Heteroaggregation of Silver Nanoparticles with Clay Minerals in Aqueous System

Thesis

Presented in Partial Fulfillment of the Requirements for the Degree Master of Science in the Graduate School of The Ohio State University

By

Jibin Liu, B.S.
Graduate Program in Civil Engineering

The Ohio State University
2014

Dissertation Committee:
John J. Lenhart, Advisor
Paula J. Mouser
Ethan J. Kubatko
Abstract

In this study, we investigated the heteroaggregation behavior of silver nanoparticles with clay minerals (montmorillonite and illite) in neutral pH solutions. Bare and Tween-coated silver nanoparticles with a nominal diameter of 60.9 ± 0.5 nm were synthesized following established methods. Illite (IMt-2) and montmorillonite (SWy-2) were purchased from the Clay Mineral Society (Indiana) and pretreated to obtain monocationic (Na-clay) and dicationic (Ca-clay) suspensions. 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 (DLS). 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. All six combinations of bare silver nanoparticles and clays in binary systems (i.e., f-f, f-e, e-e, NP-f, NP-e, NP-NP) were barrier-controlled (i.e., high electrolyte concentration is needed to overcome the energy barrier to form aggregates). We attribute this to weakly charged or negatively charged clay edges (e), negatively charged silver nanoparticles (AgNPs), as well as permanently negatively charged basal plane surfaces (f) of the clays at pH 7. The results suggest that the binary system of montmorillonite/illite and bare silver nanoparticles can be treated as a single component system of clays under the experimental conditions studied, and the fate of silver
nanoparticles in aqueous system may be controlled by their heteroaggregation of clay minerals.

However, under neutral conditions, the stability of the binary system was greatly increased when bare silver nanoparticles were changed to Tween-coated ones. The CCCs of the binary system contain Tween-AgNPs are all above 100mM in either NaCl, NaNO3, or CaCl2, and in some systems such as Ca-montmorillonite with Tween-AgNPs, the CCCs cannot even be determined in all the electrolyte solutions. The adsorption of Tween 80 on the clay surface was proposed to explain the changes among different clays and electrolytes. The present results showed that coated silver nanoparticles are more mobile than uncoated ones, and their interactions with clay minerals will be greatly affected by the existence of polymer/surfactant in the medium.
Dedication

This document is dedicated to my family and my girlfriend.
Acknowledgements

First and foremost, I would like to express my sincere gratitude to my advisor, Dr. John Lenhart, for his continuous support and guidance throughout these two years of my graduate study at The Ohio State University. His guidance helped me all the time during the experiments and thesis writing. Without his persistent help and encouragement, I could never make this thesis completed or written. One simply could not wish to have a better advisor and mentor.

I would like to thank my dissertation committee members: Dr. Paula Mouser and Dr. Ethan Kubatko for their encouragement, invaluable advice and insightful comments for this research project and my graduate study.

I am indebted to Dr. Yu-Sik Hwang, for his guidance and interest in the project.

I would also like to thank Dr. Xuan Li, for his assistance and guidance in the preparation and characterization of the silver nanoparticles. I am greatly indebted to Mr. Matthew Noerpel, for his technical assistance and valuable help in collecting the TEM images and ICP-OES data. Also, I gratefully acknowledge the assistance of Ms. Elsa Burrow, for her commitment and enthusiasm for the project and Ms. Yen-Ling Liu, for her help in preparing the clay minerals.

My special thanks go to Dr. Carolyn Merry, for her invaluable advice and support to my graduate studies and job-seeking. I remembered the days when she took me to different
luncheons and taught me how to network with other professionals. Also, I gratefully thank Dr. Jason Cheng, for his assistance and guidance in using various analytical instruments and generous help in revising my resume.

I would also like to thank my former and current lab mates (Zongsu Wei, Mengling Stuckman, Chenyi Yuan, Shuai Liu, Zuzana Bohrerova, Daniel Kekacs, John Krinks, Katie Heyob, Maggie McHugh, Kelsie Senuta, Mary Evert, Mike Jindra, Michael Brooker, Natalie Sakian, Stephanie Brim, Yilong Xiao, Chunyan Xu, Lifang Yu, Xieran Li, Youjia Zhong, Jay Hunter) for the wonderful time that we shared together in the lab and the office. My sincere gratitude extends to my friends at the Benchball Soccer Club and The Ohio State University, who make my life in Columbus much more joyful.

Last but not least, I would like to sincerely appreciate the selfless love and support given from my parents. Their love is the biggest motivation when I am moving forward. My special thank also goes to my loving girlfriend, who always stands beside me at both the happy and tough time.

This project was funded by the Korea Institute of Toxicology (KIT), Daejon, South Korea and done in collaboration with the Department of Civil, Environmental and Geodetic Engineering (CEGE) at The Ohio State University, Columbus, Ohio.
Vita

2012…………………………………….B.S. Civil Engineering, China

Hunan Agricultural University

2013 – 2014………………………….Graduate Research Associate, Department of

Civil, Environmental and Geodetic Engineering

Summer, 2014…………………………GIS intern, New York City Department of City

Planning

Fields of Study

Major Field: Civil Engineering
Table of Contents

Abstract..........................................................................................................................ii
Dedication.........................................................................................................................iv
Acknowledgements.........................................................................................................v
Vita.....................................................................................................................................vii
List of Tables.....................................................................................................................xii
List of Figures...................................................................................................................xiii
Chapter 1: Introduction......................................................................................................1
  1.1 Background of Nanoparticles..................................................................................1
    1.1.1 Applications of Nanoparticles in Environmental Researches.........................2
    1.1.2 Facts about Silver Nanoparticles......................................................................4
    1.1.3 Fate of Silver Nanoparticles in Aqueous System..............................................6
    1.1.4 DLVO and non-DLVO interactions..................................................................8
  1.2 Background of Clay Minerals..................................................................................10
  1.3 Heteroaggregation...................................................................................................12
  1.4 Research Objectives...............................................................................................15
  1.5 Dissertation Overview............................................................................................16
  1.6 References..............................................................................................................17
  1.7 Tables and Figures..................................................................................................28

Chapter 2: Heteroaggregation of Bare Silver Nanoparticles with Clay Minerals in Aquatic
Chapter 3: Heteroaggregation of Tween-coated Silver Nanoparticles with Clay Minerals in Aquatic Systems

3.1 Introduction

3.2 Materials and Experimental Methods

3.2.1 Materials

3.2.2 Clay Preparation

3.2.3 Silver nanoparticles Synthesis and Characterization

3.2.4 Aggregation Kinetics

3.3 Results and Discussion

3.3.1 Homoaggregation of Tween-coated Silver Nanoparticles

3.3.2 Heteroaggregation of Tween-AgNPs with Clay Minerals

3.3.2.1 Tween-coated Silver Nanoparticles and Montmorillonite

3.3.2.2 Tween-coated Silver Nanoparticles and Illite

3.4 Conclusion

3.5 References

3.6 Tables and Figures

Chapter 4: Conclusions

4.1 Conclusions

4.2 Recommendation for Future Studies

4.3 References

Appendix A: Preparation and Characterization of Kaolinite

A.1 Preparation of Kaolinite

A.2 Characterization of Kaolinite
A.3 Aggregation experiments with Kaolinite.................................................116
A.4 References..........................................................................................119
A.5 Figures.................................................................................................120
Bibliography...............................................................................................122
List of Tables

Table 1.1 Highlighted properties of nanoparticles……………………………………………….28

Table 1.2 Highlighted applications of nanoparticles in environmental remediation
fields……………………………………………………………………………………………………29

Table 1.3 Highlighted applications of nanoparticles in membranes………………………….30

Table 1.4 Summary of toxicological effects of silver nanoparticles on animals………………31

Table 1.5 Experiments of aggregation of clay minerals……………………………………….32

Table 2.1 Highlighted experimentation on aggregation of clay minerals………………….68

Table 2.2 Estimated Critical coagulation concentration (CCC) of suspensions in different
electrolyte types………………………………………………………………………………69

Table 2.3 Comparison of fastest \( \frac{dr}{dt} \) for single component systems…………………..70

Table 2.4 Comparison of fastest \( \frac{dr}{dt} \) for binary components systems…………………..71

Table 3.1 Comparison of fastest \( \frac{dr}{dt} \) for single component systems…………………..106

Table 3.2 Comparison of fastest \( \frac{dr}{dt} \) for Tween-contained binary components
systems…………………………………………………………………………………………….107
List of Figures

Figure 1.1 Comparison of processes relevant to determine the fate of organic chemicals (left) and to nanoparticles (right). Image from Praetorius et al.……………………………………33

Figure 1.2 Energy profile of classical DVLO model consist of van der Waals attractive and electrostatic repulsive forces………………………………………………………………………..34

Figure 1.3 Unit structures of different types of clay minerals: (a) kaolinite (TO) and (b) montmorillonite/illite (TOT)..................................................................................................................35

Figure 2.1 Unit structures of different types of clay minerals: (a) kaolinite (TO) and (b) montmorillonite/illite (TOT)..................................................................................................................72

Figure 2.2 Characterization of the silver nanoparticles suspended in background NaCl/NaHCO₃ electrolyte: (a) TEM image and (b) UV-vis absorption spectrum………..73

Figure 2.3 TEM image of clay mineral samples suspended in background NaCl/NaHCO₃ electrolyte: (a) montmorillonite and (b) illite.................................................................74

Figure 2.4 Zeta potential of montmorillonite and illite from pH 4 to 10 in systems with 1mM NaCl.........................................................................................................................75

Figure 2.5 Zeta potential of clay mineral samples in the systems with 1 – 500 mM NaCl (upper) and 0.1 – 10 mM CaCl₂ (lower): (a) montmorillonite and (b) illite ……………………76

Figure 2.6 Aggregation profiles of silver nanoparticles at pH 7.0 as a function of electrolyte concentrations: (a) NaCl and (b) NaNO₃ .................................................................77
**Figure 2.7** Inverse stability ratio (1/W) of silver nanoparticles as a function of NaCl, NaNO₃ and CaCl₂ concentration. The arrows indicate the CCCs for different systems.

**Figure 2.8** Inverse stability ratio (1/W) of montmorillonite as a function of NaCl, NaNO₃ and CaCl₂ concentrations: (a) Na-montmorillonite and (b) Ca-montmorillonite. The arrows indicate the CCCs for different systems.

**Figure 2.9** Inverse stability ratio (1/W) of Na- and Ca-montmorillonite as a function of NaCl and CaCl₂ concentration.

**Figure 2.10** Inverse stability ratio (1/W) of illite as a function of NaCl, NaNO₃ and CaCl₂ concentrations: (a) Na-illite and (b) Ca-illite. The arrows indicate the CCCs for different systems.

**Figure 2.11** Inverse stability ratio (1/W) of Na- and Ca-illite as a function of NaCl and CaCl₂ concentrations.

**Figure 2.12** 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), NaNO₃ (b and e) and CaCl₂ (c and f). The arrows indicate the CCCs for different systems.

**Figure 2.13** 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 2.14** 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), NaNO₃ (b and e) and CaCl₂ (c and f). The arrows indicate the CCCs for different systems.
Figure 3.1 Inverse stability ratio (1/W) of Tween-Ag as a function of NaCl and CaCl$_2$ concentrations............................................................108

Figure 3.2 Inverse stability ratio (1/W) of Tween-AgNPs and 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 .................................................................109

Figure 3.3 Inverse stability ratio (1/W) of Tween-Ag and 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.........................................................110

Figure A.1 TEM image of kaolinite suspended in background NaCl/NaHCO$_3$ electrolyte..........................................................................................................................120

Figure A.2 Homoggregation profile of kaolinite at pH 7.0 as a function of electrolyte concentrations: (a) NaCl, (b) NaNO$_3$ and (c) CaCl$_2$.................................................................121
Chapter 1: Introduction

1.1 Background of Nanoparticles

Products manufactured in the field of nanotechnology are various and can be broadly classified into three groups based on their morphology: nanomaterials, with one dimension of less than 100nm (e.g., nanofilms); nano-objects, with two dimensions of less than 100nm, and nanoparticles which have three dimension less than 100nm [1]. Nanofilms are typically used in solar cells and catalysis [2]. Carbon nanotubes are one example nano-object and they can exhibit either metallic or semiconducting properties making them technologically important in electrical applications [3]. Nanoparticles typically refer to particles in the range of 1 to 100nm which are made of inorganic or organic chemicals and they exist as particulate dispersions or solid particles [4].

Nanoparticles differ from bulk material not only in terms of size [5] and optical properties (e.g., color), but also in terms of physical and chemical properties such as composition, shape, surface layer, reactivity, and toxicity (Table 1). For example, gold nanoparticles are widely used in biomedicine due to their enhanced photophysical properties [6]. When irradiated with light (visible and near-infrared region), gold nanoparticles are able to enhance the local electromagnetic field, and enlarge the signal reflected from the surface of nanoparticles, a property which is exploited by surface-
enhanced spectroscopic techniques [6]. Nanoparticles also exhibit size-dependent toxic effects. For example, Wang et al. [7] studied the toxicity of nano-sized and bulk-sized metal oxide materials to nematodes. They found that the 24 h lethal concentrations of Al₂O₃ (82 mg L⁻¹) and TiO₂ (80 mg L⁻¹) nanoparticles were lower than that of bulk materials, which were 153 mg L⁻¹ and 136 mg L⁻¹, respectively. Their results indicate some metal oxide nanoparticles may be more toxic to organisms when compared to their bulk materials [7].

1.1.1 Applications of Nanoparticles in Environmental Researches

Due to their unique properties, nanoparticles are widely applied for environmental remediation (Table 2). For instance, Kanel et al. [8] synthesized surface-modified iron nanoparticles (S-INP) to remove arsenic – one of the most toxic and widespread contaminants in groundwater – from contaminated aquifers. Tween-20 was used as a surface layer to prevent particle aggregation and increase the efficiency of As(III) removal. A sand-packed column fed with an influent solution containing 0.5mg/L As(III) was amended with S-INP, and provided more than 2.5 months’ of arsenic-free water [8]. Zero-valent iron nanoparticles (ZVIs) are also commonly used, and are efficient at removing Cr(VI) and Pb(II) from contaminated water [9]. ZVIs remove Cr(VI) and Pb(II) from water by reducing them to insoluble forms, Cr(III) and Pb(0), respectively, while oxidizing the Fe(0) to goethite (alpha-FeOOH) [9]. Due to the high surface area, the rate of the removal by ZVI is nearly 30 times greater than that provided by an equal amount of iron filings [9].
Engineered nanoparticles are also utilized in membrane technology to maximize the performance of polymeric and ceramic membranes used in wastewater treatment and drinking water purification (Table 3). Membranes are widely used to remove contaminants from water, but they face a significant problem from fouling [10]. Membrane fouling is due to the interaction between the membrane and solids (e.g., bacteria, cell debris and inorganic particles) in the fluid [11]. There are two types of fouling in membrane: (1) reversible fouling caused by the deposition of solids on the surface of membrane, and (2) irreversible fouling where flux through the membrane is hindered due to the adsorption of organic matter or other material within the pores of the membrane [11]. The rise of nanotechnology gives the opportunity for researchers to not only improve membrane performance but also to design membranes that resist fouling. For example, Taurozzi et al. impregnated silver nanoparticles into polysulfone membranes via the reduction of ionic silver by a polymer solvent [12]. The resulting composite membrane was observed to have large silver nanoparticles at the membrane surface and small ones homogenously distributed within the membrane. The resulting membrane resisted fouling because the silver nanoparticles prevented the growth of biofilms via the release of silver ions from the composite membrane [12]. Similarly, Kim et al. incorporated TiO\textsubscript{2} nanoparticles into a thin-film-composite (TFC) membrane to design a hybrid TFC membrane which exhibited promising anti-biofouling ability due to its photocatalytic bactericidal effect when illuminated by UV light [13].
1.1.2 Facts about Silver Nanoparticles

Among engineered nanoparticles, silver nanoparticles (AgNPs) are given specific attention because of their antimicrobial properties. AgNPs are widely incorporated into daily use products such as clothing, wound dressings, footwear, sunscreens, food containers and surgical equipment [14-18]. These widespread beneficial applications are countered by many reports detailing adverse effects to organisms exposed to AgNPs. Some of this literature reporting the toxicology of AgNPs to animals is summarized in Table 4. AgNPs are toxic to both mammals and non-mammals and target different organs (Table 4). One of the bactericidal mechanism of AgNPs is related to their release of silver ions which can strongly bind with thiol groups of vital microbial enzymes resulting in microbe deactivation [19]. Silver ions released from AgNPs may also prevent the replication of bacteria [20]. In addition, there is also evidence indicating that AgNPs themselves may be toxic to water plant as well as human cells. Navarro et al. [21] found a higher toxicology of AgNPs than Ag$^+$ to Chlamydomonas reinhardtii, when related the results to total Ag$^+$ concentrations. AshaRani et al. [22] observed dose-dependent production of reactive oxygen species (ROS) as starch-coated AgNPs interrupted ATP synthesis in human lung fibroblast cells and glioblastoma cells. These changes may lead to DNA damage in human cells [22]. The bactericidal and toxic effects of AgNPs have raised concern of their possible adverse effects on human beings as well as the environment should they be discharged to the environment in significant quantities.

The estimated concentration of silver nanoparticles predicted by a life-cycle model is nearly 0.03 µg L$^{-1}$ in the water worldwide [23]. In the U.S., about 0.116 µg L$^{-1}$ and 21.0
µg L\(^{-1}\) of AgNPs are predicted to be present in surface water and the effluent of sewage treatment plants, respectively [24]. Thus, possible risks to aquatic organism as well as human beings may be brought about by persistent exposure to silver nanoparticles [24]. Possible exposure pathways of nanoparticles to human beings include food and water ingestion, inhalation and skin penetration [25-28]. For example, nanoparticles can enter plants (e.g., pumpkin, rice, bean and wheat plants) through their roots or leaves and then accumulate and be transported to other tissues in the plants [29-31]. Consumption of these plants may lead to possible expose to human beings. The occurrence of respiratory diseases (e.g., inflammation and asthma) can also make it possible for inhalable nanoparticles to pass through the barriers which are built by our body and used for prevent us from foreign particles [32, 33]. Some nanoparticles are used as oral carriers for drugs and vaccines, thus uptake of these products may also increase the risks of nanoparticle exposure [34]. Polyvinylpyrrolidone-coated AgNPs were observed to penetrate both intact and damaged human skin and exist in the cells under the skin [28]. The amount of AgNPs passing through damaged skin was five times more than that through undamaged skin [28]. Moreover, after entering our bodies, nanoparticles have the potential to pass through blood-brain barrier (BBB) and reach to the nervous system by passive diffusion or endocytosis [35]. However, it is necessary to note that in these toxicology studies, coating agents and sonication were applied to prevent the aggregation of nanoparticles [28, 32]. The toxicity of silver is also varies when in the form of dissolved ions or nanoparticles [19-21]. Thus it is important to understand what form AgNPs take in the environment and how they transport in different medium in order to minimize their effects to human beings and nature.
1.1.3 Fate of silver nanoparticles in aqueous system

After entering a water body, the fate of AgNPs is greatly affected by the complexity of the aqueous system. The organic and inorganic components in water can produce physical and chemical transformations of AgNPs, such as homoaggregation (aggregation between the same or similar particles), dissolution, and alteration of surface layers (Figure 1). Many environmental factors can affect the aggregation of AgNPs, such as pH, ionic strength, electrolyte type, coating layer and dissolved organic matter [36-45]. For instance at low and neutral pH, high concentrations of electrolytes and the presence of bivalent or multivalent cations leads to instability of AgNP suspensions and aggregation of the particles [38, 39]. Aggregation is sensitive to the presence of specific capping agents, with capping agents like Tween 80 and polyvinylpyrrolidone preventing aggregation, even at higher electrolyte concentrations, while agents such as citrate and sodium dodecyl sulfate little impacting stability [37, 39].

Dissolution of AgNPs (release of Ag⁺ ions) also affects their fate in aqueous environments. The dissolution can occur slowly, as during storage or upon inhibition by organic matter [46, 47], or quickly as catalyzed by specific electrolytes [38, 40]. Liu and Hurt [47] observed the dissolution of citrate-coated silver nanoparticles was inhibited in the presence of humic or fulvic acid (Suwannee River humic acid II and fulvic acid I standards, International Humic Substances Society) at pH 5.6. Higher concentrations of natural organic matter (NOM) resulted in, fewer silver nanoparticles dissolving [47]. These results suggest that NOM sorption to the surface of nanoparticles could prevent the oxidation reactions that lead to particle dissolution [48]. Liu et al. [49] systematically
studied the possible factors that may influence Ag$^+$ release from silver nanoparticles, which was primarily due to the oxidation reactions. The release rate of Ag$^+$ was affected by the particle size – the smaller the size was, the larger its surface area was and thus the faster Ag$^+$ will release. The release of Ag$^+$ can also be greatly accelerated by pre-oxidation by ozone. On the other hand, modification of silver nanoparticles by citrate, sodium sulfide or 11-mercaptoundecanoic acid (MUA) will inhibit ion release. Citrate and MUA may prevent the ion release by covering the reactive site on the particles surface. Sodium sulfide inhibited the release in a similar way, but by the formation of sulfide film which was insoluble in water. Meanwhile, Cl$^-$ was reported to dissolve the surface of AgNPs and change the morphology of AgNPs as well as the stability of nanoparticle colloids [38].

Based on the intended purpose, different coating agents are applied on AgNPs to tailor the surface properties. The coating layers of amphiphilic hyperbranched macromolecules were reported to enhance the attachment of silver nanoparticles on glass slides and also prevented the particles from being washed off by water when the AgNP-coated slides were used for antimicrobial tests [50]. On the other hand, silica shell coatings can be used to control the distance between adjacent AgNPs depending upon the thickness of the shell [51]. Coating agents are used to prevent the aggregation of AgNPs and these agents can be divided into three categories based on their mechanism and functional groups: electrostatically stabilized (e.g., citrate and sodium borohydride), sterically stabilized (e.g., polyvinylpyrrolidone (PVP) and Tween 80), and electrosterically stabilized (e.g., branched polyethyleneimine (BPEI)) [39]. As a consequence, stability, dissolution and
particle interactions will differ depending upon the surface layer. PVP- and Tween 80-coated AgNPs are more stable than uncoated and citrate-coated particles, even under high electrolyte concentrations [37, 39]. Citrate-coated AgNPs, however, behave like uncoated particles as the stability of nanoparticles changed little when coated by citrate [37, 42]. The coating layer also impacts the rate and extent of particle dissolution. For example, AgNPs with Tween 80 as coating layers released Ag\(^+\) ions quicker than uncoated and citrate-coated nanoparticles in natural water under pH \(\sim 7.7\) and low electrolyte concentrations [36], while organic coatings (e.g., humic or fulvic acids) diminished the release of silver ions from nanoparticles [47, 52].

In addition to processes and reactions that result in the transformation of the AgNPs, the AgNPs can also interact with other particles or organic matter in water. Such aggregation between dissimilar particles in termed heteroaggregation as opposed to aggregation between identical particles which is homoaggregation (aggregation between dissimilar particles) [53]. Further details of heteroaggregation will be provided in section 2.3.4. The net result of these physical and chemical transformations and interactions dictate whether AgNPs dissolve, deposit or are transported in particulate form in conjunction with the flow of water [53].

1.1.4 DLVO and non-DLVO interactions

The interaction of AgNPs (bare or surface-modified) and other particulate material in water can be described using the classic Derjaguin-Landau-Verwey-Overbeek (DLVO) and non-DLVO [54] theoretical frameworks for particle interactions. Classical DLVO
interactions incorporate van der Waals interactions with electrostatic interactions to describe particle behavior. Due to the many instances where the classical DLVO framework fails to describe particle behavior many invoke non-DLVO interactions as means to improve model fits to experimental results, where non-DLVO effects include hydrogen bonding, hydration pressure, and steric interactions [54-56].

van der Waals forces exist regardless of the chemical properties of the particles or medium and are always attractive between similar particles [57]. In specific liquid medium, van der Waals forces may be repulsive between dissimilar particles, when the sum of the interactions of the dissimilar particles with the medium molecules is larger than the sum of the interactions between these two dissimilar particles as well as between medium molecules [58]. Nanoparticles and other colloids usually have either a positive or negative surface charge which induces an electrostatic surface force of similar magnitude. Approaching particles with similar charges will be repulsed as the like charged surfaces produce an electrostatic repulsive force [57]. The opposite occurs when the surface charges are opposite. Both van der Waals and electrostatic forces can be calculated as a function of the distances between particles [54]. The classic DLVO theory simplifies interactions between particle surfaces by summing up the interaction energy of van der Waals ($V_A$) and electrostatic forces ($V_R$) to determine whether the net interaction energy is attractive ($-V_T$) or repulsive ($+V_T$) (Figure 2) [59, 60].

However, variations in nanoparticle size, shape, composition and surface layers has challenged the classic DLVO theory to describe particle interactions [59]. Thus,
researchers extend the theory by including non-DLVO forces. For instance, aqueous environments provide the potential for hydrogen bonding to occur between water molecules and nanoparticles [54]. In addition, polymer molecules bound to the surfaces of particles can extend away from the surface. The orientation of these molecules can also change based on the environmental conditions [54]. This change of orientation and the alteration in colloid system stability is termed steric interaction. In colloidal system, particles are stabilized when the sum of repulsive forces exceed the sum of attractive forces. Under these conditions aggregation between particles (either homo- or hetero-) is limited.

The stability of colloidal systems can be interrupted by introducing electrolytes which screen the surface charges of particles and suppress their electrostatic double layers [61]. This process will then lead to the aggregation of particles in which the aggregation rate is positively related to the amount of electrolyte. When the electrolyte is sufficient to diminish attractive forces between the particles, fast aggregation will be reached and the rate of aggregation will not increase with the increase of electrolyte [61]. The lowest concentration of electrolyte that induces this fast aggregation is the critical coagulation concentration (CCC).

1.2 Background of Clay Minerals

Clay minerals are one of the dominant particles naturally existing in aqueous system (approximately 30% of total particulate mass) [62], thus how they interact with AgNPs will greatly influence the fate of AgNPs in water system. The basic structure of clay
minerals is a two-dimensional array formed by sheets of silica tetrahedron (T) and sheets of alumina octahedron (O) [63]. Clay minerals are present in a TO configuration (e.g. kaolinite), which means one silica tetrahedra sheet binds with one alumina octahedra sheet, or a TOT configuration (illite and montmorillonite) in which one alumina octahedra sheet is shared by two silica tetrahedra sheets (Figure 3).

The surface charge of clay particles arise from both the basal plane and the clay edge. The basal plane of clay minerals has a permanent negative charge due to isomorphic substitution, while the charge of the edge is pH-dependent because of the exposed >Al-OH and >Si-OH groups [63]. The point of zero charge (PZC) is often used to determine the charge of the edge under the pH condition of interests. The PZC represents the value of pH under which the edge of a clay mineral is neither negatively nor positively charged. The edge is positively charged when the pH is below the PZC and negatively charged when pH is above the PZC. For example, the PZC of kaolinite and montmorillonite is in the range of 6 – 6.5, while it is around 3.5-4.5 for illite [63-65]. When the pH is below the PZC of a clay mineral, a small amount of electrolyte can disturb the stability of clay colloids which aggregate between negatively charged edge and oppositely charged basal plane. However when the pH is above the PZC, higher concentrations of electrolyte are needed to change stability because both the edge and basal of the clay particles are negatively charged. The charge of the edge is also significant for determining the predominant interaction of clay minerals such as edge-to-edge, edge-to-face, and face-to-face. It will also be reflected in interactions that occur between the clay and AgNPs.
The aggregation of clay minerals is affected by many conditions, such as natural organic matter, saturating cations, particle size, surface charge, pH and electrolyte (Table 5). For instance, the CCC of K-illite is reported to be three times less than those of Na-illite [66]. Due to the higher affinity of illite for K\(^+\) than Na\(^+\), the zeta potential for K-illite (-19 mV) is less negative than that for Na-illite (-51 mV), which in turn leads to a lower CCC for K-illite [66, 67]. Phosphate, as the anions, can exchange with the –OH group on the surface of montmorillonite and increase the surface charge of both edge and basal plane of the clay. The predominant interactions between montmorillonite were then changed from edge-to-face to face-to-face and a higher CCC was observed [68]. Finally, the addition of soil humic acids into the system (in this case the humic acids were extracted from two specific soil horizons) increased the CCC of kaolinite by a factor of 50 as the adsorbed humic acids changed the edge of kaolinite from positively to negatively charged [69, 70].

1.3 Heteroaggregation

Heteroaggregation describes aggregation between two or more dissimilar particles [71]. The same as homoaggregates, heteroaggregates can be stable or unstable depending on the composition of the solution and the magnitude of interactions between the particles [72]. Two modes of particle interactions occur in heteroaggregate systems [73]. If the dissimilar particles are similar in size, the particles will interact in a random manner and form irregular composites [73]. If the dissimilar particles are quite different in size, then the smaller particles deposit on the larger ones. When the larger particles are fully covered by smaller particles, the surface properties of the larger particles will mimic the
properties of the smaller ones [73]. Since heteroaggregates are formed by particles which differ in terms of shape, size, surface layers and charges, non-DLVO forces are also sometimes involved [72].

Heteroaggregation related to nanoparticles has been studied for decades and different factors that affect the process have been researched. Nanosilica particles (4.3, 19, 43, 105 and 285 nm) can destabilize alumina (310 nm) dispersions as an example of small particles cover the surface of larger particles and form heteroaggregates by charge neutralization and bridging [74]. However, the surface coverage of nanosilica on the alumina particles did not reach 100%, due to repulsion between the deposited silica nanoparticles [74]. As the size of the nanosilica particles increased from 4.3 to 285 nm (the resulting size ratio increased roughly from 0.01 to 1), the coverage of the alumina surface with silica was lower and fewer silica particles are needed to reach the optimal aggregation rate. Yates et al. proposed that when the size ratio was above 0.155, each silica particle may attach to more than one alumina particles, and thus fewer silica particles were needed to induce the optimal aggregation.

Huynh et al. [75] studied the heteroaggregation of multiwalled carbon nanotubes (MNTs) and hematite nanoparticles (HNPs) and their results showed faster heteroaggregation at diffusion-limited aggregation regime compared to the homoaggregation of HNPs. The heteroaggregation rate of the binary system was also found to be dependent on the mass ratio between MNTs and HNPs, with an optimal ratio of 0.0316 [75]. Under this ratio, either lower or higher, the heteroaggregation rates were lowered. The dependence of
heteroaggregation rate on the mass concentration ratio appeared to reflect that under relatively lower ratios the small amount of MNTs limited the number of attached HNPs which prevented the formation of large heteroaggregates [75]. Under relatively higher mass ratios, the amount of MNTs exceeded that of HNPs and a composite was formed when each HNP attached to a MNT. The MNT may then act as a long arm of the composite and prevent further attachment of other HNPs or MNTs [75]. However, under the optimal mass ratio the MNTs can effectively bridge the HNPs as well as other MNTs to form an extensive network of particles, which in turn lead to larger heteroaggregates as well as faster heteroaggregation rates [75].

Afrooz et al. also studied the heteroaggregation of carbon nanotubes, in this case pluronic acid-coated single-walled carbon nanotubes (SNTs), with gold nanospheres (AuNS) [76]. They observed typical DLVO-type aggregation in the binary system, with a lower aggregation rate at the reaction-limited aggregation regime and a faster rate at the diffusion-limited regime when compared to the homoaggregation of AuNS [76]. The proposed mechanism behind the heteroaggregation involves SNTs increasing the distance between AuNS at lower electrolyte concentrations, which prevents aggregation, while at higher electrolyte concentrations the SNTs act as the collector to form larger heteroaggregates [76].

Cornelis et al. [77] studied the transport of polyvinylpyrrolidone (PVP)-coated silver nanoparticles in eleven natural soil samples which were sieved to <2mm and centrifuged in cellulose acetate filters. The experiments were run under the natural pH of soil samples.
which were in the range of 4 – 7. The conventional understanding of PVP coating layers is that they can prevent the aggregation of nanoparticles and increase the stability of the suspension, which in turn increase the mobility of silver nanoparticles in the water [78]. However, their column studies indicated that polyvinylpyrrolidone (PVP)-coated silver nanoparticles rapidly attached to the surface of natural colloids in the soil and as a result they were less mobile in water systems. What Cornelis et al. [77] have observed indicates that the coating layers of silver nanoparticles may also change the way that they interact with other particles and is worth for further investigations.

1.4 Research Objectives

Although data exists describing the homoaggregation of AgNPs or clay minerals, there is very little information for the heteroaggregation between these two. Since it is likely that native particles such as clay will greatly outnumber nanoparticles in environmental systems studies evaluating the impact of these native particles are needed. Thus, the purpose of this study is to determine the key factors that influence the heteroaggregation between clay minerals and AgNPs. Based on this purpose, the specific objectives of this research were to:

1) Understand the heteroaggregation of silver nanoparticles with two clay minerals (montmorillonite and illite) as a function of saturating cation (Na⁺ and Ca²⁺) and ionic strength.

2) Investigate how the heteroaggregation of silver nanoparticles with two clay minerals changed with the addition of coating layers.
The silver nanoparticles used in this research were synthesized following the procedure described by Li et al. [37]. Three kinds of clay minerals (montmorillonite, kaolinite and illite) were purchased from the Clay Minerals Society and prepared following the methods described by either Essington et al. or Gu et al. [79, 80]. However, only montmorillonite and illite samples were used in the aggregation experiments, since preparation of a stable kaolinite suspension proved to be exceedingly difficult. Aggregation kinetics for both the homoaggregate and heteroaggregate systems were determined by measuring the initial time rate of change in the average hydrodynamic radius of the particle suspensions using dynamic light scattering (DLS). The morphology and size of the dispersed silver nanoparticles and clays were observed using a Technai G2 Spirit Transmission Electron Microscope (TEM).

1.5 Dissertation Overview

The dissertation contains four chapters to address the purpose of this research. Chapter 1 includes the introduction and background. Chapter 2 describes the effects of electrolyte type, ionic strength, valence of cation, and clay type on the heteroaggregation between bare silver nanoparticles and clay minerals. Chapter 3 addresses the change of the heteroaggregation kinetics of the binary system of silver nanoparticles and clay minerals by capping Tween 80 onto the surface of nanoparticles. Chapter 4 describes the conclusion and future work of this study. Supporting data of this research can be found in the Appendices.
1.6 References


1.7 Tables and Figures

Table 1.1 Highlighted properties of nanoparticles

<table>
<thead>
<tr>
<th>Properties of Nanoparticles</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[5]</td>
</tr>
<tr>
<td></td>
<td>[81, 82]</td>
</tr>
<tr>
<td></td>
<td>[83]</td>
</tr>
<tr>
<td></td>
<td>[84]</td>
</tr>
<tr>
<td></td>
<td>[85]</td>
</tr>
<tr>
<td></td>
<td>[81, 82]</td>
</tr>
<tr>
<td>Controllable sizes</td>
<td>√</td>
</tr>
<tr>
<td>Surface area</td>
<td>√</td>
</tr>
<tr>
<td>Various composition</td>
<td>√</td>
</tr>
<tr>
<td>Shape</td>
<td>√</td>
</tr>
<tr>
<td>Surface layer</td>
<td>√</td>
</tr>
<tr>
<td>Electrochemistry</td>
<td>√</td>
</tr>
<tr>
<td>Reactivity</td>
<td>√</td>
</tr>
<tr>
<td>Optical properties</td>
<td>√</td>
</tr>
</tbody>
</table>
Table 1.2 Highlighted applications of nanoparticles in environmental remediation fields

<table>
<thead>
<tr>
<th>References</th>
<th>Nanoparticles</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>[8]</td>
<td>Surface-modified iron nanoparticles (S-INP)</td>
<td>S-INP can remove 100% of As(III) and provide long-term arsenic free water.</td>
</tr>
<tr>
<td>[9]</td>
<td>Zero-valent iron nanoparticles (&quot;Ferragles&quot;)</td>
<td>Rate of removal of Cr(VI) and Pb(II) are 30 times higher for Ferragles than for equal weight of iron filings.</td>
</tr>
<tr>
<td>[86]</td>
<td>Ferromagnetic carbon-coated Fe nanoparticles</td>
<td>Strong ability to remove over 95% of Cr(VI) efficiently.</td>
</tr>
<tr>
<td>[87]</td>
<td>Palladized nanoscale iron particles</td>
<td>Rapid removal of tetrachloromethane (CT) and trichloromethane (CF) was achieved within 1h.</td>
</tr>
<tr>
<td>[88]</td>
<td>amphiphilic polyurethane (APU) nanoparticles</td>
<td>Used in PAHs removal and can be modified to change the affinity of APU particles for specific contaminants such as phenanthrene (PHEN).</td>
</tr>
<tr>
<td>[89]</td>
<td>maghemite nanoparticles</td>
<td>Maghemite nanoparticles can selectively remove Cr(VI), Cu(II) and Ni(II) from wastewater under different pHs.</td>
</tr>
<tr>
<td>[90]</td>
<td>Zero-valent iron nanoparticles (INP)</td>
<td>Under both oxic and anoxic conditions, INPs can remove uranium in the wastewater to &lt;1.5% of its initial concentration within 1h.</td>
</tr>
<tr>
<td>[91]</td>
<td>MgO nanoparticles</td>
<td>Over 98% of azo and anthraquinone dyes can be adsorbed by MgO nanoparticles under optimum conditions.</td>
</tr>
<tr>
<td>[92]</td>
<td>bio-precipitated and encapsulated palladium nanoparticles</td>
<td>Bio-Pb can dechlorinate 100ppm trichloroethylene within 1 hour.</td>
</tr>
<tr>
<td>[93]</td>
<td>cellulose acetate (CA) supported Ni/Fe nanoparticles</td>
<td>TCE can be removed by CA through sorption on CA support and reduction by metal nanoparticles.</td>
</tr>
<tr>
<td>[94]</td>
<td>Biogenic Uraninite Nanoparticles</td>
<td>Successful bioremediation of uranium by biogenic Uraninite nanoparticles is possible when strictly anaerobic conditions are continuously provided.</td>
</tr>
<tr>
<td>[95]</td>
<td>silver nanoparticles covered by mercaptosuccinic acid (MSA)</td>
<td>Ag@MSA was able to remove 0.8g mercury per gram in the pH range of 5-6.</td>
</tr>
</tbody>
</table>
Table 1.3 Highlighted applications of nanoparticles in membranes

<table>
<thead>
<tr>
<th>References</th>
<th>Nanoparticles</th>
<th>Membrane</th>
<th>Achievement</th>
</tr>
</thead>
<tbody>
<tr>
<td>[12]</td>
<td>Silver nanoparticles</td>
<td>polysulfone membranes</td>
<td>The addition of silver nanoparticles decreased the hydraulic resistance and inhibited the growth of biofilm.</td>
</tr>
<tr>
<td>[96]</td>
<td>Titanium dioxide (TiO$_2$)</td>
<td>Poly(phthalazine ether sulfone ketone) (PPESK) membrane</td>
<td>TiO$_2$-entrapped PPESK membranes performed better in antifouling and enhancing other mechanical properties</td>
</tr>
<tr>
<td>[97]</td>
<td>Titanium dioxide (TiO$_2$)</td>
<td>Polyethersulfone (PES) membrane</td>
<td>Compared to pure PES membrane, the permeation properties of PES-TiO$_2$ composite membranes was improved by nanoparticles, as was the mechanical strength. In addition, the pore size was controllable by the amount of TiO$_2$ that was used.</td>
</tr>
<tr>
<td>[98]</td>
<td>TiO$_2$ nanoparticle</td>
<td>poly(styrene-alt-maleic anhydride)/poly(vinylidene fluoride) (SMA/PVDF) blend membrane</td>
<td>Compared to pure PVDF/SMA blend membrane, the nanoparticle composite membranes were significantly improved in permeability and antifouling.</td>
</tr>
<tr>
<td>[99]</td>
<td>Alumoxanes nanoparticles</td>
<td>asymmetric ultrafiltration ceramic membranes</td>
<td>The pore size of alumoxane-derived ceramic membranes was controllable by the size of nanoparticles.</td>
</tr>
<tr>
<td>[100]</td>
<td>Ferroxane nanoparticles</td>
<td>ceramic membranes</td>
<td>Ultrafiltration ceramic membranes were able to produce with the addition of ferroxane nanoparticles. This new process can take place in aqueous environment with no use of hazardous agents and low energy use.</td>
</tr>
<tr>
<td>[101]</td>
<td>fullerene C$_{60}$</td>
<td>ceramic alumina membranes</td>
<td>The number of bacteria on the membranes were decreased due to the decrease of zeta-potential and increase of hydrophobicity brought by fullerene nanoparticles.</td>
</tr>
<tr>
<td>References</td>
<td>Size</td>
<td>Coating layers</td>
<td>Species</td>
</tr>
<tr>
<td>------------</td>
<td>------------</td>
<td>----------------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>[102]</td>
<td>60nm</td>
<td>None</td>
<td>Sprague-Dawley rats</td>
</tr>
<tr>
<td>[103]</td>
<td>18nm</td>
<td>None</td>
<td>Sprague-Dawley rats</td>
</tr>
<tr>
<td>[104]</td>
<td>8-20nm</td>
<td>starch and bovine serum albumin (BSA)</td>
<td>zebrafish embryos</td>
</tr>
<tr>
<td>[105]</td>
<td>13-15nm</td>
<td>None</td>
<td>6-week-old SD rats</td>
</tr>
<tr>
<td>[106]</td>
<td>15 ± 6 nm</td>
<td>None</td>
<td>Crassostrea virginica</td>
</tr>
<tr>
<td>[107]</td>
<td>22.18 ± 1.72 nm</td>
<td>None</td>
<td>C57BL/6 mice</td>
</tr>
</tbody>
</table>
### Table 1.5 Experiments of aggregation of clay minerals

<table>
<thead>
<tr>
<th>References</th>
<th>Type of Clay</th>
<th>Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>[63]</td>
<td>kaolinite, montmorillonite</td>
<td>Huge aggregates of kaolinite were only formed at pH &lt; 7. The electrolyte tolerance of both kaolinite and montmorillonite increased with the increase of pH of clay suspensions.</td>
</tr>
<tr>
<td>[66]</td>
<td>illite</td>
<td>The CCC of illite increased with the increase of pH. K-illite was observed to have higher CCC than Na-illite, due to a higher affinity of K of illite.</td>
</tr>
<tr>
<td>[108]</td>
<td>montmorillonite, kaolinite, 10A mica</td>
<td>The surface properties of clay minerals are similar to each other, due to the natural organic and metallic coatings. The aggregation of clay minerals are dominated by large particles.</td>
</tr>
<tr>
<td>[109]</td>
<td>montmorillonite</td>
<td>The zeta potential of montmorillonite was independent of the change of pH. However, the electrokinetic behavior of clay suspensions was significantly affected by the valence of cations.</td>
</tr>
<tr>
<td>[68]</td>
<td>sodium montmorillonite</td>
<td>The anions phosphates, polyphosphate and tannate stabilized the montmorillonite suspension by increasing the charge density of its edge, while carboxy methylcellulose sterically stabilized the clay particles.</td>
</tr>
<tr>
<td>[110]</td>
<td>montmorillonite, sericite, kaolinite, halloysite and allophane</td>
<td>The charge of sericite was more sensitive to the change of pH than montmorillonite and kaolinite. Both positive and negative charges were observed on halloysite at higher pH.</td>
</tr>
<tr>
<td>[111]</td>
<td>kaolinite</td>
<td>Kaolinite was highly aggregated at low pH regardless of the electrolyte concentrations due to the strong edge-face interactions. However, higher electrolyte concentration was needed to floculate kaolinite suspension at high pH.</td>
</tr>
<tr>
<td>[112]</td>
<td>kaolinite</td>
<td>The size of kaolinite aggregates was larger in the presence of anionic polyacrylamides (PAM) than cationic PAM. But the increase of surface charge of either anionic or cationic PAM can lower the aggregates size of kaolinite.</td>
</tr>
<tr>
<td>[113]</td>
<td>smectite and illite</td>
<td>The smectite clay was observed to be more sensitive to sodicity than illite loams. And the structural stability of clay suspension was greatest under high organic matter content.</td>
</tr>
</tbody>
</table>
Figure 1.1 Comparison of processes relevant to determine the fate of organic chemicals (left) and to nanoparticles (right). Image from Praetorius et al. [53].
Figure 1.2 Energy profile of classical DVLO model consist of van der Waals attractive and electrostatic repulsive forces.
Figure 1.3 Unit structures of different types of clay minerals: (a) kaolinite (TO) and (b) montmorillonite/illite (TOT).
Chapter 2: Heteroaggregation of Bare Silver Nanoparticles with Clay Minerals in Aquatic Systems

2.1 Introduction

Engineered nanoparticles are intentionally produced particles with at least one dimension less than 100 nm. Owing to their small size, the particles’ properties are drastically different from those for the bulk material of the same composition [1]. For example, nano-sized gold is an excellent catalyst while bulk gold is catalytically inert [2]. With the increased application of nanotechnology, many engineered nanoparticles have been introduced to our daily life. However, as engineered nanoparticles are released to the environment during use or disposal, questions arise regarding their potential to cause adverse effects to the environment and human health [1, 3]. Routes of entry to water bodies or air of engineered nanoparticles may come from point sources such as landfills and factories, or from non-point sources such as wet deposition, storm water runoff, and the degradation or disposal of discarded nanomaterial-containing products [4]. After entering a water body, the fate of the engineered nanoparticles is controlled by transport (aggregation, adsorption, sedimentation, and bioaccumulation) and transformation (oxidation-reduction, dissolution, and bio- or UV-degradation) processes [5]. These processes can act independently or mutually and their role in determining the fate of
nanoparticles remains poorly understood [3, 4]. An accurate determination of fate is critical to determining the risk of nanoparticles to humans, organisms, and the environment [4] and thus studies addressing ecotoxicological effects must also properly account for the processes that control the environmental transport of nanomaterials.

Among the metallic engineered nanoparticles currently being produced, silver nanoparticles (AgNPs) are unique in their extensive use in commercial products [6]. This is a reflection of their utility as a non-specific antibiotic and thus they are utilized in products such as clothing, surface coatings, wound dressings, fashion accessories, and food containers [7]. However, when these nanoparticles are discharged into the environment, such properties could also produce unforeseen adverse effects on aquatic biota and thus there is considerable interest in determining the mechanisms and processes responsible for dictating the fate of these particles in different settings, such as aquatic environments [8]. One of the dominant processes affecting the fate of silver nanoparticles in aquatic systems is aggregation and recent research provides insight into the effects of electrolyte solutions, ionic strength, coating layer and organic matter on the aggregation of silver nanoparticles [9-11]. For example, NaCl, NaNO₃, and CaCl₂ produce “dissolution-accompanied” aggregation of silver nanoparticles, meaning the particles simultaneously aggregate and dissolve [11]. In these systems more dissolution was produced in chloride-containing AgNPs suspensions and aggregates with smooth continuous surfaces were formed, while discrete aggregates were formed in nitrate-containing suspension with less dissolution [11]. Aggregation of AgNPs is a function of the capping layer and electrolyte, with AgNPs coated with large organic molecules such
as the surfactant Tween resisting dissolution and aggregation more than those coated with smaller organic molecules, such as citrate or sodium dodecyl sulfate [10]. These studies have covered most of the transformation processes of AgNPs themselves, which are important when understanding the fate of AgNPs in aqueous system.

While these and similar studies do provide insight into the environmental fate of silver nanoparticles, they do so based on the analyses of model systems that do not necessarily correspond well with natural systems. For example, these studies do not account for interactions that may arise between silver nanoparticles introduced into a system and the native particles that are already present in a system, a process that can be termed heteroaggregation. Heteroaggregates form between two or more dissimilar particles and heteroaggregation is thus used to describe the stability of particle suspensions that contain more than one type of particle, which may differ in size, shape, surface charge, etc. [12]. One of the more dominant native particle types in aquatic systems are clay minerals [13] and thus an initial attempt to study the influence of heteroaggregation on silver nanoparticles should naturally start by characterizing interactions between natural clay minerals and silver nanoparticles.

Heteroaggregation experiments involving nanoparticles have been studied for years. Yates et al. [14] discovered that the addition of nano-sized silica particles (4.3–285 nm) to stable alumina dispersions formed large aggregates that settled out. Cerbelaud et al. [15] also found that heteroaggregates formed between submicrometer Al₂O₃ particles and SiO₂ nanoparticles. They proposed silica nanoparticles deposited on the alumina particles
resulting in the production of attractive interactions between the silica-coated alumina particles. Thus, the process comprised two steps consisting of the: 1) deposition of silica nanoparticles on alumina particles, and 2) aggregation between the silica-covered alumina particles [15]. Huynh et al. [16] observed faster aggregation between negatively charged carbon nanotubes and positively charged hematite nanoparticles, when compared to the homoaggregation of hematite nanoparticles. They proposed heteroaggregation occurred due to hematite nanoparticles being bridged by carbon nanotubes thereby increasing the overall rate of aggregation [16]. However, little is known regarding the heteroaggregation of silver nanoparticles under environmentally relevant conditions. Zhou et al. [13] observed faster aggregation in binary systems (i.e., systems that contains two types of colloidal particles) of silver nanoparticles and montmorillonite at pH near 4, compared to single component system (i.e., systems that only contains one type of colloidal particles) under similar conditions. Under these conditions the edge of the clay particles was positively charged, and its interaction with negatively charged silver nanoparticles decrease the stability of this binary system. Nevertheless, they didn’t examine heteroaggregation in different electrolyte solutions or with different clay minerals. Thus in our study, the purpose is to provide more specific results for predicting the fate of silver nanoparticles in natural water system.

In this study, two common clay minerals, montmorillonite and illite, were chosen to evaluate their effects on the heteroaggregation with silver nanoparticles. The basic structure of clay minerals is a two-dimensional array comprised of a sheet of silica tetrahedra (T) bound to sheets of alumina octahedra (O) [17]. Clay minerals are present
in the form of two or three layer configurations, such as 1:1 type kaolinite with one silica sheet and one alumina sheet (TO) (Figure 2.1a), or 2:1 type montmorillonite and illite with one octahedral alumina sheet sharing oxygen atoms with two tetrahedral silica sheets (TOT) (Figure 2.1b) [17-19]. The basal plane of the clay lamella is negatively charged due to isomorphic substitution of Si- and Al-ions for ions of lower valence, while the charge of the edge is pH-dependent because of pH-dependence in the exposed >Al-OH and >Si-OH surface groups [17]. The edge is positively charged when the pH is below the point of zero charge (PZC) of the exposed functional groups and negatively charged when the pH is above the PZC [17, 20-22]. Extensive experimentation on the aggregation of clay minerals (see Table 1) shows their behavior follows expected trends and depends upon pH, electrolyte solutions, ionic strength, and saturating cations [17, 20-22]. Although the heteroaggregation of clay particles with other nanoparticles has been studied [23, 24], except for the study of Zhou et al. [13] the aggregation of clay minerals with silver nanoparticles remains little studied.

The overall goal of our research is to elucidate the fundamental processes responsible for determining the fate of silver nanoparticles in natural aquatic environments, with the specific objective of this study being to evaluate the influence of heteroaggregation. In this chapter I detail progress toward understanding the heteroaggregation of silver nanoparticles with two clay minerals (montmorillonite and illite) as a function of saturating cation (Na+ and Ca2+) and ionic strength. To compare to previous experiments evaluating the homoaggregation of silver nanoparticles [11], the pH in this studied was maintained at ~ 7 and the electrolytes (i.e., NaCl, NaNO3 or CaCl2), temperature and
measurement methods applied in all the experiments remained unchanged. Our results
did not show significant differences in the stability, as defined by the critical coagulation
concentration (CCC), of binary systems of silver nanoparticle and clays when compared
to the single component systems under the same conditions. However, the broader
aggregation behavior of the binary systems more closely mimicked that for the clay
minerals and thus it appears the aggregation kinetics of binary systems can be
approximated based upon knowledge of just the single component clay systems.

2.2 Experimental Methods and Materials

2.2.1 Materials

AgNO₃ (≥99.8%) and D-maltose monohydrate (99%) were purchased from Sigma-
Aldrich and used without further purification. Ammonium hydroxide (20-22% as NH₃,
trace metal grade) was bought from Fisher Scientific. All other reagents were analytical
grade or higher. The deionized water used in the experiments was supplied by Millipore
(Milli-Q) with a resistivity of 18.2 MΩ·cm. The electrolyte solutions (NaCl, NaNO₃, and
CaCl₂), buffer solution (NaHCO₃), and solutions employed in silver nanoparticle
synthesis were filtered through 0.1 μm cellulose ester membranes (Millipore) before use.
All labware and glassware were thoroughly cleaned and soaked in 5% nitric acid for at
least one day before use, followed by a thorough rinse with deionized water and oven-
drying. The labware was immediately used or stored in a dust-free environment prior to
use.
2.2.2 Clay Preparation

Montmorillonite (SWy-2), kaolinite (KGa-2), and illite (IMt-2) were obtained from the Clay Minerals Society and prepared for use as follows. Monocationic suspensions of montmorillonite were prepared for the experiments following Essington et al.’s protocol [25]. To begin, 5g of the montmorillonite was briefly dispersed in 250mL deionized water, and rapidly mixed for 45 min on a stir plate. The less than 2 μm size fraction was isolated into the supernatant by overnight gravity sedimentation of > 2 μm particles. The supernatant was decanted and the electrolyte concentration was adjusted to be 1M NaCl, followed by fast mixing for 15 min. The clay was separated through centrifugation at 3600 rpm for 30 min. The supernatant was decanted and fresh 0.01M NaCl was added. The clay suspension was vigorously shaken to re-suspend the clay particles and then subsequently centrifuged once again at 3600 rpm for 30min. To keep the preparation procedures as consistent as possible for all three clays, the washing procedure was repeated 5 times. The suspension was then dialyzed against 0.01M NaCl. The solution was changed daily until the conductivity of the clay suspension was the same as the 0.01M NaCl.

Illite was prepared following the procedure of Gu et al. [26] that was revised to be consistent with the procedures used to prepare montmorillonite and kaolinite (see Appendix A for kaolinite preparation and characterization). Approximately 5g of the illite was dispersed in 250mL deionized water and the solution was rapidly stirred for 45 min. The less than 2 μm size fraction was collected in the supernatant through overnight sedimentation. The supernatant was collected and then brought to 1M NaCl. The
suspension was adjusted to pH 3 with 10% HCl and stirred for two hours. The less than 2 μm size fraction was collected by centrifugation at 3600 rpm for 30 min, and then re-suspended in 0.01M NaCl followed by stirring for two hours. The suspension was then centrifuged at 3600 rpm for 30 min and the supernatant was decanted. The washing process was repeated 5 times. After that, the suspension was dialyzed against 0.01M NaCl. The solution was changed daily until the conductivities of the inner and outer phases were the same.

The calcium-saturated clay samples were prepared following the methods previously described with the exception that NaCl was replaced with CaCl₂. All of the clays were stored as concentrated suspensions in the dark at 4 °C.

2.2.3 Silver Nanoparticle Synthesis

Monodisperse suspensions of silver nanoparticles were synthesized following Li et al.’s method [11]. In short, 2 mL of 0.01M AgNO₃ was pipetted into a 50 mL glass beaker followed by 10 mL of 0.02M ammonium hydroxide. The solution was stirred using a small Teflon-coated magnetic stir bar. The solution pH was adjusted to ca. 11.5 through the addition of 250 μL of 0.1M NaOH, after which 8 mL of 0.025M D-maltose was introduced to reduce the Ag[(NH₃)₂]⁺ complex to form metallic silver nanoparticles. After the addition of all reagents, the suspension was equilibrated for 30 min in the dark at room temperature (20 ± 1 °C).
The freshly synthesized silver nanoparticles were dialyzed against deionized water using a cellulose ester membrane (Spectra/Por, 8-10k MWCO) over a period of 24 hours. The deionized water was periodically changed (minimum of 4 times), which Li. et al. [11] report is sufficient time to remove residual ions. Six such batches of silver nanoparticles were synthesized and combined to form a 120 mL stock suspension. This stock was stored in a polypropylene bottle in the dark at 4 °C. The concentration of the stock suspension was determined using an inductively coupled plasma optical emission spectrometer (ICP-OES; Varian Vista AX) to be 60 mg-Ag/L, which yields to 55% of the initial AgNO₃ solids.

2.2.4 Particle Characterization

The hydrodynamic diameter and UV-vis spectra of the silver nanoparticles was determined on a sample that was prepared by diluting the stock suspension 25 times in a sodium bicarbonate – sodium chloride buffer solution that maintained the pH at 7.0 ± 0.3 and ionic strength at 1mM. The hydrodynamic diameter was measured by dynamic light scattering (DLS) (90Plus, Brookhaven Instruments Corp., Holtsville, NY). The UV-vis spectrum was collected over the wavelength range of 200 – 700 nm using a Shimadzu UV-4201PC UV-vis spectrophotometer.

The morphology and size of the dispersed silver nanoparticles and clays were observed using a Technai G2 Spirit Transmission Electron Microscope (TEM) with a 120 kV electron beam, which located in the Campus Microscopy and Imaging Facility at The Ohio State University. Samples were prepared by placing one drop of the working
suspension on a 100 mesh copper grid that was dried under nitrogen. Samples of dispersed silver nanoparticles and clays were prepared using concentrated stock suspensions which were sonicated before use. The morphology of the heteroaggregates was also evaluated using the TEM, where one drop of the suspension generated from the heteroaggregation experiments was used instead.

The electrophoretic mobility of Na-/Ca-montmorillonite and illite was measured by a Brookhaven Instrument Corp. ZetaPALS instrument. The Smoluchowski equation was used to calculate the zeta potential from the corresponding mobility values for a particle of arbitrary shape with a nominal diameter that is much larger than the thickness of the electrical double-layer [27]. The measurements were conducted at a temperature of $22 \pm 0.5 \, ^\circ C$ across the pH range of 4.0 - 10.0 in 1mM NaCl solutions. The samples were equilibrated for 5 min and for each pH value the data comprised ten individual measurements collected and averaged for three separate samples. The effects of NaCl (0.1mM – 10mM) and CaCl$_2$ (1mM – 500mM) on the electrophoretic mobility of the clay minerals were evaluated as well at pH 7.

2.2.5 Aggregation Kinetics

Aggregation kinetics for both the homoaggregate and heteroaggregate systems was determined by measuring the initial time rate of change in the average hydrodynamic radius of the particle suspensions using DLS. The instrument was equipped with a 678 nm laser with a detection angle of 90 degrees and the experiments were conducted at a temperature of $22 \pm 0.5 \, ^\circ C$. For homoaggregation and heteroaggregation experiments, the
Intensity-weighted autocorrelation functions (ACF) were generated from the fluctuating signal caused by the random motion of particles as:

\[ g(t) = \int G(\Gamma)e^{-\Gamma t}d\Gamma \]  

(1)

where the left hand side is the measured data, \( \Gamma \) is the average decay rate (rad/sec) and \( G(\Gamma) \) is the desired distribution information. \( \Gamma \) is then determined by

\[ \Gamma = D \ q^2 \]  

(2)

where \( D \) is the translational diffusion coefficient (cm\(^2\)/sec) used to calculate particle diameter, and \( q \) is the scattering vector defined by scattering angle \( \theta \), wavelength of the laser \( \lambda_0 \), and the index of refraction of the suspending liquid \( n \) as:

\[ q = \frac{4\pi n}{\lambda_0} \sin \frac{\theta}{2} \]  

(3)

The average particle diameter \( (d) \) is then calculated by

\[ D = \frac{k_B T}{3\pi \eta d} \]  

(4)

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, and \( \eta \) is the viscosity of the liquid.

All stock suspensions were prepared in a 5.0 \( \times \) 10\(^{-2} \) mM sodium bicarbonate buffer at pH 7.0 \( \pm \) 0.3. The particle concentrations were kept the same for both the homoaggregation and heteroaggregation experiments. All working suspensions were briefly sonicated in an ultrasonic water bath before each experiment.

For the homoaggregation experiments, 3 mL of the particle suspension of interest was pipetted into a disposable acrylic cuvette. The cuvette was prepared before use by
washing using 5% HNO₃ followed by a thorough rinse with deionized water. Predetermined amounts of electrolyte and buffer solutions were then added to the cuvette to obtain the desired ionic strength, while maintaining the total volume at 4 mL. The cuvette was then covered with a plastic lid, quickly hand-shaken and inserted into the DLS sample holder. The heteroaggregation experiments were the same except that 1.5 mL of silver nanoparticles and 1.5 mL of the clay suspensions of interest were used. In either case, measurements were begun immediately upon insertion of the cuvette into the DLS. For the silver nanoparticle system, the hydrodynamic diameters were collected over a period of 15 min with 90s intervals between measurements, while the single clay and binary component systems were collected over a period of 5 min with 30s intervals between measurements.

The stability of the suspensions was analyzed by comparing variations in the inverse stability ratio with ionic strength (IS). The inverse stability ratio, 1/W, is defined as the ratio of the experimental aggregation rate constant (kₑxp) to that determined for rapid aggregation (k₁rap), or diffusion-limited aggregation, as shown in following expressions [28]:

\[ k_{\text{exp}} = \frac{1}{aNr_0} \frac{dr}{dt} \]  \hspace{1cm} (5)

\[ \frac{1}{W} = \frac{k_{\text{exp}}}{k_{\text{rapid}}} \]  \hspace{1cm} (6)

where \( N \) is the initial particle concentration, \( r_0 \) is the initial particle radius, and \( a \) is an optical factor. The \( k_{\text{exp}} \) value was calculated by conducting a linear least-squares regression analysis on the time-rate of change of the hydrodynamic radius (\( \frac{dr}{dt} \)), while
the $k_{\text{rapid}}$ value was determined as the average value of the $k_{\text{exp}}$ values under a diffusion-limited aggregation condition. This latter value was specific to each homoaggregation or heteroaggregation system and electrolyte. The relationship between $1/W$ and ionic strength can be used to identify the critical coagulation concentration (CCC) of a specific system with different types of electrolytes. The CCC can be determined as the intersection point of two straight lines, which represent the changes of $1/W$ as a function of ionic strength in the reaction and diffusion-limited aggregation regimes, respectively \[27\].

2.3 Results and Discussions

2.3.1 Characterization of Silver Nanoparticles

The hydrodynamic diameter of the synthesized silver nanoparticles determined by DLS was $60.9 \pm 0.5$ nm. TEM images show the silver nanoparticles’ morphology as smooth and roughly spherical with a diameter similar to that measured by DLS of ca. 60 nm (Figure 2.2a). Based on this size, the concentration of stock suspension ($60 \text{ mg L}^{-1}$), and the density of metallic silver ($10.5 \text{ g cm}^{-3}$), we calculate the particle concentration of the stock suspension to be $5.05 \times 10^{10}$ particles mL$^{-1}$. With a 25 times dilution, the number concentration of the working suspension for the aggregation experiments was $2.02 \times 10^{9}$ particles mL$^{-1}$.

The UV-vis spectrum (Figure 2.2b) of freshly synthesized silver nanoparticles showed a maximum absorption peak at a wavelength of 432.5 nm, which was consistent with the reported location of the surface plasmon absorption band of silver nanoparticles
synthesized using this method [29]. The observed red-shift in the position of the absorption peak compared to that for monodispersed silver nanoparticles with a diameter below 100 nm with no adsorbed or oxidized layer, as well as the broadening of the absorption band are evidence for the existence of an oxidized layer on the particle surface [11].

According to Li. et al. [11], synthesized silver nanoparticles have a negative zeta potential across the pH range of 4.0 to 10.0, and this value remains relatively unchanged at -45.8 ± 0.9 mV under neutral and alkaline conditions. Li et al. [11] rationalize that since the surface charge of bare silver nanoparticles should theoretically be zero, the measured negatively charged surfaces may be due to the existence of an oxide surface layer and the adsorption of other anions during the synthesis (e.g., hydroxide).

2.3.2 Characterization of Clay Minerals

2.3.2.1 Characterization of Montmorillonite

The diameter of dispersed montmorillonite lamellae ranged from 200 nm to 700 nm (Figure 2.3a), consistent with the method of preparation [25]. The concentrations of Na- and Ca-montmorillonite (Na-MONT and Ca-MONT) stock suspensions were determined by gravimetric analysis as 24.7 g L⁻¹ and 41.4 g L⁻¹, respectively, resulting in estimated number concentrations of diluted working suspensions of ca. 1 × 10¹⁰ particles mL⁻¹ and 8 × 10⁹ particles mL⁻¹, respectively.
The zeta potential of the sodium- and calcium-forms of the montmorillonite in 1 mM NaCl remained unchanged at -46.5 ± 7.14 mV and -22.6 ± 2.88 mV, respectively, across the pH range 4.0 to 10.0 (Figure 2.4). These results are consistent with those published for this montmorillonite suspended in NaCl as the electrolyte [13, 30]. Under the experimental conditions studied, the zeta potential of Ca-montmorillonite was less negative than that for Na-montmorillonite. The reason for this could be incomplete ion exchange during the measurement in the case of Ca-montmorillonite dispersed in NaCl solution [30, 31] because the electrolyte concentration (1mM) was too low and the time during sample preparation (less than 30 min) was too short for ion exchange to be fully completed. Thus, Ca\(^{2+}\) still dominates in the sheets of the Ca-montmorillonite particles, since montmorillonite has a higher affinity for Ca\(^{2+}\) than Na\(^{+}\) [30].

The zeta potential of the two forms of montmorillonite across the NaCl and CaCl\(_2\) concentrations corresponding to those studied in the aggregation experiments were also measured (Figure 2.5a). At low electrolyte concentration, the zeta potential for Ca-montmorillonite was less negative than that for Na-montmorillonite. As the electrolyte concentration increased, however, the zeta potential for both forms of clays converged to similar values. Unlike what was observed for the pH-dependence of the zeta potential of both forms of montmorillonite (Figure 2.4), similarities in the zeta potentials of the sodium and calcium form of the clay in the different electrolytes may reflect the higher electrolyte concentrations forced the ion exchange between Ca\(^{2+}\) and Na\(^{+}\). The same trend exists for both CaCl\(_2\) and NaCl. It is more pronounced for NaCl, however, as the zeta potential of Na-montmorillonite became less negative as NaCl was increased from
30mM to 500mM. Likely, this reflects compression of the electrical double layer in the presence of electrolyte and the subsequent decrease in the potential at the plane of shear [27]. Below a NaCl concentration of 30mM, the absolute value of the zeta potential of Na-montmorillonite increased from ca. 40mV to ca. 65mV, as NaCl concentration increased from 1mM to 30mM. According to Delgado et al. [32] this reflects that montmorillonite can undergo rapid hydrolysis at circumneutral pH, whereby H⁺, exchanged for bound Na⁺, results in the release of Al³⁺ and Mg²⁺ from montmorillonite producing the observed increase in the magnitude of the zeta potential. Delgado et al. [32] described this hydrolysis as two steps: (1) a rapid exchange of hydrogen ions in the solution with Na⁺ originally attached to the montmorillonite and (2) a slow penetration of the exchanged H⁺ into the sheets of montmorillonite. The attack of hydrogen ions decomposes montmorillonite thereby releasing Al³⁺ and Mg²⁺ into the solution. These multivalent cations could produce a compression of the electrical double layer producing a less negative zeta potential. At the same time, however, the loss of those cations would produce a decrease in the zeta potential of montmorillonite. Thus the decrease of zeta potential of clay is the result of these combined actions.

This hydrolysis process is kinetically hindered at elevated electrolyte concentrations and thus it tends to be observed during relatively low electrolyte concentrations, typically less than 10⁻³ M [32-34]. However, Callaghan et al. [35] and Rossi et al. [36] observed a decrease in the zeta potential (increase in the magnitude) at a NaCl concentration above 10⁻² M and they also attributed to the release of residual cations. This suggests the phenomenon occurs for a broader range of electrolyte concentrations. Considering the
sensitivity of clay surfaces to the method of preparation and storage [34], our results are similar in magnitude to previous results.

When Ca-montmorillonite was suspended in NaCl in the range of 1 to 30mM, a similar trend of decreasing zeta potential with increasing NaCl concentration was observed. However, in this case the origin of the trend likely reflects the exchange of Ca$^{2+}$ bound to the clay with Na$^+$ ions in the solution. The net loss of cation charge would result in a lower zeta potential. The time needed for complete replacement of Ca$^{2+}$ by Na$^+$ is reported to be around 24 h since montmorillonite has a higher affinity for Ca$^{2+}$ than Na$^+$ [34] and presumably given sufficient time the two data sets would converge. Since the equilibration time was much less than 24 hours, Ca-montmorillonite had a consistently higher (less negative) zeta potential than did Na-montmorillonite.

In systems with CaCl$_2$, the zeta potential for Na-montmorillonite increased as the electrolyte concentration increased (Figure 2.5a). This reflects both the exchange of bound Na$^+$ with solution phase Ca$^{2+}$ and the enhanced compression of the electrical double layer induced by the divalent calcium cations. However, except for an increase in the standard error of the zeta potential with increasing electrolyte, no significant change in the zeta potential of Ca-montmorillonite was observed in the range of 10$^{-4}$ to 10$^{-2}$ M CaCl$_2$ (Figure 2.5a). While the reason for this result is not known with certainty, it seems possible that the release of cations from montmorillonite counterbalances the expected increase of zeta potential caused by Ca$^{2+}$. As a result, the overall zeta potential remained unchanged.
2.3.2.2 Characterization of Illite

The illite flakes ranged in size from roughly 50 to 200 nm and differed from montmorillonite and kaolinite in that illite had irregular and curved outlines (Figure 2.3c). In some locations, individual illite lamella appeared to orient perpendicular to the imaging plane, and the resulting cluster of illite flakes formed a wheel-like formation. This wheel-like structure indicates an edge-to-face orientation of illite which allows small angles between each flake (sub-parallel orientation), when compared to the parallel orientation in kaolinite samples (see Appendix A for kaolinite characterization). This result is consistent with O’Brien’s results for illite in both distilled and saline water which show a close circle with stair-step arranged illite flakes [37]. However, except for these mostly isolated wheel-like formations, it appeared that the majority of the illite sample was oriented face-to-face. The concentrations of Na- and Ca-illite in the respective stock suspensions were 1.2 g L⁻¹ and 3.6 g L⁻¹, resulting in estimated number concentrations in the diluted working suspensions of ca. $7 \times 10^9$ particles mL⁻¹ and $5 \times 10^9$ particles mL⁻¹, respectively.

At a pH of 7, the zeta-potential of Na-illite was -44 ± 4 mV, while for Ca-illite it was -21 ± 2 mV. Similar trends were found for the zeta-potential of illite in the pH range 4 to 10 as was measured for montmorillonite (Figure 2.4). This was expected considering both clay minerals had the same basic TOT structure. As was observed for montmorillonite, the calcium-form of illite had a less negative zeta potential than did the Na form, reflecting the presence of the bound divalent cations.
The zeta potential for both Na- and Ca-illite generally increase (trend to a less negative value) as the NaCl concentration increased from 1mM to 500mM (Figure 2.5b). Different than what was observed for Na-montmorillonite, however, no significant decrease in the zeta potential was observed for Na-illite at < 30 mM NaCl. Illite is a nonexpanding clay mineral with no extractable interlayer ions [38] and although it has a 2:1 layer structure similar to that for montmorillonite, the cation exchange capacity (CEC) of illite is lower than that of montmorillonite [39]. For the samples in this study, the reported CEC of the montmorillonite is 1040 mmol kg\(^{-1}\) [25], while that for the illite is 231 mmol kg\(^{-1}\) [26]. Na-illite has a smaller amount of internal cations (i.e., potassium ions) available for release than does Na-montmorillonite. Thus, as a result of the compression of the electrical double layer induced by the increasing electrolyte, Na-illite showed a continuous decrease in the magnitude of the negative zeta potential as NaCl was increased from 1 mM to 500 mM. Similar to Ca-montmorillonite, the exchange of clay-bound Ca\(^{2+}\) associated with Ca-illite with solution-phase Na\(^+\) remains possible and if it occurred it could have produced the reduction in the magnitude of the zeta potential at NaCl below 30 mM.

The effect of CaCl\(_2\) on the zeta potentials of both Na- and Ca-illite (Figure 2.5b) reveals that illite has a higher affinity for Ca\(^{2+}\) than Na\(^+\). Since illite is a nonexpanding clay, suspending Na-illite in CaCl\(_2\) was assumed to lead to more rapid and complete exchange of Na\(^{+}\) with Ca\(^{2+}\) than that for Na-montmorillonite. As a result, the zeta potential of Na-illite was very close to that for Ca-illite from 1mM to 10mM CaCl\(_2\).
2.3.3 Homoaggregation of Single Component Systems

2.3.3.1 Homoaggregation of Silver Nanoparticles

Dissolution-accompanied aggregation was observed for the silver nanoparticles (Figure 2.6a and 7b). In the monovalent electrolyte solutions, the initial diameter decreased at the initial time of aggregation for electrolyte concentrations increasing from 10mM to 200mM. However, since the dissolution of silver nanoparticles was accompanied by aggregation, this initial decrease in size was soon followed by an overall increase in hydrodynamic size with time as aggregation of the particles proceeded. Li. et al. [11] reported the size decrease to be the result of the dissolution of the oxidized surface layer as shown in the following reaction:

\[
Ag_2O(s) + H_2O = 2Ag^+ + 2OH^- \tag{7}
\]

According to Li et al. [11], this reaction is influenced by the concentration and type of electrolyte. When the electrolyte is NaCl, AgCl\(_{(s)}\) precipitates on the nanosilver particle surface, resulting in a modification of the silver nanoparticles morphology [11]. NaNO\(_3\), however, did not produce a precipitate nor did it change aggregate morphology [11]. Regardless, the aggregation of nanosilver in these two electrolytes was similar (Figure 2.7) and was consistent with other data presented in the literature [11]. In our experiments, the CCC of silver nanoparticles in NaCl was ca. 40mM, while it was ca. 35mM in NaNO\(_3\). These results are consistent with those presented by Li. et al. [11], which indicates the behavior of AgNPs synthesized in this experiments is similar to that in previous studies.

When the electrolyte was CaCl\(_2\) the CCC of silver nanoparticles was much lower (ca. 2mM) than that in NaCl/NaNO\(_3\) (Figure 2.7). According to the Schulze-Hardy rule [27],
$\text{CCC}_{\text{Na}}/\text{CCC}_{\text{Ca}}$ equals $z^6$ for particles with a large zeta potential ($|\zeta| > 50\text{mV}$), and $z^2$ for those with a low zeta potential ($|\zeta| < 50\text{mV}$), where $z$ is the counterion charge (i.e., $z = 2$ in the case of Ca$^{2+}$). In our experiments, the ratio of $\text{CCC}_{\text{Na}}$ and $\text{CCC}_{\text{Ca}}$ was approximately proportional to $z^4$. This intermediate value between the two predicted by the Schulze-Hardy rule (i.e., $z^6$) is consistent with previous measurements, and according to Li et al. [10, 11] indicates the modification of surface charge due to the adsorption of cations on the surface of the silver nanoparticles.

### 2.3.3.2 Homoaggregation of Montmorillonite

Typical two-regime, Derjaguin-Landau-Verwey-Overbeek (DLVO) type aggregation kinetics was observed for sodium-saturated montmorillonite in NaCl, NaNO$_3$ and CaCl$_2$ (Figure 2.8a). DLVO-type aggregation refers to aggregation controlled by the combined influence of electrostatics and van der Waals interactions [40, 41]. At low electrolyte concentrations (e.g., 1 - 50 mM NaCl or 0.5 - 1 mM CaCl$_2$), an increase in the electrolyte concentration led to a corresponding increase in the aggregation rate (Figure 2.8a). Above these electrolyte concentrations, the aggregation rate reached a maximum value that did not significantly vary as electrolyte concentrations increased further. For a monovalent electrolyte, similar CCC values of ca. 50 mM were determined for Na-montmorillonite in NaCl and NaNO$_3$ (Figure 2.8a). This CCC value is comparable to those reported by Tombácz et al., of ca. 25, 50, and 100 mM NaCl at pH 4, 6.5, and 8, respectively [20]. The pH of 6.5 approximates the PZC of edges of the clay [13] where the edge of montmorillonite transitions between weakly positive and negative charged states [20]. When the pH is below the PZC of the edge, the edge will be positively charged and its
interaction with negatively charged face becomes significant and decreases the stability of the montmorillonite suspension. However, when the pH is above the PZC of the edge, both the edge and basal plane of the clays are negatively charged which limits the influence of edge-face interactions resulting in an increase in the stability of the suspension. Thus, the CCC of montmorillonite at pH ~ 7 was between that measured at a pH value below the PZC of the edge (e.g., ~ 4) and above the PZC of the edge (e.g., ~ 10).

In systems containing Na-montmorillonite equilibrated in CaCl$_2$, a CCC value of ca. 1.5mM CaCl$_2$ was determined (Figure 2.8a). The ratio of the CCC$_{[Na]}$/CCC$_{[Ca]}$ was 33:1, proportional to $z^5$. This value is similar with that predicted by the Schulze-Hardy rule of $z^6$ [42]. One possible reason for the lack of an exact agreement could be the difficulty in preparing a pure monocationic montmorillonite because of potential release of multivalent cations (Mg$^{2+}$, Al$^{3+}$) from the clay minerals [42]. It could also reflect the exchange in surface cations by the added electrolyte during the aggregation experiments [31, 43].

The same CCC of ca. 50 mM NaCl and ca. 2mM CaCl$_2$ were observed for both Na-montmorillonite and Ca-montmorillonite at pH ~7 (Figure 2.8b). It seems the cation used to saturate the basal surface planes of montmorillonite had little to no impact on the suspension stability (Figure 2.9). This was consistent with the similar values of zeta potentials for Na- and Ca-montmorillonite (Figure 2.5a). The ratio of CCC$_{[Na]}$/CCC$_{[Ca]}$ for Ca-montmorillonite was 25:1, or approximately $z^{4.6}$, which is close to that of Na-montmorillonite. A similar result was obtained by Tombácz et al. [31] and as a result they
hypothesized that montmorillonite aggregation depends only on the electrolyte, not the original cations present in the montmorillonite. A similar CCC of 70 mM was determined for Mg-montmorillonite at pH 7 in KCl [44], indicating these results span a range of electrolyte and cation types.

2.3.3.3 Homoaggregation of Illite

Typical two-regime, DLVO-type aggregation kinetics were also observed for Na- and Ca-illite in NaCl, NaNO$_3$ and CaCl$_2$ (Figure 2.10a and 2.10b). The CCCs of ca. 70mM NaCl or NaNO$_3$ and ca. 2mM CaCl$_2$ was determined for Na-illite at pH 7, while ca. 50mM NaCl or NaNO$_3$ and ca. 1mM CaCl$_2$ for Ca-illite. Unfortunately, literature data for the aggregation of Na-illite at neutral pH conditions is limited and quite variable. At pH 7, reported CCC values of Na-illite vary from 7 to 40 mM NaCl [22, 42, 45, 46]. In these studies, the illite samples were not only obtained from different sources they were also prepared differently, which likely resulted to the reported variations in the CCC. For example, Hesterberg et al. [22] first washed their illite sample with concentrated NaClO$_4$ and KClO$_4$ solutions, then followed by a two-step washing (NaClO$_4$ and HClO$_4$ at pH 3.5 followed by NaClO$_4$ at pH 7 – 10). The KClO$_4$ was used to maintain the illite’s structural K. In the end, their illite samples were used as stock suspension at pH 7 with residual NaClO$_4$ and KClO$_4$. On the other hand, Oster et al. [42] prepared their sample by washing the clay in a 1M NaCl solution, followed by distilled water washing until it was free of Cl$^-$. Their sample was then freeze-dried. Only homoionic aggregation data was found for Ca-illite [47], in which < 0.5mM CaCl$_2$ was reported to be the CCC of Ca-illite. In our experiments, the ratios of CCC$_{Na}$/CCC$_{Ca}$ for both the sodium- and calcium-
form illite were $z^{5.13}$ and $z^{5.64}$, respectively. These results were close to the prediction of the Schulze-Hardy rule, with differences again possibly reflecting the release of residual cations from the clays [42].

Similar to montmorillonite, the type of bound cation had little effect on the stability of illite (see Figure 2.11). The CCCs of Ca-illite and Ca-montmorillonite were similar, whereas the CCCs of Na-illite were slightly higher than those for Na-montmorillonite (Table 2). Oster et al. [42] similarly observed that the CCC of Na-illite was higher than that of the CCC for Na-montmorillonite, while the CCCs of the two calcium forms of the clays were similar. They concluded that the irregular surfaces and terraced planar orientation (i.e., wheel like orientation in the TEM image of Na-illite in Figure 2.3b) of Na-illite lead to smaller edge-to-face attraction forces, and eventually a higher CCC for Na-illite than for Na-montmorillonite. At the same time, the PZC of illite ranges from 3.5 to 4.5 [48-50] and thus considering its structure is similar to montmorillonite (both TOT structure) a higher CCC value of illite than that of montmorillonite seems reasonable.

2.3.4 Heteroaggregation of Binary Component Systems

2.3.4.1 Silver Nanoparticles and Montmorillonite

The stability of the mixed silver nanoparticle and montmorillonite (either Na- or Ca-saturated) systems was little changed compared to that for the single-particle systems (Figure 2.12). At neutral pH, both the edge and the face of the montmorillonite flakes were negatively charged [20]. The silver nanoparticles were also negatively charged under these conditions [11]. Thus, as a result the aggregation behavior assumed a form
characteristic of typical two-regime aggregation. TEM imaging (Figure 2.13) of the mixture in 100mM NaCl showed the silver nanoparticles were primarily associated with the basal planes of the montmorillonite, but not the edges. This was consistent with the negatively charged edge on the montmorillonite repelling the negatively charged silver nanoparticle. The basal plane, while also negatively charged, was saturated with either Na\(^+\) or Ca\(^{2+}\) ions which might act to form a cation-bridge between the clay basal face and silver nanoparticles [51].

The montmorillonite flakes were roughly five times larger than the silver nanoparticles (Figure 2.2a and 2.3a) and the particle number of montmorillonite was also nearly five times more than that of silver nanoparticles. This could explained that the rate of heteroaggregation was dominated by the montmorillonite (See Table 2.3 and 2.4). Zhou et al. [13] mentioned a possible non-DLVO force - the depletion force - could form in binary systems that have a large ratio in particle sizes. The depletion force could exist in colloidal suspensions when large particles are suspended in a dilute solution of smaller ones [52]. It occurs when the distance between two large particles is less than the diameter of the smaller ones resulting in the small particles being pushed out to leave a “free volume” between the large particles. This “free volume” will then lead to an imbalance of pressure around the large particles, which in turn may form either attractive or repulsive forces between these same particles [53]. The attractive form of the depletion force can lead to the flocculation of particles [52]. However, the limited change in the stability of the mixture suggests any such depletion force was negligible, if present at all, in this binary system.
Thus, we propose that the heteroaggregation of silver nanoparticles and montmorillonite was comprised of separate steps. The first step entailed the deposition of the nanoparticles onto montmorillonite flakes during the initial stage of the experiment [54]. In essence, montmorillonite acts as a mobile collector in a manner that is analogous to the deposition of silver nanoparticles onto the surface of sand [55] or silica [56]. The deposition of silver nanoparticles on the clay minerals can be described as the interaction between a sphere and an infinite flat plate [57], since both the basal planes and the edges of montmorillonite are negatively charged under neutral condition. In addition, based on the size of nanoparticles (~60nm) and clay particles (200 – 400nm), the basal planes of clay particles can provide most of the spaces for nanoparticle deposition. As previously discussed, only the van der Waals attraction force and electrical double layer repulsion force are considered to be involved into their interactions [13, 58]. This step is followed by the second step, where the combined NP-clay particles aggregate more or less at the same rate as that for the clay-only systems. Because of the larger particle number concentration of montmorillonite, the deposition of bare silver nanoparticles onto the illite appears to have little effect on its stability, which also explains the lack of a change in the CCC of the heteroaggregate systems.

2.3.4.2 Silver Nanoparticles and Illite

The stability of the mixture of silver nanoparticles and illite (either Na- or Ca-form) was also little changed from that for the single-particle systems (Figure 2.14). Illite has negatively charged edge and basal planes at pH 7 according to the reported PZC value of
3.5 [50] and thus as hypothesized for the binary system with montmorillonite, these results also suggest the nano-sized silver first associated with the basal illite face and then its fate was bound to the subsequent aggregation of the clay [54]. This seems reasonable due to the large particle size and higher number concentration of illite in these systems compared to that for the silver nanoparticles.

2.4 Conclusions

Our results did not show significant differences in the stability of binary component systems of silver nanoparticle and clays at pH 7 when compared to the single particle systems at the same pH. We attribute this to weakly charged or negatively charged clay edges, as well as permanently negatively charged basal plane surfaces of the clays at pH 7, thus all six combinations between silver nanoparticles and the clays in binary systems (i.e., face-to-face, face-to-edge, edge-to-edge, nanoparticle-to-nanoparticle, face-to-nanoparticle, edge-to-nanoparticle) are barrier-controlled (i.e., high electrolyte concentration is needed to overcome the energy barrier to form aggregates). While we cannot completely neglect possible non-DLVO forces that arise from size asymmetry, such as depletion forces, the lack of differences observed in the single- and binary-particle systems suggests their influence under the conditions studied was negligible. Thus, the result indicates that the binary system of montmorillonite/illite and silver nanoparticles can be treated as single component system of clays under neutral conditions, when studying the aggregation kinetics of the mixture. This substitution can simplify the process to predict the fate of silver nanoparticles in the existence of clay minerals.
2.5 References


### 2.6 Tables and Figures

**Table 2.1** Highlighted experimentation on aggregation of clay minerals

<table>
<thead>
<tr>
<th>References</th>
<th>Type of Clay Minerals</th>
<th>Saturating Cations</th>
<th>Electrolyte</th>
<th>pH</th>
<th>Aggregation Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>[17]</td>
<td>Kaolinite from Zettlitz kaolin (Germany)</td>
<td>Na⁺</td>
<td>NaCl</td>
<td>4–8</td>
<td>Huge aggregates were formed only below pH~7 in kaolinite suspensions, with CCC around 1 mM NaCl. The CCC measured in the alkaline region was ~ 100 mM NaCl.</td>
</tr>
<tr>
<td>[20]</td>
<td>Montmorillonite from Wyoming bentonite (Swy-1 and Swy-2 samples)</td>
<td>Na⁺</td>
<td>NaCl</td>
<td>4–8.5</td>
<td>The CCC of montmorillonite suspensions was reported as ~ 25 mM and ~ 100 mM NaCl at pH ~ 4 and ~ 8, respectively. The CCC at the pH of PZC of edges (~ 6.5) approximated as ~ 50mM NaCl.</td>
</tr>
<tr>
<td>[21]</td>
<td>Montmorillonite from Cheto, Arizona (SAz-1) and kaolinite from Georgia (KGa-1). Both were obtained from The Clay Minerals Society’s Source Clays Repository.</td>
<td>Na⁺, Ca²⁺, and Mg²⁺</td>
<td>NaCl, CaCl₂, or MgCl₂ to match the saturating cations of the clays.</td>
<td>5–10</td>
<td>The CCC of all types of clays were found to be pH-dependent. The effect of pH was greater for the kaolinite than the montmorillonite.</td>
</tr>
<tr>
<td>[22]</td>
<td>Silver Hill illite (IMt-1) from the Source Clays Repository of the Clay Mineral Society</td>
<td>Na⁺ and K⁺</td>
<td>NaClO₄ and KClO₄ for Na- and K-illite, respectively.</td>
<td>6–11</td>
<td>K⁺ was three times more effective than Na⁺ for flocculating illite due to greater surface complexation of K-illite.</td>
</tr>
</tbody>
</table>
Table 2.2 Estimated Critical coagulation concentration (CCC) of suspensions in different electrolyte types

<table>
<thead>
<tr>
<th>Particle type</th>
<th>Critical Coagulation Concentration (CCC) (mM)</th>
<th>NaCl</th>
<th>NaNO₃</th>
<th>CaCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare silver nanoparticles</td>
<td></td>
<td>40</td>
<td>35</td>
<td>2</td>
</tr>
<tr>
<td>Na-MONT</td>
<td></td>
<td>50</td>
<td>50</td>
<td>1.5</td>
</tr>
<tr>
<td>Ca-MONT</td>
<td></td>
<td>50</td>
<td>50</td>
<td>2</td>
</tr>
<tr>
<td>Na-Illite</td>
<td></td>
<td>70</td>
<td>70</td>
<td>2</td>
</tr>
<tr>
<td>Ca-Illite</td>
<td></td>
<td>50</td>
<td>50</td>
<td>1</td>
</tr>
</tbody>
</table>
Table 2.3 Comparison of fastest $dr/dt$ for single component systems

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Bare-AgNP</th>
<th>Na-MONT</th>
<th>Ca-MONT</th>
<th>Na-illite</th>
<th>Ca-illite</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.10</td>
<td>5.53</td>
<td>4.41</td>
<td>0.53</td>
<td>1.24</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>0.12</td>
<td>7.52</td>
<td>5.47</td>
<td>1.04</td>
<td>1.06</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>0.14</td>
<td>6.83</td>
<td>2.66</td>
<td>1.33</td>
<td>1.35</td>
</tr>
</tbody>
</table>
Table 2.4 Comparison of fastest $dr/dt$ for binary components systems

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$dr/dt$ (nm/s)</th>
<th>AgNP + Na-MONT</th>
<th>AgNP + Ca-MONT</th>
<th>AgNP + Na-illite</th>
<th>AgNP + Ca-illite</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td></td>
<td>5.73</td>
<td>5.60</td>
<td>0.63</td>
<td>1.41</td>
</tr>
<tr>
<td>NaNO₃</td>
<td></td>
<td>4.92</td>
<td>4.57</td>
<td>1.04</td>
<td>1.16</td>
</tr>
<tr>
<td>CaCl₂</td>
<td></td>
<td>7.44</td>
<td>2.99</td>
<td>1.24</td>
<td>1.21</td>
</tr>
</tbody>
</table>
Figure 2.1 Unit structures of different types of clay minerals: (a) kaolinite (TO) and (b) montmorillonite/illite (TOT).
Figure 2.2 Characterization of the silver nanoparticles suspended in background NaCl/NaHCO₃ electrolyte: (a) TEM image and (b) UV-vis absorption spectrum.
Figure 2.3 TEM image of clay mineral samples suspended in background NaCl/NaHCO₃ electrolyte: (a) montmorillonite and (b) illite.
**Figure 2.4** Zeta potential of montmorillonite and illite from pH 4 to 10 in systems with 1mM NaCl.
Figure 2.5 Zeta potential of clay mineral samples in the systems with 1 – 500 mM NaCl (upper) and 0.1 – 10 mM CaCl₂ (lower): (a) montmorillonite and (b) illite.
Figure 2.6 Aggregation profiles of silver nanoparticles at pH 7.0 as a function of electrolyte concentrations: (a) NaCl and (b) NaNO₃.
Figure 2.7 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 different systems.
Figure 2.8 Inverse stability ratio \((1/W)\) of montmorillonite as a function of \(\text{NaCl}, \text{NaNO}_3\) and \(\text{CaCl}_2\) concentrations: (a) Na-montmorillonite and (b) Ca-montmorillonite. The arrows indicate the CCCs for different systems.
Figure 2.9 Inverse stability ratio (1/W) of Na- and Ca-montmorillonite as a function of NaCl and CaCl$_2$ concentrations.
Figure 2.10 Inverse stability ratio (1/W) of illite as a function of NaCl, NaNO₃ and CaCl₂ concentrations: (a) Na-illite and (b) Ca-illite. The arrows indicate the CCCs for different systems.
Figure 2.11 Inverse stability ratio (1/W) of Na- and Ca-illite as a function of NaCl and CaCl₂ concentrations.
Figure 2.12 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), NaNO₃ (b and e) and CaCl₂ (c and f). The arrows indicate the CCCs for different systems.
Figure 2.13 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 2.14 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), NaNO₃ (b and e) and CaCl₂ (c and f). The arrows indicate the CCCs for different systems.
Chapter 3: Heteroaggregation of Tween-coated Silver Nanoparticles with Clay Minerals in Aqueous Systems

3.1 Introduction

Nanotechnology is rapidly progressing and its applications involve industries such as manufacturing, medicine, materials, electronics and environmental remediation [1, 2]. Because of its antibacterial properties, silver nanoparticles have received the most attention and broadest application [3]. Silver nanoparticle-included products account for over 23.6% of all the recorded commercial nanotechnology-based products [4], and include clothing, sunscreens, paints, food containers, and filtration membranes [3, 5]. The unique optical properties of silver nanoparticles also find them being used in biomedicine and photochemistry fields [3, 6]. The wide usage of silver nanoparticles has also raised people’s concern on possible risks to their health and the environment. There is extensive literature reporting the toxicology of silver nanoparticles to animals as well as human beings [7-14]. The possible exposure pathways of nanoparticles to human beings include ingestion, inhalation and skin penetration [13, 15-17]. As a result, a better understanding of the fate and transport of silver nanoparticles in environmental media is important to evaluate their potential risk to human health.

In order to prevent particle aggregation and tailor the particle surface for introducing
functionality, various coating agents are applied to the surface of silver nanoparticles [18-22]. For example, the application of silica layers not only prevents the aggregation of silver nanoparticles, but it also promotes the binding of large molecules (e.g., DNA and protein) allowing the particles to be used for medical purposes [18]. In addition, polymer-coated silver nanoparticles are reported to have better resistance to chloride-rich biological environments resulting in lower release of Ag\(^+\) ions[6].

However, the use of these coating agents makes it more difficult and complicated to predict the transport of silver nanoparticles, particularly when aggregation plays a role [23]. Based on their structure, charge, flexibility, and pH-dependent properties, coating layers will provide electrostatic stabilization, steric stabilization or electrosteric stabilization [24]. Citrate and sodium borohydride, for example, stabilize nanoparticles by adsorbing charged groups on the nanoparticle surfaces. However, according to both Li et al. [25] and Badawy et al. [24], such electrostatically stabilized silver nanoparticles behave similarly to uncoated particles. Although citrate-coated AgNPs have a less negative zeta potential than bare particles, the possible existence of steric interactions provided by adsorbed citrate countered the decrease of stability due to the reduced magnitude of the zeta potential [25, 26]. Tween-coated silver nanoparticles, on the other hand, are much more stable than bare and citrate-coated particles at neutral conditions due to the additional steric interactions provided by the adsorbed Tween molecule [25]. Polyvinylpyrrolidone (PVP)-coated AgNPs are also highly stable attributed to the additional steric repulsion, regardless of the pH, ionic strength or electrolyte valence [24]. As an example of electrosterically stabilized particles, branched polyethyleneimine
(BPEI)-coated AgNPs exhibited aggregation that was more pH-dependent than sterically stabilized particles (e.g., PVP-AgNPs) [24]. BPEI is a cationic polyelectrolyte which results in positive charge on the surface of AgNPs. The zeta potential of BPEI-AgNPs decrease from 45 to 2 mV, as the pH increase from 4 to 10. The BPEI-coated particles were less stable and more sensitive to changing electrolyte at pH < 7.0 due to the predominance of electrostatic repulsion. However, at pH > 7.0 the increase of ion strength has little effects on the sizes of these particles under pH > 7.0, which may attribute to the override of steric repulsion [24].

As noted above, various coating layers have been applied on silver nanoparticles, and the aggregation and interaction of coated silver nanoparticles themselves have been studied as well. However, in natural water environments these particles usually exist along with other particulate material, such as clays, organic matter and microorganisms. Thus understanding interactions between coated silver nanoparticles and other particles is also important to determining the fate of nanoparticles in aqueous system. Although ample literature detailing aspects of the homoaggregation of coated silver nanoparticles exists, the heteroaggregation of AgNPs with other particles is less studied. For example, Whitley et al. [27] studied the behavior of PVP- and citrate-coated AgNPs in the soil by analyzing the concentration of both AgNPs and dissolved Ag$^+$ ions in the soil pore water at different time periods. Coated AgNPs were incubated with either soil (control group) or municipal sewage sludge (observation group), before adding into soil and analyzing the partition of AgNPs and Ag$^+$ ions in soil pore water. The pre-incubation with sewage sludge can cause sulfidation of AgNPs which neglected the effect of initial PVP or citrate
coating, when studying the behavior of AgNPs in solid. However, in the absence of sewage sludge, the behavior of AgNPs in soil was found to be affected by initial coating layers. A higher concentration of citrate-coated AgNPs was observed in the pore water than that of polyvinylpyrrolidone (PVP)-coated AgNPs, which was attributed to heteroaggregation of PVP-coated AgNPs and the solid soil grains [27]. Whitley et al. indicated the PVP-coated AgNPs were uncharged and had a high affinity to the soil, which was a sandy loam soil, while the negatively charged citrate layers were repulsed from the same negatively charged soil surfaces [27]. Similar trends were also observed by Xiao and Wiesner [28] and Lin et al. [29] in their investigations of the deposition of PVP-coated AgNPs on clean glass beads. However, PVP-coated AgNPs were more mobile than uncoated particles in columns of biofilm-coated sand [30]. Mitzel and Tufenkji [30] explained that steric repulsion between the PVP-coated surfaces and the biofilm prevented the deposition of nanoparticle on the sand [30]. Zhou et al. studied the heteroaggregation of citrate-coated AgNPs with montmorillonite, and they found the aggregation to be pH-dependent due to the pH-dependence in the charge of the edge of montmorillonite particles [31]. Both the citrate-coated AgNPs and montmorillonite were negatively charged under pH 8 and the stability of the binary system didn’t change when compared to single component systems. A similar trend was also found in our previous experiments with uncoated AgNPs and montmorillonite or illite under neutral pH (see Section 2.3.4). Below pH 4, however, the edge of the montmorillonite was positively charged, which in turn facilitated its interaction with negatively charged AgNPs to form heteroaggregates leading to an increase in the aggregation rate [31].
None of the previous literature has investigated the heteroaggregation of sterically stabilized AgNPs with clay particles. Thus, in this chapter we examine the effects of ionic strength and electrolyte type on the heteroaggregation of Tween-coated AgNPs and two different clay minerals (montmorillonite and illite) at neutral pH conditions. Silver nanoparticles (c.a. 60 nm) were synthesized and coated by Tween 80. Monocationic (sodium- and calcium-form) montmorillonite and illite were prepared and stored as diluted suspension. The hydrodynamic diameter of particles was obtained using dynamic light scattering (DLS) over a period of time and a range of different electrolytes (NaCl, NaNO₃ and CaCl₂) as well as concentrations. Our results show big changes in the stability of the binary system with Tween-coated AgNPs when compared to those with uncoated AgNPs.

3.2 Materials and Experimental Methods

3.2.1 Materials
AgNO₃ (≥99.8%) and D-maltose monohydrate (99%) were purchased from Sigma-Aldrich and used without further purification. Tween 80 was also purchased from Sigma-Aldrich in the form of viscous liquid (BioXtra) and used without further purification. Ammonium hydroxide (20-22% as NH₃, trace metal grade) was bought from Fisher Scientific. All other reagents were analytical grade or higher. The deionized water used in the experiments was supplied by Millipore (Milli-Q) with a resistivity of 18.2 MΩ·cm. The electrolyte solutions (NaCl, NaNO₃, and CaCl₂), buffer solution (NaHCO₃), and solutions employed in silver nanoparticle synthesis were filtered through 0.1 μm cellulose ester membranes (Millipore) before use. All labware and glassware were thoroughly
cleaned and soaked in 5% nitric acid for at least one day before use, followed by a thorough rinse with deionized water and oven-drying. The labware was immediately used or stored in a dust-free environment prior to use.

3.2.2 Clay Preparation
Montmorillonite (SWy-2) and illite (IMt-2) were obtained from the Clay Minerals Society. Monocationic montmorillonite was prepared following the protocol from Essington et al. [32], while monocationic illite was prepared using the procedure provided by Gu et al. [33]. The details of the preparation procedures are described in Chapter 2.

3.2.3 Silver Nanoparticle Synthesis and Characterization
Bare silver nanoparticles were synthesized following the method of Li et al. [34]. The average hydrodynamic diameter of bare silver nanoparticles was measured as 60.9 ± 0.5 nm by DLS. The details for synthesis and characterization are provided in Chapter 2.

The synthesis of Tween-coated silver nanoparticles was based on Li et al.’s protocol [25]. Specifically, 20mL of the bare silver nanoparticle suspension was introduced into a 50mL polycarbonate tube, followed by the addition of calculated volumes of NaHCO₃ buffer and Tween-80 to achieve 10 mM Tween concentration and pH ~7. The dilution of the particle suspensions was less than 3% after the addition of the agents. The polycarbonate tube was then tightly sealed and covered using aluminum foil to protect the sample from the light. The tubes were then slowly shaken using an orbital shaker for 24h under room
temperature to reach equilibrium [35]. The suspension was subsequently dialyzed against DI water using a cellulose ester membrane with a MWCO of 8-10 kDa. It should be noted that the MWCO of the membrane used here was lower than that used in Li et al.’s [25] experiments, which was 50 kDa. The dialysis process was continued for 24h, within which the DI water was changed four times. The resulting particle suspension was stored in the dark at 4 °C and was diluted 25 times using buffer solution before the experiments. The size of the coated silver nanoparticles was measured using DLS with the same method as bare particles discussed in Chapter 2.

3.2.4 Aggregation Kinetics

Aggregation kinetics for both the homoaggregate and heteroaggregate systems were determined by measuring the initial time rate of change in the average hydrodynamic radius of the particle suspensions using DLS (90Plus, Brookhaven Instruments Corp., Holtsville, NY). During the measurements, the intensity-weighted autocorrelation functions were determined at different time intervals and the mean hydrodynamic diameters of the aggregates were calculated as a function of time using cumulant analysis, as described in chapter 2. All stock suspensions were prepared in a 5.0 × 10^{-2} mM sodium bicarbonate buffer at pH 7.0 ± 0.3. The particle concentrations were kept the same for both the homoaggregation and heteroaggregation experiments. All working suspensions were briefly sonicated in an ultrasonic water bath before each experiment. Further detail of these measurements is provided in Chapter 2.
The stability of the suspensions was analyzed by comparing variations in the inverse stability ratio with ionic strength. The inverse stability ratio, $1/W$, is defined as the ratio of the experimental aggregation rate constant ($k_{\text{exp}}$) to that determined for rapid aggregation ($k_{\text{rapid}}$). The $k_{\text{exp}}$ value was calculated by conducting a linear least-squares regression analysis on the change of hydrodynamic radius over time ($dr/dt$), while the $k_{\text{rapid}}$ value was determined as the average value of the $k_{\text{exp}}$ values under a diffusion-limited aggregation condition, which was calculated for each electrolyte system. The relationship between $1/W$ and ionic strength can be used to identify the critical coagulation concentration (CCC) of a specific system with different types of electrolytes.

3.3 Results and Discussion

3.3.1 Homoaggregation of Tween-coated Silver Nanoparticles

The average hydrodynamic diameter of Tween-AgNPs was measured as 68 ± 1.3 nm, which is about 8 nm higher than the bare-AgNPs. The increase of the hydrodynamic diameter indicates a ~4 nm thick Tween coating layer [25]. The stability of particle suspension was greatly enhanced by Tween coating layers (Figure 3.1). When the electrolyte was NaCl, the CCC of Tween AgNPs increased from 40 mM NaCl measured for the bare AgNPs to 500 mM. The measured zeta potential of Tween-AgNPs was less negative than bare AgNPs and approached zero at pH 7, due to the adsorption of neutral charged Tween molecules on the nanoparticle surface. Colloidal suspension with lower zeta potential is normally less stable and has lower CCCs [36]. However in fact, Tween-AgNPs had higher CCCs than bare ones. This result is consistent with that of Li et al.
[25] who concluded that Tween 80 coating layers were able to sterically stabilize the suspension of silver nanoparticles.

When the electrolyte was calcium chloride, a CCC of ~700mM was determined for the Tween-AgNPs (Figure 3.1), which is consistent with Li et al.’s results [25]. According to DLVO theory, aggregation in multivalent electrolyte solutions should proceed more rapidly than in monovalent electrolytes, a relationship that can be estimated with the Schulze-Hardy rule, which would predict a CCC of 7.8 mM CaCl\(_2\) calculated from 500mM NaCl [37]. In the case of Tween-AgNPs, however, the estimated CCC from the Schulze-Hardy rule was different than that measured, reflecting a dependence in the steric repulsion provided by the Tween coating on the cation valence. Moreover, the maximum aggregation rate of Tween-Ag in CaCl\(_2\) was only 13.7% of that measured in NaCl, and 15.4% of the rate for Bare-Ag in CaCl\(_2\) (See Table 3.1). Two possible mechanisms to explain the relative lack of aggregation of Tween-AgNPs in CaCl\(_2\) proposed by Li et al. [25] include: 1) divalent Ca\(^{2+}\) screen the surface charge of Tween-AgNPs, or 2) the dehydration of Ca\(^{2+}\) and Tween layers.

The Tween-AgNPs did not exhibit aggregation when equilibrated with NaNO\(_3\). When the concentration of NaNO\(_3\) was increased to 1M, the hydrodynamic diameter of Tween-AgNPs remained unchanged at 71.15 ± 0.31 nm. Although the average diameter of nanoparticles during the 15 minute experiments increased from 68 to 71nm when the NaNO\(_3\) concentration increased from 100mM to 1M, no large aggregates of Tween-AgNPs was produced during the 15 min time period of measurement. Similar results for
the electrolyte-dependence in the aggregation of Tween-coated particles were reported by Li et al., but the reason for the marked difference in the aggregation kinetics of Tween-AgNPs in NaCl and NaNO₃ was not determined [25]. Nevertheless, these results suggest that differences in how NO₃⁻ and Cl⁻ interact with the Tween-AgNPs may affect the heteroaggregation kinetics.

3.3.2 Heteroaggregation of Tween-AgNPs with Clay Minerals
3.3.2.1 Tween-coated Silver Nanoparticles and Montmorillonite

The stability of binary systems of Tween-silver nanoparticles and montmorillonite (either sodium- or calcium-form) was greatly increased, compared to the binary system of bare-silver nanoparticles and montmorillonite. The CCCs for the binary systems of AgNPs and Na-montmorillonite increased from 60, 70 and 1.5 mM for bare AgNPs in NaCl, NaNO₃, and CaCl₂, respectively, to 150, 300 and 15 mM for Tween-coated particles (Figure 2.12 and 3.2). In the binary system of Tween-AgNPs and Ca-montmorillonite, no CCCs can be determined as the hydrodynamic diameter did not increase in any of the electrolytes (Figure 3.2). The aggregation rate of the tween-coated binary system was less than 50% of that of the single component Na-montmorillonite system in all three electrolytes, and even lower in NaNO₃ (See Table 3.2). The increase of the CCCs in the tween-coated system may reflect that the coating layer provides an additional steric repulsion between particles, which in turn increases the stability of the system [25, 38].

When compared the binary system contain Na-montmorillonite or Ca-montmorillonite, the latter seems to be more stable than the former. It was previously mentioned that the
dialysis membrane applied in this experiment to clean the particle suspensions after the coating procedure had a lower MWCO than did the membrane used in Li. et al. [25]. Based on this, it was possible that the amount of Tween 80 left in the nanoparticle suspension after dialysis may be higher than that remaining in the suspensions studied by Li. et al. [25]. Tween 80 is a nonionic surfactant, however, the amount of nonionic surfactant adsorbed by clay and other surfaces can still be significant [39-41]. For example, Parfitt and Greenland [42] studied the adsorption of the nonionic surfactant, poly(ethylene glycols) (PEG), on montmorillonite and observed a maximum surface sorbed concentration of 390mg g\(^{-1}\) Ca-montmorillonite. The adsorption was also observed to be molecular weight dependent in that higher molecule weight fractions of PEG were adsorbed more readily by montmorillonite [42]. Moreover, McFarlane et al. [43] studied the adsorption rate of nonionic polyacrylamide homopolymer (PAM N) and non-ionic polyethylene oxide (PEO) on kaolinite and smectite samples at pH 7.5. Their results showed that nonionic polymer adsorption on these clay samples can be completed within 2 minutes. On the other hand, the length of our aggregation experiments was 5 minutes. Based on this, it seems reasonable to hypothesize that the adsorption of Tween 80 to the clay surfaces in these systems could have occurred and might have an impact on the aggregation behavior of the binary system.

The adsorption of nonionic surfactant on clay is primarily through hydrogen bonding between its polar-groups and oxygen-rich clay surfaces and typically does not include direct interaction with exchangeable cations [42, 44, 45]. The adsorption energies are proposed mainly coming from desorption of water molecules during the process [42].
Parfitt and Greenland [42] found that Na-montmorillonite has a stronger adsorption of PEG 300 than Ca-montmorillonite. Their calculated non-standard free energies for the adsorption process also supported their observations. Moreover, Krishna et al. [46] reported a higher Freundlich constants of Tween 80 adsorption on unmodified smectite (mostly montmorillonite) than those of PEG-300. This indicated that Tween 80 had a higher affinity to montmorillonite than PEG-300. If we assume that Tween 80 is similar to the nonionic surfactant PEG, it seems reasonable that Tween 80 adsorption to montmorillonite would occur and that more Tween 80 would adsorb to Na-montmorillonite than Ca-montmorillonite.

Lin et al. [29] observed that coating silver nanoparticles with PVP prevented aggregation, but the same coating layers increase the attachment of silver nanoparticles to bare silica surfaces. Based on these results, they proposed the coated particles were stable via steric repulsion whereas the same particles were attracted to the silica surface via the formation of PVP bridges [29]. They also observed that silica surfaces pre-coated by PVP were not attractive to the PVP-coated particles as the steric repulsion between the coated nanoparticles and silica surface prevented the deposition of nanoparticles on the surface. Thus, in our experiments, Na-montmorillonite, which should have more adsorbed Tween 80 that reduces the potential deposition of Tween-silver nanoparticles. The binary system with Na-montmorillonite should then be more stable because large heteroaggregates may be inhibited to form due to more steric repulsion between Tween-AgNP with Na-montmorillonite particles than that with Ca-montmorillonite. However, our aggregation data indicated the reverse occurred, with the binary system with Na-montmorillonite
being less stable than the corresponding system with Ca-montmorillonite. We can rule out particle concentration differences since the estimated particle concentrations of montmorillonite in the aggregation experiments were ca. $1 \times 10^{10}$ particles mL$^{-1}$ and $8 \times 10^9$ particles mL$^{-1}$ for Na-montmorillonite and Ca-montmorillonite, respectively (see Section 2.3.2.1). Thus, there are other factors should be considered when evaluating the effects of Tween 80 on the aggregation of binary systems.

The particle concentration of montmorillonite in the heteroaggregation experiments was 5-10 times larger than that of silver nanoparticles. Thus, interactions between clay particles should be more frequent than those involving the nanoparticles. Mpofu et al. [40] studied the effects of polymers on the flocculation of solid smectite (contained 95% Na-montmorillonite and 5% quartz). At pH 7.5, they observed at low polymer concentrations ($<200$ g/t solid) that the smectite settled slowly ($<0.5$ m h$^{-1}$), with the settlement rate increasing at higher polymer concentrations. They attributed this to the lack of bridging effects between clay particles at lower polymer concentrations [40]. As we hypothesized previously, Ca-montmorillonite should have less Tween 80 on its surface than Na-montmorillonite, and thus more silver nanoparticles will deposit on its surface and form heterocomposites. However, the lack of Tween 80 on its surface decreases the possibility for the heterocomposites to attract each other and form large aggregates. On the other hand, Na-montmorillonite which should have more Tween 80 on its surface will limit the deposition of silver nanoparticles, the Tween 80 may actually bridge clay particles to form large aggregates. Although the exact reason in the observed differences in the stabilities of the binary systems with sodium- and calcium-
montmorillonite remained unclear, our experiments indicate the exchangeable cations of the clay particles may affect the stability of the binary system of clay and Tween-AgNPs.

3.3.2.2 Tween-coated Silver Nanoparticles and Illite

The stabilities of the binary systems with illite were also increased by the presence of Tween-coated silver nanoparticles (See Figure 3.3). However, unlike the binary systems with montmorillonite, the binary systems with sodium- or calcium-illite behaved similarly. A similar CCC of ca. 800mM was determined for both of the binary systems in NaCl and CaCl₂, while in NaNO₃ no obvious aggregation was observed for both systems. As in the montmorillonite systems, the adsorption of Tween 80 may also occur in the illite suspensions[42]. However, in this case existing results show the amount of PEG 300 adsorbed was close for both Na- and Ca-illite samples in the range of equilibrium concentrations from 0.2 to 0.8 g/100 mL [42]. Thus, similar interactions may occur between illite particles (either Na- or Ca-saturated) and silver nanoparticles [29] as well as the clay particles themselves [40], which could lead to similar aggregation results for both of the binary systems. Meanwhile, we should point out the adsorption of nonionic polymers on illite is typically lower than that for montmorillonite because the surface area of the illite is typically smaller than montmorillonite [42, 47]. The average specific surface areas of our clay samples are 22.7 and 17.5 m²/g for montmorillonite[48] and illite [49], respectively. This difference may also be the reason that the binary system of illite and Tween-Ag behaved differently than that of montmorillonite and Tween-Ag.
3.4 Conclusion

The heteroaggregation of silver nanoparticles and clay minerals was greatly affected by the Tween coating layers. The CCCs of the binary systems containing Tween-AgNPs were all above 100mM in either NaCl, NaNO₃, or CaCl₂, and in some systems (such as Ca-montmorillonite with Tween-AgNPs) the CCCs cannot be determined in all the electrolyte solutions. The changes in the stability of the binary systems were proposed to reflect adsorption of Tween 80 on clay particles [39-41]. The amount of Tween 80 adsorbed on the clay surfaces will affect the interactions between clay particles and nanoparticles as well as that between the clay particles themselves. The more Tween 80 adsorbed, the less the affinity clay particles will have to the nanoparticles as the Tween could induce steric repulsion [29]. However, the more Tween 80 adsorbed on clay surface may destabilize clay suspension through bridging which in turn can lower the stability of the binary systems [40]. Although more experimental data is needed to support our hypothesis (e.g., homoaggregation of clay minerals in the presence of Tween 80), the present results showed that coated silver nanoparticles were more mobile than uncoated ones, and their interactions with clay minerals were greatly affected by the existence of polymer/surfactant in the medium. It also indicates that the heteroaggregation between AgNPs and clay particles in water can be diminished by the addition of sterically stabilized coating layers, and thus increases the risks of exposure to nanoparticles.
3.5 References


3.6 Tables and Figures

**Table 3.1** Comparison of fastest $dr/dt$ for single component systems

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Bare-AgNP</th>
<th>Tween-AgNP</th>
<th>Na-MONT</th>
<th>Ca-MONT</th>
<th>Na-illite</th>
<th>Ca-illite</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.10</td>
<td>0.16</td>
<td>5.53</td>
<td>4.41</td>
<td>0.53</td>
<td>1.24</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>0.12</td>
<td>0.002</td>
<td>7.52</td>
<td>5.47</td>
<td>1.04</td>
<td>1.06</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>0.14</td>
<td>0.02</td>
<td>6.83</td>
<td>2.66</td>
<td>1.33</td>
<td>1.35</td>
</tr>
</tbody>
</table>
Table 3.2 Comparison of fastest $dr/dt$ for Tween-contained binary components systems

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Tween-AgNP + Na-MONT</th>
<th>Tween-AgNP + Ca-MONT</th>
<th>Tween-AgNP + Na-illite</th>
<th>Tween-AgNP + Ca-illite</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>2.29</td>
<td>0.81</td>
<td>0.51</td>
<td>0.94</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>1.05</td>
<td>0.35</td>
<td>0.002</td>
<td>0.11</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>2.80</td>
<td>0.08</td>
<td>0.19</td>
<td>0.33</td>
</tr>
</tbody>
</table>
Figure 3.1 Inverse stability ratio (1/W) of Tween-Ag as a function of NaCl and CaCl$_2$ concentrations.
Figure 3.2 Inverse stability ratio (1/W) of of Tween-AgNPs and Na-montmorillonite (left)/Ca-montmorillonite (right) as a function of electrolyte concentrations: NaCl (a and d), NaNO₃ (b and e), and CaCl₂ (c and f). The arrows indicate the CCCs of different systems.
Figure 3.3 Inverse stability ratio (1/W) of Tween-Ag and Na-illite (left)/Ca-illite (right) as a function of electrolyte concentrations: NaCl (a and d), NaNO₃ (b and e), and CaCl₂ (c and f). The arrows indicate the CCCs of different systems.
Chapter 4: Conclusions

4.1 Conclusion

The extensive use of silver nanoparticles benefits people’s lives in many ways; however, these benefits come with the potential risk that the discharge of silver nanoparticles to the environment may result in adverse effects to ecosystems and human beings. Many factors control the fate of silver nanoparticles in aqueous system, such as dissolution, aggregation, and settling. In this study, the heteroaggregation of nanoparticles with clay minerals was evaluated. To elucidate the effects of heteroaggregation on the fate of silver nanoparticles in aquatic systems, a series of single- and binary-particle experiments were conducted with silver nanoparticles (bare and Tween-coated) and clay minerals (montmorillonite and illite) under varying conditions of ionic strength, electrolyte type, and cation valence.

In summary, the results collected at a pH ca. 7 did not show significant differences in stability between the binary component systems and the single component systems, regardless of the type of electrolyte. We attribute this to weakly positively charged (i.e., montmorillonite) or negatively charged (i.e., illite) edges of the clay particles under neutral condition. Even though the basal plane surfaces of the clays have a permanent
negative charged, high concentrations of electrolytes are needed to flocculate the mixture of particle suspensions under these circumstances. Typical two-regime, DLVO-type aggregation kinetics were observed for both the binary- and single-particle systems, which indicates interactions between the bare silver nanoparticles and clay minerals were likely dominated by electrostatic and van der Waals forces.

The particle concentration of the clay suspensions were fixed at almost ten times higher than that for the nanoparticles in order to simulate the natural water conditions and as a result the clay particles dominated the stability of the binary component systems. The aggregation rate in the heteroaggregation systems was higher than that observed during the homoaggregation of silver nanoparticles, and was similar to that observed during the homoaggregation of the clay minerals. The CCCs of the binary components systems were also close to those measured during clay homoaggregation. Thus, the following two-step process is proposed to explain the heteroaggregation of silver nanoparticles and clay minerals: 1) deposition of the nanoparticles onto the clay flakes during the initial stage of the experiment, and 2) AgNP-clay particles aggregate with at an aggregation rate similar to that for the single clay particles [1].

4.2 Recommendation for Future Studies

Different coating layers applied to the surfaces of the silver nanoparticles to tailor their properties to their intended purpose dramatically alter particle stability [2]. These coating layers can also be removed or partially modified as the particles are exposed to environment conditions where organic matter, sunlight and biota exist [3]. Thus, one
obvious next step is to evaluate heteroaggregation using silver nanoparticles “aged” under environmentally relevant conditions.

Although the basal plane of the clays studied carries a permanent negative charge, that for the edge is pH-dependent. When the pH is lower than the PZC, the edge is positively charged, while it is negatively charged when the pH is higher than the PZC. We hypothesize that a positively charged edge could promote fast aggregation with negatively charged silver nanoparticles. Thus, future efforts to evaluate heteroaggregation could target lower pH conditions should those pH conditions be considered relevant for natural or engineered systems under consideration.

Finally, natural organic matter, such as humic acid and fulvic acid, change the stability of clay suspensions [4] and also affect the release of Ag$^+$ ions from AgNPs [5, 6]. When added to clay suspensions, humic acid (HA) enhances the formation of face-HA-face orientations, which can disrupt or prevent the edge-edge and edge-face association that promote aggregation [7]. This require higher electrolyte concentration of compress the double layers of face-HA-face orientation. Thus, the effect of humic substance on homo- and heteroaggregation merits additional study as well.
4.3 References


Appendix A: Preparation and Characterization of Kaolinite

A.1 Preparation of Kaolinite

Kaolinite (KGa-2) was obtained from the Clay Minerals Society and prepared for use as follows. Monocationic kaolinite suspensions were prepared following Essington et al.’s [1] procedure. Briefly, 5g of the kaolinite was dispersed into 250mL deionized water and the suspension was rapidly stirred for 45 min. The suspension pH was adjusted to 9.5 with CO$_2$-free 0.1M NaOH and the less than 2 μm size fraction was isolated in the supernatant by overnight sedimentation. The supernatant was decanted and the electrolyte concentration was adjusted to 1M NaCl. The suspension was rapidly stirred for 15 min, and adjusted to pH 3 with 10% HCl to facilitate flocculation. The clay was collected by centrifugation at 3600 rpm for 30 min. After centrifugation, the supernatant was decanted and replaced by fresh 0.01M NaCl. The clay was vigorously shaken and then centrifuged at 3600 rpm for 30min. The washing procedure was repeated (usually 5 times) until the pH of the supernatant was 5.5. The washed kaolinite was then dialyzed against 0.01 NaCl. The solution was changed daily until the conductivity of the clay suspension was the same as the 0.01M NaCl.

The calcium-saturated clay samples were prepared following the methods previously described with the exception that NaCl was replaced with CaCl$_2$. All of the clays were
stored as concentrated suspensions in the dark at 4 °C.

### A.2 Characterization of Kaolinite

The basic structure of Kaolinite is also a two-dimensional array comprised of a sheet of silica tetrahedra (T) bound to sheets of alumina octahedra (O) [2]. However, different with montmorillonite and illite (2:1 type) which present in the form of TOT, kaolinite (1:1 type) is consist of only one silica sheet and one alumina sheet and thus in the form of TO (Figure 2.1a) [2-4]. Kaolinite is a flat, hexagonal-shaped lamella, and in this study the sizes were ca. 100 to 400 nm (Figure A.1). The TEM images show a structure comprised of clusters of face-to-face flakes. O’Brien [5] suggests this structure is the consequence of a compression of the electrical double layer of each lamella, which increases the effect of the van der Waals force of attraction and thus promotes the face-to-face parallel orientation.

### A.3 Aggregation experiments with Kaolinite

Pre-experiments to examine the aggregation behavior of kaolinite under pH ~7.0 were conducted using the method described in Section 2.2.5. When the sonification time of diluted kaolinite sample before the aggregation experiments was set to five minutes, the resulting hydrodynamic diameters exceeded the highest limit of the DLS device, which is 2µm. The measured hydrodynamic diameters of kaolinite were much bigger than that estimated from its TEM images, which was around 100 – 400 nm (Figure A.1). Two more batches of the kaolinite samples were then prepared. However, all of them generated the similar results that exceeded the measurement limit of the device. The
inconsistent results between DLS and TEM results indicate that aggregation may have already started during the storage under 10mM NaCl background solution. In order to separate the possible aggregates, sonification time was then increased to 30 minutes. The aggregation profiles of sodium-kaolinite in different electrolytes were shown in Figure A.2. The aggregation rate of kaolinite, with 10mM NaCl and 300mM NaCl, are the same under pH ~7. Moreover, the particles sizes of kaolinite samples were in the range of 400 – 800nm. When the electrolyte was changed to NaNO₃, the particles sizes were in the range of 1200 – 2000nm. The aggregation rate at low electrolyte concentrations (<40mM) was also similar to that at higher concentrations (>100mM). However in CaCl₂ solutions, the particles sizes decreased with the increase of the CaCl₂ concentrations. In addition, under different CaCl₂ concentrations, kaolinite samples showed little aggregation in the time periods. Based on these DLS measurement results, there wasn’t any CCC can be determined in the range of electrolyte concentrations that we applied.

When compared to other’s work, Tombácz and Szekeres [2] observed similar CCCs (~100mM NaCl) of kaolinite and montmorillonite under pH > 7, due to the same negatively charged basal and edge of the clay particles. Berka and Rice [6] also studied the aggregation of KGa-2 samples obtained from the Source Clay Minerals Repository. The initial particle size of kaolinite stock suspension was reported as 110 ± 10 nm, and a CCC of ca. 85mM NaCl was determined under pH ~9.5. The PZC of the edge of kaolinite was reported around 6 – 6.5 [2]. Thus under our neutral conditions, a similar CCC of should be determined at NaCl when compared to other’s work. On the other hand, the particles sizes of the kaolinite in different electrolytes also varied a lot and
without reasonable explanations, which made it hard to control the behavior of kaolinite in the experiments. Thus, kaolinite samples were not applied into following heteroaggregation experiments.
A.4 References


A.5 Figures

Figure A.1 TEM image of kaolinite suspended in background NaCl/NaHCO3 electrolyte.
Figure A.2 Homoggregation profile of kaolinite at pH 7.0 as a function of electrolyte concentrations: (a) NaCl, (b) NaNO₃ and (c) CaCl₂.


