Iowa State University

Digital Repository

2007

Interaction of m-Dinitrobenzene (DNB) with Calcium and Potassium saturated reference smectites in aqueous suspensions

Ritushree Chatterjee
Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/rtd

Part of the Environmental Sciences Commons

Interaction of *m*-Dinitrobenzene (DNB) with Calcium and Potassium saturated reference smectites in aqueous suspensions

by

Ritushree Chatterjee

A thesis submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Environmental Science

Program of Study Committee:
David A. Laird, Co-major Professor
Michael L.Thompson, Co-major Professor
Patricia A. Thiel

Iowa State University

Ames, Iowa

2007

UMI Number: 1447484

UMI®

DEDICATION

I would like to dedicate this thesis in loving memory of my mother. I love you, Mom!

TABLE OF CONTENTS

ACKNOWLEDGEMENTS

I am most grateful to my advisor Prof. David A. Laird for giving me the opportunity to work with him and introducing me to the world of Smectites. I also thank him for his patience, guidance and words of encouragement throughout the course of my graduate study. I am grateful to Dr. Michael Thompson, my co-advisor, for his valuable suggestions and guidance.

I would also like to acknowledge National Research Initiative Competitive grant No. 2005-35107-15232 from USDA Cooperative States Research, Education, and Extension Service, which supported my research.

The support and encouragement of my father, brother, parents-in-law, my sister-in-law, and above all my husband has been invaluable throughout the course of my graduate study and otherwise.

I would also like to thank all my friends in Ames because it is only because of them my time here has been the most enjoyable and memorable one.

CHAPTER 1

GENERAL INTRODUCTION

Introduction

Soil is the top layer of earth's crust made up of mineral fractions, organic matter, water, air, and living organisms. It is a non-renewable source and plays many vital functions such as storage, filtration, and food and biomass production. Soil also serves as a habitat and plays host to the gene pool as well as acts as a platform for various human activities and provider of raw materials. These functions are of socio-economic as well as environmental importance and hence need to be protected. Soil degradation in the form of loss of organic matter, compaction, salinization, and contamination is accelerating with negative effects on natural ecosystems as well as human health.

Organic pesticides, insecticides, fungicides, industrial chemicals and various other organic compounds are introduced into the soil as effluents or through agricultural practices each year. The fate of an organic compound, i.e., its transport, retention and degradation, depends upon its chemical and physical properties. The various processes that a pesticide can undergo are shown in the Figure 1.
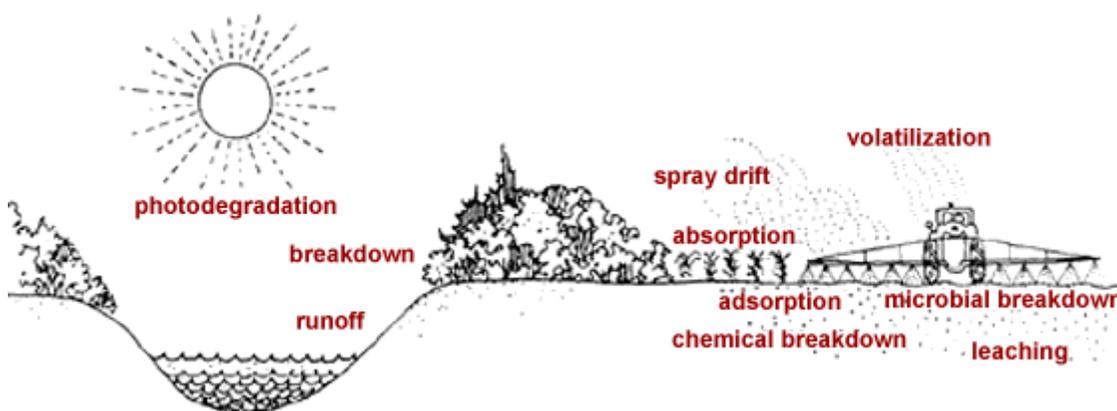
Figure 1: Shows the various pathways that affect the fate and transport of pesticides. This figure is taken from the website of Government of British Columbia, Department of Agriculture and Lands (http://www.agf.gov.bc.ca/pesticides/c_2.htm#1a)

Sorption of pesticides to soil is an important determinant of their behavior and fate in the environment. Bonding interactions between soil components and organic compounds is a complex topic as there are various factors that influence the behavior of sorbents and sorbates (Sposito, 1994).

The physical and chemical properties of soil organic matter and clay minerals make them the two dominant sorptive phases for organic contaminants and pesticides in soil.

Among the soil clay minerals, smectites have the greatest potential for sorption due to their abundance, large surface area, swelling property and high cation exchange capacity (Weissmahr, 1998, Laird 1992, Johnston 1992). It is important to understand the interaction between smectites and organic contaminants to gain further perspective into the factors that influence sorption.

Smectites

Smectites, belonging to the expansible 2:1 phyllosilicate class of silicate minerals, comprise one of the major groups of clay minerals in temperate region soils. The term

smectite is derived from the Greek word smecktos, meaning 'soap' and denotes a group of highly adsorbent clay mineral.

Composition

Silicon tetrahedra and aluminum octahedra, the basic building blocks of phyllosilicates, are arranged as planar sheets, forming a layered, 'leaf-like' structure. Each layer of a 2:1 phyllosilicate mineral has two sheets of Si-O tetrahedra sandwiching one sheet of Al-O octahedra.

The 2:1 phyllosilicates are also classified as triocatahedral, where all the possible sites in an octahedral sheet are occupied by divalent cations (typically Mg^{2+}) and as dioctahedral when just two-thirds of the possible sites are occupied by a trivalent cation, typically Al^{3+}, and each cation shares two anions with each of the three neighboring cations.
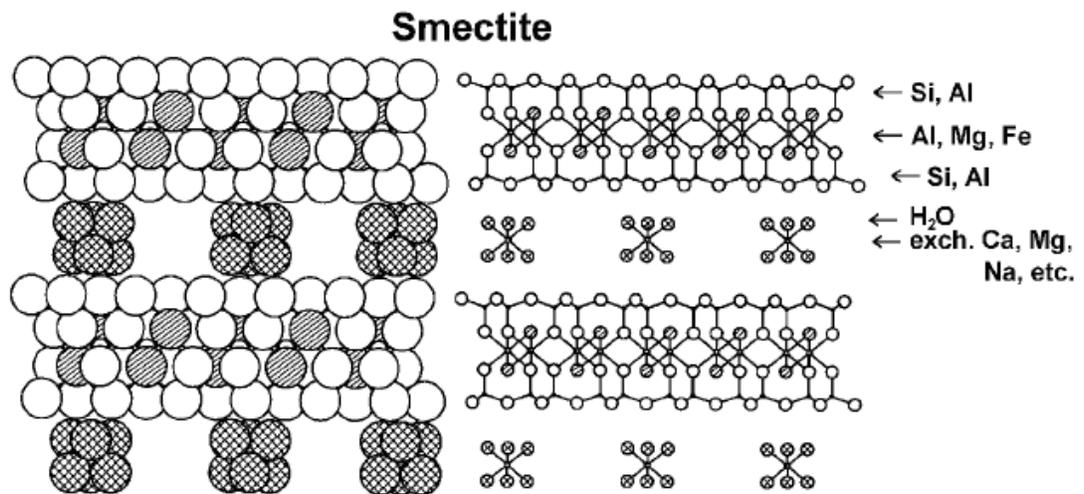

Figure 2: Structural representation of smectite (taken from class notes of Environmental Soil Chemistry, Spring 2006)

Origin of charge

There are two main sources of surface charge in smectites: permanent charge and variable or pH-dependent charge. Permanent charge is mainly due to isomorphic substitution in either the octahedral sheet or the tetrahedral sheet. If Al^{3+} is replaced by Fe^{2+} or Mg^{2+} in the octahedral sheet, the resulting excess negative charge is distributed over ten basal oxygen atoms, whereas if Si^{4+} is isomorphically substituted by Al^{3+} in the tetrahedral sheet, the negative charge is distributed only over three basal oxygen atoms of one tetrahedron (Reid-Soukup and Ulery, 2002). This net negative surface charge is balanced by the hydrated exchangeable cations present in the interlayer, such as Na^+, Ca^{2+}, and K^+. These cations participate readily in cation exchange reactions and contribute to the high cation exchange capacity of smectites.

Unsatisfied bonds at the terminal ends of minerals result in variable charge. It can be a positive or a negative charge, depending upon the pH and is sometimes called the pH-dependent charge. It is mainly due to protonation and deprotonation of the non-bridging hydroxyls present along the edges. Polar organic compounds can react with these variable charge sites through hydrogen bonding, ligand exchange, and direct charge neutralization (Laird and Sawhney, 2002).

Crystalline swelling

Smectites have in general a relatively low layer charge, varying from 0.2-0.6 per formula unit (Bailey, 1980), as compared to other silicate minerals present in the soil. Due to this lower layer charge the layers are capable of separating to large distances in water giving this class of silicate minerals the unique shrink-swell property. It is necessary to distinguish between two types of swelling, namely, crystalline swelling and osmotic swelling.

Crystalline swelling occurs when the interlayer spacing increases and osmotic swelling occurs between quasi crystals because of the differences in ion concentration close to the clay surface and in bulk solution which results in large separation distances (Norrish 1954).

The forces of attraction and repulsion present in the interlayer and between adjacent 2:1 layers play an important role in understanding this complex phenomenon of crystalline swelling (Norrish 1954, Parker 1986, Laird 1996). The main attractive force is the electrostatic force of attraction between the negatively charged layers and the interlayer cations. This force depends on the origin of the charge, the separation between positive charge and site of negative charge, and surface charge density of the clay. The Van der Waals forces of attraction acts between the atoms of the surfaces of two adjacent layers depends upon layer separation and structure.

The main repulsive force is due to the hydration of the interlayer cations and the negative charge sites (Newman, 1987). The electrostatic forces of attraction cause a partial dehydration of the interlayer cations and the negative charge sites. This difference in hydration status of cations in the interlayer and in the bulk solution causes a osmotic pressure which opposes the electrostatic attraction.

A balance between these forces of attraction and repulsion largely govern crystalline swelling (Norrish 1954, Kittrick 1969). In 1996, Laird modeled this phenomenon as a balance of potential energies of attraction and repulsion, and an equation describing the same was proposed. The potential energy of attraction is the sum of the potential energies of attraction between the negative charge sites and the interlayer cation and the Van der Waals forces of attraction between the layers. The potential energy of repulsion is the sum of the net potential hydration energy of the interlayer cations and the Born repulsion energy.

Layer charge and the origin of negative charge also play a significant role in crystalline swelling. The charge developed in the octahedral sheet is more diffuse than the charge developed in the tetrahedral sheet, which is more localized. A lower layer charge smectite will be more prone to swelling due to less electrostatic attraction. As the layer charge increases, there will be greater electrostatic force of attraction and the clay will tend to collapse and hence lead to a decrease in the extent of swelling (Laird, 2006). This can also be explained by the equation proposed by Laird in 1996, where the potential energy of attraction between the interlayer cations and the surface charge sites increases with the square of the surface charge density, where as the potential energy of repulsion due to hydration increases linearly with surface charge density.

The interlayer cation also influences the extent of crystalline swelling as the primary interaction between the cation and the negative charge sites is through the hydration of the interlayer cation. An interlayer cation with high hydration energy and smaller size will cause more swelling than a cation with smaller hydration energy; for example, K^+. In 2006, Teppen et al. showed that interlayer region and the bulk solution are two different phases. In the interlayer, only partial hydration of the interlayer cation is possible. Therefore, when a mixed ionic system is present, with cations of same charge, the cation with lower hydration energy will tend to be in the interlayer.

Cation Exchange

Cation exchange capacity (CEC) is one of the most fundamental properties of smectites. It can be defined as "quantity of cations reversible adsorbed (expressed as moles of positive charge) per unit weight of mineral" (McBride, 1994, pg 63). Ion exchange

reactions involve the displacement of the interlayer cations and replacement with cations that co-exist in aqueous phase (Garrels and Christ, 1965).

The CECs of relatively pure smectites range from 70 and 130 cmol/kg. According to Weaver and Pollard (1973), about 80% of the CEC is due negative charges resulting from to isomorphic substitution, and about 20% is due variable charge sites at the edges of crystals.

Selectivity for a particular cation depends on various factors like the type and charge of the ion, the hydration energy, the activity of the cation in solution, the extent of swelling and also the layer charge density of the smectite. Previous researchers have proposed various models for understanding cation exchange selectivity, namely, the Erickson model (1952) and the Eisenman model (1962). Using Eisenman's model, it was indicated that as the layer charge density increased, there was a preference for lesser hydrated cation in the interlayer and that layer charge and interlayer hydration were important factors influencing cation exchange selectivity (Eberl, 1980). Maes and Cremers (1980) pointed out that as the layer charge increases, the tendency to dehydrate the interlayer also increases. As the layer charge increases, the effective hydration number decreases. However, the hydration of smectites is influenced by the interlayer volume available for hydration and the cations retained on external surfaces, which have larger hydration numbers than cations in the interlayers (Laird, 1999).

In 1995, Laird et al. found that hysteresis was inherently associated with crystalline swelling in smectites. In 1997, Laird et al. proposed a model that linked selectivity, interlayer ionic composition and the extent of swelling through a feedback loop. The model suggests that selectivity of the clay for a particular cation influences the interlayer ionic composition, which in turn has an influence on the extent of swelling and the extent of swelling influences

selectivity. More recently, studying the Cs-K exchange on montmorillonites, a partitioning concept was put forward, i.e., the weakly hydrated cations partition into the less hydrated interlayer phase (Teppen and Miller, 2006).

Interaction of organic compounds with smectites

Smectites have a great potential for influencing the fate of various organic contaminants because of their large surface area and abundance in soil and sediments. Sorption from aqueous solution to solid surfaces is the key process that controls the fate of organic pollutants in soils.

The interaction of pesticides with soil minerals, in general, have been well documented by Laird and Sawhney (2002), where various factors that influence such interaction, namely, variable charge sites, permanent charge due to isomorphic substitution, and surface acidity have been discussed.

In the 90s, a study by Li et al. between aromatic molecules in water and smectites indicated that there was a direct interaction between the aromatic compound and the siloxane surface located between the sites of isomorphic substitution. Smectites are significant contributors to herbicide adsorption (Laird et al., 1992).

More recently, Pills et al. (2007) investigated the sorption of tetracycline and Chlortetracycline on Ca and K saturated soil clays, humic substances and clay humic substances and found that the maximum sorption was by the clay component and suggested cation bridging and cation exchange contribute to the sorption.

Laird (1992) investigated the effect of surface charge density on sorption of atrazine and found that affinity of smectites for Atrazine increased with decreasing surface charge density. Chappell et al. (2005) studied the influence of hydration status and swelling of

smectites on atrazine sorption and found that both these factors have a great influence on sorption of the organic molecule.

Interaction of nitroaromatic compounds with smectites

Nitro aromatics compounds (NAC) are industry's only source of aromatics with nitrogen bound to the ring and are therefore extremely important to the chemical industry (Rickert, 1984). They are widely used as pesticides, herbicides, and insecticides, and as intermediates in manufacture of dyes and drugs and as solvents.

Some groups attached to the benzene ring make it more reactive, like a methyl or an electron-donating group, whereas electron-withdrawing groups such as NO_2 deactivate the ring. The benzene ring serves as a source of electrons and may undergo electrophillic substitution reactions.

NACs find their way into the soil environment where they may pose a risk to the health of various organisms including humans. Soil organic matter and clay minerals are considered to be the most active soil components. Smectites are especially important due to their abundance in soil, high surface area, cation exchange capacities and surface reactivity (McBride, 1994).

Adsorption behaviors of NACs have been studied since the early 90s. In 1993 and 1996, Haderlein et al. studied the adsorption of a large number of NACs to mineral surfaces and concluded that adsorption in the presence of strongly hydrated cations was negligible whereas adsorption increases when clays are saturated with cations of low hydration energies, for e.g., K^+ and NH_4^+. It was also shown that the type and position of the nitro group could influence sorption of the organic compounds. They proposed an electron donor acceptor (EDA) mechanism according to which the electron withdrawing nitro groups result

in electron-deficient aromatic ring. The sites of negative charge, due to isomorphic substitution, provide electrons to the electron-deficient nitro groups, forming EDA complexes.

Quantum calculations done by Boyd et al. in 2001 showed that the charge on the nitro aromatic ring remained constant, irrespective of the type of substituent present, which conflicted with the proposed EDA mechanism. They said that the interaction between the secondary substituents along with the nitro group with the interlayer cation was mainly responsible for the sorption of nitro aromatic compound by smectites.

In 2001 Johnston et al. performed FTIR studies to understand the sorption mechanism between various NACs and smectites. Their results indicated that complexation reactions occur between the nitro group and the interlayer cation (K^+, Cs^+). The hydration status of the interlayer cation affects the complexation between cation and the nitro aromatic compound and the extent of swelling of the clay.

Hui Li et al., 2004, studied enthalpies for the adsorption of 1, 3-dinitrobenzene, 1, 4-dinitrobenzene and 1, 3, 5-trinitrobenzene by Ca and K smectites. Their results indicated that the adsorption enthalpy for Ca-smectite was smaller than for the K-smectite, which was consistent with greater sorption capacity of the K-saturated smectite for NACs. Their X-ray diffraction study on air-dried films indicated that a basal spacing of 12.2 Å was the optimum spacing required for the sorption of NACs in the interlayer of the clay as the nirtoaromatic molecule would fit into the interlayer and could interact simultaneously with both opposing siloxane surfaces.

Hui Li et al. in 2005 studied the sorption of pesticide by smectites in a mixed ionic system (Ca^{2+}/K^+). The results indicated that different amounts of $CaCl_2/KCl$ influenced the

amounts of K^+ and Ca^{2+} present on the exchange sites. Interstratifications of collapsed K-domains among the Ca-domains were indicated. Also, an increase in sorption of the pesticide with an increase in K^+ in the exchange sites was also observed.

Another study by Hui Li et al. in 2005, indicated that as the ionic strength of KCl increased, there is a more ordered formation of smectite quasicrystals and shrinkage of the interlayer distance, which enhanced the sorption of pesticides.

Chappell et al. in 2005 studied the effect of the sorption of an aromatic compound, atrazine, on basal spacing of the clay. They demonstrated that the sorption of the aromatic compound induces the formation of quasicrystals as well as dehydrates the interlayer and that sample treatment (like air drying) could influence the sorption of aromatic compounds. More recently, Pereira et al. in 2006 showed that sorption of 1, 3-dinitrobenzene enhanced the formation of quasicrystals and also shrinkage of the interlayer distance. Charles et al. (2006) showed the influence of the hydration status of the interlayer cation on the sorption of a NAC. Clay saturated with a weakly hydrated cation (K^+, Cs^+) adsorbs more NAC than when it is saturated with a strongly hydrating cation (Ca^{2+}, Mg^{2+}).

Hypothesis and Objective

Previous studies have investigated the role of smectite properties such as layer charge, exchangeable cations and the extent of interlayer hydration on the affinity of smectite for nirtoaromatic compounds such as *m*-dinitrobenzene (DNB). Previous studies have also reported a complex feedback interaction between cation exchange selectivity, interlayer cation and the extent of swelling. Figure 3 depicts the facts that have already been established.

No studies have, however, investigated how adsorption of an organic compound influences the affinity of a smectite for inorganic cations or the complex interaction between cation exchange selectivity, clay swelling and the adsorption of organic compounds in aqueous systems.
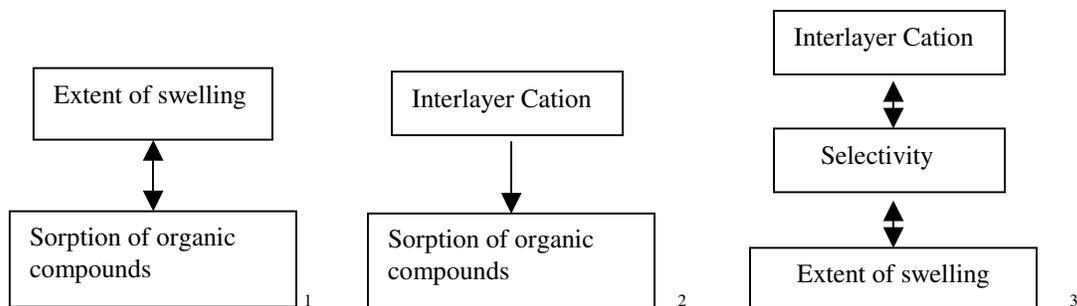
Extent of swelling
↕
Sorption of organic compounds

1

Interlayer Cation
↓
Sorption of organic compounds

2

Interlayer Cation
↕
Selectivity
↕
Extent of swelling

3

Figure 3: Facts that have been established by previous studies

[1]Chappell et. al, 2005. Influence of smectite hydration on atrazine sorption, Env. Sci. Tech. 39:3150-3156. Li et.al, 2007. Ionic strength induced formation of quasicrystals enhances nirtoaromatic compounds. Env. Sci. Tech. 41:1251-1256.
[2] Charles et. al, 2006. Exchangeable cation hydration properties strongly influence soil sorption of nitroaromatic compounds. Soil. Sci. Soc. Am. J. 70:1470-1479.
[3] Laird et al., 1997. Relationship between cation exchange selectivity and crystalline swelling in expanding 2:1 phyllosilicates. Clays and Clay Minerals 45:681-689.

We hypothesized that the adsorption of m-DNB in the interlayer of Ca and K saturated smectites, in a mixed K/Ca aqueous system, will increase the affinity of the clay towards the low hydration energy cation, i.e., K, in aqueous systems which in turn will increase sorption of m-DNB in the interlayer of the smectites.

The specific objectives of this study are (1) to determine the effect of sorption of m-DNB on cation exchange selectivity of Ca and K smectites, and (2) to determine the interaction between sorption of m-DNB, extent of swelling and cation exchange selectivity for Ca and K smectites.

Thesis organization

This thesis has been organized into four chapters. This, the first chapter is a general introduction and review of the literature. The second chapter reports the preliminary study done for the method development for the analysis of *m*-DNB. The third chapter is a report of the study of the effect of the sorption of *m*-DNB on the interlayer cation of Ca and K smectites and the interaction between selectivity, cation exchange and sorption of *m*-DNB in the interlayer of the clay. The third chapter has been compiled according to guidelines acceptable to be published in a scientific journal. The final chapter presents the conclusion of the study. The appendix includes additional supporting data not specifically used in the other chapters.

References

Bailey, S.W. 1980**.** Structure of layer silicates. Pg. 28-39. *In Crystal Structure of Clay Minerals and their X-ray Identification*, G.W. Brindley and G. Brown, eds, Mineralogical Society, London.

Boyd, S.A., G. Sheng, B.J. Teppen, and C.T. Johnston. 2001. Mechanisms for the adsorption of substituted nitrobenzenes by smectite clays. *Environ. Sci. Technol*. 35: 4227-4234.

Chappell, M.A., D.A. Laird, M.L. Thompson, H. Li, B.J. Teppen, V. Aggarwal, C.T. Johnston and S.A. Boyd. 2005. Influence of Smectite hydration and swelling on Atrazine sorption Behavior**.** *Environ. Sci. Technol.* 39:3150-3156

Charles, S., B.J. Teppen, H. Li, D.A. Laird, and S.A. Boyd. 2006. Exchangeable cation hydration properties strongly influence soil sorption of nitroaromatic compounds. *Soil. Sci. Soc. Am. J*. 70: 1470-1479

Eberl, D.D. 1980. Alkali cation selectivity and fixation by clay minerals. *Clays and Clay minerals*. 28:161-172.

Eisenman, G. 1962. Cation selectivity glass electrodes and their mode of operation. *Biophys J* 2(Supplement): 259-323.

Eriksson, E. 1952. Cation exchange equilibria on clay minerals. *Soil Sci*. 74:103-113.

Garrels, R.M, and C.L. Christ. 1965. Solution, Minerals and Equilibria. Harper & Row, New York, NY.

Haderlein, S.B., and R.P. Schwarzenbach. 1993. Adsorption of substituted nitrobenzenes and nitrophenols to mineral surface. *Environ. Sci. Technol*. 27:316-326.

Haderlein, S.B., K.W. Weissmahr, and R.P. Schwarzenbach. 1996**.** Specific adsorption of nitroaromatic explosives and pesticides to clay minerals. *Environ. Sci. Technol.* 30:612-622.

Johnston, C.T., M.F. Oliveira, B.J. Teppen, G. Sheng, and S.A. Boyd. 2001. Spectroscopic study of nitroaromatic-smectite sorption mechanisms. *Environ. Sci. Technol*. 35:4767-4772.

Johnston, C.T., M.F. De Oliveira, B.J. Teppen, G. Sheng, and S.A. Boyd. 2002. Spectroscopic study of Dinitrophenol herbicide sorption on smectites. *Environ. Sci. Technol.* 36:5067-5074.

Kittrick, **J.A.** 1969. Interlayer forces in Montmorillonite and Vermiculite. *Proc. Soil Sci. Soc. A*. 33:217-221.

Laird, D.A., E. Barriuso, R.H. Dowdy, and W.C. Koskinen. 1992. Adsorption of atrazine on smectites. *Soil Sci. Soc. Am. J*. 56:62-67.

Laird, D.A., C. Shang, M.L. Thompson. 1995. Hysterisis in Crystalline Swelling. *J. Colloid Interface Sci*. 171:240-245

Laird, D.A. 1996. Interactions between Atrazine and Smectite Surfaces. Pg 86-100. In: *Herbicide Metabolites in Surface Water and Groundwater* (M.T. Meyer and E.M. Thurman, editors). ACS Symposium Series 630. American Chemical Society, Washington, D.C.

Laird, D.A. 1996. Model for Crystalline Swelling of 2:1 Phyllosilicates. *Clays and Clay Minerals.* 44:553-559.

Laird, D.A. 1999**.** Layer Charge Influences on the Hydration of Expandable 2:1 Phyllosilicates. *Clays and clay Minerals.* 47:630-636.

Laird, D.A., and B.L. Sawhney. 2002. Reactions of pesticides with soil minerals. Pg. 765-793. In J.B. Dixon and D. Schulze (ed.) *Soil mineralogy with environmental applications.* SSSA Book Ser. 7. SSSA, Madison, WI.

Laird, D.A, and C. Shang. 1997. Relationship between cation exchange selectivity and crystalline swelling in expanding 2:1 Phyllosilicates. *Clay and Clay Minerals*. 45:681-689.

Laird, D.A. 2006. Influence of layer charge on swelling of smectites. *Appl. Clay Sci.* 34:74-87.

Li, H., G. Sheng, B.J. Teppen, C.T. Johnston, and S.A. Boyd. 2002 Adsorption of Dinitrophenol Herbicides from water by Montmorillonites. *Clay and Clay Minerals*. 50:25-34.

Li, H., T.R. Pereira, B.J. Teppen, D.A. Laird, C.T. Johnston, and S.A. Boyd. 2006. Effects of increasing potassium and calcium chloride ionic strength on pesticide sorption by potassium and calcium saturated smectites. *Soil Sci. Soc. Am. J.* 70:1889-1895.

Li, H., B.J. Teppen, C.T. Johnston, and S.A. Boyd. 2004**.** Thermodynamics of nitroaromatic compound adsorption from water by smectite clay. *Environ. Sci. Technol.* 38:5433-5442.

Li, H., T.R. Pereira, B. J. Teppen, D.A. Laird, C.T. Johnston, and S.A. Boyd. 2007. Ionic strength induced formation of smectite quasicrystals enhances nitroaromatic compound sorption. *Environ. Sci. Technol*. 41:1251-1256.

McBride, M.B. 1994. *Environmental Chemistry of Soil.* Oxford University Press, New York

Newman, A.C.D. 1987. Interaction of water with clay mineral surfaces. In *Chemistry of Clays and clay minerals*, J Wiley and Sons. Pg 235-270.

Norrish, K. 1954. Crystalline swelling of Montmorillonite. *Nature*. 173:255-257.

Parker, J.C. 1986. Hydrostatics of porous media. *In* Sparks D.L, editor. *Soil Physical chemistry*. Boca Raton, FL: CRC Press. Pg 209-296.

Pils, R.V.J, and D.A. Laird. 2007. Sorption of Tetracycline and Chlortetracycline on K and ca-Saturated Soil clays, Humic Substances, and Clay-Humic Complexes. *Appl. Clay Sci*. 35:201-211.

Reid-Soukoup, D.A., and A.L. Ulery. 2002. Smectites. Pg 467-499. *In* J.B. Dixon and D. Schulze (ed.) *Soil mineralogy with environmental applications.* SSSA Book Ser. 7. SSSA, Madison, WI.

Rickert, D.E. 1985. *Toxicity of nitroaromatic compounds*. Hemisphere Publishing Corporation, Washington.

Sheng, G., B.J. Teppen, C.T. Johnston, and S. A. Boyd. 2001**.** Potential Contribution of Smectite clays and Organic matter to Pesticide Retention in Soils. *J. Agric. Food Chem.* 49:2899-2907

Sparks, D.L. 1995. *Environmental soil chemistry*. Academic press, San Diego, CA.

Sposito, G. 1994. *Chemical Equilibria and kinetics in soils*. Oxford University press, New York.

Teppen, B.J., and D.M. Miller. 2006. Hydration Energy determines Isovalent Cation Exchange Selectivity by Clay Minerals. *Soil Sci. Soc. Am. J.* 70:31-40.
.

Weaver, C.E., and D.L. Pollard. 1973. *The Chemistry of Clay Minerals*. New York, Amsterdam: Elsevier.

Weissmahr, K.W., S.B. Haderlein, and R.P. Schwarzenbach. 1998. Complex formation of soil minerals with nitroaromatic explosives and other Π-acceptors. *Soil Sci. Soc. Am. J.* 62:369-378.

CHAPTER 2

METHOD DEVELOPMENT FOR ANALYSIS OF *m*-DINITROBENZENE

Introduction

Nitroaromatic compounds are extremely important class of compounds in the chemical industry as they are the only source of aromatics with nitrogen attached to the ring (Rickert, 1985). *m*-Dinitrobenzene (DNB) is a raw material used for the manufacture of industrial chemicals, like TNT. It is an organic contaminant that enters soil environments and affects animal and human health.

Exposure to high concentrations of 1, 3-DNB can reduce the ability of blood to carry oxygen and can cause skin to become bluish in color. Prolonged exposure to 1, 3-DNB a reduction (or loss) in the number of red blood cells (anemia) could develop. Other symptoms of 1, 3-DNB exposure include headache, nausea, and dizziness (Agency for Toxic Substances and Disease Registry (ATSDR). 1995. Toxicological profile for 1, 3-dinitrobenzene and 1, 3, 5-trinitrobenzene. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service).

The crystal structure of *m*-DNB has been investigated by many researchers. The benzene ring in *m*-DNB is completely planar, with the nitrogen lying in the plane, but the oxygen atoms are completely out of plane. The deviation from planarity has been attributed to intermolecular forces in the crystal (Trotter, 1960). The benzene ring may undergo electrophillic substitutions. Presence of groups such as the NO_2 group, which is an electron withdrawing group, deactivates the benzene ring. During the formation of nitrobenzene, a

carbocation, called the benzonium ion is formed, which stabilizes itself through resonance.
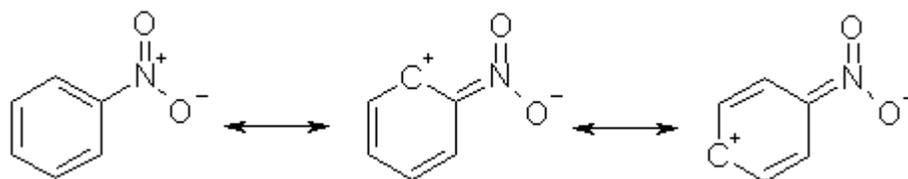

Figure 1: The resonance structures of nitrobenzene. Image taken from WebMO
(http://www.webmo.net/index.html)

Sorption of *m*-DNB by smectites has been studied by various researchers. In 1993, Haderlein studied the sorption of various nitrobenzene and nitrophenols to soil minerals and demonstrated that nitroaromatic compounds (NAC) could adsorb specifically to the siloxane surface of kaolinite. To analyze the organic solutes, they used reversed-phase high-performance liquid chromatography (HPLC). In 1998, Weissmahr et al. studied the interaction between soil minerals and many nitroaromatic pollutants like *m*-DNB and concluded that strong electron donor complexes were formed between the two. Along with HPLC they also used UV-diode array detection to determine the organic compound.

In another study by Li et al., 2004, the solubility of NACs were measured by using the batch equilibrium method and they were analyzed using the HPLC. Johnston et al. (2001) investigated the sorption mechanisms of various nitrobenzenes including *m*-DNB. Infrared spectra were obtained using Fourier transform infrared spectrometer (FTIR) for the aqueous suspension with the sorbed NAC. They also used HPLC to analyze the organic compound.

More recently, Pereira (2005) in her master's thesis work investigated the interaction between 4, 6-dinitro-o-cresol (DNOC) and smectites in aqueous suspensions. She used spectrophotometry to measure the absorbance of the organic compound in her samples. The absorbance values were then converted to concentrations. The amount sorbed was calculated

from the difference between the initial concentration and the concentration of DNOC in final solution.

For this research thesis, a preliminary study was performed on the organic compound to be used, *m*-DNB, to study the various factors that could affect the behavior of *m*-DNB that would be helpful in the design of the experiment and in developing a method for the analysis of *m*-DNB during the course of the experiment.

Materials and Methods

m-DNB was obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI) with purity >97 %. Reagent grade KCl and $CaCl_2$ salts were used to prepare the salt solutions. M-DNB was analyzed spectrophotometrically using the Milton Roy Spectronic 601 spectrophotometer with an ultra violet detector, in a quartz cuvette.

For this study a 500 mL of stock solution of 500 ppm (mg/L) of *m*-DNB was prepared in de-ionized water and all subsequent concentrations of DNB were prepared by dilution. The wavelength was varied from 200 nm to 450 nm, with a step size of 5 nm throughout the study.

Stability

From the 500 ppm *m*-DNB stock solution, a 100 mL 20 ppm *m*-DNB solution was prepared by dilution and the absorbance was measured. After 8 days, with the containers on the work bench at room temperature, the absorbance was measured again. The same was repeated with 20 ppm *m*-DNB solutions prepared in 0.005 M $CaCl_2$ and in 0.01 M KCl solutions, respectively.

Effect of pH

A 20 ppm *m*-DNB solution was put into six Pyrex 100-mL Erlenmeyer flasks. The pH of each was set from pH 3 to pH 6 by adding a few drops of very dilute HCl or a few drops of very dilute NaOH. The pH was measured using an electrode pH meter and the absorbance was measured on the spectrophotometer. The solutions were properly corked and kept at room temperature, on the work bench, for 6 days, after which the pH of each solution was measured again along with the absorbance.

Effect of ionic strength

The effect of ionic strength on the absorbance values of *m*-DNB was studied by preparing 20 ppm *m*-DNB solutions in $CaCl_2$ and KCl salt solutions respectively with varying concentrations. Salt solutions were prepared with concentrations varying from 0.01 M to 0.05 M such that the ionic strength would vary from 0.01 to 0.05. These ionic strengths were chosen, as the actual ionic strength of equilibrating solutions in the experiment would be between these values. Ionic strengths were calculated using the formula $I = 0.5 \sum Z_j^2 M_j$, where *j* is the total number of ionic species in solution and M is the concentration of each species *i*. The absorbance of *m*-DNB solutions were measured at each ionic strength.

Absorption by various containers

In order to determine the best possible container material that could be used for storing and carrying out the experiments with *m*-DNB solutions, the absorbance of *m*-DNB by various types of containers was measured. Absorbance was also measured after passing *m*-DNB solution through the 0.02 µm anotop filter and a 5-mL syringe that would be used in the experiment. A 20 ppm solution of *m*-DNB was prepared and stored in a Pyrex

Erlenmeyer flask. Its absorbance was taken as the reference. Approximately the same amount of 20 ppm *m*-DNB were also stored in a stainless steel centrifuge tube, a corex centrifuge tube, polyethylene centrifuge tube, polycarbonate centrifuge bottle, Servol centrifuge bottle, polypropylene bottle and their absorbance measured. They were equilibrated for 2 days and the absorbance was measured again.

Results and Discussion

Stability

Table 1 shows the absorbance values for the *m*-DNB solution in deionized water, KCl and in $CaCl_2$ salt solutions. It also shows the same after a period of 8 days, during which the samples were kept on the work table. Figure 2 shows the spectra of the same. The λ_{max} for *m*-DNB was at 240 nm. There was no significant change in the absorbance values for the DNB solutions prepared in deionized water, KCl, and $CaCl_2$ solution. There was also no significant change in the measured absorbance during the period of eight days. There was also no significant difference in the spectra obtained. Hence, aqueous *m*-DNB solutions are stable for at least 8 days, even when exposed to light, in a laboratory environment.

Table 1: Stability of *m*-DNB in demonized water, 0.01 M KCl and in 0.005 M $CaCl_2$

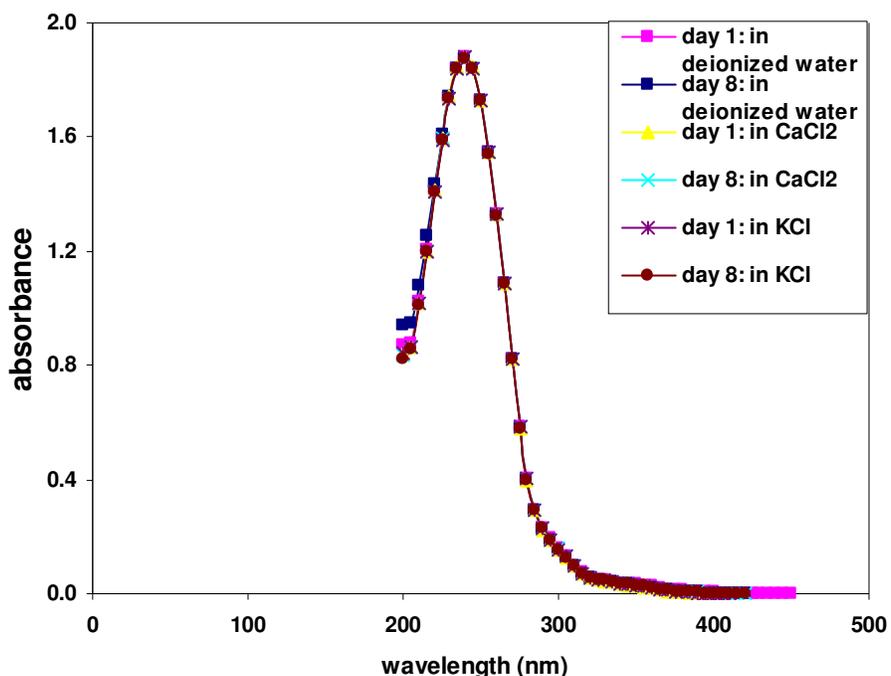|	Day 1	Day 8
Absorbance of 20 ppm m-DNB in deionised water	1.879	1.878
Absorbance of 20 ppm m-DNB in 0.01M KCl	1.880	1.876
Absorbance of 20 ppm m-DNB in 0.005 M CaCl2	1.884	1.880

Figure 2: Absorbance spectra of *m*-DNB in deionized water, KCl, and CaCl$_2$ solution

Effect of pH

Table 2 shows the change in absorbance values of 20 ppm *m*-DNB solution over a period of 8 days, at different pH values. The pH remained mostly constant at 2, 4, and 6. But pH 5.2 increased to 5.8, and pH 7 and 8 decreased to 6.2 and 6.8 respectively. Although the reason for this is not known, it could be speculated to be due to CO_2 being dissolved in the solution. There was a slight decrease observed on the absorbance values at 240 nm, the reason for which is not known.

Table 2: Effect of pH on the absorbance value of *m*-DNB

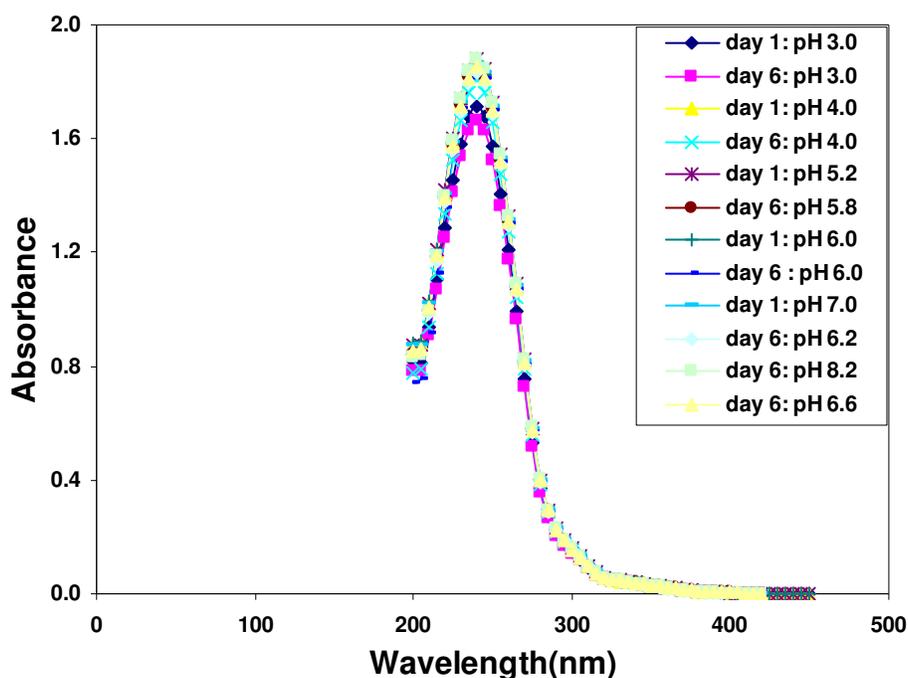| pH on day 1	Absorbance	pH on day 6	Absorbance
3.0	1.710	3.0	1.661
4.0	1.869	4.0	1.801
5.2	1.880	5.8	1.857
6.0	1.861	6.0	1.848
7.0	1.866	6.2	1.833
8.2	1.882	6.6	1.850

Figure 3: Absorbance spectra of 20 ppm *m*-DNB at various pH over a period of 6 days

Effect of ionic strength

The absorbance values, at 240 nm, were compared at different ionic strengths for *m*-DNB solutions prepared in KCl and in $CaCl_2$. The values are shown in Table 3. Figure 4 shows the absorbance spectra for the same. There was no significant difference in the absorbance values at all ionic strengths, for both *m*-DNB solutions prepared in KCl and in $CaCl_2$ solutions. Hence, ionic strength between 0.01 and 0.05 did not have a significant effect on the stability of *m*-DNB.

Table 3: Effect of ionic strength on *m*-DNB solutions in KCl and in CaCl$_2$

CaCl2		KCl	
Ionic Strength	**Absorbance**	**Ionic Strength**	**Absorbance**
0.0096	1.879	0.01	1.882
0.0189	1.888	0.02	1.887
0.0297	1.886	0.03	1.863
0.0384	1.881	0.04	1.849
0.0498	1.886	0.05	1.860
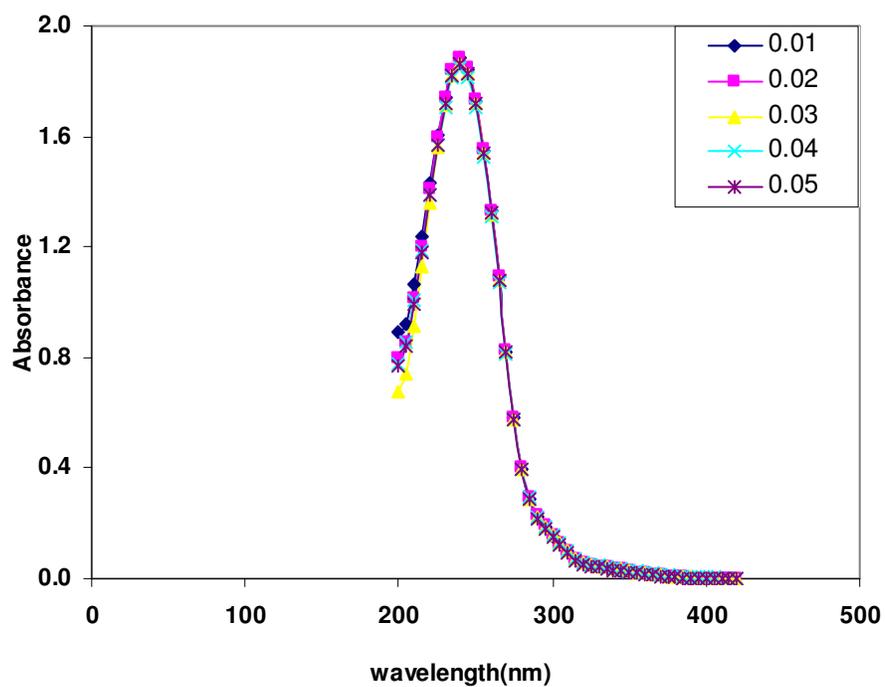
Figure 4a: Absorbance spectra of *m*-DNB solutions in varying ionic strength solutions of KCl
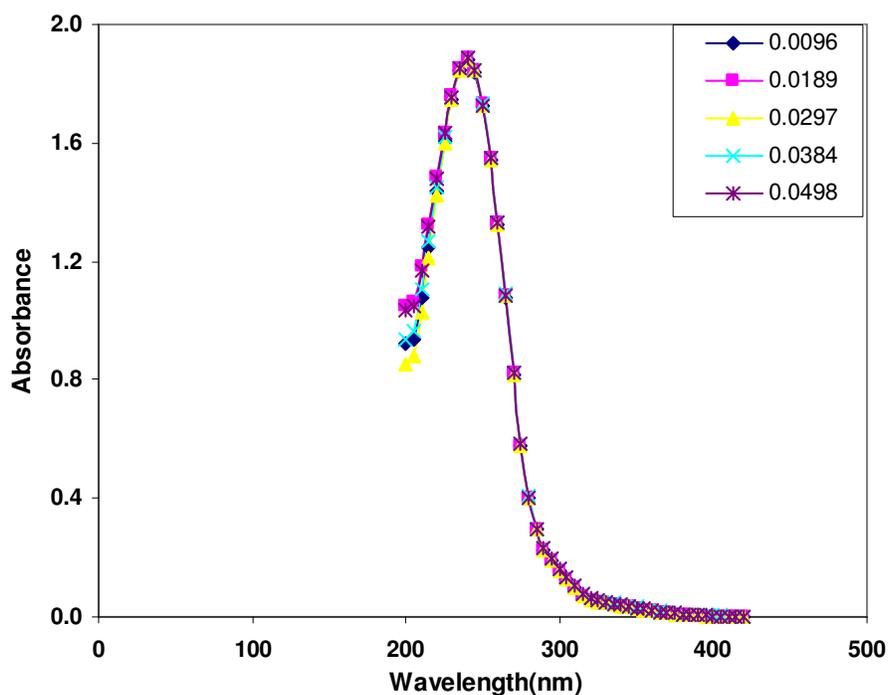
Figure 4b: Absorbance spectra of *m*-DNB solutions in varying ionic strength solutions of CaCl$_2$

Absorption by various containers

The absorbance results of *m*-DNB when stored in different containers are shown in Table 4. There was no significant change in absorbance values observed except when stored polycarbonate, Servol, polypropylene bottles and the polyethylene centrifuge tube. This could be due to absorption of the *m*-DNB by these containers. The absorbance spectra are shown in Figure 5.

Table 4: Absorbance values at 240 nm for 20 ppm *m*-DNB when stored in different containers. The absorbance with Pyrex container was chosen as the reference.

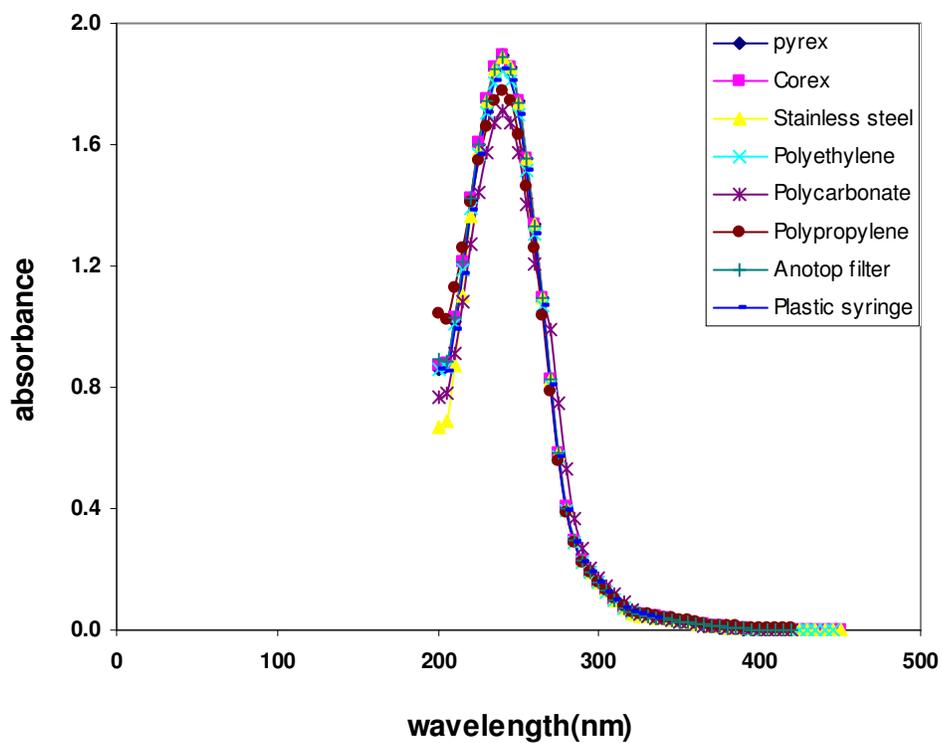| Type	Absorbance
Pyrex container	1.892
Stainless steel centrifuge tube	1.891
Corex centrifuge tube	1.893
Polyethylene centrifuge tube	1.844
Polycarbonate centrifuge bottle	1.709
Servol Centrifuge bottle	1.861
Polypropylene bottle	1.778
Anotop filter	1.888
Glass syringe	1.848
Plastic syringe	1.848

.

Figure 5: Absorbance spectra of 20 ppm *m*-DNB solution stored in different containers.

Calibration curve

To test the accuracy and precision a calibration curve was plotted between absorbance

and concentration of *m*-DNB. The concentration of *m*-DNB solution was varied from 1 ppm

to 33 ppm, after which the absorbance values were out of the range of the instrument. The

absorbance was measured both before and after passing the DNB solutions through the 0.02

µm anotop filter. A straight line was obtained in both the cases, which confirmed the

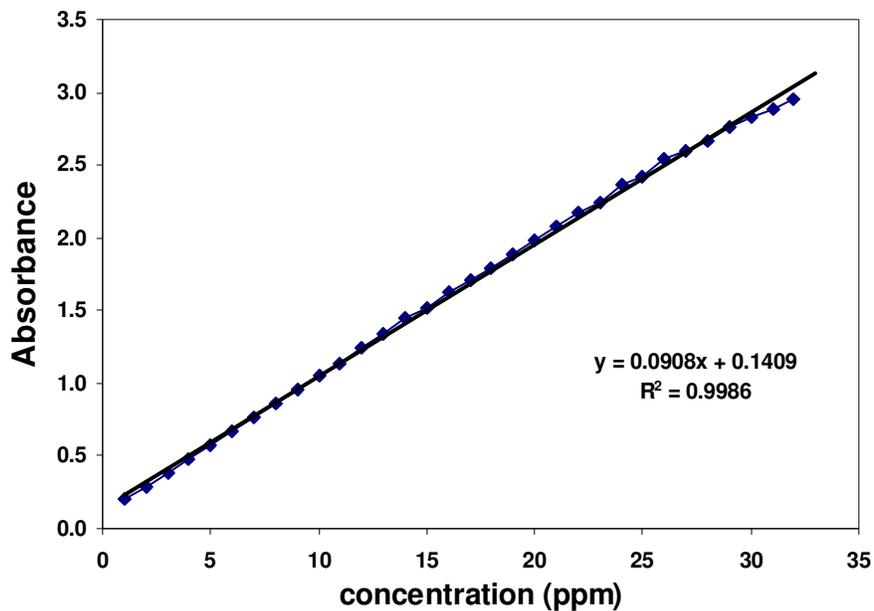accuracy of the instrument. The results are shown in Figure 6 and 7.

Figure 6: Calibration curve of *m*-DNB without passing through anotop filter
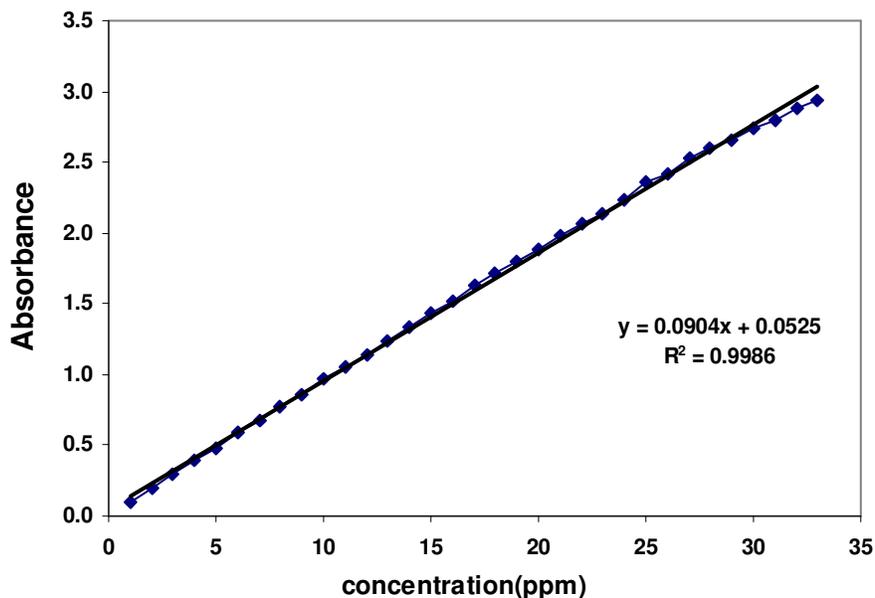
Figure 7: Calibration curve of *m*-DNB after passing through anotop filter

Conclusions

This study helped us to develop a method for the analysis of *m*-DNB in our

experiment**.** It was found that *m*-DNB is a fairly stable compound and not affected

significantly by light or temperature in the laboratory. But as a precaution, all the *m*-DNB

solutions prepared for the experiment were stored in dark-colored glass bottles. These bottles

were kept on the work bench throughout the course of the experiment. Since, *m*-DNB was

absorbed by polypropylene, polycarbonate, and polyethylene bottles, the use of these types of

containers was avoided. The equilibration solutions in the experiment were 0.01 M KCl and

0.005 M $CaCl_2$ and their mixtures. Ionic strength of the resulting solutions was between 0.01

and 0.05, and hence, would not affect the absorbance of *m*-DNB, as found from the study.

All centrifugation was done in corex centrifuge tube, and equilibration in Pyrex Erlenmeyer

flasks**.**

References

Rickert, D.E. 1985. *Toxicity of nitroaromatic compounds*. Hemisphere Publishing Corporation, Washington.

Weissmahr, K.W., S.B. Haderlein, and R.P. Schwarzenbach. 1998. Complex formation of soil minerals with nitroaromatic explosives and other Π-acceptors. *Soil Sci. Soc. Am. J.* 62:369-378.

Johnston, C.T., M.F. De Oliveira, B.J. Teppen, G. Sheng, and S.A. Boyd. 2001. Spectroscopic Study of Nitroaromatic-Smectite Sorption Mechanisms. *Environ. Sci. Technol.* 35:4767-4772.

Haderlein, S.B., and R.P. Schwarzenbach. 1993. Adsorption of substituted nitrobenzenes and nitrophenols to mineral surface. *Environ. Sci. Technol.* 27:316-326.

Li, H., B.J. Teppen, C.T. Johnston, and S.A. Boyd. 2004**.** Thermodynamics of nitroaromatic compound adsorption from water by smectite clay. *Environ. Sci. Technol.* 38:5433-5442.

Pereira, T.R. 2005. Interaction between 4, 6-dinitro-o-cresol (DNOC) and Potassium and Calcium saturated Smectites in aqueous suspension. *Master of Science dissertation, Iowa State University*.

CHAPTER 3

INTERACTION BETWEEN SMECTITE SWELLING, CATION EXCHANGE SELECTIVITY AND SORPTION OF m-DINITROBENZENE

Abstract

Smectites are the most commonly found clay mineral in many temperate region soils. It exhibits variability in shrink – swell behavior and sorption of organic molecules. Previous research has established the relationship between extent of swelling and sorption of organic compounds by smectites. The effect of the interlayer cation on sorption of organic compounds and the inter-relationship between cation exchange selectivity and extent of swelling has also been demonstrated. We investigated the effect of sorption of an organic compound on cation exchange selectivity and the interaction between organic sorption, cation exchange, and clay swelling. Our hypothesis was that adsorption of organic molecules in the interlayers of smectite influences the affinity of the clay for inorganic cations in aqueous systems. Ca- and K- saturated SPV (bentonite) and SAz-1 were equilibrated with mixed salt solutions containing 0.01 M KCl and 0.005 M $CaCl_2$ in the presence or absence of 200 ppm m-dinitrobenzene (DNB). Concentrations of Ca and K in solution and on the clay and concentrations of m-DNB were measured. The clay suspensions, both with and without the m-DNB, were also analyzed on the x-ray diffractometer to study the clay structure and the d-spacing. In general, SPV that was initially saturated with Ca sorbed more m-DNB than the SPV that was initially saturated with K. In general, the SPV sorbed more m-DNB than the SAz-1. Sorption of m-DNB on SPV increased preference for K relative to Ca for samples initially saturated with Ca, but it had little effect on exchange selectivity for samples that

were initially saturated with K. The net effect of *m*-DNB was to decrease the magnitude of the hysteresis loop for Ca-K exchange. There was little effect of *m*-DNB on K-Ca exchange for the SAz-1. Sorption of *m*-DNB also collapsed the clay and enhanced the formation of quasicrystals. This is more prominent for the SPV than the SAz-1. The type of cation initially saturating the clay influenced the sorption of *m*-DNB, and sorption of *m*-DNB altered the structure of quasicrystals. Our results demonstrated that adsorption of organic molecules in the interlayer of smectites influences the affinity of the clays for inorganic cations and that hysteresis in cation exchange influences sorption of organic molecules. It also demonstrated that sorption of organic molecules influenced the extent of swelling and clay organization.

Introduction

The wide use of nitroaromatic compounds (NAC) as pesticides, explosives, and as intermediates in the manufacture of dyes, solvents and other chemicals has resulted in the contamination of soils, sediments, and aquifers (Rickert, 1985; Hardelein et al.,1995; Leuenberger et al.,1988). Sorption of the NACs by soil minerals plays a significant role in their transport, mobility, availability, and reactivity in soil environments. Organic matter has long been believed to be the dominant sorbent of nonionic organic contaminants in soils and sediments (Karickhoff, 1981; Kile et al. 1995; Chiou et al., 2002). But recent research has shown that soil minerals may also sorb large quantities of several pollutants such as atrazine and NACs (Haderlein et al., 1996; Johnston et al., 2002; Laird et al., 1992). In order to predict the fate of nitro aromatic compounds in the environment, it is necessary to understand the role of soil minerals and the factors that influence their sorption. Among the many

minerals found in the soil, smectites play an important role due to their abundance, large surface area, and high cation exchange capacities (CEC).

Many recent studies have demonstrated the contribution of smectites to pesticide retention in soils. Laird and Sawhney in 2002 described the various factors that influence pesticide sorption by smectites, namely, permanent and variable charge sites, uncharged surfaces and surface acidity. They also discussed various mechanisms and clay–pesticide interactions. Sorption of organic compounds in aqueous suspensions by smectites is greatly influenced by the properties of the sorbent, i.e., the clay type, interlayer cation present on the exchange sites, layer charge density, and the interlayer volume, along with the type and position of substituents on the aromatic ring of the sorbate (Haderlein et al., 1993; Sheng et al., 2002). Laird et al. (1992), observed an inverse relationship between layer charge and sorption affinity for an organic compound (atrazine). Lower surface charge density smectites typically have greater sorption affinity for organic compounds due to more available siloxane surfaces (Laird et al., 1992; Laird, 1996; Sheng et al., 2002).

Smectites in aqueous suspensions may exist as quasicrystals, which are stacks of 2:1 phyllosilicate layers, combined parallel to each other. In 2006, Li et al. studied the effect of ionic strength on the sorption of 1, 3-dinitrobenze by Ca- and K-saturated reference smectite (SWy-2). They observed an increase in sorption of the NAC as the ionic strength of KCl increased. The x-ray diffraction (XRD) patterns did not indicate formation of quasicrystals at 0.01 M KCl, but addition of the *m*-DNB caused the formation of quasicrystals with the interlayer spacing of 12.3 Å. Their results indicated that sorption of the NAC enhanced the formation of quasicrystals along with collapsing and dehydrating the interlayer space.

Chappell et al. (2005) studied the influence of the extent of crystalline swelling on the sorption of atrazine by reference smectites in aqueous systems. X-ray diffraction analysis of never-dried K-Panther Creek (PC) smectite showed that it was dominated by three layers of interlayer water molecules, whereas the air dried-resuspended K-PC had intrastratification of layers with one or two layers of interlayer water molecules. The X-ray diffraction patterns for air dried-resuspended and never dried Ca-PC did not show much difference in the interlayer spacing, and both samples were dominated by quasicrystals with four layers of interlayer water molecules. The air dried-resuspended K-PC smectite had an order of magnitude higher affinity for atrazine than the never dried K-PC smectite indicating that the hydration status of the clay interlayer influenced the sorption of the organic compound by this smectite.

Previous studies have demonstrated that hydration energy of the interlayer cation affects the sorption of NACs. Less strongly hydrated cations (e.g., K^+) leave neutral siloxane surfaces more exposed and available for adsorption (Li et al., 2003). Boyd et al. in 2001 showed that due to the ease of displacing the waters of hydration, the weakly hydrated cation enhanced sorption of organic compounds by the formation of inner-sphere complexes. Charles et al. (2005) studied the contribution of soil organic matter and the mineral fraction and the effect of the exchangeable cation on the sorption of NACs by whole soil, mineral fraction, and soil organic matter. Their results demonstrated that smectites saturated with weakly hydrated cations (K^+, Cs^+) adsorb more of the organic compound than clays saturated with strongly hydrated cations such as Ca^{2+} or Mg^+. The interlayer spacing of 12.3 Å was found to be the optimum for pesticide sorption (e.g., dinitro-o-cresol) as the organic compound can interact directly with both opposing siloxane surfaces and minimize the hydration of the compound (Sheng et al., 2001, Li et al., 2004a).

Various concepts and models have been developed to explain the cation exchange selectivity exhibited by smectites in aqueous systems, e.g., Erickson model (1952), Eisenman's model (1962), and the hard acid-soft base (HASB) concept put forward by Pearson (1962). According to HASB theory, the driving force for cation exchange selectivity was the inner-sphere complexation between alkali cation and smectites. Xu and Harsh (1992) used this concept to calculate thermodynamic parameters for the cation exchange reactions. Using the Eisenman model, it was indicated that as the layer charge density increased, there was a preference for lesser hydrated cations in the interlayer and that layer charge and interlayer hydration were important factors influencing cation exchange selectivity (Eberl, 1980). Maes and Cremers (1980) pointed out as the layer charge increases, the tendency to dehydrate the interlayer also increases. As the layer charge increases, the effective hydration number decreases (Laird, 1999).

In 1997, Laird and Shang proposed a model describing the relationship between selectivity and swelling. The model postulated that cation exchange was controlled by an interaction between cation exchange selectivity, nature of the interlayer cation, and the extent of swelling, all being connected through a feedback loop. It said that crystalline swelling has an effect on the selectivity of the clay, selectivity influenced the interlayer ionic composition, and the interlayer ionic composition influenced the basal spacing. More recently, studying the Cs-K exchange on montmorillonites, a partioning concept was put forward, i.e., the weakly hydrated cations partition into the less hydrated interlayer phase (Teppen and Miller, 2005). Also, it has been suggested that clay microstructure also influences cation exchange selectivity (McBride, 1980).

Smectites exist as dynamic quasicrystals, consisting of multiple sets of the 2:1 phyllosilicate layers. In suspensions, these quasicrystals are dynamic in nature, i.e., small quasicrystals join together to form one bigger quasicrystal or larger quasicrystals break to form many smaller quasicrystals. Cation demixing may be defined as the distribution of monovalent and divalent cations in different regions of the clay structure (Fink et al., 1971). Demixing of cations suggests that internal surfaces of quasicrystals have selectivity different from external surfaces. At low electrolyte concentration, for Na^+-Ca^{2+} montmorillonites system, it has been demonstrated that Na^+ is preferred on the external surfaces and Ca^{2+} was preferred by the internal surfaces of quasicrystals (Shainberg et al., 1980; Oster et al., 1980). As discussed earlier, in 1997 Laird et al. proposed a feedback mechanism between extent of crystalline swelling and cation exchange selectivity to explain the process of demixing. In a mixed cation system, at low ionic strength, demixing occurs and monovalent cations tend to be on the external surfaces whereas the divalent cations occur on the internal surfaces (Pills et al., 2007).

From all the previous studies, the following facts can briefly be summarized: (1) the extent of swelling influences the sorption of organic compounds (2) the nature of interlayer cations influences the sorption of organic compounds, and (3) there is a relationship between cation exchange selectivity, interlayer cation composition, and the extent of smectite swelling. No research, however has addressed the effect that sorption of an organic compound will have on cation exchange selectivity and the interaction between organic–sorption, cation–exchange and clay swelling.

In this study, we hypothesized that the adsorption of organic molecules in the interlayers of smectites will influence the affinity of the clay for inorganic cations and that

sorption of organic molecules, cation exchange selectivity, and extent of swelling are all inter-related through a complex feedback interaction. The specific objectives of this study were: (1) to determine the effect of sorption of *m*-dinitrobenzene (DNB) on cation exchange selectivity for K and Ca by two reference smectites and (2) to determine the interaction between sorption of *m*-DNB, the extent of swelling, and the cation exchange selectivity for K and Ca by these reference smectites.

Materials and Methods

Smectites and m-Dinitrobenzene:

The reference smectites studied were Na-SPV ('Volclay'), a Wyoming bentonite, obtained from the Beroid Division of National Lead Company, Houston, Texas; and the Ca-SAz-1, a Ca-Montmorillonite ('Cheto') from the Apache County, Arizona, obtained from the Source Clay repository at Purdue University. *m*-DNB was used as the organic compound for the adsorption studies. It was obtained from Aldrich Chemical Company, Inc (Milwaukee, WI) with purity >97 %.

Test for presence of carbonates

The reference smectites were checked for the presence of carbonates by adding few drops of dilute HCl to the clay. No effervescence was observed, which confirmed the absence of carbonates in both samples.

Size fractionation

Both the reference smectites were Na-saturated prior to size fractionation. This was done by equilibrating 150 g of clay in 4 L of 1 M NaCl. The mixture was stirred, settled and decanted and then fresh NaCl was added after every 4 hours. This was repeated 5 times.

Thereafter, the <2 μm fraction was separated from the Na-saturated clay by sedimentation. The Na-clay was dispersed by adding deionized water. The suspension was kept undisturbed for 8 hours, after which the top 10 cm was siphoned into an autoirrigation flask. This procedure was repeated for over a week until sufficient amount of the clay fraction was obtained. The auto irrigation flask was used to dewater the clay suspension.

Ion saturation

Portions of about 30 g of the <2 μm Na-saturated SPV and SAz-1 were saturated with calcium and potassium. The samples were suspended in 1 M KCl or $CaCl_2$ by sonication in Nalgene centrifuge bottles. These bottles were then shaken on a reciprocating shaker at room temperature for 4 hours, centrifuged at 8000 rpm for 8 minutes. The supernatant was decanted and fresh salt solution was added. This was repeated 5 times. Initially Ca and K saturated SPV were termed as Ca-SPV and K-SPV respectively. Similarly, initially Ca and K saturated SAz-1 were termed as Ca-SAz-1 and K-SAz-1 respectively.

Removal of excess salt and freeze drying

Following ion saturation, the excess salt was removed by dialyzing the saturated clay suspensions, using Spectra/Por 3 dialysis membrane, against deionized water for 5 days. The water was changed thrice daily until no white precipitate was obtained for the silver nitrate test for the presence of chloride ions and a constant electrical conductivity obtained. The samples were then freeze dried, labeled, and stored in bottles.

Preparation of equilibrating solutions

Stock solutions of 0.005 M $CaCl_2$ and 0.01 M KCl were prepared, 18 L each, and mixed in proportions as shown in Table 1a. For preparing the 200 ppm *m*-DNB solutions, another set of 0.005 M $CaCl_2$ and 0.01 M KCl, 18 liters each, were prepared. To each of the

second set of salt solutions, 3.6 g of *m*-DNB were added and the solutions were heated to

about 50 º C with continuous stirring to help the crystals dissolve. They were then mixed in

proportions shown in Table 1b.

Table 1a: Equilibrating solutions without *m*-DNB

Salt Solutions (mL)	A	B	C	D	E	F	G	H	I	J	K
0.01 M KCl	1000	900	800	700	600	500	400	300	200	100	0
0.005 M CaCl$_2$	0	100	200	300	400	500	600	700	800	900	1000

Table 1b: Equilibrating solutions containing *m*-DNB

Salt Solutions containing 200 ppm *m*-DNB (mL)	A	B	C	D	E	F	G	H	I	J	K
0.01 M KCl	1000	900	800	700	600	500	400	300	200	100	0
0.005 M CaCl$_2$	0	100	200	300	400	500	600	700	800	900	1000

Equilibrating procedure

The prepared K- and Ca- saturated clay samples (300 mg each) were equilibrated

with 200 mL of the various equilibrating solutions in Erlenmeyer flasks corked with Teflon

stoppers, on the reciprocating shaker for 2 days at room temperature. Thereafter, about 60

mL of the suspension was withdrawn, centrifuged for 5 min at 8000 rpm, to separate the solid

and the liquid phases and then the supernatant was filtered by passing through a 0.02 μm

Whatman Anotop filter.

ICP sample analysis

To determine the amounts of Ca^{2+} and K^+ sorbed on the clay and in the solution

phase, an ICP experiment was set up. A Thermo Jarell Ash Model 61 E, inductively coupled

plasma –atomic emission spectrometer was used the ICP analysis.

Solution phase: The ICP was optimized for determination of K by increasing the observation

height and decreasing the resolving power. Both of these would allow easy detection of

atomic emission by K. The solution-phase samples were prepared by adding 5 mL of the

prepared internal solution containing an internal standard (90 ppm Cd) and 10 mL of the

supernatant obtained after filtration, in small polypropylene bottles, and these were shaken

and then analyzed on the ICP for K and Ca.

Clay phase: Suspension nebulisation was used for elemental analysis of the clay phase

(Laird et al., 1990). The clay obtained after centrifugation was washed with ethanol until a

constant electrical conductivity, close to that of pure ethanol, was obtained and then air dried.

60 mg of the air dried clay was suspended in 50 mL of solution containing an ICP internal

standard and matrix modified by sonication and the suspension was analyzed on the ICP for

Si, Al, Ca, Fe, Mg, Zn, Mn, Ti, and K simultaneously.

Calculation of equivalent fractions of sorbed Ca^{2+} and K^+

A sum of oxides method was used to calculate the cation exchange capacity and the

equivalent fractions of sorbed Ca^{2+} and K^+. First, the elemental concentrations in the clay

suspensions, as determined by the ICP suspension nebulisation technique, were multiplied by

the oxide/element ratios to express the results as oxides. Then, the sum of oxides was

obtained for each sample. Thereafter, the elemental concentration of each element in mmol/L

was divided by the atomic weight (g/mol) and the sum of oxides to determine the relative

concentration of each element in the clay (mmol/g-sum of oxides). The cation exchange capacity (CEC) in mmol / g- of sum of oxides was determined by using the formula (2* (mmol Ca^{2+} /g-sum of oxides) + (mmol K^+/g-sum of oxides))*1000. The CEC for Ca-saturated reference smectite equilibrated with 0.005 M $CaCl_2$ solution was used as the CEC for all the samples for that particular reference smectite. To calculate the equivalent fraction of K^+ retained by the clay the equivalent of Ca^{2+} /g of oxide was subtracted from the CEC and the result was divided by the CEC.

By using this method for calculation, the errors due to the varying water content of the samples, inaccuracies in measuring sample weights, and those occurring during ICP analysis such as fluctuations in the plasma, and variation in rates of sample introduction were all minimized. To determine the concentration (in ppm) of Ca^{2+} and K^+ in the solution phase, the equilibrating solutions were analyzed after equilibration with the clay samples. From the concentrations in ppm, equivalent fractions of K^+ and Ca^{2+} in solution, after equilibration, were calculated.

Spectrophotometric analysis

To quantify the amount of *m*-DNB sorbed by the clay samples, the supernatants obtained after centrifugation and filtration of the suspensions that had been equilibrated with mixed salt solutions containing 200 ppm *m*-DNB were analyzed on the spectrophotometer. The supernatants were first filtered by passing through a 0.02 μm anotop filter and then diluted to one-eighth of their concentration. The absorbance was measured in a quartz cuvette, fitted in a Milton Roy Spectronic 601 spectrophotometer with an ultra violet detector. The λ_{max} for *m*-DNB was 240 nm. The concentration of *m*-DNB was determined using the calibration curve. The initial concentration of *m*-DNB was the absorbance of the

stock salt solutions containing *m*-DNB, taken after a one-tenth dilution. The amount of *m*-DNB sorbed on the clay was calculated by difference between the initial concentration of *m*-DNB added and the final concentration in solution after equilibration.

XRD Analysis

Suspension x-ray diffraction (XRD) studies (Shang et al., 1995) were performed to determine the effect of the sorption of the organic compound on the basal spacing and the organization of the smectites. After equilibrations with salt solutions, both with and without the *m*-DNB, and withdrawal of a portion of the suspension for ICP analysis, the remaining suspension was transferred to a Nalgene centrifuge bottle and centrifuged at 8000 rpm for 7 min. The equilibration solution was then decanted carefully, and the clay was transferred to a scintillation vial using a spatula. The vials were pre-marked at 10 mL. Then, the equilibration solution was added to the clay till the mark; vials were closed tightly and stored in the refrigerator.

Prior to XRD analysis, the vials were shaken vigorously, and then about 1 mL of suspension was injected into a transmission XRD cell. The transmission cells, 1 mm in thickness, were made by cutting a 5-cm-diameter circle from a 1-mm thick plastic sheet and then making a 3-cm-diameter hole. The clay suspension was held in between the Mylar sheets, stuck on both sides of the disk. The sample cell was mounted in the transmission stage and was perpendicular to the zero plane of the goniometer, which allowed the radiation to pass through the suspension, and a diffraction pattern was recorded. The transmission stage was rotated at the minimum speed of 15 rpm to avoid settling of the clay in the suspension during data acquisition.

XRD patterns were obtained using CuKα radiation at 30mA and 40kV on a Braker D-5000 θ-θ diffractometer. A θ-2θ configuration, 1mm detector slit, and stepwise scan, over a range of 2 to 12 ° 2θ was used to run the samples. A step size of 0.05 ° 2θ and a speed of 0.1 ° 2θ /min for the Ca- saturated smectites and each sample took about 1hr. For K- saturated smectites, a step size of 0.05 ° 2θ and a speed of 0.05 ° 2θ /min were used, and each run took about 1h 50 min.

Results

Cation exchange selectivity

Cation exchange selectivity exhibited by SPV is illustrated by the relationship between equivalent fraction of K on the clay (X_K^C) and equivalent fraction of K in final solution (X_K^S) (after equilibration), measured with and without 200 ppm *m*-DNB in solution (Figure 1). The same plots for SAz-1 are shown in Figure 2. For all the studied samples, the amount of K on the clay increases with the X_K^S indicating the cation exchange reaction. At equilibrium, the samples that were initially K saturated have more X_K^C than the samples that were initially Ca saturated, which is an indication of hysteresis in the cation exchange reaction. For Ca-SPV (Figure 1a), at any given X_K^S, the amount of K on the clay is less without the *m*-DNB in solution than in its presence. The amount of K on the clay for K-SPV is about the same both with and without the *m*-DNB in solution (Fig 1b). For $X_K^S < 0.6$, K-SAz-1 has similar amounts of K on the clay, both with and without the *m*-DNB in solution. For $X_K^S > 0.6$, however, the amount of K on the clay is greater in the presence of *m*-DNB (Figure 2b) than in its absence. A similar trend is observed for Ca-SAz-1 (Fig 2a).
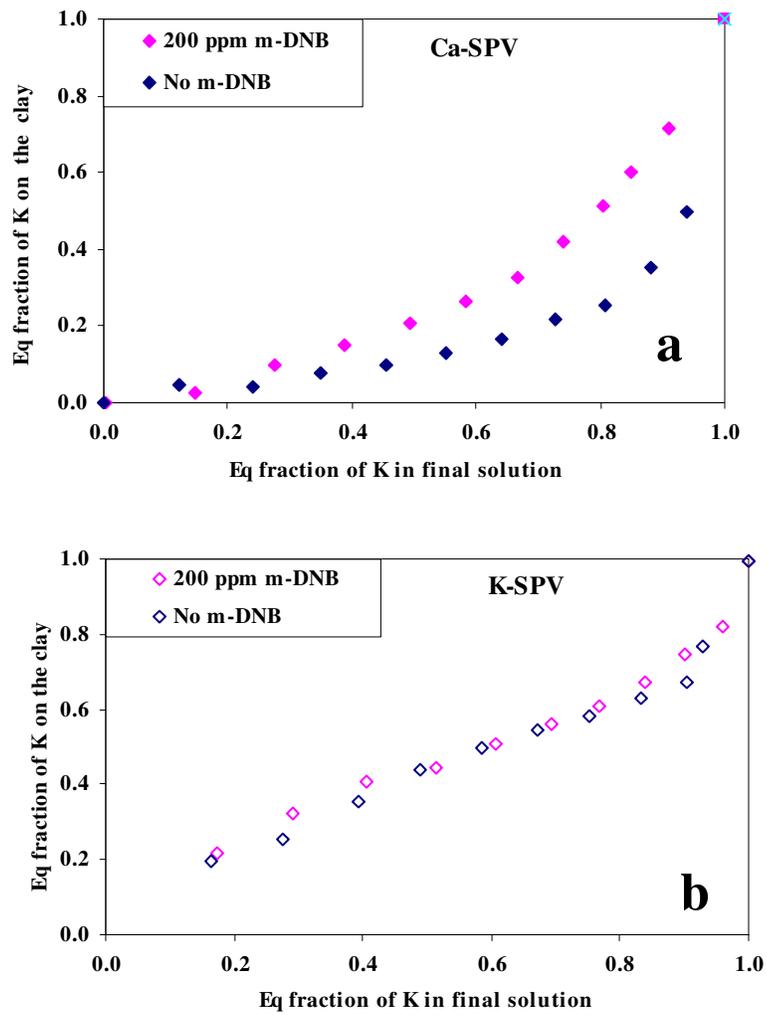
Figure 1: Cation exchange plot of Ca-SPV (a) and K-SPV (b) when equilibrated with and without 200 ppm *m*-DNB.
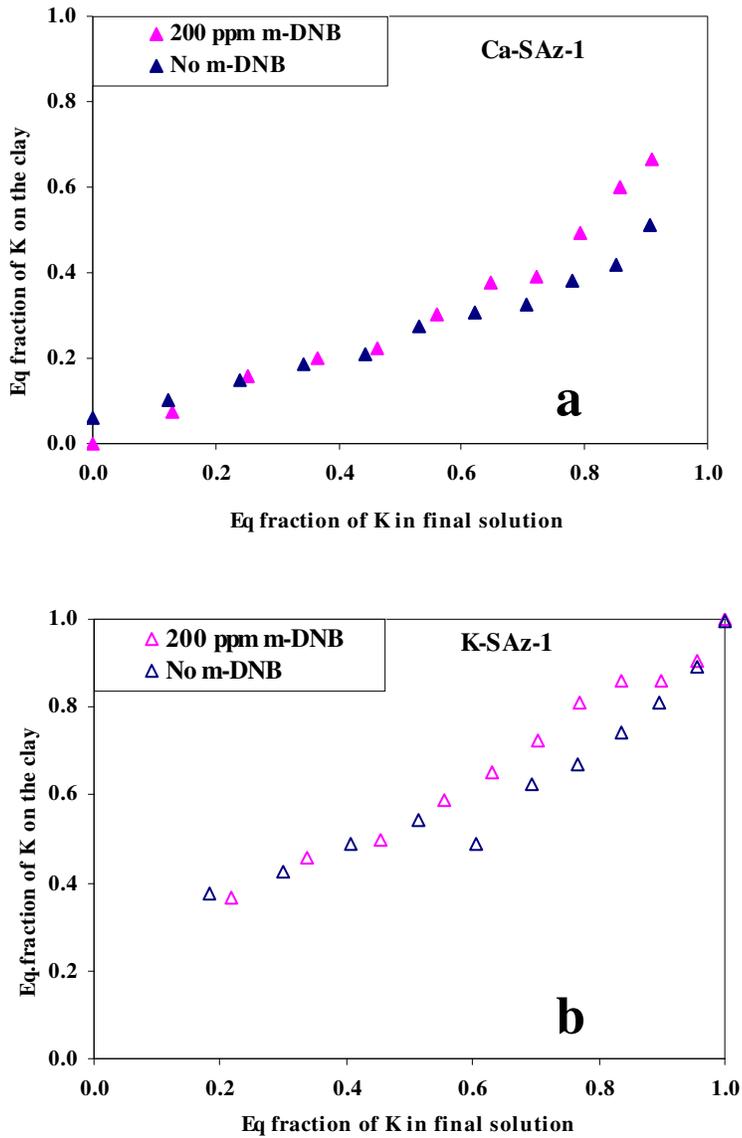
Figure 2: Cation exchange plot of Ca-SAz-1 (a) and K-SAz-1 (b) when equilibrated with and without 200 ppm *m*-DNB.

In Figures 3a and 3b, the hysteresis associated with the cation exchange reaction is depicted, both in the presence and absence of *m*-DNB, for SPV. In Figures 3c and 3d, the hysteresis for the Ca/K cation exchange reaction for the higher-charged SAz-1 is shown. The

presence of *m*-DNB suppressed the hysterisis for the SPV. The same effect is observed for the SAz-1, but to a lesser extent.
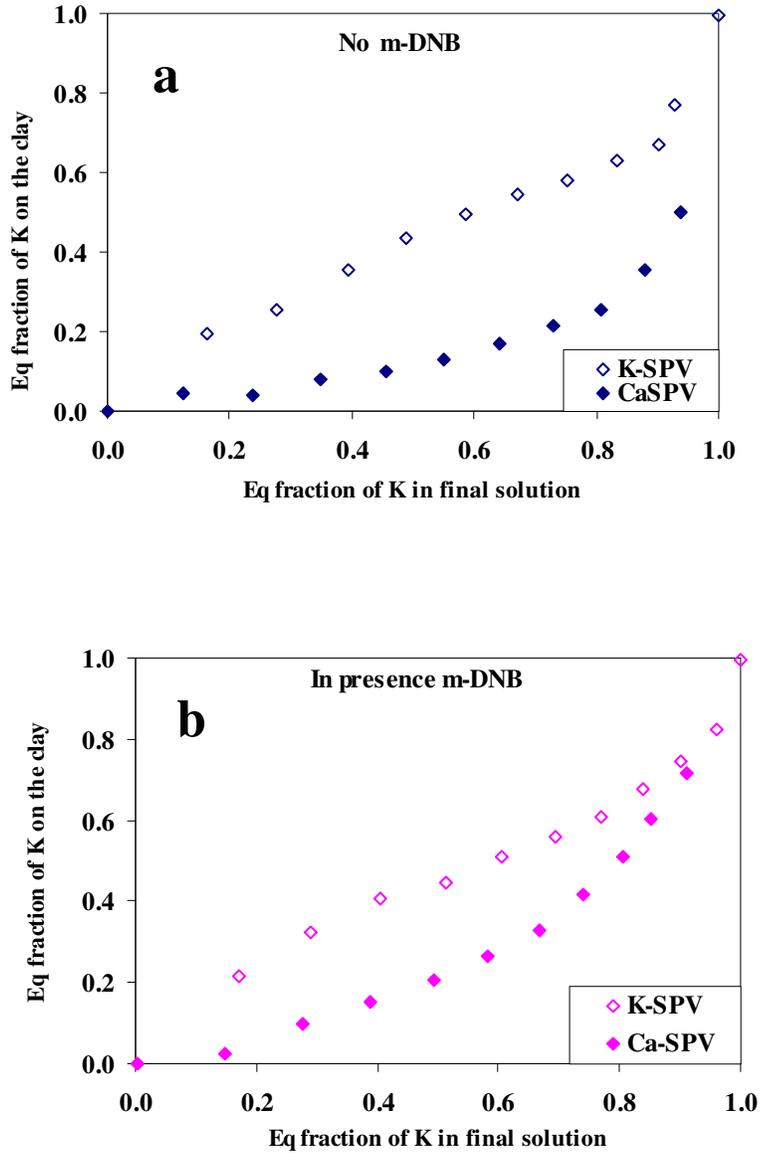

Figure 3: Hysteresis associated with Ca/K exchange reaction for SPV in the absence of *m*-DNB (a) and hysteresis associated with Ca/K exchange reaction for SPV in the presence of *m*-DNB (b).
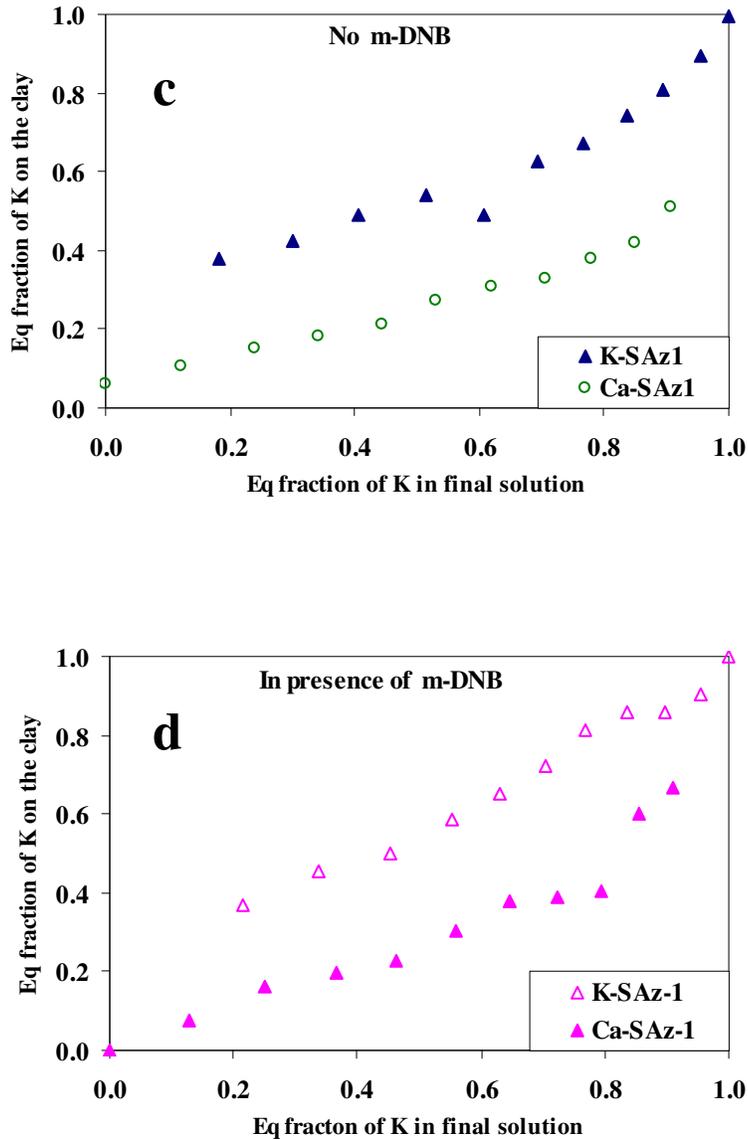
Figure 3: Hysteresis associated with Ca/K exchange reaction for SAz-1 without *m*-DNB (c) and hysteresis associated with Ca/K exchange reaction for SAz-1 in the presence of *m*-DNB (d).

Sorption of m-DNB

The sorption of *m*-DNB by the two reference smectites relative to X_K^C is shown in

Figure 4. In general, the amount of *m*-DNB on the clay increases as the X_K^C increases for all

the smectites. The amount of *m*-DNB adsorbed by the clay at any X_K^C is higher for the SPV

than for SAz-1. Hysteresis is also clearly observed for the sorption of *m*-DNB by the Ca- and

K-SPV but is not evident for the Ca- and K-SAz-1. For $X_K^C > 0.4$, the Ca-SPV sorbed more

m-DNB than K-SPV. Figure 5 shows the relationship between the amount of DNB adsorbed

by the clay and X_K^S. From figures 5, it can be seen that at $X_K^S > 0.8$, the Ca-SPV has higher

amount (mg-DNB/kg-clay) m-DNB sorbed on the clay than the K-SPV but it is not so for the
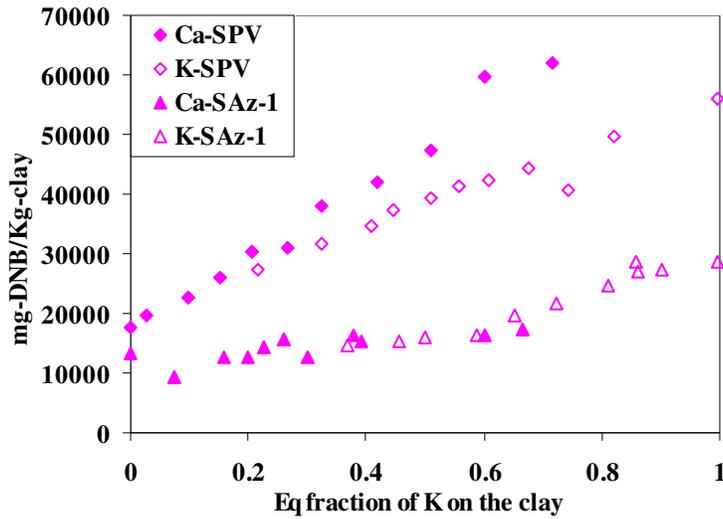
SAz-1.

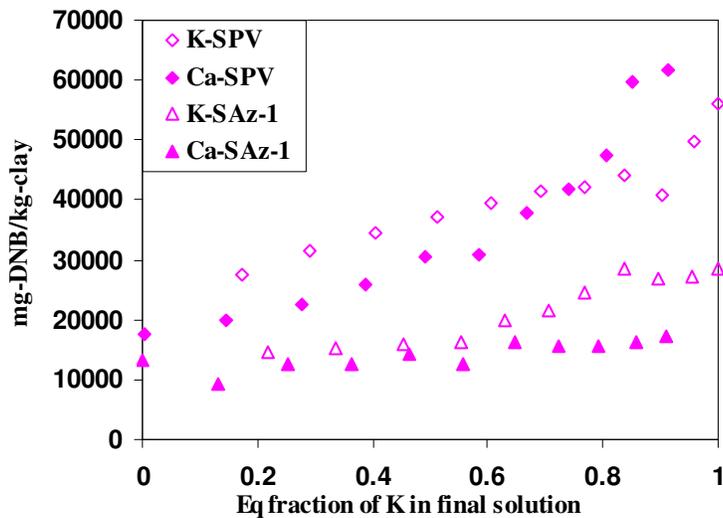Figure 4: Sorption of m-DNB by saturated smectites.

Figure 5: Sorption of m-DNB by saturated smectites.

XRD patterns for the clay suspensions

Suspension x-ray diffraction (XRD) patterns were obtained for four samples for each set of reference smectite. These four samples were equilibrated with 100% KCl, 60:40 KCl: CaCl$_2$, 40:60 KCl: CaCl$_2$ and 100% CaCl$_2$ salt solutions. These clay suspensions have different amounts of K and *m*-DNB on the clay.

Figure 6a presents the suspension XRD patterns for Ca-SPV in the absence of *m*-DNB. Clay suspension equilibrated with 100% KCl show only a broad and diffuse peak indicating that K-SPV quasicrystals are small and poorly organized. As the amount of Ca in the equilibrating solution increased, the XRD peaks were sharper and more intense, which indicates that more 2:1 phyllosilicate layers are aligned parallel to each other and the number of layers per quasicrystals increases. All peaks are centered on 19.4 Å.

Figure 6b presents the same Ca-SPV equilibrated with mixed salt solutions containing the 200 ppm *m*-DNB. The presence of *m*-DNB caused both a decrease in the basal spacing and in the intensity of the XRD peaks. For the Ca-SPV equilibrated with 100% KCl, the very broad 19.4 Å XRD peak (Fig 6a) collapsed to 12.9 Å in the presence of *m*-DNB. The presence of the 12.9 Å peak suggested that *m*-DNB induced the formation of K-SPV quasicrystals in the aqueous suspensions.

No peaks were evident in the XRD patterns for the K-SPV equilibrated with 100% KCl (Fig 7a) indicating that K-SPV quasicrystals were highly disorganized or delaminated in aqueous suspensions. The organization in the quasicrystals increased as the amount of Ca in the equilibrating solution increased, as indicated by a broad XRD peak centered at 19.6 Å. The peaks were sharper and more intense as the amount of Ca increased in the solution but

were substantially broader and lower in intensity than peaks obtained for the Ca-SPV sample (Figure 6a).

In the presence of *m*-DNB, a peak centered near 12.5 Å (Figure 7b) was observed for the K-SPV suspension equilibrated with 100% KCl, 60:40 KCl: CaCl$_2$, 40:60 KCl: CaCl$_2$ solutions. When the K-SPV was equilibrated with 100% CaCl$_2$, a very broad peak with a d-spacing of 18.8 Å was observed. This result indicated that *m*-DNB stabilized the K-SPV quasicrystals inhibiting cation exchange.

For the higher-charge smectite, no peaks were observed when the K-SAz-1 was equilibrated with 100 % KCl solution (Figure 8a). As the amount of Ca in the equilibrating solution increased, a very weak peak centered at 19.2 Å was observed in the absence of *m*-DNB. In the presence of *m*-DNB (Figure 8b), no XRD peaks were observed for the 100% KCl, 60:40 KCl: CaCl$_2$, 40:60 KCl: CaCl$_2$ treatments. For the K-SAz-1 sample equilibrated with 100 % CaCl$_2$, there was a broad XRD peak centered at 19.4 Å. Although *m*-DNB did have subtle effects on the XRD patterns for K-SAz-1, the effects were minimal and much less apparent than noted previously for the K-SPV.

Figures 9a and 9b show the XRD patterns for Ca-SAz-1, equilibrated with mixed salt solutions without and with the *m*-DNB, respectively. In the absence of *m*-DNB, the d-spacing was about 19.2 Å for 100 % CaCl$_2$, 60:40 KCl: CaCl$_2$, 40:60 KCl: CaCl$_2$ treatments. For the 100 % KCl treatment, the peak was shifted slightly to 18.4 Å. In the presence of *m*-DNB (Figure 9b), the XRD peaks were at approximately at the same positions as without *m*-DNB, however the relative intensities of the peaks were higher in the 100 % KCl and 60:40 K/Ca solutions and weaker in the 100 % CaCl$_2$. These results suggest that the presence of *m*-DNB inhibited the formation of large Ca-SAz-1 quasicrystals.
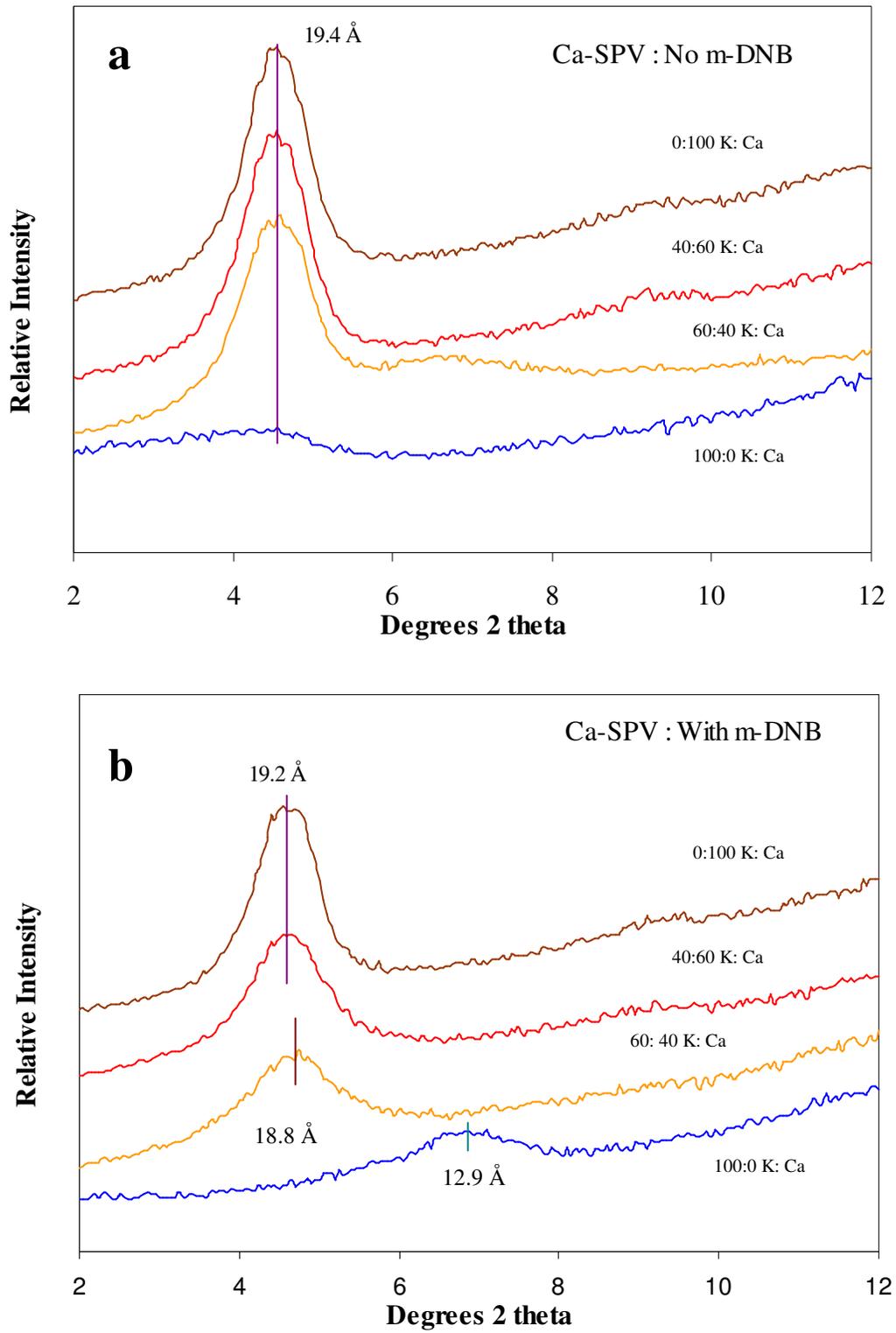
Figure 6: The XRD patterns for Ca-SPV without the *m*-DNB (a) and in presence of *m*-DNB (b). The relative intensities have been obtained by either adding or subtracting a constant. The maximum and minimum on the x-axis are same for both plots.
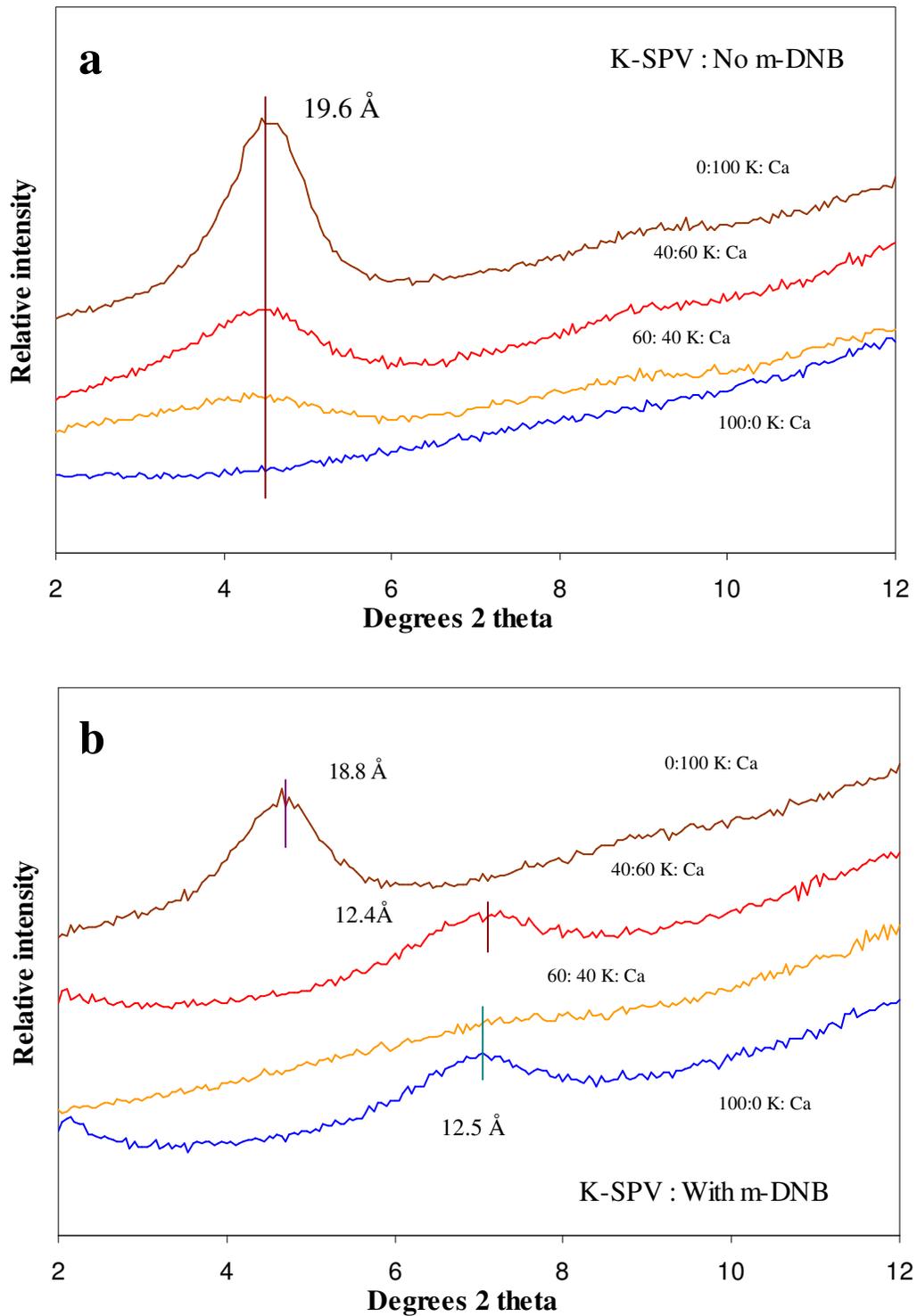
Figure 7: XRD pattern for K-SPV equilibrated with mixed salt solutions without *m*-DNB (a) and containing 200 ppm *m*-DNB (b). The relative intensities have been obtained by either adding or subtracting a constant. The maximum and minimum on the x-axis are same for both plots.

Figure 8: XRD pattern for K-SAz-1 equilibrated with mixed salt solutions without 200 ppm *m*-DNB (a) and containing *m*-DNB (b). The relative intensities have been obtained by either adding or subtracting a constant. The maximum and minimum on the x-axis are same for both plots.

Figure 9: XRD pattern for Ca-SAz-1 equilibrated with mixed salt solutions without the 200 ppm *m*-DNB (a) and containing the 200 ppm *m*-DNB (b). The relative intensities have been obtained by either adding or subtracting a constant. The maximum and minimum on the x-axis are same for both plots.
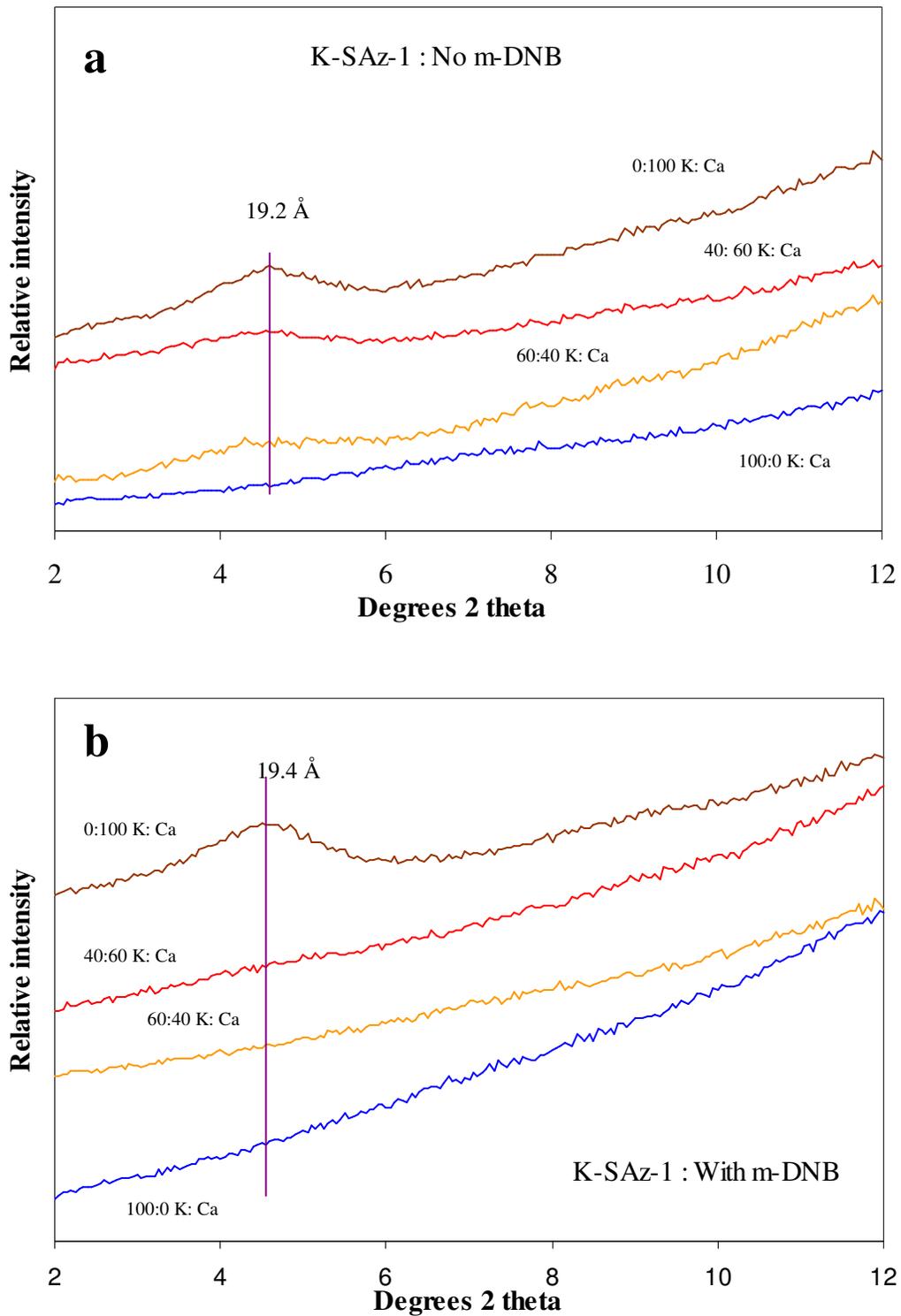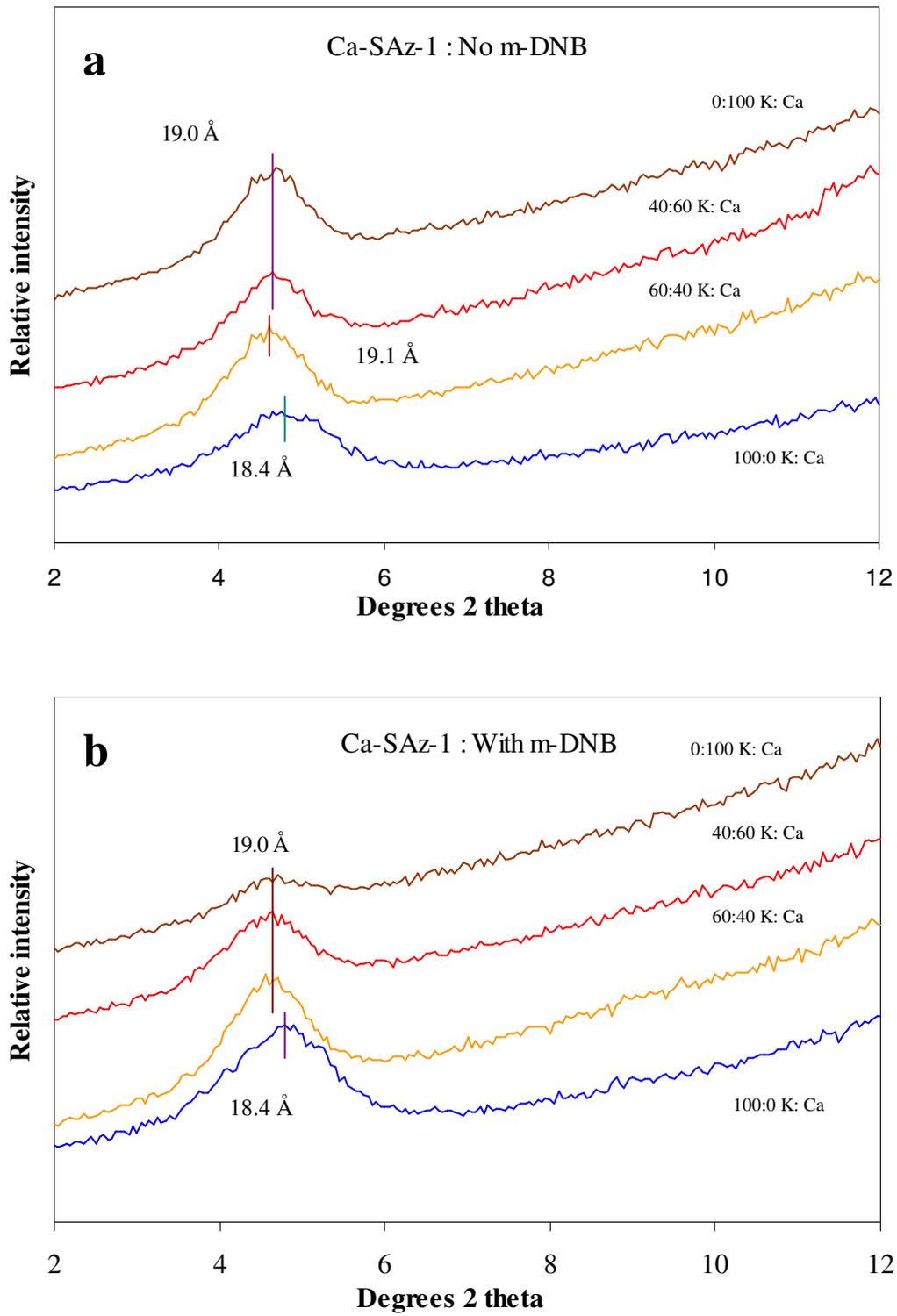
Discussion

The cation exchange selectivity isotherm (Figure 1a) for Ca-SPV shows that the presence of *m*-DNB increases the preference of the clay for K relative to Ca. By contrast, there is no apparent effect of *m*-DNB on selectivity for K on the K-SPV sample (Figure 1b). The higher-charge SAz-1 shows a slight preference towards K in the presence of *m*-DNB, only when the clay was equilibrated with solutions with $X_K^S > 0.6$ (Figure 2a and 2b). This result from the cation exchange isotherms supports our hypothesis that sorption of *m*-DNB increases selectivity of smectites for K. The reverse trend, i.e., clay saturated with weakly hydrated cations show greater affinity for *m*-DNB than do Ca-saturated clays, has already been demonstrated in previous research (Charles et al., 2006).

Overall, the higher-charge smectite, SAz-1, has more K on the clay than the SPV when equilibrated with the same solution. This is consistent with previous research, which has shown that higher-charge smectite is prone to collapse, which increases its selectivity towards weakly hydrated cations, K^+ in this case (Laird, 1996; Laird and Shang, 1997).

The amount of *m*-DNB sorbed by the smectites increases as the amount of K on the clay increases (Figure 4). This is consistent with previous research (Charles et al., 2006; Boyd et al., 2001) and has been attributed to the fact that smectites saturated with weakly hydrated cations, K^+, have larger adsorption domains between the exchange sites than Ca-saturated smectites. Hence, we also see the interrelationship between selectivity of the clay towards a specific cation and sorption of *m*-DNB.

The XRD patterns for Ca-clay (Figure 6a and 9a) showed more distinct peaks than the XRD patterns for K-clay (Figure 7a and 8a), implying that the Ca-clays have better organized

quasicrystals than the K-clays. The presence of *m*-DNB caused a decrease in both the basal

spacing and the intensity of the XRD peaks for the Ca-SPV (Figures 6a and 6b), which

suggests the breakup of Ca-quasicrystals due to enhanced K uptake (Figure 1a). By contrast,

for the K-SPV, the presence of *m*-DNB induced the formation of K-quasicrystals (Figure 6b

and 7b), which is consistent with previous research (Li et al., 2006).

Hysteresis in cation exchange reactions involving smectites is most pronounced when

cations of different hydration status are involved like K^+ and Ca^{2+} (Newman, 1970). Here we

demonstrate that hysteresis associated with the Ca-K cation exchange reaction for SPV is

much larger in the absence of *m*-DNB (Figure 3a) than in the presence of *m*-DNB (Figure

3b). By contrast there was relatively little effect of *m*-DNB on the hysteresis in the cation

exchange reaction for the high charge SAz-1 (Figures 3c and 3d). This could be due to the

difference in layer charge. Due to the higher layer charge and the tendency of high charged

clay to collapse, it has a greater preference for the weakly hydrated cation, K^+, and hence the

preferential selectivity towards a specific cation on *m*-DNB sorption is somewhat masked

and hysteretic effect is relatively small (Figure 3c and 3d). Also the SPV adsorbed

substantially more *m*-DNB than did the SAz-1 (Figure 4). Hence any effect of *m*-DNB on

K/Ca exchange reaction would be less for SAz-1 than for SPV.

Hysteresis is also visible in the sorption of *m*-DNB (Figure 4), where again it is more

evident for the SPV than for the SAz-1. Sorption of *m*-DNB causes a change in extent of

swelling, manifested by a decrease in basal spacing. It has already been demonstrated in

previous work that hysteresis in cation exchange reactions is inherent with crystalline

swelling (Laird et al., 1994).

Further insight into the sorption of *m*-DNB is obtained by the relationship between the amount of *m*-DNB sorbed and X_K^C (Figure 4). The lower charged clay (Ca/K- SPV) adsorbs more *m*-DNB than the higher charge clay. This difference in affinity could be attributed to the difference in charge densities of the smectites. For the lower charged SPV, the negatively charged sites are farther apart and there is ample room between charge sites for the sorption of organic molecules. By contrast, space for retention of organic molecules is limiting in higher charge clay (Li et al., 2003).

Figure 4 demonstrates an increase in sorption of *m*-DNB with an increase in the X_K^C on the clay, this is consistent with previous reports that saturation of clays with weakly hydrated cations such as K, increases the affinity of clays for nitroaromatic compounds (Charles et al., 2006; Weissmahr et al., 1997; Boyd et al., 2001; Sheng et al., 2002)

At a given equivalent fraction of K on the clay the Ca-SPV sorbed more *m*-DNB (mg DNB/kg-clay) than K-SPV (Figure 4). This result is surprising because K-SPV is collapsed to ~ 12.5 Å (40:60 K/Ca, 60:40 K/Ca, Figure 7b), whereas Ca-SPV is expanded to ~ 19 Å in the same X_K^S range (Figure 6b). Previous research has observed greater sorption of NACs by the K-saturated clays than the Ca-saturated smectite clays. This has been attributed to the formation of inner and outer sphere complexes between the exchangeable cations and the nitro group of the NACs. An optimum basal spacing of ~12.3 Å was identified wherein the aromatic ring could directly interact with opposing neutral siloxane surfaces (Boyd et al., 2001; Li et al., 2004). The strongly hydrated Ca^{2+} expands the interlayer to ~19 Å and also reduces the size of adsorptive domains by obstructing access to the siloxane surfaces (Haderlein et al., 1996; Li et al., 2003; Sheng et al., 2001).

In previous work K^+/Ca^{2+} exchange reactions have been shown to alter the organization of quasicrystals and to alter the extent of sorption of organic compounds, which is assumed to be proportional to $X_K{}^C$ (Li et al., 2004). But we have observed that Ca-SPV adsorbs more *m*-DNB at a given $X_K{}^C$ than K-SPV; this indicates that quasicrystal organization is complex and depends not only on $X_K{}^C$ but also on sample history.

Chappell et al. (2005) noted that collapse of the clay interlayer enhanced the sorption of atrazine in the interlayer. In this study, we see that although K-SPV collapsed from ~19 Å to about 12.8 Å (Figure 6b), the Ca-SPV has higher affinity for *m*-DNB than does K-SPV at a given $X_K{}^C$. This could be due to the difference in the polarity of *m*-DNB and atrazine. *m*-DNB does not have hydrophobic alkyl side chains that enhance collapse of the clay. Thus *m*-DNB may be able to enter the mixed Ca-K-interlayers and simultaneously interact with K ions and water molecules, whereas atrazine was strongly sorbed only in dehydrated K-interlayers.

The XRD patterns for Ca-SPV show a peak centered on 19.4 Å, which is typically the basal spacing with Ca in the interlayers, suggesting four layers of interlayer water molecules (Figure 6a). The peaks become sharper as the amount of Ca in the solution increases, suggesting more organization of the clay layers and existence of larger quasicrystals. In the presence of *m*-DNB (Figure 6b), there is a decrease in intensity and more diffuse peaks, which suggest that smaller quasicrystals are formed on *m*-DNB sorption.

For the K-SPV samples treated with 100:0 K/Ca solutions there is a peak shift to 12.9 Å, which suggests that the coherently scattering domains are dominated by K. A basal spacing of about 12.4 Å is typical when NACs are sorbed in the interlayers with K present (Sheng et al., 2002; Boyd et al., 2001). Further, a collapse from 19.4 Å to about 18 Å,

suggests that there is some interstratifications of collapsed K-domains amongst the Ca-dominated domains, which could also be one of the reasons for the greater sorption of *m*-DNB by the Ca-SPV than the K-SPV.

The XRD pattern for K-SPV at 100:0 K/Ca indicates that it was largely delaminated (Figure 7a). As the amount of Ca increased in the equilibrating solution, there was more organization in the clay interlayers and more coherently scattering domains were formed. In the presence of *m*-DNB (Figure 7b), there is a collapse of the clay interlayers. At 100:0 K/Ca and 40:60 K/Ca equilibrating solutions, there was a peak shift from about 19.6 Å to about 12.4 Å, indicating the formation of coherently scattering domains dominated by K and suggesting that sorption of *m*-DNB induced the formation of K-quasicrystals (Li et al., 2006) with a basal spacing near 12.4 Å, which is optimum for NAC sorption (Sheng et al., 2002; Boyd et al., 2001).

The XRD pattern for K-SAz-1 (Figure 8a) at 100 % KCl, shows no peak suggesting, that the clay is delaminated with no formation of quasicrystals. As the amount of Ca increases in the equilibrating solution, a peak centered at 19.2 Å is observed. Although the peaks are broad, with increasing amount of Ca in the system, the peaks gain intensity. This implies better organization of the clay structure and formation of larger number of quasicrystals, dominated with Ca, but with a lesser number of layers per quasicrystals than Ca-SAz-1. But in presence of *m*-DNB (Figure 8b), the clay was delaminated with no peak observed until the clay suspension was equilibrated with 100 % $CaCl_2$ when a peak was obtained centered at 19.4 Å. Hence, only with high amount of Ca in the equilibrating solutions were quasicrystals dominated by Ca formed.

In Figure 8a, Ca-SAz-1 equilibrated with 100 % KCl shows a peak centered at 18.4 Å. With increasing amounts of Ca in the equilibrating solution, the peaks become sharper and gained intensity. This implies that more coherent scattering domains were formed and there was better organization in the clay structure. At higher amounts of Ca in the equilibrating solution, the peaks were centered on 19.0 Å, which implies that there was some interstratifications of K within the Ca dominated quasicrystals. In the presence of *m*-DNB (Figure 9b), there was no collapse of the clay and the peaks were centered on the same value of d-spacing but there is some loss in intensity which suggests that bigger quasicrystals are broken down into smaller ones with a lower number of coherently scattering domains.

By comparing the XRD patterns for the clay suspension that have approximately the similar X_K^C in the absence of *m*-DNB, we can infer the effect of initial clay saturation on the sorption of *m*-DNB and clay organization. For example, Ca-SPV in 100:0 K/Ca and K-SPV in 40:60 K/Ca have a X_K^C of ~ 0.5 (Table 1). By examining the XRD pattern for Ca-SPV (Figure 6a) in 100:0 K/Ca, we see that a low intensity, broad peak centered at 19.4 Å is obtained, suggesting that very few Ca-dominated quasicrystals are formed. By contrast, the XRD pattern for K-SPV in 40:60 K/Ca (Figure 7a) has a more intense and sharper peak centered at 19.61 Å, which implies a better organization of the clay structure with more quasicrystals dominated by Ca in the interlayers. In the presence of *m*-DNB, the 100:0 K/Ca Ca-SPV (Figure 6b) collapsed and a distinct peak was observed at 12.9 Å. This peak indicates that more quasicrystals are formed and dominated by K. There was also a collapse of the K-SPV to 12.4 Å (Figure 7b).

By comparing the XRD patterns for Ca-SAz-1 in 100:0 K/Ca (Figure 8a) and K-SAz-1 in 40:60 K/Ca (Figure 9a) both of which have X_K^C of ~ 0.5 (Table 1), the Ca-SAz-1 has a

shaper peak centered at 18.4 Å, which suggests a better organization of the clay structure

with more quasicrystals dominated by Ca but with some interstratifications of K domains. K-

SAz-1 has a diffuse and broad peak centered at 19.2 Å. The broad nature of the peak implies

disorganization of the clay structure and that a smaller number of quasicrystals formed.

The differences discussed above demonstrate hysteresis in clay structure formation

and stabilization. Formation of K-dominated domains in the Ca-clay may enhance the

sorption of m-DNB by the Ca-clay more than on the K-clay although the Ca-clay has X_K^C. It

has already been shown in previous research that the presence of K enhances the sorption of

m-DNB (Charles et al., 2006). However the legacy of an initial Ca saturation influences the

spatial distribution of K and Ca in clay domains and alters the microstructure of the Ca-clay

in a way that enhances sorption of m-DNB.

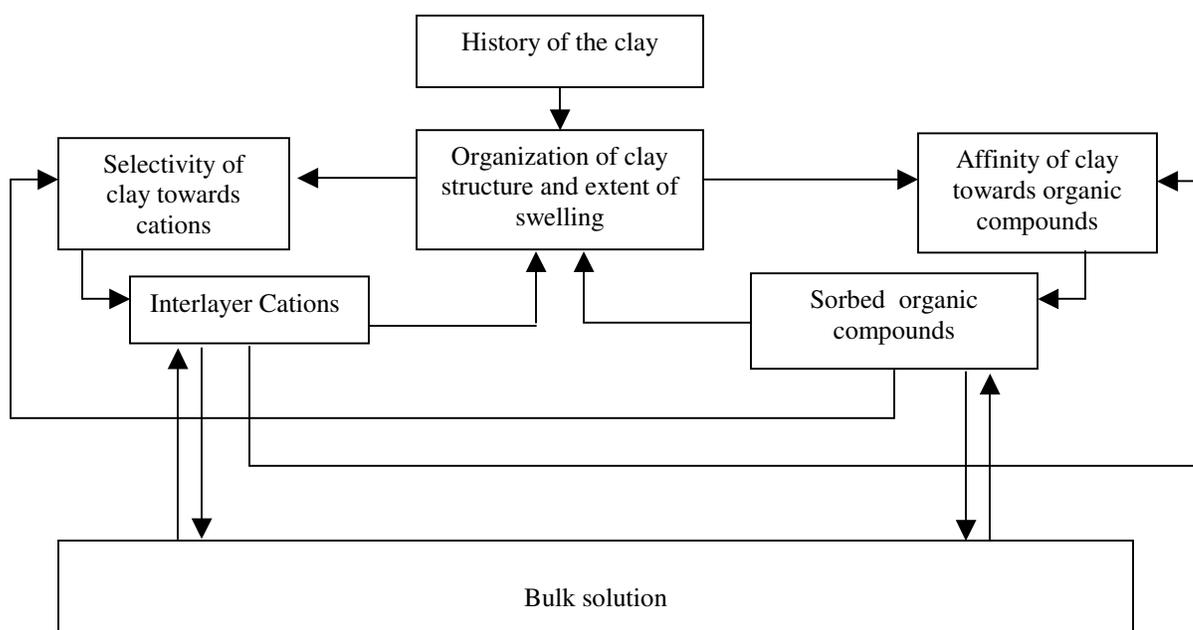All these trends can be depicted by a conceptual model as depicted in Figure 10.

Figure 10: Conceptual model of the various factors that influences the interaction between sorption of m-DNB and cation exchange reactions for the reference smectites.

According to the conceptual model, there is a complex feedback mechanism that operates influencing various factors that contribute to the interaction and sorption of *m*-DNB by the Ca- and K- reference smectites. Both cation exchange and the adsorption/desorption of organic molecules by smectites may be viewed as are thermodynamically reversible reactions, but only to the extent that these reactions do not alter the organization, structure or extent of swelling of the clay. Any change in the organization, structure, or the extent of swelling of smectite quasicrystals will alter both the affinity of the clay for the organic molecules and selectivity exhibited by the clay for various inorganic cations. Because changes in organization, structure, and extent of swelling of smectite quasicrystals are inherently hysteretic, any such change that occurs during a reaction will induce hysteresis in cation exchange or organic adsorption/desorption reactions.

Laird et al., (1997) proposed a feedback model linking cation exchange selectivity, extent of smectite swelling and interlayer cationic composition. In our study, we have demonstrated a similar feedback interaction. For all the studied samples, the amount of K on the clay increased with X_K^S. On examining the XRD patterns for the same samples, we see that samples treated with 100:0 K/Ca had a broad and diffuse pattern with no prominent peak, indicating that the clay was largely delaminated with very few coherently scattering domains. As the amount of Ca in the equilibrating solution increased, the XRD patterns gained intensity and a clear peak was visible, which demonstrates that there was better formation and increased number of quasicrystals. This also shows the difference of the hydration status of the interlayer when saturated with Ca^{2+} and K^+. The Ca^{2+} can interact with

two opposing negative-charge sites simultaneously, and it forms larger quasicrystals than K-saturated smectites

Overall the K-clay has more amount of K on the clay than the Ca-clay. This is manifested in the clay organization as shown in the XRD patterns. The XRD patterns for K-Clay are diffused, broad, and low in intensity whereas the XRD patterns for Ca-clay are sharper and more intense showing better quasicrystal formation and greater number of coherently scattering domains.

In general, the higher-charge SAz-1 has more X_K^C than the SPV. This is consistent as higher-charged clays are prone to collapse and therefore have a greater preference for the weakly hydrated cation.

Chappell et al. (2005) demonstrated that clay organization and extent of swelling affected the affinity of smectites for atrazine. It was shown that the air-dried K-smectite, dominated by basal spacing of 13.8 Å, had an order of magnitude greater affinity for atrazine sorption than the never-dried K-smectite, which had a basal spacing of about 17Å. Hui et al. (2007) showed that sorption of *m*-DNB induced the formation of quasicrystals as well as collapsed and dehydrated the interlayer.

Our study integrated the previous research by demonstrating that sorption of *m*-DNB increased the selectivity of the clay towards K (Figure 1a). As discussed earlier, the increased preference for K is more prominent in Ca-SPV than the K-SPV. The higher-charge SAz-1 showed a preference towards K only at $X_K^S > 0.6$ (Figure 2a and 2b). Further, as the amount of K increased on the clay sorption of *m*-DNB also increased. Hence the dominant interlayer cation influenced the sorption affinity of the clay towards *m*-DNB. In our study we also

observed that upon *m*-DNB sorption, there was a collapse of the clay and that it also induced the formation of quasicrystals and better organization of the clay structure.

The initial clay saturation plays a significant role as it affects the clay structure and organization and the extent of swelling. The XRD pattern for K-SPV in 100:0 K/Ca shows that the clay was delaminated, as there was no evident peak observed (Figure 6a), whereas the XRD pattern for Ca-SPV in 0:100 K/Ca (Figure 7a) shows a clear peak at ~19Å which indicates better formation of quasicrystals and more coherent scattering domains.

The clay conformation also influences the cation exchange selectivity because it changes the number of layers per quasicrystals, which affects the ratio of internal surface to external surface changes, which in turn influences the type of cation present in the interlayer (Shainberg and Otoh 1986; Fink et al., 1971). For smectites, in general, in a mixed cationic aqueous system, the divalent cation would prefer to be in the interlayer where it can interact with four negative charge sites, two on each side of the basal plane, with ease through water molecules. Due to large distances separating charge sites on external surfaces, the weakly hydrated cation K^+ would preferably be on the external surface and interact with two negative charge sites.

In our study we also demonstrated the significance of clay organization on *m*-DNB sorption. As discussed earlier, the XRD patterns for the samples with similar equivalent fraction of K on the clay demonstrated the formation of K-domains in between Ca-domains. It showed that the legacy of initial Ca saturation in the system influences the spatial distribution of Ca and K and alters the microstructure of the clay. This influenced the sorption of *m*-DNB and hence may explain the greater sorption of *m*-DNB by the Ca-SPV than by the K-SPV, although the Ca-SPV had less K on the clay than the K-SPV.

Sorption of *m*-DNB and selectivity of the clay towards a specific cation influences the clay organization and extent of swelling. Both of these factors alter the property of the interlayer region and any change in the nature of the material alters the equilibrium between the aqueous and solid phases which is analogous to a phase change. This explains the hysteresis associated with sorption of *m*-DNB as well as cation exchange selectivity.

From all the discussion above, we see that clay organization and extent of swelling is the most influential factor that affects sorption of *m*-DNB and cation exchange selectivity. The interlayer region and the bulk solution represent two different phases with different dielectric constants. Any change in the interlayer cationic composition, type of interlayer cations present, extent of swelling and clay structure, sorption of organic compounds or even the arrangement of water molecules alters the dielectric property of the interlayer. The difference in the dielectric constant between the interlayer region and the bulk solution is the driving force of cation exchange selectivity and affinity of clay for organic compounds. And any change in the dielectric property of the interlayer will change the selectivity of the clay for inorganic cations and affinity for organic molecules. Therefore, the interlayer is dynamic in nature and changes in the nature of the material is an indication of a phase change which accounts for hysteresis in crystalline swelling and cation exchange selectivity (Laird et.al, 1995; Laird and Shang, 1995).

Hence, we see that all the factors mentioned in the conceptual model are interrelated and influence one another. Sorption of *m*-DNB influenced the extent of swelling and the clay organization. It also influenced the selectivity of the clay towards a specific cation. The extent of swelling, clay microstructure, and initial clay saturation influenced the sorption of *m*-DNB. The interlayer cation present influenced the extent of swelling as well as the

sorption of *m*-DNB. Therefore, the underlying complex feedback loop depicted in Figure 10 operates and interweaves the various trends observed in this study.

References

Boyd, S.A., G. Sheng, B.J. Teppen, and C.T. Johnston. 2001. Mechanisms for the adsorption of substituted nitrobenzenes by smectite clays. *Environ. Sci. Technol.*, 35: 4227-4234.

Chappell, M.A., D.A. Laird, M.L. Thompson, H. Li, B.J. Teppen, V. Aggarwal, C.T. Johnston and S.A. Boyd. 2005. Influence of Smectite hydration and swelling on Atrazine sorption Behavior**.** *Environ. Sci. Technol.* 39(9):3150-3156

Charles, S., B.J. Teppen, H. Li, D.A. Laird, and S.A. Boyd. 2005. Exchangeable cation hydration properties strongly influence soil sorption of nitro aromatic compounds. *Soil. Sci. Soc. Am. J.* 70:1470-1479.

Chiou, C.T. 2002. *Partition and Adsorption of Organic Contaminants in Environmental Systems.* John Wiley & Sons, Hoboken, New Jersey.

Eberl, D.D. 1980. Alkali cation selectivity and fixation by clay minerals. *Clays and Clay minerals.* 28:161-172.

Eisenman, G. 1962. Cation selectivity glass electrodes and their mode of operation. *Biophys J.* 2:259-323.

Eriksson, E. 1952. Cation exchange equilibria on clay minerals. *Soil Sci.* 74:103-113.

Fink, D.H., F.S. Nayakama, B.L. McNeal. 1971. Demixing of exchangeable cations in free swelling Bentonite clay. *Proc. Soil Soc. Am.* 35:552-555.

Haderlein, S.B., and R.P. Schwarzenbach. 1993. Adsorption of substituted nitrobenzenes and nitrophenols to mineral surface. *Environ. Sci. Technol*. 27:316-326.

Haderlein, S.B., K.W. Weissmahr, and R.P. Schwarzenbach. 1996**.** Specific adsorption of nitroaromatic explosives and pesticides to clay minerals. *Environ. Sci. Technol.* 30:612-622.

Johnston C.T., and S.A. Boyd. 2005. Influence of Smectite hydration and swelling on atrazine sorption behavior. *Environ Sci Technol*. 39:3150-3156.

Johnston, C.T., M.F. Oliveira, B.J. Teppen, G. Sheng, and S.A. Boyd. 2001. Spectroscopic study of nitroaromatic-smectite sorption mechanisms. *Environ. Sci. Technol*. 35: 4767-4772.

Johnston, C.T., M.F. De Oliveira, B.J. Teppen, G. Sheng, and S.A. Boyd. 2002. Spectroscopic study of Dinitrophenol herbicide sorption on smectites. *Environ. Sci. Technol.* 36:5067-5074.

Karickhoff, S.W., D.S. Brown, and T.A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Res.* 13:241-248.

Kile, D.E., C.T. Chiou, H. Zhou, H. Li, and O. Xu. 1995. Partition of non polar organic pollutants from water to soil and sediment organic matters. *Environ. Sci. Technol.* 29:1401-1406.

Kittrtick, J.A. 1969. Interlayer forces in Montmorillonite and Vermiculite. *Proc. Soil Sci. Soc. A*. 33:217-221.

Laird, D.A., and R.H. Dowdy. 1990. Elemental recoveries for clay minerals analyzes by inductively coupled plasma atomic emission spectrometry using slurry nebulisation. *J. Anal. At. Spectrom.* 5:515-518.

Laird, D.A., E. Barriuso, R.H. Dowdy, and W.C.Koskinen.1992. Adsorption of atrazine on smectites. *Soil Sci. Soc. Am. J.* 56:62-67.

Laird, D.A., C. Shang, M.L. Thompson. 1995. Hysterisis in Crystalline Swelling. *J. Colloid Interface Sci.* 171:240-245.

Laird, D.A. 1996. Interactions between Atrazine and Smectite Surfaces. Pg 86-100. In: *Herbicide Metabolites in Surface Water and Groundwater* (M.T. Meyer and E.M. Thurman, editors). ACS Symposium Series 630. American Chemical Society, Washington, D.C.

Laird, D.A. 1996. Model for Crystalline Swelling of 2:1 Phyllosilicates. *Clays and Clay Minerals.* 44:553-559.

Laird, D.A. 1999**.** Layer Charge Influences on the Hydration of Expandable 2:1 Phyllosilicates. *Clays and Clay Minerals*, 47:630-636.

Laird, D.A., and B.L. Sawhney. 2002. Reactions of pesticides with soil minerals. Pg. 765-793. In J.B. Dixon and D. Schulze (ed.) *Soil mineralogy with environmental applications.* SSSA Book Ser. 7. SSSA, Madison, WI.

Laird, D.A., and C. Shang. 1997. Relationship between cation exchange selectivity and crystalline swelling in expanding 2:1 Phyllosilicates. *Clay and Clay Minerals*. 45:681-689.

Laird, D.A. 2006. Influence of layer charge on swelling of smectites. *Appl. Clay Sci.* 34:74-87.

Li, H., G. Sheng, B.J. Teppen, C.T. Johnston, and S.A. Boyd. 2002 Adsorption of Dinitrophenol Herbicides from water by Montmorillonites. *Clay and Clay Minerals*. 50(1):25-34.

Li, H., B.J. Teppen, C.T. Johnston, S.A. Boyd. 2004**.** Thermodynamics of nitroaromatic compound adsorption from water by smectite clay. *Environ. Sci. Technol.* 38: 5433-5442.

Li, H., T.R. Pereira, B.J. Teppen, D.A. Laird, C.T. Johnston, and S.A. Boyd. 2006. Effects of increasing potassium and calcium chloride ionic strength on pesticide sorption by potassium and calcium saturated smectites. *Soil Sci. Soc. Am. J*. 70:1889-1895.

Li, H., T.R. Pereira, B.J. Teppen, D.A. Laird, C.T. Johnston, and S.A. Boyd. 2007. Ionic strength induced formation of smectite quasicrystals enhances nitroaromatic compound sorption. *Environ. Sci. Technol*. 41:1251-1256.

McBride, M.B. 1994. *Environmental Chemistry of Soil.* Oxford University Press, New York

Oster, J.D., I. Shainberg, and J.D.Wood.1980.Flocculation value and gel structure of sodium/calcium Montmorillonite and illite suspensions. *Soil Sci. Soc. Am. J.* 44:955-959.

Pearson, R.G. 1962. Hard and Soft Acid and Bases. *J. Am. Chem. Soc*. 85:3533-3539.

Pils, R.V.J., and D. A. Laird. 2007. Role of cation demixing and quasicrystal formation and breakup on the stability of smectitic colloids. *Appl. Clay Sci.* 35: 201-211.

Rickert, D.E. 1985. *Toxicity of nitroaromatic compounds*. Hemisphere Publishing Corporation, Washington.

Shang, C., D.A. Laird, and M.L. Thompson. 1995. Transmission X-Ray diffraction technique for measuring crystalline swelling of smectites in electrolyte solutions. *Clay and Clay Minerals.* 43:128-130.

Shainberg, I., J. Oster, and J.D. Wood.1980. Sodium/calcium exchange in montmorillonite and illite suspensions. *Soil Sci. Soc. Am. J*. 44:960-964.

Sheng, G., B.J. Teppen, C.T. Johnston, and S.A. Boyd. 2001**.** Potential Contribution of Smectite clays and Organic matter to Pesticide Retention in Soils. *J. Agric. Food Chem.* 49:2899-2907

Teppen, B.J., and D.M. Miller. 2006. Hydration Energy determines Isovalent Cation Exchange Selectivity by Clay Minerals. *Soil Sci. Soc. Am. J*. 70:31-40.
.
Weaver, C.E., and D.L. Pollard. 1973. *The chemistry of clay minerals*. New York, Amsterdam: Elsevier.

Weissmahr, K.W., S.B. Haderlein, and R.P. Schwarzenbach. 1998. Complex formation of soil minerals with nitroaromatic explosives and other Π-acceptors. *Soil Sci. Soc. Am. J.* 62:369-378.

CHAPTER 4

GENERAL CONCLUSIONS

This study was conducted to provide further insight into the interaction and sorption of *m*-DNB on reference smectites saturated with Ca and K in aqueous suspension.

In Chapter 2, results for a preliminary study used to develop an analytical method for *m*-DNB are reported. Tests were conducted to determine the effects of pH, and ionic strength on the stability of *m*-DNB. Tests were also conducted to see whether the laboratory containers sorbed any *m*-DNB by measuring the absorbance of *m*-DNB stored in these containers. The absorbance values were taken as an index of concentration. These tests were carried out to foresee any parameter that could have an effect during the course of the experiment. Thereafter a calibration was prepared to test the linear range of the spectrophotometer method for quantifying *m*-DNB.

The results indicate m-DNB is a fairly stable compound and not affected significantly by light or temperature. But as a precaution, all the m-DNB solutions prepared for the experiment were stored in dark glass bottles. These bottles were kept on the work bench throughout the course of the experiment. *m*-DNB was adsorbed by polypropylene, polycarbonate, and polyethylene bottles; the use of these types of containers was avoided. Ionic strength between 0.01 and 0.05 did not affect the absorbance of m-DNB.

In Chapter 3, we reported the interaction between sorption of m-DNB, cation exchange selectivity, and extent of swelling on Ca/K saturated SPV and SAz-1. We hypothesized that sorption of m-DNB would increase the affinity of the clay towards a specific cation. The specific objectives were (1) to determine the effect of sorption of m-

dinitrobenzene on cation exchange selectivity of Ca and K smectites, and (2) to determine the interaction between sorption of m-DNB, extent of swelling and cation exchange selectivity for Ca and K-smectites.

From the cation exchange reaction our first significant observation was that on m-DNB sorption, the clay selectively preferred K^+ over Ca^{2+}. This was more pronounced for the Ca-SPV than for the K-SPV and by both the Ca/K SAz-1 at $X_K^C > 0.6$. The m-DNB sorption data shows that with an increase in the amount of K on the clay, the sorption of m-DNB also increased. With a weakly hydrated cation in the interlayer, the $-NO_2$ groups can interact with the K ions while the aromatic ring interacts with the neutral siloxane surfaces. In contrast, a strongly hydrated cation could mask these favorable adsorptive domains on the clay surfaces. Hysteresis associated with the cation exchange reaction was also observed. It was more pronounced for SPV clay than in the case of the SAz-1 clay. On m-DNB sorption hysteresis in the cation exchange reaction was suppressed for SPV as there was an increased preference for K^+ on the Ca-SPV but not on the K-SPV.

The basal XRD peaks for the K-smectites were broad and more diffuse than the basal peaks for Ca-smectites. The Ca^{2+} can interact with negative charge sites on opposing surfaces simultaneously and forms larger quasicrystals than K-smectites. On m-DNB sorption, a collapse of the clay was observed, and it also induced the formation of quasicrystals dominated by K in the interlayer.

Although it was observed that sorption of m-DNB increased with the amount of K on the clay, a significant observation was the greater sorption of m-DNB by the Ca-SPV than by the K-SPV for the same X_K^C. The XRD patterns of suspensions with the same amount of K on the clay, both with and without the m-DNB in the equilibrating solution, significant

difference in clay quasicrystal organization was noted which demonstrates the hysteresis in clay structure formation and stabilization. The formation of K-domains in the Ca-clay could enhance the sorption of *m*-DNB by the initially Ca-saturated SPV. The legacy of initial Ca-saturation altered the clay microstructure and influenced the distribution of K and Ca, which, in turn, led to greater sorption of *m*-DNB by Ca-clay.

To organize the various results, a conceptual model is proposed, which is an extension of an earlier model proposed by Laird et al. (1997). According to the earlier model, the extent of swelling of the clay, the nature of the interlayer cation and selectivity of the clay for various cations are all interrelated by a feedback loop. According to the proposed model, the type of initial clay saturation influences the clay structure through the formation of quasicrystals and the extent of swelling. Sorption of *m*-DNB influences the selectivity of the clay towards a specific cation, which in turn affects the interlayer cations present and thus the extent of swelling. Sorption of *m*-DNB in this was regulates the extent of swelling and clay structure and the dominant interlayer cation present. Hence, again, all these inter-related factors are interdependent on one another via feedback loops; changing any one of them affects the others. These results can be summarized as:

Initial saturation → Clay organization and extent of swelling

Clay organization and extent of swelling ↔ Sorption of *m*-DNB

Sorption of *m*-DNB → Selectivity of clay towards K ion

Selectivity of clay towards a cation → Interlayer cation present

Interlayer cations present ↔ Sorption of *m*-DNB

APPENDIX

The supplemental plots and results not used in Chapter 2 are provided here. The experiments conducted with 200 ppm *m*-DNB were also conducted using mixed salt solutions containing 20 ppm *m*-DNB. The concentrations of the salt solutions were the same and equilibrating solutions prepared in the same manner as described in Chapter 2. The experiment was conducted in the manner described in chapter 2.The results for cation exchange reactions and sorption of *m*-DNB are shown in the following plots.
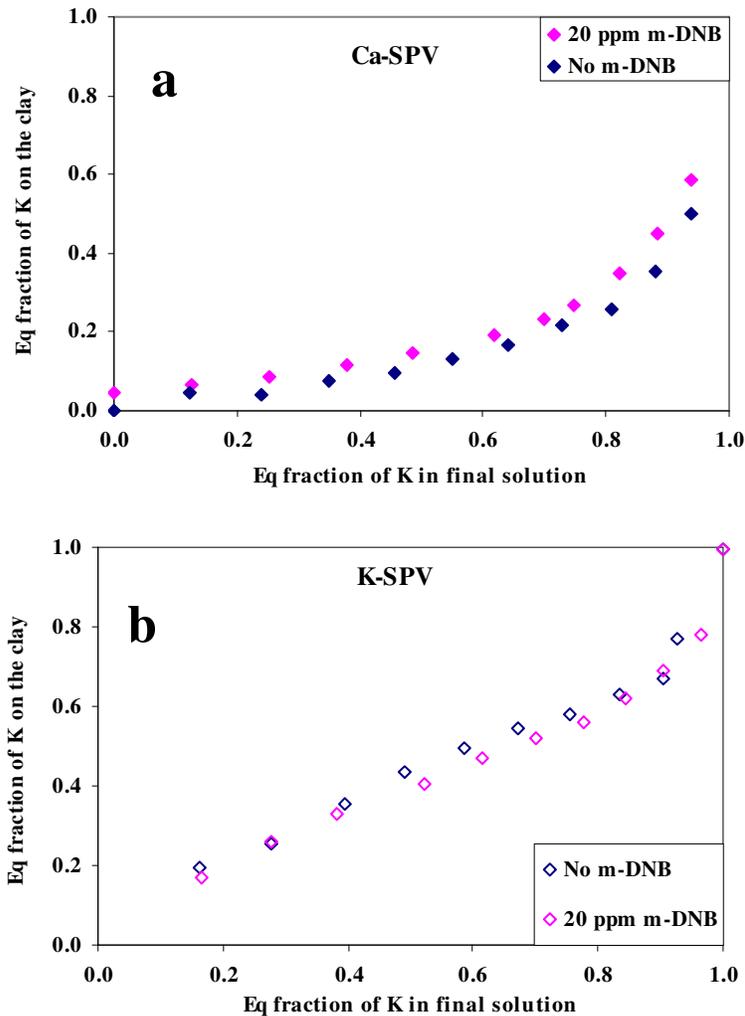

Figure 11: Cation exchange plot of K-SPV (a) and Ca-SPV (b) when equilibrated with and without *m*-DNB.
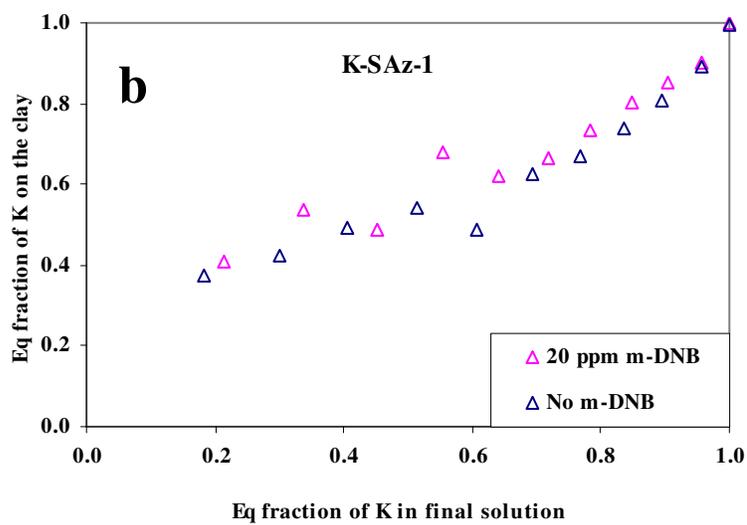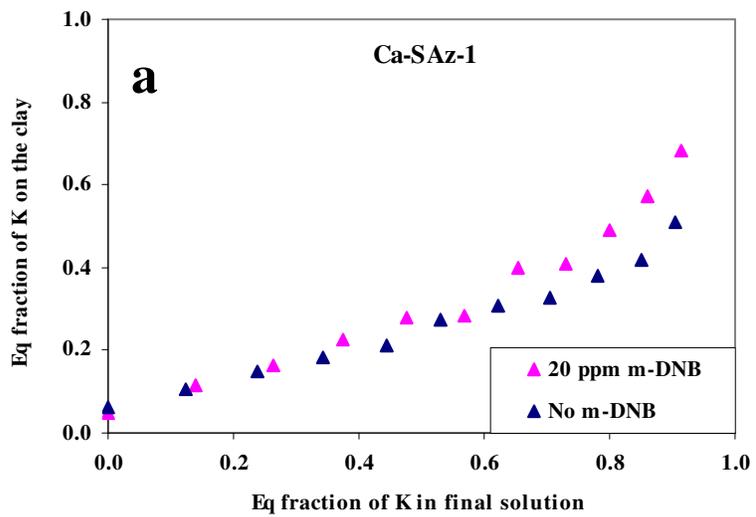
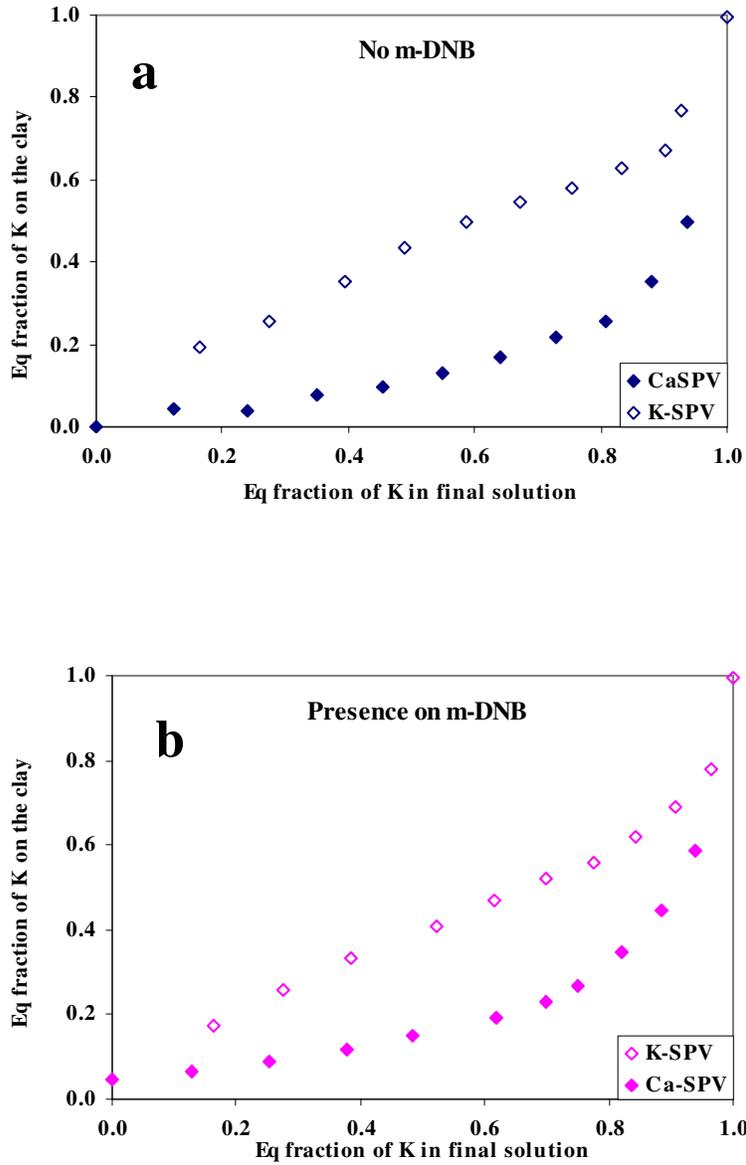Figure 12: Cation exchange plot of K-SAz-1 (a) and K-SAz-1 (b) when equilibrated with and without *m*-DNB.

Figure 13: Hysteresis associated with Ca/K exchange reaction for SPV in the absence of *m*-DNB (a) and hysterisis associated with Ca/K exchange reaction for SPV in the presence of *m*-DNB (b).
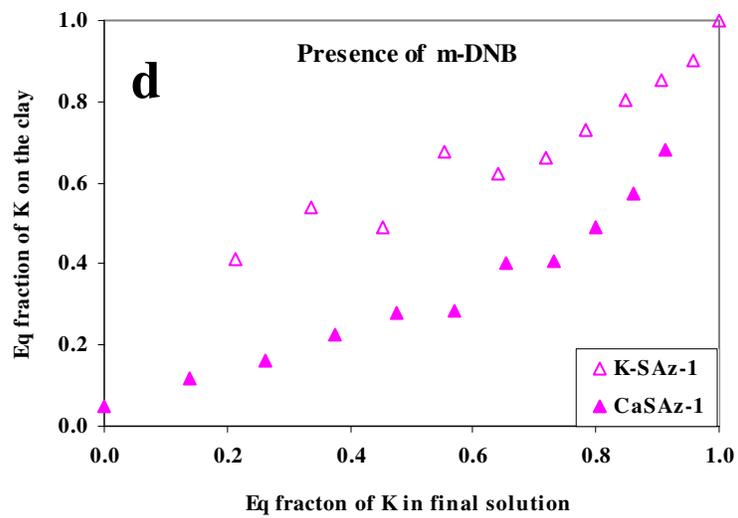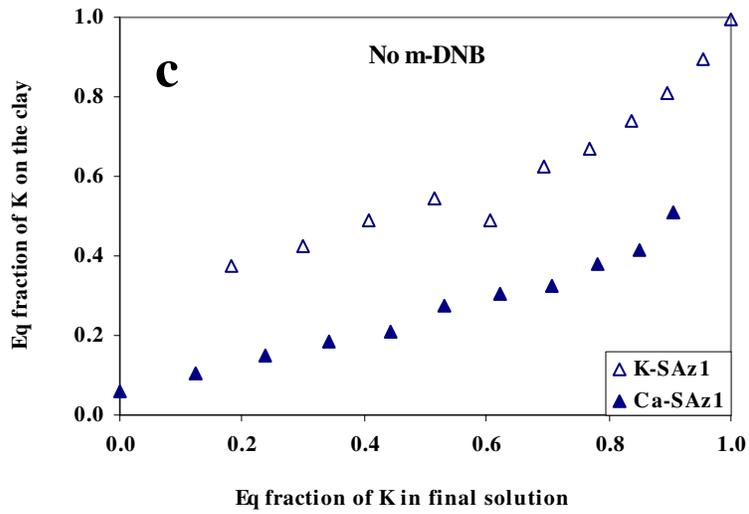
Figure13: Hysteresis associated with Ca/K exchange reaction for SAz-1 without *m*-DNB (c) and hysteresis associated with Ca/K exchange reaction for SAz-1 in the presence of *m*-DNB (d).
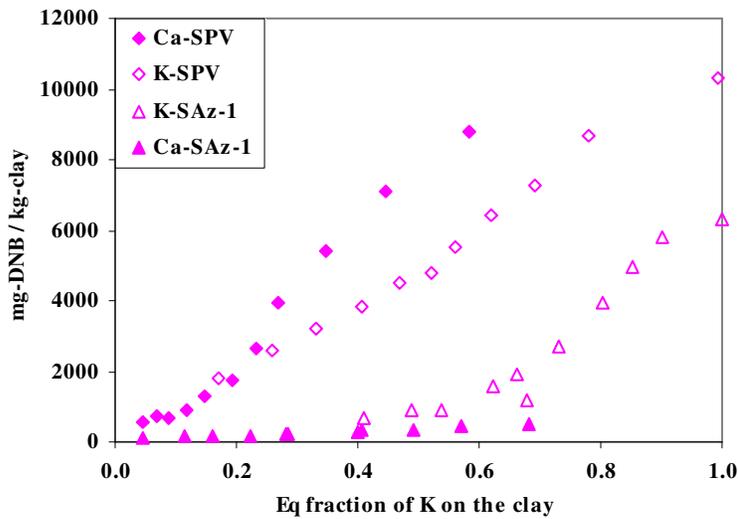
Figure 14: Sorption of 20 ppm *m*-DNB by reference smectites
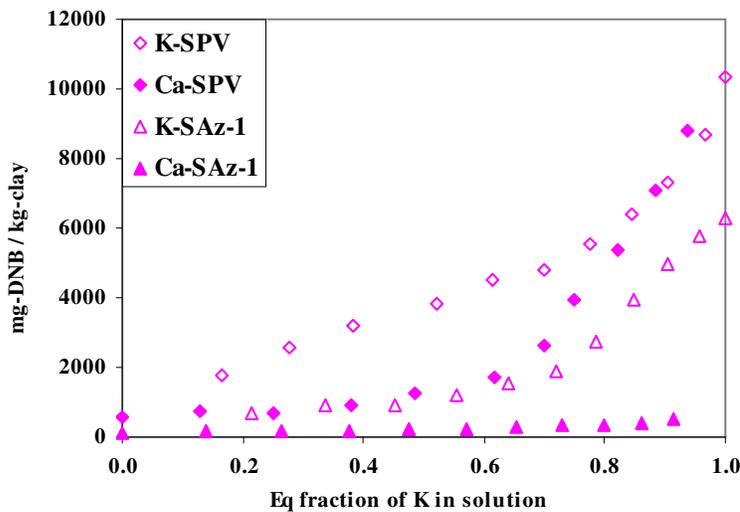
Figure 15: Sorption of 20 ppm *m*-DNB by reference smectites.

The cation exchange plots (Figures 11 and 12) show that in the presence of *m*-DNB, even at a low concentration, there was a slight preference for the K by all the reference smectites. Suppression of hysteresis is also observed but is more prominent in the case of SPV. The significant observation was the sorption data which showed the same trend as in the case of 200 ppm *m*-DNB (Figure 14 and 15). In Figure 14, we see

that with increasing amount of K on the clay, sorption of *m*-DNB also increases for all the reference smectites. But the initially Ca-saturated SPV has more of *m*-DNB on the clay than the initially K-saturated SPV for equivalent fractions of K on the clay >0.2. But the reverse trend is seen in the case of SAz-1.

Below is the table that has the equivalent fractions of K and Ca on the clay and in the solution phase obtained by the ICP analysis as described in Chapter 3.

Sample	Ca-SAz-1		K-SAz-1		Ca-SPV		K-SPV	
	Eq fraction of K on the clay	Eq fraction of K in final solution	Eq fraction of K on the clay	Eq fraction of K in final solution	Eq fraction of K on the clay	Eq fraction of K in final solution	Eq fraction of K on the clay	Eq fraction of K in final solution
Without 200 ppm m-DNB								
A	0.510	0.91	0.995	1.00	0.499	0.94	0.993	1.00
B	0.417	0.85	0.893	0.96	0.353	0.88	0.768	0.93
C	0.381	0.78	0.810	0.90	0.256	0.81	0.671	0.90
D	0.327	0.71	0.740	0.84	0.216	0.73	0.628	0.83
E	0.306	0.62	0.670	0.77	0.168	0.64	0.580	0.75
F	0.273	0.53	0.625	0.69	0.130	0.55	0.544	0.67
G	0.210	0.44	0.489	0.61	0.098	0.46	0.497	0.59
H	0.184	0.34	0.543	0.51	0.078	0.35	0.437	0.49
I	0.149	0.24	0.491	0.41	0.040	0.24	0.354	0.39
J	0.105	0.12	0.426	0.30	0.044	0.12	0.255	0.28
K	0.061	0.00	0.377	0.18	0.000	0.00	0.195	0.16
With 200 ppm m-DNB								
A	0.667	0.91	0.998	1.00	0.717	0.91	0.997	1.00
B	0.600	0.86	0.903	0.96	0.603	0.85	0.821	0.96
C	0.403	0.79	0.861	0.90	0.511	0.80	0.744	0.90
D	0.391	0.72	0.858	0.84	0.419	0.74	0.674	0.84
E	0.379	0.65	0.812	0.77	0.326	0.67	0.610	0.77
F	0.301	0.56	0.724	0.70	0.265	0.58	0.558	0.69
G	0.225	0.46	0.650	0.63	0.205	0.49	0.509	0.61
H	0.198	0.36	0.587	0.55	0.151	0.39	0.446	0.51
I	0.159	0.25	0.500	0.45	0.097	0.28	0.409	0.40
J	0.074	0.13	0.457	0.34	0.027	0.15	0.324	0.29
K	0.000	0.00	0.369	0.22	0.000	0.00	0.215	0.17

Below is the sorption data of *m*-DNB by the saturated reference smectites as described in Chapter 3.

	Ca-SAz-1			K-SAz-1		
Sample	Eq. Of K on the clay	Eq fraction of K in final solution	mg-DNB/kg-clay	Eq. Of K on the clay	Eq fraction of K in final solution	mg-DNB/kg-clay
A	0.667	0.91	17294	0.998	1.00	28621
B	0.600	0.86	16409	0.903	0.96	27264
C	0.258	0.79	15701	0.861	0.90	27028
D	0.391	0.72	15465	0.858	0.84	28503
E	0.379	0.65	16173	0.812	0.77	24609
F	0.301	0.56	12515	0.724	0.70	21718
G	0.225	0.46	14403	0.650	0.63	19830
H	0.198	0.36	12574	0.587	0.55	16350
I	0.159	0.25	12515	0.500	0.45	15878
J	0.074	0.13	9447	0.457	0.34	15229
K	0.000	0.00	13400	0.369	0.22	14580

	Ca-SPV			K-SPV		
	Eq. Of K on the clay	Eq fraction of K in final solution	mg-DNB/kg-clay	Eq. Of K on the clay	Eq fraction of K in final solution	mg-DNB/kg-clay
A	0.717	0.91	61836	0.997	1.00	56095
B	0.603	0.85	59653	0.821	0.96	49801
C	0.511	0.80	47441	0.744	0.90	40774
D	0.419	0.74	41895	0.674	0.84	44196
E	0.326	0.67	37883	0.610	0.77	42190
F	0.265	0.58	30863	0.558	0.69	41305
G	0.205	0.49	30450	0.509	0.61	39417
H	0.151	0.39	26025	0.446	0.51	37176
I	0.097	0.28	22544	0.409	0.40	34580
J	0.027	0.15	19830	0.324	0.29	31512
K	0.000	0.00	17589	0.215	0.17	27382