



**HAL**  
open science

## Heteroaggregation between particles modified by polyelectrolyte multilayers

Manuella Cerbelaud, Yasmine Bennani, Claire Peyratout

► **To cite this version:**

Manuella Cerbelaud, Yasmine Bennani, Claire Peyratout. Heteroaggregation between particles modified by polyelectrolyte multilayers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2022, 650, pp.129572. 10.1016/j.colsurfa.2022.129572 . hal-03820917

**HAL Id: hal-03820917**

**<https://hal.science/hal-03820917>**

Submitted on 19 Oct 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Heteroaggregation between particles modified by polyelectrolyte multilayers

Manuella Cerbelaud\*, Yasmine Bennani, Claire Peyratout  
*Univ. Limoges, CNRS, IRCER, UMR 7315, F-87000 Limoges, France*

---

## Abstract

The heteroaggregation of particles is interesting in many fields and particularly in the field of ceramic shaping. In general, heteroaggregation is obtained by mixing powders with opposite surface charges, which may require in some cases surface modifications of the particles.

Here we propose to study the behavior of suspensions composed of a mixture of particles with positive and negative charges, created by the adsorption of polyelectrolyte multilayers on their surface. Particular attention is paid to the effect of the number of layers of adsorbed polyelectrolytes and of the ionic strength.

This study shows that these surface modifications allow, whatever the number of layers, to have heteroaggregation in the absence of salt. Moreover, depending on the number of adsorbed layers, the addition of salt has a different effect on the suspension behavior. These phenomena can be explained by screening effects already mentioned in the literature for unmixed suspensions of particles modified by polyelectrolyte multilayers. As a consequence, this study highlights that the study of heteroaggregation in these systems is a very simple way to analyze this effect of screening which is difficult to observe on non-mixed suspensions.

*Keywords:* Heteroaggregation, colloid surface modifications, polyelectrolyte multilayers, salt effect

---

## 1. Introduction

2 For the last few years, the phenomenon of heteroaggregation of particles has been studied  
3 since it occurs in many fields ranging from pharmaceuticals to foodstuffs, including the man-

---

\*Corresponding author

*Email address:* manuella.cerbelaud@unilim.fr; Tel: +33 (0)5 87 50 23 47 (Manuella Cerbelaud)

4 manufacture of textured materials [1]. In the case of the shaping of ceramics, heteroaggregation  
5 was for example used to manufacture millimetric spheres, porous materials or even more  
6 recently ceramics presenting an oriented structure similar to nacre [2, 3, 4, 5].

7 In most heteroaggregated systems, particles carry surface charges of opposite sign, allowing  
8 them to heteroaggregate. Moreover, to obtain a good distribution of colloids in the aggre-  
9 gates, particles of the same nature must be sufficiently charged to avoid homoaggregation.  
10 That is why, in most cases, suspensions are obtained from powders with very different iso-  
11 electric points and for which there is a zone of pH values where the particles carry surface  
12 charges of opposite sign. The optimal conditions for heteroaggregation are then often ob-  
13 tained by adjusting the pH value [6, 7]. This method limits the possibilities of using certain  
14 powders which would have, for example, close isoelectric points. In this case, the range of  
15 pH values where the particles are of opposite sign is too small. This is why it can be of  
16 interest to modify the surface of the particles to obtain the necessary conditions for their  
17 heteroaggregation.

18 In this study, we propose to investigate the possibility of modifying the surface of the parti-  
19 cles by adding layers or multilayers of polyelectrolytes to obtain sufficiently stable particles  
20 with opposite charge. Indeed, the adsorption of polyelectrolyte multilayers on the surface of  
21 particles has already been widely studied and it has been shown that this adsorption, simple  
22 to implement, can be carried out on natural polymers [8], or inorganic powders [9] such as  
23 silica [10], calcium carbonate [11] or alumina [12].

24 The principle of polyelectrolyte multilayer formation consists in the progressive adsorption  
25 of polyelectrolytes of opposite signs on particles that exhibit surface charges. The first layer  
26 is made with polyelectrolyte with a charge opposite to that of the particle surface. Then the  
27 next layer is obtained with a polyelectrolyte of opposite charge to the previous polyelectrolyte  
28 (thus of the same sign as the particle surface) and so on. This method allows to control not  
29 only the surface charge of the particles but also the spacing between the particles by steric  
30 effects due to the presence of polymeric chains.

31 Numerous studies have already been carried out to understand the kinetics of formation of  
32 these multilayers, the organization between the polymers or the ionic distribution within  
33 these multilayers [13, 14, 15, 16, 17, 18]. However, to our knowledge, few studies have been  
34 performed on the possibility of using these multilayers to control the behavior of inorganic

35 colloidal suspensions. That is why, the aim of this study is to verify whether such sur-  
36 face modifications by electrolyte multilayers can be used to broaden the range of materials  
37 that can be used in ceramic shaping processes using heteroaggregation. Thus, we propose  
38 to study the heteroaggregation between silica particles which surface was modified with  
39 polyelectrolyte multilayers of poly-sodium 4-styrenesulfonate (PSS, negatively charged) and  
40 polydiallyldimethylammonium chloride (PDADMAC, positively charged). Since the presence  
41 of salt in these systems has a great influence on the conformation of the multilayers [18, 19],  
42 the possibility of using salt to control heteroaggregation is also investigated.

## 43 **2. Experimental methods**

### 44 *2.1. Raw materials*

45 Tetraethyl orthosilicate 98% (TEOS) and ammonia solution 28% (NH<sub>4</sub>OH) are obtained  
46 from Acros Organic. Absolute ethanol is provided by BDH Prolabo. 3-aminopropyl-triethoxysilane  
47 99% (APTES), fluorescein isothiocyanate isomer I 90% (FITC), rhodamine B isothiocyanate  
48 (RBITC), poly sodium 4-styrenesulfonate solution 30 w.% of Mw= 70000 (PSS), poly dial-  
49 lyldimethylammonium chloride solution 20 w.%, of Mw= 200000 (PDADMAC) and anhy-  
50 drous sodium chloride (NaCl) are obtained from Sigma-Aldrich. All reagents are used as  
51 received.

### 52 *2.2. Experimental characterizations*

53 Zeta potentials are measured using a Zetasizer Nano ZS from Malvern.  
54 Aggregation is observed via sedimentation tests. All suspensions are prepared at 3.vol.% with  
55 distilled water. In the case of mixed suspensions, the different powders are introduced simul-  
56 taneously in water. NaCl solutions are then introduced to adjust the salt concentration to  
57  $1.25 \times 10^{-3}$  M,  $2.50 \times 10^{-3}$  M,  $5.00 \times 10^{-3}$  M,  $7.50 \times 10^{-3}$  M and  $1.00 \times 10^{-2}$  M respectively. The  
58 concentration of the added saline solution is adjusted to add an identical volume of saline  
59 solution to each suspension in order not to change the volume fraction of particles. The  
60 suspensions are then mixed with an ultrasonic treatment (300 W, 30 s, pulse on 3 s, pulse off  
61 1 s). Immediately after their preparation, the suspensions are sealed in test tubes and left to  
62 rest. The heights of the sediments are analyzed after one week.  
63 The suspensions of fluorescently-labeled particles are observed with an epifluorescence micro-

64 scope Axio Imager 2 from Zeiss and with a confocal microscope LSM 880 from Zeiss. Images  
65 are processed with imageJ software.

### 66 **3. Results and discussion**

#### 67 *3.1. Powder synthesis*

68 In this study, it is proposed to investigate heteroaggregation in model systems composed  
69 of spherical, fluorescent silica particles covered with PDADMAC/PSS polyelectrolyte multi-  
70 layers. The silica particles are synthesized following the protocol described in reference [20],  
71 which is a modified Stöber synthesis. First, silica seeds are synthesized by the hydrolysis of  
72 TEOS in the presence of ammonia and ethanol. Then, a fluorescent dye (RBITC or FITC)  
73 previously associated with APTES, is introduced. Finally, a coarsening step by progressive  
74 addition of TEOS is performed. The synthesized powders are centrifuged and rinsed three  
75 times with ethanol before being dried. The obtained fluorescent spherical silica particles have  
76 a diameter of about 600 nm.

77 These particles are then surface modified by adsorption of polyelectrolyte multilayers follow-  
78 ing protocols proposed in References [10] and [21]. The principle of the surface modification  
79 is based on the progressive addition of the silica suspension into a previously prepared saline  
80 solution of polyelectrolytes. PSS or PDADMAC solutions (1.5 mg/mL) with a NaCl con-  
81 centration of 0.5 M are used. The silica suspension, prepared with 1 g of powder in 40 mL  
82 of distilled water, is then introduced dropwise into 100 mL of polyelectrolyte solution, under  
83 magnetic stirring. The mixture is stirred for 20 minutes. It is then centrifuged for 5 min at  
84 3000 rpm and rinsed three times with distilled water to remove excess or poorly adsorbed  
85 polyelectrolytes molecules.

86 Since silica is negatively charged, the first layer of polyelectrolytes adsorbed is PDADMAC.  
87 Then, layers of PSS and PDADMAC will be alternatively adsorbed until the desired number  
88 of layers is obtained. Once the surface modification is completed, the powders are dried  
89 overnight at 50°C.

90 After each modification, the zeta potential is measured to check that there is a change in  
91 sign of the surface charge. Figure 1 shows the evolution of the zeta potential of a rhodamine-  
92 labeled silica powder as a function of the number of adsorbed polyelectrolyte layers. Data  
93 show that the particles have an absolute value of zeta potentials at around 40 mV and that

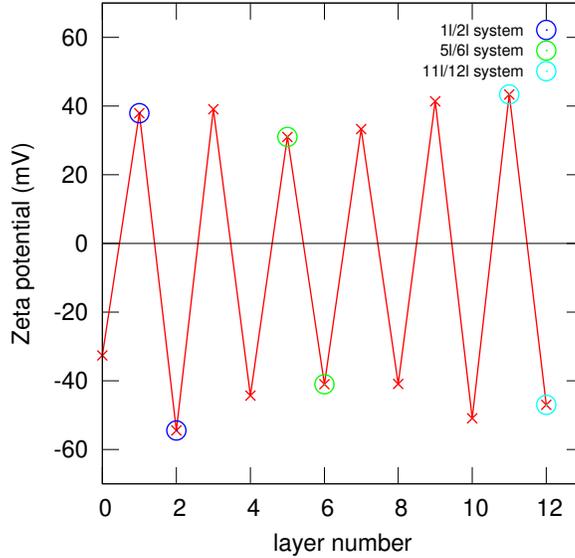


Figure 1: Evolution of the zeta potential as a function of the number of adsorbed polyelectrolyte layers for rhodamine-labeled silica particles. The circles show the binary systems used to study heteroaggregation.

94 there is indeed an alternation of the sign of the surface charge according to the number of  
 95 layers.

96

97 Zeta potential measurements, performed on suspensions prepared with dried powder after  
 98 surface modification show surface potential values similar to those obtained before drying,  
 99 which suggests that this drying step does not alter the charges of modified surfaces.

100 These surface modifications allow thus to have strongly charged particles, however they do  
 101 not allow to tune precisely the absolute value of the zeta potential.

102

103 In the following, the study will focus on the heteroaggregation, i.e. on suspensions where  
 104 negative and positive particles are mixed together. To see the influence of the number of  
 105 layers, three systems will be analyzed:

- 106 • System 11/21: mixture of modified silica with 1 layer (positively charged) and modified  
 107 silica with 2 layers (negatively charged),
- 108 • System 51/61: mixture of modified silica with 5 layers (positively charged) and modified  
 109 silica with 6 layers (negatively charged),

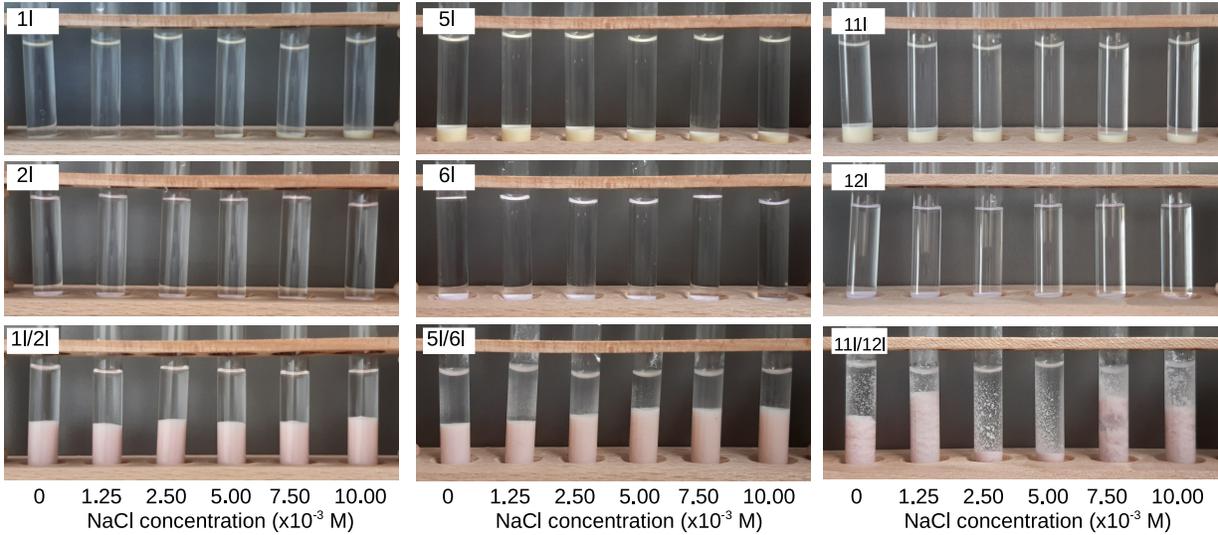


Figure 2: Sedimentation tests showing the influence of salt concentration in the aggregation of surface modified silica particles for the system 1l/2l, 5l/6l and 11l/12l. Pictures are taken one week after the preparation of suspensions. On the top row: fluorescein-labeled silica particles modified with an odd layer number (positively charged); on the middle row: rhodamine-labeled silica particles modified with an even number of layers (negatively charged); on the bottom row: binary system composed of 50% of silica modified with an odd number of layers and 50% of silica modified with an even number of layers.

- System 11l/12l: mixture of modified silica with 11 layers (positively charged) and modified silica with 12 layers (negatively charged).

The modified particles with an odd number of layers, *i.e.* positively charged will be marked by fluorescein. They will therefore appear green in epifluorescence/confocal microscopy. The modified powders with an even number of layers, *i.e.* negatively charged, will be marked by rhodamine and will appear red in epifluorescence/confocal microscopy.

### 3.2. Analysis of the heteroaggregation in the binary systems 1l/2l, 5l/6l and 11l/12l

Aggregation in the binary systems is studied by sedimentation tests in the presence of different amounts of salt, and therefore for different ionic strength values. Figure 2 shows pictures of the sedimentation tubes taken after one week for the three binary systems analyzed in this study (1l/2l; 5l/6l and 11l/12l respectively). For each system, tests are performed with only the positive powder (top row), with only the negative powder (middle row) and with both powders mixed at 50% (bottom row).

123 In all systems, in the absence of salt, it is observed that the deposits obtained with the  
124 positive particles alone, or negative alone, are of low heights, reflecting that these suspensions  
125 are stable and that the identical particles have a low tendency to aggregate. On the other  
126 hand, as soon as the positive and negative powders are mixed in equal proportion, a sediment  
127 of greater height is obtained rapidly (less than 30 minutes), revealing a strong aggregation  
128 in these mixed systems. In the absence of salt, these tests give results similar to what is  
129 observed in systems where the powders heteroaggregate [20]. These results show that the  
130 different surface modifications performed allow heteroaggregation between oppositely charged  
131 particles and limit homoaggregation between particles of the same sign.  
132 Since polyelectrolyte multilayers are sensitive to the presence of salt [19], sedimentation  
133 tests are also performed with increasing NaCl concentration up to  $C = 10^{-2}$  M. In this range  
134 of NaCl concentration, no major changes are observed for suspensions composed of only  
135 negative particles. The sediments are of low height and the suspensions are stable whatever  
136 the concentration of NaCl used. For the suspensions of positive particles, upon increasing salt  
137 concentration, the sediments remain of low heights and the suspensions thus remain rather  
138 stable. However, in the 11/2l system, the sediment height seems to increase a little with the  
139 amount of salt while in the other two systems (5l/6l and 11l/12l) it seems to decrease slightly.  
140 For the mixed systems, the behavior of the 11/2l and 5l/6l systems is similar. A sediment of  
141 almost constant height is observed whatever the salt concentration used, which attests to a  
142 strong heteroaggregation even in the presence of salt.

143 The behavior of the 11l/12l system is different from the other two systems. While the  
144 11/2l and 5l/6l systems show little evolution according to the amount of salt, the 11l/12l  
145 system shows different sediment heights according to the salt concentration. In the absence  
146 of salt or at low concentration ( $C = 1.25 \times 10^{-3}$  M), we observe a sediment of great height.  
147 However, as the salt content continues to increase, the sediment height decreases and then  
148 increases again. In addition, the appearance of the deposits obtained is very different. The  
149 highest sediments have a high porosity compared to that obtained in systems with fewer  
150 layers (11/2l and 5l/6l systems) and aggregates are stuck to the walls of the tubes (see Fig-  
151 ure 2 at  $C = 10^{-2}$  M). The sediments have also a more gelled appearance, which could be  
152 explained by the presence of a greater amount of polymers in this system.

153

154 To better understand the aggregation in these mixed 11l/12l systems, the aggregates  
155 are observed by epifluorescence and confocal microscopy. Images obtained for different salt  
156 concentrations are reported in Figure 3.

157 In the absence of salt or for a NaCl concentration of  $C = 1.25 \times 10^{-3} \text{ M}$ , the presence of  
158 large heteroaggregates is clearly observed. The particles are well distinguished and one can  
159 see an alternation between red and green particles in the aggregates, which is a typical dis-  
160 tribution for heteroaggregates [20]. For a salt concentration equal to  $C = 2.5 \times 10^{-3} \text{ M}$ , where  
161 sedimentation tests show a low sediment height, the aggregates observed by microscopy are  
162 smaller and more compact. They are still composed of red and green particles, evidence  
163 of heteroaggregation. As the salt concentration increases to  $C = 5.00 \times 10^{-3} \text{ M}$ , which still  
164 corresponds to a low height sediment, small compact heteroaggregates are observed but also  
165 individual particles, both red and green, showing that for this concentration of salt, there are  
166 deflocculated particles. As we continue to increase the salt concentration, we again observe  
167 large aggregates composed of heteroaggregated particles.

168 In all cases, we never observed crystallized zones in the aggregates. Moreover, we do not  
169 observe linear heteroaggregates. This can be explained by a short range of repulsive inter-  
170 actions between particles of the same nature, which does not allow to push them far enough  
171 from each other to obtain a linear sequence.

172 To understand the behavior of these complex systems, it is necessary to take into account not  
173 only electrostatic effects but also effects specific to the presence of polyelectrolyte layers, such  
174 as steric effects. We will discuss this point in the following. In this article, we do not focus  
175 on the shape of the aggregates but on the possibility to form them while the suspension is at  
176 rest, that is why we will analyze the behavior of the suspensions only from the interparticle  
177 interactions without taking into account the hydrodynamic effects, which can influence the  
178 kinetics of aggregation and the aggregate shapes [22].

179 As a comparison, to clearly distinguish the role of polymer-level interactions and elec-  
180 trostatic interactions, sedimentation tests are performed on a model system composed of  
181 rhodamine-labeled silica particles and fluorescein-labeled silica particles modified on the sur-  
182 face by grafting APTES molecules (SLF APTES/SIR system). Previous studies have al-  
183 ready shown that for these systems, there is a strong heteroaggregation at pH 6 without  
184 addition of salt [23]. Sedimentation tests are thus performed at pH 6 for the different NaCl

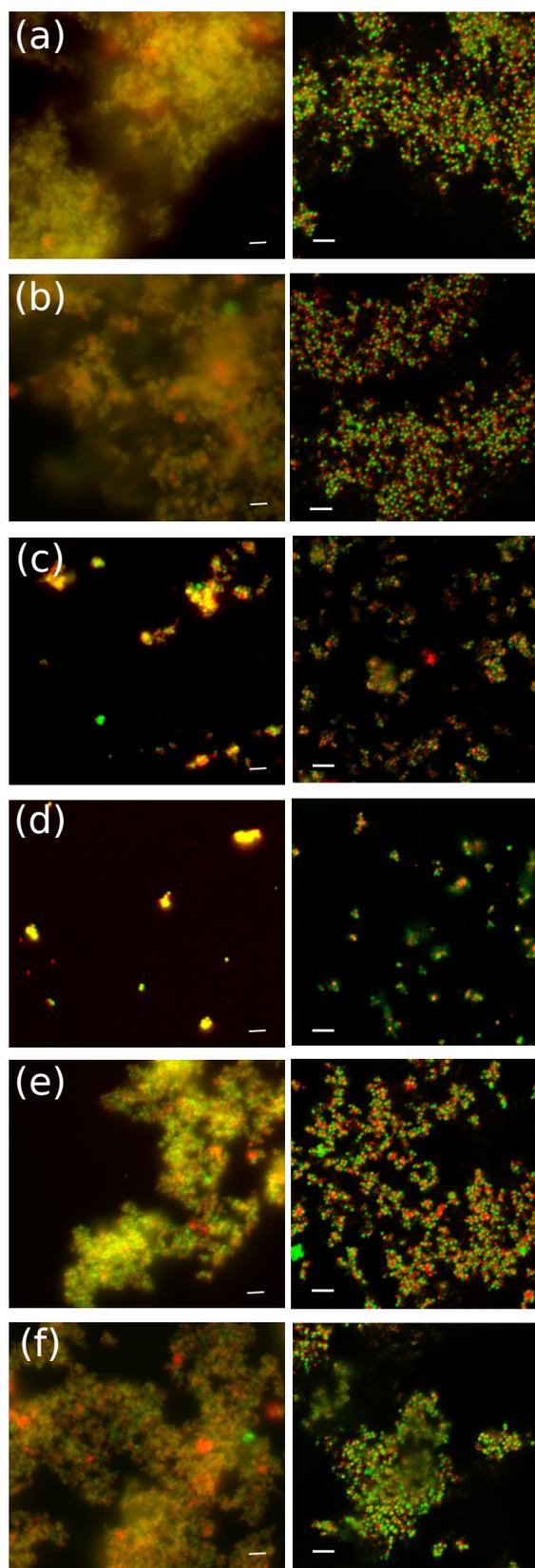


Figure 3: Aggregates observed by epifluorescence microscopy (left) and confocal microscopy (right) in the system 11l/12l as a function of NaCl concentration: (a) without salt, (b)  $C=1.25 \times 10^{-3}$  M, (c)  $C=2.50 \times 10^{-3}$  M, (d)  $C=5.00 \times 10^{-3}$  M, (e)  $C=7.50 \times 10^{-3}$  M and (f)  $C=1.00 \times 10^{-2}$  M. Scale bar =  $6\mu\text{m}$

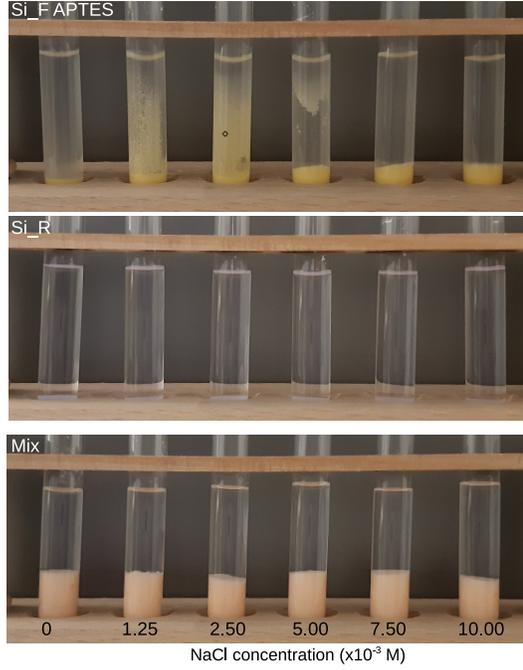


Figure 4: Sedimentation tests showing the influence of salt concentration in the aggregation for the system Si\_F APTES, SLR and mix (50% of Si\_F APTES and 50% of SLR). Pictures are taken one week after the preparation of suspensions.

185 concentrations previously used. Images of the sedimentation tubes are reported in Figure 4.

186 The results obtained with the latter system are very similar to those obtained for the  
 187 1l/2l system. The behavior of these Si\_F APTES/ Si\_R and 1l/2l systems can be interpreted  
 188 in the same way. Indeed, it does not seem necessary to take into account steric effects to  
 189 understand the 1l/2l system even if polymers are present. For these both systems, where  
 190 there are no or few polyelectrolyte layers, the behavior of the suspensions can be explained  
 191 only by a change of electrostatic interactions. Indeed, for native charged oxide particles  
 192 (without polymers), it is known that the behavior of the suspensions can be described by the  
 193 so-called Derjaguin, Landau, Verwey and Overbeek (DLVO) potential, which results from the  
 194 sum of an attractive potential due to van der Waals forces and of an electrostatic potential.  
 195 The van der Waals contribution can be expressed as follows [24]:

$$U_{ij}^{vdW} = -\frac{A_{ij}}{6} \left\{ \frac{2a_i a_j}{r_{ij}^2 - (a_i + a_j)^2} + \frac{2a_i a_j}{r_{ij}^2 - (a_i - a_j)^2} + \ln \left[ \frac{r_{ij}^2 - (a_i + a_j)^2}{r_{ij}^2 - (a_i - a_j)^2} \right] \right\}, \quad (1)$$

196 with  $a_i$  the radius of colloid  $i$ ,  $r_{ij}$  the distance between colloids  $i$  and  $j$  and  $A_{ij}$  called constant  
 197 of Hamaker which is related to the nature of the colloids and of the solvent (here silica in

198 water  $A = 4.6 \times 10^{-21}$  J [25]). The electrostatic contribution can be modeled by [26]:

$$U_{ij}^{elHHF} = \pi\epsilon \frac{a_i a_j}{a_i + a_j} (\psi_i^2 + \psi_j^2) \left\{ \frac{2\psi_i \psi_j}{(\psi_i^2 + \psi_j^2)} \ln \left[ \frac{1 + e^{-\kappa h_{ij}}}{1 - e^{-\kappa h_{ij}}} \right] + \ln [1 - e^{-2\kappa h_{ij}}] \right\}, \quad (2)$$

199 with  $h_{ij} = r_{ij} - (a_i + a_j)$  the distance between the surfaces of particles  $i$  and  $j$ ,  $\epsilon = \epsilon_r \epsilon_0$  the  
 200 dielectric constant of the solvent (here water), the surface potential of the particle  $i$  and the  
 201 inverse of the Debye length defined for a symmetrical electrolyte by the equation [27]:

$$\kappa = \sqrt{\frac{2e^2 z^2 N_a I 10^3}{\epsilon k_B T}} \quad (3)$$

202 where  $z$  is the valence of the ions in the electrolyte (here  $z = 1$ ),  $N_a$  is Avogadro's num-  
 203 ber,  $k_B$  is Boltzmann's constant and  $T$  is the temperature ( $T=293$  K).  $I$  is the ionic strength  
 204 expressed in mol/L which is deduced from the quantity of salt present in the suspension.

205 These expressions are valid when the particles have homogeneous surface properties. How-  
 206 ever, when polyelectrolytes are adsorbed on colloids, there can be surface inhomogeneities  
 207 which lead to attractions between the particles which can be considered as attractions be-  
 208 tween patch-charge heterogeneities [28]. In this study, although such surface inhomogeneities  
 209 may exist, they do not seem to govern the behavior of the suspensions, since as shown in  
 210 Figure 2, taken individually the suspensions are not aggregated. This is why we will neglect  
 211 the effects of surface inhomogeneities in the following.

212

213 When salt is added, the Debye length is decreased, resulting in a screening of the sur-  
 214 face charges and thus a decrease in the range of electrostatic interactions in favor of van  
 215 der Waals interactions, which may result in an increase in aggregation between like particles  
 216 (see Figure 5). This screening could be the reason for the small increase in sediment in the  
 217 case of positive particles as a function of salt in the SLF APTES/SLR systems and the  
 218 1l/2l systems. However, for the systems studied here, the surface potentials are high, on the  
 219 order of 40 mV (see Figure 1 and Reference [23]) and the presence of salt is not sufficient to  
 220 strongly screen the surface charges and thus has little influence on the global aggregation.  
 221 DLVO curves plotted for surface potentials of 40 mV indeed show a decrease in the range  
 222 of interactions with increasing salt concentration, but this is not sufficient to create strong  
 223 homoaggregation and thus has little influence on heteroaggregation (see Figure 5).

224

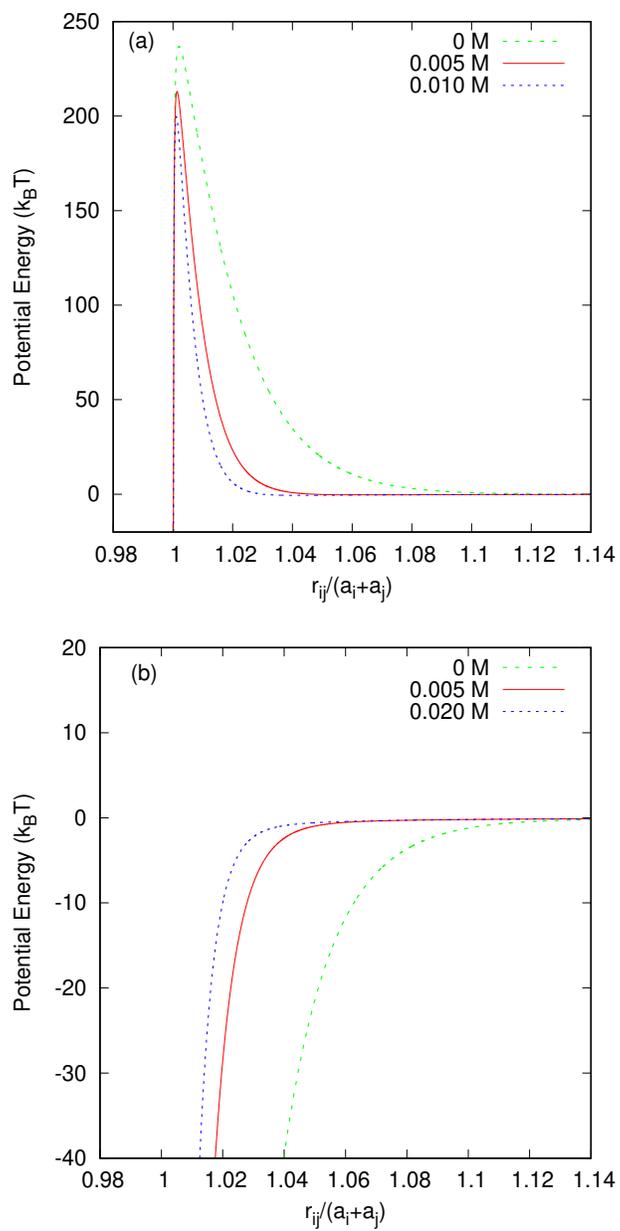


Figure 5: DLVO potentials for 600 nm silica particles dispersed in water with a surface potential of 40 mV in absolute value for different NaCl concentrations: (a) particles of same charge; (b) particles of opposite charge

225 To explain the behavior of the 11l/12l mixed system, which is quite different from that  
226 observed in the previous systems (SLF APTES/SLR and 1l/2l systems), it is necessary to  
227 take into account what happens in the polyelectrolyte multilayer. The electrostatic inter-  
228 actions between coated particles, and therefore the DLVO interactions are not sufficient to  
229 understand the suspension behavior.

230 For the PDADMAC/PSS combination, it is known that the thickness of the layers increases  
231 strongly with the number of layers and the salt concentration used during the synthe-  
232 sis [18, 29, 13]. Indeed, the strong electrolytes used here must be well adsorbed, especially  
233 because of the high ionic concentration used during the synthesis (here  $C_{\text{NaCl}} = 0.5 \text{ M}$ ). For  
234 the 11l/12l system, a much thicker layer of polyelectrolytes is thus present on the surface of  
235 the particles compared to the two other systems considered in this study. Because of that, it  
236 is assumed that the behavior of this system is essentially due to the polyelectrolyte multilayer  
237 interactions (the van der Waals potential being active at a short separation distance). When  
238 polyelectrolytes are adsorbed in the presence of salts, extrinsic charge compensation can be  
239 achieved with the presence of ions and water in the structure of the multilayers [30, 18],  
240 which cause the layers to swell. As already mentioned, the presence of ionic species makes  
241 them sensitive to ionic strength [31]. Many studies have indeed shown that the conformation  
242 of multilayers and in particular the swelling properties vary with the concentration of salts  
243 and the nature of the last adsorbed layer [32, 33, 19]. Authors have also shown that swelling  
244 is reversible and that swelling/shrinking cycles of multilayers are possible by modifying the  
245 concentration and/or the nature of the salts present in suspension [34, 35, 36].

246 For the PDADMAC/PSS systems, it was shown that the ions trapped in the multilayer were  
247 mobile and could be partially removed leading to a shrinkage of the layers or replaced by ions  
248 of a different nature, which could lead to a swelling or even a destruction of the layers [35].  
249 These behaviors could be explained by screening effects within the multilayer. When the  
250 polyelectrolyte layers are in the presence of water, the ions are extracted from the multilayer  
251 and the charge compensation between polyelectrolytes is extrinsic, so that the multilayer  
252 can shrink (the surface charges are then essentially due to the charges of the last adsorbed  
253 polyelectrolyte). Then, when the salt concentration is increased, the ions penetrate again  
254 into the multilayer, leading first to their electrostatic screening and then again to an extrin-  
255 sic charge compensation regime with a possible swelling of the multilayer. When the salt

256 concentrations become important (higher than the one used during the synthesis), there can  
257 finally be a destruction of the multilayer [35, 19]. The salt concentrations used in this study  
258 being much lower than that used during the synthesis of the multilayers, it is unlikely to  
259 obtain this destruction.

260 These screening phenomena help to explain the aggregation in the 11l/12l system. This is  
261 summarized in Figure 6.

262 Since powder are rinsed in water, they may be few ions in the multilayer and thus an intrinsic  
263 charge compensation between polymers is expected in suspensions without added salt. The  
264 charge of particle is thus created by the latest adsorbed polyelectrolyte layer, which is highly  
265 charged. Therefore, in the absence of salt or at very low ionic concentration, mixing powder  
266 with 11 layers (positive) and powder with 12 layers (negative) will allow the heteroaggregation  
267 while avoiding aggregation between identical particles.

268 However, when the amount of salt is increased ( $C= 2.5 \times 10^{-3}$  M and  $C= 5. \times 10^{-3}$  M),  
269 the charge of the multilayers is progressively screened, which decreases the heteroaggrega-  
270 tion phenomena. Moreover, the presence of a thick polymer layer on the surface, create a  
271 steric effect which will slows down the aggregation between particles. Some particles will  
272 even be deflocculated. When the salt concentration increases again, the ions penetrate the  
273 multilayer and the extrinsic charge compensation takes place again. The particles become  
274 strongly charged again and the heteroaggregation phenomena are again observed. Moreover,  
275 experimentally, confocal microscopy observations show a diffusion of the fluorescence signals  
276 which could be explained by a swelling of the polymer for the highest salt concentration (see  
277 Figure 3 (f)).

278 For suspensions composed only of 12 layers surface modified particles, sedimentation tests  
279 show always a small sediment. However, it has previously been stated that the sediment  
280 heights obtained with only the powders modified with 11 layers of polyelectrolytes are higher  
281 and decrease with the addition of salt. This phenomenon can be link to previous reported  
282 observations in literature which have shown the influence of the latest layer nature on the  
283 swelling properties. Indeed, for example, it has already been shown that 17-layers multilayer,  
284 with PDADMAC as last layer, shrink more and lost more water when exposed to NaCl so-  
285 lution compared to 16-layers multilayers, with PSS as last layer [36].

286

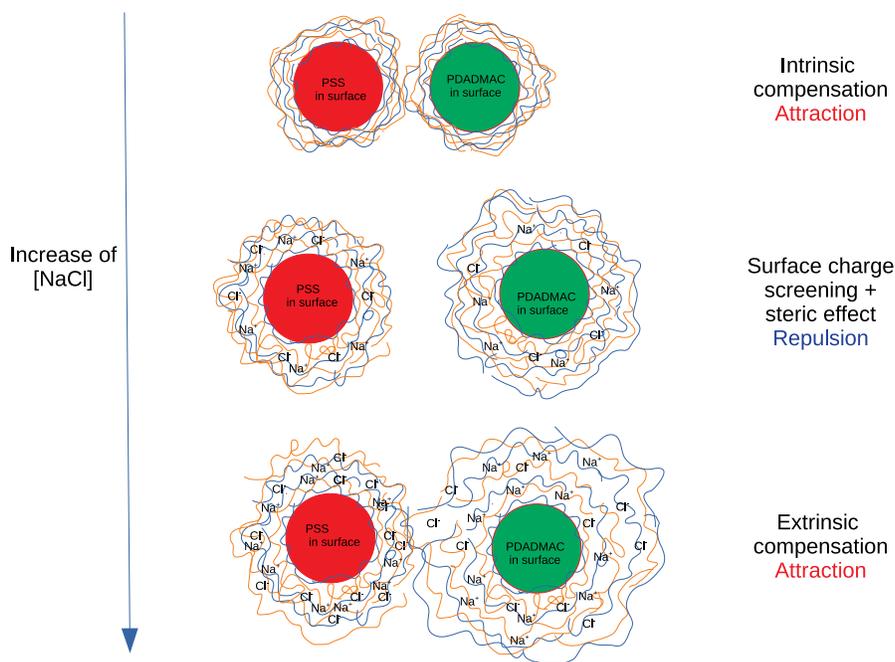


Figure 6: Schematic diagram to explain the variation of aggregation as a function of salt for the 111/121 system

287 For the mixed 5l/6l system, it seems that the number of adsorbed layers is not sufficient to  
 288 observe clearly the screening phenomenon. Previous studies show indeed different structural  
 289 changes and charge compensation mechanisms between systems composed of only a few  
 290 layers and those composed of at least a dozen layers [37]. As already reported in literature,  
 291 the structure of the multilayers can be modeled in 3 different zones [38]. The first zone is  
 292 located near the surface of the substrate and is generally composed of a few layers. The  
 293 polyelectrolytes line up along the substrate and have little mobility. Then, a second zone,  
 294 which actually composes the multilayer is observed. And on the surface, a third zone of low  
 295 thickness makes the transition between the second zone and the solution environment. In the  
 296 case of the 5l/6l system, the second zone where the polyelectrolytes no longer feel the effect of  
 297 the substrate must be very small and this system seems less sensitive to the variation of the  
 298 ionic strength. Nevertheless, it is observed that suspensions with particles modified with 5  
 299 layers seem to be somewhat more stabilized with the addition of salt than particles modified  
 300 with 11 layers. However, there is no significant effect observed on the heteroaggregation in  
 301 the mixed 5l/6l systems.

302 All these results confirm that for polyelectrolyte multilayers of around dozzain of layers, salt

303 has a significant effect on the multilayer properties as previously mentioned in literature [19].  
304 This study reveals also that studying the heteroaggregation is a very simple way to see these  
305 effect.

#### 306 4. Conclusion

307 In conclusion, first silica particles are surface modified by multilayers of PADMAC/PSS  
308 polyelectrolytes. An even number of layers is used to obtain negative particles while an odd  
309 number of layers is used to obtain positive particles. Then, this study focuses on the sus-  
310 pension behavior of mixtures of positive and negative particles as a function of the number  
311 of adsorbed layers and the ionic strength. The results clearly show that in absence of salt,  
312 heteroaggregate systems can be obtained if we mix modified particles with an even number  
313 of layers and others with an odd number of layers whatever the number of adsorbed layers.  
314 This results open thus perspectives to use such modification to allow new combination of  
315 particles in ceramic shaping processes using heteroaggregation.

316 It is also observed that if the number of adsorbed layers is low, the behavior can be explained  
317 by the DLVO theory and an addition of salt in the suspension has little effect on the aggre-  
318 gation. On the other hand, for a higher number of layers (here 11l/12l system), the effects of  
319 the presence of the multilayer, and especially steric effects must also be taken into account  
320 to understand the aggregation of mixed suspensions in presence of salt. Results indeed show  
321 that for particles covered with a large number of multilayers, size of heteroaggregates can be  
322 controlled by adjusting the ionic strength. It appears also that some particles can even be  
323 sterically stabilized at a given concentration of salt because of steric repulsion. This could  
324 be interesting for ceramic shaping processes, such as direct coagulation casting process for  
325 example. In this case, sterically stabilized mix suspensions could be heteroaggregated in situ  
326 by an increase of salt concentration.

327 This study also shed light that studying heteroaggregation in the presence of multilayer  
328 covered particles is actually a very simple way to see how the presence of salt affects the  
329 properties of polyelectrolyte multilayers. Indeed, the screening effects of multilayers induced  
330 by salt is very visible in mixed systems that heteroaggregate.

## 331 Acknowledgments

332 The authors thank Claire Carrion for her help on the confocal microscope.

## 333 CRediT author statement

334 **Manuella Cerbelaud**: Conceptualization, Investigation, Writing - Original Draft, Su-  
335 pervision; **Yasmine Bennani**: Investigation, Writing - Review & Editing; **Claire Peyratout**:  
336 Conceptualization, Writing - Review & Editing

## 337 Funding

338 This research did not receive any specific grant from funding agencies in the public,  
339 commercial, or not-for-profit sectors.

- 340 [1] N. B. Alsharif, S. Murath, B. Katana, I. Szilagyi, Composite materials based on heteroag-  
341 gregated particles: Fundamentals and applications, *Advances in Colloid and Interface*  
342 *Science* 294 (2021) 102456. doi:<https://doi.org/10.1016/j.cis.2021.102456>.
- 343 [2] S. Perko, A. Dakskobler, T. Kosmac, High-performance porous nanostructured ceram-  
344 ics, *J. Am. Ceram. Soc.* 2010 (2010) 2499–2502. doi:[https://doi.org/10.1111/j.1551-](https://doi.org/10.1111/j.1551-2916.2010.03835.x)  
345 [2916.2010.03835.x](https://doi.org/10.1111/j.1551-2916.2010.03835.x).
- 346 [3] Y. Ji, L. Black, P. Weidler, M. Janek, Preparation of nanostructured materials  
347 by heterocoagulation-interaction of montmorillonite with synthetic hematite particles,  
348 *Langmuir* 20 (2004) 9796–9806. doi:<https://doi.org/10.1021/la0495579>.
- 349 [4] P. Garcia-Perez, C. Pagnoux, A. Pringuet, A. Videcoq, J.-F. Baumard, Agglom-  
350 eration of alumina submicronparticles by silica nanoparticles: application to pro-  
351 cessing spheres by colloidal route, *J. Colloid Interface Sci.* 313 (2007) 527–536.  
352 doi:<https://doi.org/10.1016/j.jcis.2007.04.050>.
- 353 [5] M. Munoz, M. Cerbelaud, A. Videcoq, H. Saad, A. Boulle, S. Meille,  
354 S. Deville, F. Rossignol, Nacre-like alumina composites based on heteroag-  
355 gregation, *Journal of the European Ceramic Society* 40 (15) 5773–5778.  
356 doi:<https://doi.org/10.1016/j.jeurceramsoc.2020.06.049>.

- 357 [6] P. Dušak, A. Mertelj, S. Kralj, D. Makovec, Controlled heteroaggregation of two types  
358 of nanoparticles in an aqueous suspension, *J. Colloid Interface Sci* 438 (2015) 235–243.  
359 doi:<https://doi.org/10.1016/j.jcis.2014.09.086>.
- 360 [7] J. Lee, S. Lee, K. Ahn, S. Lee, Nanoparticle-induced gelation of bimodal slurries with  
361 highly size asymmetric particles: effect of surface chemistry and concentrations, *Lang-*  
362 *muir* 31 (2015) 13639–13646. doi:10.1021/acs.langmuir.5b03752.
- 363 [8] T. Mendoza-Dorantes, U. Pal, J. Vega-Acosta, C. Márquez-Beltrán, Encapsulation and  
364 surface charge manipulation of organic and inorganic colloidal substrates by multilayered  
365 polyelectrolyte films, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*  
366 434 (2013) 253–259. doi:<https://doi.org/10.1016/j.colsurfa.2013.05.027>.
- 367 [9] G. Decher, M. Eckle, J. Schmitt, B. Struth, Layer-by-layer assembled multicomposite  
368 films, *Current Opinion in Colloid & Interface Science* 3 (1951) 32–39. doi:10.1016/S1359-  
369 0294(98)80039-3.
- 370 [10] M. Dubois, M. Schönhoff, A. Meister, L. Belloni, T. Zemb, H. Möhwald, Equation of  
371 state of colloids coated by polyelectrolyte multilayers, *Phys Rev E* 74 (2006) 051402.  
372 doi:<https://doi.org/10.1103/PhysRevE.74.051402>.
- 373 [11] J. Lee, K. Sim, H. Youn, Effect of salt concentration in polyelectrolyte multilayering  
374 on properties of modified gcc and filled paper, *Nordic Pulp & Paper Research Journal*  
375 32 (2) (2017) 309–316. doi:<https://doi.org/10.3183/npprj-2017-32-02-p309-316>.
- 376 [12] W. Zhang, P.-I. Au, X. Zhang, H. Fan, C. Sun, M. Saunders, Y.-K. Leong, Spher-  
377 ical  $\alpha$   $\text{Al}_2\text{O}_3$  suspensions layered sequentially with anionic and cationic polyelec-  
378 trolytes: Chemistry, rheology and tem images, *Powder Technology* 338 (2018) 716–724.  
379 doi:<https://doi.org/10.1016/j.powtec.2018.07.068>.
- 380 [13] E. Guzman, H. Ritacco, J. E. F. Rubio, R. G. Rubio, F. Ortega, Salt-induced  
381 changes in the growth of polyelectrolyte layers of poly(diallyl- dimethylammonium  
382 chloride) and poly(4-styrene sulfonate of sodium), *Soft Matter* 5 (2009) 2130–2142.  
383 doi:10.1039/b901193e.

- 384 [14] E. Guzman, H. A. Ritacco, F. Ortega, R. G. Rubio, Growth of polyelectrolyte layers  
385 formed by poly(4-styrenesulfonate sodium salt) and two different polycations: New in-  
386 sights from study of adsorption kinetics, *The Journal of Physical Chemistry C* 116 (29)  
387 (2012) 15474–15483. doi:10.1021/jp304522t.
- 388 [15] E. Guzman, H. Ritacco, F. Ortega, R. G. Rubio, Evidence of the influence of adsorp-  
389 tion kinetics on the internal reorganization of polyelectrolyte multilayers, *Colloids and*  
390 *Surfaces A* 384 (2011) 274. doi:10.1016/j.colsurfa.2011.04.005.
- 391 [16] Y. C. Rachel L. Abbett, J. B. Schlenoff, Self-exchange of polyelectrolyte in multilayers:  
392 Diffusion as a function of salt concentration and temperature, *Macromolecules* 54 (2021)  
393 9522–9531.
- 394 [17] Y. E. Ghossoub, M. Zerbball, H. M. Fares, J. F. Ankner, R. von Klitzing, J. B. Schlenoff,  
395 Ion distribution in dry polyelectrolyte multilayers: a neutron reflectometry study, *Soft*  
396 *Matter* 14 (2018) 1699–1708. doi:10.1039/C7SM02461D.
- 397 [18] E. Guzman, R. G. Rubio, F. Ortega, A closer physico-chemical look to the layer-by-  
398 layer electrostatic self-assembly of polyelectrolyte multilayers, *Advances in Colloid and*  
399 *Interface Science* 282 (2020) 102197. doi:https://doi.org/10.1016/j.cis.2020.102197.
- 400 [19] L. Han, Z. Mao, H. Wuliyasu, J. Wu, X. Gong, Y. Yang, C. Gao, Modulating the struc-  
401 ture and properties of poly(sodium 4-styrenesulfonate)/poly(diallyldimethylammonium  
402 chloride) multilayers with concentrated salt solutions, *Langmuir* 28 (1) (2012) 193–199.  
403 doi:https://doi.org/10.1021/la2040533.
- 404 [20] M. Piechowiak, A. Videcoq, F. Rossignol, C. Pagnoux, C. Carrion, M. Cerbelaud,  
405 R. Ferrando, Oppositely charged model ceramic colloids: Numerical predictions and  
406 experimental observations by confocal laser scanning microscopy, *Langmuir* 26 (2010)  
407 12540–12547. doi:https://doi.org/10.1021/la101027d.
- 408 [21] G. B. Sukhorukov, E. Donath, H. Lichtenfeld, E. Knippel, M. Knippel, A. Budde,  
409 H. Möhwald, Layer-by-layer self assembly of polyelectrolytes on colloidal particles, *Col-*  
410 *loids and Surfaces A: Physicochemical and Engineering Aspects* 137 (1) (1998) 253–266.  
411 doi:https://doi.org/10.1016/S0927-7757(98)00213-1.

- 412 [22] A. Tomilov, A. Videcoq, M. Cerbelaud, M. Piechowiak, T. Chartier, T. Ala-Nissila,  
413 D. Bochicchio, R. Ferrando, Aggregation in colloidal suspensions: evaluation of the  
414 role of hydrodynamic interactions by mean of numerical simulations, *J. Phys. Chem.*  
415 Bdoi:<https://doi.org/10.1021/jp407247y>.
- 416 [23] M. Cerbelaud, A. Aimable, A. Videcoq, Role of electrostatic interactions in oil-in-water  
417 emulsions stabilized by heteroaggregation: An experimental and simulation study, *Lang-*  
418 *muir* 34 (2018) 15795–15803. doi:<https://doi.org/10.1021/acs.langmuir.8b02922>.
- 419 [24] H. C. Hamaker, The London-van der Waals attraction between spherical particles, *Phys-*  
420 *ica* 4 (1937) 1058–1072. doi:[https://doi.org/10.1016/S0031-8914\(37\)80203-7](https://doi.org/10.1016/S0031-8914(37)80203-7).
- 421 [25] L. Bergström, Hamaker constants for inorganic materials, *Adv. Colloid Interface Sci.* 70  
422 (1997) 125–169–A163. doi:[https://doi.org/10.1016/S0001-8686\(97\)00003-1](https://doi.org/10.1016/S0001-8686(97)00003-1).
- 423 [26] R. Hogg, T. Healy, D. Fuerstenau, Mutual coagulation of colloidal dispersions, *Trans.*  
424 *Fraday Soc.* 62 (1966) 1638–1651. doi:<https://doi.org/10.1039/TF9666201638>.
- 425 [27] M. Elimelech, X. Jia, J. Gregory, R. A. Williams, *Particle Deposition & Aggregation:*  
426 *Measurement, Modelling and Simulation*, Butterworth-Heinemann, 1998.
- 427 [28] M. Borkovec, G. Papastavrou, Interactions between solid surfaces with adsorbed poly-  
428 electrolytes of opposite charge, *Current Opinion in Colloid & Interface Science* 13 (2008)  
429 429–437. doi:<https://doi.org/10.1016/j.cocis.2008.02.006>.
- 430 [29] R. v. Klitzing, J. E. Wong, W. Jaeger, R. Steitz, Short range interactions in polyelec-  
431 trolyte multilayers, *Current Opinion in Colloid & Interface Science* 9 (1) (2004) 158–162.  
432 doi:<https://doi.org/10.1016/j.cocis.2004.05.022>.
- 433 [30] R. Koehler, R. Steitz, R. von Klitzing, About different types of water in swollen poly-  
434 electrolyte multilayers, *Advances in Colloid and Interface Science* 207 (2014) 325–331.  
435 doi:<https://doi.org/10.1016/j.cis.2013.12.015>.
- 436 [31] H. Jomaa, J. Schlenoff, Salt-induced polyelectrolyte interdiffusion in multilay-  
437 ered films: a neutron reflective study, *Macromolecules* 38 (2005) 8473–8480.  
438 doi:<https://doi.org/10.1021/ma050072g>.

- 439 [32] S. T. Dubas, J. B. Schlenoff, Swelling and smoothing of polyelectrolyte multilayers by  
440 salt, *Langmuir* 17 (25) (2001) 7725–7727. doi:<https://doi.org/10.1021/la0112099>.
- 441 [33] J. Irigoyen, L. Han, I. Llarena, Z. Mao, C. Gao, S. Moya, Responsive poly-  
442 electrolyte multilayers assembled at high ionic strength with an unusual col-  
443 lapse at low ionic strength, *Macromol Rapid Commun.* 33 (2012) 1964–1969.  
444 doi:<https://doi.org/10.1002/marc.201200471>.
- 445 [34] K. Köhler, P. Biesheuvel, R. Weinkamer, H. Möhwald, G. Sukhorukov, Salt-induced  
446 swelling-to-shrinking transition in polyelectrolyte multilayer capsules, *Phys Rev Lett* 97  
447 (2006) 188301. doi:<https://doi.org/10.1103/PhysRevLett.97.188301>.
- 448 [35] J. T. O’Neal, E. Y. Dai, Y. Zhang, K. B. Clark, K. G. Wilcox, I. M. George, N. E.  
449 Ramasamy, D. Enriquez, P. Batys, M. Sammalkorpi, J. L. Lutkenhaus, Qcm-d investi-  
450 gation of swelling behavior of layer-by-layer thin films upon exposure to monovalent ions,  
451 *Langmuir* 34 (3) (2018) 999–1009. doi:<https://doi.org/10.1021/acs.langmuir.7b02836>.
- 452 [36] J. J. I. Ramos, I. Llarena, S. E. Moya, Unusual collapse of highly hydrated polyelec-  
453 trolyte multilayers with the ionic strength, *Journal of Polymer Science Part A: Polymer*  
454 *Chemistry* 49 (11) (2011) 2346–2352. doi:<https://doi.org/10.1002/pola.24662>.
- 455 [37] R. A. Ghostine, M. Z. Markarian, J. B. Schlenoff, Asymmetric growth in polyelec-  
456 trolyte multilayers, *Journal of the American Chemical Society* 135 (20) (2013) 7636–  
457 7646. doi:[10.1021/ja401318m](https://doi.org/10.1021/ja401318m).
- 458 [38] G. Ladam, P. Schaad, J. C. Voegel, P. Schaaf, G. Decher, F. Cuisinier, In situ deter-  
459 mination of the structural properties of initially deposited polyelectrolyte multilayers,  
460 *Langmuir* 16 (3) (2000) 1249–1255. doi:<https://doi.org/10.1021/la990650k>.