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Abstract
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TUNING PARTICLE AGGREGATION IN SUSPENSIONS: FROM MONOVALENT IONS TO POLYELECTROLYTES

THÈSE D’HABILITATION

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par

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7. I. Szilagyi: Formulation of carrier nanoparticles: Towards highly stable delivery systems *Invited presentation at the EMN Meeting on Energy, Materials and Nanotechnology* Dubrovnik (4-7 May 2016) Croatia


11. E. Horvath, L. Forro, **I. Szilagyi**: Aggregation of titanate nanowires in the presence of polyelectrolytes *5th International Colloids Conference* Amsterdam (21-24 June 2015) The Netherlands

12. E. Horvath, L. Forro, T. Szabo, **I. Szilagyi**: Formulation of multifunctional titanate nanowire dispersions by polyelectrolytes *Smart and Green Interfaces Conference* Belgrade (30 March - 1 April 2015) Serbia


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ABSTRACT

The present thesis summarizes the research activity of the author in the period of 2010-2017. It focuses on colloidal stability and related interactions between particles in the presence of various aggregating agents. Colloidal particles include functionalized polystyrene latex beads, layered double hydroxide platelets and titanate nanowires. Surface charge characteristics were explored by electrophoresis, aggregation processes were followed in static and dynamic light scattering experiments, while the interparticle forces were measured by atomic force microscopy. Solid state characterization techniques involved transmission electron microscopy and X-ray diffraction and were used to confirm the formation of the inorganic hydroxide and titanate materials. The results are presented according to the type of the aggregating agents and can be briefly summarized as follows.

The stability of aqueous particle suspensions is sensitive to the physico-chemical properties of monovalent anions and cations present in the solution. Such ion specific effects lead to different charging and aggregation behaviour depending on the hydration state of the salt constituents. The classical Hofmeister series, developed to order cations and anions on the basis of their ability to aggregate charged particles, was verified and extended. The origin of the interparticle forces was found to be electrostatic and can be explained adequately with the classical DLVO theory. Multivalent ions destabilize particle suspensions more effectively than the monovalent ones due to their higher affinity to oppositely charged surfaces. The adsorption process and related charging properties depend on the valence of counterions, however, the predominating surface forces are of DLVO origin. Accordingly, the trend in particle aggregation follows the Schulze-Hardy rule, if the counterion valence is varied. Natural and synthetic polyelectrolytes acted as either aggregating or stabilizing agents depending on their dose in the samples. They strongly adsorb on oppositely charged surfaces leading to charge neutralization and subsequent charge reversal by increasing the concentration. Unstable suspensions were observed in the absence of surface charge and highly stable samples were obtained once the particles were completely coated with the macromolecules. The amount and the hydrodynamic layer thickness of the adsorbed polyelectrolytes were determined and correlated with the charging and aggregation processes. The same orientation of the elongated particles was found in aggregated clusters, regardless of the type of the aggregating agents.

These results were published in 31 scientific papers and presented at 31 conferences and research meetings in the form of oral presentation. The findings shed light on important relationships between particle interactions and the chemical content of the surrounding solutions. The applicability of existing theories was clarified and they were extended for specific systems in order to be able to predict colloidal stability from the composition and the structure of the particles and the aggregating agents present in the samples.
Ce manuscrit d’habilitation à diriger des recherches résume les activités scientifiques de l’auteur durant la période 2010-2017. Cette thèse se concentre principalement sur la stabilité des colloïdes ainsi que sur leurs interactions avec les nanoparticules en présence de divers agents d’agrégation. Plusieurs types de particules ont été étudiés: des billes de polystyrène latex fonctionnalisées, des hydroxyles doubles lamellaires et des nanofilaments de titane. La charge surfacique a été déterminée par électrophorèse, l’agrégation des particules par diffusion dynamique de la lumière tandis que les forces interparticulaires ont été identifiées grâce la microscopie à force atomique. La caractérisation des matériaux solides a été effectuée par microscopie électronique à transmission et par diffraction des rayons X. Les résultats dans ce manuscrit seront présentés en fonction du type d’agent d’agrégation.

En présence d’ions monovalents, la stabilité des particules en suspension dans les solutions aqueuses est sensible aux propriétés physicochimiques des anions et des cations. La spécificité des ions résultent en des différences de charge et d’agrégation des particules en fonction de la composition et donc de l’état d’hydratation des sels. La série de Hofmeister qui définit l’ordre des cations et des anions en fonction de leur capacité à agréger les particules chargées a été validée et étendue. L’origine des forces interparticulaires s’avère être de nature électrostatique et peut être décrite de manière adéquate par la théorie DLVO. Les ions multivalents déstabilisent d’avantage les particules en suspension que les ions monovalents dus à une plus grande affinité avec les particules de charges opposées. L’adsorption des ions et les propriétés de charges dépendent de la valence des contre-ions, cependant, les forces prédominantes sont d’origine DLVO. Par conséquent, l’agrégation des particules suit la règle de Schulze-Hardy, si la valence du contre-ion est modifiée. Les polyélectrolytes naturels et synthétiques s’avèrent être à la fois des agents d’agrégation mais aussi de stabilisation en fonction de leur dose dans l’échantillon. Ils s’adsorbent fortement sur les surfaces de charges opposées résultant en une neutralisation des charges puis à une inversion des charges si leur concentration est augmentée. Des suspensions instables ont pu être observées en l’absence de charges surfaciques alors que des échantillons extrêmement stables ont pu être obtenus une fois les particules entièrement fonctionnalisées avec les macromolécules. La quantité ainsi que le rayon hydrodynamique de la couche de polyélectrolytes adsorbés ont été déterminés.

L’ensemble de ces résultats ont été publiés dans 31 papiers scientifiques et présentés lors de présentations orales dans 31 conférences scientifiques et réunions de recherches. Ils ont permis de mettre en lumière d’importantes relations sur les interactions entre les particules en fonction de la composition de la solution. L’applicabilité des théories existantes a été validée et a été élargie pour des systèmes spécifiques dans le but de prédire la stabilité colloïdale à partir de la composition et de la structure des particules et des agents d’agrégation.
Chapter 1
INTRODUCTION

1.1. Application of particle dispersions

Particle dispersions (or so-called colloids) are widely used systems in various applications in environmental, industrial or biomedical processes (Figure 1) [1-3]. The dispersed solid particles may possess dimensions from a few nanometers to micrometers. Their compositional and morphological diversity is large, therefore, spherical (e.g., metals, polymers and oxides) or elongated (e.g., clays, carbon derivatives and chalcogenides) particles exist.

![Figure 1. Occurrences of particle dispersions in various processes.](image)

The stability of the particle dispersions is a critical issue in the applications. Stable dispersions (high colloidal stability) contain mainly primary particles homogeneously distributed in the continuous liquid phase. On the other hand, fast aggregation of the particles leads to unstable
dispersions (low colloidal stability) and to the formation of doublets at short and large clusters at longer time periods. Such large aggregates may interlink giving rise to phase separation [4]. The main factors influencing the colloidal stability of the particles are the composition, concentration and surface charge. The latter property originates from the structure (structural charge) or the protonation equilibria of the surface functional groups (pH-dependent charge) of the particles. In addition, adsorption of ionic compounds also affects the charging behaviour. Let us now discuss the role of particle aggregation in some applications.

For instance, suspensions composed of cellulose fibers and fillers are important systems in the papermaking process [5]. Fillers are naturally occurring clay, silica, titania or calcite particles of sizes in the sub-micrometer range. They are used to tune the properties of the paper and to reduce the production costs. These particles and fibers are aggregated with sufficient polymeric flocculants in order to achieve an efficient separation from the liquid phase and to obtain the raw material [6]. The samples contain mainly negatively charged particles, cellulose fibers and microcrystals, whereas positively charged flocculants are used as retention aids to keep these materials in the paper.

Paints are also important disperse systems. One of the biggest recent achievements was the development of water-based products to avoid the use of toxic organic solvents. These paint suspensions generally consist of water, pigments, fillers and stabilizing agents. Titania is almost indispensable in white pigments due to its high refractive index [7], however, latex particles have also shown excellent anti-corrosion properties in protective paintings due to their good environmental stability in long-term applications [8]. Cheap minerals, such as calcite, clay or silica particles are the filling materials, while polymeric or surfactant stabilizers of various composition and structure are responsible for achieving homogeneous particle distribution in these complex systems.

The above particles, together with others used in consumer products and industries, became a significant part of wastewaters, which also contain dissolved electrolytes, biomolecules and natural organic matter including humic acid derivatives. The removal of the particles during the primary water treatment is essential, since harmful bacteria can adsorb on them leading to a special protection against disinfectants. In drinking water production, the particles are aggregated and then sedimented and filtered. Aggregating agents usually include organic polymers [9] or multivalent metal ions [10]. The use of the first ones is more advantageous, because smaller amounts of the agents are required. In addition, the polymer-induced aggregation process leads to smaller sludge volume and lower amount of ionic components in the treated water. However, the usage of multivalent metal ions such as Al$^{3+}$ or Fe$^{3+}$ reduces the cost of the water purification process.
Recently, biomedical application of nano-sized particles is an important and continuously growing field. For instance, inorganic materials (e.g., layered double hydroxides (LDHs, see subsection 2.2 for more information) and iron oxides) of dimensions in the nanometer range are widely used in drug and gene delivery processes [11]. The carrier particles are generally loaded with drug or gene molecules and decorated with specific ligands, which recognizes the target cells. One of the central questions in these applications is the stability of the nanocarriers in the biological medium, since their aggregation is common in such a complex environment [1]. The formation of large and irregularly shaped clusters can lead to inefficient delivery, uncontrolled drug release and they can also block the veins. High resistance against aggregation can be achieved by the preparation of a biocompatible macromolecule layer on the carrier particles [12].

Besides, synthetic particles (or so-called engineered nanomaterials) suspended in liquid media are widely used in cosmetics and food products [2]. For instance, titania is used in sunscreens due to its high ultraviolet absorption properties. Stabilization in the products is typically solved by particle coating with polymeric or inorganic compounds [13]. Foods are complex multiphase systems containing various solid materials and macromolecules, where particles are commonly applied to stabilize emulsions and foams [14]. Silica or protein-based nanomaterials are widely used in such samples, as they stabilize food colloids due to accumulation at the oil-water (emulsion) or air-water (foam) interfaces. The extended usage of various particles in these products required comprehensive studies on their behaviour in life cycles, where change in specific properties (e.g., size, surface area and composition) may have enormous effect on the living organisms [15]. Therefore, a detailed understanding and control of the properties of such particles is necessary. In addition, the stage of their aggregation is a critical issue, since this process can have dramatic effects on the behaviour of the nanomaterials.

1.2. Colloidal stability

The above examples shed light on the fact that the stability of particle suspensions plays a key role in many applications. Accordingly, certain products (e.g., paints, foods or cosmetics) can be described as stable colloid systems, while destabilization of particle suspensions by sufficient aggregating agents is required in other processes such as papermaking or water treatment. Besides, both stabilization and destabilization occur at different stages of the procedure when nanoparticles suspended in a liquid are used as catalysts. Stable dispersions of primary particles are required during the catalytic run, while they are removed by aggregation and subsequent filtration after the reaction terminated [16-18]. Let us now discuss briefly the origin of the interparticle forces usually responsible for the colloidal stability of suspensions. More detailed information on the system specific interactions and related stabilizing effects will be provided in the latter subsections.
Neutral particles in a liquid attract each other by van der Waals forces. Colloidal particles in water often carry substantial charges leading to the formation of an electrical double layer (EDL) around the particles, which, therefore, repel each other by Coulomb forces. However, the van der Waals forces are always present. The extent of the overall interparticle force acting between the charged particles is determined by the superposition of the repulsive and attractive forces. This theory was developed by Derjaguin, Landau, Verwey and Overbeek (DLVO) [19-21]. These scientists also observed that the repulsive forces can be screened by adding salts to the samples and that the EDL vanishes at appropriately high salt concentrations leading to the predominance of the van der Waals forces and to fast aggregation of the particles. For particle suspensions, therefore, the aggregation rates of the charged grains are small or not even detectable at low ionic strengths, while the particles aggregate rapidly at high electrolyte concentrations. These two regimes are separated by the critical coagulation (equivalent to the term aggregation) concentration (CCC), which represents a sharp transition between the slow and fast aggregation of the particles. Accordingly, the rate of aggregation increases progressively with the ionic strength and remains constant above the CCC. Figure 2 illustrates this tendency for the early stages of the aggregation, where mainly particle dimers form. Further details and the quantitative description of the DLVO theory will be given in subsection 3.3.

It is often difficult to keep colloidal systems salt-free, therefore, stabilizing agents have to be used in order to maintain the stability of the samples. Polymeric materials have been widely used to stabilize particle suspensions. They can be neutral or charged and different techniques have been developed to anchor them on particle surfaces. Here, focus is made only on the latter case, where charged polymers, or so-called polyelectrolytes [22], are involved in the stabilization process (Figure 3). In the grafting methods, the particles are prepared first and initiators are attached to their surface. Monomers are then added to the sample and the polymerization is carried out with a suitable technique (e.g., photo-emulsion polymerization or controlled radical polymerization) and the chains are being grown directly from the surface [23]. Such procedure results in spherical polyelectrolyte brushes covalently bound to the particles. The structure and the thickness of the polyelectrolyte layer depend on the experimental conditions such as pH, ionic strength and type of solvent. The surface of the charged particles can also be coated by adsorbing oppositely charged polyelectrolytes, however, the strength of the attachment is weaker than in case of the chemically bound brushes. The mass and the thickness of the adsorbed layer...
can be tuned by varying the molecular mass or the ionic strength [24]. The first method results in high grafting density, while the latter one doesn’t require complicated chemical reactions.

Figure 3. Left: Schematic representation of polyelectrolyte-coated particles prepared by adsorbing or grafting the charged macromolecules on the surface. Right: some examples of charged functional groups present in polyelectrolyte chains.

For polyelectrolyte covered particles, the repulsive forces can originate from electrostatic and steric interactions. In the first case, the interparticle forces are the same as the ones predicted by the DLVO theory, however, the magnitude of the surface charge density is sufficiently increased due to the adsorbed polyelectrolyte chains giving rise to stronger Coulomb repulsion between the particles. This can typically occur in the case of electrostatically adsorbed polyelectrolytes [25]. For covalently bound polyelectrolytes, monovalent counterions are confined in the brushes and cause higher osmotic pressure leading to stretching of the polyelectrolyte chains and hence, to higher hydrodynamic radius than that would have been expected from a random coil conformation or from an extended chain of identical molecular weight in the solution [26]. Repulsive forces act upon overlap of the brushy layers and are called steric forces. However, both electrostatic and steric (electrosteric) repulsions are responsible for the stabilization of polyelectrolyte-grafted particles giving rise to highly stable suspensions even at elevated ionic strengths, where the electrostatically adsorbed polyelectrolytes usually desorb from the surface and where the particles rapidly aggregate [27].

Certain industrial processes (e.g., papermaking and water treatment) are based on destabilization of colloidal suspensions. Aggregation of charged particles can be induced in various ways. Monovalent electrolytes destabilize the suspended particles by surface charge screening, while multivalent ions by the joint effect of adsorption and screening [28]. Polyelectrolytes can also be used as aggregation agents, but their dose has to be explicitly known, since applying them at too high concentration leads to electrostatic stabilization, as discussed above [29].
1.3. Tuning particle aggregation

In the following part of the thesis, specific examples for both aggregating and stabilizing substances reported in the literature will be summarized with a focus on the aggregation mechanism and on the origin of interparticle forces. Stability of charged particles in the presence of monovalent salts, multivalent ions and polyelectrolytes will be discussed.

1.3.1. Monovalent ions

Particle aggregation in monovalent electrolyte solutions has been extensively studied in the past decades. The DLVO theory considers only the concentration and the charge of the electrolyte constituents irrespectively of their chemical nature. Therefore, it predicts the same effect of monovalent electrolytes of different compositions on the colloidal stability. At low ionic strength, stable dispersion of primary particles exists, while at higher salt concentrations, the aggregation becomes fast. The CCC is an important measure of the destabilization power of a certain salt. Although the DLVO theory cannot distinguish different types of ions of the same valence, ion specificity can be introduced by assuming that the salt constituents may specifically interact with the surface. This assumption relies on the fact that the affinity of the ions to the particle surfaces differs considerably, and hence, their adsorption modifies the surface charge differently. For counterions, the adsorption reduces the charge and weakens the EDL forces [30-34].

Indeed, the presence of ions of the same valence may lead to different CCCs [35-43]. The shift in the CCC can be explained by the Hofmeister series, which classifies ions according to their hydration level and affinity to surfaces [44-47]. These series was originally developed to express the stabilization power of simple electrolytes in protein solutions [45]. Although ions of higher valence were also included in the original Hofmeister series, they should be excluded in the case of particle aggregation, since they follow the Schulze-Hardy rule [48-50], which will be discussed later. Therefore, the case of monovalent ions will be detailed in this part of the thesis.

The CCCs of negatively charged hydrophobic particles follow the direct Hofmeister series shown in Figure 4. Accordingly, the ions on

![Figure 4. The Hofmeister series for anions and cations. The order is valid for hydrophobic particles of low surface charge in the presence of monovalent electrolytes.](image-url)
the left (e.g., N(CH$_3$)$_4^+$ or H$_2$PO$_4^-$) induce lower CCC, while the ions on the right (e.g., Li$^+$ or SCN$^-$) destabilize the suspensions at higher CCC. The aggregation behaviour of positively charged hydrophobic particles can be described by the indirect Hofmeister series, in which the ions on the left side induce higher CCC, while the ions on the right a lower one. The order is reversed for hydrophilic particles, accordingly, negatively charged particles follow the indirect Hofmeister series, while the shift in the CCCs can be explained by the direct series for positively charged hydrophilic particles [51].

Both direct and indirect Hofmeister series can be related to the hydrophobicity (i.e., level of hydration) of the ions. Small and strongly hydrated anions appear on the left side, while large and poorly hydrated ones are located on the right. The cations are disposed in the opposite way. Large and poorly hydrated cations are on the left side, while strongly hydrated ones are located on the right. Let us discuss the case of suspensions of hydrophobic particles. Poorly hydrated ions adsorb on such surfaces more strongly than the well-hydrated ones. Adsorption of cations on a negatively charged particle reduces the surface charge and hence, leads to lower CCC. Binding of anions will increase the magnitude of the surface charge and gives rise to higher CCCs. Concerning the positively charged particles, adsorption of anions will reduce the surface charge, while adsorption of cations will increase it. Accordingly, the aggregation of negatively charged hydrophobic particles can be described by the direct Hofmeister series, while the positively charged ones follow the indirect series. Once the surface is hydrophilic, well-hydrated ions will adsorb strongly on such grains, while the extent of the adsorption of poorly hydrated ions is much weaker. Therefore, stability of negatively charged hydrophilic particles follows the indirect Hofmeister series, while positively charged ones the direct series. This picture may be more complicated in the presence of additional forces induced by adsorption of the ions. These forces are normally not included in the DLVO theory, since they are usually short-ranged, typically act within a few nanometers. At short distances, the DLVO model has some limitations [52,53]. While the additional forces may partly change the sequences within the Hofmeister series, similar qualitative interpretation can be applied for the CCCs in those systems too.

The surface charge density of hydrophobic particles often varies systematically with the type of the surrounding ions. For example, the positive charge of alumina particles decreased in the Cl$^-$ > Br$^-$ > I$^-$ order indicating the indirect Hofmeister series [30]. The same tendency was shown for positively charged latex particles [35,36,38,54]. The charge density of negatively charged alumina beads increased in magnitude from Cs$^+$ to Na$^+$ in agreement with the direct Hofmeister series [30]. In addition, similar trends were reported for other negatively charged particles (e.g., hematite, titania and silica) [33,55]. However, the behaviour of the latter sample is atypical, since silica is usually highly charged and it follows the indirect Hofmeister series in agreement with the prediction for hydrophilic substrates [31,32]. Similar tendency was reported for silver halide colloids [56].
Besides, positively charged LDH particles showed higher affinity to HCO$_3^-$ than to Cl$^-$ or NO$_3^-$ [57,58], as shown in electrophoretic experiments. Such a trend agrees with the direct series for positively charged hydrophilic particles. However, the HCO$_3^-$ ions are strongly bound to the alkaline surface through Coulomb attraction and extended hydrogen bonding network between the surface hydroxyl groups and the HCO$_3^-$, while the LDH particles are considered to be hydrophobic. Therefore, the difference from the indirect Hofmeister series for HCO$_3^-$ is only due to specific interaction of these anions with the LDH surface [59]. This fact has been confirmed in electrophoretic experiments, where the surface charge of LDH decreased in the Cl$^-$ > SCN$^-$ order indicating the validity of the direct Hofmeister series [60].

From the trends in the observed CCCs, one can conclude that surfaces of colloidal particles are usually hydrophobic. Accordingly, negatively charged polystyrene latex or clay particles follow the direct Hofmeister series, whereas the CCCs of metal oxides or polystyrene particles of positive charge can be predicted by the indirect one [35,36,38-40,42]. Although the same tendency was observed for negatively charged silver halide particles too [43], the behaviour of this system looks irregular, since the surface charge densities follow the reverse trend [56]. Regarding polystyrene latex particles, the literature data is incomplete, since only a few cations have been investigated so far. Protein-coated latex or calcined titania behaved as expected for hydrophilic surfaces [37-41]. CCCs of LDH particles decreased in the Cl$^-$ > Br$^-$ > SCN$^-$ order in agreement with the indirect Hofmeister series for positively charged hydrophobic particles [61]. However, ion specific effects on the colloidal stability were absent for iron oxide, titania and carboxyl latex particles of low surface charge density [39,40].

On the basis of the determined CCCs, a transition between the direct and indirect Hofmeister series was observed for titania upon heat treatment [39]. The as-prepared particles followed the indirect series under alkaline conditions, as one would expect for a hydrophilic surface. After performing the heat treatment, the surface becomes hydrophobic due to the loss of the surface hydroxyl groups and the direct Hofmeister series was found. A similar transition between the direct and indirect series was also observed for silica surface once the pH was varied [34]. Under acidic experimental conditions, the silica surface is hydrophobic owing to the protonated stage of the surface hydroxyl groups and thus, it follows the direct series. Under basic experimental conditions, however, the surface becomes more hydrophilic due to the ionization of the silanol groups and hence, agrees with the indirect Hofmeister series. It was also reported that the charge density of silica may follow the direct [55] or the indirect [31,32] Hofmeister series. This fact could also be related to this hydrophobic to hydrophilic transition by varying the experimental conditions. In some systems, partial reversal of the Hofmeister series was reported too [31,39,40] and this finding has also been supported by computer simulations [51].
1.3.2. Multivalent ions

As discussed in the previous subsection, the types of salts are not directly considered in the DLVO model, however, this theory takes into account the valence of ions, which are present in the bulk solution around the particles [62]. One can show the dependence of the CCCs of colloidal particles on the valence ($z$) as [4,50,63]:

$$\text{CCC} \propto z^n$$  \hspace{1cm} (1)

Indeed, Schulze and Hardy have already recognized more than hundred years ago that metal salts containing ions of higher valence possess greater power in destabilisation of dispersions of charged particles than the ones composed of monovalent ions [64]. This phenomenon is widely utilized in applications, e.g., in water purification processes as discussed earlier.

The so-called Schulze-Hardy rule has been initially established empirically by studying the stability of colloidal suspensions of particles of either positive or negative charge in the presence of various salts. In these studies, the dependence of the CCCs on the valence was reported to be close to $n = 6$. However, this strong decrease of the CCC on the valence can be derived from the DLVO theory only for surfaces of unrealistically high magnitude of charge (around 1000 mC/m$^2$), while commonly used colloidal particles possess much lower surface charge density (typically between 15 and 150 mC/m$^2$ in absolute value). For such weakly charged surfaces of low surface potential, $n = 2$ applies in equation (1) [63].

The aforementioned rules were established for multivalent counterions, which have opposite charge compared to the particle surface. Besides, a weak dependence ($n = 1$) of the CCCs on the valence of the coions can also be derived from the DLVO theory [65], which has also been confirmed experimentally for both negative and positive latex particles in the presence of multivalent inorganic ions [66].

As one of the first systematic particle aggregation studies, the validity of the Schulze-Hardy rule has been tested on silver halide particles with a wide number of multivalent counterions [43,67,68]. In these studies, the CCCs were determined on the basis of the turbidity of the solutions and no aggregation rate coefficients were determined. The question of multivalent ion-induced aggregation was revisited in a wide range of systems. For instance, turbidity and electrophoretic measurements were performed with negatively charged silver halides in the presence of K$^+$, Ba$^{2+}$ and La$^{3+}$ cations [69]. Absolute aggregation rates of polystyrene latex particles were determined in Na$^+$, Ba$^{2+}$ and La$^{3+}$ salt solutions. A decrease in the obtained CCCs was always found by increasing the valence [70]. Test tube experiments, carried out on the basis of visual inspection, with anionic clay minerals confirmed such trend with Na$^+$, Ba$^{2+}$ and La$^{3+}$ ions [61]. Aggregation of hematite particles was investigated by light scattering in the presence
of various mono, di and trivalent metal cations. The CCCs strongly decreased with increasing the valence confirming the validity of equation (1) [71].

Moreover, size and electrophoretic mobility measurements revealed that CCCs of positively charged LDH platelets changed in the presence of multivalent anions (SO$_4^{2-}$, CO$_3^{2-}$ and HPO$_4^{2-}$) and shifted towards lower concentrations by increasing the valence [60]. The higher affinity of multivalent ions to LDH surfaces resulted in charge reversal (also called as charge inversion or overcharging) in the presence of AsO$_4^{3-}$, CrO$_4^{2-}$, Fe(CN)$_6^{3-}$ and citrate anions, however, CCCs were not reported in these publications [58,72,73]. Besides, CCCs of several other type of particles including fullerenes [74,75], carbon nanotubes [76] and bacteria [77] strongly depended on the valence of counterions indicating the generality of the Schulze-Hardy rule.

As shown in Figure 5, the aggregation data obtained with some of the above mentioned particles adequately agrees with the Schulze-Hardy rule. The relative CCCs decrease with increasing the valence in all case, however, the values are different due to system specificity. By interpreting the data, one can recognize some common trends. First, multivalent anions aggregate colloidal suspensions at lower CCCs than most of the multivalent cations. Second, the power law shown in equation (1) describes the majority of the experimental data with $n=6$ relatively well. The classical Schulze-Hardy rule fits to the experimental results satisfactorily, however, the DLVO theory doesn’t predict such a strong dependence for these weakly charged colloids, but it proposes rather $n=2$ for symmetric ($z:z$) electrolytes. To clarify this issue and the origin of the additional interactions responsible for the $n=6$ dependence, further investigations are needed.

In the recent past, the role of multivalent ions in interactions between charged colloidal particles has been revisited due to the discovery that the DLVO theory may fail in the presence of multivalent ions. Indeed, attractive interactions were observed in the presence of multivalent ions in situations, where the classical DLVO model would predict repulsion. Adsorption of the multivalent counterions also induced charge reversal of oppositely charged silica and latex surfaces [78,79]. The presence of additional (non-DLVO) attractive forces is obvious, however, their origin and effect on particle aggregation rates have to be still clarified. It is also not clear whether the

![Figure 5. Relative CCCs (normalized to the monovalent case) of positively (filled symbols) and negatively (empty symbols) charged colloidal particles as a function of the valence of counterions. The solid lines show the dependence using equation (1) with the two limits.](image-url)
adsorption occurs due to short-ranged specific interactions or due to ion correlation effects. This aspect is also addressed in this thesis by investigating aggregation rates and interparticle forces between the colloidal particles in the presence of various types of multivalent ions.

1.3.3. Polyelectrolyte-induced aggregation or stabilization

Polyelectrolytes are charged macromolecules containing ionized or ionizable groups located either in the polymeric backbone or as a side group of the chain [80]. They can be linear or branched due to their structure, natural or synthetic owing to their origin as well as strong or weak depending on the ionization constant of their functional groups and on the acidity of the solution [22]. As already mentioned in subsection 1.2, they are widely used as stabilizing agents for colloidal particle suspensions, since polyelectrolyte coating often results in enhanced electrostatic and steric repulsion leading to highly stable colloids. For some examples of chemical structures, see Figure 6.

![Figure 6. Chemical structure of various polyelectrolytes in their ionized form. The negatively charged ones include heparin, PSS, PAA and P(AA-BA), while PAMAM dendrimers, linear PEI and PDADMAC possess positive charge at appropriately low pH. The abbreviations are defined at the end of the thesis on page 135.](image)
Charging and aggregation in various dispersions containing nano or colloidal particles and polyelectrolytes will be discussed in this subsection. Regarding the type of particles, focus is made mainly on spherical latexes, elongated LDHs and titanates. Literature examples for stabilization by electrostatically adsorbed polyelectrolytes will be discussed, however, the topic of particles with covalently grafted polyelectrolyte brushes [23] will not be elaborated.

In general, polyelectrolytes adsorb strongly on oppositely charged particles leading to charge neutralization and charge reversal at appropriate doses [24]. For instance, the adsorption of positively charged PAMAM dendrimers (structure is shown in Figure 6) on oppositely charged polystyrene latexes resulted in neutral particles at the isoelectric point (IEP) and positively charged ones at higher doses [81]. The adsorption continued until the onset of an adsorption saturation plateau (ASP), which corresponds to the maximum amount of PAMAM, which can adsorb on the particle surface (Figure 7). It was also found that the IEP and ASP values were shifted towards higher concentrations with increasing dendrimer generation, i.e., the molecular weight, from G4 to G10. This phenomenon is due to counterion condensation meaning that the dendrimers bind substantial amount of anions leading to an effective charge [82]. This effective charge became significantly smaller than the structural or bare charge with increasing generation, therefore, higher amount of dendrimers was necessary to neutralize the particle surface and hence, the IEPs were shifted towards higher doses from G4 to G10.

The colloidal stability was assessed by time-resolved dynamic light scattering (DLS) in the same systems giving rise to the following conclusions. The particle aggregation was fast near the IEP and was slow far below and above it. Accordingly, stable samples were observed at low and high PAMAM doses, while unstable ones at concentrations close to the IEP. The latter regime was shifted towards higher dendrimer loadings with increasing the generation due to the effect of the counterion condensation [82].

The aggregation rates were also sensitive to the ionic strength due to the screening effect of the background electrolyte on the charge of bare or PAMAM-coated latexes. The presence of two types of interparticle forces was assumed. Accordingly, the major ones were of DLVO origin,
i.e., repulsive double layer and attractive van der Waals forces. Besides, an additional attraction was reported at partial coverage close to the IEP due to patch-charge interactions [83]. These forces arise from surface charge heterogeneities upon the inhomogeneous adsorption of the dendrimers leading to a Coulomb attraction between the positively charged PAMAM patches and negatively charged empty places on the latex surfaces (Figure 8). The strength of this additional attraction increased with dendrimer generation and decreased with increasing the ionic strength indicating its electrostatic origin.

Similar results were reported for positively charged amidine latexes in the presence of PSS of different molecular masses [84]. PSS adsorption led to charge neutralization and charge reversal. Unstable samples were observed near the IEP, where aggregation was driven by van der Waals and patch-charge attractions. The extent of the latter force decreased with increasing the ionic strength. The thickness of the adsorbed polyelectrolyte layer was also measured by DLS. It was found that increase in molecular mass or salt level resulted in thicker polyelectrolyte layers on the particle surface.

Such a characteristic charging and aggregation behaviour of latex particles of different functional groups on their surface have been reported with other polyelectrolytes too. These studies include measurements of electrophoretic mobilities and aggregation rates of sulfate latex in the presence of oppositely charged PEI [85], PDMAEMA [86,87], P(DADMAC-NMVA) copolymer [88] and PDADMAC [89,90] (the abbreviations are defined at the end of the thesis on page 135). In general, the charging behaviour at different polyelectrolyte doses determines the aggregation processes in the suspensions, however, the location of the corresponding stability regimes is system specific and depends strongly on the pH, ionic strength as well as on the charge density of the particles and polyelectrolytes. Such latex suspensions have appeared to be suitable model systems for exploring the effect of polyelectrolyte adsorption on fundamental processes, e.g., adsorption or aggregation mechanisms and related interparticle forces, in aqueous heterogeneous systems.

Besides, surfaces of particles of elongated structures were modified by polyelectrolyte adsorption for different purposes. Among them, colloidal stability of LDH platelets was extensively studied due to their potential application as drug or gene carriers in biomedical delivery processes [91-93]. Drug or gene molecules of negative charge were adsorbed between the LDH layers and on the outer surface. However, aggregation of the composite materials often led to the formation of irregularly shaped clusters in the biofluids, which prevented the successful targeted delivery.
Therefore, the use of powerful stabilizing agents was found to be important to achieve homogeneous distribution of the carrier particles in the living organisms. Aggregation was impeded by coating the platelets with biocompatible polyelectrolytes, which were electrostatically or covalently bound to the surface.

PAA adsorption on LDH particles of different composition also gave rise to charge neutralization and overcharging at appropriate polyelectrolyte concentrations, however, the colloidal stability was not assessed in these samples [58]. LDH platelets showed excellent resistance against aggregation once they were prepared together with PAA-b-PAM hydrophilic block copolymers in the reaction mixture [94]. In this study, the nature of the interaction between the metal ions and the polymer as well as the charge balance during the synthetic procedure was extensively investigated. Such a stable LDH colloids are promising candidates in biomedical delivery processes, nevertheless, the biocompatibility of the copolymer has to be still verified.

In addition, the colloidal stability of LDH particles as potential drug carriers was improved with other suitable stabilizers too. Serum albumin, as a natural blood constituent polyelectrolyte of high negative line charge density under physiological conditions, was adsorbed on drug-intercalated LDH platelets and the aggregation behaviour was extensively investigated. Due to its relatively high affinity to the LDH surface, the adsorption of BSA led to overcharging of the LDH [12]. The dispersion stability of the BSA-coated platelets was studied at high ionic strengths and under biological conditions similar to the environment in the cells. It was found that the order of reagents added to the synthetic mixture and the size of the charge compensating interlayer anions influenced the dispersions stability significantly.

The colloidal stability of the above drug-intercalated LDH-BSA system was further improved by covalently linking the BSA molecules adsorbed on the particle surface with glutaraldehyde linkers (Figure 9) [95]. The composite materials obtained by this crosslinking process could be easily redispersed in aqueous medium and showed excellent cellular uptake in the drug delivery tests. The developed bionanocomposites did not show any toxicity and thus, they were recommended as effective drug delivery systems.

Figure 9. Schematic representation of the BSA adsorption (LDH-BSA) on a LDH platelet and glutaraldehyde crosslinking (LDH-BSA-GTA).
Surface charge properties and aggregation behaviour of Cl\(^{-}\), CO\(_3\)^{2-} or dodecylsulfate-intercalated LDH particles were investigated in simulated biological fluids containing BSA [96]. Light scattering data confirmed the formation of BSA corona on the particles due to the strong adsorption of the protein leading to charge inversion of the positively charged LDHs. It was found that repulsive forces of steric origin were responsible for the improved colloidal stability. Moreover, the BSA corona prevented the platelets from dissolution at slightly acidic pH, where the bare particles may dissolve. The interlayer anions strongly influenced the above features and the application of Cl\(^{-}\) or CO\(_3\)^{2-}-intercalated LDHs in drug delivery systems was suggested rather than the one modified with dodecylsulfate anions.

Preparation of membranes containing dispersed LDH lamellae in alginate matrix was also reported [97]. Alginate is a natural polysaccharide with large number of hydroxyl and carboxylic groups in its chain. These functionalities deprotonate at sufficiently high pH, therefore, alginate can be considered as a negatively charged polyelectrolyte. To achieve homogeneous distribution of the LDH particles, they were delaminated in formamide and mixed with alginate followed by removal of the solvent by extensive washing with water. The polyelectrolyte adsorption led to highly stable colloids and impeded the re-formation of the lamellar structure, which happened in the alginate-free samples. The LDH-alginate hybrid was thermally more stable than the polyelectrolyte without the particles.

The above discussion clearly focused on oppositely charge systems, i.e., the particles possessed positive charge and the polyelectrolytes were of negative charge. However, neutral polymers may also affect the aggregation behaviours [98] and this issue definitely deserves a discussion. Accordingly, adsorption of EPE1100 block copolymer of non-ionisable functional groups was reported on the LDH surface. Such an adsorption led to the formation of surface aggregates of the polymer and to different particle morphology. Results of solution depletion experiments pointed out that the saturation of the LDH surface occurred around the critical micelle concentration (CMC). At this concentration, the polymers participate in both micelle formation and surface aggregation processes. The surface charge was shaded by the adsorbed polymer layer of neutral charge and the positive zeta potential of the bare LDH decreased with the increase of polymer dose. Non-aggregating colloids were observed at adequately high EPE1100 dose even at high ionic strengths, where the bare LDH forms unstable dispersion. The electrostatic stabilization is negligible in this situation, however, the presence of repulsive hydration and steric forces gave rise to excellent colloidal stability of the LDH-EPE1100 composite.

Furthermore, interaction between LDH platelets and cationic starch has also been investigated [99]. In this case, the particles and the polyelectrolytes possessed the same sign of charge. The positive charges of the starch were obtained by covalent modification with quaternary
ammonium groups. Although electrostatic repulsion between the particles and the polymers should hinder the adsorption process, low-affinity Langmuir-type isotherms determined in batch experiments unambiguously confirmed the polyelectrolyte adsorption on the LDH. The electrokinetic potential remained constant during adsorption. Most likely, hydrogen bonding between the surface hydroxyl groups and the polyelectrolyte as well as an entropic gain due to the release of solvent molecules and counterions upon adsorption induced the polymer immobilization on the LDH. The adsorbed amount increased at higher ionic strengths due to charge screening, while this effect was more pronounced in the presence of multivalent cations, because of the formation of negatively charged metal-hydroxo complexes serving as bridges between the LDH and the polyelectrolyte. Moreover, the starch adsorption could be enhanced at higher pH or temperature. The colloidal stability of the suspensions were not assessed in this case, therefore, future particle aggregation experiments would be useful to clarify the aggregation behaviour of the particles.

Another important class of materials used in various fields is the titanate derivatives. Applications include, for instance, water treatment, drug delivery and preparation of composite materials to be used in sensors, catalysts or solar cells [100,101]. Among them, spherical nanoparticles are the most commonly used structures, however, they may be overruled in the future due to the potential development and use of titanate derivatives of elongated shape (e.g., nanowires and nanosheets).

Given the fact that titanate or titania suspensions are used in most of the application processes, detailed understanding of particle aggregation in such samples is crucial. Accordingly, colloidal stability of titanate derivatives of various compositions and shapes has been studied in some systems, as discussed later. However, in spite of the growing number of applications and predictable future importance of titanate nanosheets, nanotubes and nanowires, only a few articles can be found in the literature, which deal with the control of colloidal stability in aqueous dispersions. In addition, most of these studies approach the problem in a qualitative way and no considerable quantitative data (e.g., surface charge density, aggregation rate or CCC) have been disseminated yet.

Colloidal stability of titanate nanotubes and their titania-modified derivatives has been investigated by zeta potential and size measurements [102]. The latter materials are composed of broken nanotubes with spherical titania on the outer surface. The charging and aggregation at different pH and ionic strength were found to be very similar for these compounds due to the similarity in their chemical composition. The particles possessed no charge around pH 3.5 (commonly expressed as point of zero charge (PZC) in the literature) and were negatively charged above this pH value. Humic acids (a class of natural polyelectrolyte-type materials of significant negative charge) adsorbed on the surfaces in both cases. Given the same sign of
charge for the polyelectrolyte and the surface, the adsorption was driven by non-electrostatic interactions such as hydrogen bonding and entropy gain due to the release of solvent molecules and counterions upon adsorption. The interfacial humic acid layer formation resulted in higher zeta potential and improved the colloidal stability. It was assumed that the aggregation was prevented by both electrostatic and steric repulsions. Similar electro-steric stabilization mechanism has also been reported in dispersions containing humic acids and magnetite nanoparticles [103].

In a recent article, the effect of PEI adsorption on the aggregation in titanate nanotube suspensions was studied [104]. These nanotubes are potential candidates as carriers in biotechnology applications, however, their colloidal stability has to be improved. They were synthesized in a hydrothermal process from rutile. Zeta potential measurements at different PEI doses indicated that the polyelectrolyte adsorption on the oppositely charged nanotube surface led to charge neutralization and subsequent charge reversal at appropriate doses. The coating procedure gave rise to a relatively high coverage and to highly positive zeta potentials at polyelectrolyte doses, where the titanates were fully covered. The turbidity of the samples was measured in time-resolved experiments through monitoring of the absorption band with a spectrophotometer. It was reported that the bare nanotubes settled down quickly, while the PEI-coated ones showed greater stability. This correlates well with the zeta potential data, therefore, electrostatic stabilization by repulsive double layer interactions was suggested as the stabilizing force. In addition, the polyelectrolyte covered nanotubes were found to be biocompatible and showed good cellular uptake. These facts indicate their suitability as carrier particles in biomedical applications.

As discussed above, the effect of polyelectrolyte adsorption on the stability of colloidal particles has a huge importance in various fields. Although considerable amount of quantitative results have been published with spherical latex particles, it is still not possible to predict the suspension behaviour solely from the composition of the systems, i.e., type of latex and aggregating agents. The situation is even less clear for LDH and elongated titanate particles due to the lack of extensive studies on colloidal stability in the presence of aggregating agents such as multivalent ions or polyelectrolytes. To further clarify the picture and to better understand these systems, several issues (e.g., influence of shape, size and chemical composition on the aggregation rates and on the structure of the aggregates) have to be addressed in future systematic investigations. To handle these challenges, the present thesis deals with the effect of monovalent salts, multivalent ions and polyelectrolytes on colloidal stability of latex, LDH and titanate particles. Conclusions will be drawn on the basis of experimental results obtained by various techniques, in addition, future research directions will be suggested.
Chapter 2

COLLOIDAL PARTICLES

In this chapter, the colloidal particles discussed in the thesis are introduced. The particles include spherical latexes, LDH platelets and titanate nanowires. Their composition, size, charge and some other important properties will be summarized.

2.1. Functionalized polystyrene latexes

Polystyrene-based latex beads (Figure 10) were used to investigate charging, aggregation and interparticle forces in the presence of various additives in aqueous suspensions. These particles are widely used in biotechnology [105], sensing [106] and materials science to prepare novel composites [23,107-109]. In addition, they proved to be excellent spherical beads of well-defined size and surface charge properties to explore fundamental phenomena in aqueous suspensions [24,35,70,110,111]. The latexes to be discussed in the present thesis are surface functionalized commercial products purchased from Interfacial Dynamic Corporation (Portland, USA). They were used after purification by dialysis against ultrapure water to remove the dissolved contaminants from the dispersions.

![Schematic representation of the structure of latex particles.](image)

**Figure 10.** Schematic representation of the structure of latex particles. The polystyrene beads are functionalized with sulfate (SL), amidine (AL) and carboxylic (CL) groups.
They can be dispersed in water due to their surface functionalities. SL, AL and CL particles are polystyrene-based beads functionalized with sulfate, amidine and carboxylic groups on the surface, respectively. The SL and CL particles are negatively charged in aqueous suspensions at appropriately high pH, while the AL ones possess positive charge at low pH due to the protonation equilibria of the functional groups. In general, the charge is higher for the AL and CL particles in magnitude than for the SL in the fully ionized stage. All of these particles are considered to be partially hydrophobic due to the relatively low surface coverage of the functional groups.

The CML (carboxylate modified latex) particles are largely different in composition and in charging properties from the SL, AL and CL beads. These particles are prepared by copolymerizing carboxylic acid containing polymers leading to a highly charged and hydrophilic surface layer of carboxylate groups. The formation of such layer resulted in that high pH was required to deprotonate all of the functional groups of the particles. Data about the composition, size and charge of these latex particles are presented in Table 1.

**Table 1.** The characteristic size and charge data of the latex particles to be discussed in the thesis.

<table>
<thead>
<tr>
<th>symbol</th>
<th>surface functionality</th>
<th>pK$^a$</th>
<th>particle diameter (nm)</th>
<th>CV$^d$ (%)</th>
<th>SCD$^e$ (mC/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>TEM$^b$</td>
<td>DLS$^c$</td>
<td></td>
</tr>
<tr>
<td>SL-100</td>
<td>sulfate</td>
<td>~2.0</td>
<td>100</td>
<td>116</td>
<td>7.9</td>
</tr>
<tr>
<td>SL-190</td>
<td>sulfate</td>
<td>~2.0</td>
<td>190</td>
<td>194</td>
<td>3.1</td>
</tr>
<tr>
<td>SL-270</td>
<td>sulfate</td>
<td>~2.0</td>
<td>270</td>
<td>290</td>
<td>5.9</td>
</tr>
<tr>
<td>SL-470</td>
<td>sulfate</td>
<td>~2.0</td>
<td>470</td>
<td>476</td>
<td>2.6</td>
</tr>
<tr>
<td>SL-530</td>
<td>sulfate</td>
<td>~2.0</td>
<td>530</td>
<td>556</td>
<td>2.0</td>
</tr>
<tr>
<td>SL-980</td>
<td>sulfate</td>
<td>~2.0</td>
<td>980</td>
<td>1100</td>
<td>2.2</td>
</tr>
<tr>
<td>SL-3100</td>
<td>sulfate</td>
<td>~2.0</td>
<td>3100</td>
<td>N/A</td>
<td>5.6</td>
</tr>
<tr>
<td>AL-220</td>
<td>amidine</td>
<td>~10.5</td>
<td>220</td>
<td>234</td>
<td>4.3</td>
</tr>
<tr>
<td>AL-400</td>
<td>amidine</td>
<td>~10.5</td>
<td>400</td>
<td>412</td>
<td>3.3</td>
</tr>
<tr>
<td>AL-950</td>
<td>amidine</td>
<td>~10.5</td>
<td>950</td>
<td>1060</td>
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<tr>
<td>CL-1000</td>
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<td>1000</td>
<td>1032</td>
<td>4.5</td>
</tr>
<tr>
<td>CML-308</td>
<td>carboxylic</td>
<td>N/A</td>
<td>308</td>
<td>312</td>
<td>4.2</td>
</tr>
</tbody>
</table>

$^a$The dissociation constant values were reported by the manufacturer. $^b$Determined by transmission electron microscopy (TEM). $^c$Measured by DLS in stable dispersions. $^d$Coefficient of variation in size obtained by TEM. $^e$Surface charge density (SCD) reported by the manufacturer on the basis of conductometry measurements. They refer to the fully ionized stage.
The diameters of the particles determined by DLS were always higher than the values obtained by TEM. This is due to the stagnant layer of hydrated ions around the particles and to the finite polydispersity of the original samples, since the particles of higher size contribute significantly to the scattered intensity in the DLS measurements, much more than the smaller ones.

2.2. Layered double hydroxides

Layered double hydroxide (LDH) is the general term for the hydrotalcite-type anionic clays containing lamellar mixed hydroxides with exchangeable anions and water between the layers [112-116]. Their shape can be standard or rounded hexagon depending on the synthetic procedure. The structure of the lamellar LDHs originates from brucite (Mg(OH)$_2$) with octahedral coordination around the metal ions. Some of the Mg$^{2+}$ ions are substituted to trivalent cations (e.g., Al$^{3+}$ or Fe$^{3+}$) with similar coordination properties. The general structure of LDHs is illustrated in Figure 11.

![Figure 11. Schematic representation of the structure of LDHs. The general elemental composition is also indicated. The figure was reprinted from reference [117] with permission from John Wiley & Sons, Inc.](image-url)
This isomorphous substitution results in positively charged layers neutralized electrostatically by anions (NO$_3^-$, Cl$^-$, CO$_3^{2-}$, etc.). Accordingly, LDHs possess considerable ion exchange capacity and the anions may be exchanged with other negatively charged substances. Water molecules also exist in the interlayer space, therefore, the LDHs can be described with a general formula as [M$_{1-x}$M$_x$(OH)$_2$]$^x$[A$^{n-}$]$_{y/n}$·yH$_2$O, where M$^{2+}$ and M$^{3+}$ are the di and trivalent metal cations, while A$^{n-}$ is the intercalated charge compensating anion [118,119].

Although LDHs are less frequent than the cationic clays in nature, their synthesis is simple. Coprecipitation is the most common method to prepare them in large amounts, however, other processes (e.g., anion exchange, rehydration and hydrothermal methods) are also known and used [120,121]. Intercalation of negatively charged molecules (metal complexes, enzymes, various types of organic and inorganic anions etc.) into LDHs was comprehensively studied in the past decades [91,122-125]. The obtained nanocomposites have been used, for example, in catalysis, sensing, water treatment, coating and various biomedical processes [16,92,126-132]. In spite of the large number of applications in liquid media, their aggregation and related colloidal behaviour was poorly characterized.

The LDHs discussed in the present thesis (Table 2) were prepared by the flash co-precipitation method followed by hydrothermal treatments. In a typical synthesis, NO$_3^-$, HCO$_3^-$ or CO$_3^{2-}$ salts of Mg$^{2+}$ and Al$^{3+}$ ions were dissolved together in water and added quickly to a sodium hydroxide solution until the final pH reached 10. The samples were aged for a couple of hours at the same pH. The resulting suspensions were subjected to hydrothermal treatments at higher temperature for a few hours. The size and polydispersity of the particles could be controlled in this step by varying the experimental conditions [133-135]. The solid materials were then filtered, washed and redispersed in water. The formation of the layered materials was confirmed by X-ray diffraction and IR spectroscopy. In this way, colloidal LDHs with relatively narrow particle size distribution were prepared.

Table 2. The characteristic size and charge data of the LDH particles discussed in the thesis.

<table>
<thead>
<tr>
<th>symbol</th>
<th>cations$^a$</th>
<th>anions$^b$</th>
<th>size (nm)$^c$</th>
<th>PDI$^c$</th>
<th>SCD (mC/m$^2$)$^d$</th>
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<tbody>
<tr>
<td>LDH-272</td>
<td>Mg$^{2+}$ &amp; Al$^{3+}$</td>
<td>CO$_3^{2-}$</td>
<td>272</td>
<td>0.274</td>
<td>+15</td>
</tr>
<tr>
<td>LDH-632</td>
<td>Mg$^{2+}$ &amp; Al$^{3+}$</td>
<td>CO$_3^{2-}$</td>
<td>632</td>
<td>0.265</td>
<td>+15</td>
</tr>
<tr>
<td>LDH-336</td>
<td>Mg$^{2+}$ &amp; Al$^{3+}$</td>
<td>NO$_3^-$</td>
<td>336</td>
<td>0.390</td>
<td>+10</td>
</tr>
<tr>
<td>LDH-180</td>
<td>Mg$^{2+}$ &amp; Al$^{3+}$</td>
<td>NO$_3^-$</td>
<td>180</td>
<td>0.150</td>
<td>+11</td>
</tr>
</tbody>
</table>

$^a$Layer-forming metal ions. $^b$Interlayer anions. $^c$Hydrodynamic diameter and polydispersity index (PDI) measured by DLS in stable dispersions. $^d$Obtained by electrophoresis.
Table 2 shows the composition, size and surface charge of the obtained LDHs. Lamellar materials containing Mg\(^{2+}\) and Al\(^{3+}\) layer-forming cations, which are coordinated by hydroxyl groups, were prepared. The type of the interlayer charge compensating anion was varied. The CO\(_3^{2-}\) ions have higher affinity to the LDH surface, while the NO\(_3^-\) can be replaced by other negatively charged compounds [127]. The obtained platelet-like particles had a lateral dimension of a few hundreds of nanometers and a thickness of about 10 nm. The LDHs possess positive structural charge due to the aforementioned isomorphous metal ion substitution. This charge is constant in the pH range of 7-10 and its magnitude is much lower than the ones reported for the positively charged latex beads. Negative charge can also be generated on the surface by deprotonation of the surface hydroxyl groups, but such process is negligible in the pH range used in the present study.

2.3. Titanate nanowires

Titanate nanowire (TiONW) is an elongated titanate derivative and this material is widely used in sensors, nanocarriers and catalysts [101,136-139]. During the synthesis of the nanocomposites for these applications, functionalization of the titanate surface is often required to tune the aggregation of the particles in order to improve the material properties, such as porosity and grain boundaries. The structure and pH-dependent electrophoretic mobility values of the TiONW are shown in Figure 12.

The TiONWs were synthesized in a two-step hydrothermal process [140,141], in which anatase was reacted first with sodium hydroxide solution at high temperature. The intermediate product was collected and the previous step was repeated. The white product was then filtered off and washed extensively with water and neutralized with hydrochloric acid. The latter process exchanged the Na\(^+\) ions to H\(^+\) in the interlayer space. Finally, the TiONWs were dried and suspended in water. The formation of the nanowires was confirmed by X-ray diffraction, TEM and elemental analysis.

The structure of the TiONWs can be indexed as multilayered trititanate of H\(_2\)Ti\(_3\)O\(_7\) (or Na\(_2\)Ti\(_3\)O\(_7\) in the sodium form) composition with a gallery spacing of 0.5-0.8 nm between the layers, which consist of TiO\(_6\) octahedra sharing edges and corners as represented in Figure 12. The nanowires are not perfect cylinders, but rather resemble to rolled-up carpets. The length of the TiONW can be tuned by changing the growth conditions (e.g., temperature and composition of the starting mixture in the synthesis). The TiONWs discussed in this thesis have typical lengths of 300-600 nm and an average diameter of 30-40 nm. The samples were moderately polydisperse with a PDI of 0.260 (related to the longest dimension) as determined in stable dispersions by DLS [142].
Similarly to other titanate derivatives [143-145], the charge of the nanowires is pH-dependent due to the protonation equilibria of the surface hydroxyl groups and the adsorption of OH⁻ ions under alkaline conditions. The PZC was found to be 4.1 [146], accordingly, the TiONWs are positively charged below this pH, while their charge becomes negative at higher pH, as indicated by the electrophoretic mobilities in Figure 12.

![Figure 12](image)

**Figure 12.** The structure of the TiONWs in the sodium exchanged case. The hydrogen atoms are not shown for clarity. The electrophoretic mobilities of TiONWs measured in aqueous suspensions at different pH values and at 1 mM ionic strength (adjusted by the added HCl or NaOH solutions) are also presented. The electrophoretic mobility data were taken from reference [146].

Relatively low surface charge densities (+7 mC/m² at pH 3 and –20 mC/m² at pH 11) were determined in electrophoretic mobility measurements carried out in aqueous suspensions at different ionic strengths [146]. Such charges were found to be high enough to stabilize the TiONW suspensions at low salt concentrations, while the particles were aggregated close to the PZC. Addition of low amount of monovalent electrolytes gave rise to aggregation of the particles regardless of the pH.
Chapter 3

**METHODS TO STUDY PARTICLE STABILITY**

The colloidal stability of particles can be characterized by following the charging and aggregation processes in the suspensions. In addition, the direct measurement of the predominant interparticle forces may shed light on the mechanism of particle aggregation or stabilization. In this chapter the following experimental techniques will be discussed in detail: static and dynamic light scattering to measure aggregation rates, electrophoresis to determine mobilities and electrokinetic potentials as well as the multiparticle colloidal probe technique to measure interparticle forces.

### 3.1. Measuring aggregation rates by static and dynamic light scattering

Aggregation processes in particle suspensions lead to the formation of dimers at the early stages (Figure 13). Since the particle aggregation is irreversible, trimers, tetramers and bigger aggregates form in the late stages giving rise to sedimentation or creaming depending on the material properties [147]. At higher particle concentration, the aggregated clusters interlink and colloidal gels can be formed [148]. A large variety of experimental techniques have been used to explore particle aggregation in suspensions [149]. For instance, larger particles were studied in turbidity measurements, nevertheless, this technique can be applied for particles of smaller size only at high concentration, which condition results in the formation of higher ranked aggregates quickly [150,151]. To study the early stages of aggregation, time-resolved light scattering methods have proved to be suitable to determine aggregation rates of dimer formation in both static (SLS) and dynamic (DLS) mode [152,153]. These techniques permit to measure the size of particles ranging from a few nanometers to a micrometer.

In the present thesis, only the early stages of aggregation, where mainly dimers form, will be discussed for spherical latex and anisometric LDH and TiONW particles. In general,
aggregation is irreversible if the particles are sufficiently large and each collision of the primary particles (A) leads to doublet (AA) formation (Figure 13). The formation of each dimer gives rise to the loss of two primary particles and the corresponding rate law can be written as [152]:

$$\frac{dC_{AA}}{dt} = k\frac{C_A^2}{2}$$

(2)

where \(C_{AA}\) and \(C_A\) are the number concentration of the dimers and monomers, respectively, \(k\) is the aggregation rate coefficient and \(t\) is the time. The concentrations at very short time intervals can be calculated as:

$$\frac{C_A}{C_0} = 1 - kC_\eta t + ...$$

$$\frac{C_{AA}}{C_0} = \frac{C_0kt}{2} + ...$$

(3)

where \(C_0\) is the initial number concentration of the particles meaning that \(C_0 = C_A + 2C_{AA}\), provided only dimer formation occurs. If the particles undergo Brownian motion, i.e., the aggregation is controlled solely by their diffusion, the aggregation rate constant for doublet formation can be given by the Smoluchowski’s rate (\(k_s\)) as [149]:

$$k_s = \frac{8k_BT}{3\eta}$$

(4)

where \(k_B\) is the Boltzmann constant, \(T\) is the absolute temperature and \(\eta\) is the dynamic viscosity of the medium. The half-time of aggregation (\(T_{1/2}\)) refers to the time interval necessary to aggregate half of the monomers in the original dispersion. In an unstable sample, where diffusion controlled particle aggregation takes place, it can be calculated as:

$$T_{1/2} = \frac{2}{kC_0}$$

(5)

Considering equations (4) and (5), one can realize that at a given temperature, the value of \(T_{1/2}\) depends only on the particle concentration and the viscosity of the medium.

In SLS, the initial rate of change in the scattered intensity is followed in time-resolved measurements performed at one or several angles (Figure 14a). The scattering light intensity (\(I\)) determined by SLS measurements in aggregating dispersions can be written as [152,154]:

$$I(q,t) = I_A(q)C_A(t) + I_{AA}(q)C_{AA}(t)$$

(6)

where \(I_A\) and \(I_{AA}\) are the scattering intensities (or so-called form factor) of the monomer and dimer, respectively, whereas \(q\) is the magnitude of the scattering vector, which is defined as follows:
\[ q = \frac{4\pi n}{\lambda} \sin \left( \frac{\theta}{2} \right) \]  

(7)

where \( n \) is the refractive index of the medium, \( \lambda \) is the wavelength of the laser beam and \( \theta \) is the scattering angle.

\[ k_{\text{SLS}} = \frac{1}{I(q,0)} \left( \frac{dI(q,t)}{dt} \right)_{t=0} = \left( \frac{I_{\lambda\lambda}(q)}{2I_\lambda(q)} - 1 \right) kC_0 \]  

(8)

To describe the optical part in equation (8), the form factors of the monomers and dimers can be defined using the Rayleigh-Gans-Debye theory developed for weakly scattering particle systems as [147]:

\[ \frac{I_{\lambda\lambda}(q)}{2I_\lambda(q)} - 1 = \frac{\sin(2Rq)}{2Rq} \]  

(9)

where \( R \) is the geometric radius. If one knows the particle concentration and the refractive index of the solvent accurately, \( k_{\text{SLS}} \) can be obtained from the initial slope of the scattering intensity versus time plot by performing a linear fit. Its value depends on the scattering angle as shown in Figure 14a. Besides, the average hydrodynamic radius \( \langle R_\lambda \rangle \) can be measured by DLS in time-resolved experiments, similar to the SLS method discussed above [156].
Provided only monomers and dimers are present in the suspension, the average $R_h$ can be defined as follows [157]:

$$\frac{1}{R_h(t)} = \frac{I_A(q)C_A(t)/R_{hA}(t) + I_{AA}(q)C_{AA}(t)/R_{hAA}(t)}{I_A(q)C_A(t) + I_{AA}(q)C_{AA}(t)}$$

where $R_{hA}$ and $R_{hAA}$ are the hydrodynamic radii of the monomer and dimer, respectively, and $R_{hAA} = 1.39R_{hA}$ [4]. The apparent dynamic rate constants ($k_{DLS}$), which describe the initial increase of $R_h$, is given as:

$$k_{DLS} = \frac{1}{R_h(q,0)}\left(\frac{dR_h(q,t)}{dt}\right)_{t=0} = \frac{I_{AA}(q)}{2I_A(q)}\left(1 - \frac{R_{hA}}{R_{hAA}}\right)kC_0$$

Consequently, the $k_{DLS}$ can be experimentally determined from the slopes of the apparent hydrodynamic radius versus time plots. The value of $k_{DLS}$ also depends on the scattering angle, as shown in Figure 14b. If one combines equations (8) and (11), the absolute aggregation rate can be calculated without knowing the form factor of monomers and dimers as [70,152]:

$$kC_0 = \frac{R_{hAA}}{R_{hAA} - R_{hA}k_{DLS}}k_{SLS}$$

As shown in Figure 15, plotting the apparent static rates versus the dynamic rates, the intercept of the straight line gives $k$, while the hydrodynamic factor can be calculated from the slope.

The colloidal stability can also be expressed in terms of the stability ratio ($W$), which is the fast aggregation rate coefficient ($k_{fast}$) divided by the one ($k$) measured in the actual experiment [147,152,158-160]:

$$W = \frac{k_{fast}}{k}$$

Obviously, the value of $W$ can also be calculated from the apparent rates determined in time-resolved SLS ($k_{SLS}$) or DLS ($k_{DLS}$) measurements without knowing the optical and hydrodynamic factors of the monomers and dimers. Considering equation (13), it can be easily realized that higher stability ratios are measured for slow particle aggregation, while the values close to unity indicate rapidly aggregating particles.
3.2. Surface charge properties by electrophoresis

The electrical properties of charged colloidal particles suspended in a salt solution are determined by the spatial distribution of ions around the surfaces (Figure 16a). They originate from dissolved salts leading to the presence of coions (same sign of charge as the surface) and counterions (oppositely charged than the particles) in the samples. The distribution of these point-like charges from the surface gives rise to the formation of the EDL or electrical interfacial layer [62]. This layer contains a larger number of counterions than coions, as shown in a typical charge distribution in Figure 16b.

Accordingly, the positively charged interface is characterized by a localized layer of charged surface groups. Compensation of this positive charge takes place by the accumulated anions in the diffuse layer. Usually two types of ions can be distinguished in regard to their interaction with the surfaces. Indifferent ions adsorb on the interface only weakly by attractive Coulomb forces. Specifically adsorbing ions have strong affinity to the surface in addition to the generic Coulomb interaction. It has been already discussed in Chapter 1 that adsorption of the latter ions can also lead to charge reversal, where the sign of the surface charge is reversed after the adsorption process [24,161,162].

As illustrated in Figure 16c, the potential corresponding to the solid surface in contact with the electrolyte solution is the surface potential ($\psi_0$). The potential at the origin of the diffuse part of the EDL is called diffuse layer potential ($\psi_D$). The zeta (or electrokinetic) potential ($\zeta$) is positioned at the slip plane (or shear plane), which determines the distance from the surface, at which a hydrodynamically stagnant layer is present and moves together with the particle in an external electrical field [163]. However, this stagnant layer is very thin, therefore, the value of $\zeta$ is almost the same (at low electrolyte concentrations) or slightly smaller (at high electrolyte concentrations) than $\psi_D$.
Electrophoresis is a widely used method to investigate charging properties of colloidal particles in dispersions in the presence of surface active agents [24,164,165]. This technique explores the movement of charged particles or macromolecules suspended in a liquid under the influence of an external electric field. Two electrodes are used and the positively charged objects move towards the negatively charged electrode and the negatively charged grains toward the positive electrode. The relation between the value of the velocity ($v$) and the electrophoretic mobility ($u$) of the particles can be written as [62]:

$$v = uE$$

(14)

where $E$ is the magnitude of the electric field strength. The $v$ can be determined by light scattering techniques (e.g., laser Doppler velocimetry or phase analysis light scattering). The simplified mobility of an isolated charge, which moves due to the electric field is:

$$u = \frac{Q}{f}$$

(15)

where $Q$ refers to the charge ($Q = e\zeta$, $e$ is the elementary charge) and $f$ indicates the friction coefficient described by Stokes ($f = 6\pi\eta R$). In a suspension, the particles move together with the stagnant layer of ions and thus, the electrophoretic mobility values are proportional to the zeta potentials.

Different models are available to convert the electrophoretic mobilities to electrokinetic potentials, however, their applicability is limited and depends on the charge and size of the particles as well as on the ionic strength applied in the suspensions [163]. The concentration of the background electrolyte is included in the Debye length ($\kappa^{-1}$) through the ionic strength ($I$) as follows:

$$\kappa^{-1} = \sqrt{\frac{\varepsilon \varepsilon_0 k_B T}{2 N_A e^2 I}}$$

(16)

where $N_A$ is the Avogadro number, $\varepsilon_0$ is the permittivity of vacuum and $\varepsilon$ is the dielectric constant. For charged surfaces, the presence of the neutralizing diffuse layer of counterions leads to the formation of the EDL, as shown in Figure 16. The thickness of EDL can be estimated with the Debye length [62].

In the situation when $\kappa R \gg 1$ and the potential is low ($|\zeta| \leq 50$ mV), the theory developed by Helmholtz and Smoluchowski is applicable and $\zeta$ can be calculated as [62]:

$$\zeta = \frac{u\eta}{\varepsilon_0 \varepsilon}$$

(17)
If $\kappa R \ll 1$ (i.e., small particles and low ionic strength), the Hückel-Onsager equation is recommended to use:

$$\zeta = \frac{2u\eta}{3\varepsilon_0\varepsilon}$$  \hspace{1cm} (18)

The situation between the limits of these models (i.e., between low and high $\kappa R$ values) can be handled by Henry's formula as follows [166]:

$$\zeta = \frac{2u\eta}{3\varepsilon_0\varepsilon} f(\kappa R)$$  \hspace{1cm} (19)

where $f(\kappa R)$ is Henry's function, which varies from 1 (the case of equation (18)) to 1.5 (equation (17)) depending on the concentration of the background electrolyte in the suspensions. Note that equation (19) is valid only for potentials smaller than about 50 mV in magnitude.

Once the electrostatic potential is high and thus, the relaxation effect (it is owing to the deformation of the EDL in the electric field applied during electrophoresis) becomes significant, the O’Brien-White theory [165] is more accurate to perform the conversion. This model assumes that the electrokinetic potential is equal to the electrostatic potential at the particle surface.

Therefore, the most appropriate conversion model can be selected on the basis of the size of the particles (measured by an independent technique), the salt concentration (controlled during sample preparation) in the suspension and the magnitude of the potential.

One of the most important parameters, which can be estimated from the electrokinetic potentials, is the surface charge density ($\sigma$) of the particles. Two theories were evolved to describe the ionic strength dependence of the potentials (Figure 17). First, the Gouy-Chapman model was developed to calculate $\sigma$ from the potentials in case of charged planar surfaces immersed in salt solutions. Accordingly, this theory defines the decay of the potential with the ionic strength by the following relation [167]:

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure17.png}
\caption{Electrostatic potential values as a function of the ionic strength. The experimental points (circles) were measured by electrophoresis with negatively charged TiONW particles in LiCl electrolyte at pH 9. The solid and dashed lines were calculated with the Gouy-Chapman and the Debye-Hückel models, respectively, applying a surface charge density of -11 mC/m$^2$.}
\end{figure}
\[
\psi_0 = \frac{2k_B T}{e} \text{asinh}\left(\frac{e\sigma}{2k_B T \varepsilon \varepsilon_0 \kappa}\right)
\]  

(20)

The above relation is also called as Grahouette equation and it was developed on the basis of the Poisson-Boltzmann description of the charge distribution in the EDL [19-21].

Second, the Debye-Hückel theory defines the change of the potential with the electrolyte concentration for spherical colloids or planar surfaces as [4]:

\[
\sigma = \varepsilon \varepsilon_0 \kappa \psi_0
\]

(21)

This equation is also derived from the Poisson-Boltzmann theory by linearizing equation (20) and it is valid for low potential ranges. The discrepancy between these models is illustrated in Figure 17, accordingly, the Gouy-Chapman theory gives a more accurate solution for high potentials, while it agrees well with the Debye-Hückel model at low potentials (i.e., lower than approximately 25 mV in magnitude), where both of them provide reliable results.

### 3.3. Determination of interparticle forces by atomic force microscopy

Although the principles of the DLVO theory have been previously discussed in subsection 1.2, let us now revisit this issue in a more quantitative fashion. In case of charged colloidal particles suspended in an electrolyte solution, the EDL forms. The thickness of these layers have an important role in the particle stability, since upon their overlap an osmotic pressure is built up, which leads to repulsive interparticle forces. However, attractive forces are always present between the particles irrespectively of the charge. These are the van der Waals forces originating from moving dipoles of atoms and molecules. The DLVO theory states that the overall force acting between the particles can be approximated by the sum of these repulsive and attractive forces, as illustrated in Figure 18 [19-21]. In some cases, non-DLVO forces may also play important role. The nature of these interactions can be either repulsive or attractive. They usually originate from ion-ion correlation [168,169], surface charge heterogeneities [170], charged macromolecule adsorption on oppositely charged surfaces [27,103], depletion interactions [171] or hydrophobic effects between surfaces [172].

The DLVO-type interactions for charged spherical particles can be quantified as follows. This theory is based on the assumption that the total interaction energy \( V(h) \) between two identical particles at a separation distance \( h \) is the sum of the energies from the van der Waals \( V_{vdW}(h) \) and double layer \( V_{EDL}(h) \) interactions as:

\[
V(h) = V_{vdW}(h) + V_{EDL}(h)
\]

(22)
The attractive van der Waals interaction energy can be calculated within the Derjaguin approximation, which is valid for particles of significantly larger size than the ranges of the interactions, with the following equation [4,173]:

\[ V_{vdw}(h) = -\frac{RH}{12h} \]  

(23)

where \( R \) is the particle radius and \( H \) is the Hamaker constant. The latter parameter depends on the composition of the materials [4].

To quantify the double layer interaction energy, the Debye-Hückel superposition approximation can be applied, if the surface charge density (i.e., the surface potential) is low. This is the simplest situation, where \( V_{EDL}(h) \) can be given as:

\[ V_{EDL}(h) = 2\pi\varepsilon_0\varepsilon R\psi_0^2 e^{-\kappa h} \]  

(24)

For higher surface charge densities (i.e., particles of high electrostatic potential) and at smaller surface separations, the repulsion between the double layers can be quantified by solving the more complex Poisson-Boltzmann equation between two identical plates [62,173].

The relation between the total interaction energies and the forces acting between the particles (Figure 18) can be written as:

\[ V(h) = \int_{h}^{\infty} F(h')dh' \]  

(25)

Once \( V(h) \) is known, the aggregation rate of particle dimer formation can also be predicted within the DLVO theory as follows [147]:

\[ k = \frac{4k_BT}{3\eta R} \left[ \int_{0}^{\infty} \frac{B(h)}{(2R+h)^2} \exp \left[ \frac{V(h)}{k_BT} \right] dh \right]^{-1} \]  

(26)

where \( B(h) \) is the hydrodynamic resistance function. Accordingly, the absolute aggregation rates measured by the above discussed light scattering techniques in suspensions can be compared to the one calculated from the force profile between the particles [172,174,175]. However, the same experimental conditions (e.g., ionic strength, temperature and pH) have to be applied.
The interaction forces between surfaces can be determined with various techniques. For instance, the surface force apparatus [169,176,177] measures forces involved with curved mica surfaces across liquids, however, the force resolution is moderate. The most suitable methods to directly determine the force profile between colloidal particles are the optical tweezers [178] and the colloidal probe technique [179,180].

The latter measurements can be performed with an atomic force microscope (AFM) with only particles or particles and planar substrates. A force resolution of 1-50 pN can be achieved with this technique. Using the asymmetric sphere-plane mode, the colloidal particle is immobilized on a tipless cantilever and it approaches the substrate with an AFM scanner (Figure 19). The substrate can be silica or glass for instance and it has to be often modified to achieve sufficiently strong attachment of the probes. The interparticle forces can be obtained from the deflection of the cantilever. This is quantified by measuring the reflection of a laser beam focusing on the cantilever. In the sphere-sphere geometry (e.g., in the multiparticle colloidal probe technique), one of the particles has the same position as the one in the sphere-plane mode, however, a second particle is immobilized on the surface of the substrate [181,182]. In this symmetric mode, the particles have to be centered laterally (e.g., with an optical microscope) and such a setup allows investigating interaction forces between the particles directly.

The multiparticle mode measurements, which contain large number of particles with a huge internal surface area, provide several advantages over the traditional colloidal probe techniques. First, one works in the suspensions of the particles, where the experimental conditions (pH, background electrolyte, dose of any additives, etc.) can be more precisely controlled. Second, to avoid the presence of bubbles in the system, the particles are attached to the cantilever and to the substrate under liquid. Otherwise bubbles of similar sizes as the particles may form and they can interfere with the measurements. Third, force measurements can be performed between particles from the same batch, but also between particles differing in composition and size [183].

Comparison between aggregation rates measured directly by light scattering and calculated from the force profiles determined by the multiparticle colloidal probe technique will be presented in this thesis. When exactly the same particles were used, the quantitative agreement between the values will be given, while in other cases the origin of the interparticle forces and the aggregation mechanisms will be clarified by interpreting the measured data.
Chapter 4
AGGREGATION BY MONOVALENT IONS

In this chapter, the effect of monovalent ions on charging and aggregation of polystyrene latex and LDH particles will be discussed. Monovalent ions include simple inorganic electrolytes as well as ionic liquid (IL) constituents. The location of the ions in the Hofmeister series, which classify anions and cations on the basis of their efficiency in destabilizing protein solutions or particle suspensions, will be clarified. These series will be extended for IL constituent ions.

4.1. Polystyrene latexes

4.1.1. Aggregation in the presence of inorganic salts

Surface charge properties and colloidal stability of sulfate (SL-530) and amidine (AL-220) latex particles were investigated in monovalent salt solutions at pH 4 [184]. Accordingly, N(CH$_3$)$_4$Cl, NH$_4$Cl, CsCl, KCl, NaCl and LiCl salts were used to vary cations, while the influence of anions was investigated in the presence of NaH$_2$PO$_4$, NaF, NaCl, NaBr, NaNO$_3$ and NaSCN. Therefore, the effect of both counter and coions on the charging and aggregation was assessed. Given the fact that these ions are included in the Hofmeister series, the relationship between the location of the CCCs and the position of the ions within this series was explored.

As shown in Figures 20 and 21 on the next page, the absolute values of the electrophoretic mobilities decreased with increasing the electrolyte concentration (i.e., the ionic strength). Such a decrease can be explained by the screening of the surface charge. The negative and positive mobilities measured for the SL-530 and AL-220 particles at low salt levels reflect the charge of the ionized surface functional groups. The deviation between the electrophoretic mobility plots by varying the salt composition indicates specific ion adsorption on the particles. Stability ratios (equation (13)) measured under identical experimental conditions as in the mobility studies are shown for the SL-530 particles in Figure 20 and for the AL-220 latexes in Figure 21. Note that the inverse of the stability ratio value is equal to the fraction of the collisions, which leads to dimer formation. Slow (at low salt concentration) and fast (at high salt concentration) aggregation regimes were identified, which were separated by the CCC, as the transition point between the slow and fast aggregation regions in good qualitative agreement with the DLVO theory. In addition, the deviation of the CCCs in different type of electrolyte solutions shed light on the importance of ion specific effects on the particle aggregation processes.
Figure 20. Charging and aggregation of negatively charged SL-530 particles as a function of the concentration of various monovalent salts at pH 4. Cl$^-$ salts of different cations (a) and sodium salts of some anions (b). Electrophoretic mobilities are shown in the left column, while stability ratio values are plotted in the right one. Stability ratio close to one refers to rapid particle aggregation, while higher values indicate slower aggregation. Reprinted with permission from reference [184]. Copyright (2015) American Chemical Society.

Ion specific effects on the aggregation rates above the CCCs, i.e., in the fast aggregation regime, were studied at high electrolyte concentrations, where the viscosities of concentrated electrolyte solutions may significantly deviate from that of pure water. Therefore, rate constants in the diffusion controlled regime may be different, since the diffusion coefficient of the particles depends on the solution viscosity. Such an effect of the dynamic viscosity especially at high ionic strengths was considered [184,185]. To compare the experimental values, the absolute aggregation rate coefficients, determined in simultaneous SLS and DLS (SSDLS) measurements (equation (12)), were normalized with the diffusion controlled aggregation rate coefficient obtained from Smoluchowski’s theory (equation (4)), which contains the viscosity of the medium. It was found that the composition of the monovalent salts did not influence the normalized rates.
Accordingly, these normalized rate coefficients were almost identical for the two types of particles used ((0.26±0.01) for the SL-530 latex and (0.23±0.01) for the AL-220) irrespectively to the nature of the salt constituents. This fact indicates that the origin of the interparticle forces in the fast aggregation regime is similar regardless of the type of ions present.

The observed trends in mobilities and in CCCs were interpreted for both particles. The magnitude of the electrophoretic mobilities at the same salt concentrations, decreased in the \(\text{N} (=\text{CH}_3)_4^+ < \text{NH}_4^+ < \text{Cs}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+\) sequence for the SL-530 latex, in agreement with the direct Hofmeister series [186]. Such a tendency can be explained by the different affinity of the cations to the surface. Accordingly, larger and less hydrated \(\text{N} (=\text{CH}_3)_4^+\) ions adsorb most strongly on the hydrophobic latex particle surface of negative charge. The adsorption processes results in partial charge compensation and thus, lower mobilities. On the contrary, the well-hydrated \(\text{Li}^+\)
ions have lower affinity to the particle surface and prefer to stay in the bulk. Therefore, the magnitudes of the surface charge and of the mobility are the largest in the presence of this ion.

The CCC systematically varies with the type of cation and it shifts from low to high values (Figure 22a) following the order in the direct Hofmeister series (\(\text{N(CH}_3\text{)_4}^+ < \text{NH}_4^+ < \text{Cs}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+\)) suggested for a negatively charged hydrophobic particles [51]. As discussed above, adsorption of \(\text{N(CH}_3\text{)_4}^+\) ions reduced the magnitude of surface charge and also the CCC, while the diffuse layer charge is high due to weak adsorption of the \(\text{Li}^+\) ions. Molecular dynamic simulations on hydrophobic surfaces also confirms these findings [53]. However, the CCC values for the \(\text{Li}^+\) and \(\text{Na}^+\) ions were very similar indicating the indifferent nature of these cations. Other type of hydrophobic particles of negative charge also followed the direct Hofmeister series in the presence of monovalent electrolytes. Accordingly, the same tendency was reported with clay, silver iodide, polystyrene latex and heat-treated titania particles on the basis of results of aggregation experiments [36,37,39,42,43].

Figure 22. CCCs for SL-530 (a) and AL-220 (b) particles as a function of the ions included in the Hofmeister series. The effect of cations is shown in the left column, while the trend with the anions in the right one. The arrows indicate the tendency predicted by the direct or indirect Hofmeister series. Reprinted with permission from reference [184]. Copyright (2015) American Chemical Society.
Data shown in Figure 20b and Figure 22a indicates no specific effect of the coions on the charging and aggregation of SL-530, since both electrophoretic mobilities and CCCs were very similar for all ions investigated. Hence, it can be assumed that the particles of highly negative surface charge repel the anions and thus, they do not adsorb on the surface. CCC values reported earlier for colloidal particles in the presence of various coions showed also the absence of interaction between the ions and the surface of the same sign of charge [35-37].

For the AL-220 particles in the presence of simple coions (Cs\(^+\), K\(^+\), Na\(^+\) and Li\(^+\)), the measured electrophoretic mobilities and CCCs were very similar (Figures 21a and 22b). The indirect Hofmeister series for positively charged hydrophobic particles predicts decreasing affinity of these ions towards the surface in this sequence and hence, the CCCs should decrease. However, the CCCs remained constant within the experimental error ((200±10) mM) indicating negligible interaction of these ions with the highly charged surface. Moreover, lower CCCs were measured for AL-220 in the presence of the N(CH\(_3\))\(_4\)\(^+\) and NH\(_4\)\(^+\) ions. This finding is in contrast with the trend in the indirect Hofmeister series, which predicts higher CCCs for these ions. It was assumed that hydrogen bonding between the amidine groups on the particle surfaces and the nitrogen containing cations is responsible for the ion adsorption on the AL-220 surface and for the atypical aggregation behaviour. Similar discrepancies in the sequence of the CCCs were also reported for positively charged latex particles [36,37].

Varying the counterions, the electrophoretic mobility at given concentration decreased approximately in the sequence of H\(_2\)PO\(_4\)^– > F\(^–\) > Cl\(^–\) > Br\(^–\) > NO\(_3\)^– > SCN\(^–\) at sufficiently low salt concentration (Figure 21b) in agreement with the indirect Hofmeister series [51]. The tendency can be again explained by the different affinity of the counterions to the AL-220 surface. Accordingly, well-hydrated anions (e.g., H\(_2\)PO\(_4\)^–) do not adsorb on the hydrophobic latex particles, while the less hydrated anions (e.g., SCN\(^–\)) adsorb strongly and thus, reduces the charge. The affinity of SCN\(^–\) to the surface is so high that charge reversal occurred.

The trend in the mobilities corresponds to the order in the CCCs, which partly reflects the indirect Hofmeister series (Figures 21b and 22b). The discrepancy is due to the very similar CCCs determined in the presence of H\(_2\)PO\(_4\)^–, F\(^–\) and Cl\(^–\) anions, where a decrease in the CCCs is expected in this order. However, a pronounced decrease of the CCC was detected in the sequence of Cl\(^–\) > Br\(^–\) > NO\(_3\)^– > SCN\(^–\) in agreement with the indirect series.

The origin of interparticle forces was explored using the DLVO theory (see subsection 3.3 for more details). Converting the electrophoretic mobilities to electrokinetic potentials with the Smoluchowski’s model (equation (17)), the surface charge density was determined by fitting the potentials at different salt levels with the Debye-Hückel charge-potential relationship shown in
The DLVO-type interaction energies (equation (22)) were used to calculate the CCCs as follows. If one applies the Derjaguin and superposition approximations [147], the repulsive double layer interaction energies can be estimated with equation (24), while the attractive van der Waals interaction energies with equation (23). The CCC can then be estimated, assuming that the energy barrier vanishes, as:

$$CCC = \frac{0.365}{N_A L_n} \left( \frac{H e e_0}{\varepsilon \varepsilon_0} \right)^{2/3} \sigma^{4/3}$$  \hspace{1cm} (27)

where $L_n$ is the Bjerrum length (the distance, where the electrostatic interaction between two charges is comparable in magnitude to the thermal energy), which can be calculated with the following formula [4]:

$$L_n = \frac{e^2}{4 \pi \varepsilon_0 \varepsilon k_B T}$$  \hspace{1cm} (28)

It is important to mention that equation (28) is valid only when the energy barrier completely vanishes at the CCC [63]. The calculated and experimental data are given in Figure 23. A good correlation between the CCCs and the surface charge densities was found. The results of the DLVO calculations are in relatively good accordance with the experimental data. However, a significant deviation was observed with the NH$_4^+$ ion, which is most likely due to its specific interaction with the surface amidine groups. To achieve the best agreement between the calculated and measured values, a Hamaker constant of $1.2 \times 10^{-20}$ J was applied in equation (27). For the SL-530, the surface charge density measured by conductometric titration ($-77$ mC/m$^2$) agrees quite well in magnitude with the highest charge densities shown in Figure 23. On the other hand, a significantly lower charge ($+30$ mC/m$^2$) than the titrated one ($+132$ mC/m$^2$) was found for the AL-220 particles.

The fact that the experimental CCCs could be well-predicted with the DLVO theory indicates that the predominant interparticle interaction is electrostatic.
forces are of similar origin regardless of the type of ions. However, the ion specific dependence in the CCCs is owing to the modification of the surface charge through adsorption of these ions. For the counterions, less hydrated ones adsorb strongly on the hydrophobic surface and hence, decrease the magnitude of the surface charge density leading to lower CCC. Well-hydrated counterions have lower affinity to the particle surface and they do not influence the surface charge giving rise to higher CCCs. In addition, no interaction was evidenced between the coions and the particles. The Hamaker constant used to fit the data is in good agreement with the value \(1.0 \times 10^{-20}\) J obtained from the full Lifshitz calculation, but it is larger than the ones reported for other latex particles [170,187,188].

4.1.2. Direct measurement of interparticle forces

In another set of experiments, stability ratios measured by SSDLS were compared with the ones calculated from the force profile determined by AFM for the same AL-950 particles [172]. The choice of the latex size, which was 950 nm in diameter, is an adequate compromise, since aggregation rates can be accurately measured by light scattering and it is large enough to use it in the AFM measurements. To study the ion specific effects on colloidal stability and the related interparticle forces, \(\text{Cl}^-, \text{Br}^-, \text{SCN}^-\) anions were used, while the cation was \(\text{Na}^+\). The measured force profiles were quantitatively interpreted and the stability ratios were predicted to compare with experimental results.

The AFM-based multiparticle colloidal probe technique (see part 3.3 for more details) was used to directly determine forces between AL-950 particles. Figure 24 shows a selection of measured interparticle force profiles at different NaCl concentrations. The forces were qualitatively very similar for all anions studied. Accordingly, strongly repulsive and long-ranged forces were measured at lower ionic strength, where the double layer repulsion predominates over the attractive van der Waals forces. Increasing the salt concentration, the range of the double layer force became shorter. This is due to the decrease of the Debye length with increasing ionic strength (equation (16)), which determines the thickness of the EDL. At higher salt level, the repulsive forces further weaken and a
long-ranged attraction was observed. Such longer-ranged attractions are due to the van der Waals forces. In principle, the DLVO-type interactions were applied to quantitatively analyse the force profile. However, the overall interparticle forces at shorter distances were more attractive than in the case, where only forces of electrostatic origin were considered. The resulting forces are:

\[ F(h) = F_{vdW}(h) + F_{EDL}(h) + F_s(h) \]  

where \( F_{vdW}(h) \) is the van der Waals, \( F_{EDL}(h) \) is the double layer and \( F_s(h) \) is the attractive short-ranged force. The latter one is responsible for the deviation between the measured and the DLVO-type force profiles. This additional contribution is mainly determined by the hydrophobic force rising between the particles at short separation distances.

The total interaction energy was determined from the sum of the interparticle forces (equation (25)) and used to calculate the aggregation rate coefficients (equation (26)) and the stability ratios (equation (13)). The comparison between the stability ratios measured by light scattering and calculated from the AFM experiments for the three anions is shown in Figure 25.

Figure 25. Measured (by DLS, symbols) and calculated (from AFM data, solid lines) stability ratios of the AL-950 latex particles at pH 4. The results obtained using only the DLVO theory to fit the interparticle forces are also shown (dashed line). Reprinted with permission from reference [172]. Copyright (2015) American Chemical Society.

The agreement between the measured and calculated CCCs is particularly good. The CCC decreases in the \( Cl^- > Br^- > SCN^- \) order in good agreement with the indirect Hofmeister series suggested for positively charged hydrophobic particles [51]. Such a sequence was also found with the AL-220 particles, as discussed earlier. Nevertheless, discrepancies could be discovered in the experimental and calculated slopes of the stability plots in the slow aggregation regime below the CCCs. Similar differences were also observed in other systems [189,190] and lateral charge heterogeneities on the particle surfaces were assumed to be responsible for the smaller stability ratios obtained in the SSDLS measurements. This effect was not included in the model during the interpretation of the force profiles.
Looking at the data in Figure 25, one can easily realize that the DLVO predictions are less accurate than the ones including the additional attractive non-DLVO force. This finding sheds light on the importance of the additional short-ranged forces to obtain the correct prediction of the CCC. Using solely the EDL and van der Waals forces in the interpretation gives rise to higher CCCs than the ones determined by light scattering. The different extent of the counterion adsorption seemed to be responsible for the different CCCs, since the contribution from the short-ranged forces is the weakest for SCN\(^-\) (strongly adsorbing anion) and the highest for Cl\(^-\) (indifferent anion). This fact indicates that specific ion adsorption decreases the strength of the hydrophobic interaction leading to the predominance of DLVO-type forces.

### 4.1.3. Aggregation in the presence of ionic liquid constituents

To extend the traditional Hofmeister series of cations, charging and aggregation of negatively charged SL-530 particles have been studied in the presence of Cl\(^-\) salts of IL constituent cations by measuring electrophoretic mobilities and stability ratios [191]. They included Cl\(^-\) salts of 1-alkyl-3-methylimidazolium cations, in which alkyl refers to octyl (OMIM\(^+\)), hexyl (HMIM\(^+\)), butyl (BMIM\(^+\)) and ethyl (EMIM\(^+\)) groups, while 3-methylimidazolium (MIM\(^+\)) was also used. The hydrophobicity of these ions decreases with decreasing the length of the alkyl chains (see Figure 26 for the structures), therefore, different affinities to the oppositely charged hydrophobic latex surfaces are expected.

![Figure 26.](image)

**Figure 26.** Electrophoretic mobilities (a) and stability ratio values (b and c) of SL-530 particles in the presence of ILs composed of Cl\(^-\) anion and 1-alkyl-3-methylimidazolium cations of different alkyl chain lengths. The measurements were performed at pH 4. The lines serve to guide the eyes only. The structures of the cations are shown on the top. Reproduced from reference [191] with permission from the PCCP Owner Societies.
It was found that the electrophoretic mobilities increase with the IL concentration (Figure 26a). To interpret this tendency, one has to consider the effects of charge screening and the adsorption of the cations on the oppositely charged surface. These processes are present in different extent in the systems depending on the structure of the 1-alkyl-3-methylimidazolium cations. For MIM\(^+\) and EMIM\(^+\), the increase in the mobility is due to the screening effect of the salt on the surface charge, therefore, negatively charged particles were observed within the entire concentration range investigated. For BMIM\(^+\), however, charge neutralization and a slight charge reversal occurred indicating the adsorption of these cations. Such an overcharging was even more pronounced in the presence of HMIM\(^+\) and OMIM\(^+\). Similar results have been already reported with the latter cation in systems contained negatively charged kaolinite particles [192]. Further increasing the IL concentration, the positive charge of the particles is screened by the Cl\(^-\) ions leading to a decrease in the mobilities.

The trend in the stability ratios measured in the same systems can be explained with the charging properties discussed above. The stability plots measured with the BMIM\(^+\), EMIM\(^+\) and MIM\(^+\) cations (Figure 26b) show very similar behaviour to the ones presented for monovalent electrolytes in part 4.1.1. Accordingly, slow aggregation at low concentrations, fast aggregation at high concentrations and these two regimes are separated by the CCC. For the HMIM\(^+\) and OMIM\(^+\), however, the shape of the stability ratio versus IL concentration curves is significantly different (Figure 26c). These systems are stable at low IL dose indicated by high stability ratios. Increasing the concentration, they decrease to unity near the charge neutralization point first and increase till a maximum observed at IL doses, where the extent of the charge inversion is the highest. The stability ratios decrease again at larger concentrations and reach unity. The clear difference between the systems containing HMIM\(^+\) or OMIM\(^+\) counterions is that the intermediate maximum is much more pronounced in the latter case due to the weaker charge reversal of HMIM\(^+\) as discussed above in the electrophoretic mobility study. In general, adsorption of OMIM\(^+\) is the strongest in the series and the strength decreases with decreasing the chain length in the 1-alkyl-3-methylimidazolium cations.

Furthermore, one has to consider the possible formation of micelles and corresponding CMCs for the HMIM\(^+\) and OMIM\(^+\) cations. Literature data report a CMC of 900 mM for HMIM-Cl and 220 mM for OMIM-Cl [193]. The value for HMIM\(^+\) is in the concentration range, where the charge of the positive particles was screened by the Cl\(^-\) ions giving rise to unstable suspensions. Therefore, the micelle formation does not play a role here. The situation is similar in the OMIM\(^+\) system too, in which the CMC is located in the charge screening regime. The particle surface is completely covered with OMIM\(^+\) at this concentration and hence, the adsorption of the cations could not influence the aggregation processes at the CMC. Summarily, micelles form only at high concentrations in the systems and do not affect the colloidal stability of the SL-530 particles.
The data shown in Figure 26c for HMIM\(^+\) and OMIM\(^+\) clearly indicate that the dependence of the stability ratio on the IL concentration cannot be interpreted with one CCC anymore. Therefore, three CCCs were considered. Accordingly, the first CCC was caused by the charge neutralization process and their values were found to be very similar to the IL concentrations at the IEP (Figure 26a). The restabilization of the SL-530 particles due to the charge inversion induced by the cation adsorption on the surface is responsible for the second CCC, which was found after the first minimum in the stability ratios. The location of the third CCC is defined by the charge screening process by the Cl\(^-\) ions at higher concentrations after the maximum in the stability ratio. The aggregation became fast again at this IL dose.

![Figure 27. Stability map including the CCC values of SL-530 particles in the presence of IL cations of different alkyl chain lengths. The circles indicate the first CCC, squares show the second and diamonds refer to the third CCC. Reproduced from reference [191] with permission from the PCCP Owner Societies.](image)

Let us now summarize the results obtained with the SL-530 particles in the presence of simple monovalent anions (subsection 4.1.1) and IL constituents. Considering the CCC values (only the first ones for HMIM\(^+\) and OMIM\(^+\)), the Hofmeister series for cations can be extended as follows.

![Decreasing Destabilization Power - Direct Hofmeister Series](image)
Hydrophobic cations of longer alkyl chains are positioned on the left hand side and they induce lower CCCs due to their stronger adsorption on the particle surface. The more hydrophilic ones on the right hand side adsorb more weakly or not at all leading to higher CCCs. Since the SL-530 particle is negatively charged and hydrophobic, this sequence indicates the direct Hofmeister series of cations. Such an order was suggested in part on the basis of protein stabilization experiments [194], but this is the first time when the location of these IL cations was clarified within the Hofmeister series on the basis of results obtained in particle aggregation studies.

4.2. Aggregation of layered double hydroxides

Colloidal stability of positively charged LDH-336 particles (see Table 2 in subsection 2.2) was investigated by electrophoresis and time-resolved DLS in the presence of monovalent inorganic electrolytes over wide range of concentrations. The salt composition, i.e., the type of anions, was systematically varied in the samples. Note that the anions are the counterions, while K⁺ coion was used in the experiments. The results were compared to the ones obtained with the aforementioned latex particles in similar electrolyte solutions [59].

Electrophoretic mobilities were measured first with Cl⁻, NO₃⁻, SCN⁻ and HCO₃⁻ anions (Figure 28a). Very similar trend was observed in the mobilities for the first three anions and the change in magnitudes resembles to those obtained with the AL-220 particles in the presence of the same anions, as discussed in subsection 4.1.1. The structural charge of the LDH-336 platelets resulted in positive mobilities in the entire concentration range for the Cl⁻, NO₃⁻ and SCN⁻ ions. The electrophoretic mobilities decreased with increasing the ionic strength and were close to zero at high concentrations. Like in the monovalent systems discussed in the previous parts, such a decrease originates from the screening effect by the salts and the adsorption of the anions on the oppositely charged LDH-336 surface. Similar to the case observed with AL-220 latex (Figure 21b), the adsorption process led to charge neutralization in the presence of SCN⁻ at high ionic strengths. The tendency in the electrophoretic mobility values at a given concentration followed the Cl⁻ > NO₃⁻ > SCN⁻ order indicating different extent of ion adsorption on the platelets.

Concerning the behaviour of the HCO₃⁻ anion, its affinity to the LDH-336 surface was much higher and led to charge neutralization at the IEP and subsequent charge inversion. Such a strong interaction between the HCO₃⁻ and the LDH particles has already been reported in other systems [58,127]. It was assumed that this effect is due to the extended hydrogen bonding network between the anions and the surface functional groups. A decrease in the magnitude of the mobilities can be observed at higher salt levels, where the platelets are negatively charged and the K⁺ ions screen the surface charge.
Stability ratios were determined under the same experimental conditions to study the aggregation processes in the suspensions (Figure 28b). The shape of the stability ratio versus salt concentration plots was similar for all anions and they resembled to the ones determined with charged particles in the presence of monovalent electrolytes [172,184,191]. Namely, slow and fast aggregation regimes separated by the CCC were observed. The observed trend in the stability ratios is in good agreement with the DLVO theory.

However, the variation in the CCCs deserves further discussion. Only one CCC was determined from the stability plots in each case and they decreased in the Cl\(^-\) > NO\(_3^−\) > SCN\(^−\) > HCO\(_3^−\) order (Figure 29). The sequence with the first three ions is identical with the one predicted by the indirect Hofmeister series for positively charged hydrophobic particles. The same trend was found in the case of AL-220 latexes earlier (see Figure 22b in subsection 4.1.1) and similar explanation can also be put forward. Accordingly, the less hydrated SCN\(^−\) anions adsorb on the particles leading to lower surface charge and lower CCC. The well-hydrated Cl\(^−\) anions remain in the bulk and do not adsorb on the platelets giving rise to higher surface charge and the highest CCC within the anions studied here.
Let us now discuss the case of HCO$_3^-$, where the CCC value indicated atypical behaviour. If one applies the indirect Hofmeister series for positively charged hydrophobic surfaces, the CCC should be the highest for the HCO$_3^-$ anion (see Figure 4 in subsection 1.3.1). Nevertheless, the lowest CCC was measured for this ion. Such a discrepancy from the traditional series is due to the strong adsorption of the HCO$_3^-$ ions on the LDH-336 surface, which induced charge neutralization and significant charge inversion of the platelets (Figure 28a). The CCC in the presence of the HCO$_3^-$ is located at the IEP and hence, it is lower than for the other ions, where the destabilization occurred mainly by charge screening.

The origin of the interparticle forces was further explored by studying the relation between the CCCs and the surface charge densities in the presence of different anions. First, the electrophoretic mobilities were converted to zeta potential using equation (17) and then the Debye-Hückel model was applied to calculate the surface charge densities (equation (21)). Second, the CCC was estimated from the DLVO theory (equation (27)) [4,62,63]. The results are presented as solid line in Figure 29, where the calculated surface charge density values varied between +1 and +22 mC/m$^2$. In agreement with the tendency in the mobility experiments, the Cl$^-$ > NO$_3^-$ > SCN$^-$ > HCO$_3^-$ sequence was found for the magnitude of the surface charge. This order follows the indirect Hofmeister series suggested for positively charged hydrophobic particles with the exception of the HCO$_3^-$. This anion adsorbs strongly due to its specific affinity to the LDH-336 surface giving rise to the lowest surface charge. The CCCs measured by light scattering agreed well with the calculated ones. Since only DLVO-type forces were included in the calculations, this finding confirms that the predominating interparticle forces are of DLVO origin. However, the ion specific interactions also play an important role through the extent of the counterion adsorption, which leads to different surface charge densities and to significant deviation in the strength of the repulsive double layer forces.

For the Cl$^-$, NO$_3^-$ and SCN$^-$ anions, the observations are in line with the results obtained with the AL-220 particles, however, the absolute CCC values are dissimilar due to the different composition and surface hydrophobicity of the LDH and latex particles. These results show that the LDH-336 surface is less hydrophilic than the AL-220 due to the surface functionalization with positively charged amidine groups in the latter case.
Chapter 5

AGGREGATION BY MULTIVALENT IONS

This chapter deals with the effect of various multivalent ions on the charging and aggregation of latex and LDH particles. For the first ones, aggregation rates measured by light scattering and calculated from direct force measurements performed in the presence of inorganic multivalent counterions will be compared. In addition, the influence of oligoamines and oligocarboxylates of different chain length on colloidal stability of latex particles will be discussed. The chapter will end with the general interpretation of the Schulze-Hardy rule, where the effect of specific ion adsorption on the CCCs will be clarified.

5.1. Latex particles

5.1.1. Aggregation in the presence of inorganic multivalent ions

Charging and aggregation of two types of negatively charged colloidal particles in the presence of various counterions of different valence were studied first [28]. The particles include carboxylic (CL-1000) and sulfate (SL-530) modified spherical polystyrene latexes (Table 1), while Cl\(^{-}\) salts of K\(^{+}\), Mg\(^{2+}\) and La\(^{3+}\) cations were used. At pH 4, where the experiments were carried out, these cations do not hydrolyse, however, about 10% of the La\(^{3+}\) ions are in the form of LaCl\(^{2+}\) above 100 mM salt concentration [195] leading to a loss in the ionic charge. Electrophoretic mobilities and stability ratios were measured to explore surface charge properties and aggregation of the particles.

Absolute aggregation rate coefficients were determined in multiangle SSDLS measurements in 1.0 M KCl solutions. These experimental conditions correspond to the fast aggregation regime. Aggregation rates of (2.0±0.2)×10\(^{-18}\) and (3.3±0.1)×10\(^{-18}\) m\(^3\)/s were obtained for CL-1000 and SL-530, respectively. These values were compared to the value (1.2×10\(^{-17}\) m\(^3\)/s) obtained by Smoluchowski for hard core interactions (equation (4)) [152]. The measured rate coefficients are smaller than the Smoluchowski’s value. This discrepancy mainly originates from the fact that this theory neglects van der Waals forces and hydrodynamic interactions between the particles. In addition, apparent dynamic rates at other conditions were obtained from time-resolved DLS measurements applying equation (11) and these rates were converted to absolute rate coefficients by normalization to the respective measurement at 1.0 M KCl. Finally, stability ratios were calculated from these aggregation rates using equation (13).
In general, similar charging and aggregation behavior were found for the two particles. Figure 30a summarizes the electrophoretic mobility of CL-1000 and SL-530 particles under the same experimental conditions. One observes that the mobility increases with increasing salt concentration in each case. This increase originates from the screening effect of the counterions on the surface charge and their adsorption on the oppositely charged particles. The latter process led to charge neutralization in the presence of divalent ions and to charge reversal for the trivalent cations. The mobilities of SL-530 are much higher in magnitude indicating that these particles are more strongly charged than the CL-1000 latexes.

Figure 30. Electrophoretic mobilities (a) and stability ratios (b) of CL-1000 (left column) and SL-530 (right column) particles as a function of the concentration of cations (squares: K⁺, triangles: Mg²⁺ and circles: La³⁺) of different valence. The data were taken from reference [28].
The dependence of the stability ratios on the electrolyte concentration are shown in Figure 30b. Similarly as in the presence of the monovalent electrolytes, the stability ratios are high at low concentrations, but decreases rapidly with increasing the salt level in this slow aggregation regime. At higher concentrations, the stability ratios are constant. The CCC values decreased with increasing valence of the cations in good qualitative agreement with the Schulze-Hardy rule (equation (1)) [49,50]. The quantitative interpretation of the CCCs in terms of this theory will be discussed later.

Moreover, the aggregation slows down significantly at very high La$^{3+}$ concentration as indicated by an increase in the stability ratio values. It was assumed that the higher stability ratios originate from the increased viscosity and the subsequent slower aggregation of the particles. Accordingly, the diffusion of the particles is slower, because the viscosity increases at high salt levels. Such an increase in the stability ratios can also be observed with MgCl$_2$, but not with KCl. Aggregation rates normalized by the dynamic viscosity of the solutions unambiguously confirmed that this slowdown in the aggregation is solely caused by the increased viscosity [28]. Although La$^{3+}$ induces a substantial charge reversal, especially for the CL-1000, the extent of this charge inversion is too small to inducerestabilization similar to other multivalent ions or polyelectrolytes [24,59,196]. The electrokinetic potential, where the charge inversion occurred, is around +5 mV, which is too low to induce a restabilization due to double layer repulsion [63].

Moreover, electrophoretic mobilities and stability ratios of AL-950 latexes were measured in the presence of K$^+$ salts of anions of different valences, such as Cl$^-$, SO$_4^{2-}$, Fe(CN)$_6^{3-}$ and Fe(CN)$_6^{4-}$ at pH 4 [174]. The particles are positively charged under the experimental conditions investigated, while protonation only takes place for the Fe(CN)$_6^{4-}$ leading to the formation of HFe(CN)$_6^{3-}$ species and a 20% decrease in the ionic strength compared to the fully deprotonated stage [197]. SSDLS measurements yielded an absolute aggregation rate of $(3.8\pm0.2)\times10^{-18}$ m$^3$/s in 1.0 M KCl solution, which was used as $k_{\text{fast}}$ in equation (13) to calculate stability ratios.

Electrophoretic mobilities are shown in Figure 31a at different salt concentrations. For KCl and K$_2$SO$_4$, positive mobilities were measured in the entire concentration range due to the protonation of the amidine groups on the particle surface. They pass through a maximum, as predicted by the standard electrophoretic model [165,198] and decrease with the salt concentration thereafter. This decrease is due to surface charge screening and to moderate adsorption of the counterions on the latexes. Such adsorption process is stronger for the divalent anions, therefore, the magnitude of the electrophoretic mobilities at the same salt level is always smaller for K$_2$SO$_4$ than for KCl. For the K$_2$Fe(CN)$_6$ and K$_4$Fe(CN)$_6$ solutions, the particles are positively charged at low concentrations. The adsorption of these multivalent anions gives rise to low mobilities in much diluted solutions and also to charge reversal at higher concentrations, which is more
enhanced for the tetravalent ions. The mobilities start decreasing in magnitude with salt concentration after a minimum because of the high concentration of the counterions (which are the K\(^+\) for the overcharged AL-950) and also due to their screening effect on the surface charge.

The charging behaviour is well-reflected in the colloidal stability of the samples (Figure 31b). Accordingly, slow and fast aggregation regimes, separated by the CCCs, were observed for the AL-950 for mono and divalent anions indicating the presence of DLVO-type interparticle forces.

The main difference between the KCl and K\(_2\)SO\(_4\) systems is that the CCC is significantly shifted towards lower salt levels when divalent ions are present, in accordance with the Schulze-Hardy rule. The tri and tetravalent ions are even more powerful destabilizing agents, since the fast aggregation regime has already been reached in the sub-millimolar concentration range. However, the stability ratio features an intermediate maximum due to overcharging for both K\(_3\)Fe(CN)\(_6\) and K\(_4\)Fe(CN)\(_6\). Such a maximum corresponds to higher stability ratios for the tetravalent anions because of the more enhanced charge reversal and higher negative charge of the particle leading to stronger double layer repulsive forces between the latexes. Unstable suspensions were observed at very high salt concentrations, where the K\(^+\) ions screen the surface charge and the repulsive forces vanish. The aggregation is controlled entirely by the diffusion of the particles in this regime indicated by stability ratio values close to unity, which remained the same by further increasing the electrolyte concentration.

The origin of interparticle forces in this system will be discussed in more detail later. The quantitative interpretation of the change in the CCCs by changing the valence of the counterions and the effect of anion adsorption on the CCCs will be discussed in subsection 5.3.
5.1.2. Comparison of aggregation and direct force measurements

Direct force measurements between the CL-1000 and AL-950 particles were performed with AFM in aqueous solutions containing multivalent ions. The negatively charged carboxylated particles were studied in the presence of KCl, MgCl$_2$, LaCl$_3$ and ZrCl$_4$ electrolytes [195], while the positively charged AL-950 in KCl, K$_2$SO$_4$, K$_3$Fe(CN)$_6$ and K$_4$Fe(CN)$_6$ solutions [174]. The measured interparticle forces were fitted quantitatively with a modified DLVO theory and the stability ratios were predicted on the basis of these results using equations (13) and (26). The obtained values were compared with the ones measured by light scattering. The latter measurements, with the exception of the ZrCl$_4$ system, were discussed in subsection 5.1.1, therefore, the following part will focus on the comparison.

In the suspensions of CL-1000 particles, similar forces were measured in the presence of KCl and MgCl$_2$ salts. It was found that DLVO theory works adequately beyond surface separation distances of 5 nm, but fails to describe the strong attraction discovered at distances of 2-3 nm. In order to describe the force curves in these regimes as well, the force profile was modified with the short-ranged attractive force acting between hydrophobic particles, as mentioned in part 4.1.2 for monovalent electrolytes (equation (29)) [172]. This additional attraction can be described with an exponential term as:

$$F_S(h) = -A_S e^{-q_S h}$$

where $q_S^{-1}$ characterizes its range, while $A_S$ defines its strength. The $A_S$ values were very similar for KCl and MgCl$_2$ and they decrease with increasing salt level. This short-ranged non-DLVO force probably originates from a hydrophobic attraction between the particles and depends on their surface charge densities.

The interparticle forces determined in the LaCl$_3$ and ZrCl$_4$ samples cannot be fitted with the classical DLVO theory even at larger separation distances. This discrepancy results from the fact that attractive forces are stronger than the van der Waals forces detected in the monovalent system. It was assumed that this additional attraction originates from the patch-charge heterogeneity of the substrate [24,199]. The overall force profiles can now be interpreted with the following relation:

$$F(h) = F_{vdW}(h) + F_{EDL}(h) + F_S(h) + F_{pc}(h)$$

where $F_{pc}$ is the additional attraction due to the patch-charge distribution caused by surface heterogeneities owing to the adsorption of the tri and tetravalent ions. As shown in the above equation, the DLVO-type forces are complemented by two additional forces for the LaCl$_3$ and ZrCl$_4$ samples. The value of $F_{pc}$ can be given for a square lattice as:
\[ F_{\text{PC}}(t) = -A_{\text{PC}} e^{-q_{\text{PC}} h} \]  

(32)

where \( q_{\text{PC}} \) is the range and \( A_{\text{PC}} \) is the amplitude of \( F_{\text{PC}} \) [195]. The diffuse layer potentials obtained from the fits of the force profiles are given and compared to the zeta potentials, which were converted from the electrophoretic mobilities using equation (19), in Figure 32a.

For \( \text{LaCl}_3 \) and \( \text{ZrCl}_4 \), charge reversal can be observed in the potentials obtained from AFM measurements, which is weak for the trivalent cation and very pronounced in the presence of the tetravalent one. The extensive overcharging in the latter system can be explained by the presence of the highly charged \( \text{Zr}_4(\text{OH})_8^{8+} \) species due to the hydrolysis and subsequent formation of hydroxo complex of the \( \text{Zr}^{4+} \) ions at this pH [195]. Such a charge reversal was also confirmed by the electrokinetic potentials measured by electrophoresis with identical particles. In general, potentials obtained with different techniques in the same samples agree well for all ions.

Particle aggregation was followed with time-resolved SSDLS and the obtained aggregation rates are presented as stability ratios in Figure 32b. For KCl, MgCl\(_2\) and LaCl\(_3\) solutions, the typical tendency was detected, namely, high salt concentrations induced fast aggregation, whereas at lower concentrations, the aggregation slowed down. In accordance with the Schulze-Hardy rule, the CCCs decreased with the valence of counterions [49].
However, only a very narrow unstable regime was observed for the ZrCl$_4$ solutions. Since the presence of highly charged Zr$_4$(OH)$_8^{8+}$ species induced a significant charge reversal (Figure 32a), restabilization of the particles occurred by the repulsive EDL forces. A minor increase in the stability ratios was also observed at higher concentration in the LaCl$_3$ solutions due to the increase in the dynamic viscosity at elevated salt levels [28].

The total interaction energy potentials were obtained from the forces and used in equation (26) to calculate the aggregation rates followed by the calculation of the stability ratios with equation (13). As shown in Figure 32b, the stability ratios predicted by the force profiles agree very well with the ones measured experimentally with SSDLS. The calculated values for the KCl samples are shifted towards lower salt levels. Such a deviation may originate from the inaccuracies in the force profiles at small surface separations. The fast absolute rate coefficient ($6.8 \times 10^{-18}$ m$^3$/s) obtained from the AFM experiments was similar to the one ($2.0 \times 10^{-18}$ m$^3$/s) from SSDLS.

Forces and aggregation rates with particles from the same dispersions were also measured with positively charged AL-950 latexes in the presence of multivalent counterions [174]. The size of the particles allowed the application of both the multiparticle colloidal probe and the multilang SSDLS techniques. Inorganic salts included KCl, K$_2$SO$_4$, K$_3$Fe(CN)$_6$ and K$_4$Fe(CN)$_6$. The charging and aggregation behaviour observed in these systems have been detailed in subsection 5.1.1, therefore, the nature of the force profiles and the comparison between stability ratios obtained from AFM and light scattering measurements will be discussed here.

Figure 33. Interparticle forces measured between AL-950 latexes by the AFM-based colloidal probe technique in the presence of Fe(CN)$_6^{4-}$ anions at low (left) and high (right) concentrations at pH 4 [174]. The solid lines are the best fits including repulsive EDL forces as well as attractive van der Waals and patch-charge interactions. Reprinted with permission from reference [174]. Copyright (2013) American Chemical Society.
Interparticle forces in the presence of monovalent and divalent ions could be fitted with the classical DLVO theory using a Hamaker constant of $4.0 \times 10^{-21}$ J remarkably well. However, the force profiles for tri and tetravalent ions (Figure 33) cannot be described only with DLVO-type interactions due to the presence of additional long-ranged attractions. Similar to the CL-1000 systems discussed above, this additional attraction originates from surface charge heterogeneities and subsequent patch-charge interactions, which can be quantified with equation (32). The short-ranged attraction, which was present with the CL-1000 latexes, (equation (30)) was not detected.

Figures 34a and 34b show the comparison of the stability ratios determined by light scattering and calculated from the force profiles. Monovalent and divalent counterions induce the typical salt dependence on colloidal stability, i.e., slow aggregation regime at low salt concentrations and fast aggregation at high concentrations. For tri and tetravalent counterions, the stability ratios went through an intermediate maximum due to charge inversion, as discussed before. The experimental SSDLS fast aggregation rate ($3.8 \times 10^{-18} \text{ m}^3/\text{s}$) agreed sufficiently with the one calculated using the modified DLVO theory ($6.5 \times 10^{-18} \text{ m}^3/\text{s}$).

![Figure 34](image)

**Figure 34.** Stability ratios of AL-950 particles versus concentration of Cl$^-$, SO$\text{\textsubscript{4}}^{2-}$ (a), Fe(CN)$_6^{3-}$ and Fe(CN)$_6^{4-}$ (b) ions. Comparison of experimental data (symbols) with predictions based on the force profiles (solid lines) is also shown. The stability map (c) shows the valence of the counterions and the location of the CCC obtained by light scattering (symbols) or AFM (lines). Reprinted with permission from reference [174]. Copyright (2013) American Chemical Society.

The CCCs are summarized in a stability map for all counterions (Figure 34c). It was found that the experimental CCCs could be reproduced adequately with the AFM-based calculations for all types of ions. For Cl$^-$ and SO$\text{\textsubscript{4}}^{2-}$, a good agreement was found between the measured and the calculated CCCs. Nevertheless, the agreement was only semi-quantitative for the Fe(CN)$_6^{3-}$ and Fe(CN)$_6^{4-}$. The deviation was well-visible near the intermediate maximum (Figure 34b). Similar to the CL-1000 system, it was assumed that these differences originate from lateral surface charge heterogeneities caused by the adsorption of the multivalent ions.
In summary, combination of the AFM-based direct force measurements and aggregation studies with the same CL-1000 or AL-950 particles revealed that the traditional DLVO theory is only applicable in some cases. For most of the systems, additional non-DLVO attractive forces were observed. These attractive forces could be originated from short-ranged hydrophobic interactions and surface charge heterogeneities depending on the particles used. In addition, ion-ion correlation effects induced substantial charge reversal in the presence of ions of higher valences and enhanced surface charge heterogeneities leading to stronger patch-charge attractive forces.

5.1.3. Oligoamines and oligocarboxylates

Colloidal stability of aqueous dispersions of CML-308 particles (Table 1) was studied in the presence of multivalent linear oligoamines from N1 (methylamine) through N3 (diethylenetriamine) to N6 (pentaethylenehexamine) [196]. Electrophoretic mobility measurements were performed to study the charging properties, while particle aggregation was investigated by time-resolved DLS. The obtained stability ratios were compared to theoretical ones calculated by the classical DLVO theory.

Electrophoretic mobilities of CML-308 particles as a function of the oligoamine (from N1 to N6) concentration are shown in Figure 35 [196]. The distribution of the charged species and the degree of ionization was calculated from the protonation constants of the oligomers. Accordingly, the protonation is complete for N1 and N2 under the experimental conditions applied in the measurements (pH 4 and 1 mM KCl added salt). The degree of ionization decreased with increasing number of the amino group in the chain and 70% of them were ionized in the case of N6.

For N1 and N2, the electrophoretic mobilities increased with the dose, however, they were negative in the entire concentration range studied. This result indicated their negligible affinity to the oppositely charged surface and that the increase in the mobilities was due to charge screening. The adsorption of N3, N4, N5 and N6 gave rise to charge neutralization and charge reversal at appropriate oligoamine doses. The latter process was the most pronounced in the presence of N6. In

![Figure 35. Electrophoretic mobility of CML-308 particles as a function of the concentrations of different oligoamines at pH 4. The solid lines are empirical functions for data interpolation. Reprinted from reference [196], Copyright (2013), with permission from Elsevier.](image-url)
addition, the charge neutralization point shifted towards lower concentrations with increasing the valence. Given the fact that charge inversion became more pronounced with increasing valence, the adsorption of the oligoamines was increasingly important. Such an increasing affinity of the aliphatic amines with their size explained the shift of the charge neutralization point too. Moreover, the contribution of the non-adsorbed oligoamines, which were dissolved in the bulk, to the ionic strength is stronger for the molecules of higher valence leading to a more emphasized screening effect.

The aggregation processes of the CML-308 particles were assessed in time-resolved DLS under identical experimental conditions as applied in electrophoresis [196]. Accordingly, aggregation rates were calculated with equation (11) and converted to stability ratios with equation (13). As shown in Figure 36, oligoamines of lower valence (N1, N2 and N3) followed the classical behaviour described for simple salts. The stability ratios measured for oligoamines of higher valence (N4, N5 and N6) showed more complicated behaviour and two fast aggregation regimes were discovered. These findings were similar to the ones obtained in other systems containing multivalent ions and oppositely charged colloidal particles [59,174,200], as discussed in subsection 5.1.1. Once the oligoamine dose increased, the stability ratio decreased first and reached unity in the first fast regime. When the concentration was further increased, the aggregation slowed down giving rise to increasing stability ratio values, which passed through a maximum and decreased again until

![Figure 36. Stability ratios of CML-308 versus the oligoamine concentrations. The solid lines are calculations based on the DLVO theory. Reprinted from reference [196], Copyright (2013), with permission from Elsevier.](image-url)
one. This aggregation behaviour led to three CCC values and thus, very similar situation could be concluded as with the IL constituent cations in part 4.1.3.

Let us now interpret the results of the aggregation study by considering the charging behaviour discussed above. The results of the electrophoretic mobility measurements did not indicate significant adsorption of N1 and N2 amines on the particles, therefore, the destabilization of the dispersions occurred by charge screening effect in these cases. This situation is similar to the one observed for simple monovalent ions in Chapter 4. It is evident from the mobilities that oligoamines of higher valence (N4, N5, and N6) adsorbed on the particle surface. The charge neutralization and the charge reversal induced by these molecules clearly confirm they considerable affinity to the surface. Similarly to the other multivalent ions as well as the HMIM\(^+\) and OMIM\(^+\) IL cations discussed earlier, three CCCs were observed in these systems. Their origin can be interpreted in the same way. Accordingly, the first CCC is due to charge neutralization, the second one is caused by the restabilization of the CML-308 particles owing to the charge inversion process, while the third CCC is owing to the charge screening by the Cl\(^-\) ions. The border between these two different aggregation mechanisms was observed at N3. Although the adsorption of this oligoamine led to a slight charge inversion, no particle restabilization took place and hence, only one CCC could be determined.

To further explore the origin of the interparticle forces, stability ratios were calculated by involving only DLVO-type forces in the model (equations (13), (22) and (26)). The attractive van der Waals interaction energy was calculated by equation (23) using a Hamaker constant of 9.0\(\times\)10\(^{-21}\) J [201]. Zeta potentials were converted from interpolated electrophoretic mobility values shown in Figure 35 using the Henry model (equation (19)). The repulsive EDL forces were obtained within the Debye-Hückel approximation (equation (24)) [62]. In these data analysis processes, the ionization of the individual oligoamines and the added KCl concentration were considered to calculate the ionic strength. Accordingly, the distribution of the charged species was determined at pH 4 using the known protonation constants of the oligoamines [168,196,202]. The Henry model and the Debye-Hückel theory could be considered as good approximations under these experimental conditions, since the magnitude of the electrokinetic potentials was always below 30 mV.

The results of the model calculations shown in Figure 36 indicate that the dependence of the stability ratio on the oligoamine concentration is captured sufficiently well. Moreover, the calculated and measured CCCs were in good agreement. However, slight deviations were observed from the DLVO theory. First, the intermediate restabilization region was predicted as too narrow for N5. Second, the decrease of the stability ratios with increasing concentration in the slow aggregation regime was always steeper than the one measured by DLS, especially in the restabilization region after the charge neutralization point, where Cl\(^-\) anions are the counterions
due to the charge inversion of the CML-308 particles. In this situation, the barrier in the interaction potential is located at small separation distances, where the DLVO theory is not accurate [110,190]. Furthermore, short-ranged hydrophobic interaction and patch-charge attraction can also be responsible for the deviation between the experimental and the calculated stability ratios. These forces are not included in the DLVO model, however, they were directly measured by AFM between other latex particles, as discussed in subsection 5.1.2 [174,195].

The CCC values obtained from Figure 36 are shown in Figure 37 [196]. As discussed above, one CCC was determined for N1, N2 and N3, while the charge reversal and subsequent restabilization processes resulted in three CCCs for N4, N5 and N6. The first CCCs decreased with increasing the ionic valence in agreement with the Schulze-Hardy rule. The dispersions were stable at low oligoamine concentrations. The narrow channel in the unstable regime corresponds to the IEP, while the smaller stable region was caused by the charge inversion and the establishment of the EDL forces under these experimental conditions.

Similar stability behaviour was reported for other latex particles in the presence of multivalent ions (Figure 34c) and also with monovalent 1-alkyl-3-methylimidazolium cations (Figure 27). Comparing the charging (Figures 26a and 35) and aggregation (Figure 26c and 36) properties of the latter systems with the present ones, very similar tendencies can be discovered with increasing concentration of the aggregating agents. The trends in the electrophoretic mobilities and stability ratios obtained with oligoamines of higher valence and with 1-alkyl-3-methylimidazolium cations of longer alkyl chains are identical. One can assume therefore that the interactions, which drive the adsorption and aggregation processes, are similar in these systems. Accordingly, the hydrophobicity of the oligoamines and the IL cations increases with increasing chain length giving rise to stronger adsorption on the hydrophobic latex particles. Such a strong affinity to the surface induces significant charge reversal for the less hydrated cations (e.g., N6 or OMIM\(^+\)) and overlap between the re-entering EDL stabilizes the dispersions. The more hydrated cations (e.g., N1 or MIM\(^+\)) adsorb on the particles in small extent and hence, do not change the surface charge properties significantly. Similar conclusions were also made with inorganic multivalent ions (part 5.1.2). To distinguish between the importance of charge and hydrophobicity in the adsorption processes further experiments are required.

**Figure 37.** Stability map including the CCC values of CML-308 latex in the presence of oligoamines of different chain length. Squares indicate the first CCC, triangles show the second one and circles refer to the third CCC. The data were taken from reference [196].
Almost the same tendencies were observed in the charging and aggregation behaviour with AL-220 particles in the presence of acrylic acid oligomers of different valence, namely, monomers, dimers, trimers, tetramers and hexamers [200]. In brief, it was found that adsorption of highly charged oligomers (e.g., hexamers) induced charge neutralization at the IEP and charge reversal at appropriately high concentrations. This feature has already been observed for the trivalent anions. Similar to the multivalent systems of higher valences discussed before, three CCCs could be determined in the stability plots. The aggregation was rapid, where the charge of the particles is compensated by the adsorbed oligocarboxylates, while the suspension became stable away from this point. At high oligomer concentrations, fast aggregation occurred again due to the screening effect of the counterions. The monomer (acetate) did not induce charge reversal and slow aggregation was observed at low concentrations, while the stability ratios were close to unity at high doses.

The stability ratios were calculated with the DLVO theory (equations (13) and (26)) and compared to the ones measured by DLS. To estimate the repulsive EDL forces, the potentials were converted from the electrophoretic mobilities with equation (19), while a Hamaker constant of 2.0×10^{-21} J was used to calculate the van der Waals interaction energies using equation (23). The CCCs were captured well by the model calculations. However at higher concentrations, where the charge inversion caused restabilization of the suspensions, the DLVO theory predicted higher stability ratios than the ones measured experimentally. This finding was similar to the case of oligoamines of higher valence, as discussed on the previous pages.

Accordingly, the interparticle forces were of DLVO-type near the IEP, whereas additional attractive non-DLVO forces were present at higher oligocarboxylate doses. As revealed by multiparticle colloidal probe measurements in similar suspensions containing latex particles and multivalent ions [174,195], these forces originate from hydrophobic and patch-charge interactions between the particle surfaces. Ion-ion correlation could be also important in inducing the charge inversion. In addition, the increasing hydrophobicity with the oligocarboxylate chain length enhanced their adsorption leading to significant decrease in the first CCCs in accordance with the Schulze-Hardy rule.

5.2. Charging and stability of layered double hydroxides

In this subsection, the effect of multivalent anions on charging and aggregation of positively charged LDH-336 particles will be discussed [59]. LDHs of different compositions are widely used to capture anions in water purification processes [128,203], therefore, their effect on colloidal stability has to be well-understood to design stable suspension for the ion exchange process. To emphasize the environmental relevance, the list of anions was extended with
HAsO$_4^{2-}$ and HPO$_4^{2-}$, which are often targeted in water treatments by ion exchange. Note that the anions are the counterions and their K$^+$ salts were used in the measurements.

First, the colloidal stability of LDH-336 particles was studied in the presence of divalent anions (SO$_4^{2-}$, HAsO$_4^{2-}$, and HPO$_4^{2-}$). As detailed in subsection 2.2, LDHs possess permanent positive charge due to their structure. Indeed, positive mobilities were measured at low salt concentrations in each case (Figure 38a). The adsorption of the anions gave rise to charge neutralization, where the dose at the IEP decreased in the SO$_4^{2-}$ > HAsO$_4^{2-}$ > HPO$_4^{2-}$ order. Further increasing the salt concentration, charge reversal occurred owing to the significant affinity of these ions to the surface. The increase in the mobilities at salt concentrations higher than 10 mM is due to charge screening by the K$^+$ ions. Similar charging phenomena have already been reported for other LDHs in the presence of divalent anions [58,60,73].

Furthermore, the extent of the adsorption was the largest for HPO$_4^{2-}$ and led to the most negative electrophoretic mobilities in the charge reversed stage, followed by the ones measured in the presence of HAsO$_4^{2-}$ and SO$_4^{2-}$. This fact together with sequence of IEPs indicated different affinity of the individual divalent anions to the LDH-336 surface. Such an affinity increased in the SO$_4^{2-}$ < HAsO$_4^{2-}$ < HPO$_4^{2-}$ order. Similar finding was also reported earlier, but only for HPO$_4^{2-}$ and HAsO$_4^{2-}$ ions [204].

**Figure 38.** Electrophoretic mobilities (a) and stability ratios (b) of LDH-336 platelets versus the anion concentration. K$^+$ salts of the divalent anions were used throughout the experiments, which were performed at pH 9. The lines are just to guide the eyes. Reproduced from reference [59] with permission from the Royal Society of Chemistry.

The stability ratios measured by DLS under exactly the same experimental conditions as in the mobility study are shown in Figure 38b. For the SO$_4^{2-}$ and HAsO$_4^{2-}$ anions, the classical trend
was observed in the stability ratios. Namely, slow and fast aggregation regimes with well-defined CCCs were observed in qualitative agreement with the DLVO theory [4]. The aggregation behaviour of the platelets was, however, completely different in the presence of HPO$_4^{2-}$ anions. Similar to the case of multivalent ions of higher valences (Figures 34 and 36) as well as the HMIM$^+$ and OMIM$^+$ cations (Figure 26), three CCCs were obtained. Comparing the tendencies in the mobilities and stability ratios, it is evident that the first CCC is due to the charge neutralization, while the second CCC originated from the restabilization effect owing to charge inversion. In addition, the aggregation rates increased and fast aggregation occurred again at higher concentrations leading to the establishment of the third CCC. In case of the SO$_4^{2-}$ and HAsO$_4^{2-}$ anions, the charge reversal did not result in sufficiently high surface charge density (as one can see in Figure 38a), therefore, the repulsive EDL forces were not strong enough to induce restabilization of the suspensions.

Besides, electrophoretic and time-resolved DLS experiments were carried out with the LDH-336 particles in K$_3$Fe(CN)$_6$ and K$_4$Fe(CN)$_6$ solutions. The mobilities were measured first (Figure 39a) and qualitatively similar trends were discovered as with the HPO$_4^{2-}$ ions (Figure 38a).

![Figure 39.](image)

Figure 39. Electrophoretic mobility (a) and stability ratio (b) values of LDH-336 particles versus the anion concentration for K$^+$ salts of Fe(CN)$_6^{3-}$ and Fe(CN)$_6^{4-}$ anions. The measurements were carried out at pH 9, where the tetravalent anion is completely deprotonated [197]. The lines serve to guide the eyes. Reproduced from reference [59] with permission from the Royal Society of Chemistry.

The remarkably lower concentration at the charge neutralization point and the large extent of the charge inversion clearly indicated extremely strong affinity of the Fe(CN)$_6^{4-}$ to the LDH-336. Looking at the trend in the mobilities obtained in the presence of Fe(CN)$_6^{3-}$, the charging behaviour was very similar to the case of HPO$_4^{2-}$. The magnitude of the mobilities was twice
higher after the charge reversal occurred with the tetravalent ions. Such a significant change in the surface charge upon anion adsorption was experienced only in LDH-polyelectrolyte systems so far [58,205,206]. Moreover, the mobilities increased after the minimum at higher concentrations due to the screening effect of the K$^+$ counterions.

Three CCCs were obtained for the LDH-336 platelets in the solutions of the tri and tetravalent ions (Figure 39b). The interpretations of their origin are the same as for other multivalent ions adsorbing on oppositely charged colloidal particles, as described previously in the thesis. Accordingly, the first CCC occurred at the IEP, the second CCC is due to charge reversal and subsequent restabilization, while the third CCC was the result of the charge screening effect by the K$^+$ ions.

The similarity between the charging and aggregation behaviours of the Fe(CN)$_6^{3-}$ and HPO$_4^{2-}$ anions is so striking that it deserves further discussion. Due to the almost identical IEP and CCC values, one could assume that the HPO$_4^{2-}$ deprotonates upon adsorption and thus, the characteristic surface charge features resemble to the situation with a trivalent anion. This hypothesis, however, was not confirmed unambiguously on the basis of experimental results. Another interesting finding is that the adsorption of the Fe(CN)$_6^{4-}$ anions resulted in such an enormous charge reversal that stability ratios could not be measured in this intermediate concentration range. However, the third CCC could be determined at higher salt level, where the K$^+$ concentration was high enough to screen the EDL.

Figure 40 shows the stability ratios for the Cl$^-$, SO$_4^{2-}$, Fe(CN)$_6^{3-}$ and Fe(CN)$_6^{4-}$ together. The first CCCs decreased with the valence indicating an increasing affinity and stronger adsorption on the particle surface. The second and third CCCs were present only for the Fe(CN)$_6^{3-}$ and Fe(CN)$_6^{4-}$ anions. The second CCC also decreased with the valence, whereas, a higher third CCC was obtained for the tetravalent ion compared to the case of the trivalent one. Such a charging feature can be interpreted with the extent of the charge inversion. Accordingly, significantly more K$^+$ counterions are needed to screen the surface charge of the Fe(CN)$_6^{4-}$-modified particles of highly negative charge. This leads to a higher third CCC than in the trivalent system, where the less effective charge reversal process gave rise to weaker repulsion by the overlapping EDLs.

**Figure 40.** Stability ratios of LDH-336 particles versus the concentration of K$^+$ salts of mono, di, tri and tetravalent anions at pH 9. The data were taken from reference [59].
Analogously to the latex particle systems, it was assumed that the hydration stage of the anions plays a crucial role here as well. Poorly hydrated anions tend to adsorb on the hydrophobic surfaces stronger leading to lower CCCs. Such adsorption reduces the surface charge and hence, the particles aggregate at lower salt concentrations. On the other hand, well-hydrated ones adsorb only weakly or not at all and remain in solution giving rise to higher CCCs. A more detailed interpretation of the first CCCs and their relation to the Schulze-Hardy rule will be discussed in the following part.

5.3. The dependence of the CCC on the valence

5.3.1. The Schulze-Hardy rule

The dependence of the CCCs on the valence of the counterions was further explored and compared to the Schulze-Hardy rule [50]. This rule can be derived from the DLVO theory, which predicts that the EDL forces decrease with the valence of the counterions at the same salt concentrations. Such a decrease leads to a characteristic dependence of the CCCs on the counterion valence, as shown in equation (1) in part 1.3.2. An effect of the valence of coions can also be calculated on the basis of the DLVO theory [65,66], nevertheless, this issue is not discussed in the present thesis, because determination of CCCs in systems containing latex or LDH particles together with multivalent coions was not performed.

For symmetric \((z\cdot z)\) electrolytes, the value of \(n\) in equation (1) can be varied between 2 and 6 as follows [63]. In case of weakly charged particles, the Debye-Hückel model is appropriate to describe the double layer forces, in which the inverse Debye length (equation (16)) includes the ionic strength and the valence enters through it as:

\[
I = \frac{1}{2} \sum_i z_i^2 c_i
\]

where \(c_i\) is the molar concentration of the ionic species in the solution. Performing the suitable derivation, one obtains that the Debye-Hückel theory predicts \(n = 2\) in equation (1). However, for highly charged surfaces with high surface potentials, the Poisson-Boltzmann model must be used to describe the EDL interactions [62]. Using the Poisson-Boltzmann theory to calculate the CCCs, their dependence on the valence becomes stronger with increasing surface charge, but the classical Schulze-Hardy dependence \((n = 6)\) would only be recovered for systems with enormously high charge densities (above 1000 mC/m\(^2\)), which is unrealistically high for the most commonly studied colloidal particles (e.g., the ones in Tables 1 and 2).
Moreover, symmetric electrolytes of higher valences are rare and hardly soluble. In the more common asymmetric (z:1 or 1:z) salt solutions, the dependence of the CCC on the valence is slightly different. At fixed ionic strength, the double layer forces weaken, when the valence of the counterions increases or when the valence of the coions decreases. Therefore, equation (1) can be derived from the DLVO theory with \( n = 1.6 \) for surfaces of lower charge and with \( n = 6.5 \) for highly charged particles [207]. Figure 41 shows these dependencies together with the experimental data discussed in Chapter 5.

The relative CCCs decrease for both positively and negatively charged particles with increasing the valence of the counterions in qualitative agreement with the Schulze-Hardy rule. Although the data corresponding to the same valence scatter due to ion specific effects, some tendencies can be still observed. Accordingly, multivalent anions are more effective in destabilizing colloidal suspensions of oppositely charged particles (AL-950, AL-220 and LDH-336) than multivalent cations for negatively charged particles (CML-308, SL-530 and CL-1000). In addition, equation (1) fits the data with \( n = 6.5 \) better than with \( n = 1.6 \). This result is surprising given the fact that the CCCs were measured with particles of low surface charge, where the Debye-Hückel model should be applied with \( n = 1.6 \). It can be assumed therefore that the observed agreement with \( n = 6.5 \) is likely only a coincidence. The CCC also increases with the diffuse layer potential as [63]:

\[
CCC \propto \frac{\psi_0^4}{z^2} \quad (34)
\]

Moreover, it is obvious from the electrophoretic mobility data shown in Chapter 5 that the increase in the valence of the counterions enhances their adsorption and decreases the surface potential of the oppositely charged particles. Therefore, this issue also influences the dependence of the CCC on the valence and higher dependency than \( n = 1.6 \) is expected for weakly charged surfaces leading to a shift of \( n \) towards higher values. Summarily, the classical Schulze-Hardy rule with \( n = 6 \) in equation (1) is the result of both the low potential due to counterion adsorption and the decrease in the CCC with the counterion valence as predicted by the DLVO theory.
5.3.2. The polyelectrolyte rule

In the previous subsection, the dependence of the CCCs on the valence was discussed only up to tetravalent ions. However, the studies with the oligoamines and oligocarboxylates were extended to further explore the effect of the adsorption of counterions of higher valences on particle aggregation. In part 5.1.3, oligomers (oligoamines and oligocarboxylates) up to six monomers were discussed. Follow-up investigations were performed with systems containing the same latexes and polyelectrolytes of higher degree of polymerization [29]. Accordingly, stability ratios were measured for CML-308 particles in the presence of linear PEI of 58 and 5800 monomers, while for AL-220 latexes with PAA of 88 and 1200 monomers. The charging and aggregation processes will be detailed later for the polyelectrolyte systems, here, focus is made only on the dependence of the CCC on their valence.

As discussed earlier, ions of lower valence induce particle aggregation by surface charge screening (e.g., N1) and the larger oligomers (e.g., N6) by charge neutralization at the IEP. Similar to the latter situation, PEI and PAA also induce charge reversal leading to fast aggregation at the IEP [208,209]. According to the Schulze-Hardy rule for multivalent ions, the first CCCs decrease with the valence of the counterions as shown in subsection 5.3.1. On the other hand, the position of the IEP and hence, the location of the CCC, is independent of the valence of the PEI and PAA of higher degree of polymerization, i.e., at higher molecular weights of the polyelectrolytes.

This so-called polyelectrolyte rule is illustrated in Figure 42 [29]. Note that the traditional Schulze-Hardy rule is presented in the graph with $n = 6$ in equation (1). The transition between these two rules occurs at a valence of about 10. In other words, the classical Schulze-Hardy rule breaks down above valences higher than 10 and the CCCs no longer depend on the charge of the multivalent ions or polyelectrolytes. These results are of especial importance for formulation of particle dispersions with mixtures of multivalent ions and polyelectrolytes. The next chapter will further detail the characteristic charging and aggregation behaviour of latex, LDH and TiONW particles in the presence of charged polymers.

![Figure 42. CCC versus the valence for CML-308 latexes with linear amines and for AL-220 particles with carboxylates. Solid lines show the dependencies expected from the Schulze-Hardy and polyelectrolyte rules. Reprinted with permission from reference [29]. Copyright (2012) American Chemical Society.](image-url)
Chapter 6

POLYELECTROLYTE CONTROLLED AGGREGATION

The following chapter deals with the stability of various colloidal particles in the presence of oppositely charged polyelectrolytes (the terms of polymers, charged polymers or macromolecules are also used in the text). Charging and aggregation of latex, LDH and TiONW particles will be explored, in addition, the structure of the adsorbed polyelectrolyte layer and the orientation of the particles upon aggregation will be discussed. The origin of the interparticle forces responsible for the stability of the suspensions will also be clarified on the basis of the results obtained from direct force measurements by AFM.

6.1. Polyelectrolyte adsorption on latex particles

6.1.1. Charging and aggregation

6.1.1.1. Negatively charged latexes – PEI

The colloidal stability of negatively charged SL-270 and CML-308 (Table 1) latexes was assessed in the presence of linear PEI (see Figure 6 on page 26 for the structure) polyelectrolyte [208]. The CML-308 particles contained a highly charged and hydrophilic surface layer of carboxylate groups, while the SL-270 latex had a more hydrophobic character. PEI is a polyamine, its charging properties are determined by the ionization constants of the primary and secondary amino groups of the chain and by the interactions between these groups. The present experiments were carried out at pH 4, where about 65% of the functional groups of the PEI are protonated [210]. The surface charge properties were studied with electrophoresis, while stability ratios were measured in time-resolved DLS experiments (see equations (11) and (13)).

In the systems containing SL-270 particles and PEI of a molecular mass of 250 kg/mol, the mobilities were negative at low polymer doses due to the negatively charged bare or partially neutralized particles (Figure 43a). The polyelectrolyte adsorption led to a characteristic IEP and continued beyond the charge neutralization point giving rise to charge reversal. Further increasing the PEI concentration, the electrophoretic mobility curves saturated at the onset of the ASP, which indicates that the adsorbed amount reached its maximum and that any further added polymer remained dissolved in solution. It was found that PEI adsorbs quantitatively (i.e., no partitioning between the surface and the bulk) below the ASP, since the electrophoretic
mobilities measured at the same PEI dose, but at different particle concentrations were the same within the experimental error [211].

A very similar behaviour was observed with the CML-308 latex (Figure 43b). Accordingly, the strong adsorption of the oppositely charged PEI led to charge neutralization of the particles at the IEP and subsequent charge reversal at higher doses. Such surface charge properties resemble the ones induced by adsorption of multivalent ions of higher valences on similar latex particles, nevertheless, the extent of the charge reversal was considerably smaller in the latter systems, as discussed in subsection 5.1.

Figure 43. Electrophoretic mobility (top) and stability ratio (bottom) of SL-270 (a) and CML-308 (b) as a function of the dose of PEI of molecular mass of 250 kg/mol at pH 4 for different ionic strengths adjusted by KCl. The mg/g unit of the PEI dose refers to mg polyelectrolyte per gram of latex. The lines serve to guide the eyes. Reprinted from reference [208], Copyright (2011), with permission from Elsevier.
Polyelectrolyte adsorption on oppositely charged surfaces usually leads to such a charge inversion [24,212,213]. The continuation of the adsorption beyond the IEP can be explained with the presence of one or more of the following driving forces. Hydrophobic interactions between the polyelectrolyte chains can enhance the adsorbed amount [214]. In addition, entropy gain due to the release of solvent molecules and counterions of the charged polymers upon adsorption [215] as well as ion-ion correlations [162] can be equally responsible for the charge reversal process.

The electrophoretic measurements were repeated at different ionic strengths. The concentration of the background electrolyte significantly influenced the mobility values. Accordingly, their magnitude decreased with increasing salt level at low polyelectrolyte doses due to the screening of the counterions of the partially neutralized particle surfaces. This finding is evident if one compares these electrophoretic data with ones measured with the bare latexes at the corresponding ionic strengths. For SL-270, similar tendency was observed in the mobilities at the saturation plateau, as they increased by decreasing ionic strength. However, a non-linear dependence of the mobilities beyond the ASP was discovered for the CML-308 particles. This trend can be adequately interpreted with the standard electrokinetic model [165], which was also used to explain the non-monotonic dependence of the electrophoretic mobilities of latex particles with increasing the concentration of monovalent salts.

The effects of the ionic strength on the IEP and the onset of ASP values are shown in Figure 44. Concerning the IEPs, only a weak influence was observed in the SL-270 systems and the values increased with the salt level. This result clearly indicates that the charge of the adsorbed PEI is partially neutralized by interacting Cl$^-$ ions. This is the so-called counterion condensation phenomenon, which has been previously reported in other polymer-colloidal particle systems [81,82]. The IEPs followed the same tendency in the CML-308 suspensions, i.e., only a weak increase was observed, indicating the same adsorption mechanism as in case of SL-270.

The charging ratio (CR) defines the numbers of elementary charges of a polyelectrolyte, which are necessary to neutralize the charge on the surface upon adsorption. Its value is unity whenever the process is...
stoichiometric meaning that one charge of the bare polyelectrolyte compensates one charge of opposite sign on the particle. For SL-270, the CR lies between 5 and 7 depending on the ionic strength. Such so-called super-stoichiometric charge neutralization also indicated that a substantial fraction of the PEI charge was neutralized by the condensed Cl\(^-\) anions. In case of CML-308, the magnitude of the surface charge density was high due to the thick layer of carboxylate groups giving rise to a CR of 0.3, which was about the same for all ionic strengths. This value indicates that a fraction of the negative particle charge was neutralized by co-adsorbed K\(^+\) cations, which accumulated in the highly charged brushy layer on the CML-308 surface.

The data in Figure 44 also indicate that CML-308 particles adsorbed a much higher amount of PEI than SL-270 due their higher magnitude of charge. However, the tendency in both cases was that the adsorbed amount increased with the ionic strength. It was assumed that the location of the ASP was determined by electrostatic forces and such an increase could be interpreted with the weaker repulsion between the adsorbed PEI chains. Accordingly, at low salt level, the polyelectrolytes are surrounded with an extended diffuse layer leading to repulsion between the polymers on the surface and to a smaller absorbed amount. This repulsion is weaker at high ionic strength due to charge screening by the background salt and hence, the polyelectrolyte can adsorb in a more compact configuration giving rise to higher PEI amount on the particle surface.

Let us now discuss the aggregation processes investigated in the above systems. For both SL-270 and CML-308, the aggregation was rapid near the IEP indicated by stability ratios close to unity (Figure 43). However, oppositely charged polyelectrolyte-particle systems usually show different behaviour and an acceleration of the fast aggregation rate at the IEP is observed at low salt levels leading to stability ratio values less than one [81,84,87]. This would be a clear signal of the presence of non-DLVO attractive forces.

The aggregation process slowed down on both sides of the IEP, wherever the particles possessed sufficiently high surface charge and an EDL formed. At low PEI concentrations, the negative charge of the particles was only partially neutralized due to the small amount of adsorbed polyelectrolytes, while at doses above the IEP, the particle was positively charged due to overcharging. In both cases, the overlapping EDLs induced repulsive forces, which stabilized the dispersions. Obviously, these forces were absent at the IEP and thus, attractions between the particles led to rapidly aggregating samples. Moreover, plateaus were observed in the stability ratios at low and high PEI concentrations suggesting similar aggregation mechanism for the bare and the polyelectrolyte-coated particles. This issue will be further discussed later in detail.

The stability ratio data shown in Figure 43 indicates that the concentration of the background electrolyte significantly influenced the colloidal stability of the suspensions. Accordingly, the
unstable region near the IEP was wider at high ionic strength due to the weaker repulsive EDL forces at higher salt levels. Such a charge screening process was also responsible for that the stability ratio values at the plateaus at high PEI dose decreased with increasing the KCl concentration from 10 mM to 100 mM.

The effect of the molecular mass on the charging and aggregation was also studied using PEIs of 2.5, 25 and 250 kg/mol. For the SL-270 particles, the electrophoretic mobilities changed only slightly by varying the molecular mass and no dependences were observed with the CML-308. These findings are similar to the ones reported for suspensions containing positively charged latexes and negatively charged polyelectrolytes [84] and indicated that the adsorption process is close to stoichiometric. However, in other systems, where high CR values were determined, the IEP shifted towards higher doses with increasing the molecular mass [81].

Further investigation on the colloidal stability of the above systems confirmed that the aggregation processes were also independent of the molecular mass of the PEI. Accordingly, the shapes of the stability ratio versus PEI dose curves were the same within the experimental error at different molecular masses for both SL-270 and CML-308 latexes. The absence of dependence of the colloidal stability on the molecular mass is atypical comparing to other polyelectrolyte-particle systems published earlier [81,84,216], where marked acceleration of the aggregation rate was found in both the slow and fast regimes at higher molecular masses.

The fact that these results do not suggest the presence of interparticle forces of non-DLVO origin (e.g., patch-charge or hydrophobic interactions) indicates homogeneously adsorbed PEI layer on the particle surface and hence, homogeneous surface charge distribution. It was assumed that the absence of charge heterogeneities resulted from the weakly charged stage of the PEI under these experimental conditions [210], which adsorb in a more extended configuration. This situation is similar to the one described as the semi-dilute 2-D Wigner liquid regimes applied for polyelectrolyte adsorption mechanisms [217].

The adsorbed polyelectrolyte layer is usually heterogeneous and the chains are well-separated on the surface when patch-charge interactions are present (see Figure 8 on page 28). However, in their absence, the adsorbed polymer film is usually more homogeneous and the individual chains are adsorbed in an extended configuration. This case was found for linear PEI here. Furthermore, the PEI chains crossed each other frequently on the surface, which leads to a random network. Although heterogeneities may be discovered on length scales smaller than the mesh-size of this network, it looks homogeneous on larger length scales leading to the presence of only DLVO-type (repulsive double layer and attractive van der Waals) interparticle forces. In addition, the PEI can be considered as a rather hydrophilic polyelectrolyte, since the charges are located on
the backbone and hence, it does not show any tendencies to interact with hydrophobic surfaces or polyelectrolytes.

The origin of interparticle forces was further explored by the AFM-based multiparticle colloidal probe technique using SL-3100 particles (Table 1) and linear PEI polyelectrolytes of 2.5 and 250 kg/mol [218]. The charging properties were followed by electrophoresis in the same suspensions. Note that the only difference between the SL-270-PEI and the present system is the size of the particles, therefore, qualitative comparison between the colloidal stabilities of the two systems will be made. Figure 45 shows the force profiles for different doses of PEI of a molecular mass of 250 kg/mol.

![Figure 45. Forces between SL-3100 particles as a function of the separation distance for various PEI doses at pH 4 and 1.1 mM ionic strength adjusted by KCl. The solid lines are the fits using the Poisson-Boltzmann theory. Polyelectrolyte dose (a) below and at the IEP (0.28 mg/g) and (b) at the IEP and above. Note that the mg/g unit refers to mg PEI per one gram of latex particle. Reprinted with permission from reference [218]. Copyright (2011) American Chemical Society.](image)

Repulsive forces were measured for the bare SL-3100 latexes (0 mg/g in Figure 45a) because of the predominance of the EDL forces over the attractive van der Waals interactions. In the presence of PEI, the polyelectrolyte adsorbs on the surface leading to a decrease of the electrophoretic mobilities with increasing the polyelectrolyte dose. Such a decrease in the charge resulted that the double layer repulsion weakened and an attractive force was observed at short distances. At the IEP, which was located at 0.28 mg/g PEI dose, the EDL forces disappeared due to the lack of surface charge and the interaction was purely attractive. A CR of about 3 was calculated at the charge neutralization point indicating super-stoichiometric charge compensation due to counterion condensation [82].
Figure 45b shows the force profiles at doses above the IEP, where the PEI adsorption gave rise to charge reversal and the surface of the SL-3100 latex became positively charged. Again, an EDL built up around such particles and the suspensions were stabilized due to repulsive forces upon their overlap. The adsorption process continued until the onset of the ASP, where the surface saturated and further added polyelectrolytes remained in the bulk. The maximum adsorbed amount of PEI was found to be 1.1 mg/g. The surface charge density remained constant after this dose due to the constant adsorbed amount and the same repulsive forces were determined under these experimental conditions.

The Poisson-Boltzmann model was used to fit the repulsive part of the forces determined at PEI doses below and above the IEP. The good agreement between the experimental and calculated data shown in Figure 45 indicates that DLVO-type forces were the major interactions between the particles and no additional (e.g., patch-charge, steric or hydrophobic) forces were present. The tendency in the interparticle force profiles determined at different polyelectrolyte doses qualitatively supports the results obtained in the charging and aggregation measurements with SL-270 particles in the presence of PEI, as discussed earlier [208].

To further investigate the origin of the interactions, the attractive forces were measured at the IEP in the presence of PEI of 250 kg/mol and 2.5 kg/mol molecular masses. Note that the repulsive EDL forces vanished at this dose. The charge neutralization with the higher molecular mass PEI resulted in lower attractive forces than for the 2.5 kg/mol one at short distances. Additional important information was that the tendency in the forces at larger distances was the same regardless of the molecular mass and the ionic strength. Since additional attractive interactions of non-DLVO origin (patch-charge, ion-ion correlation, polyelectrolyte bridging, etc.) are usually sensitive to the amount of the background electrolyte, these findings further confirmed that solely van der Waals forces were acted between the particles.

Such behaviour is atypical in dispersions of charged latex particles in the presence of oppositely charged polyelectrolytes at the charge neutralization points. As revealed by colloidal probe measurements with similar systems [170,187,188], significantly stronger attractive forces were observed than the ones in the SL-3100-PEI dispersions. In addition, the forces were sensitive to both ionic strength and molecular mass indicating that they originated from surface charge heterogeneities induced by polyelectrolyte adsorption. However, in excellent agreement with the colloidal stability study performed with the smaller SL-270 particles, the present results suggest that the layer of adsorbed PEI is homogeneous. For instance, this feature is utilized in preparation of multilayered polyelectrolyte films, where PEI is adsorbed as the first layer on the substrate and thus, it provides a smooth surface for the additional polyelectrolyte layers [219].
6.1.1.2. Carboxyl latex – PAMAM dendrimer

This part of the thesis deals with the investigation of charging, interparticle forces and aggregation in systems containing CL-1000 particles and PAMAM dendrimers of different generations, such as G4, G7 and G10 [175]. PAMAM dendrimers are composed of an ethylenediamine core and charge determining primary amino groups on the outer spheres (Figure 6). The connections between the units are set by oligoamide chains [220]. Charged PAMAMs possess spherical structures in solutions. Under the experimental conditions applied here (pH 5.8 and ionic strength of 1 mM adjusted by KCl), the carboxyl latex particles are negatively charged and the PAMAM dendrimers are of positive charge [221].

Electrokinetic potentials (Figure 46) were converted from electrophoretic mobilities using the O’Brien-White theory [165]. In general, the charging behaviour of the CL-1000 particle in the presence of the dendrimers was similar to other systems containing latexes and oppositely charged polyelectrolytes discussed in the previous part of the thesis. Accordingly, the negative potentials at low doses corresponded to the charge of the bare particles, while dendrimer adsorption led to charge neutralization at the IEP and subsequent overcharging, which continued until the onset of the ASP. Unlike in the SL-270-PEI and CML-308-PEI suspensions, the IEPs shift towards higher PAMAM doses with increasing the molecular mass of the macromolecules. It was assumed that the condensation of the Cl\(^-\) ions into the dendrimers gave rise to loss of the bare charge and this phenomenon was more pronounced with PAMAMs of higher generations [82]. Due to the lower effective charge, higher amounts of dendrimer are necessary to neutralize the particles. Similar results were reported with latex-PAMAM dendrimer systems earlier [81].

The predominant interparticle forces were determined with the colloidal probe technique with exactly the same samples as used in the electrophoresis. Qualitatively similar force profiles were observed in the systems, which were different only in the size of the PAMAM molecules. Accordingly, repulsive interactions were detected at low dendrimer doses, while the forces were attractive at the IEP. At higher PAMAM concentrations above the IEP, where the CL-1000 latexes were positively charged, the particles repelled each other again.
The interparticle force profiles in the presence of different doses of PAMAM dendrimers could be well-described by DLVO-type repulsive EDL and attractive van der Waals forces, however, an additional attractive force originating most likely from patch-charge interactions had to be also included:

\[ F(h) = F_{vdW}(h) + F_{EDL}(h) + F_{PC}(h) \]  

(35)

Such a force profile is similar to the ones obtained for latex-multivalent ion systems [174,195], as discussed in subsection 5.1.2 and also for other latex-PAMAM dispersions [170].

The origin of the patch-charge attractions can be interpreted as follows. The charge density of the PAMAM dendrimers is higher than the CL-1000 particles. Once the overall charge neutrality occurred, a fraction of the surface charged sites are still available, because the average distance between two surface site neighbours is higher than the size of a PAMAM molecule. Therefore, the adsorbed dendrimers accumulate islands of positive charges (patch) among negatively charged bare sites (charge) on the surface. Such charge heterogeneities leads to Coulomb attraction between the oppositely charged parts of the particles and thus, to the presence of attractive patch-charge interactions. The strength of these dendrimer-induced patch-charge forces is much higher than the ones experienced in the presence of multivalent ions. However, such an additional attraction was not present in the earlier discussed SL-3100-PEI system due to homogeneous polyelectrolyte adsorption and smooth particle surfaces.

To further confirm the above assumptions, 3-D height topographic AFM images of G10 PAMAM dendrimers adsorbed on CL-1000 particles were taken at different doses. The bumps in Figure 47 indicate dendrimer molecules adsorbed on the surface. The increased adsorbed amount with increasing the dose was well-visible in the images allowing the quantification of the macromolecules on the latexes.
Figure 47c indicates that the PAMAM dendrimers covered the CL-1000 surface only partially, in contrast to other polyelectrolytes of linear or branched structures [24,222]. This finding can be explained by the electrostatic repulsion between the charged macromolecules adsorbed on the surface. Such a repulsive interaction is usually more pronounced at low ionic strength leading to lower adsorbed amount, while the polyelectrolytes can be adsorbed in a more compact way at high salt levels due to charge screening and hence, the adsorbed amount is higher in this case.

To determine the extent of the patch-charge forces caused by the adsorption of the PAMAM dendrimers of different generations, the interparticle forces were measured at the charge neutralization points, where the repulsive EDL forces vanished. However, it is extremely difficult to hit the IEP accurately, therefore, the forces recorded close to the IEP still contained a slightly repulsive part. To simplify the picture and focus better on the patch-charge and DLVO attractions, the contribution from the EDL repulsion was eliminated from the curves shown in Figure 48.

Let us compare the van der Waals force determined in 1 M salt solution with the bare CL-1000 latex with the forces measured in the presence of the dendrimers. The difference is striking, since the attraction induced by the PAMAM adsorption is significantly stronger than the van der Waals attraction and the obtained force profiles cannot be fitted with the DLVO model.

Another interesting feature was that the forces became more attractive in the G4 < G7 < G10 order. This sequence is due to the increasing size of the dendrimers. Adsorption of a higher generation PAMAM gave rise to a higher patch size.

Considering equation (32), which describes the strength of the patch-charge forces through the amplitude and decay length, it is obvious that the bigger patch size leads to a higher value of both the amplitude and the decay length. Therefore, the non-DLVO interparticle attractions of patch-charge origin become stronger with increasing the size of the adsorbing molecules.
The comparison of the stability ratio values calculated from the AFM experiments (equations (13) and (26)) and measured by time-resolved DLS (equations (11) and (13)) in the systems containing CL-1000 particles and PAMAM dendrimers is shown in Figure 49.

**Figure 49.** Measured (symbols, DLS) and calculated (solid lines, AFM) stability ratios as a function of the doses of G4, G7 and G10 PAMAM dendrimers. Reprinted from reference [175], Copyright (2014), with permission from Elsevier.

To interpret the stability ratio values, let us recall the tendency in the electrokinetic potentials (Figure 46) measured in the same systems. In general, similar observations were taken as for the PEI-particle suspensions discussed in subsection 6.1.1.1. Accordingly, at low PAMAM doses below the IEP, the particles are negatively charged and hence, the repulsive EDL forces predominate between the particles leading to stable dispersions. The aggregation became faster with increasing the dendrimer dose and the stability ratio values went through a minimum near the IEP, where only attractive forces were present owing to the lack of surface charge. Suspensions of primary particles were observed again at high dendrimer doses, where the charge of the CL-1000 latex was reversed due to PAMAM adsorption and the repulsive EDL forces were strong enough to prevent particle aggregation. These conclusions were generic for all systems, however, the following differences can be discovered for the colloidal stability of the particles in the presence of dendrimers of different generations.

First, stability ratios could be measured in wider ranges by increasing the generation, i.e., the curves became narrower in the G10, G7 and G4 sequence (Figure 49). This phenomenon was also reflected in the slopes in the slow aggregation regime and smaller slopes were detected by increasing the generation. Second, the fast aggregation region appeared at higher doses with increasing the molecular mass of PAMAM in accordance with the mobility data, which also indicated similar shift in the IEPs, where such diffusion controlled aggregation occurred. Third, the stability ratios in the fast aggregation regime were close to unity for G4, however, they were lower than one for G10 indicating an acceleration in particle aggregation due to the presence of an attractive interparticle force of non-DLVO origin.
These observations can be explained by considering the effects of patch-charge interaction and counterion condensation. The shallower slopes at low and high doses indicate faster aggregation processes with increasing the PAMAM generation. As mentioned before for the force measurements, the extent of patch-charge interaction increasing in this way and thus, higher attractive forces and lower stability ratio values can be expected with increasing the molecular mass of dendrimers at identical doses. The same effect is responsible for the acceleration in the fast aggregation rates at higher PAMAM generations. In addition, counterion condensation takes place and leads to an effective charge lower than the bare one, as discussed earlier in case of the electrophoretic data. The extent of this effect increases again with the generation and hence, higher amount of dendrimers is needed to neutralize the surface charge with G10 than G4. Since charge neutralization determines the fast aggregation regimes, they also shift towards higher doses by increasing the PAMAM generation.

Moreover, the stability ratios measured by DLS were compared with the ones calculated from the AFM results. The latter results are shown as solid lines in Figure 49 and they were calculated by including DLVO-type and patch-charge interparticle forces (equation (35)). For G4, the agreement between experimental and theoretical values was good, however, significant deviations were observed by increasing the generation. Although the calculated fast aggregation regimes agreed well with the experimental ones in all case, the AFM results indicated narrow ranges of the stability ratios, most likely due to the steep transition of the electrokinetic potentials around the IEP values (Figure 46).

The other reason for such differences in the stability ratios could be again the different extent of patch-charge attractions in the DLS and AFM experiments. Namely, the CL-1000 particles were immobilized on the substrate and on the tip-less cantilever, therefore, they cannot rotate freely during the AFM measurements. On the contrary, the samples in the DLS study contained latexes in a suspension and the particles could find their preferred orientation in order to locate the oppositely charged patches by the charged surface sites. Accordingly, the patch-charge interactions were more visible in the latter case, while they were partly hidden in the AFM experiments due to the fixed position of the CL-1000 particles.

6.1.2. Stabilization mechanism

As discussed before, coating of latex particles with oppositely charged polyelectrolytes at different doses can change the colloidal stability significantly. To further explore the origin of the interparticle forces, additional experiments were carried out to probe the effect of the ionic strength on the aggregation of charged colloidal particles coated with polyelectrolytes [25].
As discussed earlier, polyelectrolytes strongly adsorb on oppositely charged colloidal particles leading to charge neutralization at the IEP and subsequent charge reversal. The adsorption continues until the onset of the ASP, where the surface of the particles is saturated by the polyelectrolyte layer. It is relatively clear that mainly van der Waals attractions are responsible for the destabilization near the IEP. Other type of attractive forces (e.g., patch-charge or hydrophobic interactions) may be also present depending on the system. However, the origin of the predominant forces arising between the overcharged particles due to polyelectrolyte adsorption is still not identified unambiguously. Several scientists recommended repulsive steric forces as the main stabilizing interaction, while others suggested that the suspensions of polyelectrolyte-coated particles are stable due to the repulsion between the EDLs upon their overlap [13,89,223,224]. In addition, the presence of both steric and electrostatic repulsion was also reported in certain polyelectrolyte-particle systems [27,103,159].

To address this issue, electrophoretic mobilities and stability ratios were measured at different ionic strengths in the following samples. SL-190 and SL-270 were used as negatively charged particles as well as AL-220 and AL-400 as positively charged ones (see Table 1 on page 35 for more details). The latexes were coated with PEI, PDADMAC, PSS and PAA (structures are shown in Figure 6 on page 26) at the dose of the onset of the ASP. These polyelectrolytes are of high line charge density and their strong affinity to oppositely charged surfaces, which gives rise to charge inversion of the particles, has been confirmed [84,90,208,209].

The dependence of the mobilities and stability ratios in dispersions of polyelectrolyte-coated latex particles on the ionic strength adjusted with KCl indicates that the repulsive EDL forces have major contribution in the stabilization mechanism. Figure 50a shows the electrophoretic mobilities of the bare SL-270 and AL-400 latexes at different salt levels. The mobility values went through a maximum or minimum, respectively and they decreased in magnitude with increasing the ionic strength. The former phenomena can be well-described with the electrokinetic effect [165,198], while the decrease is owing to the surface charge screening by the salt and subsequent lowering of the absolute value of the electrostatic surface potential.

Let us discuss the corresponding stability data (Figure 50b), which followed similar tendency as discussed earlier for charged particles in monovalent salt solutions. Accordingly, slow aggregation and stable samples were observed at low KCl concentrations and the dispersions became unstable at high ionic strength indicated by stability ratios close to one. These regimes were separated by well-defined CCCs. This behaviour is typical in systems, where the major interparticle forces originate from DLVO-type interactions, i.e., the superposition of the repulsive EDL and attractive van der Waals forces determines the colloidal stability of the dispersions. As discussed Chapter 4, DLVO theory predicts the location of CCC between 0.1 M
and 1.0 M in monovalent salt solutions, in agreement with the experimental results presented for the bare particles in Figure 50b.

It is evident from the tendency of the mobilities and stability ratios that the colloidal stability of these latex particles with and without an adsorbed polyelectrolyte layer is very similar. Concerning the electrophoretic mobilities (Figure 50a), their dependence on the ionic strength remains the same for the bare and coated latexes, however, the corresponding signs are reversed due to the charge reversal process. The trend in the stability ratios as a function of the KCl concentration is again analogous for the bare the polyelectrolyte-coated particles. Accordingly, slow and fast aggregation regimes separated by the CCC were observed. Due to the very similar behaviour of the bare and coated particles in these measurements, one can assume that the
stabilization mechanism is the same. Since the DLVO theory describes the stability of the bare particles in monovalent electrolyte solutions, therefore, the governing interparticle forces must be also the same in suspensions containing the same latexes, but with an adsorbed polyelectrolyte layer on their surface.

In spite of the similarity in the trends of the stability ratios, a striking deviation in the slopes of the slow aggregation regime was observed. In this region, the increase of the stability ratios was found to be steeper with decreasing the ionic strength for the bare particles indicating that the attractive forces are somehow stronger for the covered latexes. If one assumes only DLVO-type forces for the bare particles, an attractive interaction of non-DLVO origin must be present in the other case. It was assumed that this attraction originates from the lateral heterogeneity of the adsorbed polyelectrolyte layer, which leads to patch-charge interactions and thus, acceleration in the aggregation. Similar patch-charge forces were identified with other polyelectrolytes and also with multivalent ions [24,174,175,182,187,195,225].

Apart from these attractive interactions, the repulsion between the EDLs was still the major stabilization force in these systems. The importance of the repulsive double layer forces was confirmed by direct force measurements in the SL-3100-PEI (subsection 6.1.1.1) and also in other particle-polyelectrolyte systems using the AFM-based multiparticle colloidal probe technique [24,181,187,218,226]. In those experiments, only electrostatic repulsion was detected at high polymer doses, above the onset of the ASP. However, AFM images of polyelectrolyte monolayers confirmed the lateral heterogeneity in the adsorbed layer and hence, additional forces may play a role in certain extent [24]. In addition, no evidence was found for the presence of repulsive steric forces between the adsorbed polyelectrolytes. These types of interactions are probably present for weakly charged macromolecules or neutral polymers, where the strength of the adsorption is smaller. However, the effect of steric repulsion on the colloidal stability was found to be negligible in the present dispersions containing highly charged polyelectrolytes and particles.

6.1.3. Structure of the polyelectrolyte layer

To better understand the interfacial processes in particle-polyelectrolyte systems at high polymer doses (where the latex surfaces are completely coated with the macromolecules), information on the amount and the thickness of the adsorbed polyelectrolyte layer is needed. However, the accurate determination of these parameters is not trivial. Electrophoresis and DLS techniques were used to develop procedures in order to accurately measure the adsorbed mass and the hydrodynamic layer thickness in systems containing latex particles and oppositely charged polyelectrolytes [227-229].
Thickness of adsorbed polyelectrolyte layers measured by DLS was reported in the range of 1-100 nm [89,230-234] indicating that such measurements have to be carried out carefully and several factors have to be considered. Increase in the hydrodynamic radius may be resulted from different processes such as the formation of the adsorbed polymer layer or particle aggregation (Figure 51). The latter phenomena can be eliminated with dilution of the dispersions, however, the scattered intensity has to be high enough for reliable determination of the hydrodynamic radii by the DLS methods.

The most important requirement is that the particle dispersion has to be stable during the entire experiment (i.e., in the absence and also in the presence of polyelectrolyte). If no aggregation occurs, the measurement of the hydrodynamic layer thickness is straightforward, as summarized below.

The hydrodynamic radius \( R_i \) of the bare particles can be measured by DLS in a time-resolved experiment and this value is subtracted from the one determined after addition of the polyelectrolyte at sufficiently high concentration \( R_j \). Accordingly, the hydrodynamic thickness of the adsorbed polyelectrolyte layer \( L \) can be calculated from the difference between these radii as:

\[
L = R_j - R_i
\]

In order to carry out accurate layer thickness measurements in particle-polyelectrolyte systems by DLS, the following issues must be considered. First, the colloidal particles may aggregate in the presence of the oppositely charged polymers. This can occur even at high polyelectrolyte doses, where the dispersions were reported to be stable, since the adsorption process passes through the IEP. At this dose, a fraction of the latexes are not charged during a short time interval and thus, the hydrodynamic radius slightly increases due to particle aggregation. Such an increase has to be distinguished from the one caused by the adsorbed polyelectrolyte layer. However, aggregation of colloidal particles usually gives rise to a steady increase of the hydrodynamic radius, while the increase due to the adsorbed polymer layer is constant in time. Therefore, the different type of increases can be easily distinguished, if the time-resolved DLS experiments are carried out carefully.
The second issue is that the size of the particles must be suitable for such layer thickness measurements. Equation (36) suggests that small particles are better to use, because the difference between \( R_1 \) and \( R_2 \) will be bigger upon polyelectrolyte adsorption and hence, the error will be smaller. Nevertheless, there is a second phenomenon, which should be considered at this point. The unwanted aggregation processes are eliminated with sufficient dilution of the suspensions, but the intensity of the scattered light from these diluted samples should be high enough to perform reliable DLS measurements. Therefore, relatively large particles of diameters typically in the 100-500 nm range have to be used to accurately determine the hydrodynamic thickness of the saturated polyelectrolyte layers on particles.

Negatively charged SL-270 and CML-308, as well as positively charged AL-400 were used as particles and two negatively (PSS and PAA) and one positively (PEI) charged polyelectrolytes were applied. The hydrodynamic layer thickness was obtained by DLS, while the saturated adsorbed mass by electrophoresis. The effects of the molecular mass and the ionic strength on these quantities were systematically studied. The influence of the latter parameter on the adsorption strength and mechanism is especially important to understand, since the background salt screens the charges of both the surface and the polyelectrolyte and hence, it can significantly modify the nature of the interaction between the macromolecules and the latex particles [217,234,235].

The precision of the measurements was further improved by performing time-resolved multiangle DLS experiments in the dispersions. Using this technique, polyelectrolyte layers with thicknesses of only a few nanometers can be determined. Note that the hydrodynamic radii measured at different scattering angles vary about \( \pm 5 \) nm due to the polydispersity of the latexes, since the particles of higher sizes are weighted more in the diffusion coefficients. Although \( R_1 \) and \( R_2 \) depend on the scattering angle, their difference is independent and therefore, a typical accuracy of \( \pm 0.5 \) nm was obtained once the \( L \) values measured in multiangle DLS experiments were averaged.

The obtained hydrodynamic thicknesses of the adsorbed polyelectrolyte layers are shown in Figure 52. Two important conclusions can be made on the basis of these data. The value of \( L \) increases with the ionic strength and also depends on the molecular mass of the polymers. More precisely, the polyelectrolyte layer has only a thickness of around 2-3 nm at low salt levels (e.g., at 0.1 mM in Figure 53), which is constant regardless of the molecular mass (\( M \)). However at higher ionic strengths (e.g., at 100 mM in Figure 53), the thickness reaches a plateau, where its dependence on \( M \) can be quantified as:

\[
L \propto M^{0.1}
\]

(37)
The layer thickness values determined in four types of suspensions containing latex particles and polyelectrolytes of different molecular masses at various ionic strengths clearly indicated that the above trend is generic. The data in Figure 53 further confirm this observation at low and high salt levels for flat or swollen layers, respectively. In addition, the exponent presented in equation (37) is significantly smaller than the ones reported earlier for adsorbed layers of neutral or weakly charged polymers [236,237].

Figure 52. Hydrodynamic thicknesses of adsorbed saturated polyelectrolyte layers measured in the SL-270-PEI, AL-400-PAA and AL-400-PSS dispersions as a function of ionic strength adjusted by KCl and for different molecular masses at pH 4. The solid lines are just to guide the eyes. The data were taken from references [228,229].

Figure 53. Left: hydrodynamic layer thickness for different polyelectrolytes at low (0.1 mM) and high (100 mM) ionic strengths. Solid lines are fits with equation (37). Right: schematic representation of the conformation of adsorbed polyelectrolyte chains. Reproduced from reference [228] with permission from the PCCP Owner Societies.
The data obtained during the layer thickness measurements were compared with previously published Monte Carlo simulation results, in which the conformation of a single adsorbed polyelectrolyte chain under different experimental conditions was investigated [238]. The theoretical results indicated that the layer thickness is small and independent of the molecular mass at low ionic strengths, while the adsorbed polyelectrolyte swells and hence, its thickness increases until a plateau with increasing the salt level. In addition, the thickness of the layers at this plateau increases with the molecular mass of the polymers.

Comparing these observations to the experimental results presented above, full agreement can be concluded. The only discrepancy is that the theoretical dependence on the molecular mass indicates a higher exponent in equation (37) than the one fitted with the experimental data. A possible explanation for the deviation in the exponents can be that only electrostatic interactions were considered in the simulations, but additional (e.g., hydrophobic or hydrogen bonding) attractions between the polyelectrolytes and the particles may also play a role in the adsorption mechanism. Indeed, the fact that the polymers are adsorbed on the surface even at high salt level clearly suggests the presence of non-electrostatic attractions, since the purely electrostatic interactions are screened by the background electrolyte at high ionic strengths leading to the desorption of the polyelectrolytes from the substrate [217,238].

Despite the difference in the exponents obtained by simulations or DLS, the very similar tendency in the data affirms that the conformation of the single polyelectrolyte chains is responsible for the thickness of the polymer layer. Figure 53 illustrates such changes in the confirmation at different salt levels and molecular masses. Accordingly, the polyelectrolyte chains adopt flat configuration at low ionic strength regardless of the molecular mass. At high salt levels, the thickness of the layers increases with increasing the molecular mass due to the larger lateral enlargement of the adsorbed polyelectrolyte.

It was found that this mechanism is generic in systems containing spherical latexes and oppositely charged polymers, regardless of the sign of the particle or the polyelectrolyte charge. However, this hypothesis is valid only for adsorbed polyelectrolyte monolayers, where the major attractive forces are of electrostatic origin, while different mechanisms may occur in case of multilayers or covalently grafted polymers [219,239,240].

Besides, it was demonstrated previously in the thesis that the characteristic overcharging of latex particles upon addition of oppositely charged polyelectrolytes can be adequately followed by electrophoresis. It was clarified that the onset of the ASP indicates the maximum adsorbed amount of polymers at surface saturation. These quantities were determined in some particle-polyelectrolyte systems. Figure 54 shows that the adsorbed mass of the polyelectrolytes on
oppositely charged latex particles increased with the ionic strength and slightly decreased with increasing the molecular mass. In the latter case, the relation can be given as follows:

\[ \Gamma \propto M^{-0.06} \]  

(38)

Figure 54. Molecular mass dependence of the amount of polyelectrolytes adsorbed on oppositely charged latex particles at different ionic strengths (adjusted by KCl) measured in the SL-270-PEI, AL-400-PAA and AL-400-PSS systems at pH 4. Solid lines are fits with equation (38). The data were taken from reference [228].

The generality of the above discussed tendencies was confirmed in three types of suspensions containing latex particles and oppositely charged polyelectrolytes of different molecular masses at various salt levels. Although the adsorbed mass values are different due to system specificity, the molecular mass dependence is analogous and the same exponent was found for equation (38) in all of the systems investigated.

6.2. Polyelectrolyte-stabilized layered double hydroxides

6.2.1. Tuning the colloidal stability by polyelectrolytes

6.2.1.1. LDH – P(AA-BA) copolymer

In this part, the surface charge properties and aggregation behaviour of LDH-180 particles will be discussed in the presence of P(AA-BA) copolymer (structure is shown in Figure 6 on page 26). LDH-180 consists of Mg\(^{2+}\) and Al\(^{3+}\) layer-forming cations and NO\(_3^-\) intercalated anions (see Table 2 on page 37 for more details). It was synthesized by the flash co-precipitation method [121,130]. The P(AA-BA) copolymer (which will also be referred to as polyelectrolyte) is a short statistical copolymer containing 7.5 acrylic acid and 7.5 butyl acrylate monomers and 4-cyano-4-
thiothiopropylsulfanyl pentanoic functional group. This compound was synthesized by reversible addition fragmentation chain transfer (RAFT) polymerization. It is a representative of the macroRAFT agents, which are typically employed in macroRAFT-assisted encapsulating emulsion polymerization processes, where inorganic materials embedded in a polymeric matrix can be synthesized [241-243]. However, it is very important to investigate the dispersion characteristics and suggests experimental conditions, where the P(AA-BA)-coated LDH-180 particles are stable and can be used in the polymerization procedures later.

The LDH-180 platelets have positive structural charge, which are pH-independent between pH 6 and 10. Besides, each P(AA-BA) chain possesses an average of 8.5 negative charges due to the deprotonation of 7.5 acrylic acid units plus the carboxylic acid end group at pH 9, where the investigations were carried out. Electrophoretic mobility measurements were performed at different polyelectrolyte doses and ionic strengths, while the concentration of LDH-180 particles was kept constant in each experiment.

Strong adsorption of the copolymer on the platelets was observed (Figure 55a). The electrophoretic mobilities were positive at low P(AA-BA) concentrations and the values were close to the ones measured for the bare LDH at the corresponding ionic strengths (Figure 55b). The mobilities decreased with increasing P(AA-BA) dose due to the fact that the adsorbed...
copolymers progressively neutralized the charge of the LDH-180. Such a neutralization process led to well-defined IEPs and their location decreased with increasing the concentration of the background electrolyte. Similar to the latex-polyelectrolyte systems in subsection 6.1 and also to other suspensions containing charged colloidal particles and oppositely charged polyelectrolytes [29,84,89,142,243], the adsorption of the P(AA-BA) continued until the onset of the ASP and gave rise to overcharging. Very similar electrophoretic mobilities were measured at the plateau at the 1 mM and 10 mM salt level. However, these plateau values were significantly lower in the 100 mM system due to the more enhanced charge screening by the K$^+$ cations.

Apparent dynamic rate coefficients (equation (11)) and stability ratios (equation (13)) were determined in time-resolved DLS measurements in the same systems as used in the mobility study. The results obtained at three ionic strengths are illustrated in Figure 55c. The colloidal stability of the suspensions was very sensitive to the salt concentration at low P(AA-BA) doses. Below 1 mg/g polyelectrolyte loading, the stability ratios of the particles of the same P(AA-BA) coverage decreased rapidly with increasing the ionic strength. For instance, unstable suspensions were observed at 100 mM salt level in this regime and stability ratios close to one indicated that the aggregation is controlled solely by the diffusion of the platelets. Such a destabilization occurred owing to the salt screening effect and subsequent vanish of the repulsive EDL forces. Comparing these findings to the ones obtained with the latex-polyelectrolyte systems (Figures 43 and 49), the difference is striking. The latexes were found to be more resistant against salt-induced aggregation in the presence of small amount of adsorbed polyelectrolyte chains below the IEP. This difference most likely originates from the higher surface charge density and thus, stronger repulsive EDL forces of the bare latex particles [25,208,209].

Moreover, the aggregation of the P(AA-BA)-modified LDH-180 particles was fast at doses near the IEP regardless of the ionic strength due to the lack of stabilizing double layer repulsions and the predominance of the van der Waals attractions. Further increasing the polyelectrolyte dose, the stability ratios rapidly increased and highly stable dispersions were found at high doses. The slopes of the stability ratio versus polyelectrolyte dose curves in this regime did not depended significantly on the KNO$_3$ concentration indicating that interparticle forces of non-electrostatic origin play also an important role in the aggregation mechanism. Similar tendencies were reported with gibbsite platelets in the presence of anionic macroRAFT agents [243].

Concerning the extent of the repulsive EDL interactions, the situation at lower polyelectrolyte doses is discussed above. The contribution of the double layer repulsion to the stabilizing forces at high P(AA-BA) concentrations deserves further discussion. Electrophoretic measurements indicated that the onset of the ASP is located at 300 mg/g dose. This is the amount needed to completely coat the platelets and it roughly corresponds to a polyelectrolyte surface density of 1.7 mg/m$^2$. Although this value is notably lower than the grafting density of polymer brushes
(10-20 mg/m$^2$) [240], but higher than the ones reported for suspensions of polyelectrolyte functionalized polymer [228], magnetite [103] or silica [89] particles. The onsets of the ASPs were also found to be lower for the latex-polyelectrolyte systems discussed in subsection 6.1. Accordingly, more P(AA-BA) copolymer can be adsorbed on the particles than other polyelectrolytes of high line charge density. It was assumed that the randomly distributed butyl groups enhance adsorption through hydrophobic attraction between the adsorbed copolymer chains and with the LDH-180 surface. As discussed also in part 4.1.3, substances of increased hydrophobicity show higher affinity to particle surfaces leading to higher adsorbed amount and hence, higher extent of the overcharging.

The effect of the butyl chains on the onset of the ASP was illustrated by comparing the values determined with P(AA-BA) and pure PAA of the same molecular mass under identical experimental conditions (Figure 56). It was found that the onset of the ASP was shifted towards higher concentration once the copolymer was applied. This finding unambiguously shows that the butyl groups are responsible for the higher adsorbed amount most probably due to hydrophobic interactions between the adsorbed P(AA-BA) chains and the surface. Furthermore, the IEPs followed the same tendency, namely, the charge neutralization by PAA occurred at significantly lower polyelectrolyte dose than by the copolymer. It was suggested that the structure of the saturated P(AA-BA) layers are more extended laterally (e.g., the chains form tails and loops upon adsorption) than the ones form upon adsorption of polyelectrolytes of high line charge density.

On the basis of this information one can conclude that the repulsive forces originate from steric repulsion between the chains as well as from EDL forces. However, the latter interactions are of similar strength than for PAA, since the magnitude of the mobilities of the charge reversed particles was very similar. Accordingly, the extra stabilization effect is clearly caused by the butyl groups of the copolymer, which allows the formation of a laterally more extended polymer layer on the particles leading to the presence of the steric repulsive forces due to the rising osmotic pressure upon the overlap of the P(AA-BA) chains.

![Figure 56. Electrophoretic mobility of LDH-180 particles in the presence of PAA and P(AA-BA) polyelectrolytes of identical molecular mass (1800 g/mol) at 1 mM ionic strength adjusted by KNO$_3$ and pH 9. Reprinted with permission from reference [205]. Copyright (2015) American Chemical Society.](image-url)
6.2.1.2. LDH - Heparin

The effect of heparin (structure is shown in Figure 6 on page 26) adsorption on charging and aggregation of CO$_3^{2-}$-intercalated LDH particles of different sizes (LDH-272 and LDH-632, see their properties in Table 2) was investigated [206]. Low molecular weight heparin was used, which is a natural polyelectrolyte having the highest negative charge density among the biological macromolecules [244]. Heparin is widely used in biomedical applications as injectable stabilizing agent. On the other hand, LDH particles are promising candidates as drug carriers in delivery processes, however, their stability have to be improved to prevent aggregation in such applications [92,127,245]. Therefore, the aim of this work was to study the colloidal stability of LDH particles in the presence of heparin and to suggest experimental conditions, where highly stable dispersions can be obtained.

Charging properties of LDH-272 was investigated with electrophoresis in a wide range of polyelectrolyte doses at pH 7. As mentioned before, the particles are positively charged owing to their structural properties, while the heparin is negatively charged due to the ionization of its functional groups at the pH applied. Only the polymer concentration was varied in a set of measurement, i.e., pH, LDH-272 concentration and ionic strength was kept constant. In addition, three sets of experiments were carried out at different salt levels to probe the electrostatic interactions between the particles and the polyelectrolytes. The data presented in Figure 57a indicates that the electrophoretic mobilities followed similar tendencies as the ones showed in the LDH-180-P(AA-BA) system.

![Figure 57. Electrophoretic mobility (a) and stability ratio (b) values for LDH-272 particles as a function of the heparin dose at different ionic strengths adjusted by NaCl at pH 7. The mg/g unit refer to mg heparin per gram of LDH-272. Reproduced from reference [206] with permission from the Royal Society of Chemistry.](image-url)
Heparin adsorption on the oppositely charged particle surface gave rise to a decrease of the mobilities with increasing the polyelectrolyte dose. Charge neutralization occurred at the IEP, which was located in the range of 12-26 mg/g. Although the location of the IEPs varied by changing the ionic strength, no clear trend was observed. The adsorption continued after the IEP leading to the charge inversion phenomena, as often reported for oppositely charged particle-polyelectrolyte systems [24, 199, 246]. The onsets of the ASPs were found around 100 mg/g dose indicating that less amount of heparin is needed to completely coat the particles than P(AA-BA) in the previously discussed LDH-180-P(AA-BA) system.

Similar results were published with carboxylate derivatives adsorbing on CO$_3^{2-}$ and Cl$^-$-intercalated LDHs [58]. In that work, systematic zeta potential measurements carried out at different doses revealed that charge neutralization and overcharging occurred due to the adsorption process. However, much higher particle concentration was applied there and thus, higher absolute amount of the carboxylate compounds were necessary to significantly change the surface charge properties of the particles.

Moreover, the trend in the magnitude of the electrophoretic mobilities at different ionic strengths can be interpreted as follows. At very low polyelectrolyte doses, the electrophoretic mobility values decreased with increasing the salt level. In this regime, the charge of the platelets is very similar as for the bare LDH-272 due to the small amount of adsorbed heparin. Therefore, the screening effect of the salt on the surface charge is responsible for the decrease in the mobilities at higher ionic strength. At elevated heparin doses above the onset of the ASP, the mobilities did not change linearly with the salt level. The surface of the LDH-272 was completely covered with the polyelectrolyte under these experimental conditions, therefore, different issues have to be considered to explain this finding. These are the electrokinetic effect on the mobilities [165], counterion condensation into the heparin structure [82] and screening of the surface charge by the salt. Therefore, this topic requires further interpretation of the effect of ionic strength on the stability of the coated LDH-272, which will be given in subsection 6.2.2.

To assess the colloidal stability in the above systems, time-resolved DLS experiments were performed to determine stability ratios under the same conditions as in the electrophoretic study. The aggregation behaviour of the LDH-272 particles was qualitatively analogous with the one observed in the LDH-180-P(AA-BA) suspensions. The speed of particle aggregation depended considerably on both polyelectrolyte dose and ionic strength (Figure 57b). Unstable dispersions were observed near the IEP, while more stable suspensions formed at higher heparin doses, where the platelets were negatively charged due to the charge inversion phenomenon. The colloidal stability was extremely sensitive to the concentration of the background electrolyte at low polyelectrolyte doses.
At first sight, such a behaviour can be explained by the classical DLVO theory [62]. Accordingly, repulsive EDL forces stabilize the samples, wherever the charge of the particles is sufficiently high and attractive van der Waals forces predominate around the IEP, where the double layer vanishes. Similar findings were reported in other suspensions containing polymeric latex [84], titanate [142,151,205] or silica [216,247] particles and oppositely charged polyelectrolytes. However, the situation in the present system is more complicated especially at high heparin coverage and the origin of the interparticle forces will be further discussed in subsection 6.2.2.

The stability ratios determined at low polyelectrolyte doses strongly depend on the ionic strength (Figure 57b). Relatively narrow U-shaped curve was obtained at 1 mM NaCl concentration, which widened at 10 mM and became almost open at the low dose side at 100 mM salt level. In the latter situation, the stability ratios were around three meaning that every third particle collision led to dimer formation. On the contrary, the stability ratio values were insensitive to the NaCl concentration at high heparin loading. The same values were measured within the experimental error at doses above the fast aggregation regime regardless of the salt level.

The dependence of the stability ratios on the ionic strength at low polymer coverage resembles to the one experienced in the LDH-180-P(AA-BA) suspensions [205] and it is in line with the DLVO theory. Accordingly, the charge screening effect by the added background electrolyte weakened the repulsive EDL forces and hence, the aggregation rates increased with increasing the ionic strength at the same heparin dose. At high polyelectrolyte concentration, however, the polymer-coated LDH-272 platelets were stable even at 100 mM ionic strengths. Given their relatively low surface charge density, the bare particles rapidly aggregate at this NaCl concentration. The stabilizing effect of the saturated heparin layer will be revisited shortly.

The lateral dimension of the LDH platelets may change the charging and aggregation behaviour even in the presence of a polyelectrolyte. To address this issue, similar experiments as shown in Figures 57 were carried out with the notably larger LDH-632 particles. No significant differences were discovered in the tendencies of the electrophoretic mobilities and stability ratios measured at various heparin doses. This fact indicates the same polyelectrolyte adsorption and aggregation mechanisms for the LDH-272 and LDH-632 particles regardless of the difference in size. However, the ionic strength dependence of the colloidal stability slightly changed in the case of LDH-632 and mobilities close to zero were measured at low heparin level at 100 mM NaCl concentration leading to unstable suspensions at all doses below the IEP. In addition, the stability of the platelets increased with decreasing the salt level at low polymer doses. These results clearly indicate that the predominating interparticle forces are of electrostatic origin in this regime and the aggregation mechanism can be described by the DLVO theory. However at high heparin coverage, the LDH-632 dispersion was stable irrespectively to the ionic strength due to the stabilizing effect of the adsorbed polyelectrolyte layer.
Given the lamellar structure of the LDH platelets, heparin may be intercalated into the interlayer space or adsorb on the outer surface of the particles. Indeed, immobilization of heparin between LDH layers was previously reported [248]. Nevertheless, no clear experimental evidences (e.g., increase in the interlayer spacing upon addition of heparin) were found for this phenomenon in the present systems.

### 6.2.2. Stability of polyelectrolyte-coated LDHs

In this part, the extent and mechanism of stabilization of the particles with a saturated layer of P(AA-BA) for LDH-180 and heparin for LDH-272 and LDH-632 is discussed. Highly stable suspensions were reported in these systems at high polyelectrolyte doses, therefore, doses corresponding to the onset of the ASP were applied in the individual systems. The influence of the polyelectrolyte layer on the colloidal stability was explored by comparing electrophoretic mobilities and stability ratios determined with the bare and covered LDHs at different salt levels (Figure 58).

![Figure 58](image.png)

Figure 58. Comparison of electrophoretic mobilities (a) and stability ratios (b) of bare (empty symbols) and polyelectrolyte-coated (filled symbols) LDHs of different size and composition as a function of the ionic strength. The data were taken from references [205,206].

Let us first discuss the differences between the bare particles. In general, the mobilities decreased with the ionic strength due to the screening effect of the counterions on the surface charge and remained very close to zero at higher electrolyte concentrations. The electrophoretic mobilities of the LDH-272 and LDH-632 particles were the same within the experimental error especially
at higher salt levels, while the mobilities of the LDH-180 were systematically lower in the entire concentration range (Figure 58a). This finding is in line with previous results discussed in subsection 4.2. Accordingly, NaCl salt was used to adjust the ionic strength for the LDH-272 and LDH-632 platelets, whereas KNO$_3$ for the LDH-180. The Hofmeister series for positively charged hydrophobic LDH platelets predicts that Cl$^-$ ions adsorb only weakly, while the more hydrophobic NO$_3^-$ shows higher affinity leading to stronger adsorption on the surface and thus, to lower electrophoretic mobilities at the same salt concentration [59].

Polyelectrolyte adsorption at the dose corresponding to the onset of the ASP resulted in negatively charged particles due to the overcharging process illustrated in Figures 55 and 57. The mobility data shown in Figure 58a indicates a deviation in the values at low ionic strengths. However, very similar electrophoretic mobilities were measured at higher salt levels. The tendency in the magnitude of the mobilities of bare and coated platelets was identical. Namely, they passed through a maximum at the beginning owing to the electrokinetic effect [198] and they decreased with increasing the ionic strength thereafter.

To quantify the extent of the surface charge, the mobilities were converted to electrokinetic potentials by equation (17) and the surface charge densities were estimated using the Debye-Hückel approximation (equation (21)) [62,142]. In case of the heparin-coated LDH-272 and LDH-632 particles, the best fit to the experimental values was found with (-30±5) mC/m$^2$ surface charge density. This finding indicates that the polyelectrolyte coverage resulted in at least two-time higher surface charge in magnitude compared to the bare particles (Table 2). Such a change in the charging behaviour is expected to have significant effect on the colloidal stability.

Figure 58b shows the stability ratios for the bare and polyelectrolyte-coated particles at different ionic strengths. They follow the typical trend suggested for charged colloids in the present of monovalent electrolytes (see Chapter 4). Accordingly, slow aggregation occurred at low salt level, while the particles were unstable at high ionic strengths.

For the bare particles, the CCC values were similar, however, significant deviation between the slopes in the slow aggregation regimes indicated different aggregation mechanism at low electrolyte concentrations. The tendency can be correlated with the size of the particles, since the slopes decreased with increasing the size of the LDH of the same composition (LDH-272 and LDH-632). Indeed, the attractive van der Waals forces increase with the size of the particles in general [4,62,173]. Given the fact that the Hamaker constant is the same for materials of the same composition, the attractive interaction energy is bigger for larger particles (see equation (23)). Therefore, the attractive force is stronger for LDH-632 than for LDH-272. The stability ratios decreased accordingly confirming that the acceleration of the aggregation process at the same ionic strength originates from the different size of the particles.
Regarding the heparin-coated particles, no deviation was observed in the slopes in the slow aggregation regime for LDH-272 and LDH-632. The lack of the size dependence on the aggregation rates at low ionic strength suggests the presence of additional non-DLVO forces. The CCCs were found to be in the same concentration range and they were located at much higher salt levels than the ones for the bare LDHs. More precisely, the heparin coverage resulted in a 20-time higher CCC of both LDH-272 and LDH-632 platelets. Such an enormous stabilization effect of the saturated heparin layer cannot be caused solely by the EDL forces, therefore, the presence of steric repulsion was also assumed.

For the P(AA-BA)-coated LDH-180 particles, a very high CCC was found too, which is more than a magnitude higher than the CCC of the bare particles (Figure 58b). The shape of the curve indicated the predominance of DLVO-type forces, however, the stability ratios in the slow aggregation regime were systematically lower than the ones determined for the heparin-coated LDH-272 and LDH-632 at the same ionic strengths. This increase in the aggregation rates could originate from the attractive interaction between the adsorbed P(AA-BA) chains, in which the butyl acrylate units tend to interact through attractive hydrophobic interactions. Such attractions result in an acceleration of the aggregation and to lower stability ratios. Another sensible explanation would be the presence of patch-charge attraction, but no evidences have been found for them around the IEP (Figure 55) were such an interaction is usually the most pronounced [81,167,249].

Although such a polymer coating was found to be an excellent tool to stabilize LDH particles of low surface charge density, this process did not result in considerable shifts in the CCCs for latex particles (Figure 50). Most likely, the high surface charge of the latexes is responsible for this behaviour, since the large EDL repulsion provides a relatively high stability already for the bare particles. Polyelectrolyte-coating did not increase the magnitude of the charge significantly, therefore, the strength of the EDL forces were similar as for the bare particles. In addition, the adsorption of the macromolecules was stronger on the latexes due to their higher charge and hence, the lateral extension of the polyelectrolyte layer towards the bulk was smaller than in the case of LDHs. Such a more compact layer led to the absence of the steric repulsion between the polymer chains and thus, to the lack of the non-DLVO stabilization for the coated latexes.

In summary, the polyelectrolyte coverage led to an enormous increase in the colloidal stability of the LDHs and highly stable dispersions were obtained. These particle systems are promising candidates in delivery processes, in which aggregation must be prevented in solutions containing electrolytes at high concentrations.
6.2.3. Structure of the aggregates

TEM analysis was performed on samples containing different LDHs and polyelectrolytes to visualize the orientation of the platelets in the aggregates. Note that the suspensions were dried during the TEM experiments, which could also cause some aggregation. The dispersions were imaged at the dose of the IEPs (Figure 59a), where fast aggregation of the materials occurred and also at the onset of the ASP (Figure 59b), where the surfaces were saturated with the polyelectrolyte layers leading to the formation of stable suspensions.

The images confirmed the tendency discussed earlier in the colloidal stability studies (Figures 55 and 57). Primary particles can be seen at the dose of the onset of the ASP due to the high colloidal stability of the samples under this experimental condition. However, the suspensions were unstable at the charge neutralization points leading to the formation of LDH clusters. Figure 59a also indicates that the orientation of the platelets in the clusters was the same in both systems. Accordingly, the LDHs adopted face-to-face orientation in the aggregates (Figure 59c), which spread laterally and form a film of a few LDH thickness. Similar results were obtained with the bare LDH-180 [205] upon salt-induced aggregation and also with LDH systems containing other aggregating agents [195,196]. Different structures, which correspond to face-to-edge [197] or edge-to-edge [198,199] aggregation reported for clay materials of similar morphology, were not observed in the images. This information is especially important once such dispersions are used to prepare hybrid materials, where the structure of aggregates influences the structural properties of the composites.

![Figure 59. TEM images of LDH-180 and LDH-272 particles in the presence of P(AA-BA) and heparin, respectively. The applied polyelectrolyte dose was at the IEP (a) and at the onset of ASP (b). The first condition refers to unstable, while the latter one to stable suspensions. The general scheme of LDH aggregation is also shown (c). The images were taken from references [205,206].](image)
Since the same structure of the aggregates was found also for the bare LDH platelets, therefore, one can assume the presence of the same type of attractive forces in both bare and polyelectrolyte modified LDH systems. For bare particles, the face-to-face position was also confirmed with AFM images recorded in aqueous dispersions [205] indicating that the drying process during the TEM measurements did not affect significantly the platelet orientation in the aggregates. Therefore, the shape of the clusters obtained by particle aggregation is similar regardless of the type of aggregating agents and composition of the LDH particles.

6.3. Stability of titanate nanowires

6.3.1. Polyelectrolyte-induced aggregation

6.3.1.1. TiONW – PSS

As detailed in subsection 2.3, the hydrothermally synthesized TiONWs possess pH-dependent charge being positively charged at low and negatively charged at higher pH with a PZC of 4.1 (see Figure 12 on page 39). Charging and aggregation have been studied first at pH 3 in the presence of oppositely charged PSS (chemical structure is shown in Figure 6) [167]. PSS is a strong polyelectrolyte carrying one negative charge on each monomer under the experimental conditions applied. It was shown previously in part 6.1.3 that adsorption of PSS on oppositely charged latex particles gives rise to the formation of a saturated polyelectrolyte layer of a few nanometers thickness [228]. Nevertheless, detailed investigations of charging and aggregation processes in titanate dispersions in the presence of PSS are necessary to assess the colloidal stability. Therefore, the effect of polymer adsorption on the dispersion stability of the TiONW samples has been studied systematically using electrophoresis and light scattering as experimental techniques (Figure 60).

Figure 60. Electrophoretic mobility (squares) and stability ratio (circles) data for TiONW particles versus the PSS dose at 1 mM ionic strength and pH 3. The data were taken from reference [167].
In the electrophoretic study, the particle concentration was kept constant in the experiments and the dose of PSS was increased. The electrophoretic mobilities at low PSS concentrations were very similar to the one determined for the bare TiONW under the same experimental conditions, but without any added polymer. Increasing the dose, PSS adsorption took place on the oppositely charged nanowire surface leading to charge neutralization at the IEP and subsequent overcharging. The latter process continued until the onset of the ASP and the mobility values were constant thereafter, regardless of the amount of further added PSS. Comparing the electrophoretic mobilities of the bare and the PSS-coated (at a dose of the onset of the ASP) nanowires, one can conclude that the charge inversion resulted in higher magnitude of the surface charge. This tendency is typical for polyelectrolyte-particle systems as shown previously in subsections 6.1 and 6.2.

Besides, electrophoretic mobilities were measured at different TiONW concentrations, but at the same PSS loading (mg polyelectrolyte per gram of nanowire) to probe the strength of the adsorption. The values were the same within the experimental error. It was reported earlier that such curves shift upon significant partitioning of the polyelectrolytes between the surface and the bulk [211]. In other words, no influence of the particle concentration on the electrophoretic mobilities measured at the same dose clearly indicates a strong polyelectrolyte adsorption on the TiONW surface. Therefore, all of the added PSS molecules adsorbed on the nanowires at doses below the onset of the ASP. Such an irreversible interaction was also reported with other strong polyelectrolytes adsorbing on various surfaces [24,250].

The colloid stability graph, determined for the system containing the nanowires and the polyelectrolyte under the same experimental conditions as used in the electrophoretic measurements, is shown in Figure 60. The stability ratios follow the typical tendency observed upon interaction of polyelectrolytes and oppositely charged particles. Accordingly, the dispersions were stable at low PSS concentrations, were the TiONW charge is only partially neutralized and the nanowires possessed significant charge. The stability ratio decreased with increasing the PSS loading and rapid particle aggregation and unstable systems were observed around the charge neutralization point. Higher load of the PSS resulted in stable suspensions. Unlike other inorganic particle-polyelectrolyte systems [142,205,249,251], the stability ratios changed steeply before and after the fast aggregation regime. This finding indicates a remarkable stability of the bare particles. The unstable region around the IEP was broad compared to previously published results obtained at low ionic strength, where the stability curves widened only at higher background salt concentrations [84,90,208].

Besides, the stability ratios were constant within the experimental error at very low and high PSS doses. These plateaus refer to the colloidal stability of the bare and PSS-coated TiONWs and indicate similar stabilization mechanism in both cases. Such a similarity in the aggregation of the
bare and fully coated TiONWs predicts DLVO-type interparticle forces under these experimental conditions. In addition, the U-shaped curve of the stability ratios discussed above also indicates that the forces are of DLVO origin. Similar conclusions were made with latex particles and polyelectrolytes of high line charge density in subsection 6.1.

Another interesting finding in this system was that the stability ratios were systematically lower than one in the fast aggregation regime. Remember that the value of the stability ratio is one if the particle aggregation is entirely controlled by the diffusion. Such condition can be achieved in excess of an inert electrolyte, where the interactions between the nanowires are governed only by van der Waals forces due to the lack of the EDL repulsion [25,62,147]. Therefore, stability ratios below unity clearly indicate the presence of an additional attraction, which is certainly not a DLVO-type force. Such acceleration in the aggregation process can be interpreted by assuming the formation of surface charge heterogeneities upon PSS adsorption and thus, the presence of patch-charge attractions. These types of forces acted between particles and other surfaces, wherever polyelectrolytes of high line charge densities adsorbed and the surface coverage was incomplete [83,84,187].

6.3.1.2. TiONW – PDADMAC

Colloidal stability of TiONWs has also been studied in the presence of PDADMAC polyelectrolyte under alkaline conditions, where the nanowires are negatively and the polymer is positively charged. The effect of PDADMAC adsorption on the charging and aggregation properties was investigated [142,252]. PDADMAC is a strong polyelectrolyte, each monomer holds a pH-independent positive charge. Although this polyelectrolyte has been used to tune stability of various colloidal particles [89,90,247], its interaction with elongated titanate materials has not been assessed yet.

The charging behaviour (Figure 61a) resembled to a general particle-polyelectrolyte system, similar to the ones reported in the previous part of the thesis and published in the literature [24,175,205,206,208]. At low polyelectrolyte loading, the electrophoretic mobilities were similar to the one measured for the bare TiONW at the same ionic strength at pH 9. Strong polyelectrolyte adsorption occurred and thus, the surface charge was progressively reduced with increasing the PDADMAC dose due to charge neutralization. The mobilities passed through the IEP and increased until the onset of the ASP. Accordingly, the characteristic overcharging phenomena took place and the mobilities of the completely coated TiONWs considerably depended on the level of the background electrolyte owing to the screening effect of the salt on the surface charge. The ionic strength dependence of the mobilities at the ASP will be further discussed later.
The stability ratios measured at different PDADMAC doses at three ionic strengths are shown in Figure 61b. Remarkable differences can be discovered between the three sets of measurements especially at low doses, where the TiONW surface is only partially covered with the polyelectrolytes and hence, the charge is similar to the bare nanowires. At 0.1 mM ionic strength, the suspensions were stable at low PDADMAC loading and the stability ratio values decreased with increasing the dose. The fast aggregation regime was reached around the IEP. The charge reversal process stabilized the suspensions and the aggregation slowed down at high PDADMAC concentrations.

The tendency in the stability ratio versus PDADMAC dose curves changed extremely at higher ionic strengths. The plot measured at 1 mM salt level was wider, however, the same trend was observed as at 0.1 mM. Moreover at 10 mM ionic strength, the nanowires rapidly aggregated already at low doses due to the fact that this KCl concentration is above the CCC of the bare TiONW. The stability ratios increased with the PDADMAC loading in the charge reversal regime and they reached a plateau at PDADMAC concentrations higher than the onset of the ASP. Similar plateau were found in the TiONW-PSS system [167] at low pH and also with latex particles in the presence of oppositely charged polymers [25]. It was assumed that the ionic strength dependence of such plateaus indicates that the major interparticle forces are of electrostatic (DLVO) origin. However, the difference in the slopes of the curves in the slow aggregation regime measured at 0.1 mM and 1 mM salt levels can be assigned to the presence of additional patch-charge attractions.
To further explore the adsorption mechanism, IEP and onset of ASP values were determined at various ionic strengths in electrophoretic experiments. The trend in the measured mobilities indicated an increase of the onset of ASP with the salt level. However, the dose needed to neutralize the charge of the TiONW decreased with the ionic strength. These findings are clear signals for that the electrostatic interactions between the polyelectrolyte chains and the surface play a major role in the adsorption mechanism. In addition, the magnitude of the IEP and onset of ASP values agreed well with the ones measured in the earlier discussed particle-polyelectrolyte suspensions. Similar increase of the adsorbed amount with the salt level was also found for latex particle systems [24,228]. To interpret the ionic strength dependence of the adsorption behaviour, the electrostatic interactions between the polyelectrolyte chains on the surface has to be considered. While the Coulomb attraction between the PDADMAC and the TiONW induced adsorption, the polymers repelled each other on the surface. The extent of this repulsion decreases with increasing the concentration of the background electrolyte due to charge screening. Therefore, the nanowires could adsorb higher amount of PDADMAC at elevated ionic strengths leading to higher onset of ASP and lower IEP values. In addition, counterion condensation [82] also gives rise to decreasing charge neutralization points with increasing salt concentration.

6.3.1.3. TiONW – PAMAM dendrimers

The charging and aggregation of TiONWs have been tuned with PAMAM dendrimers in alkaline solutions, where the nanowires were of negative charge, while the macromolecules were positively charged [249]. The ionization of the dendrimers is moderate at pH 9 and low ionic strength, since only about 30% of the amino groups are protonated under these experimental conditions [221].

Concerning their potential applications in biomedical processes, it was found that the toxicity of PAMAMs depends on their size and concentration [220,253]. Biocompatibility of PAMAM dendrimers [254] and also their composite materials [255,256] has been already reported in the literature. For this reason, they are promising candidates to tune the colloidal stability of nanoparticles to be used in delivery processes in living systems. Therefore, the main goal of this investigation was to find the conditions, where PAMAM dendrimers are able to stabilize the TiONW dispersions even at higher electrolyte concentrations, e.g., higher than 160 mM, which is the ionic strength in the blood plasma [257].

The effect of the dendrimer adsorption on the charging properties of the TiONWs was explored with PAMAMs of different generations (G2, G6 and G10). The measured electrophoretic mobilities are shown in Figure 62a. In spite of the low degree of ionization, the dendrimers
adsorbed on the oppositely charged particles and the trend in the mobilities indicated typical polyelectrolyte-type behaviour for the PAMAM [24]. Accordingly, the mobility values increased with increasing the dose leading to charge neutralization and subsequent charge reversal at appropriate dendrimer loadings. Similar to other particle-polyelectrolyte systems discussed earlier in this thesis, the onsets of ASPs indicated the maximum amount of PAMAM adsorbed on the TiONW.

![Figure 62. Electrophoretic mobility (a) and stability ratio (b) values as a function of the dendrimer dose measured in TiONW dispersions at 1 mM ionic strength adjusted by KCl at pH 9 for three generations (G2, G6 and G10) of PAMAM. Reprinted with permission from reference [249]. Copyright (2015) American Chemical Society.](image)

It was somewhat surprising that the location of the IEP and ASP was independent of the size of the dendrimers, since a clear influence of the generation on the charge neutralization point and saturation maximum was reported earlier in the presence of oppositely charged latex particles [81,175]. However, those studies were performed with highly charged PAMAMs at low pH. Under that condition, significant amount of counterions are bound to the polyelectrolytes leading to much lower effective charge of the dendrimers than the bare structural one.

Similar onsets of the ASPs (around 500 mg/g) were determined for all generations. However, this is significantly larger than the ones (50-100 mg/g) determined in other TiONWs systems [142,167], where polyelectrolytes of high line charge densities were used. On the other hand, similar value was measured in the LDH-180-P(AA-BA) system. Since the PAMAMs are only partially protonated in the present suspensions, the electrostatic repulsion between the adsorbed dendrimers is notably less giving rise to higher adsorbed amount on the surface. Moreover, the situation is similar to the case of LDH-180-P(AA-BA) samples, where the presence of the neutral butyl acrylate monomers reduced the charge density of the copolymer and thus, the
chains could adsorb in a more compact way giving rise to higher onset of ASP. Another possible explanation for this phenomenon may be the formation of dendrimer multilayers on the TiONW surface driven by hydrophobic interactions between the PAMAMs and entropy gain [215,258]. However, no unambiguous experimental evidences were found for these processes.

The stability ratios of the nanowires determined in time-resolved DLS measurements in the presence of G2, G6 and G10 PAMAMs are shown in Figure 62b. The pH, particle concentration, range of dendrimer dose and ionic strength were the same as in the electrophoretic study. The colloidal stability plots were very similar for G2 and G6, while some deviations were observed for G10 especially at high PAMAM concentrations. In general, the suspensions were stable at low and high polyelectrolyte doses, below and above the IEP, respectively. Rapid particle aggregation and unstable dispersions were observed around the charge neutralization point. Similar tendency of the stability ratios was also observed in other particle-polyelectrolyte systems discussed in the previous subsections. Such behaviour qualitatively agrees well with the classical DLVO theory.

Despite the mainly DLVO-type aggregation mechanism, the fact that the stability ratios are systematically lower than unity in the fast aggregation regime indicated the presence of additional attractive forces. Since the reference fast aggregation rate coefficient was determined in suspensions, where the bare particles undergo diffusion controlled aggregation due to the presence of the attractive van der Waals forces, the additional attraction must be induced by the dendrimers on the nanowire surface. As discussed earlier, polyelectrolyte adsorption often occurs in a heterogeneous fashion giving rise to the formation of surface charge heterogeneities and to attractive patch-charge interactions. It was assumed that they also play a role in the present system leading to an acceleration of the aggregation process around the IEP, where the PAMAMs cover the TiONW surfaces only partly. Similar patch-charge forces have already been discussed in the thesis in systems containing particles and multivalent ions, polyelectrolytes or dendrimers [24,81,83,167,188].

Moreover, the rapid particle aggregation regime was shifted towards higher dendrimer concentrations for G10. This result is similar to the one reported with latex-PAMAM systems in acidic solutions [81]. Such phenomenon was interpreted with the effect of the counterion condensation [82]. Accordingly, the amount of the negatively charged ions incorporated into the structure of the dendrimers is higher for PAMAMs of larger size (G10, which is the biggest available PAMAM dendrimer) than for G2 or G6. Therefore, a considerable part of the PAMAM’s charge is neutralized leading to lower effective charge. As a consequence, higher amount of dendrimer is needed to neutralize the TiONW surface. The electrophoretic mobility measurements were most likely not sensitive enough to observe this effect.
The nature of the interactions responsible for the adsorption and aggregation processes was further explored in electrophoretic and DLS experiments carried out at different ionic strengths (at 1, 10 and 100 mM KCl concentration) in the TiONW-G6 system. It was found that the electrophoretic mobilities are sensitive to the salt concentration especially at low polyelectrolyte coverage. Accordingly, the magnitude of the mobilities decreased at higher ionic strengths at low dendrimer doses due to the salt screening effect on the surface charge. At the ASP, however, the charge of the PAMAM-coated particles was very similar regardless of the salt concentration. This result indicates that significant ion condensation takes place and thus, the screening effect of the salt is less pronounced than for the partially covered TiONWs, where such condensation is negligible due to the lower amount of dendrimers on the surface.

Concerning the colloidal stability of the TiONWs in the presence of G6 dendrimers at different ionic strengths [249], rapid particle aggregation was observed below the IEP once the salt level was higher than the CCC of the bare nanowires, which was found to be 8 mM at pH 9 [142]. The small amount of dendrimers adsorbed on the TiONWs at these low doses did not change the surface charge properties significantly, therefore, the aggregation behaviour was similar to the one observed for the bare particles. In addition, the stability ratios decreased with increasing the PAMAM loading until they reached the fast aggregation regime, where stability ratios lower than one were observed owing to the presence of the attractive patch-charge forces.

Furthermore, the suspensions were stabilized by the charge inversion process at high PAMAM concentrations. The slopes in these slow aggregation regimes decreased with increasing the salt level. Since patch-charge attractions are usually absent at such high surface coverage, the ionic strength dependence of the stability ratios is due to the screening effect of the background electrolyte. However, this effect was not detected in the electrophoretic measurements, where similar mobilities were measured at higher PAMAM doses. The fact that the stability ratio values were the same within the experimental error in the fast aggregation regime irrespectively of the KCl concentration indicated that the structure of the adsorbed PAMAM molecules did not change considerably with the ionic strength. This result is in contrast to previous findings obtained in acidic latex-PAMAM suspensions [81] probably due to the significantly higher charge of the dendrimers in the latex systems.

6.3.2. Effect of polyelectrolyte coating on TiONW stability

To further explore the stabilization mechanism and the origin of interparticle forces between polyelectrolyte-coated TiONW particles, electrophoretic and DLS measurements were carried out over a wide range of ionic strength at different pH [142,167,249].
The magnitude of the mobilities of the bare particles showed similar tendency by changing the salt level regardless of the pH (Figure 63a). Accordingly, they decreased with increasing the ionic strength due to charge screening by the electrolyte. However, the change is slighter with the positively charged TiONW under acidic conditions. The same salt (KCl) was used to adjust the ionic strength in all experiments, therefore, this difference can be attributed to the different affinity of the anions and cations to the surface. The K$^+$ ions adsorb more on the negatively charged particles and hence, the mobilities increased till zero at high concentrations. On the other hand, the nanowires possess significant positive charge in this concentration regime at pH 3 due to the negligible adsorption of Cl$^-$ ions on the TiONW.

![Figure 63. Charging and stability of bare (left column) and polyelectrolyte-coated (PAMAM dendrimers, PSS and PDADMAC, right column) TiONWs. Electrophoretic mobilities (a) and stability ratios (b) as a function of the ionic strength adjusted by KCl. The experimental conditions applied in the measurements are detailed in Table 3. The lines are just to guide the eyes. The data were taken from references [142,167,249].](image-url)
Coating the particles with the polyelectrolytes (PSS, PDADMAC, G6 and G10 PAMAM dendrimers) resulted in significantly higher surface charge densities than for the bare ones (Table 3). Note that the PSS-coated particles are negatively charged at pH 3 and the other ones (covered with PDADMAC, G6 and G10 PAMAM dendrimers) are positively charged at pH 9 due to the pH-dependent charge of the TiONW. The doses used for the coating processes corresponded to the onset of the ASP determined earlier (Figures 60, 61 and 62) and they were lower for strong polyelectrolytes (PSS and PDADMAC) indicating that the electrostatic repulsion between the adsorbed polyelectrolyte chains played a major role in the adsorption mechanism. The PAMAM dendrimers were ionized only in 30% at pH 9, therefore, such repulsion was not pronounced enough allowing the adsorption of higher amounts of PAMAM on the TiONWs.

Table 3. Characteristic dispersion properties of bare and polyelectrolyte-coated TiONWs.

<table>
<thead>
<tr>
<th>particle</th>
<th>polyelectrolyte</th>
<th>pH</th>
<th>dose (mg/g)</th>
<th>CCC (mM)</th>
<th>SCD (mC/m²)</th>
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<tr>
<td>TiONW</td>
<td>–</td>
<td>3.0</td>
<td>–</td>
<td>8</td>
<td>+7</td>
</tr>
<tr>
<td>TiONW</td>
<td>–</td>
<td>9.0</td>
<td>–</td>
<td>8</td>
<td>–8</td>
</tr>
<tr>
<td>TiONW</td>
<td>PSS</td>
<td>3.0</td>
<td>80</td>
<td>600</td>
<td>–20</td>
</tr>
<tr>
<td>TiONW</td>
<td>PDADMAC</td>
<td>9.0</td>
<td>300</td>
<td>32</td>
<td>+15</td>
</tr>
<tr>
<td>TiONW</td>
<td>G6 PAMAM</td>
<td>9.0</td>
<td>1000</td>
<td>1500</td>
<td>+25</td>
</tr>
<tr>
<td>TiONW</td>
<td>G10 PAMAM</td>
<td>9.0</td>
<td>1000</td>
<td>&gt;2000</td>
<td>+29</td>
</tr>
</tbody>
</table>

a| Dose (mg polyelectrolyte per gram TiONW) at the onset of the ASP used to coat the nanowires.
b| Obtained from the stability plots in Figure 63b. c| SCD was determined from the ionic strength dependence of the electrophoretic mobilities (see subsection 3.2 for more details).

Moreover, the electrophoretic mobilities passed through a minimum (PSS) or maximum (PDADMAC, G6 and G10) located around 10 mM ionic strength (Figure 63a), as predicted by the standard electrokinetic model developed for charged colloidal particles [165,198]. The magnitude of the mobilities decreased with increasing the salt level, but the coated TiONWs remained negative (PSS) and positive (PDADMAC, G6 and G10) even at the highest ionic strengths. Such a behaviour resembles to the case reported earlier for polyelectrolyte-coated latex and LDH particles [25,206], therefore, this phenomenon can be considered as generic for polyelectrolyte-coated colloidal particles.

Very similar stability ratios have been measured for the bare TiONWs both in the positively and the negatively charged stages (Figure 63b). The CCCs are identical within the experimental error (Table 3) and a slight difference can be observed only in the slopes of the slow aggregation regime at low ionic strengths. The shape of the curves suggests that the interparticle forces are of electrostatic origin, which is predicted by the DLVO theory, as discussed earlier. The low CCCs
indicate limited stability of the particles. In general, polyelectrolyte coating improved the resistance against salt-induced aggregation. The CCC values were shifted markedly towards higher concentration, which implies that significantly higher electrolyte concentration was necessary to destabilize the coated nanowires than the bare ones. The stabilization effect was the most enormous in the case of the G10 coating, where slow aggregation was observed even at high salt levels and the CCC could not be measured due to the solubility limit of KCl used to adjust the ionic strength.

The shape of the stability ratio versus ionic strength plots were similar to the ones obtained for the bare particles. Slow aggregation was obtained at low salt levels, while increasing the electrolyte concentration led to an increase of the aggregation rates and to the subsequent destabilization of the samples at the CCC. Again, such aggregation behaviour and tendency in the stability ratios is typical for charged colloids suspended in monovalent salt solutions and can be well-explained with the classical DLVO theory [19-21].

However, the slopes in the slow aggregation regimes were smaller for the PSS, PDADMAC and G6-coated particles, i.e., a steeper transition between the fast and slow aggregation regimes was observed in the case of bare TiONWs regardless of the sign of their charge. The DLVO theory also predicts larger slopes [62,190,196], therefore, the shallower transition for the coated TiONWs originates from additional non-DLVO attractive forces. It was assumed that the extra attraction is present because of the patch-charge interactions, as discussed before. These types of interactions are not included in the DLVO theory, which considers homogeneous surface charge distribution. However, polyelectrolyte adsorption often gives rise to heterogeneous charge distribution on the surface, as reported several times for charged particles with adsorbed polyelectrolyte layers [24,81,83].

The CCCs increase with the surface charge densities (Table 3) suggesting also mainly electrostatic stabilization mechanism, nevertheless, such a high CCC as determined for the G10 system cannot be predicted by the DLVO theory [59,184]. On the other hand, the steep transition between the slow and fast aggregation regimes in these suspensions indicates DLVO-type stabilization. On the basis of these results, the origin of the interparticle forces cannot be defined unambiguously for the polyelectrolyte-coated TiONWs and further investigation (e.g., direct force measurements with AFM) is needed to clarify this issue. In summary, it was shown that polyelectrolyte coating significantly improved the stability of the nanowires and highly stable dispersions can be obtained even at elevated ionic strengths, where the bare particles rapidly aggregate. This stabilization effect can be important, wherever (e.g., catalysis [101], water treatment [259] or drug delivery [260]) stable suspensions of primary particles are required.
6.3.3. Orientation of the TiONWs in aggregates

To obtain information on the structure of the aggregated clusters and on the alignment of the nanowires upon aggregation, AFM images were recorded in bare TiONW suspensions at an ionic strength higher than the CCC at pH 3. The nanowires were deposited on freshly cleaved mica, which possessed opposite charge than the particles. The samples contained TiONW of low concentration, therefore, images of monomers, dimers and trimers together could be taken in the same measurement (Figure 64a).

The results pointed out that the TiONWs preferred a lateral side-by-side orientation upon aggregation resulting in the formation of spaghetti-like bundles. The height profile of the particles is shown in Figure 64b and an increase from the right to the left side of the image indicated the presence of aggregated TiONWs of different generations. Similar information was obtained for the TiONW-PSS system [167], where clusters with house-of-card structure or end-to-end connections of the wires were not observed in the AFM images most probably due to the early stages of the aggregation process.

For the TiONW-PAMAM systems, the structure of the aggregates was investigated at doses close to the charge neutralization point by recording TEM images. The sample preparation process was performed in the same way as for the mobility and scattering study (Figure 62). In these experiments, aggregating TiONW samples were imaged in the presence of G2 (Figure 65a), G6 (Figure 65b) and G10 (Figure 65c) PAMAM dendrimers. In contrast to the conditions in the AFM measurements, the samples were dried prior to imaging by TEM, which process could also induce some aggregation of the nanowires.

One can easily conclude that the nanowires adopted a face-to-face orientation in the aggregates. Very similar structure was observed in the images with PAMAMs of different generation. Accordingly, spaghetti-like bundles formed regardless of the molecular weight of the dendrimers. As discussed above, the same orientation of the TiONWs was observed in AFM images recorded in acidic solutions (where the nanowires are positively charged) during salt or PSS-induced aggregation.

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**Figure 64.** TiONWs imaged by AFM at higher ionic strength than the CCC at pH 3 (a). Height profile of TiONWs measured along the red line in the image (b). The figure was reprinted from reference [167] with permission from John Wiley & Sons, Inc.
The fact that the TiONWs aggregate in the same way in the absence and also in the presence of polyelectrolytes suggests that the major interparticle forces are of the same origin in both systems. In other words, polyelectrolyte-induced aggregation led to the same structure of the aggregates as the salt-induced one. One can surely assume diffusion controlled aggregation and DLVO-type forces at ionic strength higher than the CCC in the later samples, therefore, the same structure upon aggregation shed light on the presence of similar driving forces in the aggregation process of the polyelectrolyte modified nanowires. However, other type of interactions (e.g., patch-charge attraction or steric repulsion) can also be present, but these forces are weaker than the EDL and the van der Waals forces and depend on the ionic strength and surface coverage of the particles. Moreover, such non-DLVO interactions most likely also press the TiONWs into wall-to-wall orientation in the aggregated clusters. This information can be especially useful in preparation of composites, where the structure of the aggregates defines the structural properties of the desired materials.
Chapter 7

CONCLUSIONS

In the present thesis, stability of charged colloidal particles of different shapes and compositions is discussed. Particles include spherical polystyrene latexes functionalized with sulfate, amidine or carboxylate groups on their surface, platelet-like LDHs and elongated TiONWs. The latex particles were commercial products, while the LDHs and TiONWs have been synthesized and they possess a layered structure. The charging properties, aggregation behaviour, interparticle forces and structure of the aggregates in the presence of mono and multivalent ions as well as polyelectrolytes have been studied by experimental techniques including electrophoresis, light scattering, atomic force and electron microscopy. Conclusions made on the basis of the experimental results can be summarized as follows.

Concerning particle aggregation in monovalent salt solutions, similar tendencies were observed in the stability ratios by changing the electrolyte concentrations irrespectively of the composition of the particles and the salt. The major interparticle forces could be interpreted by means of the DLVO theory in general. However, short-ranged attractive interactions of hydrophobic nature also took place between the functionalized polystyrene latexes. Although the origin of the forces was very similar in all of the systems regardless of the types of particles and electrolytes, ion specific effects were found to be important in the adsorption processes of the monovalent counterions on the oppositely charged surfaces. It was showed that poorly hydrated ions adsorbed on the particles in considerable amount leading to a significant decrease in the magnitude of the surface charge density, while the adsorption of well-hydrated counterions was negligible and the particle surfaces remained highly charged.

Based on the experimental results, it was pointed out that such a specific ion adsorption resulted in a change of the CCC values with variation of the composition of the electrolytes. For latex particles, the monovalent counterions could be ordered in the Hofmeister series of anions and cations according to their effect on the location of the CCC. It was found that the indirect Hofmeister series can be applied for positively charged amidine functionalized polystyrene beads, while the direct series for the negatively charged sulfate latexes. In the latter case, the traditional sequence of the cations was extended with IL constituents, where the strength of the interaction with the surfaces depended also on the hydrophobicity of the counterions. For positively charged LDH particles, the CCCs determined in the presence of different monovalent anions follow the classical indirect Hofmeister series with the exception of the bicarbonate ion due to its specific affinity to the LDH surface, which places this ion on the opposite side of the sequence. These
findings clarified and extended the traditional Hofmeister series of cations and anions in terms of their effect on particles aggregation and revealed the origin of the interparticle forces, which determined the colloidal stability of the suspensions.

In addition, multivalent counterions were more effective destabilizing agents for charged colloids than the monovalent ones leading to a considerable shift in the CCCs towards lower concentrations by increasing the valence of the counterions. This tendency is due to the stronger affinity of ions of higher valences to the oppositely charged surfaces, as demonstrated with functionalized polystyrene latex and LDH particles. The adsorption is mainly driven by Coulomb attraction, however, hydrophobic interactions give rise to ion specificity too. The adsorption process decreases the magnitude of the surface charge density or even reverses the sign of the particle charge. As a consequence, smaller amount of electrolyte is needed to screen the surface charges and to destabilize the samples in the presence of ions of higher valences.

Although ion adsorption decreases the surface charge density, the main aggregation mechanism could be still described by the DLVO theory. Nevertheless, additional attractive forces originating from hydrophobic interactions and surface charge heterogeneities were also present in certain extent. It can be also concluded that the often reported good agreement between the experimentally determined CCCs and the sixth power law recommended by the Schulze-Hardy rule is the result of the joint effect of the counterion adsorption and the acting interparticle forces. Moreover, it was found that this rule breaks down at valences higher than about ten and the so-called polyelectrolyte rule describes the position of the CCCs thereafter.

Besides, polyelectrolyte adsorption on oppositely charged particles led to charge neutralization and overcharging depending on the dose of the charged polymeric materials. These processes significantly influence the colloidal stability of the dispersions. For highly charged latexes, unstable samples were found around the IEP and stable ones away from it. In the case of LDH and TiONW particles, however, low polyelectrolyte coverage resulted in moderate resistance against salt-induced aggregation. The polyelectrolyte-coated inorganic particles, which possessed limited stability in the bare form, were highly stable in suspensions even at extremely high salt levels, where the DLVO theory predicts unstable systems. Therefore, a more complex force profile including DLVO-type, hydrophobic, patch-charge and steric interactions was assumed in these dispersions.

For the latex particles, structural characterization of the saturated polyelectrolyte layer revealed that the adsorbed amount increases with the ionic strength and slightly decreases with the molecular mass of the polymers. The hydrodynamic thickness of the polyelectrolyte layer increases with increasing the molecular mass and the ionic strength. These findings confirmed the importance of electrostatic interactions between the polymer chains adsorbed on the surface.
In addition, face-to-face orientation was found upon aggregation of both LDHs and TiONWs regardless of the type of the aggregation agent, i.e., salt or polyelectrolyte-induced aggregation led to the same structure of the aggregates, which indicates similar type of forces acting between the particles.

In conclusion, it was shown that colloidal stability of suspensions containing charged particles can be tuned by appropriately chosen charged species of different valences and the origin of the major interparticle forces were identified reasonably well. Nevertheless, the quantitative prediction of the interaction forces and colloidal stability is still not possible straight from the composition and the physico-chemical properties of the aggregating agents and the particles. For instance, the IEP for polyelectrolyte layers of partial coverage can be estimated by assuming stoichiometric charge neutralization, but polyelectrolytes usually adsorb in a super-stoichiometric way due to counterion condensation. The quantification of the extent of this condensation process has not been performed yet.

Besides, it was clarified that the DLVO theory can be used to describe the interactions between colloidal particles of a few hundreds of nanometers in lateral dimensions relatively well. Additional forces are also present under certain experimental conditions, but in a smaller extent. The growing interest in formulation and related colloidal stability of nanoparticles (e.g., iron oxide, silica and gold) of much smaller sizes, where DLVO-type forces might not be the major ones, calls for similar types of charging and aggregation studies in those systems. The lack of experimental information on the aggregation of such nanoparticles demands for further investigations using suitable experimental techniques.

On the other hand, given the landmark development of the unilamellar material graphene, two-dimensional compounds (e.g., delaminated dichalcogenides, clays or metal oxides) attract significant contemporary interest in the scientific communities. Their application in dispersions requires detailed understanding of their colloidal stability under certain experimental conditions. Due to the lack of comprehensive studies, the aggregation of nanomaterials of various shapes has to be investigated and understood in detail.

In order to better understand these complicated systems, these issues will be hopefully addressed in the future by combining advanced experimental and theoretical methods. The results of such investigation should definitely lead to the development of a more detailed and comprehensive picture about the predominating interactions involved in particle aggregation processes. Using the knowledge to be generated by such studies, one will be able to predict the conditions to develop particle dispersions of optimal properties for various applications in environmental, biomedical and other chemical manufacturing processes.
### LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
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<tr>
<td>AL</td>
<td>amidine functionalized polystyrene latex</td>
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<td>ASP</td>
<td>adsorption saturation plateau</td>
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<td>BSA</td>
<td>bovine serum albumin</td>
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<td>CCC</td>
<td>critical coagulation concentration</td>
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<td>CL</td>
<td>carboxyl functionalized polystyrene latex</td>
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<td>CMC</td>
<td>critical micelle concentration</td>
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<tr>
<td>CML</td>
<td>carboxylate modified latex</td>
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<tr>
<td>CR</td>
<td>charging ratio</td>
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<tr>
<td>DLS</td>
<td>dynamic light scattering</td>
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<tr>
<td>DLVO</td>
<td>Derjaguin, Landau, Verwey and Overbeek</td>
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<tr>
<td>EDL</td>
<td>electrical double layer</td>
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<tr>
<td>EPE1100</td>
<td>polyethylene oxide-polypropylene oxide-polyethylene oxide</td>
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<tr>
<td>EPM</td>
<td>electrophoretic mobility</td>
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<tr>
<td>IEP</td>
<td>isoelectric point</td>
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<tr>
<td>IL</td>
<td>ionic liquid</td>
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<tr>
<td>LDH</td>
<td>layered double hydroxide</td>
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<td>NMVA</td>
<td>N-methyl-N-vinyl acetamide</td>
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<td>PAA</td>
<td>poly(acrylic acid)</td>
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<td>PBA</td>
<td>poly(butyl acrylate)</td>
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<td>PAM</td>
<td>poly(acryl amide)</td>
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<td>PAMAM</td>
<td>poly(amido amine)</td>
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<td>PDADMAC</td>
<td>poly(diallydimethyl ammonium chloride)</td>
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<td>PDI</td>
<td>polydispersity index</td>
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<tr>
<td>PDMAEMA</td>
<td>poly(dimethylaminoethyl methacrylate)</td>
</tr>
<tr>
<td>PEI</td>
<td>poly(ethylene imine)</td>
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<td>PSS</td>
<td>poly(styrene sulfonate)</td>
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<tr>
<td>PZC</td>
<td>point of zero charge</td>
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<td>RAFT</td>
<td>reversible addition-fragmentation chain-transfer</td>
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<tr>
<td>SCD</td>
<td>surface charge density</td>
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<td>SL</td>
<td>sulfate functionalized polystyrene latex</td>
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<tr>
<td>SLS</td>
<td>static light scattering</td>
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<tr>
<td>SSDLS</td>
<td>simultaneous static and dynamic light scattering</td>
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<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
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<tr>
<td>TiONW</td>
<td>titanate nanowire</td>
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REFERENCES