Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Environmental Science
Nano

www.rsc.org/es-nano

ROYAL SOCIETY
OF CHEMISTRY

ROYAL SOCIETY
OF CHEMISTRY

rsc.li/es-nano

Heteroaggregation of Bare Silver Nanoparticles with Clay Minerals

Jibin Liu, Yu Sik Hwang[1] and John J. Lenhart[*]

Department of Civil, Environmental and Geodetic Engineering

The Ohio State University, Columbus, OH 43210, United States

[1]Future Environmental Research Center, Korea Institute of Toxicology, Jinju 660-844, Republic of Korea

*Corresponding Author, Tel.: +1-614-688-8157; Fax: +1-614-292-3780.

Email: lenhart.49@osu.edu

Nano Impact Statement

Understanding how nanoparticles interact with other particulate material in aqueous systems is essential to assess the fate of nanoparticles because these interactions directly or indirectly affect nanoparticle form, concentration, and aggregation. Clays are one of the dominant naturally occurring particle classes in aqueous system. Thus, in this study we investigated the heteroaggregation of silver nanoparticles with two clay minerals in neutral pH solutions. Our results suggest the binary clay-nanosilver systems behave nearly the same as the clay-only systems under the experimental conditions studied. Thus, to account for the influence of native particles, such as clays, on the fate of silver nanoparticles in aqueous system may simply require the understanding of the aggregation behavior of the clay minerals.

TOC Artwork
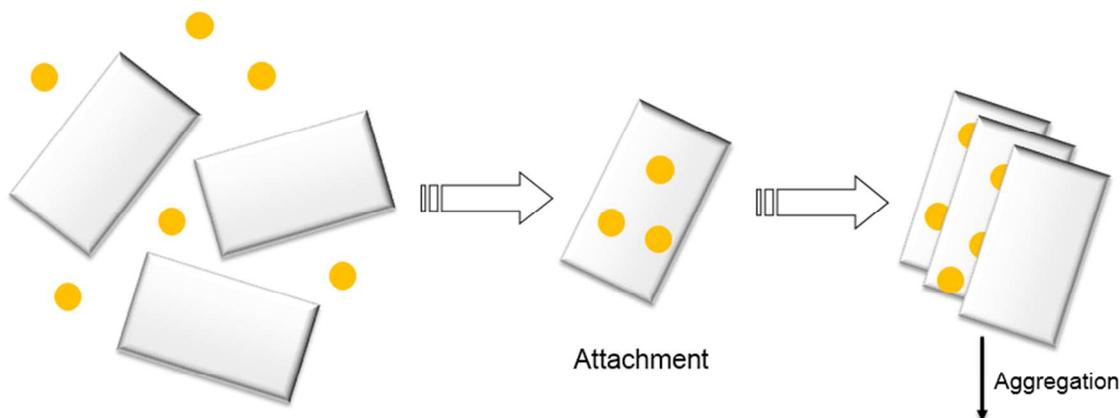
Attachment

Aggregation

Abstract

In this study, we investigated the heteroaggregation of silver nanoparticles with clay minerals in neutral

pH solutions as a function of electrolyte type and concentration. Bare nanoparticles with a nominal

diameter of 60.9 ± 0.5 nm were synthesized and their aggregation behavior with illite (IMt-2) and

montmorillonite (SWy-2), pretreated to obtain monocationic (Na-clay) and dicationic (Ca-clay)

suspensions, was studied. Aggregation was monitored as a function of electrolyte concentration in both

homo- and heteroaggregation scenarios by measuring the change in hydrodynamic diameter as a function

of time using dynamic light scattering. Our results did not show significant differences in the stability of

binary component systems of bare silver nanoparticle and clays at pH 7 when compared to the single

particle systems of clay or silver at the same pH. In each case, high electrolyte concentrations were

needed to overcome the energy barrier to form aggregates, which we attribute to weakly charged or

negatively charged clay edges, negatively charged silver nanoparticles, as well as the permanently

negatively charged basal plane surfaces of the clays at pH 7. The results suggest that a binary system of

clay (either montmorillonite or illite) and bare silver nanoparticles can be treated as a single component

system of the respective clay under the experimental conditions studied, and the fate of silver

nanoparticles in aqueous system may be controlled by their heteroaggregation with native particles, such

as clays.

Introduction

Engineered nanoparticles are intentionally produced particles with a size less than 100 nm. Owing to this small size, the particles' properties are drastically different from those for the bulk material of the same composition[1]. As the application of nanotechnology has increased, many engineered nanoparticles have been introduced to products used in our daily lives. Due to this fact, questions arise about nanoparticle release to the environment during product use or disposal as well as the potential of these released particles to cause adverse effects to the environment and human health[1, 2]. Routes of entry to the environment may originate from point sources such as factories, or from non-point sources such as wet deposition, storm water runoff, and the degradation or disposal of discarded nanomaterial-containing products[3]. In aqueous systems, the fate of engineered nanoparticles is controlled by physical transport (e.g., advection or sedimentation), chemical or biological transformation (e.g., oxidation-reduction or dissolution) and particle interaction (e.g., heteroaggregation) processes[4]. These processes can act independently or mutually and their role in determining the fate of nanoparticles remains poorly understood[2, 3]. An accurate determination of fate is critical to determining the risk of nanoparticles to humans, organisms, and the environment[3].

Among metallic nanoparticles currently being produced and utilized, silver nanoparticles (AgNPs) are unique in their widespread and extensive use in commercial products[5]. This reflects their utility as non-specific antibiotics and thus they are utilized in products (e.g., clothing, food containers, wound dressings, etc.) that exploit this effect for beneficial purposes[6]. When used, however, these products release nanoparticles and these nanoparticles can be discharged into the environment[6]. The properties that make AgNPs useful in commercial products could produce unforeseen adverse effects on aquatic biota and thus there is considerable interest in determining the mechanisms and processes responsible for dictating AgNP fate in different settings, such as aquatic environments[7]. One of the dominant processes affecting the fate of AgNPs in aquatic systems is aggregation and recent research provides insight into the effects of electrolyte type, ionic strength, coating layer and organic matter on the aggregation of AgNPs[8-10]. For example, NaCl, NaNO$_3$, and CaCl$_2$ produce "dissolution-accompanied" aggregation of silver

44   nanoparticles, meaning the particles simultaneously aggregate and dissolve[10]. More dissolution occurred

45   in chloride-containing AgNPs suspensions and the aggregates formed had smooth continuous surfaces,

46   while discrete aggregates were formed in nitrate-containing suspensions[10]. Aggregation of AgNPs is a

47   function of the capping layer, with AgNPs coated with large organic molecules such as the surfactant

48   Tween resisting aggregation more than those coated with smaller organic molecules, such as citrate or

49   sodium dodecyl sulfate[9].

50   While these and similar studies provide insight into the environmental fate of AgNPs, they do so

51   based on the analyses of model systems that do not necessarily correspond well with natural systems. For

52   example, these studies do not account for interactions that may arise between silver nanoparticles

53   introduced into a system and native particles that are already present in a system, a process termed

54   heteroaggregation.   Heteroaggregates   form   between   two   or   more   dissimilar   particles   and

55   heteroaggregation is thus used to describe the stability of particle suspensions that contain more than one

56   type of particle which may differ in size, shape, surface charge, etc.[11]. One of the more dominant native

57   particle types in aquatic systems are clay minerals[12] and thus an initial attempt to study the influence of

58   heteroaggregation on AgNPs should naturally start by characterizing interactions between AgNPs and

59   clay minerals.

60   Heteroaggregation has been researched for years and several studies have evaluated nanoparticles.

61   Yates et al.[13], for example, determined that adding nano-sized silica particles (4.3–285 nm) to stable

62   alumina dispersions produced large aggregates that readily settled out. Cerbelaud et al.[14] also found

63   heteroaggregates formed between submicrometer Al_2O_3 particles and SiO_2 nanoparticles as silica

64   nanoparticles depositing on the alumina particles produced attractive interactions between the now silica-

65   coated alumina particles.   Since the two particles were oppositely charged, the resulting process was

66   conceptualized by the following two steps: 1) deposition of the silica nanoparticles on alumina particles

67   and 2) aggregation of the silica-covered alumina particles[14]. Comparable studies with AgNPs are limited

68   and have only recently been studied. In studying interactions between AgNPs and hematite Huynh et al.[15]

69   observed rapid heteroaggregation that far exceeded that for the single-particle systems. This result was

2

70   similar to that observed by Yates et al.[11] and Cerbelaud et al.[12] and is a reflection of the attractive

71   electrostatic interactions between the two particles in these systems. Zhou et al.[12] report similar results in

72   their study of the heteroaggregation of AgNPs with montmorillonite at pH 4 where the edge sites of the

73   clay carry a positive charge. However, at pH 8 they report that mixed montmorillonite-Ag system

74   aggregation behavior was little changed compared to those for the single-particle systems. They attribute

75   this observation to the repulsive electrostatics that exist between the AgNPs and the clay face and edge

76   sites observed faster aggregation in a binary system of AgNPs and montmorillonite.

77   In this study, two common clay minerals, montmorillonite and illite, were chosen to evaluate their

78   effects on the heteroaggregation of AgNPs. These minerals are both 2:1 type clays, with one octahedral

79   alumina sheet sharing oxygen atoms with two tetrahedral silica sheets[16-18]. Montmorillonite is distinct

80   from illite in its ability to expand when it contacts water due to it lacking strongly held potassium ions in

81   the interlayer region and thus its ratio of edge to basal plane sites is greater than illite[14]. The basal planes

82   of clay lamella carry a permanent negative charge due to isomorphic substitution of Si- and Al-ions for

83   ions of lower valence, while the charge of the lamella edge is pH-dependent because of pH-dependence in

84   the exposed >Al-OH and >Si-OH surface groups[16]. The edge is positively charged when the pH is below

85   the point of zero charge (PZC) of the exposed functional groups and negatively charged when the pH is

86   above the PZC[16, 19-21]. Extensive experimentation on the aggregation of clay minerals (see Table S1)

87   shows their behavior follows expected trends and depends upon pH, electrolyte solutions, ionic strength,

88   and saturating cations[16, 19-21]. In the case of montmorillonite and illite, the greater proportion of illite edge

89   sites to basal plane sites results in it exhibiting aggregation tendencies that vary with the nature of the

90   saturating cation[14]. Although the heteroaggregation of clay particles with other nanoparticles has been

91   studied[22, 23], except for the study of Zhou et al.[12] the aggregation of clay minerals with AgNPs remains

92   little understood.

93   The overall goal of our research is to elucidate the fundamental processes that control the fate of

94   silver nanoparticles in natural aquatic environments, with the specific objective of this study being to

95   evaluate the influence of heteroaggregation. We focus our attention in this paper on expanding progress

96   made toward understanding the heteroaggregation of silver nanoparticles with clay minerals presented by

97   Zhou et al.[12], by comparing results with two clay minerals (montmorillonite and illite) as a function of

98   saturating cation (Na^+ and Ca^{2+}) and electrolyte (NaCl, $NaNO_3$ or $CaCl_2$). Although montmorillonite and

99   illite are structurally similar, the non-expanding nature of illite produces aggregation behavior with

100   greater dependence on solution composition than that for montmorillonite (see Table S1).   Thus, we

101   hypothesize that illite interactions with AgNPs will exhibit a greater dependence on solution composition

102   (e.g., saturating cation) than will montmorillonite. To facilitate comparisons to the conditions in this study

103   were the same as those previously used to evaluate the homoaggregation of silver nanoparticles[10]. Our

104   results did not show significant differences in the stability, as defined by the critical coagulation

105   concentration (CCC), of binary systems of silver nanoparticle and clays when compared to the single

106   component systems under the same conditions. They also did not exhibit much dependence on the clay

107   mineral or saturating cation, which was counter to our original hypothesis.   Instead, the broader

108   aggregation behavior of the binary systems closely mimicked that for the clay minerals and thus we

109   propose under conditions present in natural systems (e.g., circumneutral pH and excess concentration of

110   natural particles) that the aggregation kinetics of binary systems with AgNPs and natural particles, such as

111   clays, can be approximated based upon knowledge of just the single component clay systems.

112

Experimental Details

114   **Materials**

115   $AgNO_3$ ($\geq$99.8%) and D-maltose monohydrate (99%) were purchased from Sigma-Aldrich and used as

116   received. Ammonium hydroxide (20-22% as NH_3, trace metal grade) was bought from Fisher Scientific.

117   All other reagents were analytical grade or higher. All experiments used deionized water (Millipore Milli-

118   Q) with a resistivity of 18.2 MΩ·cm. The electrolyte solutions (NaCl, $NaNO_3$, and $CaCl_2$), buffer solution

119   ($NaHCO_3$), and solutions employed in silver nanoparticle synthesis were filtered through 0.1 μm cellulose

120   ester membranes (Millipore) before use. All labware and glassware were thoroughly cleaned and soaked

121 in 5% nitric acid for at least one day before use, followed by a thorough rinse with deionized water and

122 oven-drying. The labware was immediately used or stored in a dust-free environment prior to use.

123

124 **Clay Preparation**

125 Montmorillonite (SWy-2) and illite (IMt-2) were obtained from the Clay Minerals Society and prepared

126 as monocationic suspensions following established protocols[24, 25]. To begin, 5g of each clay in 250mL

127 deionized water was rapidly mixed for 45 min. The less than 2 μm size fraction was isolated into the

128 supernatant by overnight gravity sedimentation. The supernatant was decanted and the electrolyte

129 concentration was adjusted to be 1M NaCl. For montmorillonite, this step was followed by a rapid 15

130 minute mix, whereas for illite the suspension was adjusted to pH 3 with 10% HCl and stirred for two

131 hours. The clays were separated from their respective suspensions through centrifugation at 3600 rpm for

132 30 min. The supernatant was decanted and fresh 0.01M NaCl was added. The clay suspensions were

133 vigorously shaken to re-suspend the clay particles and subsequently centrifuged once again at 3600 rpm

134 for 30min. This washing procedure was repeated 5 times. The suspensions were dialyzed against 0.01M

135 NaCl. The solution was changed daily until the conductivity of the clay suspension was the same as the

136 0.01M NaCl.

137 Calcium-saturated clay samples were prepared following the methods previously described with the

138 exception that NaCl was replaced with $CaCl_2$. All of the clays were stored as concentrated suspensions in

139 the dark at 4 °C.

140

141 **Silver Nanoparticle Synthesis**

142 Monodisperse suspensions of silver nanoparticles were synthesized following Li et al.[10]. In short, 2 mL of

143 0.01M $AgNO_3$ was pipetted into a 50 mL glass beaker followed by 10 mL of 0.02M ammonium

144 hydroxide. The solution was stirred using a small Teflon-coated magnetic stir bar. The solution pH was

145 adjusted to ca. 11.5 through the addition of 250 μL of 0.1M NaOH, after which 8 mL of 0.025M D-

146 maltose was introduced to reduce the $Ag[(NH_3)_2]^+$ complex to form metallic silver nanoparticles. After

5

147   the addition of all reagents, the suspension was equilibrated for 30 min in the dark at room temperature

148    $(20 \pm 1 \,°C)$.

149   The freshly synthesized silver nanoparticles were dialyzed against deionized water using a cellulose

150   ester membrane (Spectra/Por, 8-10k MWCO) over a period of 24 hours. The deionized water was

151   changed a minimum of 4 times, which Li. et al.[10] report is sufficient time to remove residual ions. Six

152   such batches of silver nanoparticles were synthesized and combined to form the stock suspension which

153   was stored in a polypropylene bottle in the dark at 4 °C. The concentration of the stock suspension,

154   determined using an inductively coupled plasma optical emission spectrometer (Varian Vista AX), was 60

155   mg-Ag/L which corresponds to an approximate yield of 55% of the initial Ag.

156

157   **Particle Characterization**

158   The hydrodynamic diameter and UV-vis spectrum of the silver nanoparticles was determined on a sample

159   that was diluted by 25 times in a sodium bicarbonate – sodium chloride buffer solution that maintained

160   the pH at 7.0 ± 0.3 and ionic strength at 1mM. The hydrodynamic diameter was measured by dynamic

161   light scattering (DLS) (90Plus, Brookhaven Instruments Corp., Holtsville, NY). The UV-vis spectrum

162   was collected over the wavelength range of 200 – 700 nm using a Shimadzu UV-4201PC UV-vis

163   spectrophotometer.

164   The morphology and size of the dispersed silver nanoparticles and clays were imaged using a Technai

165   G2 Spirit Transmission Electron Microscope (TEM) with a 120 kV electron beam. Samples were

166   prepared by placing one drop of the working suspension on a 100 mesh copper grid that was dried under

167   nitrogen. Samples of dispersed silver nanoparticles and clays were prepared using concentrated stock

168   suspensions which were sonicated before use. The morphology of the heteroaggregates was also

169   evaluated using the TEM, where one drop of the suspension generated from the heteroaggregation

170   experiments was used instead.

171   The electrophoretic mobility of Na-/Ca-montmorillonite and illite was measured by a Brookhaven

172   Instrument Corp. ZetaPALS instrument. The Smoluchowski equation was used to calculate the zeta

6

173 potential from the corresponding mobility values for a particle of arbitrary shape with a nominal diameter

174 that is much larger than the thickness of the electrical double-layer[26]. The measurements were conducted

175 at a temperature of 22 ± 0.5 °C across the pH range of 4.0 - 10.0 in 1mM NaCl solutions. The samples

176 were equilibrated for 5 min and for each pH value the data comprised ten individual measurements

177 collected and averaged for three separate samples. The effects of NaCl (0.1mM – 10mM) and $CaCl_2$

178 (1mM – 500mM) on the electrophoretic mobility of the clay minerals were evaluated as well at pH 7.

179 **Aggregation Kinetics**

180 Aggregation kinetics for both the homoaggregate and heteroaggregate systems was determined by

181 measuring the initial time rate of change in the average hydrodynamic radius of the particle suspensions

182 using DLS. The instrument was equipped with a 678 nm laser with a detection angle of 90 degrees and

183 the experiments were conducted at a temperature of 22 ± 0.5 °C.

184 All working suspensions were prepared by diluting stock suspensions in a 0.05 mM sodium

185 bicarbonate buffer at pH 7.0 ± 0.3. Individual particle concentrations were kept the same for both the

186 homoaggregation and heteroaggregation experiments. This entailed diluting the stock particle suspensions

187 when preparing the working suspensions for the heteroaggregation experiments with a particle

188 concentration twice that for the homoaggregation experiments (see Table S2). All working suspensions

189 were briefly sonicated in an ultrasonic water bath before each experiment.

190 For the homoaggregation experiments, 3 mL of the particle suspension of interest was pipetted into a

191 disposable acrylic cuvette. The cuvette was prepared before use by washing using 5% HNO_3 followed by

192 a thorough rinse with deionized water. Predetermined amounts of electrolyte and buffer solutions were

193 added to the cuvette to obtain the desired ionic strength, while maintaining the total volume at 4 mL. The

194 cuvette was covered with a plastic lid, quickly hand-shaken and inserted into the DLS sample holder. The

195 heteroaggregation experiments were the same except that 1.5 mL of silver nanoparticles and 1.5 mL of

196 the clay suspensions of interest were used. In either case, measurements begun immediately upon

197 inserting the cuvette into the DLS. For silver nanoparticle systems, measurements were collected over a

198   period of 15 min with 90s intervals between measurements, while single clay and binary component

199   systems were measured over a period of 5 min with 30s intervals between measurements.

200   The stability of the suspensions was analyzed by comparing variations in the inverse stability ratio

201   (1/W) with ionic strength where 1/W is defined as the ratio of the experimental aggregation rate constant

202   (k_{exp}) to that determined for rapid aggregation (k_{rapid}), or diffusion-limited aggregation, as shown in the

203   following expressions[27]:

$$k_{exp} = \frac{1}{aNr_0}\frac{dr}{dt} \tag{1}$$

$$\frac{1}{W} = \frac{k_{exp}}{k_{rapid}} \tag{2}$$

206   where N is the initial particle concentration, r_0 is the initial particle radius, and a is an optical factor. The

207   k_{exp} value was calculated by conducting a linear least-squares regression analysis on the time-rate of

208   change of the hydrodynamic radius (dr/dt), while the k_{rapid} value was determined as the average value of

209   the k_{exp} values under diffusion-limited aggregation conditions. This latter value was specific to each

210   homoaggregation or heteroaggregation system and electrolyte. The relationship between 1/W and ionic

211   strength was used to identify the critical coagulation concentration (CCC) for each system and it was

212   determined as the intersection point of two straight lines that represent the change of 1/W as a function of

213   ionic strength in the reaction and diffusion-limited aggregation regimes, respectively[26].

214

Results and Discussions

Silver Nanoparticle Characterization

217   The hydrodynamic diameter of the silver nanoparticles determined by DLS was 60.9 ± 0.5 nm. TEM

218   images show the silver nanoparticles' morphology as smooth and roughly spherical with a diameter

219   similar to that measured by DLS (Figure S1a). Based on this size, the concentration of the stock

220   suspension (60 mg Ag L^{-1}), and the density of metallic silver (10.5 g cm^{-3}), we calculated a particle

221   concentration for the stock suspension of 5×10^{10} particles mL^{-1}. Based on the dilutions used to prepare

222 working solutions (see Table S2), the silver nanoparticle concentration used in aggregation experiments

223 was 1.5×10^9 particles mL^{-1}.

224 The UV-vis spectrum (Figure S1b) of freshly synthesized silver nanoparticles showed a maximum

225 absorption peak at a wavelength of 433 nm, which was consistent with the reported location of the surface

226 plasmon absorption band of silver nanoparticles synthesized using this method[28]. The observed red-shift

227 in the position of the absorption peak compared to that for monodispersed silver nanoparticles with a

228 diameter below 100 nm with no adsorbed or oxidized layer, as well as the broadening of the absorption

229 band provide evidence for the existence of an oxidized layer on the particle surface[10].

230 According to Li. et al.[10], the silver nanoparticles synthesized with this method have a negative zeta

231 potential across the pH range of 4.0 to 10.0 that remains relatively unchanged at -45.8 ± 0.9 mV in 1 mM

232 NaCl. Li et al.[10] rationalize the measured negatively charged surfaces may reflect the existence of an

233 oxide surface layer and the adsorption of anions during synthesis. Increasing the electrolyte concentration

234 or valence of the electrolyte cation decreased the magnitude of the zeta potential[10], reflecting the increase

235 in charge screening under these conditions.

236

237 **Clay Mineral Characterization**

238 *Characterization of Montmorillonite*

239 The diameter of dispersed montmorillonite lamellae ranged from 200 nm to 700 nm (Figure S2a),

240 consistent with the method of preparation[24]. From the DLS measurement of the suspensions, however,

241 the most predominant hydrated particle size for both forms of montmorillonite was ca. 200 nm. This size

242 reflects the implied assumption that the particles were spherical as DLS determines the rotationally

243 averaged particle size. Particle sizes determined using DLS are more sensitive to the major dimension of

244 the particle than they are to the minor dimension and thus we were not able to discern any differences in

245 thickness of the clay lamella for Na- or Ca-montmorillonite. According to Schramm and Kwak [29] these

246 differences are on the order of ca. 5, with Ca-forms of the clay being thicker. The concentrations of the

247 Na- and Ca-montmorillonite (Na-MONT and Ca-MONT) stock suspensions were determined by

9

248   gravimetric analysis as 25 g L^{-1} and 41 g L^{-1}, respectively. Using the spherical size determined from DLS

249   for these particles of 200nm and a density of 2.35 g cm^{-3} we estimated particle concentrations in our stock

250   clay suspensions of ca. 3×10^{15} particles mL^{-1} for Na-MONT and 4×10^{15} particles mL^{-1} for Ca-MONT.

251   The assumption of a spherical dimension may result in a lower particle concentration since it does not

252   represent the true particle size or morphology. Based upon the dilutions used (see Table S1), the

253   concentration of Na-MONT in the aggregation experiments was 7.6 x 10^9 particles/mL and that for Ca-

254   MONT was 6.3 x 10^9 particles/mL.

255   The zeta potential of the sodium- and calcium-forms of the montmorillonite in 1 mM NaCl remained

256   unchanged at -46.5 ± 7.14 mV and -22.6 ± 2.88 mV, respectively, across the pH range 4.0 to 10.0 (Figure

257   1). These results were consistent with those published for this montmorillonite suspended in NaCl[12, 30].

258   Under the experimental conditions studied, the zeta potential of Ca-montmorillonite was less negative

259   than that for Na-montmorillonite. Montmorillonite has a higher affinity for Ca^{2+} than Na^+ and the bound

260   Ca2+ can suppress the negative charge of the basal planes [30, 31] Given time, the bound Ca^{2+} could be

261   displaced when Ca-montmorillonite was dispersed in NaCl, but since the electrolyte concentration (1mM)

262   was too low and the time during sample preparation (less than 30 min) was too short such ion exchange

263   was not fully completed[30].

264   The zeta potential of both forms of montmorillonite were measured across the NaCl and CaCl$_2$

265   concentrations corresponding to those studied in the aggregation experiments (Figure 2a). At low

266   electrolyte concentration, the zeta potential for Ca-montmorillonite was less negative than that for Na-

267   montmorillonite. As the electrolyte concentration increased, however, the zeta potential for both forms of

268   the clay converged to similar values. The same trend existed for both CaCl$_2$ and NaCl. It was more

269   pronounced for NaCl, however, as the zeta potential of Na-montmorillonite became less negative as NaCl

270   increased from 30mM to 500mM. Likely, this just reflects compression of the electrical double layer at

271   elevated electrolyte concentration[26]. Below 30 mM NaCl, the absolute value of the zeta potential of Na-

272   montmorillonite increased from ca. 40mV to ca. 65mV. According to Delgado et al.[32] this reflects

273   montmorillonite can undergo rapid hydrolysis at circumneutral pH, whereby H$^+$, exchanged for bound

274   Na$^+$, induces the release of Al^{3+} and Mg^{2+} from montmorillonite which could produce the observed

275   increase in the magnitude of the zeta potential. Hydrolysis is distinct from mineral dissolution, which

276   occurs slowly (e.g., Metz et al.[33]), and is partially driven by the accumulation of H$^+$ at the clay interface

277   needed to satisfy electroneutrality in the system[23,24]. Delgado et al.[32] described this hydrolysis as two steps:

278   (1) a rapid exchange of hydrogen ions in the solution with Na$^+$ originally attached to the montmorillonite

279   and (2) a slow penetration of the exchanged H$^+$ into the sheets of montmorillonite. The penetrating

280   hydrogen ions induce the release of Al^{3+} and Mg^{2+} from montmorillonite into the solution. The released

281   multivalent cations could also compress the electrical double layer which would reduce the magnitude of

282   zeta potential. At the same time, however, the loss of these cations would decrease the zeta potential of

283   montmorillonite. The determination of the electrophoretic mobility, hence zeta potential, is also

284   influenced by the high surface conductivity of montmorillonite which is reported to also produce low

285   absolute values under dilute electrolyte conditions[34]. Thus, the observed decrease of zeta potential of clay

286   was likely the net result of these combined actions. The hydrolysis process is kinetically hindered at

287   elevated electrolyte concentrations and thus it tends to be observed at electrolyte concentrations less than

288   10^{-3} M[32, 35, 36]. Callaghan and Ottewill[37] and Rossi et al.[38] observed different trends in the zeta potential

289   that entailed a decrease (increase in the magnitude) at NaCl concentrations above 10^{-2} M. Rossi et al.[38]

290   attribute this to particle dissolution and ion release. Finally, aggregation of the montmorillonite during

291   the five minute equilibration time prior to the zeta potential determinations was possible, particularly at

292   electrolytes equal to or greater than 30 mM, and it could also have influenced these measurements.

293   Considering the obvious sensitivity of clay surfaces to methods of preparation and storage[36], our results

294   were similar in magnitude to those previously reported.

295   When Ca-montmorillonite was suspended in 1 to 30 mM NaCl, a similar trend of decreasing zeta

296   potential with increasing NaCl concentration resulted. However, in this case the origin of the trend not

297   only reflects hydrolysis and surface conductance, but also the exchange of Ca^{2+} bound to the clay with

298   Na$^+$ ions in the solution. This net loss of bound cation charge could produce a lower zeta potential. The

299   time needed for complete replacement of Ca^{2+} by Na$^+$ is reported to be around 24 h[36] and presumably

11

300 given sufficient time the two data sets would converge. Since the equilibration time was much less than

301 24 hours, Ca-montmorillonite had a consistently higher (less negative) zeta potential than did Na-

302 montmorillonite.

303 In systems with $CaCl_2$, the zeta potential for Na-montmorillonite increased as the electrolyte

304 concentration increased (Figure 2a). This reflects both the exchange of bound Na^+ with solution phase

305 Ca^{2+} and the enhanced compression of the electrical double layer induced by the divalent calcium cations.

306 However, except for an increase in the standard error of the zeta potential with increasing electrolyte, no

307 significant change in the zeta potential of Ca-montmorillonite was observed in the range of 10^{-4} to 10^{-2} M

308 $CaCl_2$ (Figure 2a). While the reason for this result was not known with certainty, it was similar to results

309 presented in the literature[39] and may reflect the influence of particle aggregation during the preparation of

310 the samples prior to these measurements .

311

312 *Illite Characterization*

313 The illite flakes ranged in size from roughly 50 to 200 nm and differed from montmorillonite in that illite

314 had irregular and curved outlines (Figure S2b). In some locations, individual illite lamella appeared to

315 orient perpendicular to the imaging plane, and the resulting cluster of illite flakes formed a wheel-like

316 formation. This wheel-like structure indicates an edge-to-face orientation of illite which allows small

317 angles between each flake (sub-parallel orientation). Similar images exist for illite in both distilled and

318 saline water[40]. Except for these mostly isolated wheel-like formations, it appeared that the majority of the

319 illite was oriented face-to-face. The concentrations of Na- and Ca-illite in the respective stock

320 suspensions were 1.2 g L^{-1} and 3.6 g L^{-1}. Following the approach used for montmorillonite, a density of

321 2.75 g cm^{-3} and diameters measured from DLS of 135 nm for Na-illite and 270 nm for Ca-illite we

322 estimated particle concentrations in our stock clay suspensions of ca. 3×10^{14} particles mL^{-1} and 1×10^{14}

323 particles mL^{-1}, respectively. Based upon the noted dilutions (see Table S1), the concentration of Na-illite

324 in the aggregation experiments was 5.1 x 10^9 particles/mL and that for Ca-illite was 3.6 x 10^9

325   particles/mL. As previously noted, the assumption of a spherical particle likely resulted in an

326   underestimate of the illite particle concentration.

327   At pH 7, the zeta-potential of Na-illite was -44 ± 4mV while for Ca-illite it was -21 ± 2mV (Figure 1).

328   Similar trends were found for the zeta-potential of illite in the pH range 4 to 10 as was measured for

329   montmorillonite. This was expected considering both clay minerals had the same basic structure. As was

330   observed for montmorillonite, the calcium-form of illite had a less negative zeta potential than did the Na

331   form, reflecting the presence of the bound divalent cations.

332   The zeta potential for both Na- and Ca-illite generally increased (trend to a less negative value) as the

333   NaCl concentration increased from 1mM to 500mM (Figure 2b). Unlike what was observed for Na-

334   montmorillonite, however, no significant decrease in the zeta potential occurred for Na-illite below 30

335   mM NaCl. Illite is a nonexpanding clay[41] and although the 2:1 layer structure is similar to that for

336   montmorillonite, the cation exchange capacity (CEC) of illite is lower than that of montmorillonite[39]. The

337   CEC of the montmorillonite in this study is 1040 mmol kg^{-1} [24], while that for illite is 231 mmol kg^{-1} [25],

338   reflecting the smaller amount of internal cations (i.e., potassium ions) available for release from illite than

339   montmorillonite[42]. Thus, the decrease in the magnitude of the negative zeta potential as NaCl was

340   increased from 1 mM to 500 mM likely reflects compression of the electrical double layer induced by the

341   increasing electrolyte. Similar to Ca-montmorillonite, the exchange of clay-bound Ca^{2+} associated with

342   Ca-illite with solution-phase Na^+ remains possible and if it occurred it could have produced the reduction

343   in the magnitude of the zeta potential at NaCl below 30 mM.

344   The effect of $CaCl_2$ on the zeta potentials of both Na- and Ca-illite (Figure 2b) reveals illite has a

345   higher affinity for Ca^{2+} than Na^+. Since illite is a nonexpanding clay, suspending Na-illite in $CaCl_2$ was

346   assumed to lead to more rapid and complete exchange of Na^+ with Ca^{2+} than that for Na-montmorillonite.

347   As a result, the zeta potential of Na-illite was very close to that for Ca-illite from 1mM to 10mM $CaCl_2$.

348

349   **Homoaggregation of Single Component Systems**

350   *Homoaggregation of Silver Nanoparticles*

351   The aggregation behavior for the silver nanoparticles exhibited trends consistent with that previously

352   observed[8c] to indicate coincident particle dissolution and particle aggregation (Figures 3a and 3b). In the

353   monovalent electrolyte solutions, the initial particle diameter decreased as the electrolyte concentration

354   increased from 10mM to 200mM. However, since the dissolution of silver nanoparticles was

355   accompanied by aggregation, this initial decrease in size was soon followed by an overall increase with

356   time as aggregation of the particles proceeded. Li. et al.[10] reported the size decrease to be the result of the

357   dissolution of an oxidized surface layer evident in the absorption spectrum (see Figure S1b). According to

358   Li et al.[10], this reaction is influenced by the concentration and type of electrolyte. When the electrolyte is

359   NaCl, $AgCl_{(s)}$ precipitates on the nanosilver particle surface, resulting in a modification of the silver

360   nanoparticles morphology[10]. $NaNO_3$, however, did not produce a precipitate nor did it change aggregate

361   morphology[10]. Regardless, the aggregation of nanosilver in these two electrolytes was similar (Figures 3a

362   and 3b) and was consistent with other data presented in the literature[10, 43, 44]. In our experiments, the CCC

363   of silver nanoparticles in NaCl was ca. 40mM, while it was ca. 35mM in $NaNO_3$. These results were

364   consistent with those presented by Li. et al.[10, 43, 44] indicating the AgNPs synthesized in these experiments

365   behaved similarly to those in previous studies.

366   When the electrolyte was $CaCl_2$ the CCC of silver nanoparticles was much lower (ca. 2mM) than that

367   in $NaCl/NaNO_3$ (Figure 4). According to the Schulze-Hardy rule[26], $CCC_{[Na]}/CCC_{[Ca]}$ equals z^6 for particles

368   with a large zeta potential ($|\xi| > 50mV$), and z^2 for those with a low zeta potential ($|\xi| < 50mV$), where z is

369   the counterion charge (i.e., $z = 2$ in the case of Ca^{2+}). In our experiments, the ratio of $CCC_{[Na]}$ and $CCC_{[Ca]}$

370   was approximately proportional to z^4. This intermediate value between the two predicted by the Schulze-

371   Hardy rule (i.e., z^6) is consistent with previous measurements, and according to Li et al.[9, 10] indicates the

372   modification of surface charge due to the adsorption of cations on the surface of the silver nanoparticles.

373

374   *Homoaggregation of Montmorillonite*

375   Although the trends in zeta potential for sodium-saturated montmorillonite did not exhibit typical trends

376   (Figure 2a), the aggregation kinetics did approximate Derjaguin-Landau-Verwey-Overbeek (DLVO) type

14

377 aggregation kinetics (Figure 5a). DLVO-type aggregation refers to aggregation controlled by the

378 combined influence of electrostatics and van der Waals interactions[45, 46]. At low electrolyte

379 concentrations (e.g., 1 - 50 mM NaCl or 0.5 - 1 mM CaCl$_2$), an increase in the electrolyte concentration

380 led to a corresponding increase in the aggregation rate (Figure 5a). Above these electrolyte concentrations,

381 the aggregation rate reached a maximum value that did not significantly vary as the electrolyte

382 concentrations increased. For a monovalent electrolyte, similar CCC values of ca. 50 mM were

383 determined for Na-montmorillonite in NaCl and NaNO$_3$ (Figure 5a). This CCC value was comparable to

384 those reported by Tombácz et al., of ca. 25, 50, and 100 mM NaCl at pH 4, 6.5, and 8, respectively[19]. The

385 pH of 6.5 approximates the PZC of clay edges[12] where the edge transitions between positive and negative

386 charged states[19]. When the pH is below the PZC of the edge, the clay edge is positively charged and its

387 interaction with the negatively charged clay face becomes significant and decreases the stability of the

388 montmorillonite suspension. When the pH is above the PZC of the edge, both the edge and basal plane of

389 the clays are negatively charged edge-face interactions are limited resulting in an increase in the stability

390 of the suspension. Thus, our montmorillonite CCC at pH ~ 7 was similar to that reported in the literature

391 at a similar pH value, which is near the PZC of the clay edge.

392 In CaCl$_2$, the CCC value of Na-montmorillonite was estimated at 1.5 mM (Figure 5a). The ratio of the

393 CCC$_{[Na]}$/CCC$_{[Ca]}$ was 33:1, proportional to z^5, which was similar with that predicted by the Schulze-Hardy

394 rule of z^6 [47]. The difference could reflect the difficulty in preparing a pure monocationic montmorillonite

395 due to the potential release of multivalent cations (Mg^{2+}, Al^{3+}) from the clay minerals[47]. It could also

396 reflect exchange of surface cations with the added electrolyte cation during aggregation[31, 48].

397 The same CCC of ca. 50 mM NaCl or NaNO$_3$ and ca. 2mM CaCl$_2$ were observed for both Na-

398 montmorillonite and Ca-montmorillonite at pH ~7 (Figure 5b). The cation used to saturate the basal

399 surface planes of montmorillonite had little to no impact on the suspension stability (Figure S3), which

400 was consistent with the similar values of zeta potentials for Na- and Ca-montmorillonite (Figure 2a). The

401 ratio of CCC$_{[Na]}$/CCC$_{[Ca]}$ for Ca-montmorillonite was 25:1, or approximately $z^{4.6}$, which was close to that

402 of Na-montmorillonite. A similar result was obtained by Tombácz et al.[31] and as a result they

403   hypothesized that montmorillonite aggregation depends only on the electrolyte, not the original cations

404   present in the montmorillonite. This was also consistent with the reported CCC of 70 mM for Mg-

405   montmorillonite at pH 7 in KCl [49].

406

407   *Homoaggregation of Illite*

408   Typical two-regime, DLVO-type aggregation kinetics were also observed for Na- and Ca-illite in NaCl,

409   NaNO$_3$ and CaCl$_2$ (Figure 6a and 6b). CCCs of ca. 70mM NaCl or NaNO$_3$ and ca. 2mM CaCl$_2$ were

410   determined for Na-illite at pH 7, while for Ca-illite the values were ca. 50mM NaCl or NaNO$_3$ and ca.

411   1mM CaCl$_2$. Literature data for Na-illite aggregation at neutral pH conditions is limited and quite variable

412   with reported CCC values of Na-illite varying from 7 to 40 mM NaCl at pH 7[21, 47, 50, 51]. This variation

413   likely reflects the different illite sources and sample preparation. For example, Hesterberg et al.[21] prepared

414   their sample by first washing it with concentrated NaClO$_4$ and KClO$_4$ solutions, followed by a

415   NaClO$_4$/HClO$_4$ wash at pH 3.5 and then concluding with equilibration in NaClO$_4$. The KClO$_4$ was used to

416   maintain the illite's structural K. In the end, their illite samples prepared as stock suspension at pH 7

417   contained residual Na$^+$ and K$^+$. These residual ions may have decreased the CCCs of illite samples in their

418   experiments, as they reported a CCC of 30mM NaClO$_4$ at a pH of 7.5. Only homoionic aggregation data

419   is available for Ca-illite[52], with a CCC value for Ca-illite of < 0.5mM CaCl$_2$. Based on these results, the

420   ratios of CCC$_{[Na]}$/CCC[Ca] for both the Na- and Ca-illite were $z^{5.13}$ and $z^{5.64}$, respectively. These were

421   close to those estimated from the Schulze-Hardy rule, with differences again possibly reflecting the

422   release of residual cations from the clays[47].

423   Similar to montmorillonite, the bound cation had little effect on the stability of illite (Figure S4). The

424   CCCs of Ca-illite and Ca-montmorillonite were similar, but the CCCs of Na-illite were slightly higher

425   than those for Na-montmorillonite (Table 1). Oster et al.[47] similarly observed the CCC of Na-illite was

426   higher than the CCC for Na-montmorillonite, while the CCCs of the two calcium forms of the clays were

427   similar. They concluded the irregular surfaces and terraced planar orientation (i.e., wheel-like orientation

428   in the TEM image of Na-illite in Figure S2b) of Na-illite lead to smaller edge-to-face attraction forces,

16

429   and eventually a higher CCC for Na-illite than for Na-montmorillonite. At the same time, the PZC of illite

430   ranges from 3.5 to 4.5[53-55] and thus considering its structure is similar to montmorillonite a higher CCC

431   value of illite than that of montmorillonite seems reasonable.

432

433   **Heteroaggregation of Binary Component Systems**

434   *Silver Nanoparticles and Montmorillonite*

435   The stability of the mixed silver nanoparticle and montmorillonite (either Na- or Ca-saturated) systems as

436   measured based on the position of the CCC was little changed compared to that for the single-particle

437   systems (Figure 7). At neutral pH, both the edge and the face of the montmorillonite flakes were

438   negatively charged[19]. The silver nanoparticles were also negatively charged under these conditions[10]. As a

439   result the aggregation behavior assumed a form characteristic of typical two-regime aggregation. TEM

440   imaging (Figure 8) of the mixture in 100mM NaCl indicates the silver nanoparticles self-aggregation was

441   limited, particularly when compared with that expected for 100 mM NaCl (see Li et al. [10]) and that many

442   were associating with the basal planes of the montmorillonite, but not the edges. This was consistent with

443   the negatively charged edge on the montmorillonite repelling the negatively charged silver nanoparticles.

444   The basal plane, while also negatively charged, was saturated with either Na^+ or Ca^{2+} ions which could

445   attract the silver nanoparticles[56]. Images collected at 10 mM NaCl not only indicate limited silver

446   nanoparticle self-aggregation, but also more limited interactions between the silver nanoparticles and the

447   clay minerals, as images collected showed the clay was devoid of deposited silver nanoparticles as well as

448   isolated silver nanoparticles (see Figure S6).

449   The rates of particle heteroaggregation at high electrolyte concentrations appeared to be dominated by

450   montmorillonite as the values for k_{rapid} for the binary-particle systems were similar to those for the

451   respective clay system as opposed to that for the silver nanoparticle system (See Tables S3 and S4). At

452   low electrolyte concentrations, however, the aggregation rates were intermediate between the two single

453   particle systems resulting in values for 1/W in the binary system being lower than those for either of the

454   single particle systems (e.g., see Figure 7a). These trends could reflect that the montmorillonite flakes

17

455   were roughly five times larger than the silver nanoparticles (Figures S1a and S2a) and the particle number

456   of montmorillonite was greater than that of the silver nanoparticles. It could also reflect non-DLVO

457   depletion force interactions that can form in binary systems that have a large ratio in particle sizes [12] when

458   the large particles are suspended in a dilute solution of the smaller ones[57]. It occurs when the distance

459   between two large particles is less than the diameter of the smaller particles resulting in the small particles

460   being pushed out to leave a "free volume" between the large particles. This "free volume" will then lead

461   to an imbalance of pressure around the large particles, which in turn may form either attractive or

462   repulsive forces between these same particles [58]. The attractive form of the depletion force can lead to the

463   flocculation of particles[57]. The limited change in the stability of the mixture compared to the clay-only

464   system suggests any such depletion force was negligible, if present at all, in this binary system.

465   Thus, we propose that as electrolyte concentrations approach the CCC for the respective binary

466   system that the heteroaggregation of silver nanoparticles and montmorillonite was comprised of two

467   simultaneous processes. The first entailed the deposition of the silver nanoparticles onto the

468   montmorillonite flakes, likely during the initial stage of the experiment[59]. In essence, montmorillonite acts

469   as a mobile collector in a manner that is analogous to the deposition of silver nanoparticles onto the

470   surface of sand[60] or silica[61] where silver nanoparticle deposition occurs at ionic strength values as low as

471   5 mM[42,43]. Since both the basal planes and the edges of montmorillonite were negatively charged at pH 7

472   as were sand[42] and silica[43] their interactions with the silver nanoparticles should be similar. Based on the

473   size of nanoparticles (~60nm) and clay particles (200 – 400nm), however, it seems more likely that the

474   basal planes of the clay particles provide sites for nanoparticle deposition. The second process involved

475   the aggregation of the combined NP-clay particles, which aggregate more or less at the same rate as that

476   for the clay-only systems. Because of the larger particle number concentration of montmorillonite, the

477   deposition of bare silver nanoparticles appears to have little effect on its stability as the CCC of the

478   heteroaggregate system was similar to that for the clay-only system.

479

480   *Silver Nanoparticles and Illite*

481   The stability of the mixture of silver nanoparticles and illite (either Na- or Ca-form) was also little

482   changed from that for the single-particle systems (Figure 9). Illite has negatively charged edge and basal

483   planes at pH 7 according to the reported PZC value of 3.5[55] and thus as hypothesized for the binary

484   system with montmorillonite, these results also suggests the nano-sized silver first associated with the

485   basal illite face and then its fate was bound to the subsequent aggregation of the clay[59]. We were unable to

486   collect images for these systems, but this proposed interaction between illite and the silver nanoparticles

487   seems reasonable due to the large particle size and higher number concentration of illite in these systems

488   compared to that for the silver nanoparticles.

489

490   **Conclusions**

491   Our results did not show significant differences in the stability of binary component systems of silver

492   nanoparticle and clays at pH 7 when compared to the single particle systems at the same pH. We attribute

493   this to weakly charged or negatively charged clay edges, as well as permanently negatively charged basal

494   plane surfaces of the clays at pH 7, thus all six combinations between silver nanoparticles and the clays in

495   binary systems (i.e., face-to-face, face-to-edge, edge-to-edge, nanoparticle-to-nanoparticle, face-to-

496   nanoparticle, edge-to-nanoparticle) are barrier-controlled (i.e., high electrolyte concentration is needed to

497   overcome the energy barrier to form aggregates). Our expectation for greater dependence in illite

498   aggregation on solution chemistry was also not evident in our experiments. While we cannot completely

499   neglect possible non-DLVO forces that arise from size asymmetry, such as depletion forces, the lack of

500   differences observed in the single- and binary-particle systems suggests their influence under the

501   conditions studied was negligible. Our results suggest under neutral pH and moderate to elevated

502   electrolyte concentrations approaching the measured CCC values that binary systems of

503   montmorillonite/illite and silver nanoparticles can be treated as single component clay systems. Further

504   research specifically highlighting conditions where the silver nanoparticles interact with clay phases and

505   the role of additional complexities such as natural organic matter are needed in order to better extend our

506   observations to predict the fate of silver nanoparticles in natural systems.

507

Acknowledgements

519

References

521 1.   M. Auffan, J. Rose, J. Y. Bottero, G. V. Lowry, J. P. Jolivet and M. R. Wiesner, *Nature

522 nanotechnology*, 2009, **4**, 634-641.

523 2.   V. L. Colvin, *Nature Biotechnology*, 2003, **21**, 1166-1170.

524 3.   M. R. Wiesner, G. V. Lowry, P. Alvarez, D. Dionysiou and P. Biswas, *Environmental

525 science & technology*, 2006, **40**, 4336-4345.

526 4.   A. Praetorius, M. Scheringer and K. Hungerbuhler, *Environmental science & technology*,

527 2012, **46**, 6705-6713.

528 5.   D.   Rejeski,   Nanotechnology   and   consumer   products,

529 http://www.nanotechproject.org/publications/archive/nanotechnology_consumer_products/,

530 (accessed June, 2014).

531 6.   T. M. Benn and P. Westerhoff, *Environmental science & technology*, 2008, **42**, 4133-

532 4139.

533 7.   B. Nowack and T. D. Bucheli, *Environmental pollution*, 2007, **150**, 5-22.

534 8.   X. Li and J. J. Lenhart, *Environmental science & technology*, 2012, **46**, 5378-5386.

20

535 9. X. Li, J. J. Lenhart and H. W. Walker, *Langmuir : the ACS journal of surfaces and*
536 *colloids*, 2012, **28**, 1095-1104.

537 10. X. Li, J. J. Lenhart and H. W. Walker, *Langmuir : the ACS journal of surfaces and*
538 *colloids*, 2010, **26**, 16690-16698.

539 11. A. Islam, B. Chowdhry and M. Snowden, *Advances in colloid and interface science*,
540 1995, **62**, 109-136.

541 12. D. Zhou, A. I. Abdel-Fattah and A. A. Keller, *Environmental science & technology*, 2012,
542 **46**, 7520-7526.

543 13. P. D. Yates, G. V. Franks, S. Biggs and G. J. Jameson, *Colloids and Surfaces A:*
544 *Physicochemical and Engineering Aspects*, 2005, **255**, 85-90.

545 14. M. Cerbelaud, A. Videcoq, P. Abélard, C. Pagnoux, F. Rossignol and R. Ferrando,
546 *Langmuir : the ACS journal of surfaces and colloids*, 2008, **24**, 3001-3008.

547 15. K. A. Huynh, J. M. McCaffery and K. L. Chen, *Environ. Sci. Technol. Lett.*, 2014, **1**,
548 361-366.

549 16. E. Tombácz and M. Szekeres, *Applied Clay Science*, 2006, **34**, 105-124.

550 17. M. Bentabol, M. D. Ruiz Cruz, F. J. Huertas and J. Linares, *Clay Minerals*, 2003, **38**,
551 161-172.

552 18. S. Laribi, B. Jouffrey and J.-M. Fleureau, *The European Physical Journal Applied*
553 *Physics*, 2007, **39**, 257-265.

554 19. E. Tombácz and M. Szekeres, *Applied Clay Science*, 2004, **27**, 75-94.

555 20. S. Goldberg and R. A. Glaubig, *Clays and Clay Minerals*, 1987, **35**, 220-227.

556 21. D. Hesterberg and A. Page, *Soil Science Society of America Journal*, 1990, **54**, 735-739.

557 22. L. Cai, M. Tong, X. Wang and H. Kim, *Environmental science & technology*, 2014, **48**,
558 7323-7332.

559 23. H. J. Kim, T. Phenrat, R. D. Tilton and G. V. Lowry, *Journal of colloid and interface*
560 *science*, 2012, **370**, 1-10.

561 24. M. E. Essington, J. Lee and Y. Seo, *Soil Science Society of America Journal*, 2010, **74**,
562 1577.

563 25. X. Gu and L. J. Evans, *Journal of colloid and interface science*, 2007, **307**, 317-325.

564 26. R. Hunter, *Foundations of colloid science*, Oxford University Press, Oxford, 2001.

565 27. J. W. Virden and J. C. Berg, *Journal of colloid and interface science*, 1992, **149**, 528-535.

566   28.   A. Panáček, L. Kvitek, R. Prucek, M. Kolar, R. Vecerova, N. Pizurova, V. K. Sharma, T.

567   j. Nevečná and R. Zboril, *The Journal of Physical Chemistry B*, 2006, **110**, 16248-16253.

568   29.   L. L. Schramm and J. C. T. Kwak, *Clays and Clay Minerals*, 1982, **30**, 40-48.

569   30.   S. Garcia-Garcia, S. Wold and M. Jonsson, *Journal of colloid and interface science*, 2007,

570   **315**, 512-519.

571   31.   E. Tombácz, J. Balázs, J. Lakatos and F. Szántó, *Colloid and Polymer Science*, 1989, **267**,

572   1016-1025.

573   32.   A. Delgado, F. Gonzalez-Caballero and J. Bruque, *Journal of colloid and interface

574   science*, 1986, **113**, 203-211.

575   33.   V. Metz, K. Amram and J. Ganor, *Geochim. Cosmochim. Acta*, 2005, **69**, 1755-1772.

576   34.   P. Leroy, C. Tournassat, O. Bernard, N. Devau and M. Azaroual, *Journal of colloid and

577   interface science*, 2015, **451**, 21-39.

578   35.   E. E. Saka and C. Güler, *Clay Minerals*, 2006, **41**, 853-861.

579   36.   Y. Horikawa, R. Murray and J. Quirk, *Colloids and surfaces*, 1988, **32**, 181-195.

580   37.   I. Callaghan and R. Ottewill, *Faraday Discussions of the Chemical Society*, 1974, **57**,

581   110-118.

582   38.   S. Rossi, P. F. Luckham and T. F. Tadros, *Colloids and Surfaces A: Physicochemical and

583   Engineering Aspects*, 2002, **201**, 85-100.

584   39.   I. Sondi, J. Bišćan and V. Pravdić, *Journal of colloid and interface science*, 1996, **178**,

585   514-522.

586   40.   N. R. O'Brien, *Clays and Clay Minerals*, 1971, **19**, 353-359.

587   41.   L. B. Williams and R. L. Hervig, *American Mineralogist*, 2002, **87**, 1564-1570.

588   42.   J. Hower and T. C. Mowatt, *American Mineralogist*, 1900, **51**.

589   43.   K. A. Huynh and K. L. Chen, *Environmental science & technology*, 2011, **45**, 5564-5571.

590   44.   A. M. El Badawy, K. G. Scheckel, M. Suidan and T. Tolaymat, *Science of the Total

591   Environment*, 2012, **429**, 325-331.

592   45.   B. Derjaguin and L. Landau, *Acta Physicochim. URSS*, 1941, **14**, 633-652.

593   46.   E. J. W. Verwey and J. T. G. Overbeek, *Theory of the stability of lyophobic colloids*,

594   Courier Dover Publications, 1999.

595   47.   J. Oster, I. Shainberg and J. Wood, *Soil Science Society of America Journal*, 1980, **44**,

596   955-959.

597   48.   H. Van Olphen and P. H. Hsu, *Soil Science*, 1978, **126**, 59.

598   49.   A. Katz, M. Xu, J. C. Steiner, A. Trusiak, A. Alimova, P. Gottlieb and K. Block, *Clays*

599   *and Clay Minerals*, 2013, **61**, 1-10.

600   50.   H. Arora and N. Coleman, *Soil Science*, 1979, **127**, 134-139.

601   51.   P. Rengasamy, *Journal of soil science*, 1983, **34**, 723-732.

602   52.   R. Greene, A. Posner and J. Quirk, *Journal*.

603   53.   M. Alvarez-Silva, A. Uribe-Salas, M. Mirnezami and J. Finch, *Minerals Engineering*,

604   2010, **23**, 383-389.

605   54.   E. Errais, J. Duplay, M. Elhabiri, M. Khodja, R. Ocampo, R. Baltenweck-Guyot and F.

606   Darragi, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2012, **403**, 69-78.

607   55.   Y. Lan, B. Deng, C. Kim and E. C. Thornton, *Geochemical transactions*, 2007, **8**, 4.

608   56.   M. Muneer and J. Oades, *Soil Research*, 1989, **27**, 411-423.

609   57.   Y. Mao, M. Cates and H. Lekkerkerker, *Physica A: Statistical Mechanics and its*

610   *Applications*, 1995, **222**, 10-24.

611   58.   B. Götzelmann, R. Evans and S. Dietrich, *Physical Review E*, 1998, **57**, 6785.

612   59.   M. Elimelech, X. Jia, J. Gregory and R. Williams, *Particle deposition & aggregation:*

613   *measurement, modelling and simulation*, Butterworth-Heinemann, 1998.

614   60.   Y. Liang, S. A. Bradford, J. Simunek, M. Heggen, H. Vereecken and E. Klumpp,

615   *Environmental science & technology*, 2013, **47**, 12229-12237.

616   61.   V. G. Pol, D. Srivastava, O. Palchik, V. Palchik, M. Slifkin, A. Weiss and A. Gedanken,

617   *Langmuir : the ACS journal of surfaces and colloids*, 2002, **18**, 3352-3357.

618

619

Table 1. Estimated Critical coagulation concentration (CCC) of suspensions in different electrolyte types

Particle type	CCC (mM)		
	NaCl	NaNO$_3$	CaCl$_2$
Bare silver nanoparticles	40	35	2
Na-MONT	50	50	1.5
Ca-MONT	50	50	2
Na-Illite	70	70	2
Ca-Illite	50	50	1

Figure Captions

Figure 1. Zeta potential of montmorillonite and illite from pH 4 to 10 in systems with 1mM NaCl.

Figure 2. Zeta potential of (a) montmorillonite and (b) illite in the systems with 1 – 500 mM NaCl or 0.1 – 10 mM $CaCl_2$.

Figure 3. Aggregation profiles of silver nanoparticles at pH 7.0 as a function of electrolyte concentrations in (a) NaCl and (b) $NaNO_3$.

Figure 4. Inverse stability ratio (1/W) of silver nanoparticles as a function of NaCl, $NaNO_3$ and $CaCl_2$ concentration. The arrows indicate the CCCs for the different systems.

Figure 5. Inverse stability ratio (1/W) of (a) Na-montmorillonite and (b) Ca-montmorillonite as a function of NaCl, $NaNO_3$ and $CaCl_2$ concentrations. The arrows indicate the CCCs for the different systems.

Figure 6. Inverse stability ratio (1/W) of (a) Na-illite and (b) Ca-illite as a function of NaCl, $NaNO_3$ and $CaCl_2$ concentrations. The arrows indicate the CCCs for different systems.

Figure 7. Inverse stability ratio (1/W) of silver nanoparticles with Na-montmorillonite (left)/Ca-montmorillonite (right) as a function of electrolyte concentrations: NaCl (a and d), $NaNO_3$ (b and e) and $CaCl_2$ (c and f). The arrows indicate the CCCs for different systems.

Figure 8. TEM image of heteroaggregated silver nanoparticles with Na-montmorillonite at 100mM NaCl. Red circles highlight the interactions between AgNPs and basal planes of Na-montmorillonite.

Figure 9. Inverse stability ratio (1/W) of silver nanoparticles with Na-illite (left)/Ca-illite (right) as a function of electrolyte concentrations: NaCl (a and d), $NaNO_3$ (b and e) and $CaCl_2$ (c and f). The arrows indicate the CCCs for different systems.
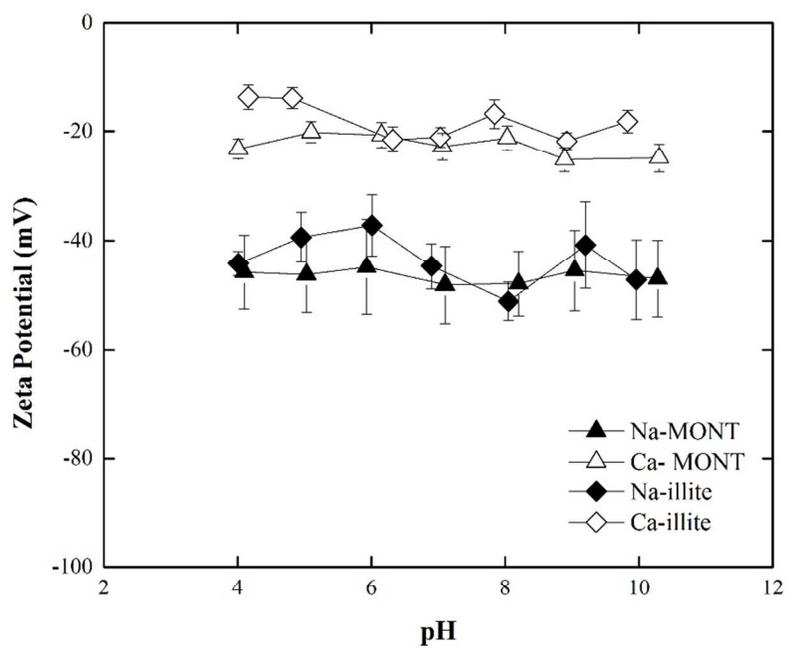
Figure 1.
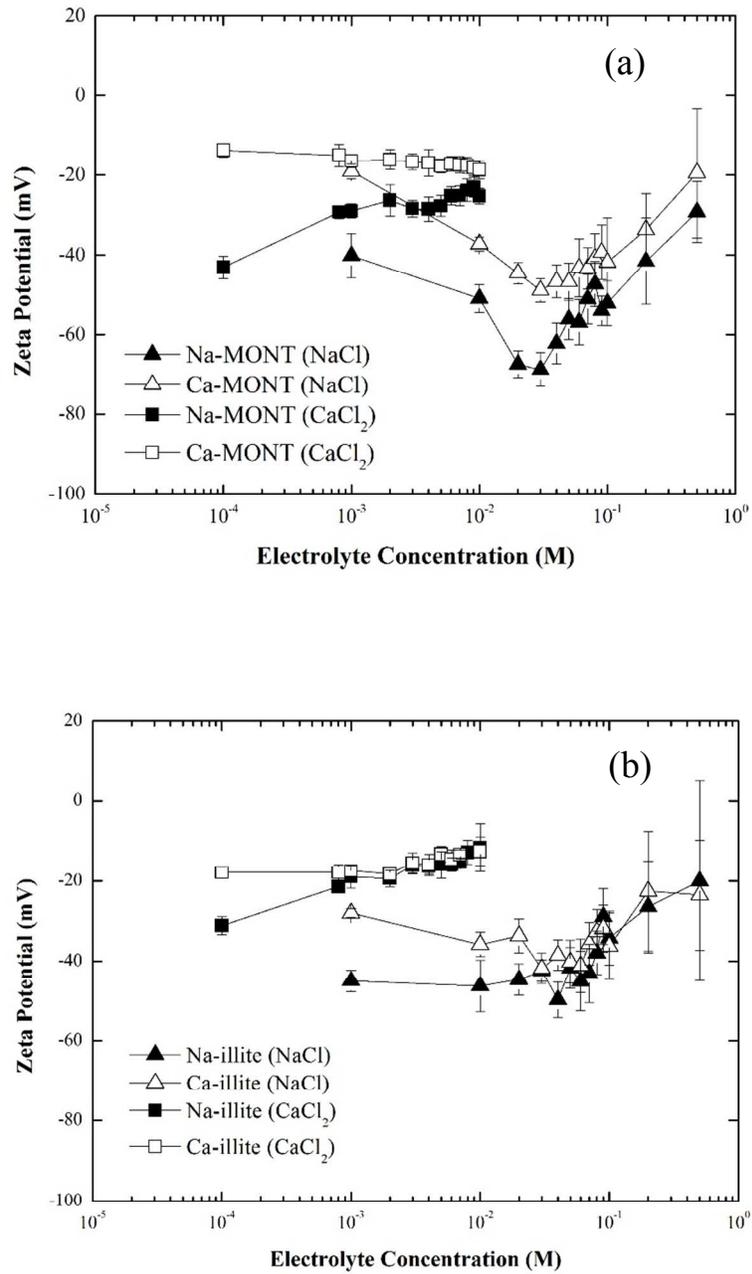
Figure 2.
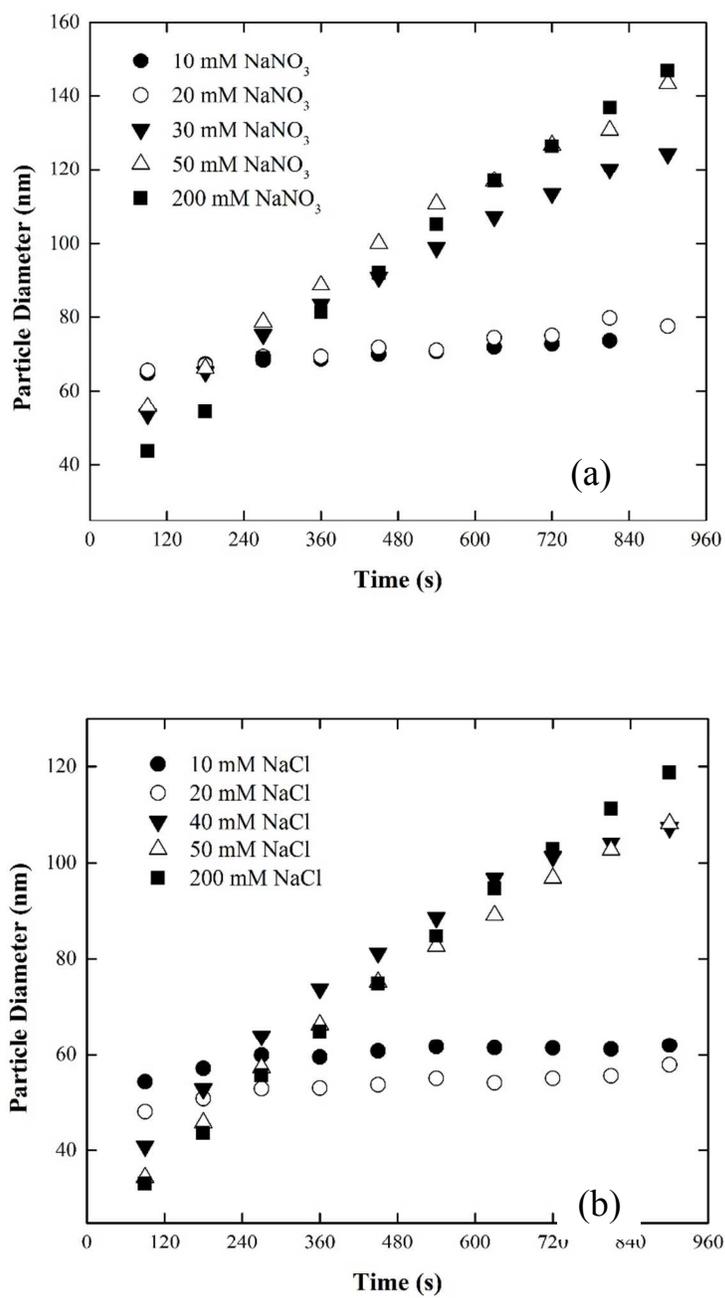
Figure 3.
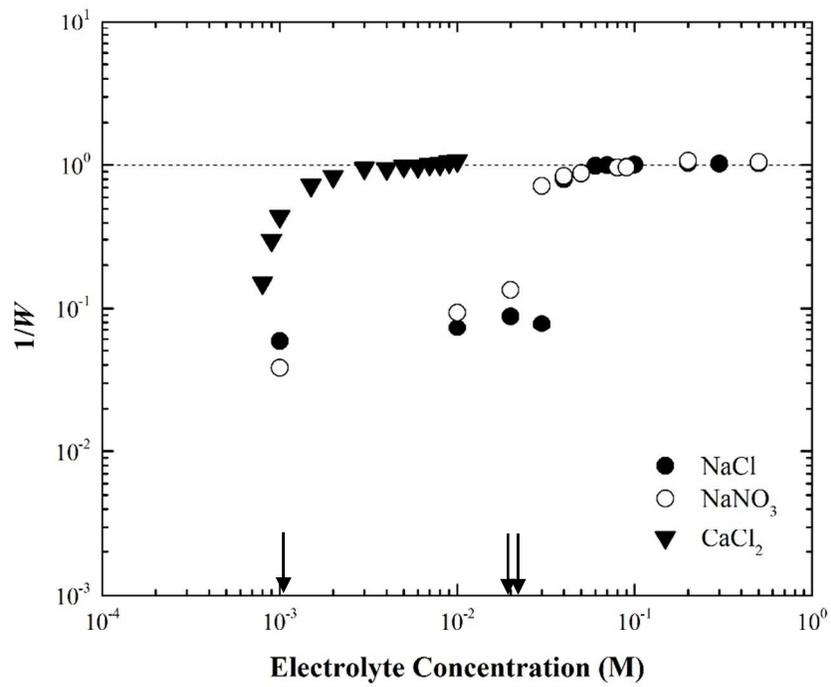
Figure 4.
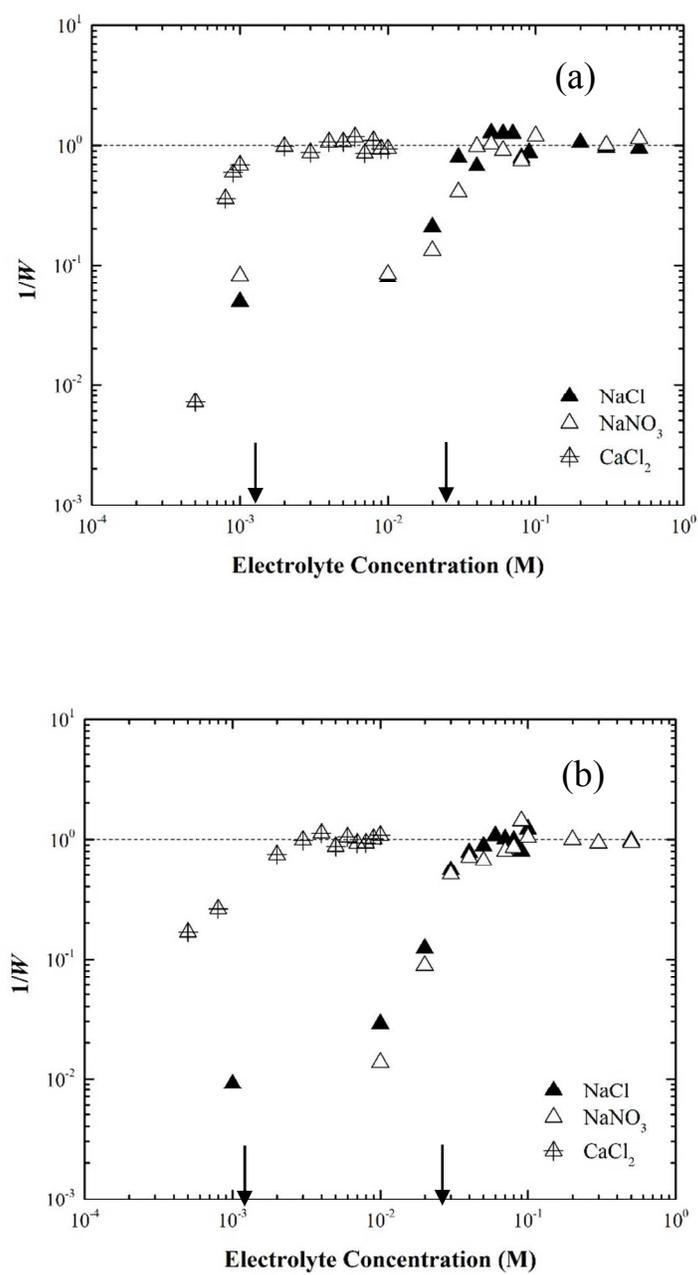
Figure 5.

Figure 6.

Figure 7.

34

Figure 8.

Figure 9.

36