back on themselves to form a significant number of intramolecular bridges.

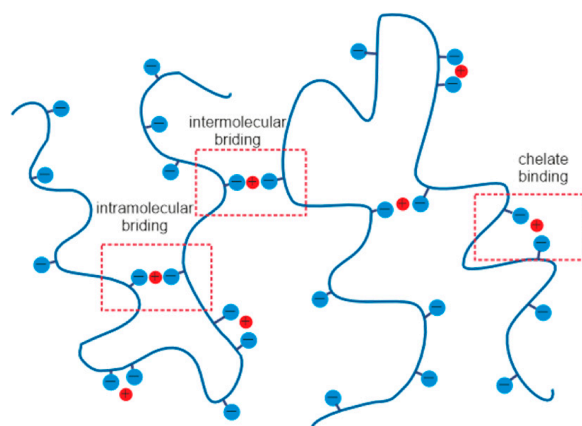


Figure 11. Type of binding of Ca^{2+} cation (red) to PSS (blue) monomer units.

Furthermore, extensive intermolecular bridging, which would induce massive particle aggregation, can also be considered. DLS results (Figure 10) indicate that aggregation of PSS-coated TiO_2 particles occurs at high CaCl_2 concentrations ($c > 0.5 \text{ mol dm}^{-3}$), which can additionally reduce the available space for the exchange of Na^+ ions with Ca^{2+} ions.

Consequently, localized chelate coordination remains probably the only structurally favorable binding mode for PSS-coated TiO_2 nanoparticles, which could explain the lower overall affinity observed in this system.

Although the apparent hydrodynamic size of polymer molecules can be strongly affected by concentration, interchain interactions, scattering intensity and the presence of

aggregates, DLS results can indirectly indicate changes in the conformation of free PSS molecules in solution. For example, Adamczyk and co-workers studied the conformations of several polyelectrolytes in electrolyte solutions by DLS, microelectrophoresis, dynamic viscosity measurements, and theoretical modeling [52–54]. They demonstrated how these macromolecules undergo conformational transitions corresponding to changes in the environment (polyelectrolyte concentration, ionic strength, pH, etc.). In this study, it was found that the hydrodynamic diameter of PSS chains in solution increases with increasing CaCl_2 concentration (Figure 9). In the absence of CaCl_2 , the hydrodynamic diameter of PSS chains in solution was 3 nm. This experimental value is almost identical to the theoretical prediction for a hydrated fully extended PSS molecule [53]. It is assumed that at low CaCl_2 concentration, PSS chains adopt an extended conformation due to the electrostatic repulsion between the charged monomer units. With increasing CaCl_2 concentration, the measured value of hydrodynamic diameter increased, becoming 6 nm for $c(\text{CaCl}_2) = 15 \text{ mmol dm}^{-3}$. This D_h value is again in accordance with the theoretical predictions calculated by Adamczyk and co-workers for a PSS molecule bent into the shape of a semi-circle [53]. The transformation of the PSS structure could be explained by a collapse of the PSS chains to a semi-circle conformation due to charge screening and attractive van der Waals interactions between monomers.

Although the primary intention of this study is fundamental, we would like to briefly refer to the applicable aspect as well. From a practical perspective, understanding the performance of ion-exchange systems is crucial for water softening applications. A key parameter evaluating this efficiency is ion-exchange capacity (IEC), a physical quantity that measures an insoluble material's capacity to exchange loosely bound ions with those in a surrounding solution. Essentially, the IEC indicates the density of active functional sites available for the ion-exchange reaction. In this study, where the primary focus is the exchange of Na^+ for Ca^{2+} , the calcium ion-exchange capacity can be formally expressed as the ratio between the amount of released Na^+ ions or bound Ca^{2+} ions (n) and the dry mass of the ion exchanger (m)

$$\text{IEC} = \frac{n}{m}. \quad (3)$$

The calculated IEC values for free PSS chains in solution and PSS adsorbed onto TiO_2 nanoparticles are summarized in Table 1, alongside comparative literature values for other polymeric ion exchangers. The amount of released Na^+ ions was determined by correcting the sodium ion activity at the end of the titration from the data in Figure 7 with the activity coefficient calculated using the Debye–Hückel extended law. In the calculation of ionic strength, the contribution of PSS anion was disregarded. Furthermore, the total mass of the PSS-coated nanoparticles was estimated as the sum of the pristine nanoparticle mass and the mass of the adsorbed NaPSS layer.

Table 1. Calcium ion exchange capacity (IEC) of free PSS(aq) chains, PSS-coated TiO_2 nanoparticles, and comparative polymeric ion exchangers reported in the literature.

Ion Exchanger	IEC/ mmol g^{-1}	Ref.
PSS(aq)	2.99	this work
PS-SA-TETATA	1.88	[55]
Amberlite IRC 748	1.18	[56]
Lewatit TP 207	0.91	[57]
PS-SA-Gly	0.90	[55]
PS-SA-Morph	0.28	[55]
TiO_2 PSS	0.26	this work
PS-SA-8AQ	0.13	[55]

All the ion exchangers listed in Table 1 are cationic, with most being based on a polystyrene matrix functionalized with sulfonic acid groups. Triethylenetetramine tetraacetic acid (PS-SA-TETATA) is a sulfonamide derivative of polystyrene resin. Among the ion exchangers compared, PS-SA-TETATA is the only one that coordinates Ca^{2+} ions in a 1:1 stoichiometric ratio, which likely accounts for its exceptionally high CaCl_2 ion-exchange capacity (IEC) [55]. While the IEC of free PSS is comparable to that of PS-SA-TETATA, the former is included for reference only; as a fully soluble polyelectrolyte, free PSS lacks structural integrity and cannot be readily recovered, limiting its direct practical application.

Amberlite IRC 748 and Lewatit TP 207 are commercial cation exchange resins featuring chelating iminodiacetic acid groups anchored to a crosslinked polystyrene-divinylbenzene matrix. For industrial applications, these macroporous resins are reported to exhibit Ca^{2+} IEC values of 1.18 mmol g^{-1} and 0.91 mmol g^{-1} , respectively [56,57]. Their high capacities are largely attributed to the highly accessible surface area of their macroporous architectures. In contrast, polystyrene-sulfonamide-glycine (PS-SA-Gly), polystyrene-sulfonamide-morpholine (PS-SA-Morph), and polystyrene-sulfonamide-8-aminoquinoline (PS-SA-8AQ) consist of solid polystyrene beads functionalized with distinct sulfonamide surface groups. Similar to the PSS-coated TiO_2 nanoparticles, these systems possess a rigid, non-porous matrix and bind a single Ca^{2+} ion *via* two ligand groups (a 1:2 binding stoichiometry). Within this group of structurally analogous ion exchangers, PS-SA-Gly exhibits the highest IEC. Interestingly, the IEC of PSS adsorbed on TiO_2 nanoparticles is similar to that of PS-SA-Morph, yet it remains higher than the capacities reported for PS-SA-8AQ [55].

Consequently, it can be concluded that PSS adsorbed on TiO_2 nanoparticles displays a low binding capacity for Ca^{2+} ions. Specifically, the IEC of the nanoparticle-bound PSS is approximately 9% of the capacity observed when the PSS chains are free in solution. To enhance the performance of adsorbed PSS for practical water-softening applications, its IEC must be optimized. One promising approach is the adsorption of PSS onto porous colloidal templates rather than solid cores, as an increased specific surface area could substantially boost the ion-exchange capacity. Furthermore, full practical implementation will require a comprehensive evaluation of the ion selectivity and regeneration efficiency of these PSS-based materials. Investigating these thermodynamic and kinetic properties on TiO_2 and other porous colloidal supports is the subject of ongoing and future research within our group.

5. Conclusions

In summary, this study demonstrates the successful coating of TiO_2 nanoparticles with poly(4-styrenesulfonate) anion at $\text{pH} = 3.0$. Thermodynamic analysis reveals that the subsequent $\text{Na}^+/\text{Ca}^{2+}$ ion exchange on PSS is endothermic, indicating a positive entropic contribution. This favorable energetic pathway is driven both by the desolvation of counterions and the stoichiometric release of a greater number of Na^+ ions into the bulk solution. The binding affinity for Ca^{2+} to PSS is found to be significantly weaker when the polyelectrolyte is bound to the nanoparticle surface than when it is free in solution. Furthermore, the combined analysis of counterion exchange and hydrodynamic diameter suggests that localized chelate binding is probably the most favored in the case of PSS-coated TiO_2 nanoparticles. Finally, the ion-exchange capacity of the nanoparticle-bound PSS was found to be approximately 9% of the capacity exhibited by free PSS ions in solution, highlighting the steric and conformational constraints imposed by surface immobilization. Taken together, these insights offer a clearer framework for designing functional polyelectrolyte-nanoparticle systems for targeted ion-capture and environmental applications.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/colloids10050067/s1>, Figure S1: PCD titration curves of the TiO₂ nanoparticle suspension with a PE4VPBr solution in acidic region; Figure S2: PCD titration curves of the TiO₂ nanoparticle suspension with a PE4VPBr solution in basic region; Figure S3: PCD titration curves of the TiO₂ nanoparticle suspension with a PSS solution; Figure S4: PCD titration curves of TiO₂ suspensions of different nanoparticle concentrations with a PE4VPBr solution at pH = 7.0; Figure S5: Surface charge densities of TiO₂ nanoparticles at different nanoparticles mass concentration obtained using the PCD at pH = 7.0; Figure S6: Hydrodynamic diameter of PSS-coated TiO₂ nanoparticles at pH = 3; Figure S7: Calibration diagram of the Na-ISE; Figure S8: Calibration diagram of the Ca-ISE.

Author Contributions: Conceptualization, J.N. and T.B.; methodology, I.V.P., T.K. and T.B.; validation, T.K.; formal analysis, I.V.P. and F.M.; investigation F.M.; resources, K.B.; writing—original draft preparation, T.K., I.V.P. and T.B.; writing—review and editing, T.B., T.K., I.V.P., J.N., K.B. and F.M.; visualization, I.V.P. and T.B.; supervision, T.K. and I.V.P.; funding acquisition, T.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the European Union—NextGenerationEU through the National Recovery and Resilience Plan 2021–2026. via Institutional grants of the University of Zagreb Faculty of Science (NextGenChem) and by the Croatian Science Foundation under the project DOK-NPOO-2023-10-2255.

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding authors.

Acknowledgments: During the preparation of this manuscript/study, the author(s) used Gemini 1.5 Pro in order to improve the English language and readability of the manuscript. The authors have reviewed and edited the output and take full responsibility for the content of this publication.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

PSS	Poly(4-styrenesulfonate) anion
NaPSS	Sodium poly(4-styrenesulfonate)
ITC	Isothermal titration calorimetry
DLS	Dynamic light scattering
PE4VPBr	Poly(<i>N</i> -ethyl-4-vinylpyridinium) bromide
PCD	Particle charge detector
PTFE	Polytetrafluoroethylene
ELS	Electrophoretic light scattering
Na-ISE	Sodium ion-selective electrode
Ca-ISE	Calcium ion-selective electrode
IEC	Ion-exchange capacity

References

1. Bolto, B.; Gregory, J. Organic Polyelectrolytes in Water Treatment. *Water Res.* **2007**, *41*, 2301–2324. [[CrossRef](#)]
2. Fauser, H.; Von Klitzing, R. Effect of Polyelectrolytes on (de)Stability of Liquid Foam Films. *Soft Matter* **2014**, *10*, 6903–6916. [[CrossRef](#)]
3. Dutkiewicz, J.K. Superabsorbent Materials from Shellfish Waste—A Review. *J. Biomed. Mater. Res.* **2002**, *63*, 373–381. [[CrossRef](#)]
4. Katić, J.; Nikolić, J.; Juračić, T.; Klačić, T.; Namjesnik, D.; Begović, T. Surface Properties and Corrosion Protection Study of a Poly(*N*-Ethyl-4-Vinylpyridine) Polyelectrolyte-Based Coating on an Electrochemically Formed Ti/TiO₂ Surface. *J. Mater. Chem. C* **2024**, *12*, 17241–17253. [[CrossRef](#)]
5. Durmaz, E.N.; Sahin, S.; Virga, E.; De Beer, S.; De Smet, L.C.P.M.; De Vos, W.M. Polyelectrolytes as Building Blocks for Next-Generation Membranes with Advanced Functionalities. *ACS Appl. Polym. Mater.* **2021**, *3*, 4347–4374. [[CrossRef](#)]

6. Smook, L.A.; Dahlin, A.; Schroën, K.; De Beer, S. Responsive Polyelectrolyte Brushes in Applications: Functions, Stimuli, and Design Considerations. *Adv. Mater.* **2025**, *37*, e09580. [\[CrossRef\]](#)
7. Borkovec, M.; Koper, G.J.M.; Piguët, C. Ion Binding to Polyelectrolytes. *Curr. Opin. Colloid Interface Sci.* **2006**, *11*, 280–289. [\[CrossRef\]](#)
8. Lopez, C.G.; Matsumoto, A.; Shen, A.Q. Dilute Polyelectrolyte Solutions: Recent Progress and Open Questions. *Soft Matter* **2024**, *20*, 2635–2687. [\[CrossRef\]](#)
9. Traeger, A.; Leiske, M.N. The Whole Is Greater than the Sum of Its Parts—Challenges and Perspectives in Polyelectrolytes. *Biomacromolecules* **2025**, *26*, 5–32. [\[CrossRef\]](#)
10. Mattai, J.; Kwak, J.C.T. Divalent Metal Ion Binding to Polyelectrolytes with Different Polyion Structure and Functional Groups. *Macromolecules* **1986**, *19*, 1663–1667. [\[CrossRef\]](#)
11. Minakata, A. Dielectric Properties of Polyelectrolytes. III. Effect of Divalent Cations on Dielectric Increment of Polyacids. *Biopolymers* **1972**, *11*, 1567–1582. [\[CrossRef\]](#)
12. Ghimici, L.; Dragan, S. Behaviour of Cationic Polyelectrolytes upon Binding of Electrolytes: Effects of Polycation Structure, Counterions and Nature of the Solvent. *Colloid Polym. Sci.* **2002**, *280*, 130–134. [\[CrossRef\]](#)
13. Winter, S.S. The Physical Chemistry of Polyelectrolytes and Ion Exchange Resins. *J. Chem. Educ.* **1956**, *33*, 246. [\[CrossRef\]](#)
14. Dubois, E.; Boué, F. Conformation of Poly(Styrenesulfonate) Polyions in the Presence of Multivalent Ions: Small-Angle Neutron Scattering Experiments. *Macromolecules* **2001**, *34*, 3684–3697. [\[CrossRef\]](#)
15. Schweins, R.; Huber, K. Collapse of Sodium Polyacrylate Chains in Calcium Salt Solutions. *Eur. Phys. J. E* **2001**, *5*, 117–126. [\[CrossRef\]](#)
16. Schweins, R.; Lindner, P.; Huber, K. Calcium Induced Shrinking of NaPA Chains: A SANS Investigation of Single Chain Behavior. *Macromolecules* **2003**, *36*, 9564–9573. [\[CrossRef\]](#)
17. Kwak, J.C.T.; Hayes, R.C. Electrical Conductivity of Aqueous Solutions of Salts of Polystyrenesulfonic Acid with Univalent and Divalent Counterions. *J. Phys. Chem.* **1975**, *79*, 265–269. [\[CrossRef\]](#)
18. Leyte, J.C.; Zuiderweg, L.H.; Vledder, H.J. An i.r. Investigation of Polyion-Counterion Interactions. *Spectrochim. Acta A* **1967**, *23*, 1397–1407. [\[CrossRef\]](#)
19. Lopez, C.G.; Horkay, F.; Schweins, R.; Richtering, W. Solution Properties of Polyelectrolytes with Divalent Counterions. *Macromolecules* **2021**, *54*, 10583–10593. [\[CrossRef\]](#)
20. Glisman, A.; Mantha, S.; Yu, D.; Wasserman, E.P.; Backer, S.; Wang, Z.-G. Multivalent Ion-Mediated Polyelectrolyte Association and Structure. *Macromolecules* **2024**, *57*, 1941–1949. [\[CrossRef\]](#)
21. Mantha, S.; Glisman, A.; Yu, D.; Wasserman, E.P.; Backer, S.; Wang, Z.-G. Adsorption Isotherm and Mechanism of Ca^{2+} Binding to Polyelectrolyte. *Langmuir* **2024**, *40*, 6212–6219. [\[CrossRef\]](#)
22. Chremos, A.; Douglas, J.F. Influence of Higher Valent Ions on Flexible Polyelectrolyte Stiffness and Counter-Ion Distribution. *J. Chem. Phys.* **2016**, *144*, 164904. [\[CrossRef\]](#)
23. Kłos, J.; Pakula, T. Lattice Monte Carlo Simulations of a Charged Polymer Chain: Effect of Valence and Concentration of the Added Salt. *J. Chem. Phys.* **2005**, *122*, 134908. [\[CrossRef\]](#)
24. Jacobs, M.; Lopez, C.G.; Dobrynin, A.V. Quantifying the Effect of Multivalent Ions in Polyelectrolyte Solutions. *Macromolecules* **2021**, *54*, 9577–9586. [\[CrossRef\]](#)
25. Kundagrami, A.; Muthukumar, M. Theory of Competitive Counterion Adsorption on Flexible Polyelectrolytes: Divalent Salts. *J. Chem. Phys.* **2008**, *128*, 244901. [\[CrossRef\]](#)
26. Shklovskii, B.I. Screening of a Macroion by Multivalent Ions: Correlation-Induced Inversion of Charge. *Phys. Rev. E* **1999**, *60*, 5802–5811. [\[CrossRef\]](#)
27. Lyklema, J. Adsorption of Polymers and Polyelectrolytes. In *Fundamentals of Interface and Colloid Science*; Elsevier: Amsterdam, The Netherlands, 1995; Volume 2, ISBN 978-0-12-460524-4.
28. De Dardel, F. Ion Exchangers. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2002; ISBN 978-3-527-30673-2.
29. Wang, J.; Yu, J.; Li, M.; Zhang, Y. Synthesis of Sodium Polystyrene Sulfonate Resins for the Removal of Methylene Blue from Wastewater. *J. Taiwan Inst. Chem. Eng.* **2024**, *159*, 105501. [\[CrossRef\]](#)
30. Pepper, K.W. Sulphonated Cross-linked Polystyrene: A Monofunctional Cation-exchange Resin. *J. Appl. Chem.* **1951**, *1*, 124–132. [\[CrossRef\]](#)
31. Holmberg, J.P.; Ahlberg, E.; Bergenholtz, J.; Hassellöv, M.; Abbas, Z. Surface Charge and Interfacial Potential of Titanium Dioxide Nanoparticles: Experimental and Theoretical Investigations. *J. Colloid Interface Sci.* **2013**, *407*, 168–176. [\[CrossRef\]](#)
32. Zhou, D.; Ji, Z.; Jiang, X.; Dunphy, D.R.; Brinker, J.; Keller, A.A. Influence of Material Properties on TiO_2 Nanoparticle Agglomeration. *PLoS ONE* **2013**, *8*, e81239. [\[CrossRef\]](#)
33. Suttiponparnit, K.; Jiang, J.; Sahu, M.; Suvachittanont, S.; Charinpanitkul, T.; Biswas, P. Role of Surface Area, Primary Particle Size, and Crystal Phase on Titanium Dioxide Nanoparticle Dispersion Properties. *Nanoscale Res. Lett.* **2010**, *6*, 27. [\[CrossRef\]](#)

34. Jukić, J.; Kovačević, D.; Cindro, N.; Fink, R.; Oder, M.; Milisav, A.-M.; Požar, J. Predicting the Outcomes of Interpolyelectrolyte Neutralization at Surfaces on the Basis of Complexation Experiments and Vice Versa. *Soft Matter* **2022**, *18*, 744–754. [\[CrossRef\]](#)
35. Jukić, J.; Juračić, T.; Josić, E.; Namjesnik, D.; Begović, T. Effects of Polyion Adsorption on Surface Properties of TiO₂. *Adsorption* **2024**, *30*, 251–264. [\[CrossRef\]](#)
36. Böckenhoff, K.; Fischer, W. Determination of Electrokinetic Charge with a Particle-Charge Detector, and Its Relationship to the Total Charge. *Fresenius J. Anal. Chem.* **2001**, *371*, 670–674. [\[CrossRef\]](#)
37. Preočanin, T.; Kallay, N. Point of Zero Charge and Surface Charge Density of TiO₂ in Aqueous Electrolyte Solution as Obtained by Potentiometric Mass Titration. *Croat. Chem. Acta* **2006**, *79*, 95–106.
38. Svecova, L.; Cremel, S.; Sirguy, C.; Simonnot, M.-O.; Sardin, M.; Dossot, M.; Mercier-Bion, F. Comparison between Batch and Column Experiments to Determine the Surface Charge Properties of Rutile TiO₂ Powder. *J. Colloid Interface Sci.* **2008**, *325*, 363–370. [\[CrossRef\]](#)
39. Panagiotou, G.D.; Petsi, T.; Bourikas, K.; Garoufalis, C.S.; Tsevis, A.; Spanos, N.; Kordulis, C.; Lycourghiotis, A. Mapping the Surface (Hydr)Oxo-Groups of Titanium Oxide and Its Interface with an Aqueous Solution: The State of the Art and a New Approach. *Adv. Colloid Interface Sci.* **2008**, *142*, 20–42. [\[CrossRef\]](#)
40. Kosmulski, M. The pH Dependent Surface Charging and Points of Zero Charge. VIII. Update. *Adv. Colloid Interface Sci.* **2020**, *275*, 102064. [\[CrossRef\]](#)
41. Llamas, S.; Guzmán, E.; Ortega, F.; Baghdadli, N.; Cazeneuve, C.; Rubio, R.G.; Luengo, G.S. Adsorption of Polyelectrolytes and Polyelectrolytes-Surfactant Mixtures at Surfaces: A Physico-Chemical Approach to a Cosmetic Challenge. *Adv. Colloid Interface Sci.* **2015**, *222*, 461–487. [\[CrossRef\]](#)
42. Guzmán, E.; Maestro, A.; Ortega, F.; Rubio, R.G. Association of Oppositely Charged Polyelectrolyte and Surfactant in Solution: Equilibrium and Nonequilibrium Features. *J. Phys. Condens. Matter* **2023**, *35*, 323001. [\[CrossRef\]](#)
43. Nylander, T.; Samoshina, Y.; Lindman, B. Formation of Polyelectrolyte–Surfactant Complexes on Surfaces. *Adv. Colloid Interface Sci.* **2006**, *123–126*, 105–123. [\[CrossRef\]](#)
44. Liu, S. Cooperative Adsorption on Solid Surfaces. *J. Colloid Interface Sci.* **2015**, *450*, 224–238. [\[CrossRef\]](#)
45. Fleer, G.J.; Stuart, M.A.C.; Scheutjens, J.M.H.M.; Cosgrove, T.; Vincent, B. Electrostatic Effects: Charged Surfaces and Polyelectrolyte Adsorption. In *Polymers at Interfaces*; Springer: Dordrecht, The Netherlands, 1998; pp. 339–371, ISBN 978-94-010-5749-3.
46. Hoogeveen, N.G.; Stuart, M.A.C.; Fleer, G.J. Polyelectrolyte Adsorption on Oxides. *J. Colloid Interface Sci.* **1996**, *182*, 133–145. [\[CrossRef\]](#)
47. Požar, J.; Bohinc, K.; Vlachy, V.; Kovačević, D. Ion-Specific and Charge Effects in Counterion Binding to Poly(Styrenesulfonate) Anions. *Phys. Chem. Chem. Phys.* **2011**, *13*, 15610. [\[CrossRef\]](#)
48. Sinn, C.G.; Dimova, R.; Antonietti, M. Isothermal Titration Calorimetry of the Polyelectrolyte/Water Interaction and Binding of Ca²⁺: Effects Determining the Quality of Polymeric Scale Inhibitors. *Macromolecules* **2004**, *37*, 3444–3450. [\[CrossRef\]](#)
49. Ospennikov, A.S.; Kwiatkowski, A.L.; Philippova, O.E. Cellulose Nanofibrils vs Nanocrystals: Rheology of Suspensions and Hydrogels. *Gels* **2025**, *11*, 926. [\[CrossRef\]](#)
50. Marcus, Y. *Ion Properties*; Dekker: New York, NY, USA; Basel, Switzerland, 1997; ISBN 978-0-8247-0011-9.
51. Mesić, M.; Klačić, T.; Kovačević, D. Specific Ion Effects of Divalent Cations on the Formation and Properties of Polyelectrolyte Multilayers. *ChemistrySelect* **2025**, *10*, e202501185. [\[CrossRef\]](#)
52. Jachimska, B.; Jasiński, T.; Warszyński, P.; Adamczyk, Z. Conformations of Poly(Allylamine Hydrochloride) in Electrolyte Solutions: Experimental Measurements and Theoretical Modeling. *Colloids Surf. A* **2010**, *355*, 7–15. [\[CrossRef\]](#)
53. Adamczyk, Z.; Jachimska, B.; Jasiński, T.; Warszyński, P.; Wasilewska, M. Structure of Poly (Sodium 4-Styrenesulfonate) (PSS) in Electrolyte Solutions: Theoretical Modeling and Measurements. *Colloids Surf. A* **2009**, *343*, 96–103. [\[CrossRef\]](#)
54. Adamczyk, Z.; Bratek, A.; Jachimska, B.; Jasiński, T.; Warszyński, P. Structure of Poly(Acrylic Acid) in Electrolyte Solutions Determined from Simulations and Viscosity Measurements. *J. Phys. Chem. B* **2006**, *110*, 22426–22435. [\[CrossRef\]](#)
55. Jeon, S.I.; Chung, I.J.; Ahn, C.-H. Surface Modification of Polystyrene Beads with Sulfonamide Derivatives and Application to Water Softening System. *Macromol. Res.* **2020**, *28*, 172–178. [\[CrossRef\]](#)
56. Yu, Z.; Qi, T.; Qu, J.; Wang, L.; Chu, J. Removal of Ca(II) and Mg(II) from Potassium Chromate Solution on Amberlite IRC 748 Synthetic Resin by Ion Exchange. *J. Hazard. Mater.* **2009**, *167*, 406–412. [\[CrossRef\]](#)
57. Jiang, S.Y.; Gao, B.; Dong, B. Ion Exchange Behaviors of Ca(II) and Mg(II) on Lewatit MonoPlus TP 207 and TP 208 Chelating Resins. *Adv. Mater. Res.* **2011**, *347–353*, 937–951. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.