


Review

Effect of Ionic Compounds of Different Valences on the Stability of Titanium Oxide Colloids

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Abstract: Titanium oxide particles of various morphologies have been prepared for applications of scientific or industrial interest in recent decades. Besides development of novel synthetic routes and solid-state characterization of the obtained particles, colloidal stability of titanium oxide dispersions was the focus of numerous research groups due to the high importance of this topic in applications in heterogeneous systems. The influence of dissolved ionic compounds, including monovalent salts, multivalent ions and polyelectrolytes, on the charging and aggregation behaviour of titanium oxide materials of spherical and elongated structures will be discussed in the present review.

Keywords: titanium oxide; colloidal stability; aggregation; surface charge; polyelectrolyte

1. Introduction

Titanium oxide is one of the most frequently studied inorganic materials due to the advantageous structural and chemical features utilized in a large number of applications. Recent reviews indicate a widespread contemporary interest in this compound and its derivatives [1–4]. For instance, the high refractive index makes it excellent pigment in white paints [5], where primary particles are homogeneously dispersed in the liquid medium. Biocompatibility is a key property in bioapplications, including delivery of bioactive molecules [6,7], tissue engineering [8], development of biosensors [9], biomimetic [10] and antibacterial materials [11]. Since the discovery of the photoelectric effect in titania [12], enormous effort has been made to develop photocatalytic systems composed of titanium oxide nanostructures or their composites [13–17]. It was also discovered that the shape [18] of the titania particles and the ionic environment [19] influences the photocatalytic activity. Moreover, novel titanium oxide-based substances were applied in solar cells [20], electrode materials [21], supercapacitors [22], inks [23] and electronics [24].

Large number of these applications relies on titanium oxides or their surface modified derivatives dispersed in a liquid medium, most frequently in aqueous solutions. Such dispersions can be directly used for example as delivery agents [6,7] or applied in synthetic processes for preparation of hybrid materials [25–27]. Colloidal stability of the particles is a key issue in photocatalytic applications, where stable dispersions of primary particles are required during the catalytic process, while aggregation, that is, destabilization of the dispersions, can be induced to eliminate the solid material by subsequent sedimentation and filtration [16,28,29]. To tune the stability of the heterogeneous systems, numerous stabilizing or destabilizing agents including simple salts or polymeric compounds have been already applied and comprehensive studies were published to describe the influence of the additives on the colloidal stability of the titanium oxide materials [5,30–33].

The aim of the present contribution is to clarify the charging and aggregation processes in such systems. Accordingly, dispersions containing titanium oxide particles of various shapes and ionic

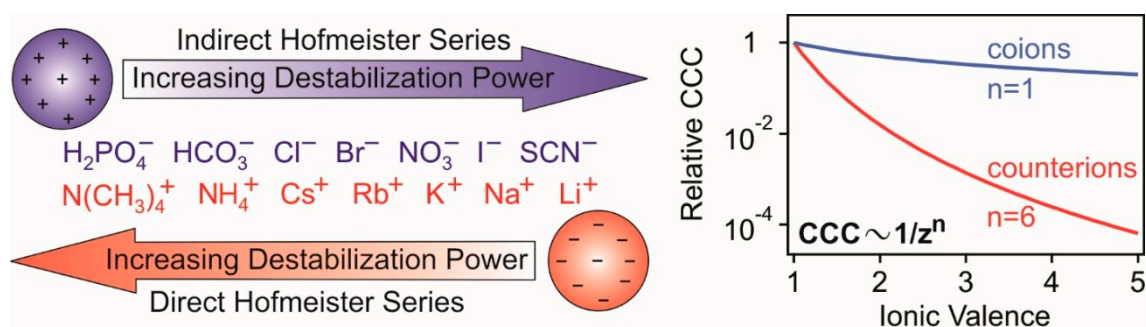
species from monovalent through multivalent ions to polyelectrolytes will be discussed and the relationship between the surface processes and the predominant interparticle forces will be ascertained. The main focus will be made on dispersed particle systems, studies performed with planar surfaces will not be discussed.

2. Stability of Titanium Oxide Particles in Electrolyte Solutions

2.1. General Considerations

In general, stable particle dispersions refer to homogeneously distributed primary particles in liquid medium, while in unstable dispersions particle aggregation occurs leading to the formation of dimers, trimers and higher ranked aggregates. The colloidal stability of charged particles dispersed in electrolyte solutions can be predicted by the classical theory developed by Derjaguin, Landau, Verwey and Overbeek (DLVO) [34,35]. This model interprets the overall interparticle forces acting between the particles in the presence of dissolved ions as the superposition of the repulsive electrical double layer forces and the attractive van der Waals forces. The first ones weaken with increasing the ionic strength, while the latter ones are always present independently of the solution composition [36]. Therefore, stable dispersions are predicted at low ionic strengths and rapid aggregation of the particles leading to unstable systems occurs at high electrolyte concentrations. These two regimes are typically separated by the critical coagulation concentration (CCC) or in other words by the critical coagulation ionic strength (CCIS). The value of these quantities is identical for monovalent salts, where the coions are of the same sign of charge as the surfaces and the counterions are oppositely charged.

Due to the fact that DLVO considers only the valence and the concentration of the ions in solution, it predicts equal CCC for the same particles dispersed in different monovalent salt solutions. However, large number of experimental literature data shows that the CCC is sensitive to the type or chemical composition of coions and counterions present in the systems [37–41]. Such a deviation from the theoretical prediction was explained by the different affinity of the ions and thus, different extent of adsorption of the surrounding anions and cations to the surfaces. This issue can be addressed by the Hofmeister series of ions (Scheme 1, left), which predicts the destabilization power of a given anion or cation considering the charge and the hydrophobicity of the particle surfaces [42–44].



Scheme 1. Left: Hofmeister series of anions and cations for hydrophobic colloidal particles. Right: representation of the Schulze-Hardy rule for counter and coions with the dependence of the CCC on the ionic valence (z).

For multivalent ions, however, DLVO takes the valence of ions into account and predicts a decrease of the CCC with increasing the valence through the Schulze-Hardy rule [45–47]. Moreover, the extent of this decrease is different for coions [48] and counterions [49] (Scheme 1, right) as well as it also depends on the magnitude of the surface charge [50]. Therefore, the ions of higher valences are more effective in destabilization of the colloid dispersions. In the next section, the colloidal stability of titanium oxide particles will be discussed on the basis of these considerations.

2.2. Effect of pH on Charging and Aggregation

It is well known that titanium oxide surfaces possess pH dependent charge due to the protonation-deprotonation equilibria of the surface hydroxyl groups [51]. Accordingly, they are positively charged under acidic conditions and negatively charged at higher pH [52]. These regimes are separated by the point of zero charge (PZC), which corresponds to the pH, where the overall charge of the particle is zero. The PZC values of numerous titanium oxide particles were determined with various techniques in the past decades [23,31,53–58] and they were found to be in the range of 4–7 [51]. In addition, adsorption of ionic species may also change the charge and the position of the PZC of the titanium oxide materials [19,59]. To demonstrate this feature, the pH profile of the electrokinetic potentials (equal to zeta potential) of titanate nanowires and titania nanosheets are shown in Figure 1 [56,59].

The surface charge is sensitive for the ionic strength applied due to the screening effect of the ions present in the solution. In general, the magnitude of the surface charge density decreases with increasing the salt level, as pointed out in potentiometric experiments with spherical titania particles [57]. However, this observation is only valid for indifferent electrolytes, that is, adsorption of ions is negligible, which do not change the position of the PZC. The presence of anions or cations with significant affinity towards the surface may induce different changes in the surface charge density and the corresponding surface potential [59].

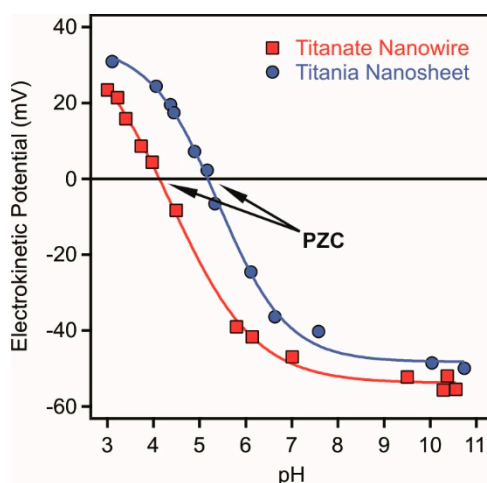


Figure 1. Electrokinetic potentials of titanate nanowires (squares, PZC 4.1) and titania nanosheets (circles, PZC 5.2) as a function of the pH at 1 mM ionic strength. The data were taken from References [56,59].

Aggregation of bare titanium oxide particles is usually governed by DLVO-type forces, therefore, the magnitude of the surface potential and the surface charge determines the strength of the repulsive forces originating from the overlapping electrical double layers formed around the particles. Colloidal stability of titania spheres of 200 nm in radius was investigated in time-resolved dynamic light scattering measurements [57], where the stability ratio values were determined to express the rate of aggregation in the dispersions (Figure 2). In the calculation of the stability ratios, the aggregation rates are normalized to the one measured in unstable dispersions, where the aggregation is controlled only by the diffusion of the particles [40,60–63]. Therefore, note that stability ratio values close to one indicate unstable dispersions, while higher values refer to more stable samples. It is clear from the stability ratio versus pH plot that the titania dispersions were stable at low and high pH indicated by large or not even measurable stability ratio values. In the intermediate pH regime, near the PZC, the stability ratios reached a minimum referring to rapid aggregation of the particles and to unstable dispersions.

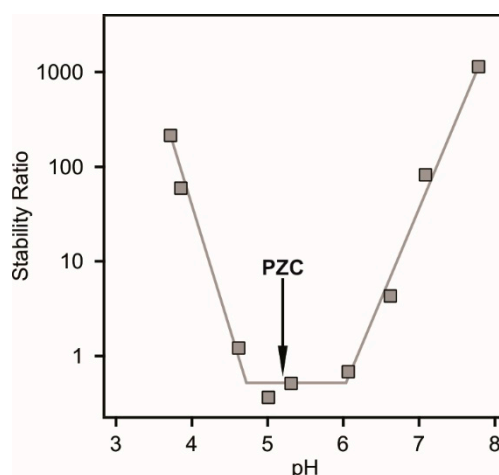


Figure 2. Stability ratio data of spherical titania particles measured at different pH at 7.5 mM ionic strength set by KCl. The particles have a PZC of 5.2 indicated with an arrow. Note that stability ratio values of one indicate that the particle aggregation is controlled solely by the diffusion of the particles, that is, each collision leads to dimer formation. Higher values are signals for slower aggregation rates. The data were taken from Reference [57].

An interesting feature in the stability ratio plot is that the values are slightly lower than one in the fast aggregation regime. This acceleration in the aggregation rates most likely originates from the interaction of the surface hydroxyl groups of different protonation stage. Although the overall charge of the particles is close to zero near the PZC, the surface may contain protonated and deprotonated groups, which can induce additional attractive electrostatic forces among the van der Waals interactions.

2.3. Colloidal Stability in the Presence of Monovalent Electrolytes

Salt-induced aggregation of titanium oxide materials was investigated by several authors and CCC values between 1–100 mM [7,59,62–66] were determined by various methods. For instance, a colloid stability study performed on spherical titania particles was carried out at different pH in KCl solutions by following particle aggregation with light scattering technique [67]. The position of the CCC varied with the pH due to the different surface charge densities and they were the lowest at pH close to the PZC. Theoretical calculations revealed that the aggregation mechanism can be adequately described by the DLVO theory, however, the roughness of the surface of the titania particles has to be taken into account.

A comprehensive study was carried out to investigate the specific effect of anions and cations on the colloidal stability of titania hydrosols [68]. The absorbance of the dispersions was measured with a spectrophotometer and stability ratios were calculated to determine the CCC. These quantities were then measured at different pH and in the presence of different monovalent anions and cations to order these ions in the Hofmeister series (Scheme 1) [44]. The CCC of titania decreased in the $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ order above the PZC, which is consistent with the prediction by the indirect Hofmeister series for negatively charged hydrophilic particles [69].

Similar sequence was found for surface charge densities of titania particles in the presence of K^+ and Li^+ ions indicating that the ion-surface interaction is responsible for the charging and aggregation processes in these systems [70]. However, this sequence was reversed once titania particles were heat treated indicating that the surface became hydrophobic during calcination and the CCC follows the direct Hofmeister series for negatively charged hydrophobic particles. The same order was found for commercial titania particles pointing to the hydrophobic nature of their surfaces [71]. Nevertheless, it was also found that ion specific effects for positively charged titania below the PZC are not significant once the surface underwent calcination [68].

Electrokinetic potentials and stability ratios were determined with titania nanosheets under acidic and alkaline conditions, that is, with negatively and positively charged surfaces, in the presence of various monovalent anions by light scattering methods [59]. Therefore, the anions were applied as counterions below the PZC, which was reported to be 5.2 [31] and as coions above it. As shown in Figure 3 (left column), ion specific effects led to significantly different electrokinetic potentials and stability ratios once the pH was acidic, that is, positively charged nanosheets were present.

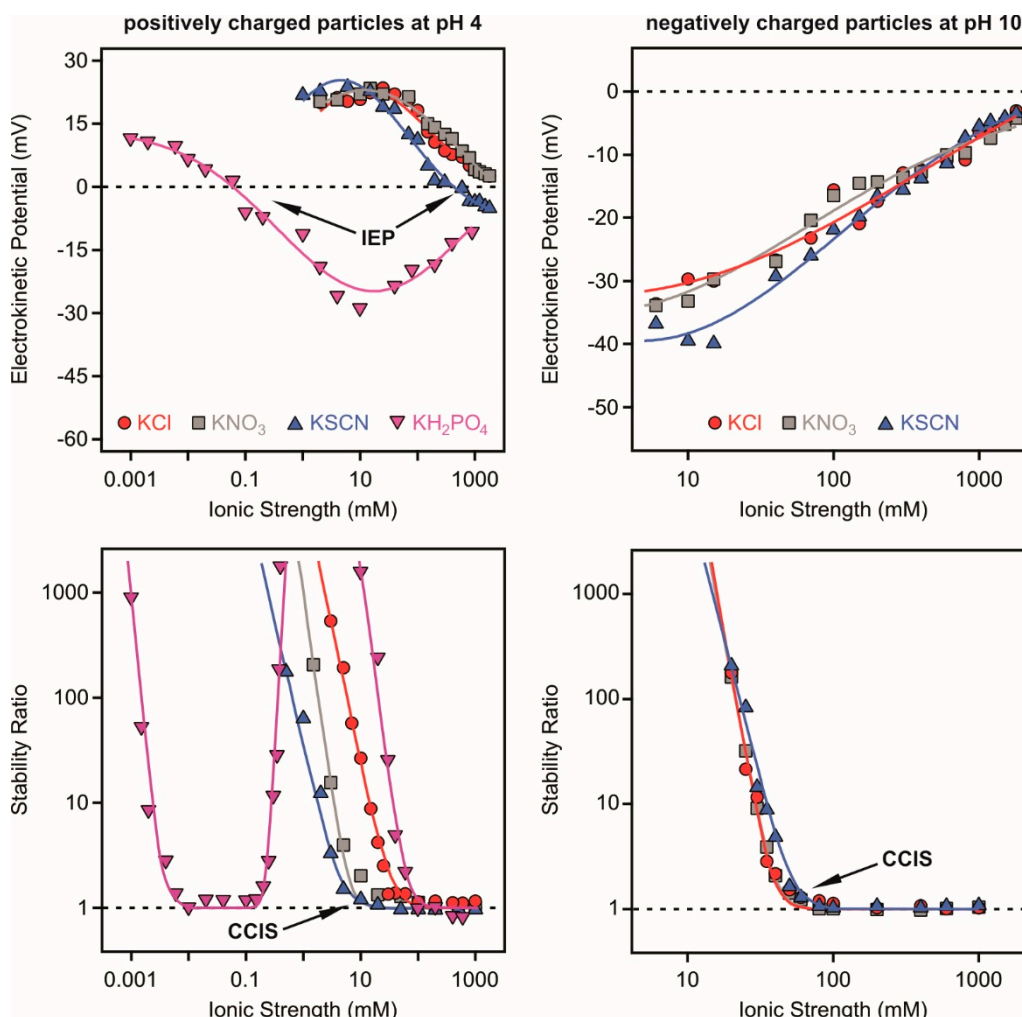


Figure 3. Electrokinetic potentials (**top row**) and stability ratios (**bottom row**) of titania nanosheets as a function of the ionic strength set by different monovalent electrolytes below the PZC at pH 4 (**left column**) and above the PZC at pH 10 (**right column**), where the nanosheets are positively or negatively charged, respectively. The particle concentration was 1 mg/L. Reprinted with permission from Reference [59]. Copyright (2017) American Chemical Society.

The affinity of the anions to the oppositely charged surface followed the $\text{H}_2\text{PO}_4^- > \text{SCN}^- > \text{NO}_3^- > \text{Cl}^-$ order and thus, the charge of the particles increases in the same sequence at the same ionic strength. The adsorption of the SCN^- ions led to charge neutralization at the isoelectric point (IEP), which refers to the concentration of the adsorbent necessary to neutralize the surface charge. Further addition of the anions gave rise to slight reversal of the sign of the charge of the nanosheets. The charge reversal was more pronounced for the H_2PO_4^- system and highly charged titania of negative charge were observed at elevated salt concentrations. Such a high extent of charge reversal is rare for systems containing monovalent electrolytes and charged colloids but rather typical for multivalent ions [37]

and polyelectrolytes [72] in the presence of oppositely charged surfaces. This issue will be discussed later in detail.

The corresponding stability ratio values measured in the same systems correlate well with the electrokinetic potential data (Figure 3, left). Accordingly, the CCIS followed the $\text{H}_2\text{PO}_4^- < \text{SCN}^- < \text{NO}_3^- < \text{Cl}^-$ sequence meaning that the lowest CCIS was found for the strongly adsorbing H_2PO_4^- and the highest for the weakly adsorbing Cl^- ions, as indicated by the measured potentials. These results clearly indicated that adsorption of ions led to different surface charge and hence, to different CCIS. The $\text{SCN}^- < \text{NO}_3^- < \text{Cl}^-$ sequence followed the indirect Hofmeister series for positively charged hydrophobic particles [37,38,40,42,69], however, the position of the H_2PO_4^- is atypical, since its presence should lead to the highest CCIS (Scheme 1). Note that the numerical value of the CCIS and CCC are the same for monovalent salts.

The shape of the stability ratio plot in the case of the H_2PO_4^- ions can be described as follows. The dispersions were stable at low salt levels and turned to be unstable at the CCIS. However, the strong charge reversal process resulted in a high magnitude of the surface charge, giving rise to a restabilization process indicated by high, or not even measurable, stability ratios in the intermediate concentration regime. Such a restabilization phenomenon was due to the strong repulsive electrical double layer forces between the negatively charged nanosheets. The dispersions became unstable again at high ionic strength, since charge screening by the salt constituents occurred.

The specific interaction between phosphate anions of different valences and titania particle surfaces has already been observed in other systems too [73–76]. On the basis of results from experimental (infrared (IR) spectroscopy) and theoretical (efficient density-functional-based tight-binding calculations) methods, it was suggested that a primary chemical bond was established between the metal ions on the surface and the oxygen atom of the phosphate ions and this interaction gives rise to the accumulation of negative charges on the particle surface.

The trend for the negatively charged particles above the PZC is simpler (Figure 3, right). For the NO_3^- and Cl^- systems, both electrokinetic potentials and stability ratios were the same within the experimental error. In the case of SCN^- ions, slight increase in the magnitude of the potentials at the same ionic strength and in the CCIS was observed. This was in agreement with the direct Hofmeister series for negatively charged hydrophobic particles in the presence of monovalent coions. However, the effect of the coions was much weaker than the influence of counterions in the case of positively charged nanosheets and the same anions.

In systems containing titanium oxide particles and monovalent electrolytes, the generic conclusions can be summarized as follows. Regardless of the surface charge and the type of ions, the major interparticle interactions were the repulsive double layer and attractive van der Waals forces. Nevertheless, the different affinity of the counterions led to different charge density of the surfaces and hence, the double layer forces weakened once the counterion adsorption was stronger. Such a decrease in the extent of the repulsive interaction led to a decrease in the CCC or CCIS. The effect of coions is less pronounced. Summarily, specific ion adsorption determines the charging properties of the particles, while the aggregation mechanism and the predominant interparticle forces can be described within the DLVO theory.

2.4. Multivalent Ion-Induced Aggregation

Similar studies were carried out with the same titania nanosheets as discussed above but in the presence of multivalent inorganic anions [59]. Accordingly, electrokinetic potential and stability ratio measurements were performed below and above the PZC, which was 5.2 [31], with positively or negatively charged nanosheets, respectively, in dispersions containing $\text{H}_2\text{PO}_4^{2-}$, SO_4^{2-} , $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ ions. The results are presented in Figure 4.

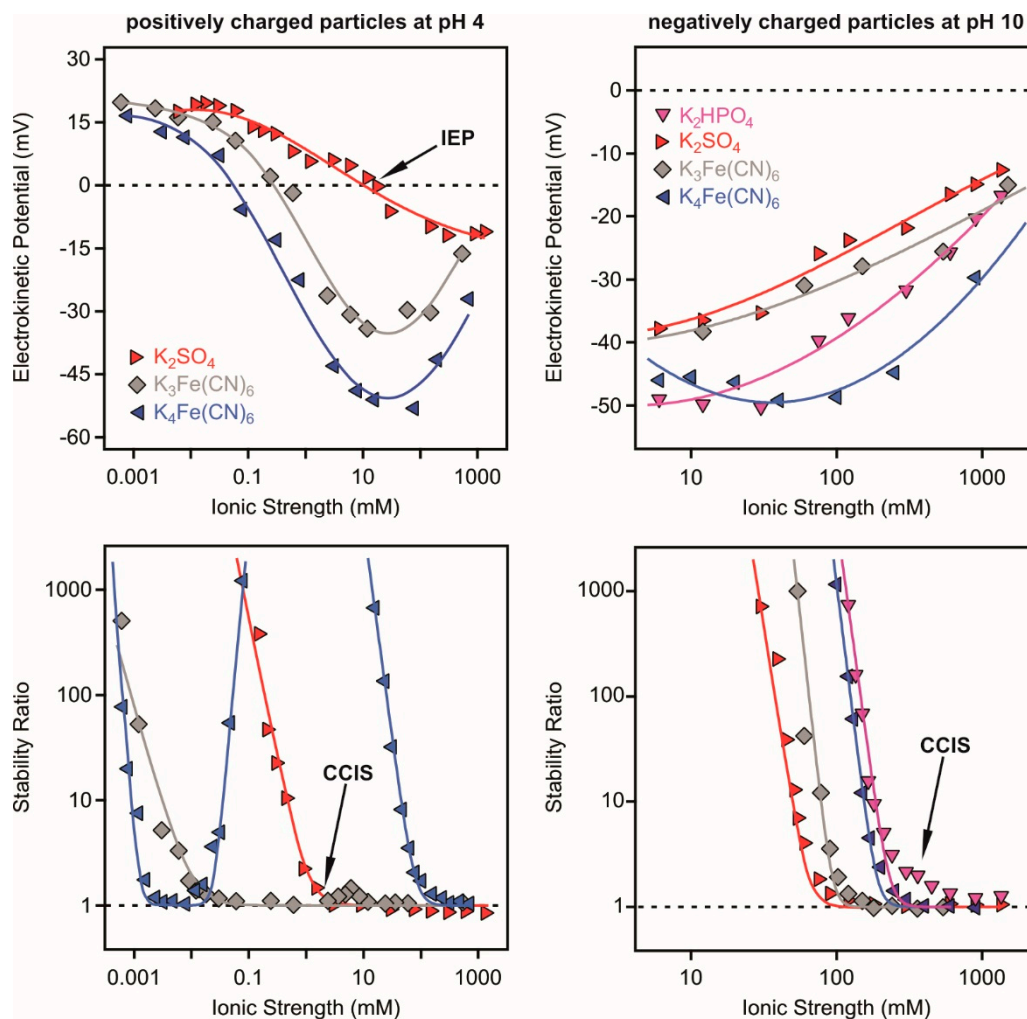


Figure 4. Electrokinetic potentials (**top row**) and stability ratios (**bottom row**) of titania nanosheets as a function of the ionic strength set by different multivalent electrolytes below the PZC at pH 4 (**left column**) and above the PZC at pH 10 (**right column**), where the nanosheets were positively or negatively charged, respectively. The concentration of the particles was kept constant at 1 mg/L. Reprinted with permission from Reference [59]. Copyright (2017) American Chemical Society.

For positively charged particles (Figure 4, left), well-defined IEP values indicated the adsorption of the anions on the oppositely charged surface. Such a charge neutralization was followed by charge reversal at higher ionic strengths and the extent of this phenomenon followed the $SO_4^{2-} < Fe(CN)_6^{3-} < Fe(CN)_6^{4-}$ order. The location of the IEP decreased in this sequence. On the basis of the measured stability ratios, one can observe slow aggregation regime at low electrolyte concentrations and fast aggregation at high salt levels separated by the CCIS values. The CCIS decreased in the $SO_4^{2-} > Fe(CN)_6^{3-} > Fe(CN)_6^{4-}$ sequence in qualitative agreement with the Schulze-Hardy rule [46,47,50] and in good correlation with the IEP values. It was concluded that multivalent ions of higher valences adsorbed stronger on the oppositely charged surface and thus, the reduced surface charge led to lower CCIS.

In addition, the tendency in the stability ratios for the $Fe(CN)_6^{4-}$ dispersions was similar to the one for the $H_2PO_4^-$ system discussed in the previous chapter. Restabilization of the nanosheets occurred in the intermediate salt concentration regime and three CCIS values could be observed. The first one is at lower ionic strength, the second one is when the restabilization started and the third one is at high salt level once the charge of the negative particles was screened by the salt constituent

ions. Such a behaviour has already been described in other oppositely charged particle-multivalent ion systems too [61].

For the negatively charged nanosheets above the PZC (Figure 4, right), the anions were the coions. The electrokinetic potentials increased in magnitude by increasing the valence of the anions indicating their adsorption on the like-charged surface. The adsorption of the $\text{H}_2\text{PO}_4^{2-}$ was much stronger compared to the SO_4^{2-} of the same valence due to the specific interaction with the surface metal ions through primary chemical bonds [73–76]. The stability ratio plots contained slow and fast aggregation regimes separated by the CCIS values, which increased in the $\text{SO}_4^{2-} < \text{Fe}(\text{CN})_6^{3-} < \text{Fe}(\text{CN})_6^{4-} < \text{H}_2\text{PO}_4^{2-}$ order. The position of the latter anion was atypical, owing to its above-mentioned accumulation on the surface but the $\text{SO}_4^{2-} < \text{Fe}(\text{CN})_6^{3-} < \text{Fe}(\text{CN})_6^{4-}$ sequence followed adequately the inverse Schulze-Hardy rule (Scheme 1) developed for the colloidal stability of charged particles in the presence of multivalent coions [48,50]. Note that this order is the opposite if one considers the CCC values in the same systems. Both direct and inverse Schulze-Hardy rules can be derived within the DLVO theory, therefore, the major interparticle forces between both positively and negatively charged titania nanosheets were originated from the electrical double layer repulsion and van der Waals attraction [59].

Results from aggregation kinetic and zeta potential measurements performed with commercial titania particles of spherical shape and mono or multivalent cations showed similar dependence in the charging and aggregation processes [71]. The particles were slightly negatively charged, therefore, the metal ions acted as counterions. The zeta potential data showed that adsorption of the divalent ions caused significant charge reversal (Figure 5, left). Moreover, the adsorption of the monovalent ions also resulted in charge reversal but in a smaller extent. This behaviour is rather unusual for monovalent ions; it likely occurred because the pH was close to the PZC, that is, the particle charge was close to zero and a small number of adsorbed cations could reverse the charge of the titania surface. The CCIS values determined in light scattering experiments was substantially smaller for Ca^{2+} ions than for the Na^+ salt (Figure 5, right) in agreement with the Schulze-Hardy rule. This tendency agreed well with calculations used to elucidate the compression of the electrical double layer at different ionic strengths.

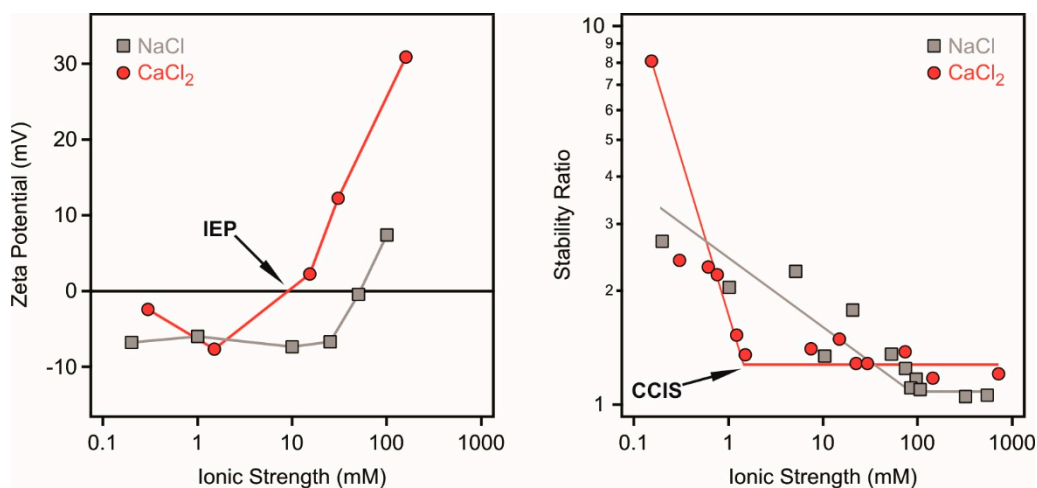


Figure 5. Zeta potential (left) and stability ratios (right) of titania particles as a function of the ionic strength adjusted by NaCl or CaCl_2 . The data were reproduced from Reference [71].

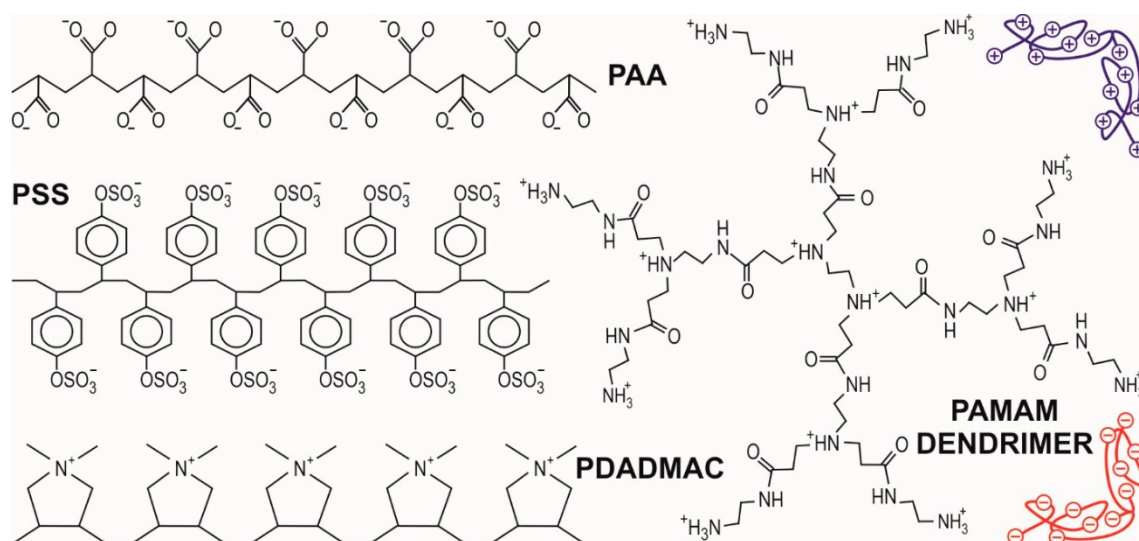
Similar charge reversal was observed with negatively charged titania spheres in the presence of Ba^{2+} ions, however, the electrokinetic potentials remained negative up to high ionic strengths for K^+ ions [57]. The stability ratios were measured with photon correlation spectroscopy and the calculated CCC shifted in the $\text{K}^+ > \text{Ba}^{2+}$ direction, as predicted by the Schulze-Hardy rule.

From the above discussed results, it is clear that multivalent counterions are more effective in destabilizing colloidal dispersions of titanium oxide materials. Their adsorption often leads to charge neutralization and charge reversal at appropriate concentrations. However, ion specific effects result in different affinity of the ions to the surface giving rise to different extent of charge reversal and to different CCIS within the ions of the same valences [59]. The CCC or CCIS values qualitatively follow the Schulze-Hardy rule but the quantitative description has to be clarified, since it depends on the magnitude of the surface charge and the stoichiometry of the electrolytes [50]. Recent data [59] indicates that effect of multivalent coions on the colloidal stability of titanium oxide particles is important and the inverse Schulze-Hardy rule [48] can be used to describe that phenomenon. However, systematic studies with variation of surface charge density and salt compositions as well as combining different techniques are needed to further pursue this issue.

3. Charging and Aggregation of Titanium Oxide Materials in the Presence of Polymers

3.1. General Remarks

Polymers and their charged derivatives, the so-called polyelectrolytes, are often used to tune the stability of colloidal particles [72,77,78]. Polyelectrolytes (Scheme 2) are especially suitable as stabilizing or destabilizing agents, since they adsorb strongly and irreversibly on oppositely charged particles and thus, change the surface charge properties leading to variation of the interparticle forces and to different colloidal stability.



Scheme 2. The structure of some polyelectrolytes (PAA—poly(acrylic acid), PSS—poly(styrene sulfonate), PDADMAC—poly(diallyldimethyl ammonium) and PAMAM—poly(amido amine) dendrimer) used to tune colloidal stability of titanium oxide particles. The polyelectrolytes are shown in their ionized forms.

Adsorption of polyelectrolytes on particles of the same sign of charge was also reported with or without addition of bridging ions between the surface and the polymers [32,33,79]. Titanium oxide surfaces were modified by polymeric species either to tune their charging and aggregation behaviour or to functionalize them to prepare hybrid materials [30,80–82] or to enhance the adsorption capacity of the particles [26,83,84]. It was shown that polymer coating improves the cellular uptake of the particles in biomedical applications [6]. Furthermore, polyelectrolytes were used to eliminate titanium oxide materials from dispersions [85]. These applications rely on the nature of polymer-particle and particle-particle interaction; therefore, these phenomena have to be understood in detail. The following section will summarize the efforts made by several research groups in the field from the point of

view of charging and aggregation and corresponding colloid stability of polyelectrolyte functionalized titanium oxide materials.

3.2. Oppositely Charged Particle-Polyelectrolyte Systems

As the first example, Figure 6 illustrates the influence of PDADMAC adsorption on negatively charged titania nanosheets [31] and titanate nanowires [63]. The polyelectrolyte possesses permanent positive charge due to the quaternary amino groups in the chain.

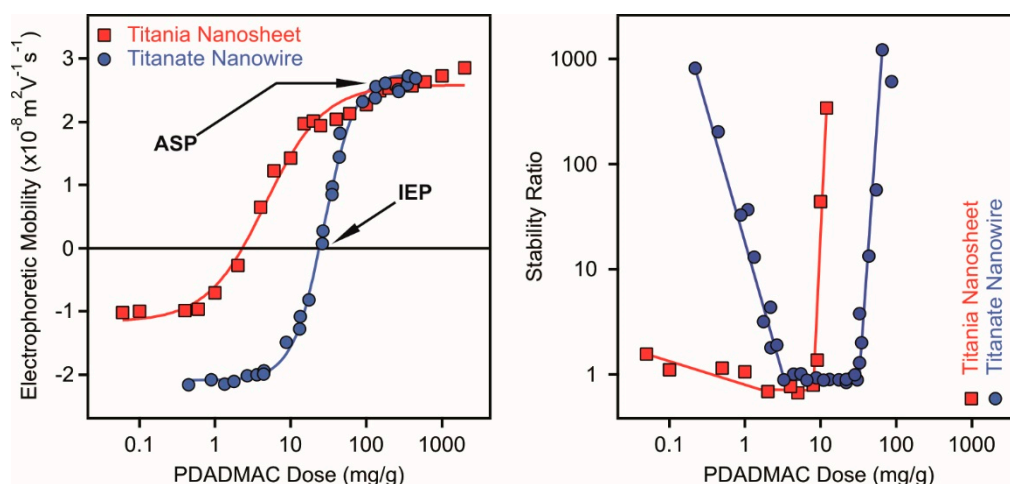


Figure 6. Electrophoretic mobilities (**left**) and stability ratios (**right**) of titania nanosheets (squares) and titanate nanowires (circles) at different doses of PDADMAC polyelectrolyte at 4.5 mM and 1 mM ionic strengths, respectively. The mg/g unit refers to mg PDADMAC per one gram of particle. The data were taken from References [31,63].

Concerning the electrophoretic mobility data (Figure 6, left), the values of both series with increasing polyelectrolyte dose showed a trend typical for oppositely charged polyelectrolyte-particle systems [37,72,78,86,87]. Accordingly, the mobilities are negative at low PDADMAC doses and correspond to the electrophoretic mobilities of the bare particles at the corresponding pH and ionic strength. Polyelectrolyte adsorption gave rise to increase in the mobilities and to charge neutralization of the particles at the IEP. The adsorption process continued beyond the IEP and charge reversal occurred. Such an inversion in the sign of the surface charge can be originated from hydrophobic interaction between the polyelectrolyte chains [88], from entropic effect due to the release of solvent molecules and counterions of the highly charged PDADMAC upon adsorption [89] and from ion-ion correlations [90]. The surface of the titanium oxides saturated with the polyelectrolyte at the adsorption saturation point (ASP), that is, further added PDADMAC remained dissolved in the solution. The mobilities were constant within the experimental error after the dose of the ASP.

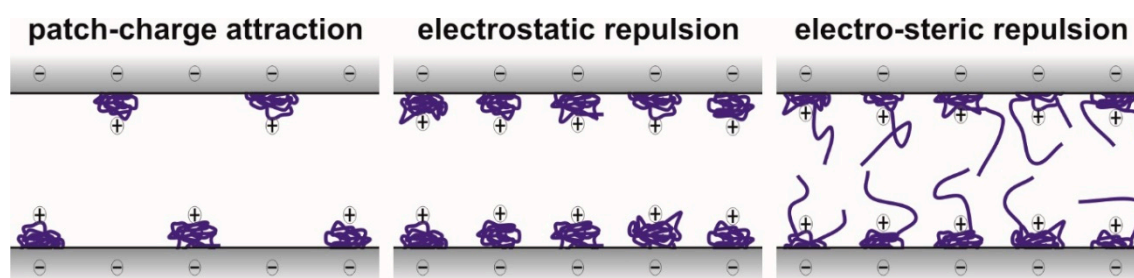
For the titanate nanowire system, the ASP values were determined at different ionic strengths and they increased with the salt level [63]. It was assumed that the electrostatic interaction between the adsorbed PDADMAC chains was responsible for such a tendency. At low electrolyte concentration, the adsorbed amount was limited, since the polyelectrolytes repelled each other on the surface. Once the ionic strength was increased, screening of the polyelectrolyte charge took place and thus, the reduced repulsion between the polyelectrolytes adsorbed on the surface led to higher adsorbed amount and to higher ASP. A decrease in the IEP data with increasing the ionic strength was also reported in the same system and the tendency was explained also with the electrostatic interaction between the adsorbed PDADMAC chains. The locations of the IEP and ASP values are system specific and depend on the surface charge densities of the titanium oxide materials, however, the above tendencies are generic in the individual systems.

The stability ratio data measured in the titania nanosheet and titanate nanowire systems (Figure 6, right) correspond well with the trend in the electrophoretic mobilities discussed above. Rapid particle aggregation and unstable dispersions were observed at doses close to the IEP, while the dispersions were more stable away from these polyelectrolyte loadings. For the nanowire particles, the samples were highly stable at low and high PDADMAC doses [63]. The stability ratio data resembled a U-shape curve, which has been already reported in other particle-polyelectrolyte systems too [37,60,72,91].

The titania nanosheets possessed limited stability at low doses indicated by lower stability ratios in this regime [31]. However, the formation of the saturated PDADMAC layer at the ASP led to stable dispersions and high or not even measurable stability ratio values were determined. Furthermore, the above observations were confirmed by imaging the particles with transmission electron microscopy at different polyelectrolyte doses. Accordingly, individual particles were imaged at low and high PDADMAC concentrations, while aggregated samples were found at doses close to the IEP.

Charging and aggregation of titania nanowires were studied in the presence of PSS (Scheme 2) below the PZC, where the nanowires are positively charged and the polyelectrolyte is of negative charge due to the deprotonation of the sulfonate functional groups [92]. The strong adsorption of the PSS on the oppositely charged surface was confirmed by electrophoretic measurements performed at different particle concentrations. The adsorption process led to charge neutralization and reversal similar to the above discussed systems, while the charge balance was the opposite due to the positively charged nanowires. Moreover, on the basis of the stability ratio data, unstable dispersions were observed near the IEP and stable ones at low and high doses. Similar results were published with titania nanosheets and titanate nanowires in the presence of protamine [62], poly(acrylamide-co-diallyldimethylammonium) chloride [31] and PAMAM dendrimers of different generations [66].

Although the overall tendencies were similar in these systems, different types of interparticle forces were observed. In general, repulsive electrical double layer and attractive van der Waals forces were always present. The latter ones were predominant close to doses of the IEP, while sufficiently charged particles were stabilized by the double layers at low and high polyelectrolyte doses. However, stability ratios lower than unity shed light on the presence of additional attractive forces especially near the IEP, at partial surface coverage [31,63,66]. It was assumed that patch-charge interaction [77,78,93] originating from electrostatic attraction between adsorbed polyelectrolyte islands and empty spaces of the partially covered surfaces was responsible for this additional attraction, which occurred with polyelectrolytes of high line charge density (Scheme 3).



Scheme 3. Illustration of different interaction forces between negatively charged particle surfaces with adsorbed polyelectrolytes of positive charge.

As discussed above, electrostatic repulsion between the polyelectrolyte coated surfaces is always present but the overlap of the adsorbed polyelectrolyte chains may give rise to the appearance of repulsive steric forces [94–96]. Such a steric stabilization can occur if the polyelectrolytes adsorb in an extended conformation and form tails on the surface, as illustrated in Scheme 3. The overlap of these tails leads to the rise of osmotic pressure, which causes repulsive interaction. These two effects (double layer and steric interaction) are often called an electrosteric stabilization mechanism [31,66,92]. One can

realize from these results that the nature of the adsorption process and the chemical composition of the polyelectrolytes and particles determine the strength of the interparticle forces of non-DLVO origin.

The stabilizing forces rose after polyelectrolyte adsorption can be demonstrated if one compares the charging and aggregation behaviour of bare and polyelectrolyte-coated titanium oxide materials. Polyelectrolyte coating refers to adsorption on the surface at a dose corresponding to the ASP, that is, the particles possess a saturated polyelectrolyte layer on their surface. Such a layer can be 2–10 nm thick depending on the experimental conditions applied [97]. Electrophoretic mobilities and stability ratios of bare and polyelectrolyte-coated titanate nanowires are shown in Figure 7.

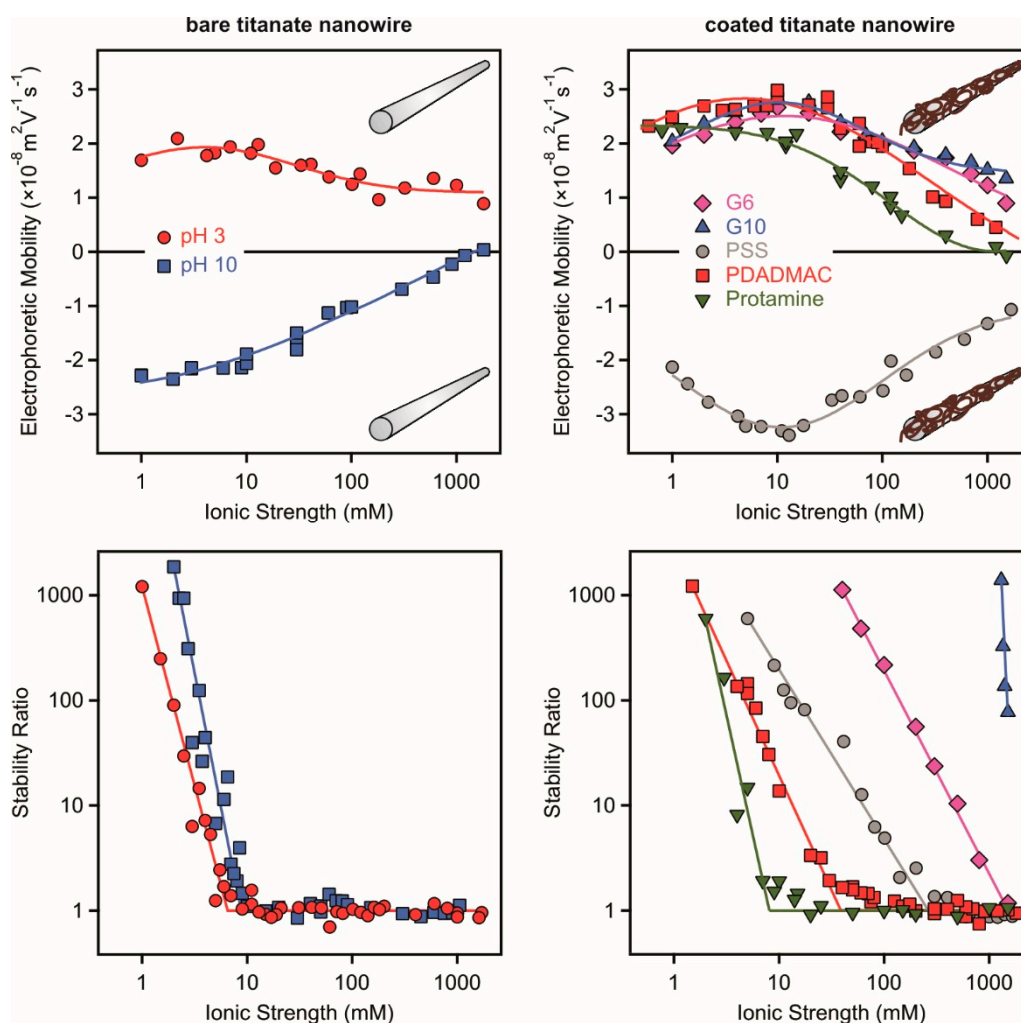


Figure 7. Charging and aggregation of bare (left column) and polyelectrolyte-coated (PAMAM dendrimers of generation 6 and 10, PSS, PDADMAC and protamine, right column) titanate nanowires. Electrophoretic mobilities (top row) and stability ratios (bottom row) as a function of the ionic strength adjusted by KCl. In the nanowire-PSS system pH 3 was set, while in the others pH 9, corresponding to positively and negatively charged particles, respectively. The data were taken from references [62,63,66,92].

The PZC of the bare nanowires is 4.1, therefore, they are positively charged at pH 3 and negatively at pH 9 (Figure 7, left). The magnitude of the electrophoretic mobilities decreases with increasing the ionic strength due to charge screening by the dissolved electrolyte constituents. Very similar CCC of about 8 mM was determined independently of the pH and the charge of the bare particles.

However, polyelectrolyte coating led to significant differences in both mobilities and stability ratios (Figure 7, right). This fact shed light on that the adsorption processes and interparticle forces

vary once different type of polyelectrolytes are used for the surface functionalization. Note that the coated particles are of the opposite charge to the bare particles, due to the charge reversal process. Although the electrophoretic mobility data also show some system specificity, the differences in the aggregation curves are more striking. Protamine coating did not give rise to significant change in the shape of the stability ratio plot or in the CCC, because this polyelectrolyte forms a homogeneous and thin layer on the nanowire surfaces and no additional (e.g., steric or patch-charge) forces were present between the functionalized particles [62].

The PDADMAC [63] and PSS [92] adsorption on the negatively and positively charged particles, respectively, resulted in remarkable increase in the CCC values (32 mM for PDADMAC and 600 mM for PSS) indicating the presence of steric stabilization among the electrical double layer repulsion. Moreover, the effect of PAMAM dendrimer layers on the colloidal stability of the titanate nanowires is the most significant compared to the other polyelectrolyte systems. The adsorption of the G6 led to a CCC of about 1500 mM, while the G10 stabilized the dispersions such that the CCC could not be determined, since it was higher than the solubility limit of KCl used to adjust the ionic strength [66]. These highly stable dispersions of primary particles are stabilized by electrosteric forces [94–96] and they are promising candidates in applications, wherever the nanowires should be resistant against salt-induced aggregation up to high ionic strengths.

3.3. Effect of Like-Charged Polyelectrolytes on the Stability of Titanium Oxide Dispersions

In this situation, the polyelectrolytes possess the same sign of charge as the particle surface and electrostatic repulsion is expected to hinder the adsorption process. However, as shown in the following examples, interaction between the like-charged polyelectrolytes and the titanium oxide particles can be promoted to tune colloid stability of the dispersions.

Adsorption of negatively charged polymethacrylate (PMA) on commercial titania spheres was reported above the PZC in the presence of Mn^{2+} ions [33]. On the basis of adsorption isotherms and results from electron paramagnetic spectroscopy experiments, it was suggested that the divalent metal ions induced the PMA adsorption and the Mn^{2+} ions adsorb directly on the titania-water interface and act as bridges between the surface and the polyelectrolyte. The formation of the titania- Mn^{2+} -PMA complex improved the colloidal stability of the dispersions significantly. Such an adsorption process of like-charged polyelectrolytes was also reported in other particle systems either in the presence [98] or in the absence [32] of multivalent bridging ions.

In another contribution, interaction of $BaTiO_3$ particles with PAA (Scheme 3) and PAA-poly(ethylene oxide) (PAA-PEO) copolymer was investigated at different ionic strengths adjusted by KCl or $BaCl_2$ salts [99]. Adsorption of both polymeric species was confirmed on the titanate surface of the same charge using total organic carbon analysis performed on the solution phase to determine the possible concentration of the non-adsorbed polymers. Addition of divalent cations caused aggregation at lower concentrations compared to the monovalent ones in the $BaTiO_3$ -PAA dispersions. The PAA-PEO macromolecules proved as excellent stabilizing agents, that is, stable samples were observed in the entire pH and salt concentration range investigated. It was suggested that the ionisable PAA part of the copolymer is adsorbed on the surface and it was shielded by the PEO chains from ion-bridging interaction, which would cause aggregation of the particles especially in the presence of multivalent ions. The PEO part also keeps the conformation of the adsorbed copolymer the same upon changes in the pH or ionic strengths, which results in stabilization of the dispersions under wide range of experimental conditions. Steric forces induced by the PEO segments played a major role in the improvement of the stability of the particle dispersions.

Titania nanoparticles were stabilized with the addition of PAA and titania-treated cotton fabric materials were prepared and investigated by light scattering, electron microscopy and in self-cleaning experiments [84]. The particles were negatively charged in a wide range of pH and no clear PZC was observed even at low pH, once PAA was present in the systems. This fact clearly indicated the adsorption of the polyelectrolyte on the like-charged surface and subsequent stabilization of the

dispersions. The distribution of the PAA modified particles on the cotton fibre surfaces was visualized on scanning electron microscopy (SEM) images.

Colloidal stability of titania spheres, nanotubes and their composites was studied in the presence of humic acid (HA) as well as mono and multivalent cations [79]. Zeta potential measurements revealed that the like-charged polyelectrolyte adsorbs on the titania surfaces. This result was also confirmed with IR spectroscopy by identifying the characteristic vibrational bands of the particles and polyelectrolytes in the spectrum recorded after HA adsorption. However, the presence of Ca^{2+} ions led to lower magnitude of the surface charge density likely due to the co-adsorption of the HA and the cations. Comparing the different titania structures, it was found that higher amount of polyelectrolyte adsorbed on the elongated materials and this finding was attributed to the higher specific surface area. The presence of HA inhibited the aggregation of the titania particles irrespectively of their shape, however, the stability was lower once Ca^{2+} and HA co-existed in the samples due to bridging effects.

To mimic the effect of natural organic matter on the charging and aggregation of spherical titania particles, the colloidal stability was investigated in the presence of HA and tannic acid (TA) [100]. Moreover, environmentally relevant cations were added to the dispersions to simulate the experimental conditions present in natural waters. Stabilizing effect of both HA and TA was reported and DLVO-type interaction qualitatively described the major interparticle forces. Polyelectrolyte adsorption led to an increase in the magnitude of zeta potentials and this phenomenon significantly contributed to the high stability through the increase in the strength of the electrical double layer forces. Adsorption of the divalent metal ions on the polyelectrolyte modified particles led to a decrease in the zeta potentials and to lower stability. However, aggregation was observed only in the presence of Ca^{2+} ions and not with the Mg^{2+} ions due to the formation of Ca^{2+} bridges between the polyelectrolyte chains adsorbed on the particle surfaces. The validity of size measurements carried out with light scattering was confirmed by SEM imaging, where similar sizes of the primary particles and aggregates were determined.

4. Conclusions

The colloidal stability of titanium oxide particles of various shapes and compositions in the presence of numerous charged species was summarized in the present review. First, it can be concluded that specific adsorption of monovalent ions on the titanium oxide surfaces determines the surface charge properties leading to different magnitude of the surface potentials. The major interparticle forces are of DLVO origin in these systems, however, the different charging behaviour due to specific ion adsorption gives rise to variation in the strength of the electrical double layer forces and thus, to different CCC values. The sequence of the CCC can usually be predicted by the Hofmeister series of ions once the charge and the hydrophobicity of the particles are correctly considered.

Second, multivalent ions are able to reverse the sign of charge of oppositely charged particles by adsorbing on their surfaces. Restabilization of the dispersions often occurs at electrolyte concentrations corresponding to the highest extent of the charge reversal. The CCC or CCIS values decrease with the valence of the counterions according to the Schulze-Hardy rule, which can be derived from the DLVO theory. Slight dependence of the CCIS on the valence can also be observed for coions, as described by the inverse Schulze-Hardy rule.

Third, polyelectrolytes can be successfully applied as stabilizing or destabilizing agents for titanium oxides. In the oppositely charged particle-polyelectrolyte systems, charge neutralization induced by polyelectrolyte adsorption destabilizes the dispersions due to the lack of repulsive electrostatic forces. Moreover, the highest stability of the samples containing primary particles was observed once a saturated polyelectrolyte layer forms on the titanium oxide materials causing charge reversal. Additional patch-charge and steric interactions also play major roles in the aggregation processes. Adsorption of like-charged polyelectrolytes is feasible with or without the help of multivalent ions, which may act as bridging agent between the polyelectrolyte chain and the surface.

Considering the results reported to date, the major future challenges in the field can be summarized as follows. Although, the influence of simple salts on the colloidal stability of titanium

oxide materials was extensively studied in the past in case of mono or multivalent counterions, there is a lack comprehensive investigation on the effect of coions of different valences. Given the widespread use of titanium oxide particles in electrolyte mixtures in environmental, biomedical or industrial applications, this issue deserves more attention. In addition, quantitative description of the aggregation processes has to be performed, since the classical theories, for example, Schulze-Hardy rule, usually gives only a qualitative prediction for the aggregation processes. Polyelectrolyte-particle systems represent an important class of materials in various fields, however, it is still not possible to quantitatively predict adsorption or aggregation processes by considering only the chemical composition of the polymers and the particles. The understanding of the contribution of different interparticle forces to the colloidal stability of such dispersions is also far from complete. To deal with these challenges, combined studies using state-of-the-art experimental and theoretical techniques should be carried out. Finally, the efficiency of the titanium oxide dispersions in various applications can be improved once researchers from different fields collaborate to understand each aspects of the process and the features of the involved materials.

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