2004

Metal -surface reactions in mixed aqueous organic solvents

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Metal-Surface Reactions in Mixed Aqueous Organic Solvents

Rafif K. Srour

**Dissertation submitted to the
Davis College of Agriculture, Forestry and Consumer Sciences
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Doctor in Philosophy
in
Agricultural Sciences**

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**Morgantown, West Virginia
2004**

**Keywords: Metal-Surface reactions, exchange, sorption, cosolvents, dielectric
constants, stability constants, pH**

ABSTRACT

Metal-Surface Reactions in Mixed Aqueous Organic Solvents

Rafif K. Srour

The effect of mixed aqueous-organic solvents on exchange and adsorption reactions onto clay minerals is examined in this study while accounting for the effect of cosolvents on metal solution properties, ionic activity and complexation. In the absence of published values, a determination of the primary association constant of selected ions in solution was conducted using conductometric methods. These stability constant values were used to correct for ion-pairing in the exchange and the adsorption experiments. A spectrophotometric determination of pH was accomplished through the quantification of the conditional dissociation constants, ${}_sK_I$, of two indicators (methyl red and phenol red) at constant ionic strength and at $25^\circ\text{C} \pm 2.0$ in ethanol and methanol-water mixtures. In these mixtures and under these conditions, solution pH was determined from measurements of the indicator absorbance ratios at two wavelength λ_{HIn} and λ_{In^-} within the range $4.5 \leq \text{pH} \leq 8.5$. Calcium-sodium exchange on Wyoming bentonite in methanol, ethanol and acetone-water systems were investigated at constant total chloride concentration and at room temperature. In all treatments, Ca-Na exchange in cosolvents was a surface-controlled phenomenon involving electrostatic and specific solvent-surface interactions. The effect of cosolvents on Cd and Zn sorption to Ca-saturated bentonite and illite in mixed alcohol-water systems at low ionic strength and low initial metal concentration in the presence of nitrate varied between metals. Cd^{2+} sorption to bentonite and illite was independent of the solvent dielectric constant suggesting a specific mechanism for Cd^{2+} sorption involving inner-sphere complexes with the surface edge sites. Zn^{2+} sorption to both clay minerals was strongly dependent on ϵ_r with both increases (illite) and decreases (bentonite) in retention observed with decreased ϵ_r . Although it is not yet possible to predict the effects of cosolvents on metal-surface reactions, it is clear that cosolvents can affect metal concentrations in solution, and therefore contaminant transport (increased hydraulic conductivity resulting from flocculation as Ca^{2+} replaces Na^+ , and hence greater risk of clay liners failure). Additional study is needed on the effects of cosolvents on surface charge density, changes in the interlayer spacing, surface acidity and pH changes before and after sorption.

To my advisor, Dr. Louis McDonald, who made me a better person

ACKNOWLEDGMENTS

I would like to express my deepest thanks to my family, my father, my mother, Dania, Rabih and Rasha, for giving me all what it takes to accomplish my degree. It was hard for them to watch me go and I apologize for all the pain I caused but I am also grateful for allowing me to pursue my dream. I would also like to thank my niece, yasmina, for bringing joy into my life.

I and heartily thankful to my friends, Mr. Charles Joukhadar and Mr. Rajesh Chintala for their enjoyable company, for constantly helping me during my experimental work and for putting up with all my craziness in the most difficult times of my work.

I would like to express my gratitude to Mr. Nicholas Salazar, Ms. Monica Lecaros and Mr. Sunny Baidwan for their encouragement and support.

I don't know how to thank Ms. Lina Gomez for being my friend and my family in all the good and the bad times.

There are no words that can express how grateful I am to Dr Riad Baalbacki, my teacher, my mentor and my friend. For Dr. Baalbacki has been my shelter everytime my world, infused with work stress and disappointment, seemed to fall apart: For this and for a lot more, I will always be in debt.

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LIST OF ABBREVIATIONS

HOAc	Acetic Acid
Ac	Acetone
HIn	Acid form of an indicator
Al	Aluminum
NH ₃	Ammonia
NH ₄ ⁺	Ammonium cation
SbCl ₅	Antimony (V) Chloride
~	Approximately
In ⁻	Base form of an indicator
Br ⁻	Bromide anion
Cd	Cadmium
Cd(NO ₃) ₂ .6H ₂ O	Cadmium Nitrate Hexahydrate
Cd(NO ₃) ⁺	Cadmium Nitrate ion-pair
Ca	Calcium
CaCl ₂	Calcium Chloride
CaCl ⁺	Calcium Chloride ion-pair
Ca(NO ₃) ₂ .4H ₂ O	Calcium Nitrate Tetrahydrate
(C ₂ H ₅) ₃ PO	Triethyl Phosphate
CCl ₄	Carbon Tetrachloride
CEC	Cation Exchange Capacity
CAS	Chemical Abstracts Service
cm	Centimeter

cmol _c kg ⁻¹	Centimole of Charge per Kilogram
cP	CentiPoise
Cl ⁻	Chloride ion
CMOS	Completely Miscible Organic Solvents
[]	Concentration
CN ⁻	Cyanide anion
°C	Degree Celsius
DMSO	Dimethyl Sulfoxide
DMF	Dimethyl Formamide
EC	Electrical conductivity
=	Equal to
Eq	Equation
e.m.f.	Electromotive force
E _X	Electromotive force of the unknown sample, X
E _{RVS}	Electromotive force of the Reference Value Standard
eq L ⁻¹	Equivalent per liter
<i>et al.</i>	<i>et alai</i> (and others)
EPA	Environmental Protection Agency
EtOH	Ethanol
EDTA	Ethylene Diamine Tetraacetic Acid
e.g.	Example
F ⁻	Fluoride anion
(g)	Gaseous phase

g	Gram
g cm^{-3}	Gram per centimeter cube
>	Greater than
DN	Gutmann's donor number
AN	Gutmann's acceptor number
hrs	Hours
HF	Hydrofluoric acid
H^+	Hydronium ion
HCl	Hydrochloric acid
pH	Hydrogen potential in aqueous solvents
${}_s\text{pH}$	Hydrogen potential in solvent <i>s</i>
${}_s\text{pH}_\text{X}$	Hydrogen potential of an unknown, X, in solvent <i>s</i>
${}_s\text{pH}_\text{RVS}$	Hydrogen potential of the Reference Value Standard in solvent <i>s</i>
<i>s</i>	
IUPAC	International Union of Pure and Applied Chemistry
Fe	Iron
I^-	Iodide
kg	Kilogram
kJ mol^{-1}	KiloJoule per mole
<	Less than
L	Liter
Li^+	Lithium ion
log	Logarithm

ln	Natural Logarithm
Mg	Magnesium
Max	Maximum
MeOH	Methanol
MR	Methyl Red indicator
μg	Microgram
mg	Milligram
mmHg	Millimeter of mercury
mmol _c kg ⁻¹	Millimole of positive charge per kilogram
mV	Millivolt
min	Minutes
μS cm ⁻¹	MicroSiemens per centimeter
mol	Mole
mol L ⁻¹	Mole per liter
mol kg ⁻¹	Mole per kilogram
nm	Nanometer
NO ₃	Nitrate
N ₂	Nitrogen gas
N	Normal
NMR	Nuclear Magnetic Resonance
No	Number
ppm	Parts per million
PMOS	Partially Miscible Organic Solvents

%	Percentage
% wt	Percentage weight
±	Plus or minus
PR	Phenol Red indicator
³¹ P	Phosphorus isotope 31
KH ₂ PO ₄	Potassium Dihydrogen Phosphate
RVS	Reference value standard
Ag ⁺	Silver ion
Si	Silicon ion
AgCl	Silver Chloride
Na	Sodium
NaOAc	Sodium Acetate
Na ₂ HPO ₄	Sodium Hydrogen Phosphate
NaOH	Sodium Hydroxide
H ₂ SO ₄	Sulfuric acid
<i>t</i> -BuOH	Tertiary butyl-hydroxide
SCN ⁻	Thiocyanate ion
UV-Vis	Ultraviolet and visible electromagnetic spectra
v/v	Volume-to-Volume
Zn	Zinc
Zn(NO ₃) ₂ ·6H ₂ O	Zinc Nitrate Hexahydrate
Zn(NO ₃) ⁺	Zinc Nitrate ion-pair
wt/wt	Weight-to-weight

LIST OF SYMBOLS & CONSTANTS

$A_{\lambda_{HIn}}^{HIn}$	Absorbance of compound HIn at λ_{HIn}
a	Combined cation and anion ion size parameter
a_{B-F}	Distance of closest approach
a_i	Debye-Hückel ion size parameter
A_{D-H}	Debye-Hückel parameter
$\text{\AA}$	Angstrom
α	Polarizability (always negative)
α_{On}	Onsager coefficient
b_a	Cell path length
b	Parameter in Fuoss definition of ion pairs
B_{D-H}	Debye-Hückel parameter
B_p	Boiling point
β	Onsager coefficient
C_i	Ion concentration
C_T	Total concentration
δ	Onsager's slope
δ_s	Solubility parameter
e_0	Electronic charge
ϵ_r	Bulk dielectric constant
ϵ_0	Permittivity of vacuum
ϵ	Molar absorptivity
E_C	Coulombic energy

F	Faraday constant
F_p	Freezing point
γ_i	single ion activity coefficient
h	Planck's constant
η	Absolute viscosity
$\{i\}$	Activity of ion i
I	Ionic strength
k	Boltzmann's constant
K	Hydraulic conductivity
K_A	Ion association constant
K_{ap}	Autoprotolysis constant
${}_sK_I$	Acid dissociation constant of indicator in solvent s
K_{1A}	Primary ion pair formation constant
K_{2A}	Secondary ion pair formation constant
K_f	Freundlich partition coefficient
K_{ow}	Octanol-partitioning coefficient
K_{sp}	Solubility product
K_v	Vanselow selectivity coefficient
κ^{-1}	Reciprocal Debye length
Λ	Equivalent conductance
Λ_0	Limiting equivalent conductance
λ_0	Single ion limiting equivalent conductance
L	Ligand

λ	Wavelength in nanometer
M	Metal ion
m	Molality
$1/n$	Freundlich parameter
N_A	Avogadro's constant
n_i	Number of ions (i)
Ω^{-1}	mohs
q	Distance parameter in Bjerrum equation
r	Distance from surface of ion or particle
r_{B-F}	Distance parameter in Bjerrum and Fuoss equation
r_i	Ionic radius
r_F	Radius in Fuoss equation
r_m	Minimum separation distance
R	Universal gas constant
ρ	Density
σ	Effective molecular distance
T	Absolute temperature in Kelvin
V_i	Volume of titrant
V_T	Total volume
V_s	Solvent volume
μ	Dipole moment
u_m	Potential energy minimum
$u(r)$	Potential energy

ν	Vibrational frequency of electrons (always negative)
z^+	Cation valence
z^-	Anion valence
z_i	Ion valence
Φ_B	Born potential energy
ζ	Proportionality constant
Φ_{vdW}	van der Waals potential
Φ_m	Minimum potential energy
Φ_r	Lennard-Jones 6-12 pair potential
ψ_x	Electrical potential at distance r from the clay particle
ψ_0	Electrical potential at the surface of the clay particle
ΔG_{el}	Electrostatic Gibbs free energy
$\Delta G_{lattice}^0$	Lattice free energy
ΔG_t^0	Standard Gibbs energy of transfer
ΔG_{soln}^0	Solution Gibbs free energy
ΔG_{solv}^0	Solvation Gibbs free energy

CHAPTER I

INTRODUCTION

1.1 Overview

The disposal of large quantities of industrial, municipal and household wastes into landfills, ponds and injection wells has been practiced for years as it was believed to be a safe practice that would isolate these contaminants from the environment. However, contaminant concentrations in soil/sediment and drinking water samples at some of these sites are far above the US EPA guidelines (Sawhney and Kozloski, 1984). This has raised concerns about groundwater pollution with potentially hazardous chemicals from those underground waste disposal sites.

Despite the increased efforts toward remediation and proper waste disposal, predicting contaminant behavior in these sites has proven difficult. The difficulty arises from the complexity of these sites where high levels of contaminants containing specific radionuclides, metals, organic ligands, and organic solvents exist in various binary and ternary combinations (Riley and Zachara, 1992). These mixtures are likely to exhibit complex geochemical behavior as a result of comingling. Certain components within these mixtures may undergo chemical interactions that either facilitate or retard their dissemination in the environment.

Studies have been conducted to identify these mixtures and the levels at which they exist in the environment (Artiola-Fortuny and Fuller, 1982; Bedient *et al.*, 1983). Fewer studies have aimed at understanding the fundamental chemical and physical nature of their interactions and the processes that result in their subsurface migration (Green *et al.*, 1983; Sheet and Fuller, 1986; Brown and Thomas, 1987).

In this context, the primary objective of this review is to provide a fundamental understanding of the major reactions controlling ion-solvent and surface-solvent interactions, in light of the major physicochemical properties of non-aqueous and mixed aqueous organic solvents. Special attention will be given to clay minerals, given their use in landfill liners and their substantial role in determining contaminant transport. A summary of the major work conducted on metal/clay interactions in water miscible organic solvents will also be presented.

It is not the objective of this review to present a complete discussion of non-aqueous and mixed aqueous organic solvent chemistry; several books have been published for this purpose (e.g; Popovytch and Tomkins, 1981; Reichardt, 1988; and Izutsu, 2002). The aim is to present a basic discussion of the important processes governing ion-solvent and surface-solvent interactions to provide a framework for understanding metal/clay behavior in non-aqueous and mixed aqueous organic solutions.

1.2 Solvent Properties & Classification schemes

Solvent properties likely to influence metal/clay interactions are given in Table 1.1 (Reichardt, 1988; Atkins, 1998). The boiling point, B_p , and the freezing point, F_p , determine the liquid range of the solvent. The vapor pressure is important when considering the problem of vaporization and toxicity of solvents. Several empirical parameters have been proposed to quantitatively express the relative acidity and basicity of solvents (Reicherdt, 1988). Gutmann's donor number, DN, is defined as the negative enthalpy of the reaction between the solvent and $SbCl_5$ in 1,2-

dichloroethane and measures Lewis base strength. The higher the donor number, the stronger is the Lewis base. The Lewis acid strength is given by the acceptor number, AN, which is measured by ^{31}P NMR shift of the reference base $(\text{C}_2\text{H}_5)_3\text{PO}$ in pure solvent. The higher the acceptor number, the stronger is the Lewis acid. It is generally agreed that in solvents with high permittivities, differences in reactions or equilibria among the solvents are often caused by differences in the solvent acidity/basicity (Izutsu, 2002). The dielectric constant, ϵ_r , (relative permittivity) influences the electrostatic interactions between charged particles (Izutsu, 2002). An electric dipole consists of two electric charges separated by a distance, r . The electric dipole moment, μ , is a vector that points from a negative charge ($-q$) to a positive charge (q), the magnitude of which is $\mu=qr$ (Atkins, 1998). Dielectric constant, dipole moment, μ , and the relative acidity and basicity of the solvents are often used as criteria to classify solvents.

Several classification schemes for solvents have been proposed because no single scheme is appropriate for all uses. Yalkowsky *et al.*, (1976), classified solvents according to their miscibility with water and their interfacial free energy. Completely miscible organic solvents (CMOS) like lower alcohols and acetonitrile were distinguished from partially miscible organic solvents (PMOS) like o-cresol and trichloroethylene. This classification is usually based on the solubility parameter, δ , (defined as $\delta=C_i^{1/2}$ where C_i is the electrolyte concentration). Miscible solvents have similar δ -values, immiscible solvents have dissimilar δ -values. Rao and coworkers (Rao *et al.*, 1990, Nkedi-Kizza *et al.*, 1985) used this approach to describe the effect of organic solvents on hydrophobic organic chemicals sorption and transport. A

commonly used scheme, originally proposed by Kolthoff (Kolthoff, 1974), uses the dielectric constant as well as the acid and base properties of the solvent (Table 1.2).

Table 1.1. Physical and chemical properties of selected solvents (Izutsu, 2002).

Solvent	B _p (°C) ²	F _p (°C) ³	Vapor Pressure (mmHg) ¹	Density (g cm ⁻³) ¹	Viscosity (cP) ¹	ε _r ^{1,4}	μ ^{1,5}	DN ⁶	AN ⁷
Water	100	0	23.8	0.9970	0.890	78.39	1.85	33	54.8
Acids									
Hydrogen Fluoride	19.6	-83.3		0.9529	0.256	84.0	1.82	20	52.9
Acetic acid	117.9	16.7	15.6	1.0439	1.130	6.19	1.68		
Alcohols									
Methanol	64.5	-97.7	127	0.7864	0.551	32.7	2.87	19	41.3
Ethanol	78.3	-114.5	59	0.7849	1.083	24.6	1.66	32	37.9
Ketones									
Acetone	56.1	-94.7	231	0.7844	0.303	20.6	2.7	17.0	12.5
Others									
Benzene	80.1	5.5	95.2	0.8736	0.603	2.27	0	0.1	8.2
Toluene	110.6	-95.0	28.5	0.8622	0.553	2.38	0.31		

¹⁾ Unless otherwise stated, the data are at 25°C.²⁾ Boiling point.³⁾ Freezing point.⁴⁾ Dielectric constant.⁵⁾ Dipole moment.⁶⁾ Donor number.⁷⁾ Acceptor number.

Table 1.2. Classification of solvents (Kolthoff, 1974)

	No.	$\epsilon_r, \mu^1)$	Acidity ²⁾	Basicity ²⁾	Examples
Amphiprotic solvents					
Neutral	1a	+	+	+	Water, methanol, ethanol
	1b	-	+	+	<i>t</i> -BuOH
Protogenic	2a	+	++	±	H ₂ SO ₄ , HF
	2b	-	++	±	CH ₃ COOH
Protophilic	3a	+	±	++	DMSO, NH ₃
	3b	-	±	++	Tetramethylguanidine
Aprotic solvents					
Dipolar protophilic ³⁾	4a	+	- (±)	++ (+)	DMSO
	4b	-	-	++ (+)	Pyridine
Dipolar protophobic	5a	+	- (±)	-	Acetonitrile
	5b	-	-	-	Methylethylketone
Inert	5c	-	-	-	CCl ₄

¹⁾ The symbol "+" is for $\epsilon_r \geq 15$ or 20, $\mu \geq 2.5$ and "-" for $\epsilon_r < 15$, or 20, $\mu < 2.5$.

²⁾ The symbol "+" is for the case comparable with water, "++" for case much stronger than water, "±" for the case somewhat weaker than water, and "-" for the case much weaker than water.

³⁾ Some solvent with $\epsilon_r < 15$ ($\mu < 2.5$) are also classified as "dipolar".

1.3 Ion-Solvent Interactions

1.3.1 Ion Solvation

The relative solubility of electrolytes in non-aqueous and mixed aqueous organic solvents are largely influenced by the extent of solvation and the changes in the solution local environment dictated by the structure and macroscopic properties (dielectric constant, viscosity, density, equilibrium constants, etc.) of the solvent, as well as the microscopic properties of the individual molecules (dipole moments, polarizability, H-bonding). Ion solvation has a significant effect on the dissolution of an electrolyte and on chemical reactions and equilibria. The ion-solvent interactions that may participate in ion solvation can be divided into electrostatic, non electrostatic and specific chemical including hydrogen bonding, coordination and acid-base reactions. The simplest model for the electrostatic component of ion-solvent interactions was introduced by Born (Born, 1926). In this model, the solvation energy is defined as the change in the Gibbs free energy (ΔG_{el}) when the ion is transferred from vacuum to a solvent and is estimated by the Born equation

$$\Delta G_{el} = -\frac{z_i^2 e^2 N_A}{8\pi\epsilon_0 r_i} \left(1 - \frac{1}{\epsilon_r}\right) \quad [1.1]$$

The choice of solvated ionic radius, r_i , and of the solvent dielectric constant, ϵ_r , are of critical importance and might explain the failure of the Born equation to adequately describe experimental data (Xue and Traina, 1996a), especially when crystallographic radii and the solvent bulk dielectric constants are used. The Born equation has been modified in various ways and recently, the so-called mean spherical approximation

(MSA), which takes into account the effect of the solvent on the ionic radii has been used in treating ion solvation.

Figure 1.1 shows the relationship between ϵ_r and ΔG_{el} for a univalent ion, at constant ionic radius. ΔG_{el} decreases rapidly in the low dielectric constant region ($\epsilon_r < 10$) and rather slowly in the high permittivity region. In the high permittivity region, the solvation of the ions is more a function of non-electrostatic ion-solvent interactions, such as the Lewis acid/base strength. Cation solvation becomes stronger with the increase in the donor number of solvents. On the other hand, anion solvation is stronger with the increase in the acceptor number. The capacity of the solvent to form hydrogen bonds becomes more important with small anions such as F^- , Cl^- , and OH^- .

A quantitative way to describe the effect of solvents on ionic solvation is through the introduction of the Gibbs energy of transfer

$$\Delta G_t^0(i, R \rightarrow S) = \Delta G_{solv}^0(i, S) - \Delta G_{solv}^0(i, R) \quad [1.2]$$

where $\Delta G_{solv}^0(i, R)$ is the solvation energy of species i in solvent R (reference solvent), $\Delta G_{solv}^0(i, S)$ is the solvation energy of i in solvent S and $\Delta G_t^0(i, R \rightarrow S)$ is the Gibbs free energy of transfer of species i from solvent R to S . Table 1.3 represents the standard Gibbs energy of transfer of some ions from water to non-aqueous solvents (Izutsu, 2002).

In mixed aqueous organic solvents, the situation gets more complicated as interactions between unlike molecules, in addition to ion-solvent interactions arise. In those systems, preferential solvation of the ionic species to the component of the mixture which leads to the more negative ΔG_{solv}^0 is observed. For instance, in a

solution of CaCl_2 in water/methanol mixtures, both Ca^{2+} and Cl^- are largely solvated by water whereas a

Figure 1.1. The effect of solvent dielectric constant on the electrostatic solvation energy of an ion ($r_i = 0.2 \text{ nm}$).

Table 1.3. Standard Gibbs energies of transfer of ions from water to non-aqueous solvents (ΔG_t^0 (I,W→S), kJ mol⁻¹).

Ions	Methanol	Ethanol	Acetone	DMF	DMSO
H⁺	10.4	11.1	--	-18	-19.4
Li⁺	4.4	11	--	-10	-15
Na⁺	8.2	14	--	-9.6	-13.6
K⁺	9.6	16.4	4	-10.3	13.0
Ag⁺	6.6	4.9	9	-20.8	-34.8
NH₄⁺	5	7	--	--	--
F⁻	16	--	57	51	40.3
Cl⁻	13.2	20.2	42	48.3	27.4
Br⁻	11.1	18.2	25	36.2	10.4
I⁻	7.3	12.9	--	20.4	-41
CN⁻	8.6	7	--	18.4	35

solution of silver nitrate in acetonitrile/water, a preferential solvation of Ag⁺ by acetonitrile and of NO₃⁻ by water was observed (Reichardt 1988 and references therein).

1.3.2 Solubility

The dissolution of a substance requires not only that the lattice energy be overcome but also the interaction energy between the solvent molecules themselves

$$\Delta G_{soln}^0 = \Delta G_{solv}^0 - \Delta G_{lattice}^0 \quad [1.3]$$

At equilibrium, ΔG_{soln}^0 relates to the solubility product, K_{sp} , of an electrolyte by

$$\Delta G_{sol}^0 = -RT \ln K_{sp} \quad [1.4]$$

For the dissociation of the hypothetical ionic solid M_pL_q

K_{sp} is defined at equilibrium by

$$K_{sp} = \{M^{+}\}^p \{L^{-}\}^q \quad [1.6]$$

where $\{ \}$ denotes the activities of the individual ions and p and q the stoichiometric coefficients of the cationic (M^+) and anionic (L^-) species respectively. Any factor affecting free ion activity will have an effect on the solubility product and hence the solubility of the studied compound.

In soil systems, important chemical reactions occur at the colloid/solvent interface or at the ion/solvent interface. In either case, the proximity of the solvent to charged surfaces significantly disrupts its bulk chemical and physical properties (Popovytch and Thomkins, 1981). As we shift from aqueous to mixed aqueous organic solvents, other factors such as volume energies and solvent-solvent interactions may affect ionic solubility. It is generally observed that ionic substances exhibit higher solubility in solvents of high dielectric strength (Reichardt, 1988). However, the relation is not always linear as predicted. In many cases, observed deviations from linearity can be attributed to the microscopic properties of the solvent molecules themselves. For instance, silver salts of large polarizable anions like SCN^- exhibit enhanced solubility in methanol as opposed to water, whereas silver salts of small anions such as Cl^- tend to be less soluble (Reichardt, 1988), a difference attributed to the ability of Cl^- to form hydrogen bonds with water molecules.

The single ion activity $\{i\}$ describes the thermodynamic behavior of a particular chemical species in solution,

$$\{i\} = \gamma_i C_i \quad [1.7]$$

where γ_i denotes the single-ion activity coefficient and C_i the molar concentration of the ionic species. The single-ion activity coefficient serves to correct for the non-ideality of the solution. In ideal dilute aqueous solutions, γ_i equals 1 and the ionic

activity equals the molar concentration. In more concentrated aqueous solutions and in complex non-aqueous solution, γ_i decreases. Several theoretical models have been proposed to calculate the single-ion activity coefficient. Among these, the extended Debye-Hückel equation is widely used

$$\log \gamma_i = - \frac{A_{D-H} z_i^2 I^{\frac{1}{2}}}{1 + B_{D-H} a_i I^{\frac{1}{2}}} \quad [1.8]$$

I is the ionic strength, a_i is the ion size parameter, and A_{D-H} and B_{D-H} are two parameters defined as

$$I = \frac{1}{2} \sum C_i z_i^2 \quad [1.9]$$

$$A_{D-H} = (2\pi N_A \sigma)^{0.5} \left[\frac{e_0^2}{4\pi \epsilon_r \epsilon_0 K T} \right]^{1.5} \quad [1.10]$$

$$B_{D-H} = e \left(\frac{2 N_A \sigma}{\epsilon_r \epsilon_0 K T} \right)^{0.5} \quad [1.11]$$

A_{D-H} and B_{D-H} are both a function of the solvent properties and the temperature of the solution. One way to calculate the single ion activity coefficient in non-aqueous and mixed system is to replace ϵ_r and σ by their respective values in the studied systems (Bates, 1973). Figure 1.2 illustrates the changes in the single ion activity coefficient as a function of ionic strength for a univalent ion at various solvent dielectric constants. As the solvent dielectric constant decreases, the single ion activity coefficient decreases more rapidly as a function of the ionic strength, I .

The solubility products for a large number of salts have been determined experimentally in non-aqueous and mixed aqueous organic solvents using

thermodynamic approaches. A list of K_{sp} in non-aqueous and mixed aqueous organic solvents is compiled by Timmermans (1960). However, the unlimited number of different solvent compositions which can be prepared from a particular binary system (e.g. organic solvent and water) requires the establishment of equations for the computation of these parameters for any solvent composition from few parameters. The lack of these equations combined with the inherent difficulty in experimentally determining these parameters, may partially explain the scarcity of research on metal/clay interactions in mixed aqueous organic systems in soil science.

1.3.3 Complexation

The effect of the dielectric constant on the ion-solvent interactions is more pronounced than what is predicted by the Debye-Hückel theory because specific ion-pairing and complexation may be responsible for a greater departure from ideality than non-specific electrostatic interactions.

Figure 1.2. Changes in the single ion activity coefficient as a function of ionic strength at various solvent dielectric constants (for $a_i = 4$ nm).

Coulomb's law is often used to quantitatively describe the energy of attraction between oppositely charged ions in solution

$$E_C = \frac{z^+ z^- e^2}{r_i \epsilon_r} \quad [1.12]$$

Coulomb's law predicts that the energy of attraction between oppositely charged ions increases as the solvent dielectric constant, ϵ_r , decreases. This phenomenon is observed as a result of the decreased shielding of charges by the surrounding solvent molecules induced by decreased ϵ_r . This increased attraction is

manifested as an increase in the magnitude of ion-pairing between these charges and the formation of new pairs, ones that would not form otherwise in aqueous solvents.

The most widely used theories on ion association include the Debye-Hückel (Bockris and Reddy, 1973), the Bjerrum (1926) and the Fuoss (1958) theories. The Debye-Hückel theory does not account for ion pairing and its effect on ionic activity. It assumes that the energy resulting from the electrostatic interactions between the ions is small and much less than the energy of thermal agitation. This holds true when the distance between interacting ions is large. As this distance decreases, the electrostatic interactions increases and approaches the energy of thermal agitation. According to Bjerrum, ionic association occurs if the two ions are at a distance r_{B-F} less or equal than q , the critical distance at which the energy of electrostatic interaction becomes equal to the energy of thermal agitation. If $r_{B-F} > q$, the ions remain unassociated. This distance r_{B-F} cannot be less than the distance of “closest approach, a_{B-F} ”, which is equal to the sum of the radii of the associated cation and anion. According to Bjerrum, the association constant, K_A is expressed by:

$$K_A = \frac{4\pi N_A}{1000} \int_{a_{B-F}}^q r_{B-F}^2 \exp\left(\frac{2q}{r_{B-F}}\right) dr_{B-F} \quad [1.13]$$

According to Fuoss, an ion pair is defined as two oppositely charged ions that are in contact, i.e. at a distance of $r_F = a_{B-F}$ and the association constant, K_A , is defined as

$$K_A = (4\pi N_A / 3000)(a_{B-F} / m)^3 \exp(2q / a_{B-F}) \quad [1.14]$$

Equation [1.15] is obtained from Eq. [1.14] using tabulated values of q :

$$\log K_A = \log(4\pi N_A a_{B-F}^3 / 3000) + 0.434 |z_+ z_-| N_A e^2 / (4\pi a_{B-F} \epsilon_0 \epsilon_r RT) \quad [1.15]$$

From this equation, a linear relationship between $\log K_A$ and $1/\epsilon_r$ is expected (Figure 1.3). Figure 1.3 shows this relationship between the ion association constant ($\log K_A$) and $1/\epsilon_r$. Accordingly, only solvents with high dielectric constants ($\epsilon_r > 40$) will be capable of reducing the strong electrostatic forces to such an extent as to prevent ion pairing. In aqueous solutions, ion association between cations and large polarizable anions is small except at high ionic strength. In these systems, hydrated ions are highly stabilized by the elevated dielectric constant of water (ϵ_r equal to 78.39 at 25°C), preventing ions from approaching each other and forming pairs. In solvents of lower dielectric constants such as methanol (32.7) or ethanol (24.5), ionic complexation is favored at extremely low electrolyte concentrations. In solvents of dielectric constants less than 10, essentially no free ions exist, except in very dilute solutions (Reichardt, 1988; Izutsu, 2002).

Both theories, Bjerrum and Fuoss, have been widely used in the interpretation of experimental data involving the association constant, K_A , of electrolytes in non-aqueous media. Often, the discrepancy between the experimentally measured and calculated (using either approach) values of K_A , is attributed to the existence of specific ion-solvent interactions (Fuoss and Edelson, 1951). If $\log K_A$ varies linearly with $1/\epsilon_r$, pairing is assumed to result solely from electrostatic interactions (Hawes and Kay, 1965; Mui and McBride, 1974; Ananthaswamy *et al.*, 1979). If not, specific solvent-solute interactions are invoked (Doe *et al.*, 1990). Xue and Traina (1996b) observed increased stability of Cu(II) and EDTA complexes in acetone and methanol water mixtures as the fraction of solvent/water increased. They attributed this phenomenon to the increased electrostatic interactions between the two compounds as

a result of decreased dielectric constant and to changes in the Gibbs energy of solvation associated with complex formations, originating from specific solvent-solute interactions. Coulombic forces are the strongest intermolecular forces in amphoteric solvents. However, in protic solvents they are of minor importance and other forces such as ion-dipole and ion-induced dipole are of greater significance (Reichardt, 1988). A detailed discussion of these theories, their applications and limitations is available (Bockris and Reddy, 1973; Yeager and Salkind, 1973; and Izutsu, 2002).

Figure 1.3. Changes in the ion association constant ($\log K_A$) as a function of the reciprocal of solvent dielectric constant ($1/\epsilon_r$) for $a_{B-F} = 0.6$ nm (Izutsu, 2002).

Ion association is further complicated by the existence of different types of ion pairs, which depending on the strength of ion-solvent interactions can vary from solvent-separated, solvent-shared to contact pairs. Triple and quadruple ion pairs have also been reported in some solvent (Salomon, 1989). Methods used to identify these pairs include infrared, Raman, and dielectric relaxation spectroscopies (Izutsu, 2002).

The most widely used standard methods for the determination of association constants include potentiometry (Gaizer *et al.*, 1985; Doe *et al.*, 1987; Mui and McBride, 1974), spectrophotometry (Ghasemi *et al.*, 2002) and conductometry (Evers and Knox, 1951; Doe *et al.*, 1990). Other methods such as specific ion EMF measurements, nuclear magnetic resonance (NMR), and polarography are used under specific circumstances (Martell and Motekaitis, 1992). NMR has been widely used to provide microscopic information on metal-ligand complexes such as the identification of protonation and metal coordination sites on ligands.

Conductance measurements constitute one the most sensitive and widely used physical method for investigating electrolyte solutions. It can be applied to a wide variety of solvents over wide temperature and pressure ranges. When combined with theoretical equations, useful information can be obtained on ionic mobility, ion-size parameters, and association constants (Yeager and Salkind, 1973). All conductance measurements consist of measuring the changes in the conductance of a solution as a function of the electrolyte concentrations. These measurements are relatively easy but require a high degree of precision, especially accurately known concentrations, true resistance readings, solvent corrections and good temperature control. For detailed consideration of techniques employed in conductometry, the reader is referred to the

textbook by Yeager and Salkind (1973) and the review by Nancollas and Tomson (1982).

Several equations have been developed to treat conductance data. The most commonly used equation for both undissociated and associated electrolytes is the Fuoss-Onsager equation (Fuoss and Onsager, 1957; and Fuoss and Onsager, 1958). Other equations such as the Shedlovsky (Shedlovsky, 1932) and the Pitt equation are also used, primarily for symmetrical electrolytes. For asymmetrical electrolytes, the most commonly used equations are the Fuoss-Edelson (Fuoss and Edelson, 1951) and the Lee-Wheaton (Lee and Wheaton, 1978) equations.

The association constants of several metal perchlorates in non-aqueous solvents have been determined using conductometric methods (Doe *et al.*, 1984, Doe *et al.*, 1990). Conductometric measurements are often limited by the assumptions of the theoretical equations used in data treatment. Most equations deal with only one kind of ion-pair; the zero valent pair for symmetric electrolytes and the monovalent pair for asymmetric electrolytes. In non-aqueous and mixed aqueous organic solvents, these assumptions are often questionable because several other pairs can be present in large concentrations.

1.3.4 pH

The effect of pH on soil chemical reactions in dilute aqueous systems is well-documented (Sposito, 1984). Soil pH plays a major role in controlling precipitation/dissolution, adsorption/desorption, flocculation/deflocculation and chelation reactions.

In dilute aqueous media, pH is defined as

$${}^w_pH = -\log {}^w a_{H^+} = -\log {}^w \gamma_{H^+} * {}^w m_{H^+} \quad [1.16]$$

The subscript and the superscript on the left side indicate the medium in which the activity coefficient is measured and the medium to which this measured value refers respectively. In aqueous systems, data related to pH definition and measurements are abundant.

In non-aqueous system, the situation is very different. The scarcity of data defining a normal pH scale in non-aqueous systems is related to the absence of an “intersolvental” scale with ultimate reference to the solvent water. This hinders any meaningful comparison with pH defined in the studied solvent and that defined in aqueous systems (Mussini *et al.*, 1985). In these systems, the s_pH value measured in the solvent s and quoted on the pH scale specific to the studied solvent can be expressed as w_pH on one “intersolvental” scale by the following conversion equation:

$${}^s_pH = -\log({}^s \gamma_{H^+} m_{H^+}) = {}^s_pH - \log({}^s \gamma_H^0) \quad [1.17]$$

with:

$${}^s \gamma_{H^+} = {}^s \gamma_{H^+} * {}^s \gamma_H^0 \quad \text{and} \quad {}^s \gamma_{H^+} \rightarrow 1 \text{ as } s \rightarrow w \quad [1.18]$$

where ${}^s \gamma_{H^+}$ is the total medium effect and ${}^s \gamma_H^0$ the primary medium effect, which incorporates the activity change associated with the change of the medium from water to solvent. Changes in the nature and composition of the solvent often produces large changes in the activity coefficient of the chemical species and consequently in the proton potential. Therefore, the single ion activity coefficient, γ_i , reflects changes in both the interionic attractions and the medium effect largely stimulated by a drop in the medium dielectric constant.

Several studies have been conducted to measure the primary medium effects in various solvents by incorporating thermodynamic principles with electrochemical measurements in galvanic cells. The inconsistency and the poor reproducibility of these results (Table 1.4) limit their use in pH calculation and the adoption of the pH/electrode measurement systems as a universal device to measure pH in non-aqueous and mixed aqueous systems.

Table 1.4. Medium effects for the proton (Molal scale) in water-methanol solvents at 25°C, determined by extrapolation methods. (Bates, 1973).

% Methanol (w/w)	Log ${}_w^s\gamma_H^0$		
	Izmailov	Feakins	Alfenaar and deligny
10	—	-0.38	-0.21
20.22	0.14	-0.69	—
50	0.43	-2.41	—
68.33	0.7	-3.44	—
87.7	—	—	-2.7
90	1.45	-4.00	—
100	3.21	-2.25	-1.45

According to Yamazaki *et al.*, (1992), the spectrophotometric method of pH measurement rivals the usual pH meter technique in both reliability and convenience. It is true that the hydrogen electrode is the fundamental standard by which values of pH are assigned (Bates, 1973), however, this normal pH scale is limited to dilute aqueous solutions and cannot be used at very high concentrations of either acids or bases, nor in non-aqueous and mixed solvents mainly because of diffusion potential problems and strong ionic activity coefficient deviations. There is also the problem of comparing the pH values of aqueous and non-aqueous solutions and the establishment of an “intersolvental” pH scale as described above.

Indicator dyes, as defined by Ostwald are “weak acids or bases that exhibit a change in color on the conversion of the acidic form to the basic form, or vice versa”. Since color changes accompany change in the relative concentration of the acid and the base form, spectrophotometric measurement of the degree of light absorption can be used to measure pH. The only problem relies in determining the dissociation constants of the indicator in the specific non-aqueous or mixed solvent. For this purpose, there is a need to combine both potentiometry and spectrophotometry to get reliable absorption and pH data. For mixed aqueous organic solvent, the IUPAC Commission on Electroanalytical Chemistry has recommended a method for pH measurements in organic solvent mixtures of high permittivity ($\epsilon_r > 30$) (Mussini *et al.*, 1985).

1.4 Surface-Solvent Interactions

This section will focus on the effect of solvents on the physical and chemical properties of clay minerals and the forces that govern their interactions with other clay minerals and inorganic pollutants. Special attention will be given to the effect of solvents on exchange and adsorption reactions, the two most important chemical processes that determine metal mobility in the environment. A review of the literature on the work on clay-solvent interactions will also be presented.

1.4.1 Clays Physicochemical Properties

Clay minerals, particularly phyllosilicates, are layer type aluminosilicates that are abundant in terrestrial biogeochemical cycles and in the containment of toxic

waste materials. Clay minerals are stacked, polymeric sandwiches of tetrahedral and octahedral sheet structures (Sposito, 1999) that are classified first into “layer types” based on the number of tetrahedral and octahedral sheets and second into “group types” differentiated by the kind of isomorphic substitution occurring in their layer structure. The 1:1 layer structures consist of one octahedral sheet and one tetrahedral sheet, with the apical O^{2-} ions of the tetrahedral sheets being shared with the octahedral sheet. The most common type of 1:1 clay minerals is kaolinite. The 2:1 layer type has one octahedral sheet fused between two tetrahedral sheets. Three clay mineral groups have these structures: illite, vermiculite and smectites. These clay minerals are differentiated by their layer charge, which generally decreases in the order illite (-1) $\rightarrow$ vermiculite (-0.9 to -0.6) $\rightarrow$ smectites (-0.6 to -0.25), and in the degree and place of isomorphic substitution (vermiculite has a higher degree of isomorphic substitution in the tetrahedral sheet than smectites). Despite their high layer charge, illite minerals have very low cation exchange capacity (20-40 $cmol_c\ kg^{-1}$ of clay). In these minerals, most of the negative charge in the interlayer spaces is balanced by the monovalent cation K^+ , whose small ionic radii and strong interaction with the siloxane cavity causes the interlayer space to collapse, reducing both the accessible surface charge and interlayer swelling of the clay. The colloidal size and large surface areas of these clay minerals endow them with unique surface reactivity that allows them to play a major role in the biogeochemical cycling of metals, nutrients and contaminants.

The reactivity of 2:1 clay minerals is largely determined by the reactivity of the siloxane cavity (a hexagonal cavity created by the corner-sharing tetrahedral Si),

which in turn depends on the nature of the charge distribution in the clay layer (Sposito, 1984). Neutral siloxane surfaces are hydrophobic surfaces that result from the absence of nearby isomorphic substitution (talc and pyrophyllite). The neutral siloxane surfaces function as weak Lewis bases with a low affinity for water. From a surface reactivity standpoint, these surfaces are inert and interact with solutes mainly via van der Waals or London forces (Johnston & Tombacz, 2002). If isomorphic substitution of structural Al by Fe (II) or Mg occurs in the octahedral sheet, the result is a delocalized excess of negative charge that makes it possible for the surface to form strong complexes with cations and with water molecules. If isomorphic substitution of Si with Al occurs in the tetrahedral sheet, the result is a more localized excess negative charge that allows a much stronger adsorption of cations to the surface. These two types of substitution usually result in the formation of constant or permanent charge sites as opposed to conditionally charged sites (also referred to as variable or pH-dependent sites). These pH-dependent sites usually occur on the edges of 2:1 and 1:1 phyllosilicates clay minerals. Their relative contribution to the total cation exchange capacity of 2:1 clay minerals is small compared to the permanent charge sites (15% in the case of montmorillonite, and 30% in the case of illite as determined by Anderson and Sposito, 1991). However, they are considered to play a major role in the specific adsorption of metals, especially at low levels of metal contamination (Ziper *et al.*, 1988; VanBladel *et al.*, 1993).

In addition to their surface reactivity, clays are also distinguished by their physical properties; most importantly surface area, elasticity and swelling potential. Smectites and vermiculite have a larger surface area ($600\text{-}800\text{ m}^2\text{ g}^{-1}$) than illite (70-

120 m² g⁻¹). Smectites have a larger swelling potential than vermiculite. Illites are considered non-expandable. The large swelling capacity of smectites is responsible for their low hydraulic conductivity.

Because clays have high surface charge, low hydraulic conductivity and large surface area, they have been used as liners in waste landfills. Nevertheless, when some contaminants in those waste disposal landfills were able to find their way into the subsurface environment (Riley and Zachara, 1992), questions were raised as to the appropriateness of clays as landfill liners. In a study conducted by Green *et al.* (1983), significant interactions of clays with organic solvents were believed to be responsible for pollutants migration to underground subsurface environment. To understand the behavior of these clays in non-aqueous and mixed-water systems, it is important to consider the effect of the solvent physicochemical properties on the reactivity as well as the structure of clay minerals.

1.4.2 Effect of Solvents on Clay Structure

The swelling and collapse of clay interlayers are governed by the same forces that control the flocculation and dispersion of clay suspensions. These forces are essentially the Born repulsive forces, van der Waals attractive forces, electrostatic or diffuse double layer forces and the hydration forces that can either be repulsive or attractive depending on the nature of the clay surface. The Born repulsive energy, Φ_B , results from the overlap of the electron clouds of two molecules approaching each other and are usually given by the following equation

$$\Phi_B = + \frac{\xi}{r^{12}} \quad [1.29]$$

The van der Waals energies are of three types: the Keesom-van der Waals arising from the attraction between permanent dipoles, the Debye-van der Waals arising from the attraction of induced dipoles and the London-van der Waals arising from oscillating charges due to the positive nucleus and the negative electron charge. The net attractive van der Waals potential (Φ_{vdW}) is expressed by the following equation

$$\Phi_{\text{vdW}} = -\frac{1}{(4\pi\epsilon_r)^2} \left(2\alpha_{0,1}\mu_1^2 + \frac{2}{3} \frac{\mu_1^4}{K_B T} + \frac{3}{4} h\nu_1 \alpha_{0,1}^2 \right) r^{-6} \quad [1.30]$$

The distribution of the electrical potential around clay particles can be described by Gouy-Chapman theory as follows:

$$\psi_r = \psi_0 e^{-\kappa r} \quad [1.32]$$

and

$$\kappa = \sqrt{\frac{(8\pi e \sum n_i z_i^2)}{(\epsilon_r kT)}} \quad [1.33]$$

where ψ_x is the potential at distance x from the clay particle, ψ_0 is the potential at the surface of the clay particle and κ^{-1} is Debye length (m^{-1}). If all chemical variables are held constant except ϵ_r , the electrical potential may be calculated and plotted as a function of r (Figure 1.4). Decreasing the medium dielectric constant as a result of changing the solvent or adding a cosolvent to water will increase the net van der Waals (Eq 1.30) attractive forces, decrease the thickness of the diffuse double layer (Eq 1.33), and promote flocculation. However, the effect is not as straightforward as it seems, decreasing ϵ_r will also decrease the ionic strength of the solution as a result of both pairing and decreased ionic activity. This will increase the thickness of the

diffuse double layer and increase the long range repulsive forces to promote clay dispersion.

The hydration force is a function of both the hydration energies of the intercalated cation and the hydration energy of the clay surface and can oscillate between attractive (for hydrophobic surfaces) and repulsive (hydrophilic surfaces). These forces are very important in controlling the swelling and collapse of 2:1 clay minerals (Israelachvili, 1987).

Figure 1.4. Changes in the electrical potential, ψ , as a function of x , the distance from the clay particle for various values of dielectric constant, ϵ_r (Fernandez and Quigley, 1985).

Numerous studies have been conducted on the behavior of clay minerals in non-aqueous solvents. Green *et al.*, (1983) studied the interactions of clay soils with water and organic solvents. He concluded that, the greater the solvent dielectric constant, the greater the swelling of a given clay soil. In his study, all clay soils evaluated contained water at optimum moisture content. Intercalation of clays involved competition between solvent molecules and water for favorable sites in the interlayer region. For this reason, weakly polar solvents such as CCl_4 did not intercalate. The high correlation between the octanol-partitioning coefficient (K_{ow}) and the degree of swelling indicated that K_{ow} is related to the solvent solubility in the soil pore water.

Fernandez and Quigley (1985) observed that the hydraulic conductivity of initially dry clays increased with decreasing solvent dielectric constant (Figure 1.6). These results were attributed to the compression of the diffuse double layer (Eq 1.33). No change in the hydraulic conductivity was observed when wet clays were permeated with water-insoluble hydrocarbons (benzene, xylene, and cyclohexane). This difference in the behavior of dry and wet clays suggests more a specific solvent-surface interactions (specific ion and surface solvation) rather than simple compression of the diffuse layer (low dielectric constant will decrease the ionic strength and increase the thickness of the diffuse layer).

Figure 1.5. Changes in the hydraulic conductivity, k , of the pore fluid of dry clay soils with reciprocal dielectric constant, ϵ_r . (Data from Fernandez and Quigley, 1985).

Additional support for the specific solvation hypothesis is provided by Brindley *et al* (1969), who studied the intracrystalline swelling of initially dry Ca-montmorillonite in water mixed organic solvents. Figure 1.6 shows different behavior of 1-2 ethandiol and methanol saturated clays even though the two solvents have similar dielectric constant. Collapse of the interlayer spacing occurred only after a threshold value of the organic solvent fraction (f_c) is reached. This threshold value was dictated by the dielectric constant of the solvent-water mixture.

Barshad (1952) observed that the interlayer expansion of vermiculite and montmorillonite depended on the hydration status of the clay: both clays failed to expand if completely dehydrated. From a calculation of the extent of expansion (Å), he concluded that expansion depended on the length of the immersion liquid molecule and on the type of packing. The important conclusions he reached were the following: expansion of these clay minerals was greater for smaller radius, low charge cations and the effect of the total charge of the crystal lattice on expansion was greater, the smaller the cation charge. Barshad (1952) rationalized his findings by invoking the important role the interlayer cations play in activating and binding the interlayer surfaces. Depending on the position of the interlayer cations (within the interlayer cavity or midplane between the two oxygen layers), it is not surprising that the ease of expansion was greater, the smaller the cation, the greater the valence of the cation and the smaller the total charge of the interlayer surfaces. When related to the dielectric constant, the expansion both increased and decreased by lowering the dielectric constant of the liquid in contact with the surfaces, depending on the starting value of

the dielectric constant under consideration. This anomaly seemed to resolve itself by a consideration of the relative magnitude of the

Figure 1.6. Effect of cosolvents on the d-spacing of Ca-montmorillonite (Brindley *et al.*, 1969).

interlayer attractive force of the crystal lattice itself and the attractive force between the crystal lattice and the adsorbed molecules. Expansion is proportional to ϵ_r as long as the interlayer attractive forces are only slightly smaller than the attractive forces between the lattice and the adsorbed molecule. But if these latter forces are greatly increased over the former, expansion would be inversely proportional to ϵ_r .

Olejnik *et al.*, (1974) observed that the intracrystalline swelling of montmorillonite in polar organic solvents increased with an increase in the solvent dielectric constant, with the magnitude of increase being larger for monovalent cations. When ϵ_r is kept constant, the degree of swelling was inversely related to the degree of methyl substitution in the organic polar solvent as a result of dipole moment.

Berkheiser and Mortland (1975) found little correlation between the intracrystalline swelling of clay and the solvent bulk physicochemical properties (dielectric constant, acid/base character, dipole moment, etc.). No relationship between the charge density and expansion occurred except in water. Considerable variety in the stereochemistry of Cu(II) ions in the interlayers was found.

Brown and Thomas (1987) conducted a study on the soil's hydraulic conductivity as affected by clay expansion in non-aqueous media. As ϵ_r decreased, the clays electrophoretic mobility and zeta potential decreased and particles were drawn closer together until they flocculated.

Sheets and Fuller (1986) studied the transport of Cd by organic solvents in soils. Ethylene glycol was found to reduce Cd adsorption in soils rich in CaCO_3 mainly because of physical coating of the clay particles with the solvent molecules,

decreased solubility of CaCO_3 , and inhibited chemisorption of Cd on the soil surfaces. In silt soils rich in smectites, the decreased adsorption was attributed to the induced collapse of the interlayer spaces. In clayey soils, mostly kaolinite, increased adsorption of Cd was related to increased electrostatic forces due to reduced competition between the solvation energy of adsorption and the solvation energy of solubilization.

1.4.3 Effect of Solvents on Clay Surface Reactivity

The effect of solvents on clay surface reactivity has been investigated for oxides, hydroxide, and silicates and excellent review is available (Kosmulski, 1999). Increased surface acidity (Leoppert *et al.*, 1979), decreased surface potential (Kosmulski and Matijevic, 1992), decreased surface charge density (Kosmulski, 1990; Kosmulski, 1996), and increased organic solvent adsorption (Kosmulski, 1993) with decreased dielectric constant are typically reported.

Leoppert *et al.*, (1979) observed that the effects of non-aqueous solvents on clay surface reactivity were largely determined by the properties of the solvent (ϵ_r , acid-base character most importantly) and the interactions between the solvent and the exposed Al and Si atoms. Organic solvents with low dielectric constant increased surface acidity, with underlying mechanisms differing from one group of solvents to the other. Protic solvents increased the surface acidity of kaolinite by allowing sharp end point detection and stabilization of atoms at the crystalline surface edges. Weakly polar solvents increased the polarity of the hydrated water whereas dipolar aprotic completely displaced hydration water from the surface sites.

In his study of rutile, Kosmulski (1990) found that the solvent adsorption was responsible for reducing the negative surface charge by complexing with some of the hydroxide ions, usually involved in surface charge formation. The situation differs in alumina, where alcohol adsorption didn't block a significant number of surface hydroxide and proved non-competitive in relation to the formation of surface charge and ion adsorption. The exact mechanisms underlying these observed differences were not fully discerned.

Xue and Traina (1996a) described an increase in the number of apparent surface sites of goethite in acetone and methanol-water mixed systems with increasing cosolvent volume fraction as compared to aqueous systems. This was attributed to the increased strength of some originally weak iron oxide and iron hydroxide bonds in water. In addition, the low dielectric constant observed at high cosolvent fractions decreased the solubility of H^+ ions and reduced the solvation forces that usually compete with surface sites for H^+ protonation.

The effect of cosolvents on the selectivity of a charged surface for a specific cation is often overlooked. Little if any work has been done on cation exchange reactions in solvents other than water. Factors such as cation properties (ionic activity, solvated radius, valency and hydration energy) and surface characteristics (total cation exchange capacity, acid-base character, and tendency to form inner/outer sphere complexes and to undergo configurational changes) affect the preference of a particular surface for one ion over the other. At constant ionic strength, monovalent cations are usually selectively exchanged for polyvalent ones in aqueous solvents. In mixed-water systems, a shift in the surface selectivity for lower valence ions is

expected to occur at high cosolvent fraction as a result of increased ion pairing, more pronounced for polyvalent ions, and changes in the mineral surface structure and reactivity.

1.5 Effect of Solvents on Adsorption

Most of the work on inorganic chemical sorption in non-aqueous systems was conducted by Kosmulski (1995 and 1994), who studied extensively the behavior of oxides in mixed systems. Decreased adsorption of Na onto oxide surfaces, and decreased surface charge density (σ_0) was observed when water was replaced with a mixed solvent. These results were explained by suggesting an electrostatic adsorption of monovalent cations as a result of an increase in the local concentration of counterions around the oxide surface without a direct surface-ion contact.

In his review of the oxide/electrolyte behavior in mixed solvents, Kosmulski (1995) presented a thorough explanation of the general laws governing the interactions between oxide/electrolyte in mixed solvents with a critical assessment of the current findings in this domain and the future needed advances. In the absence of both a common pH definition and a method to measure pH in mixed solvent, results regarding ion adsorption, surface charge reactivity, and solubility remains skeptical and of limited applicability. The adoption of the Born equation to solely explain ion behavior in mixed systems has proven inadequate because specific solvent-water and the solvent ion interactions are not considered.

The same conclusion was reached by McDonald (1995) who worked on Zn, Cd, and Sr adsorption onto Bentonite clays in ethanol-water and methanol-water

systems. The Eisenman theory of exchange reactions seemed more pertinent in qualitatively explaining the observed increases in Zn adsorption, decreases in Cd adsorption and the unchanged Sr adsorption. Eisenman attributes the total change in exchange energy to a combination of Coulombic forces, hydration enthalpies and anionic radii.

In this context, the objective of this dissertation is to examine the effect of cosolvents on metal-surface reactions onto clay minerals. This will be accomplished through the study of two types of surface reactions: exchange and adsorption. Both reactions commonly describe the retention of metals on clay surfaces with differences lying in the mechanism of this retention (Evangelou, 1998). The former involves outer-sphere complexation where non-specific long-range electrostatic forces govern the interactions between the metal and the surface, whereas the latter involve inner-sphere complexes where specific electrostatic and non-electrostatic forces are implicated. A proper modeling of cosolvent effects on metal sorption and exchange necessitates a quantification of its effect on metal solution properties, most importantly ionic activity and complexation. For this purpose and in the absence of published values, a determination of the stability constants of major ions in solution should be conducted. Moreover, a quantification of the hydrogen ion activity, pH, in cosolvents should be conducted given the importance of pH in adsorption experiments.

Of the many mixtures that are of environmental concern, metal aqueous-organic solvent interactions with clay minerals are of interest to this study primarily because of their importance as contaminants in landfill sites and the lack of scientific

knowledge regarding their geochemical dynamics in subsurface environments. The organic solvents selected for this study represent a relatively varied range of neutral amphiprotic (methanol and ethanol) and dipolar protophobic (acetone). Although both methanol and ethanol belong to the same solvent category, their properties are very different with methanol more closely related to water (in terms of dielectric constant and polarity) than ethanol (very low dielectric constant). Their major characteristics are presented in Table 1.5. Cadmium is a soft Lewis acid, calcium and sodium are hard Lewis acids and zinc is intermediate. In addition, Zn and Cd are major pollutants in soil/sediments and groundwater (Riley *et al.*, 1992).

Table 1.5. Physical properties of cosolvents at 25°C.

Solvent	% wt	ϵ_r	ρ (kg/m ³)	η (cP)
Water ^a	0	78.48	997.1	0.890
Methanol ^b	10	74.21	981.6	1.098
	30	65.19 ^c	951.4	1.444
	50	56.05	915.6	1.572
	70	46.90 ^c	871.5	1.339
Ethanol ^c	8.6	73.08 ^c	977.1	1.230 ^e
	10	72.29 ^c	981.9	1.510
	26.6	63.01 ^c	947.2	2.103 ^c
	30	61.11 ^c	953.9	2.667
	46.3	51.99 ^c	907.3	2.874 ^c
	50	49.92 ^c	913.9	2.813
	67	40.41 ^c	877.4	2.701 ^c
Acetone ^d	10	73.02	983.1	0.952
	30	61.04	953.7	1.075
	50	48.22	915.9	0.911
	70	36.42	886.7	0.747

^a ϵ_r and ρ were obtained from Janz and Tomkins, η from CRC

^b ϵ_r was obtained From Janz and Tomkins, ρ from CRC, η from Timmermans

^c ϵ_r and η were obtained From Timmermans, ρ from CRC

^d ϵ_r and ρ were obtained From Timmermans, ρ from Janz and Tomkins

^e Interpolated values

CHAPTER II

Spectrophotometric Determination of pH in Mixed Aqueous Alcohol Mixtures Using Methyl Red and Phenol Red

2.1 Introduction

pH determination in non-aqueous and mixed aqueous organic solvents is of importance in the study of metal-surface reactions in soil systems contaminated with cosolvents (Kosmulski, 1992). pH affects surface reactions both indirectly, through its effects on solution properties (complexation, solubility and ionic strength) and directly through its effects on surface charge density. Both potentiometric and spectrophotometric methods are available for pH measurement. Potentiometric pH measurements in nonaqueous and mixed aqueous organic solvents are cumbersome and involve nonthermodynamic assumptions such as a constant residual liquid junction-potential in solutions of different ionic strength than the standard buffers (Bates, 1973). These measurements require preconditioning of the pH electrode, the time of which can vary from 10-20 days (Xue and Traina, 1996a) and, at the time of taking readings, several minutes for the electrode potential to stabilize. Standard procedures for potentiometric pH measurements have been published by the IUPAC; however, they are limited to the aqueous organic solvents (ethanol, methanol, ethandiol, etc.) for which a primary reference value standard has been defined (Rondinini *et al.*, 1998).

Spectrophotometric techniques using pH indicators present an alternative to potentiometric pH measurement methods (Yamazaki *et al.*, 1992; Yamazaki *et al.*, 1993; Yao and Byrne, 2001). Since measurements are made via absorbance ratios, pH

is directly related to the indicator molecular properties and calibrating buffers are not required (Robert-Baldo *et al.*, 1985). One disadvantage of the spectrophotometric method is the *a priori* determination of the dissociation constants of the particular indicators. However, once the indicator dissociation constants have been determined, the spectrophotometric method offers a fast, reliable and accurate method to determine pH.

In this study, we determined the conditional dissociation constants, ${}_sK_I$, of two sulphonephthalein indicators, methyl red (MR) and phenol red (PR), in mixed aqueous organic solvents (at a constant ionic strength) to provide a quantitative basis for pH measurements in these solvents. MR and PR are particularly good acids to study since both their acid and base forms have strong absorption peaks in the visible portion of the spectrum. Their acid dissociation constants are not greatly affected by changes in ionic strength and temperature (Yao and Byrne, 2001; Robert-Baldo *et al.*, 1985), and their color change intervals covering a pH range of 4.5-8.5 can be conveniently obtained using a simple HOAc-NaOAc (MR) and $\text{KH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4$ (PR) buffer systems (Kolthoff, 1953). The mixed aqueous-organic solvents chosen for this study represent the solvents of interest in the study of metal-surface reactions, more specifically metal adsorption on clay minerals.

2.2 Theory

The spectrophotometric determination of pH in aqueous media can be extended to non-aqueous and mixed aqueous organic solvents using the Henderson-Hasselbach equation,

$${}_s pH = -\log {}_s[H^+] = {}_s pK_I + \log \frac{{}_s[In^-]}{{}_s[HIn]} \quad [2.1]$$

which follows from the indicator dissociation reaction

The conditional dissociation constant of the indicator species, ${}_s K_I$, is defined as

$${}_s K_I = \frac{{}_s[H^+]{}_s[In^-]}{{}_s[HIn]} \quad [2.2]$$

In these equations, the left hand subscript indicates the solvent s in which measurements are made, $[H^+]$ is the concentration of the hydrogen ion on the molal scale,

${}_s pK_I = -\log {}_s K_I$, and $[HIn]$ and $[In^-]$ are the concentrations of the protonated and unprotonated forms of the indicator species.

The use of Eq [2.1] requires determination of the ${}_s pK_I$ of the indicator species in the solvent s . In the absence of any published literature value, these ${}_s pK_I$ in non-aqueous and mixed aqueous organic solvents can be determined using buffer solutions of varying ratios and constant total ionic strength (Tobey, 1958; Yao and Byrne, 2001) by rearranging Eq [2.1]

$${}_s pK_I = {}_s pH - \log \frac{{}_s[In^-]}{{}_s[HIn]} \quad [2.3]$$

In this equation, ${}_s pH$ can be measured potentiometrically using a procedure developed by the IUPAC Commission on Electroanalytical Chemistry for organic solvent mixtures of high permittivity, $\epsilon_r > 30$, (Mussini *et al.*, 1985). In this procedure, the relationship between the ${}_s pH$ values of the sample, ${}_s pH_X$, and the Reference Value

Standard, ${}_s\text{pH}_{\text{RVS}}$, in the solvent s , and the electromotive forces (e.m.f.) of cells I, E_X , and II, E_{RVS} , is given by

$${}_s\text{pH}_X = {}_s\text{pH}_{\text{RVS}} + \frac{{}_sE_{\text{RVS}} - {}_sE_X}{(\ln 10)(RT/F)} \quad [2.4]$$

In these cells, the liquid junction potential at || is assumed to be equal. The Reference Value Standard chosen for these measurements is typically a solution of 0.05 mol kg⁻¹ potassium hydrogen phthalate prepared in the solvent s and for which a reference pH value ${}_s\text{pH}_{\text{RVS}}$ is given. At 25°C, values of pH_{RVS} in selected mixed aqueous organic solvents can be found in Rondinini *et al.*, (1997). At any temperature, these values can also be calculated using the following polynomial regression equation (Rondinini *et al.*, 1998),

$${}_s\text{pH}_{\text{RVS}} = 4.005 + 22.17x - 9.19x^{1.5} + 32.26x^2 - 0.821\varepsilon_r x + 0.01049\varepsilon_r^2 x - 1.590K_{\text{ap}}x^2 - 0.75u_1x^{0.5} \quad [2.5]$$

where $u_1z = (T - \theta) / \theta(1 + z)$, $\theta = 298.15\text{K}$, x is the alcohol mole fraction in the mixture, and K_{ap} is the autoprotolysis constant of the pure alcohol component at 298.15 K. Selected values of K_{ap} in nonaqueous and aqueous organic solvents can be found in Rondinini *et al.*, (1987). A regression equation to calculate these values for some mixed aqueous organic solvents was developed by Roses *et al.*, (1993). In this

study, values for ${}_s\text{pH}_{\text{RVS}}$ and K_{ap} were taken from the literature and are given in Table 2.1.

Table 2.1 Values of ${}_s\text{pH}_{\text{RVS}}$ in mixed aqueous alcohol solvents at 25°C (Rondinini *et al.*, 1997).

Solvent	% wt Cosolvent	${}_s\text{pH}_{\text{RVS}}^*$
Water	0	4.005
Methanol	10	4.243
	30	4.626
	50	5.125
Ethanol	10	4.230
	30	4.686
	50	5.096

* Values that were not available at a specific cosolvent fraction were interpolated from existing data.

In equations [2.1] and [2.3], the ratio $[\text{In}^-]/[\text{HIn}]$ is obtained by measuring the absorbance of a solution that contains both forms of an indicator at two wavelengths.

The first wavelength (λ_{HIn}) is chosen where the acid and not the basic form of the indicator strongly absorbs and the second wavelength (λ_{In^-}) is chosen where the basic and not the acidic form of the indicator absorbs.

If Beer's law is obeyed, the absorbances at λ_{HIn} and λ_{In^-} of a particular indicator are given by

$$A_{\lambda_{\text{HIn}}}^{\text{HIn}} = \epsilon_{(\text{HIn}, \lambda_{\text{HIn}})} \times b_a \times [\text{HIn}] \quad [2.6]$$

and

$$A_{\lambda_{\text{In}^-}}^{\text{In}^-} = \epsilon_{(\text{In}^-, \lambda_{\text{In}^-})} \times b_a \times [\text{In}^-] \quad [2.7]$$

where $A_{\lambda_{\text{HIn}}}^{\text{HIn}}$ and $A_{\lambda_{\text{In}^-}}^{\text{In}^-}$ are the absorbance of the acidic form of the indicator, HIn (right hand superscript) at λ_{HIn} (right hand subscript) and the basic form of the indicator, In^- ,

at λ_{In^-} respectively. $\epsilon_{(HIn, \lambda_{HIn})}$ and $\epsilon_{(In^-, \lambda_{In^-})}$ are the molar absorptivities of HIn at λ_{HIn}

and In^- at λ_{In^-} respectively and b_a is the cell path length. At any pH, the total concentration (C_T) of both forms of indicator is

$$C_T = [HIn] + [In^-] \quad [2.8]$$

In extremely acidic solution, where $HIn \gg In^-$ and $C_T = [HIn]$

$$A_{\lambda_{HIn}(acidic)} = \epsilon_{(HIn, \lambda_{HIn})} \times b_a \times C_T \quad [2.9]$$

Likewise, in extremely basic solution where $In^- \gg HIn$ and $C_T = [In^-]$

$$A_{\lambda_{In^-}(basic)} = \epsilon_{(In^-, \lambda_{In^-})} \times b_a \times C_T \quad [2.10]$$

At any pH, the ratio $[In^-]/[HIn]$ can be obtained by combining Eq 2.6-2.10 to give

$$\frac{[In^-]}{[HIn]} = \frac{A_{\lambda_{In^-}} (C_T / A_{\lambda_{In^-}(basic)})}{A_{\lambda_{HIn}} (C_T / A_{\lambda_{HIn}(acidic)})} \quad [2.11]$$

or

$$\frac{[In^-]}{[HIn]} = \frac{A_{\lambda_{In^-}}}{A_{\lambda_{HIn}}} \times R_I \quad [2.12]$$

where

$$R_I = \frac{A_{\lambda_{HIn}(acidic)}}{A_{\lambda_{In^-}(basic)}} \quad [2.13]$$

All the absorbances used in these equations are background corrected such that

$$A_{\lambda_{HIn}}^{HIn} = A_{\lambda_{HIn}}^{HIn}(measured) - A_{\lambda_{In^-}}^{HIn}(acidic) \quad [2.14]$$

where $A_{\lambda_{HIn}}^{HIn}$ is the corrected absorbance, $A_{\lambda_{HIn}}^{HIn}(measured)$ is the measured absorbance

and $A_{\lambda_{In^-}}^{HIn}(acidic)$ is the absorbance of HIn at λ_{In^-} from the most acidic solution

(Braun, 1982). $s.pK_I$ is then calculated by combining Eq [2.3] and [2.12]

$${}_s pK_I = {}_s pH - \log \frac{A_{\lambda_{In^-}}}{A_{\lambda_{HIn}}} \times R_I \quad [2.15]$$

using either of two equivalent methods, an algebraic method or a graphical method.

In the algebraic method, sets of ${}_s pH$ and absorbance values are substituted in Eq [2.15] and the ${}_s pK_I$ is calculated for each set. The ${}_s pK_I$ reported is then the average of the calculated ${}_s pK_I$. In the graphical method, $\log [In^-]/[HIn]$ is plotted against ${}_s pH$ and ${}_s pK_I$ is obtained as the x-intercept. The line should have a slope of -1.

For any solution and within the buffer region of the selected indicator, ${}_s pH$ can be determined by rearranging Eq [2.15]

$${}_s pH = {}_s pK_I + \log \frac{A_{\lambda_{In^-}}}{A_{\lambda_{HIn}}} \times R_I \quad [2.16]$$

In Eq [2.16], all parameters must be known except for $A_{\lambda_{In^-}}$ and $A_{\lambda_{HIn}}$ which are measured spectrophotometrically for each unknown sample.

2.3 Materials and Methods

2.3.1 Reagents

The solvents used in this study were deionized water, methanol (HPLC grade, CAS: 67-56-1, Fisher Scientific, Pittsburgh, PA) and ethanol (Reagent grade). Cosolvent fractions were prepared by weight (10%, 30% and 50%) using N_2 purged distilled water. Properties of these cosolvents are given in Table 1.5.

The stock solution of MR (5.49×10^{-3} mol L^{-1}) was prepared by dissolving an appropriate amount of reagent grade methyl red sodium salt ($C_{15}H_{14}N_3NaO_2$, CAS: 845-10-3, Acros Organics, NJ) in 95% ethanol and diluting with distilled water

(Tobey, 1958). The stock solution of PR ($5.31 \times 10^{-3} \text{ mol L}^{-1}$) was prepared by dissolving reagent grade phenol red sodium salt ($\text{C}_{19}\text{H}_{13}\text{NaO}_5$, CAS: 34427-61-1, Acros Organics, NJ) in distilled water (Kolthoff, 1953). Working solutions of acids (HCl), bases (NaOH) and buffers (HOAc, NaOAc, KH_2PO_4 , Na_2HPO_4) were prepared in various weight percent cosolvents. Concentrations of indicator in this work were $2.197 \times 10^{-5} \text{ mol L}^{-1}$ for MR and $2.125 \times 10^{-5} \text{ mol L}^{-1}$ for PR.

2.3.2 Determination of the conditional dissociation constant, pK_b , of MR and PR

The first step in this experiment involved determining the wavelengths at which HMR and MR^- and HPR and PR^- exhibited absorption maxima. For each indicator, this was done by investigating the absorbance versus wavelength relationship of two solutions: An acidic solution which contained the indicator entirely in the form HIn and a basic solution which contained the indicator entirely in the form In^- (Kolthoff, 1953). Absorption maxima and peak width were recorded in every percent weight cosolvent.

The second step involved determining the relative amounts of the acid and base forms of each indicator as a function of pH. This was done by preparing a series of solutions of constant total ionic strength ($I = 2.5 \times 10^{-3} \text{ mol L}^{-1}$), constant total amount of indicator and varying amount of buffer solutions in each percent weight cosolvent (Tobey 1958). The absorbance of the solution at λ_{HIn} and λ_{In^-} were determined using a Cary 50 UV-Vis spectrophotometer (Variance Instruments, Walnut Creek, Ca) equipped with a dip probe. In each cosolvent, baseline corrections

were done by measuring the absorbance of a blank solution containing the solvent of interest (e.g. 10% methanol) and subtracting it from the absorbance of the samples at λ_{HIn} and λ_{In^-} .

In each solution and at each cosolvent fraction, e.m.f was measured in mV using an Accumet pH meter equipped with an Sure-flow glass combination electrode (Orion®) preconditioned in a solution that contained the cosolvent of interest for at least 10 days (in order to reduce electrical potential drifts) (Xue and Traina, 1996a). Prior to any measurement, the pH electrode was calibrated using a standard 0.05 mol kg⁻¹ potassium hydrogen phthalate prepared in the cosolvent of interest and the e.m.f. was recorded (Rondinini *et al.*, 1998). Depending on the solvent type, the time needed for readings to stabilize varied from 5-20 min.

2.4 Results and Discussion

Figure 2.1 and 2.2 illustrate the type of plots obtained for PR and MR indicators respectively in 10% methanol. The absorption maxima of HIn and In⁻ for MR were $\lambda_{\text{HMR}} = 520$ nm and $\lambda_{\text{MR}^-} = 425$ nm and $\lambda_{\text{HPR}} = 433$ nm and $\lambda_{\text{PR}^-} = 558$ nm for PR. These results as well as the calculated dissociation constants for MR and PR in water correlate well with published literature values (Tobey, 1958; Yao and Byrne, 2001). No change in the wavelength at which the absorption maxima of the acidic and basic solution occurred. However, changes in the peak width among cosolvents were recorded. This change in peak width can be attributed to the presence of several species of the indicator (potential isomers) molecule (Bates, 1973).

The experimental data for PR and MR in all cosolvents are presented in Appendix A (A.1-A.12). A sample of these data (10% methanol) is presented in Tables 2.2 and 2.3 for PR and MR respectively. The properties of all acidic and basic solutions in the various alcohol-water mixtures are presented in Table 2.4. A summary of ${}_s\text{pK}_I$ is represented in Table 2.5. These ${}_s\text{pK}_I$ are calculated algebraically as the average of the various ${}_s\text{pK}_I$ determined for each indicator in each cosolvent within the indicator buffer region. These ${}_s\text{pK}_I$ are conditional dissociation constants and can only be used in the studied cosolvents under a constant ionic strength ($I=2.5\times 10^{-3} \text{ mol L}^{-1}$) and temperature ($25^\circ\text{C}\pm 2.0$). The temperature variation is somewhat large ($\pm 2.0^\circ\text{C}$) and represents the range of temperatures of all the studied solutions in the various cosolvents during the overall period of study (one month). However, the effect of temperature on the dissociation constants of phenol red and methyl red is relatively small (only apparent at the third decimal place) and can be, for the purpose of this study considered to be negligible (Yao and Byrne, 2001; Robert-Baldo *et al.*, 1985; Kolthoff, 1953).

Figure 2.3 shows the variation of the negative logarithm of the dissociation constants of MR and PR in the studied alcohol-water mixtures. As the solvent dielectric constant decreased, the dissociation constant of both PR and MR in methanol-water mixtures decreased ($78.48 < \epsilon_r < 74.21$ corresponding to $0 < \% \text{wt} < 10\%$), then increased ($74.21 < \epsilon_r < 56.05$ corresponding to $10 < \% \text{wt} < 50\%$). In ethanol-water mixtures, ${}_s\text{pK}_I$ of both indicators increased as the solvent dielectric constant decreased. The nonlinear variation of ${}_s\text{pK}_I$ with the reciprocal solvent dielectric constant indicates that the dissociation of the studied indicators in alcohol-water

mixtures is not solely a function of the solvent dielectric constant. Other specific-solvent-indicator interactions, the nature of which could not be deduced from the current study, are indicated.

In these mixtures and for the same conditions under which these dissociation constants were determined ($I=2.5 \times 10^{-3} \text{ mol.L}^{-1}$, and $T=25^{\circ}\text{C} \pm 2.0$), ${}_s\text{pH}$, on the free hydrogen ion scale, can be estimated from measurements of the indicator absorbance ratios ($A_{\lambda_{In^-}} / A_{\lambda_{HIn}}$) of any solution whose ${}_s\text{pH}$ is unknown using Eq [2.16] where ${}_s\text{pK}_I$ and R_I are obtained from Tables 2.5 and 2.4, respectively. These two indicators can be used to determine pH within the range $4.5 \leq \text{pH} \leq 8.5$.

Table 2.2. Experimental data for phenol red indicator in 10% methanol.

	KH ₂ PO ₄ /Na ₂ HPO ₄ ^b	e.m.f ^c	pH ^d	Measured Absorbance		Corrected Absorbance ^e		log [PR ⁻]/[HPR] ^f	pK _I ^g
				λ_{HPR}^{HPR} (measured)	λ_{PR}^{PR-} (measured)	λ_{HPR}^{HPR}	λ_{PR}^{PR-}		
Set I ^a	4	11	5.37	0.3694	0.0449	0.3233	0.0448	-1.3517	6.72
	2	-8.9	5.70	0.3538	0.0893	0.3077	0.0892	-1.0311	6.73
	1	-20.5	5.90	0.3388	0.149	0.2927	0.1489	-0.7869	6.69
	0.5	-38.3	6.20	0.2989	0.2609	0.2528	0.2608	-0.4798	6.68
	0.25	-52.7	6.44	0.2606	0.38	0.2145	0.3799	-0.2451	6.69
	0.2	-52.7	6.44	0.2754	0.3364	0.2293	0.3363	-0.3270	6.77
	0.1	-71.1	6.76	0.2109	0.5378	0.1648	0.5377	0.0202	6.74
	0.05	-78.8	6.89	0.1891	0.6097	0.1430	0.6096	0.1364	6.75
Set II	4	16.3	5.28	0.3592	0.0432	0.3131	0.0431	-1.3545	6.63
	2	-6.8	5.67	0.345	0.0856	0.2989	0.0855	-1.0369	6.71
	1	-23.3	5.95	0.3263	0.1502	0.2802	0.1501	-0.7644	6.71
	0.5	-41.1	6.25	0.29	0.2647	0.2439	0.2646	-0.4580	6.71
	0.25	-55.3	6.49	0.2691	0.4047	0.2230	0.4046	-0.2346	6.72
	0.2	-54.7	6.48	0.2562	0.3631	0.2101	0.3630	-0.2559	6.73
	0.1	-69.3	6.72	0.2073	0.5363	0.1612	0.5362	0.0286	6.70
	0.05	-74.3	6.81	0.1908	0.5751	0.1447	0.5750	0.1059	6.70
Acidic solution				0.3791	0.0001	0.333			
Basic solution				0.0461	1.0371		1.037		
R_{PR}^h					0.3211				

^a Each set represents individual replicate^c e.m.f is the electromotive force measured in mV for each solution^e Corrected absorbance calculated using Eq [2.14]^g Calculated using Eq [2.15]^b This column present the ratio of buffer solution used^d Calculated from Eq [2.4]^f Calculated using log Eq [2.12]^h Calculated using Eq [2.13]

Table 2.3. Experimental data for methyl red indicator in 10% methanol.

	HOAc/NaOAc ^b	e.m.f ^c	<i>s</i> pH ^d	Measured Absorbance		Corrected Absorbance ^e		log [MR ⁻]/[HMR] ^f	<i>s</i> pK ^g
				$\lambda_{MR^-}^{MR^-}$ (measured)	λ_{HMR}^{HMR} (measured)	$\lambda_{MR^-}^{MR^-}$	λ_{HMR}^{HMR}		
Set I ^a	2	120.5	3.52	0.1824	0.6527	0.1356	0.6437	-0.2244	3.74
	1.5	113.2	3.64	0.209	0.6032	0.1622	0.5942	-0.1184	3.76
	1	102.6	3.82	0.2431	0.49	0.1963	0.481	0.0548	3.76
	0.5	85	4.12	0.3106	0.3271	0.2638	0.3181	0.3586	3.76
	0.25	67	4.42	0.349	0.2027	0.3022	0.1937	0.6255	3.80
	0.2	61	4.52	0.3594	0.1627	0.3126	0.1537	0.7356	3.79
	0.1	44.1	4.81	0.3965	0.1096	0.3497	0.1006	0.9559	3.85
	0.05	28	5.08	0.4109	0.0689	0.3641	0.0599	1.1750	3.90
Set II	2	120.1	3.52	0.2007	0.6824	0.1539	0.6734	-0.1890	3.71
	1.5	113.5	3.63	0.2275	0.6267	0.1807	0.6177	-0.0818	3.72
	1	102.1	3.83	0.2686	0.5195	0.2218	0.5105	0.0900	3.74
	0.5	85.3	4.11	0.3247	0.3484	0.2779	0.3394	0.3652	3.75
	0.25	66.7	4.43	0.3714	0.2189	0.3246	0.2099	0.6414	3.78
	0.2	61.2	4.52	0.3813	0.1865	0.3345	0.1775	0.7272	3.79
	0.1	44	4.81	0.4081	0.1133	0.3613	0.1043	0.9916	3.82
	0.05	27.1	5.10	0.4192	0.0739	0.3724	0.0649	1.2108	3.88
Acidic solution				0.0468	1.0485	1.0395			
Basic solution				0.4139	0.0090	0.3671			
R_{MR}^h					2.8316				

^a Each set represents individual replicate^c e.m.f is the electromotive force measured in mV for each solution^e Corrected absorbance calculated using Eq [2.14]^g Calculated using Eq [2.15]^b This column present the ratio of buffer solution used^d Calculated from Eq [2.4]^f Calculated using log Eq [2.12]^h Calculated using Eq [2.13]

Table 2.4. Properties of the acidic and basic solutions of PR and MR in various alcohol-water mixtures.

Solvent	% wt	Phenol Red		Methyl Red	
		R_{PR}^a	Measured Absorbance ^b	R_{MR}	Measured Absorbance
Water	0	0.3270	$\lambda_{PR}^{HPR} = 0.0024$	2.9339	$\lambda_{MR}^{HMR} = 0.0737$
Methanol	10	0.3211	$\lambda_{HPR}^{PR^-} = 0.0439$	2.8316	$\lambda_{HMR}^{MR^-} = 0.0431$
			$\lambda_{PR}^{HPR} = 0.0001$		$\lambda_{MR}^{HMR} = 0.0468$
			$\lambda_{HPR}^{PR^-} = 0.0461$		$\lambda_{HMR}^{MR^-} = 0.0090$
	30	0.3226	$\lambda_{PR}^{HPR} = 0.0038$	2.9255	$\lambda_{MR}^{HMR} = 0.0908$
			$\lambda_{HPR}^{PR^-} = 0.0393$		$\lambda_{HMR}^{MR^-} = 0.0318$
	50	0.3247	$\lambda_{PR}^{HPR} = 0.0017$	2.6951	$\lambda_{MR}^{HMR} = 0.1053$
Ethanol	10	0.3263	$\lambda_{HPR}^{PR^-} = 0.0403$	2.8667	$\lambda_{HMR}^{MR^-} = 0.0224$
			$\lambda_{PR}^{HPR} = 0.0029$		$\lambda_{MR}^{HMR} = 0.0720$
			$\lambda_{HPR}^{PR^-} = 0.0413$		$\lambda_{HMR}^{MR^-} = 0.0420$
	30	0.3338	$\lambda_{PR}^{HPR} = 0.0043$	2.7097	$\lambda_{MR}^{HMR} = 0.0779$
			$\lambda_{HPR}^{PR^-} = 0.0351$		$\lambda_{HMR}^{MR^-} = 0.0239$
	50	0.3303	$\lambda_{PR}^{HPR} = 0.0002$	2.7258	$\lambda_{MR}^{HMR} = 0.1170$
			$\lambda_{HPR}^{PR^-} = 0.0401$		$\lambda_{HMR}^{MR^-} = 0.0383$

^a These values are calculated using Eq [2.13]

^b These values are needed for the corrections of measured absorbance in every solution (Refer to Eq [2.14])

Table 2.5. $s\text{pK}_I$ for PR and MR in various alcohol-water mixtures.

Solvent	% wt	$s\text{pK}_I$	
		Phenol Red	Methyl Red
Water	0	8.05 ± 0.03	5.07 ± 0.09
Methanol	10	6.71 ± 0.03	3.78 ± 0.06
	30	7.04 ± 0.04	3.94 ± 0.07
	50	8.77 ± 0.06	5.50 ± 0.04
Ethanol	10	8.09 ± 0.02	5.08 ± 0.03
	30	8.43 ± 0.03	5.46 ± 0.04
	50	8.50 ± 0.1	5.38 ± 0.06

Figure 2.1. Absorbance versus wavelength for the acidic (HPR) and the basic (PR^-) form of phenol red (PR) indicator in 10% methanol-water mixtures.

Figure 2.2. Absorbance versus wavelength for the acidic (HMR) and the basic (MR⁻) form of methyl red (MR) indicator in 10% methanol-water mixtures.

Figure 2.3. Changes in the negative logarithm of the dissociation constant, ${}_s\text{p}K_I$, of MR and PR in alcohol-water mixtures at constant ionic strength with $100/\epsilon_r$. $\square$ PR, methanol; $\blacksquare$ PR, ethanol; $\circ$ MR, methanol; $\bullet$ MR, ethanol.

CHAPTER III

Conductometric Study of Cd(II), Ca(II), Zn(II) Nitrates and Ca(II) Chlorides in Mixed Aqueous Organic Solvents at 25°C

3.1 Introduction

In the studies of soil chemical reactions, it is often necessary to keep ionic strength constant without affecting other chemical equilibria. Generally, this ionic strength varies from low (mostly in sorption studies) to high (exchange reactions). At high ionic strength, ion-pairing is often too large and is responsible for a large drop in the ionic activity. In aqueous solutions with low ionic strength, this effect is often small and enough to be ignored. In non-aqueous and mixed aqueous organic solvents with low dielectric constants, even low ionic strength solutions are capable of some degree of ionic association (Doe *et al.*, 1984). For this purpose and in the absence of published values, studies of electrolytic conductance in mixed non aqueous solvents have been initiated in order to provide experimental data on the primary ion-association constant, K_{1A} , of some electrolytes of interest in soil science studies. These electrolytes include $\text{Ca}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$ and CaCl_2 .

3.2 Materials and Methods

3.2.1 Reagents

Certified reagent grade $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Fisher Scientific, Pittsburgh, PA, CAS: 13477-34-4), $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Fisher Scientific, Pittsburgh, PA, CAS: 10022-68-1), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fisher Scientific, Pittsburgh, PA, CAS: 7779-88-6), and

anhydrous CaCl_2 (Fisher Scientific, Pittsburgh, PA, CAS: 10043-52-4) were used to prepare titrant solutions. The exact concentration of each titrant was calculated after standardization with 0.01N EDTA. The solvents used in this study were deionized water, methanol (HPLC grade, Fisher Scientific, Pittsburgh, PA CAS: 67-56-1), ethanol (Reagent grade) and acetone (HPLC grade, Fisher Scientific, Pittsburgh, PA, CAS: 67-64-1). The electrical conductivity of each solvent was recorded and the reported values were 0.39, 0.04, 0.1, and 0.01 $\mu\text{S}/\text{cm}$ for each solvent respectively. All cosolvent fractions were prepared by weight.

3.2.2 Conductometric titration

Conductivity measurements in mixed aqueous organic solvents are highly sensitive to atmospheric pressure and carbon dioxide (Yeager and Salkind, 1973). Therefore special care was taken to ensure complete isolation of the system from the atmosphere. Before each run, the water-jacketed reaction cell was rinsed several times with the solvent of interest and then flushed for approximately 10 min with highly purified nitrogen gas (Ultra Pure nitrogen, Airgas, Bowling Green, KY) which bubbled through the solvent just before entering the cell (Broadwater *et al.*, 1976). A known volume of mixed aqueous alcohol solvent, V_s , (weighed and corrected for density) was carefully transferred to the cell and purged with solvent-saturated nitrogen until the measured electrical conductivity (EC) stabilized. This value was recorded and subtracted from all subsequent EC readings. After thermal equilibrium had been attained ($25^\circ\text{C} \pm 0.1$), and the solvent EC determined, an exact volume of titrant, V_i , was added using an autotitrator (DL50, Mettler Toledo) and the solution

was allowed to equilibrate for 3 min before the specific conductivity and the solution temperature were recorded using an LF 3000 Microprocessor Conductivity meter equipped with a TetraConL conductivity measuring cell (WTW). For every V_i , the solution equivalent concentration, $(C_i, \text{eq L}^{-1})$, and the equivalent conductivity ($\Lambda, \text{ohm cm}^2 \text{eq}^{-1}$), was calculated as

$$C_i = 2\left(\frac{n_i \times V_i}{V_T}\right) \quad [3.1]$$

and

$$\Lambda = EC / C_i \quad [3.2]$$

where

$$V_T = V_s + V_i \quad [3.3]$$

n is the number of moles of titrant per liter solution, and V_T is the total solution volume in ml. At all times during the titration, the solution was continuously stirred and a solvent-saturated N_2 (g) pressure head maintained. Each titration was generally completed within one hour.

3.2.3 Data analysis

The densities, ρ , dielectric constants, ϵ , and absolute viscosity, η , used in calculations were obtained from the literature and are summarized in Table 1.5. In cases where values for a specific cosolvent fraction were not available, they were obtained by interpolation of existing data. The conductometric data was treated with the Fuoss and Edelson method (Fuoss and Edelson, 1951). For (2:1) electrolytes, the following equilibria are considered:

Fuoss and Edelson assumed that $K_{1A} \gg K_{2A}$ and hence developed the following equation:

$$\Lambda F = \Lambda_0 - XK_{1A} / \Lambda_0 \quad [3.6]$$

where

$$X = C_i \gamma_M \Lambda F (\Lambda F - \Lambda_0 / 2)$$

$$F = \{1 / (1 - \delta C_i^{0.5}) + (\Lambda_0 - \lambda_0) / 2\Lambda\} / \{1 + (\Lambda_0 - \lambda_0) / 2\Lambda_0\}$$

$$\delta = \alpha \Lambda_0 + \beta$$

$$\alpha = 5.60 \times 10^6 q / \{\epsilon_r T\}^{1.5} (1 + q^{0.5})\}$$

$$\beta = 123.8 / [\eta(\epsilon_r T)^{0.5}]$$

$$q = (2/3)(1 + \lambda_0 / \Lambda_0)^{-1}$$

Here, Λ_0 is the limiting equivalent conductance, λ_0 is the equivalent conductance of the anion, δ is the Onsager's slope for a 2:1 electrolyte, divided by Λ_0 . The ion activity coefficient of M^{2+} , γ_M was calculated using the extended Debye-Hückel equation, (Eq 1.8). In all cosolvents, the ion size parameter, a_i , for Ca and Zn was assumed equal 6 Å and for Cd, 5 Å; the values that are used in water (Kielland, 1937).

For each treatment, two replicates were performed. The values of $\lambda_0(\text{NO}_3)^{-}$ and $\lambda_0(\text{Cl})^{-}$ were not available at the various percent weight cosolvent and since they

are needed for the computation of Λ_0 and K_{1A} , they were assumed equal to their values in the pure solvent, that is for NO_3^- , these were 60.95 and 24.82 $\Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$ in methanol and ethanol respectively; and for Cl^- , these were 52.38, 21.85, and 109.30 $\Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$ in methanol, ethanol, and acetone respectively (Izutsu, 2001 and references therein). Eq 3.6 was solved for the two unknown parameters Λ_0 and K_{1A} using an iterative procedure until Λ_0 and K_{1A} became constant.

3.3 Results and Discussion

The experimental data are summarized in Appendix B (Table B.1-B.6). The errors in these tables are the standard deviations. Each series represents a separate replicate. The Fuoss-Edelson plots (Eq 3.6) for $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and CaCl_2 systems at 25°C are also presented in Appendix B (Figure B.1 and B.2). These plots represent individual data replicate and were chosen at random among the two series.

All these plots are linear which indicates that pairing other than the monovalent pair is minor (Fuoss and Edelson, 1951). Table 3.1 contains the limiting equivalent conductance, Λ_0 , the primary association constants, K_{1A} , and their standard deviations. Except for water, the values of K_{1A} and Λ_0 were interpolated graphically from the Fuoss-Edelson plots, Figures B.1 and B.2, with Λ_0 being the intercept and K_{1A} the slope * intercept. The values of $\lambda_0(\text{NO}_3)^-$ and $\lambda_0(\text{Cl})^-$, necessary for the computation of Λ_0 and K_{1A} , were assumed equal to their values in the pure solvents primarily because no data were available for the λ_0 's of all the studied electrolytes at the various mixed aqueous-organic solvent concentrations. The only data for λ_0 's

were available for Cl^- ions in ethanol-water mixtures at 25°C in Spivey and Shedlovsky (1967). However, they were not adopted in this study for consistency purpose and because the computation of these values, according to the authors, involved large errors and “their use is subject to considerable uncertainty”. Nevertheless, λ_0 does not control strongly the values of K_{1A} and Λ_0 (Doe *et al.*, 1984). The lack of data also prevented the use of transport numbers for the calculation of λ_0 's.

The values of K_{1A} of the various electrolytes in water were taken from the literature (Smith and Martell, 1976). Other values are reported elsewhere and they range from -1 to 0.98 (Lindsay, 1979, CRC). The large variation in these values reflects the differences in the methods (potentiometric, spectrophotometric, NMR etc...) as well as the assumptions (ionic strength, activity versus concentration constants, etc...) used for their determination. For all studied electrolytes, these values are lower than what we expect if we interpolate our data to zero cosolvent fractions but they still depict the large variation found in the literature.

Table 3.1. Limiting equivalent conductance ($\Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$) and ionic association constants, K_{IA} for various salts at 25°C.

Solvent	%wt	Λ_0	K_{IA}
Ca(NO₃)₂·4H₂O			
Methanol	0	130.96 ^a	10 ^{-4.80} ^b
	10	108.21±0.01	10.78±0.21
	30	79.99±0.01	14.44±0.33
	50	71.95±0.02	23.04±0.18
Ethanol	10	103.17±0.18	10.79±0.34
	30	64.14±0.01	17.20±0.08
	50	51.50±0.03	22.93±0.05
Cd(NO₃)₂·4H₂O			
Methanol	0	124.26 ^c	2.04 ^b
	10	94.80±0.01	12.38±0.06
	30	69.61±0.01	14.77±0.92
	50	63.14±0.07	28.02±0.06
Ethanol	10	90.38±0.03	13.02±0.23
	30	55.59±0.01	18.33±0.03
	50	45.36±0.02	34.12±1.10
Zn(NO₃)₂·6H₂O			
Methanol	0	124.26 ^c	2.51 ^b
	10	96.60±0.06	12.12±0.60
	30	69.56±0.02	14.92±0.01
	50	63.35±0.01	28.82±0.25
Ethanol	10	89.09±0.02	11.29±0.13
	30	55.29±0.04	19.50±0.24
	50	45.69±0.01	36.81±0.16
CaCl₂			
Methanol	0	135.7 ^a	2.63 ^b
	10	108.60±0.32	27.38±0.05
	30	77.75±0.13	31.52±0.28
	50	67.40±0.06	43.01±0.10
Ethanol	70	70.59±0.23	61.41±2.25
	10	99.33±0.28	28.69±0.73
	30	61.64±0.05	55.95±0.06
	50	48.51±0.02	58.90±0.35
Acetone	70	44.11±0.05	84.56±0.70
	10	112.16±0.16	38.23±1.84
	30	87.25±0.35	149.96±0.38
	50	76.16±0.22	219.43±1.92
	70	76.03±0.26	487.48±13.60

^a Values for the limiting equivalent conductance of the studied electrolytes in water were computed from ionic equivalent conductance data ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) using Kohlrausch's Law of Independent Migration of Ions

($\Lambda_0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0$) where $\lambda_{\text{Ca}^{2+}}^0 = 119.0$; $\lambda_{\text{Cl}^-}^0 = 76.36$; $\lambda_{\text{NO}_3^-}^0 = 71.46$ (Atkins, 1998).

^b Values for K_{IA} for water were obtained from Smith and Martell (1976).

^c The value of $\lambda_{\text{Cd}^{2+}}^0$ in water was assumed equal to $\lambda_{\text{Zn}^{2+}}^0 = 105.6 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (Atkins, 1998).

3.3.1 *Walden products*

Figure 3.1 shows the variation of the Walden products, $\Lambda_0\eta$, for nitrate salts in methanol and ethanol. For both solvents, the Walden products for $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are nearly identical. These ions have similar ionic sizes and their properties are largely masked by the strong acid properties of the solvents. The higher mobility of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is attributed to the smaller hydrated radius of Ca.

In methanol, the Walden products for all three nitrate salts are largely independent of solvent composition. This indicates that the mobility of these electrolytes in methanol is primarily determined by the solvent bulk viscosity and that the ion size parameter does not vary with methanol-water composition (Stoke's Law). In ethanol-water mixtures (Figure 3.1), the variation in the Walden products indicates that the mobility of these electrolytes is not solely dependent on the solvent bulk viscosity, but also depends on ion solvation. The observed maxima in $\Lambda_0\eta$ for the three electrolytes at about 30% ethanol agrees with the results reported by Spivey and Shedlovsky (1967) and were interpreted as the result of the large disruption caused by the addition of ethanol on water structure in the vicinity of the ions. Ion solvation is also responsible for the decrease in the Walden products of CaCl_2 in methanol, ethanol and acetone (Figure 3.2). Again, a structure enhancement is observed around 20-30% ethanol.

Figure 3.1. Variation of the Walden products, $\Lambda_0\eta$, of nitrate salts with solvent composition at 25°C. ♦, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; □, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; ▲, $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. (Error bars smaller than data points).

Figure 3.2. Variation of the Walden products, $\Lambda_0\eta$, of CaCl_2 with solvent composition at 25°C. (Error bars smaller than data points).

3.3.2 Stability constant

Figure 3.3 presents the variation in the association constant of Ca (II), Cd (II) and Zn (II) nitrates as a function of the reciprocal dielectric constant. For each electrolyte, this relationship is linear ($R^2 \geq 0.91$) suggesting that the ionic association of these electrolytes in the studied cosolvents is primarily determined by electrostatic attractions between oppositely charged ions. The large difference between $\log K_{1A}$ of $\text{Ca}(\text{NO}_3)^+$ (only observed at lower solvent dielectric constant or $\sim 50\%$ cosolvent composition) and $\log K_{1A}$ for $\text{Cd}(\text{NO}_3)^+$ or $\text{Zn}(\text{NO}_3)^+$ indicates the lower pairing potential of Ca (II) ions and may be the consequence of the harder Lewis acid character of Ca (II) (Doe *et al.*, 1984).

Formation constants for CaCl^+ were larger than for $\text{Ca}(\text{NO}_3)^+$ in all solvents and at all solvent concentrations. In methanol-water mixtures, $\log K_{1A}$ for CaCl^+ increased linearly ($R^2 \geq 0.99$) with the reciprocal of the solvent dielectric constant, ϵ_r , suggesting that in these two cosolvents, the ion-pair formation is largely regulated by the solvent dielectric constant (Figure 3.4). In ethanol ($R^2=0.86$) and acetone-water mixtures ($R^2=0.81$), other specific solvent-solute interactions are apparent especially at low acetone concentrations.

3.4 Conclusion

The stability constants of CaCl^+ and $\text{M}(\text{NO}_3)^+$ ($\text{M} = \text{Ca}, \text{Cd}, \text{and Zn}$) in ethanol and methanol-water mixtures, as determined by conductometric titration, seem to involve, in addition to electrostatic interactions, specific solvent-solute interactions. These appear to be related to the acid-base character of both the solvent and the solute. The mobility of the three nitrate salts in methanol-water mixtures, at infinite dilution, as shown by the variation in the Walden product with solvent composition, seems to be solely dependent on the bulk viscosity of the solvent. In ethanol, solvent-solvent interactions such as ion solvation and water structure disruption seem to occur. This conclusion also applies to CaCl_2 mobility at infinite dilution in the three water-mixed solvents (methanol, ethanol and acetone).

Figure 3.3 Variation of $\log K_{1A}$ with the reciprocal dielectric constant in alcohol-water mixtures at 25°C. (Error bars smaller than data points).

Figure 3.4. Variation of $\log K_{1A}$ of CaCl_2 with the reciprocal dielectric constant in cosolvents at 25°C. (Error bars smaller than data points).

CHAPTER IV

Effect of Cosolvents on Ca-Na Exchange onto Wyoming Bentonite

4.1 Introduction

In soils and waste contaminated sites, the net effect of solvents on the behavior of inorganic contaminants will result from a combination of its effects on the solution and the surfaces properties. Solvent effects on the physical properties of soils and clays have been reported (Brown and Thomas, 1987; Fernandez and Quigley, 1985), but there has been little work on solvent effects on metal surface reactions (Kosmulski, 1994; Miller *et al.*, 1992) and none on clay minerals. Studying Ca-Na exchange reactions on Wyoming bentonite in mixed aqueous organic solvents offers many advantages. This system is well studied in aqueous solvents (Van Bladel and Gheyi, 1980; Sposito *et al.*, 1983; Amrhein and Suarez, 1991; Zhang and Sparks, 1996) and it is established that, in the absence of significant ion pairing and complexation, the long range electrostatic attraction of cations to the surface favor the adsorption of Ca^{2+} as opposed to Na^+ ions. As ion-pairing increases, this selectivity tends to decrease (Sposito *et al.*, 1983). Both Ca and Na are hard Lewis acids; Ca is a divalent cation with strong hydration energy, small size and high charge density, whereas Na is a monovalent cation with low hydration energy, small size and low charge density. Calcium and Na both tend to form outer-sphere surface complexes with the hard Lewis base Wyoming bentonite.

For the exchange reaction

The Vanselow selectivity coefficient is defined as:

$$K_v = \frac{\{Na^+\}^2 N_{Ca}}{\{Ca^{2+}\} N_{Na}^2} = \frac{[Na^+]^2}{[Ca^{2+}]} \times \frac{\gamma_{Na^+}^2}{\gamma_{Ca^{2+}}} \times \frac{N_{Ca}}{N_{Na}^2} \quad [4.2]$$

where X indicates a solid phase exchanging surface with a charge of -2, { } refers to the activity of the specific cation, N_{Ca} and N_{Na} are the mole fractions of Ca and Na on the exchanger sites respectively. Eq [4.2] is rearranged

$$\frac{N_{Ca}}{N_{Na}^2} = K_v \times \frac{[Ca^{2+}]}{[Na^+]^2} \times \frac{\gamma_{Ca^{2+}}}{\gamma_{Na^+}^2} \quad [4.3]$$

The effect of a solvent on the selectivity of a surface for a particular cation would result from its combined effect on the solution properties (single ion-activity coefficients and free metal concentrations) and the surface properties (adsorbed metal fraction). Increasing cosolvent fraction will decrease $\frac{\gamma_{Ca^{2+}}}{\gamma_{Na^+}^2}$ (Figure 4.1) and decrease $[Ca^{2+}]$ due to increased ion-pairing (more pronounced for divalent Ca^{2+} than the monovalent Na^+). Assuming no changes in the exchanger activity coefficients or in K_v , this should decrease $\frac{N_{Ca}}{N_{Na}^2}$ (increase Na-loading). Increasing cosolvent concentration is in fact expected to increase selectivity of the surface by increasing Coulombic attractions ($Ca^{2+} > Na^+$). Other shifts in position on the isotherm or of the isotherm itself with cosolvent fraction, after correction for changes in the solution phase metal activity, may indicate changes in exchanger activity coefficients or some other solvent-specific effects.

It is the objective of this study to determine the net effect of cosolvents on the changes in the selectivity of Wyoming bentonite for Ca/Na ions by examining the effect of the solvent dielectric constant on both the surface and the solution properties. Given the inherent difficulty

in measuring the activities of ions in the solid phase, only the activities of ions in solution will be corrected for both changes in single-ion activity coefficient (Debye-Hückel equation) and free metal concentration (ion-pairing).

4.2 Materials and Methods

4.2.1 Na-Montmorillonite

Wyoming Bentonite clay was obtained from the American Colloid Company at Upton Plant, Wyoming. Before clay separation, soluble and insoluble salts, organic matter and iron oxides were removed according to standard procedures (Kunze and Dixon, 1986). The $<2.0\ \mu\text{m}$ clay fraction was separated by repeated washing and centrifugation. Na-saturated clays were prepared by repeated equilibration with 1M NaCl. Excess salts were removed by dialysis against distilled water until an AgNO_3 test indicated that the equilibrium solution was free of chloride ions. The salt-free gel was freeze-dried and stored for further analysis.

4.2.2 Cosolvents

The solvents used in this study were deionized water, HPLC grade methanol and acetone and reagent grade ethanol. All solvents were used without further purification. Cosolvent fractions (0, 10, 30, 50, and 70%) were prepared on weight basis for methanol and acetone. For ethanol, volume fractions were used. For ease of comparison, these volume fractions were converted to weight percentages using density data. The properties of these cosolvents are presented in Table 1.5.

Figure 4.1. Changes in the single ion activity ratio (as predicted by Debye-Hückel equation) as a function of $100/\epsilon_r$ in Δ methanol, $\square$ ethanol and $\diamond$ acetone.

4.2.3 Sodium-Calcium Exchange Experiments

In methanol and acetone experiments, 0.1 M of NaCl and CaCl_2 stock solutions were prepared by adding appropriate amounts of oven-dried (105°C overnight) anhydrous CaCl_2 and NaCl salts to 50 ml of cosolvent solution. The stock solutions were then used to prepare a series of mixed $\text{CaCl}_2/\text{NaCl}$ solutions with a constant total chloride concentration ($\text{TN}=0.03\text{N}$) and differing soluble calcium fraction, X_{Ca} . The solution compositions were 0.05, 0.1, 0.2, 0.4, 0.6

and $0.8 X_{Ca}$. Approximately 0.05g of Na-montmorillonite was added to tared 15 ml polyethylene centrifuge tubes and reacted with 10 ml of the mixed solutions for methanol and acetone.

For ethanol experiments, concentrated stock solutions of various X_{Ca} but constant total chloride concentration (0.03 mol L^{-1}) were prepared in distilled water. Appropriate volumes of water and ethanol were added to 15 ml tared polyethylene tubes containing 0.05g of Na-montmorillonite to yield 10%, 30%, 50% and 70% (v/v) solvent concentration. Exactly 0.1 ml of each of the stock solutions were then added to make a series of samples varying in their composition but having all a constant total chloride concentration ($TN = 0.03 \text{ mol L}^{-1}$). There were two replicates of each cosolvent at each cosolvent fraction.

Clays were uniformly dispersed using a vortex mixer and centrifuge tubes were equilibrated by rotating end-over-end in a rock tumbler for 12 hr. After equilibration, tubes were centrifuged at 5000 rpm for 20 min, and the supernatant solutions were collected for Ca and Na determination. Exactly 1 ml of supernatant was removed and evaporated to dryness in Pyrex tubes in a digestion block at 130°C . The evaporates were dissolved in an acidified lanthanum oxide solution and Na and Ca were determined using atomic absorption and emission spectrophotometry. These measured values of Ca and Na were used to calculate the equilibrium concentrations of Ca^{2+} and Na^{+} ions in the supernatant solution of the Na-Ca exchange reaction. The centrifuge tubes were weighed to determine the mass of the entrained solution in each clay sample. The volume of entrained solution was calculated using appropriate cosolvent density values (Table 1.5).

The clays were then extracted two times with 10 ml of concentrated $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ by shaking, centrifuging and decanting. Extracting solutions of 1 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were prepared in

corresponding cosolvent solution fractions except for 50% and 70% acetone, where 0.1 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was used. The supernatant solution from each clay sample was collected and Na and Ca were determined as described above.

4.3 Data analysis

To calculate single-ion activity coefficients, the parameters A_{D-H} and B_{D-H} (Eq 1.10 and 1.11) were calculated for each cosolvent fraction by replacing ϵ_r and ρ with their corresponding values (Table 1.5). The ion size parameters for Na, Ca, and CaCl^+ were taken as equal to their values in water that is 4.0, 6.0 and 5.1 Å, respectively (Kielland, 1937). The adsorbed metal charges of Na and Ca on the exchangers were calculated as follows:

$$q_{Na} = n_{Na} - \frac{C_{Na}V_e}{M_{Clay}} \quad [4.4]$$

$$q_{Ca} = 2 * (n_{Ca} - \frac{C_{Ca}V_e}{M_{Clay}}) \quad [4.5]$$

where n is the number of moles of Ca or Na per kilogram of clay extracted by $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solutions, C is the molar concentration of Ca and Na ions in the equilibrium supernatant solution, V_e is the volume in liters of the entrained solution and M_{clay} is the mass of clay in kg. The total adsorbed metal charge, Q, is given by the equation

$$Q = q_{Na} + q_{Ca} \quad [4.6]$$

where q_{Na} and q_{Ca} are defined in equations [4.4] and [4.5].

The non-preference isotherm for Na-Ca exchange (Sposito, 1981) was,

$$E_{Ca} = 1 - \left[1 + \frac{2\gamma_{Ca}}{(TN)\gamma_{Na}^2} \left(\frac{1}{(1-E'_{Ca})^2} - \frac{1}{E'_{Ca}} \right) \right]^{-0.5} \quad [4.7]$$

where

$$E'_{Ca} = \frac{2\{Ca\}}{2\{Ca\} + \{Na\}} \quad [4.8]$$

E'_{Ca} is the charge fraction of Ca in solution, E_{Ca} is the equivalent fraction of Ca on the exchanger and TN is the total chloride normality (0.03 N).

The adsorbed Ca^{2+} charge fraction was corrected for $CaCl^+$ by adopting the method developed by Sposito *et al.*, (1983). The total adsorbed metal charge, Q_0 is calculated as follows

$$Q_0 = q_{Na^+} + q_{Ca^{2+}} + q_{CaCl^+} \quad [4.9]$$

and q_{CaCl^+} was calculated as follows

$$q_{CaCl^+} = Q - Q_0 \quad [4.10]$$

In the objective of isolating the effect of solvents on the selectivity of bentonite surfaces for Ca and Na ions, it was important to correct for ion-pair formation in solution and its adsorption on the surface. In this context, the association constants, K_{1A} , of $CaCl^+$ were experimentally determined (Table 3.1) using conductometric methods (Fuoss and Edelson, 1951). The value of the $\log K_{1A}$ for $CaCl^+$ in water was taken from the literature (Smith and Martell, 1976). Other values were reported elsewhere. (Lindsay (1979) reports a value of -1 for the thermodynamic stability constant). The $NaCl^0$ pairs were assumed to be negligible (Spivey and Shedlovsky, 1967) and hence were not included in the calculation of the ion activities.

The adsorbed fraction of CaCl^+ on the exchanger, q_{CaCl^+} , was calculated using Eq [4.10]. The value of Q_0 can be measured by determining Q [Eq 4.9] in an exchange experiment in a medium where no ion-pair formation is expected (perchlorate, for instance) or by extrapolating Q measured in an exchange experiment conducted in chloride background to the condition of vanishing q_{Ca} . In cosolvent systems where ion-pair formation is significant even with poor-pair forming ligands such as perchlorates (Doe *et al.*, 1983), the second option seemed more appropriate to calculate Q_0 . Therefore, in every treatment and at every cosolvent fraction, Q was plotted as a function of the equivalent fraction of Ca in solution and Q_0 (Table 4.4) was taken to be equal to the cubic polynomial regression estimate of Q when the clay was Na-saturated.

4.4 Results

The equilibrium and exchanger compositions for Na-Ca exchange reactions onto bentonite clays are summarized in Tables 4.1-4.3. In each table, the fourth and the fifth column represent the equilibrium activity of Ca and Na respectively. Within a single treatment, the greater the concentration of Ca and Na, the larger the decrease in effective molar concentration (activity), this decrease being more prominent for Ca than Na. Acetone had a larger effect on ion activities than did ethanol, which in turn had a larger effect than methanol. As the solvent dielectric constant decreases, the activity of the ions is expected to decrease due to decreased single ion activity coefficient (Eq 1.8-1.10) and increased ion-pairing (Eq 1.12).

In methanol-water treatment (Table 4.1), the seventh column presents the adsorbed Ca charge in $\text{mol}_c \text{ per kg}^{-1}$, q_{Ca} , on Wyoming bentonite surfaces. Within a single cosolvent treatment and as the percent weight cosolvent increased, q_{Ca} increases with increasing X_{Ca} . This trend

coupled with the decreased activity of Ca in solution might indicate, at first sight, an increased preference of the exchanging surface for Ca ions with increasing X_{Ca} and with increasing percent weight cosolvent. In ethanol and acetone-water systems (Table 4.2 and 4.3) and within each percent weight cosolvent, q_{Ca} is increasing with increased X_{Ca} . Across treatments, q_{Ca} is rather constant.

The values of the total adsorbed metal charge in $\text{mol}_c \text{ kg}^{-1}$, Q , are reported in column 8 in Tables 4.1-4.3. Different trends are observed among various cosolvents. In methanol-water treatments and for constant X_{Ca} (Table 4.1), Q increases with increasing weight percent methanol especially at 50% and 70%. Within a single treatment, Q is fairly constant and any observed increase is within experimental error. In ethanol and acetone-water treatments, Q is fairly constant. The observed increase in the total adsorbed metal charge, Q , in methanol-water systems, at higher cosolvent weight percent, can be attributed to assigning all of the adsorbed Ca (II) species a +2 valence when in fact one of the adsorbed species is the monovalent complex, CaCl^+ (Sposito *et al.*, 1983).

Figure 4.2 presents the fractional isotherms for Na-Ca exchange on Wyoming bentonite. In these plots, the equivalent fraction of Ca in solution was corrected for single-ion activity coefficients, but not for the formation of CaCl^+ pairs. All isotherms were above the non-preference isotherm, indicating a greater selectivity of the surface for Ca ions. As the weight percent methanol increased, a shift in the isotherms toward greater Ca preference is observed at low equivalent Ca fraction (<0.2). At higher Ca fractions, all isotherms converged but showed a tendency of decreased E'_{Ca} as the percent weight methanol increased (as shown by the shift in the individual points towards the rich Na-end as the methanol concentration increased). In ethanol-

water mixtures, no increased preference for Ca was shown. At the Ca-rich end of the isotherm, increasing cosolvent concentration increased Na-loading in methanol, ethanol, and to a lesser extent in acetone. This observation is consistent with the increasing formation of CaCl^+ pairs in low ϵ_r solutions. The same effect is observed at the Na-rich end of the isotherm in ethanol and acetone. However, in methanol, increasing cosolvent concentration increased Ca-loading at the Na-rich end of the isotherm. This may indicate a methanol specific effect on metal ion activity coefficients in solution and on the surface. All isotherms converged and exhibited a greater compression towards lower E'_{Ca} and E_{Ca} as the percent solvent fraction increased. In acetone-water mixtures, increasing cosolvent concentration decreased the preference of the surface for Ca ions.

Table 4.4 presents the calculated values of Q_0 in various cosolvents. In all treatments, Q_0 is rather constant at all cosolvent weight percentage and the observed difference is considered to be within experimental error. After the determination of Q_0 , the exchange isotherms in Figure 4.1 were corrected for CaCl^+ formation both in solution and on the surface (Figures 4.3, 4.4, and 4.5 for methanol, ethanol and acetone-water treatment, respectively). In these figures, each percent weight cosolvent was plotted separately with water for ease of comparison. In all treatments, the fraction of CaCl^+ on the surface generally increased as the equivalent fraction of CaCl^+ in solution increased with some distinct trends among and within cosolvents, indicating that Ca-Na exchange on Wyoming bentonite in a chloride background involves the ternary exchange system Ca-Na- CaCl^+ . In 10% methanol, E_{CaCl^+} increases with E'_{CaCl^+} however the magnitude of increase was small (Figure 4.3). For all other cosolvent concentrations, adsorption of CaCl^+ was

significant. In acetone-water treatments (Figure 4.5), the preference of the surface for CaCl^+ increases almost linearly with E'_{CaCl^+} at all percent weight cosolvent. In the water treatment, our results are in good agreement with those described by Sposito *et al.*, (1983). Others (Amrhein and Suarez, 1991; and Zhang and Sparks, 1996) have reported no evidence for the adsorption of CaCl^+ ions in water. Demonstrating whether CaCl^+ adsorption is significant or not is not the objective of this study, it is rather the identification of the major processes that control the selectivity of bentonite for a specific cation in cosolvents where the magnitude of pairing is significant. This wouldn't be possible unless CaCl^+ formation both in solution and on the surface is accounted for.

In ethanol-water treatments (Figure 4.4), no distinct trend can be distinguished. An exact explanation for these differences in behavior among and within cosolvents is currently unavailable. However, increased stability of CaCl^+ in the solutions rather than on the surface or decreased affinity of bentonite surfaces for CaCl^+ ; as a result of greater competition between Na^+ and CaCl^+ for external surface sites at the Ca rich end, (Sposito *et al.*, 1983) in media of lower dielectric constant than water are suggested. This might explain why the affinity of bentonite for CaCl^+ in all treatment was less than that in water.

4.5 Discussion

Prior to CaCl^+ correction, our results (Tables 4.1-4.3 and Figure 4.2) indicate a preference of bentonite surfaces for Ca^{2+} ions in all solvents as measured by the relative position of each cosolvent fractional isotherm with respect to the water isotherm and to the non-preference isotherm. The change in the position of the fractional isotherm especially for acetone-

water mixtures and methanol-water mixtures at low equivalent Ca fraction (<0.2) indicate that the selectivity of bentonite for Ca ions in cosolvents is a surface-controlled phenomenon essentially driven by solvent-surface interactions. In ethanol, the preference of the surface seems driven by solution-solvent interactions.

The predicted increase in K_v in response to cosolvents was apparent in methanol and ethanol only after correcting for formation of CaCl^+ . In acetone, there was evidence of increased Na-loading at the high cosolvent fraction (Figure 4.5) but no increase in Ca^{2+} selectivity.

In ethanol and ethanol-water mixtures, the observed increase in the preference of bentonite clays for Ca^{2+} after CaCl^+ correction, is attributed to a combination of dielectric (increased Ca^{2+} adsorption with decreased ϵ_r in both methanol and ethanol-water mixtures) and specific surface-cosolvent effects. This is indicated by the gradual decrease in the surface preference for Ca^{2+} (as shown by the magnitude of difference between the water and the respective fractional isotherm), as we move from methanol to ethanol to acetone-water systems after corrections for both single ion activity coefficient and ion-pairing.

This increased preference for Ca^{2+} cannot be solely explained by enhanced Coulombic attractions between the surface and the divalent cation as a result of decreased solvent dielectric constant because if this is the case, then the magnitude of preference should decrease from acetone>ethanol>methanol. Dielectric saturation of the bentonite surfaces may be larger in methanol than in ethanol and acetone.

Table 4.1. Experimental data for Na-Ca exchange on Wyoming bentonite in methanol-water mixtures at constant total chloride concentration (TN=0.03N) at room temperature.

Solvent	X _{Ca}	C _{Na}	C _{Ca}	(Na)	(Ca)	q _{Na}	q _{Ca}	Q
Water	0.05	2.92E-02	5.59E-04	2.45E-02	2.94E-04	0.404±0.027	0.508±0.020	0.912±0.029
	0.1	2.80E-02	1.29E-03	2.34E-02	6.81E-04	0.238±0.040	0.715±0.059	0.953±0.048
	0.2	2.39E-02	3.24E-03	2.00E-02	1.70E-03	0.122±0.021	0.932±0.036	1.054±0.024
	0.4	1.72E-02	6.65E-03	1.44E-02	3.50E-03	0.042±0.012	1.004±0.029	1.046±0.023
	0.6	1.29E-02	8.83E-03	1.08E-02	4.64E-03	0.014±0.003	1.041±0.034	1.055±0.034
	0.8	7.48E-03	1.16E-02	6.26E-03	6.08E-03	0.003±0.001	1.089±0.048	1.092±0.049
10% (wt/wt) Methanol	0.05	2.95E-02	5.53E-04	2.46E-02	2.86E-04	0.580±0.026	0.689±0.005	1.268±0.031
	0.1	2.72E-02	1.17E-03	2.27E-02	6.06E-04	0.278±0.001	0.928±0.008	1.205±0.007
	0.2	2.36E-02	3.07E-03	1.96E-02	1.57E-03	0.130±0.006	1.121±0.003	1.251±0.002
	0.4	1.73E-02	6.66E-03	1.43E-02	3.30E-03	0.057±0.008	1.175±0.016	1.231±0.025
	0.6	1.24E-02	9.22E-03	1.02E-02	4.48E-03	0.037±0.011	1.201±0.015	1.238±0.004
	0.8	8.43E-03	1.14E-02	6.88E-03	5.45E-03	0.025±0.002	1.228±0.005	1.253±0.003
30% (wt/wt) Methanol	0.05	2.70E-02	4.00E-04	2.20E-02	1.90E-04	0.501±0.010	0.708±0.010	1.209±0.000
	0.1	2.67E-02	1.23E-03	2.17E-02	5.73E-04	0.263±0.006	0.979±0.003	1.241±0.003
	0.2	2.28E-02	3.48E-03	1.84E-02	1.58E-03	0.122±0.005	1.161±0.025	1.283±0.030
	0.4	1.65E-02	7.27E-03	1.31E-02	3.17E-03	0.067±0.020	1.220±0.001	1.287±0.021
	0.6	1.21E-02	1.02E-02	9.51E-03	4.30E-03	0.032±0.004	1.238±0.007	1.270±0.003
	0.8	7.96E-03	1.29E-02	6.05E-03	4.88E-03	0.028±0.003	1.260±0.000	1.288±0.004
50% (wt/wt) Methanol	0.05	2.79E-02	4.23E-04	2.17E-02	1.71E-04	0.520±0.007	0.819±0.019	1.340±0.026
	0.1	2.66E-02	1.27E-03	2.06E-02	5.07E-04	0.255±0.090	1.054±0.010	1.309±0.100
	0.2	2.34E-02	3.58E-03	1.80E-02	1.37E-03	0.148±0.009	1.215±0.027	1.362±0.018
	0.4	1.75E-02	7.58E-03	1.32E-02	2.75E-03	0.079±0.003	1.289±0.035	1.368±0.038
	0.6	1.22E-02	1.07E-02	9.09E-03	3.75E-03	0.053±0.014	1.334±0.004	1.387±0.017
	0.8	8.26E-03	1.34E-02	6.10E-03	4.55E-03	0.033±0.002	1.316±0.012	1.350±0.010
70% (wt/wt) Methanol	0.05	2.83E-02	3.44E-04	2.07E-02	1.11E-04	0.515±0.007	0.869±0.010	1.384±0.003
	0.1	2.72E-02	1.09E-03	1.98E-02	3.46E-04	0.267±0.020	1.128±0.025	1.396±0.005
	0.2	2.32E-02	3.44E-03	1.67E-02	1.06E-03	0.144±0.009	1.254±0.008	1.398±0.001
	0.4	1.73E-02	7.56E-03	1.22E-02	2.16E-03	0.081±0.012	1.334±0.014	1.415±0.026
	0.6	1.21E-02	1.07E-02	8.38E-03	2.92E-03	0.056±0.001	1.379±0.002	1.435±0.003
	0.8	8.30E-03	1.30E-02	5.70E-03	3.45E-03	0.043±0.003	1.429±0.065	1.471±0.062

Table 4.2. Experimental data for Na-Ca exchange on Wyoming bentonite in ethanol-water mixtures at constant total chloride concentration (TN=0.03N) at room temperature.

X_{Ca}	C_{Na} —mol L ⁻¹ —	C_{Ca}	(Na)	(Ca)	q_{Na}	q_{Ca} —mol _e kg ⁻¹ —	Q
<u>8.6% (wt/wt) Ethanol</u>							
0.05	2.69E-02	3.87E-04	2.26E-02	2.03E-04	0.552±0.043	0.449±0.028	1.001±0.071
0.1	2.65E-02	1.30E-03	2.21E-02	6.68E-04	0.336±0.065	0.684±0.03	1.020±0.035
0.2	2.36E-02	3.38E-03	1.95E-02	1.70E-03	0.130±0.016	0.932±0.07	1.062±0.086
0.4	1.66E-02	6.65E-03	1.36E-02	3.27E-03	0.040±0.004	0.971±0.032	1.010±0.036
0.6	1.18E-02	9.38E-03	9.67E-03	4.51E-03	0.019±0.001	1.084±0.061	1.103±0.062
0.8	8.20E-03	1.16E-02	6.66E-03	5.48E-03	0.002±0.001	0.994±0.008	0.995±0.008
<u>26.6% (wt/wt) Ethanol</u>							
0.05	2.80E-02	3.72E-04	2.26E-02	1.69E-04	0.486±0.009	0.460±0.038	0.946±0.028
0.1	2.66E-02	1.06E-03	2.14E-02	4.79E-04	0.258±0.027	0.673±0.04	0.931±0.068
0.2	2.40E-02	3.14E-03	1.91E-02	1.37E-03	0.111±0.002	0.891±0.004	1.001±0.006
0.4	1.74E-02	6.85E-03	1.37E-02	2.88E-03	0.042±0.004	1.067±0.019	1.109±0.015
0.6	1.22E-02	9.50E-03	9.50E-03	3.91E-03	0.019±0.014	1.062±0.022	1.081±0.037
0.8	8.23E-03	1.19E-02	6.38E-03	4.78E-03	0.002±0.001	1.056±0.025	1.058±0.023
<u>46.3% (wt/wt) Ethanol</u>							
0.05	2.78E-02	3.32E-04	2.11E-02	1.22E-04	0.535±0.003	0.462±0.011	0.997±0.015
0.1	2.67E-02	1.09E-03	2.02E-02	3.97E-04	0.305±0.017	0.737±0.038	1.042±0.055
0.2	2.36E-02	3.19E-03	1.77E-02	1.12E-03	0.133±0.007	0.926±0.023	1.059±0.03
0.4	1.65E-02	6.57E-03	1.22E-02	2.23E-03	0.050±0.006	1.058±0.063	1.108±0.068
0.6	1.18E-02	9.59E-03	8.63E-03	3.12E-03	0.017±0.009	1.135±0.137	1.153±0.147
0.8	7.98E-03	1.16E-02	5.78E-03	3.70E-03	0.003±0.001	1.097±0.047	1.099±0.048
<u>67% (wt/wt) Ethanol</u>							
0.05	2.61E-02	3.22E-04	1.79E-02	8.36E-05	0.563±0.007	0.456±0.02	1.019±0.027
0.1	2.51E-02	1.03E-03	1.71E-02	2.64E-04	0.326±0.004	0.716±0.03	1.041±0.034
0.2	2.29E-02	3.11E-03	1.53E-02	7.44E-04	0.172±0.003	0.957±0.019	1.129±0.016
0.4	1.56E-02	6.24E-03	1.04E-02	1.45E-03	0.065±0.007	1.031±0.028	1.096±0.035
0.6	1.14E-02	9.16E-03	7.38E-03	2.00E-03	0.022±0.001	1.182±0.016	1.204±0.017
0.8	7.79E-03	1.15E-02	4.99E-03	2.41E-03	0.006±0.001	1.153±0.071	1.158±0.073

Table 4.3. Experimental data for Na-Ca exchange on Wyoming bentonite in acetone- water mixtures at constant total chloride concentration (TN=0.03N) at room temperature.

X_{Ca}	C_{Na} mol L ⁻¹	C_{Ca}	(Na)	(Ca)	q_{Na}	q_{Ca} mol _c kg ⁻¹	Q
<u>10% (wt/wt) Acetone</u>							
0.05	3.11E-02	6.01E-04	2.57E-02	3.03E-04	0.341±0.020	0.370±0.013	0.711±0.006
0.1	2.95E-02	1.68E-03	2.43E-02	8.36E-04	0.233±0.060	0.527±0.044	0.760±0.103
0.2	2.42E-02	3.42E-03	1.99E-02	1.70E-03	0.141±0.004	0.606±0.003	0.747±0.007
0.4	1.83E-02	6.76E-03	1.50E-02	3.27E-03	0.067±0.013	0.697±0.01	0.763±0.024
0.6	1.17E-02	9.88E-03	9.55E-03	4.69E-03	0.046±0.004	0.762±0.037	0.808±0.041
0.08	6.98E-03	1.15E-02	5.68E-03	5.44E-03	0.025±0.006	0.805±0.019	0.829±0.025
<u>30% (wt/wt) Acetone</u>							
0.05	3.23E-02	4.58E-04	2.54E-02	1.92E-04	0.373±0.038	0.407±0.001	0.781±0.037
0.1	2.97E-02	1.51E-03	2.33E-02	6.30E-04	0.257±0.013	0.586±0.013	0.843±0.001
0.2	2.48E-02	3.69E-03	1.94E-02	1.52E-03	0.133±0.009	0.708±0.001	0.841±0.007
0.4	1.80E-02	7.23E-03	1.39E-02	2.88E-03	0.069±0.011	0.758±0.007	0.827±0.019
0.6	1.21E-02	1.03E-02	9.28E-03	3.99E-03	0.038±0.005	0.805±0.021	0.843±0.016
0.08	7.22E-03	1.25E-02	5.52E-03	4.78E-03	0.015±0.007	0.848±0.003	0.863±0.004
<u>50% (wt/wt) Acetone</u>							
0.05	3.00E-02	7.20E-04	2.17E-02	2.27E-04	0.392±0.021	0.256±0.006	0.648±0.027
0.1	2.87E-02	1.77E-03	2.06E-02	5.47E-04	0.253±0.011	0.426±0.009	0.678±0.002
0.2	2.35E-02	3.96E-03	1.68E-02	1.20E-03	0.151±0.013	0.547±0.022	0.698±0.009
0.4	1.53E-02	7.84E-03	1.09E-02	2.29E-03	0.079±0.005	0.640±0.001	0.719±0.005
0.6	1.12E-02	1.03E-02	7.84E-03	2.92E-03	0.035±0.001	0.676±0.013	0.712±0.014
0.08	6.85E-03	1.29E-02	4.75E-03	3.52E-03	0.024±0.001	0.663±0.026	0.687±0.027
<u>70% (wt/wt) Acetone</u>							
0.05	3.27E-02	8.43E-04	2.02E-02	1.54E-04	0.491±0.042	0.260±0.005	0.750±0.036
0.1	3.06E-02	1.89E-03	1.88E-02	3.39E-04	0.348±0.002	0.430±0.013	0.778±0.015
0.2	2.51E-02	3.97E-03	1.54E-02	7.05E-04	0.240±0.007	0.528±0.010	0.769±0.002
0.4	1.69E-02	7.62E-03	1.02E-02	1.30E-03	0.147±0.006	0.648±0.005	0.795±0.001
0.6	1.18E-02	1.02E-02	7.05E-03	1.68E-03	0.078±0.001	0.682±0.023	0.760±0.023
0.08	6.91E-03	1.22E-02	4.11E-03	1.98E-03	0.053±0.001	0.754±0.019	0.807±0.019

Figure 4.2. Ca-Na exchange isotherms on Wyoming Bentonite at 0.03 mol L⁻¹ total electrolyte concentration in methanol, ethanol and acetone-water systems.

Table 4.4. Values of Q_0 in cosolvent solutions as determined by a cubic polynomial regression of Q versus equivalent fraction of Ca in solution.

Solvent	% wt	Q_0
Methanol	0	0.865
	10	1.247
	30	1.191
	50	1.328
	70	1.384
Ethanol	8.6	1.012
	26.6	0.919
	46.3	1.008
	67	1.018
Acetone	10	0.719
	30	0.785
	50	0.640
	70	0.738

Figure 4.3. Exchange isotherms for CaCl^+ (left-hand side) and Ca^{2+} (right-hand side) on Wyoming bentonite at constant total chloride concentration (0.03 mol L^{-1}) in methanol water systems, corrected for CaCl^+ .

Figure 4.4. Exchange isotherms for CaCl^+ (left-hand side) and Ca^{2+} (right-hand side) on Wyoming bentonite at constant total chloride concentration (0.03 mol L^{-1}) in ethanol-water systems, corrected for CaCl^+ . Full symbol; water, hollow symbols; studied cosolvent.

Figure 4.5. Exchange isotherms for CaCl^+ (left-hand side) and Ca^{2+} (right-hand side) on Wyoming bentonite at constant total chloride concentration (0.03 mol L^{-1}) in acetone-water systems, corrected for CaCl^+ . Full symbol; water, hollow symbols; studied cosolvent.

When the total adsorbed metal charge, Q was corrected for CaCl^+ adsorption, no change in Q_0 was observed (Table 4.5). This implies that the observed increase in the values of Q in Table 4.1 for methanol-water systems with percent weight cosolvent were experimental artifact resulting from assigning a value of +2 to all adsorbed Ca species rather than an increase in the number of apparent sites available for adsorption as reported by Xue and Traina, (1996a) for goethite in acetone and methanol-water mixtures. In their work, this increase was mainly attributed to the increased strength of some originally weak iron oxide and iron hydroxide bonds in water because of the increased long range electrostatic bonds. In addition, the low dielectric constant observed at high cosolvent fractions decreased the solubility of H^+ ions and reduced the solvation forces that usually compete with surface sites for H^+ protonation. In this experiment, bentonite clays are predominantly permanent charge clays (>70% of total adsorbed metal charge) with a small percentage of pH-dependent charges (Anderson and Sposito, 1991). Any change in the number of apparent sites within the pH-dependent charges as a function of cosolvent fraction is likely too small to be detected in this experiment.

Decreasing the solvent dielectric constant has been reported to affect the intracrystalline swelling of clay minerals. Brindley *et al.*, (1969) reported that the intracrystalline swelling of Ca-montmorillonite increases with an increase in the fraction of organic solvent (f_c) up to a certain threshold dictated by the medium dielectric constant, after which collapse of the interlayer spacing occurs. They explained this observed phenomena through the effects of solvents on the cations hydration whereby expansion occurred as a result of water molecules being replaced

with those of the solvent. In this study, the effect of cosolvents on the intracrystalline swelling of Na-bentonite has not been experimentally determined. However visual observations of clays during the exchange experiments indicate that flocculation was much greater in solutions where the percent weight cosolvent exceeded 50%. Despite the changes in the intracrystalline swelling of Na-bentonite as a function of exchangeable Ca fraction and percent weight cosolvent, flocculation does not necessarily result in inaccessible interlayers because we note that there were no changes in Q and Q_0 as a function of cosolvent concentrations. However, the effect of exchanger composition and cosolvent concentration on physical structure of clays deserves further study.

Calcium-sodium exchange on Wyoming bentonite in chloride background in mixed-water systems can be expected to involve the ternary cation exchange (Ca^{2+} - CaCl^+ - Na^+). In the three studied cosolvents, the affinity of the surface for Ca^{2+} , after correction for CaCl^+ formation in the surface and in solution, is larger than that of Na^+ , with the magnitude decreasing as we move from methanol to ethanol to acetone. The selectivity of bentonite for Ca in cosolvents is primarily driven by solvent-surface interactions. Both electrostatic and specific surface-cosolvent interactions such as dielectric saturation are believed to control these interactions and hence the selectivity of the surface for a specific cation.

CHAPTER V

Effect of Cosolvents on the Retention Mechanisms of Cd and Zn on Clay Minerals

5.1 Introduction

Transition metal sorption to clay minerals has been widely studied in the past and various mechanisms of retention have been proposed. Authors generally agree that at low initial metal concentration, sorption is a process (Elrashidi and O'Connor, 1982) that involves physical, electrostatic (Shainberg and Kemper, 1967) and nonelectrostatic (Kinniburgh *et al.*, 1975) attractions to the surface, depending on the nature of the surface and the cation involved. In non-aqueous and mixed aqueous organic solvents, where changing the solvent properties (dielectric constant, viscosity, acidity, etc), is expected to affect both metal and surface physicochemical properties, the mechanisms of metal sorption are yet to be elucidated (Miller *et al.*, 1991).

Because of the important role played by the solvent dielectric constant in determining the electrostatic interactions between oppositely charged ions in a liquid medium (i.e. Debye-Hückel Eq, Born Eq and Coulomb's Law), it is often used as the parameter to predict the effect of solvents on chemical reactions (Izutsu, 2002).

However in solvents with high dielectric constant ($\epsilon_r > 40$) and for easily polarizable anions at low ionic strength, the electrostatic forces are too weak to affect ion pairing (Figure 3.3 and 3.4) and activity (Figure 1.2). In these media, solvent microscopic properties such as acidity/basicity, the ability to form hydrogen and covalent character bonds also affect chemical equilibria.

The effects of solvents on clay surface reactivity include increased surface acidity (Loeppert *et al.*, 1977; Loeppert *et al.*, 1979) in kaolinite, decreased surface potential of silicates, (Kosmulski and Matijevic, 1992), and decreased surface charge density coupled with increased solvent adsorption in rutiles (Kosmulski, 1990; Kosmulski, 1996). An increase in the surface charge density of goethite in acetone and methanol-water mixed systems with increasing cosolvent volume fraction as compared to aqueous systems was reported by Xue and Traina (1996a).

In aqueous systems, direct and indirect effects of pH on cation sorption include increased surface charge density induced by high pH values, and changes in metal solubility, speciation and chelation. These effects are more pronounced in variable than in permanent-charge clays (Naidu *et al.*, 1997). In these latter, the effect of pH is related to the type of adsorption sites (interlayer versus planar and edge sites) and their relative contribution to the adsorption of a particular metal. According to Abollino *et al.*, (2003), Cd^{2+} sorption on Na-montmorillonite occurs mainly through the formation of inner-sphere complexes with silanol and aluminol functional groups at the clay particle edge, whereas Zn sorption occurs mainly through ion exchange in the interlayers. For both metals, no pH effect was observed at values ranging from 5.5 to 8.0. For illite where the edge sites are the primary sorption sites, Cd sorption strongly increased within the pH range $6.0 \leq \text{pH} \leq 8.0$. In non-aqueous and mixed aqueous organic solvents, the poor control of pH makes it difficult to generate a simple model to predict the behavior of metals in hazardous systems (Kosmulski, 1995).

The objective of this study is to describe Cd and Zn sorption to two clay minerals, bentonite and illite in cosolvents of high dielectric constant at low ionic strength. The pH of the equilibrium solution was determined to provide an estimate of the pH range at which these reactions take place. The alcohol-water mixtures selected for this study represent neutral amphiprotic solvents (methanol and ethanol). Illites are nonexpanding clays with low cation exchange capacity, high surface charge density and high edge/interlayer ratio (Anderson and Sposito, 1991). Bentonites are highly expandable clays with high cation exchange capacity, lower edge/interlayer ratio and lower surface charge density than illites. Cd and Zn are both important environmental pollutants with the mechanisms of retention on bentonite and illite fairly well described in aqueous media (Ziper *et al.*, 1988; Van Bladel, 1993).

5.2 Materials and Methods

5.2.1 Clays

Wyoming Bentonite clay was obtained from the American Colloid Company at Upton Plant, Wyoming. Illite (IMt-2), Silver Hill was obtained from the Source Clay Minerals Repository, University of Missouri, MO. Before clay size separation, soluble and insoluble salts, organic matter and iron oxides were removed according to standard procedures (Kunze and Dixon, 1986). The <2.0 μm clay fraction was separated by repeated washing and centrifugation (Jackson, 1974). Ca-saturated clays were prepared by repeated equilibration with 0.5 M $\text{Ca}(\text{NO}_3)_2$. Four washings with distilled water were necessary to remove excess salts. The salt-free gel was freeze-dried and stored for further analysis. The CECs were determined by Ca-Mg exchange

and found to be 108.63 and 23.81 cmol_c kg⁻¹ for bentonite and illite respectively, which compares well to literature values (Sposito, 1998).

5.2.2 *Reagents*

The solvents used in this study were deionized water, HPLC grade methanol and reagent grade ethanol. All solvents were used without further purification. The properties of these cosolvents are presented in Table 2.1. Cd(NO₃)₂·4H₂O and Zn(NO₃)₂·6H₂O stock solutions were prepared in distilled water from reagent grade salts and were standardized against 0.01M EDTA.

5.2.3 *Adsorption studies*

Cd and Zn adsorption to Bentonite and Illite were studied using batch-type experiments. Solids concentrations were 1.0g L⁻¹ for Zn and 2.67 g L⁻¹ for Cd. The Ca-saturated samples were placed in 15-ml polyethylene centrifuge tube (Fisher Scientific, Pittsburgh, PA), found previously not to sorb Cd and Zn, with appropriate amounts of distilled water and methanol or ethanol to yield 0, 10, 30, and 50% (wt/wt) cosolvent concentrations. All experiments were conducted in 2.5 mM Ca(NO₃)₂ as the background electrolyte. Initial Cd and Zn concentrations ranged from 0 to 10⁻⁵ M. Dispersed samples were placed on an end-over-end shaker for 16 hours at room temperature for the equilibration period. The suspensions were centrifuged at 6000rpm for 20 min, (for the water treatment, an additional 20 min was necessary to settle the clays) and 5 mL of supernatant was removed, evaporated to dryness in Pyrex tubes on a Technicon BD-40 digestion block at 130°C. The evaporates were

then dissolved in 0.5M HNO₃ for metal determination. Equilibrium Cd and Zn concentrations were determined using a Perkin Elmer 400 Inductively Coupled plasma spectrometer.

5.2.4 pH determination

Equilibrium pH was determined spectrophotometrically (Yamazaki, 1992 and Yao *et al.*, 2001) using the conditional dissociation constants, $s\text{p}K_I$, (Table 2.5) and the absorptive properties (Table 2.4) of Methyl Red (MR) and Phenol Red (PR) indicators, as described in Chapter 2. Briefly, exactly 2 ml of supernatant solution were placed in 15-mL centrifuge tube with appropriate volume of either indicator solution to yield a total indicator concentration of 2.197×10^{-5} for MR and 2.125×10^{-5} mol L⁻¹ for PR, the same total concentration used for the determination of the indicators $s\text{p}K_I$'s. MR was chosen, as opposed to PR, as the appropriate indicator because both its acidic (HMR) and basic (MR) forms absorbed well at $\lambda_{\text{HMR}} = 520$ nm and $\lambda_{\text{MR}} = 425$ nm respectively, indicating that the pH of the solution was within the indicator's buffer region and hence allowing the use of its $s\text{p}K_I$ and absorptive properties for pH determination.

5.2.5 Determination of Stability Constants of the 1:1 ion-pair of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

The stability constants of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in methanol-water and ethanol-water mixtures were determined at $25^\circ\text{C} \pm 0.1$ using conductometric titrations (Table 3.6). Data were treated using the

Fuoss and Edelson equation (Fuoss and Edelson, 1951). A detailed description of the procedure followed is described in Chapter 3.

5.2.6 *Statistical analysis*

The isotherm parameters (K_f and $1/n$) for Cd^{2+} and Zn^{2+} sorption to bentonite and illite in methanol-water and ethanol-water mixtures were calculated by fitting Freundlich isotherms using both linear and power regression equations, to all data points in the treatments, before and after correction for $\text{Cd}(\text{NO}_3)^+$ and $\text{Zn}(\text{NO}_3)^+$ speciation in solution. Based on the goodness of fit, R^2 , power regression equations were fitted for all treatments except for Cd^{2+} sorption to bentonite where a linear regression equation was more appropriate ($R^2 \geq 0.98$).

A statistical analysis of the data consisted of a factorial experiment for the partitioning coefficients, K_f , for each metal assembled in a Completely Randomized Design including four factors: clay type at two levels (bentonite and illite), cosolvent type at two levels (ethanol and methanol), percent weight cosolvent at four levels (0, 10, 30, and 50%) and pairing at two levels (pairing and no-pairing). The experiment was replicated twice. Statistical analysis of variance was performed using the SAS Statistical Package. Treatment means were separated by the Tukey's Studentized Range (HSD) test at 5% significance levels. Regression analysis was conducted using Excel.

5.3 Results

In this experiment, no significant effect of pairing on the partitioning coefficients of Cd^{2+} and Zn^{2+} to clay minerals was recorded (Table 5.1 and 5.2) because of the low initial metal concentrations and the low ionic strength ($I=0.0075$) used. For Cd^{2+} , there were significant effects due to clay and solvent type and the interactions between clay and %wt cosolvent and solvent and %wt cosolvent (Table 5.1 and 5.2). For Zn^{2+} , all studied factors and their interactions, except for pairing, were highly significant ($p \leq 0.01$).

Cd^{2+} sorption to Wyoming bentonite was linear at all percent weight cosolvents in both methanol and ethanol and the linear partition coefficient, K_f , was constant across all treatments (Table 5.3). Zn^{2+} sorption to Wyoming bentonite was nonlinear for all percent weight cosolvent in both methanol and ethanol (Table 5.3). There is a general trend to decrease K_f with weight percent methanol above 10% methanol. In ethanol, K_f increased from 0 to 10%, was constant between 10% and 30% and decreased at 50% weight cosolvent. The nonlinearity of Zn^{2+} sorption to bentonite, as indicated by changes in the parameter $1/n$, decreased with increasing percent weight cosolvent in both methanol and ethanol except at 30% ethanol (Table 5.3). The relative change in isotherm nonlinearity was larger in methanol than ethanol-water mixtures.

Both Cd^{2+} and Zn^{2+} sorption to illite was nonlinear at all percent weight cosolvent (Table 5.3). For Cd^{2+} , K_f was constant across all treatments except at 50% methanol where K_f decreased. For Zn^{2+} sorption, there is a general trend to increase K_f with increasing percent weight cosolvent in both methanol and ethanol. Both clays

showed a higher affinity for Zn^{2+} than Cd^{2+} (higher K_f values) with the affinity being larger for both metals in illite than bentonite. No specific trend in isotherms nonlinearity could be discerned for Cd^{2+} or Zn^{2+} sorption to illite.

Figure 5.1 is a plot of the changes in the partition coefficient, K_f , for Cd^{2+} and Zn^{2+} sorption on bentonite and illite as a function of $100/\epsilon_r$, where, ϵ_r is the medium dielectric constant. For Cd^{2+} sorption to bentonite and illite in both alcohol-water mixtures, K_f was essentially independent of the medium dielectric constant except at 50% methanol. This indicates that forces other than Coulombic attractions may be involved in Cd^{2+} sorption to both clays in alcohol-water mixtures (Echeverria *et al.*, 2002).

Table 5.1. Analysis of variance for the partitioning coefficient, K_f , of Cd^{2+} on clay minerals in mixed aqueous alcohol mixtures.

Source of variation	Degrees of freedom	p>F
Clay	1	<0.0001
Solvent	1	<0.0001
Clay * Solvent	1	0.5071
% wt cosolvent	3	0.9837
Clay * % wt cosolvent	3	<0.0001
Solvent * % wt cosolvent	2	0.0001
Clay * Solvent * % wt cosolvent	2	0.3702
Pairing	1	0.3778

Table 5.2. Analysis of variance for the partitioning coefficient, K_f , of Zn^{2+} on clay minerals in mixed aqueous alcohol mixtures.

Source of variation	Degrees of freedom	p>F
Clay	1	<0.0001
Solvent	1	<0.0001
Clay * Solvent	1	<0.0001
% wt cosolvent	3	<0.0001
Clay * % wt cosolvent	3	<0.0001
Solvent * % wt cosolvent	2	<0.0001
Clay * Solvent * % wt cosolvent	2	<0.0001
Pairing	1	0.1575

Zn^{2+} sorption, on the other hand, did vary with ϵ_r . For illite where sorption is believed to occur primarily on the edge sites (as indicated by the higher adsorption on illite, large edge/interlayer sites ratio, as compared to bentonite, low interlayer/edge sites ratio), K_f increased almost linearly with $100/\epsilon_r$ except between 10% and 30% weight cosolvent. This suggests that electrostatic forces may be involved in Zn^{2+} retention on illite, an observation further supported by the larger K_f values in ethanol than methanol. In bentonite, K_f decreased almost linearly with $100/\epsilon_r$ in methanol. In ethanol, K_f decreased only after a threshold value of ϵ_r corresponding to 30% cosolvent weight, the same threshold found in the exchange experiment for ethanol-water mixtures (Chapter 4) and in other literature (Brindley *et al.*, 1969).

Percent coverage of bentonite and illite in various cosolvents at low ($2\mu\text{M}$) and high ($10\mu\text{M}$) initial metal concentration is plotted in Figure 5.2. Low total percent coverage was observed for both metals on both clay mineral surfaces. This is attributed to the low initial metal concentrations (0 to $10\mu\text{mol L}^{-1}$) and low ionic strength (0.0075). In all treatments, percent coverage for illite was greater than for bentonite, for both Cd and Zn. This may be related to the high charge density of edge sites (Zipper *et al.*, 1988) and lower CEC of illite. For Cd and Zn on bentonite, % coverage was essentially independent of cosolvent concentration. At higher initial metal concentrations, increasing ethanol concentration to 10% increased % coverage on illite, but increasing methanol concentration had no effect. For Zn on illite, at higher initial metal concentrations, % coverage increased linearly with increasing methanol concentration. In ethanol, the maximum % coverage was observed at 30%.

The effect of $100/\epsilon_r$ on the equilibrium solution pH is presented in Figure 5.3 for Cd and Zn on bentonite and illite. In both clay minerals, pH ranged from 4.5 to 6.9. In ethanol, there is slight increase in pH with decreased ϵ_r for both Zn and Cd on both clay minerals. In methanol, an initial decrease in pH (from 1.27 to 1.35 $100/\epsilon_r$, which corresponds to 0 and 10% methanol respectively) followed by a linear increase (after 1.35) with $100/\epsilon_r$ is observed for both metals on both clay minerals. For Cd^{2+} , higher pH values were recorded in illite as opposed to bentonite in both methanol and ethanol. For Zn^{2+} , no significant difference between clay types was observed.

5.4 Discussion

5.4.1 Mechanisms of Cd Retention

In water treatment, Cd^{2+} sorption to both bentonite and illite at concentrations ranging from 0 to $10 \mu\text{mol L}^{-1}$ was low as expressed by the low partitioning coefficients, K_f (Table 5.3) and the low percent surface coverage (Figure 5.2). This low sorption is explained by the low initial clay concentration (2.67 g L^{-1} for both clay types) and the presence of Ca^{2+} both on the clay sorbing sites and as the index cation (Naidu *et al.*, 1998). A detailed analysis of the effect of clay concentration on cation adsorption is given by Nir (1986) and a study of this effect on Cd sorption to montmorillonite is presented by Hirsh *et al.*, (1989). Briefly, increasing clay concentration should increase the total amount of Cd sorbed. The effect of index cation on metal sorption was reported by Naidu *et al.*, (1998) who observed that the sorption of Cd in the presence of $0.03 \text{ mol L}^{-1} \text{ NaNO}_3$ was at least 2-4 times more than in $0.03 \text{ mol L}^{-1} \text{ Ca(NO}_3)_2$. The effect of index cation can be attributed to

increased competition between Ca^{2+} and Cd^{2+} for sorbing sites, the effect of the divalent cation on the suspension pH and the greater specificity of the divalent Ca^{2+} and its effect on the thickness of the double layer.

In this study, the effect of decreasing ϵ_r on metal complexation in solution was negligible in all treatment and could be ignored. Therefore, any changes in the sorption of Cd^{2+} to either clay mineral can be solely attributed to the effects of cosolvents on the surface properties and its interactions with the metal. At low initial metal concentration, Cd^{2+} sorption to both bentonite and illite in various cosolvents and at various cosolvent fractions, except in 50% methanol on illite, is independent of the solvent dielectric constant and therefore may indicate inner-sphere complexes with aluminol and silanol on the clay edge sites. The edge sites are believed to be the major sites for Cd sorption because of the low initial metal concentration used, the weak ability of Cd^{2+} to compete with interlayer Ca^{2+} ions due to its large hydrated radius (9.7 Å) and its soft Lewis acid character, and the observed higher sorption of Cd^{2+} onto illite (high edge/interlayer sites ratio) as compared to bentonite (low edge/interlayer sites ratio) in all treatments (Figure 5.1). These results correlate well with data reported in aqueous systems (Abollino *et al.*, 2003; Ziper *et al.*, 1988 and Naidu *et al.*, 1994). The nature of bonding between the metal and the edge surface functional groups are believed to be nonelectrostatic as shown by the independent variation of K_f as a function of $100/\epsilon_r$ (Figure 5.1). If electrostatic interactions were involved in the sorption process, a linear increase of K_f with decreasing ϵ_r should have been observed.

Table 5.3. Freundlich constants for Cd^{2+} and Zn^{2+} sorption to Wyoming Bentonite and Illite in methanol-water and ethanol-water mixtures in $2.5 \text{ mmol L}^{-1} \text{ Ca(NO}_3)_2$ background electrolyte. (Solution phase concentrations were $\mu\text{mol L}^{-1}$, solid phase concentrations were $\mu\text{mol g}^{-1}$).

Metal	Cosolvent	% Weight Cosolvent	Bentonite		Illite	
			K_f	1/n	K_f	1/n
Cd^{2+}	Water	0	0.26	1.0	0.69	0.47
	Methanol	10	0.26	1.0	0.74	0.64
		30	0.29	1.0	0.71	0.53
		50	0.30	1.0	0.59	0.63
	Ethanol	10	0.27	1.0	0.72	0.40
		30	0.30	1.0	0.71	0.51
		50	0.31	1.0	0.69	0.43
	Water	0	1.03	0.42	1.42	0.28
Zn^{2+}	Methanol	10	1.02	0.55	1.67	0.23
		30	0.87	0.68	1.47	0.31
		50	0.64	1.05	1.63	0.40
	Ethanol	10	1.10	0.68	2.87	0.54
		30	1.11	0.57	1.59	0.64
		50	0.75	0.92	2.31	0.54

The decrease in K_f for Cd at 50% methanol onto illite clays is not clearly understood and may involve the participation of different surface functional groups in the sorption process, some of which may be activated or depressed by changing the solvent dielectric constant, ϵ_r . The percent Cd^{2+} coverage to both bentonite and illite was essentially constant and independent of the percent weight cosolvent (Figure 5.2). Any observed deviations (less than 0.5%) are considered to be within experimental error. However, this figure was plotted using the cation exchange capacity value of illite and bentonite, as measured in water and not in the various cosolvents. More specific conclusion could be drawn if CEC had been measured in the various cosolvents. An effort to measure these values was made; however procedure complications arose from increased metal complexation and precipitation when high concentration extracting solutions were used and unusually low CEC values when lower concentration extraction solutions were used. Evidence from the literature suggests both a decrease and an increase in the surface charge density in response to cosolvents (Xue and Traina, 1996a; Kosmulski, 1990). The former is related to interlayer collapse (Brindley *et al.*, 1969) or solvent molecules adsorption whereas the latter is explained by an activation of the surface functional groups as a result of decreased solvent dielectric constant (Xue and Traina, 1996a). Given the fact that Cd^{2+} is mostly adsorbed to edge surface sites, a collapse in the interlayer spacing would not affect its percent metal coverage on either bentonite or illite. Whether any solvent-surface interactions are affecting the edge surface sites on illite cannot be deduced from this study, but warrants further investigation.

Figure 5.1. Effect of $100/\epsilon_r$ on the partition coefficient, K_f , of Cd^{2+} and Zn^{2+} sorption to clay minerals in 2.5 mmol L^{-1} $\text{Ca}(\text{NO}_3)_2$ background electrolyte.

Figure 5.2. Cosolvent effect on % metal coverage at low ($2\mu\text{M}$) and high ($10\mu\text{M}$) initial metal concentrations, C_i : □, Low C_i , EtOH; ○, High C_i , EtOH; ◇, Low C_i , MeOH; △, High C_i , MeOH.

5.4.2 Mechanisms of Zn Retention

Zn sorption varied significantly between clay types in various solvents and at various cosolvent fractions (Table 5.2) suggesting different mechanisms for its retention by clay minerals. The nearly linear increase in Zn^{2+} sorption to illite in both ethanol and methanol (except between 0 and 10% weight cosolvent) with increased $100/\epsilon_r$ (Figure 5.1) supports that at least some Zn^{2+} sorption to illite is due to electrostatic interactions between the metal and the edge sorbing sites. The sharp increase in Zn^{2+} sorption to illite between 0 and 10% weight cosolvent in both methanol and ethanol coupled with an increase in the percentage surface coverage (Figure 5.3) may be explained by increased availability of functional surface sites (Xue and Traina, 1996a). The results of Figure 5.2 further support this conclusion; however due to the same limitations discussed above, further investigation is necessary. In bentonite, Zn^{2+} sorption seems to involve two mechanisms: cation exchange between Zn^{2+} and Ca^{2+} in the interlayers and formation of electrostatic bonds between Zn^{2+} and the edge surface sites. The decrease in K_f of Zn^{2+} onto bentonite in both ethanol and methanol and the threshold at which this decrease is occurring (>30% for ethanol and >10% for methanol) suggest a reduction in the surface charge density as a result of either a partial collapse in the interlayer spacing (Brindley *et al.*, 1969) or a reduction in the number of apparent surface functional group as a result of solvent adsorption (Xue and Traina, 1996a). The exchange of interlayer cations with Zn^{2+} has been reported in aqueous systems at higher initial Zn^{2+} concentration (10^{-4}M) (Abollino *et al.*, 2003), however, it cannot be excluded from this experiment given the low hydrated radius of Zn^{2+} ($7.4\text{\AA}$) and its

intermediate Lewis acid character. Why both increased (illite) and decreased (bentonite) surface charge density are believed to occur may be related to the differential participation of aluminol and silanol surface edge groups in the sorption process.

5.4.3 Effect of pH

In aqueous systems, the effect of pH on metal sorption varies between clay minerals and metal type. In the range 2.5-8.0, no effect of pH on Zn^{2+} sorption to montmorillonite is reported whereas below $\text{pH} \leq 3.5$, Cd^{2+} sorption strongly decreased (Abollino *et al.*, 2003). In illite, Cd^{2+} is strongly affected by pH values for $4.0 \leq \text{pH} \leq 6.0$ (Echeverria *et al.*, 2002). In this experiment, the equilibrium solution pH was measured and ranged from 4.5-7.0. In this range and for bentonite clays, pH is believed to have minimum effect on Cd^{2+} and Zn^{2+} sorption for the following reasons; first, the low initial metal concentration and the low percent metal coverage (0.5-4%) (Figure 5.2); second, the constant pH range within a single treatment and with increased metal concentration; and third, the lack of correspondence between changes in pH and K_f with the reciprocal dielectric constant (Figure 5.1 and 5.4). To further investigate this relationship, we calculated the equilibrium pH that would result if all sorbed Cd^{2+} and Zn^{2+} displaced H^+ ions from the surfaces. For a maximum coverage of 0.5 and 1% (Figure 5.2) and for a CEC value of $108.63 \text{ cmol}_c \text{ Kg}^{-1}$ and a solid concentration of 1.0 g L^{-1} (Zn^{2+}) and 2.67 g L^{-1} (Cd^{2+}), these values were calculated as 5.3 and 4.5 for Zn^{2+} and Cd^{2+} , respectively. For illite, these values were calculated as 5.0 and 4.9 for Zn^{2+} and Cd^{2+} , respectively (CEC $23.81 \text{ cmol}_c \text{ Kg}^{-1}$). For bentonite,

the similarity in variation between pH and pK_a of methyl red with the reciprocal dielectric constant (Table 2.5) and the range of pH calculated (for complete H^+ displacement) and measured (falling within the no pH range effect on Cd^{2+} and Zn^{2+} sorption to bentonite in water) suggest strong solvent-solvent interactions rather than metal-surface interactions. This conclusion is preliminary and needs further investigation. A better assessment of pH effect would be possible by comparing initial to equilibrium solution pH, as well as cosolvent pH to the pH of clay suspensions when no metals are added. In this way, the source of pH variation can be isolated and its effect on metal sorption identified.

This study is among the first to try to isolate the effects of solvents on metal-surface reactions. Sorption of Cd and Zn to clay minerals at low initial metal concentration and low ionic strength was dependent on metal (Zn or Cd), clay type (bentonite or illite), cosolvent type (methanol or ethanol) and cosolvent concentration. No general mechanism of metal retention in cosolvents can yet be described partly because metal-sorption appears to be species, surface and solvent specific, at least for the two metals studied. Cosolvents are clearly affecting metal surface and solution properties. Additional studies on the effects of cosolvents on clay surface properties including surface charge density, surface acidity and interlayer spacing will certainly provide useful insights.

Figure 5.3. Effect of $100/\epsilon_r$ on the equilibrium pH, as determined by spectrophotometry in Cd and Zn sorption to ■ Bentonite and □ Illite clays.

CHAPTER VI

CONCLUSION

In this study, the effect of cosolvents on metal-surface reactions, more specifically exchange and adsorption, has been investigated in an attempt to understand the major physical and chemical processes that control metal-surface interactions in waste disposal sites. Because these surface reactions are a function of metals activities, special attention was given to the effect of these cosolvents on metal single ion activity coefficients (Debye-Hückel equation) and ion-pairing. In the absence of published values for the ion association constants for our selected cosolvents, we determined those experimentally using conductometric methods. The formation of CaCl^+ and $\text{M}(\text{NO}_3)^+$ ($\text{M}=\text{Ca}$, Cd , and Zn) in the studied cosolvents involved, in addition to electrostatic interactions, specific solvent-solute interactions (interactions between the acid-base properties of both solvent and solute) and solvent-solvent interactions such as ion solvation and water structure disruption.

Given the importance of pH in describing metal adsorption processes and mechanisms onto clay minerals, an equation for pH calculation, within the range $4.5 \leq \text{pH} \leq 8.5$, in mixed methanol and ethanol-water systems under specified conditions ($I=2.5 \times 10^{-3} \text{ mol.L}^{-1}$, and $T=25^\circ\text{C} \pm 2.0$) was developed using the conditional dissociation constants, ${}_s\text{pK}_I$, and the absorbance ratios ($A_{\lambda_{m^-}} / A_{\lambda_{HIn}}$) of two sulphonephthalein indicators; methyl red and phenol red. In both cosolvents, ${}_s\text{pK}_I$ varied nonlinearly with the reciprocal solvent dielectric constant indicating that the dissociation of the studied indicators in alcohol-water mixtures is not solely a function of the solvent dielectric constant. Other specific-solvent-indicator

interactions, the nature of which could not be deduced from the current study, were indicated.

In calcium-sodium exchange on Wyoming bentonite (chloride background), the affinity of the surface for Ca^{2+} , after correction for CaCl^+ formation on the surface and in solution, was larger than that of Na^+ , with the magnitude decreasing as we moved from methanol to ethanol to acetone. This implied that specific surface-cosolvent interactions such as dielectric saturation were involved in determining the selectivity of the surface for a specific cation. This increased selectivity of bentonite clays for Ca^{2+} will result in enhanced flocculation of clays in landfill liners and a subsequent increase in hydraulic conductivity. Cadmium and Zn sorption to clay minerals was also affected by cosolvents, but the effects were not simply related to solution dielectric constant. Again, specific solvent-metal and solvent-surface interactions were apparent.

It is not yet possible to predict the effect of cosolvents on metal-surface reactions partly because they appear to be solvent and surface specific. These effects also appear to be metal-specific, at least for the two metals (Cd and Zn) tested here. However, this work suggests that these clay liners, in the presence of cosolvents, are at greater risk of failing and releasing contaminants than what is predicted by studies conducted in aqueous solutions or based on the effect of cosolvents on the physical properties of clays (interlayer spacing). Considerably more research is needed before contaminant transport in cosolvent solutions can be predicted, the way it is now for aqueous solutions. In particular, there is a need to expand the data base of metal-ligand formation constants, particularly in mixed aqueous solutions, and in solutions

that contain more than one cosolvent. Information is also needed on the effects of cosolvents on interlayer clay spacing, especially as a function of interlayer cation composition. There is also a need for an improved understanding of the role of cosolvents on the properties of mineral surface functional groups, especially those with acid-base character. And finally, there is a need to understand the effect of cosolvent type and concentration on the structure of the interfacial region. Contributions in any of these areas can only improve our understanding of contaminant fate and transport in real contaminant plumes.

APPENDIX A
Experimental Data for Indicators

Table A.1. Experimental data for phenol red indicator in water.

	KH ₂ PO ₄ /Na ₂ HPO ₄ ^b	e.m.f ^c	pH ^d	Measured Absorbance		Corrected Absorbance ^e		log [PR ⁻]/[HPR] ^f	pK _I ^g
				λ_{HPR}^{HPR} (measured)	$\lambda_{PR^-}^{PR^-}$ (measured)	λ_{HPR}^{HPR}	$\lambda_{PR^-}^{PR^-}$		
Set I ^a	4	11.3	6.65	0.3743	0.0392	0.3304	0.0368	-1.4422	8.09
	2	-4.2	6.91	0.3634	0.0717	0.3195	0.0693	-1.1532	8.06
	1	-20.6	7.19	0.3387	0.1183	0.2948	0.1159	-0.9089	8.10
	0.5	-35.8	7.45	0.3117	0.2201	0.2678	0.2177	-0.5853	8.03
	0.25	-48.7	7.66	0.2806	0.3111	0.2367	0.3087	-0.3837	8.05
	0.2	-50	7.69	0.2922	0.2985	0.2483	0.2961	-0.4090	8.09
	0.1	-68.2	7.99	0.221	0.5058	0.1771	0.5034	-0.0401	8.03
	0.05	-76.4	8.13	0.1943	0.6021	0.1504	0.5997	0.1192	8.01
Acidic solution				0.3889	0.0024	0.3450			
Basic solution				0.0439	1.0579		1.0555		
R_{PR}^h					0.3270				

^a Each set represents individual replicate

^b This column present the ratio of buffer solution used

^c e.m.f is the electromotive force measured in mV for each solution

^d Calculated from Eq [2.4]

^e Corrected absorbance calculated using Eq [2.14]

^f Calculated using log Eq [2.12]

^g Calculated using Eq [2.15]

^h Calculated using Eq [2.13]

Table A.2. Experimental data for methyl red indicator in water.

	HOAc/NaOAc ^b	e.m.f ^c	pH ^d	Measured Absorbance		Corrected Absorbance ^e		log [MR ⁻]/[HMR] ^f	pK _I ^g
				$\lambda_{MR^-}^{MR^-}$ (measured)	λ_{HMR}^{HMR} (measured)	$\lambda_{MR^-}^{MR^-}$	λ_{HMR}^{HMR}		
Set I ^a	2	112	4.95	0.1925	0.5109	0.1188	0.4678	-0.1278	5.07
	1.5	105.4	5.06	0.2143	0.412	0.1406	0.3689	0.0005	5.06
	1	95.7	5.22	0.2575	0.3351	0.1838	0.292	0.2066	5.02
	0.5	80.4	5.48	0.3204	0.267	0.2467	0.2239	0.4331	5.05
	0.2	55.5	5.90	0.3714	0.13	0.2977	0.0869	0.8273	5.07
	0.25	61.8	5.80	0.3826	0.117	0.3089	0.0739	0.8891	4.91
	0.1	39	6.18	0.4148	0.1003	0.3411	0.0572	0.9990	5.18
	0.05	21.3	6.48	0.4277	0.0537	0.354	0.0106	1.2865	5.19
Acidic solution				0.0737	1.1034		1.0603		
Basic solution				0.4351	0.0431	0.3614			
R_{MR} ^h					2.9339				

^a Each set represents individual replicate^b This column present the ratio of buffer solution used^c e.m.f is the electromotive force measured in mV for each solution^d Calculated from Eq [2.4]^e Corrected absorbance calculated using Eq [2.14]^f Calculated using log Eq [2.12]^g Calculated using Eq [2.15]^h Calculated using Eq [2.13]

Table A.3. Experimental data for phenol red indicator in 30% methanol.

	KH ₂ PO ₄ /Na ₂ HPO ₄ ^b	e.m.f ^c	pH ^d	Measured Absorbance		Corrected Absorbance ^e		log [PR ⁻]/[HPR] ^f	pK _I ^g
				λ_{HPR}^{HPR} (measured)	$\lambda_{PR^-}^{PR^-}$ (measured)	λ_{HPR}^{HPR}	$\lambda_{PR^-}^{PR^-}$		
Set I ^a	4	-19.7	5.79	0.3620	0.0741	0.3227	0.0703	-1.1532	6.94
	2	-37.5	6.09	0.3455	0.1133	0.3062	0.1095	-0.9379	7.03
	1	-55.8	6.40	0.3224	0.1894	0.2831	0.1856	-0.6747	7.07
	0.5	-72.2	6.68	0.2767	0.3358	0.2374	0.3320	-0.3457	7.02
	0.25	-81.1	6.83	0.2572	0.4078	0.2179	0.4040	-0.2232	7.05
	0.2	-85.3	6.90	0.2558	0.4085	0.2165	0.4047	-0.2197	7.12
	0.1	-90.3	6.98	0.2138	0.5411	0.1745	0.5373	-0.0029	6.98
	0.05	-109.1	7.30	0.1686	0.6804	0.1293	0.6766	0.2274	7.07
Set II	4	-21.1	5.81	0.3653	0.0646	0.3260	0.0608	-1.2206	7.03
	2	-37.9	6.10	0.3475	0.1215	0.3082	0.1177	-0.9094	7.00
	1	-56.6	6.41	0.3202	0.2021	0.2809	0.1983	-0.6426	7.05
	0.5	-74.1	6.71	0.2765	0.3450	0.2372	0.3412	-0.3334	7.04
	0.25	-86.7	6.92	0.2375	0.4668	0.1982	0.4630	-0.1229	7.04
	0.2	-86.2	6.91	0.2449	0.4377	0.2056	0.4339	-0.1670	7.08
	0.1	-97	7.09	0.2040	0.5664	0.1647	0.5626	0.0422	7.05
	0.05	-107.2	7.27	0.1768	0.6643	0.1375	0.6605	0.1902	7.08
Acidic solution				0.3810	0.0038	0.3417			
Basic solution				0.0393	1.0630		1.0592		
R _{PR} ^h					0.3226				

^a Each set represents individual replicate^b This column present the ratio of buffer solution used^c e.m.f is the electromotive force measured in mV for each solution^d Calculated from Eq [2.4]^e Corrected absorbance calculated using Eq [2.14]^f Calculated using log Eq [2.12]^g Calculated using Eq [2.15]^h Calculated using Eq [2.13]

Table A.4. Experimental data for methyl red indicator in 30% methanol.

	HOAc/NaOAc ^b	e.m.f ^c	pH ^d	Measured Absorbance		Corrected Absorbance ^e		log [MR ⁻]/[HMR] ^f	pK _I ^g
				$\lambda_{MR^-}^{MR^-}$ (measured)	λ_{HMR}^{HMR} (measured)	$\lambda_{MR^-}^{MR^-}$	λ_{HMR}^{HMR}		
Set I ^a	2	94.5	3.86	0.2600	0.5952	0.1692	0.5634	-0.0562	3.91
	1.5	87	3.98	0.2869	0.5306	0.1961	0.4988	0.0608	3.92
	1	76.4	4.16	0.3211	0.4316	0.2303	0.3998	0.2267	3.94
	0.5	59.3	4.45	0.3738	0.2868	0.2830	0.2550	0.5114	3.94
	0.2	35.3	4.86	0.4244	0.1509	0.3336	0.1191	0.9135	3.94
	0.25	41.3	4.76	0.4124	0.1760	0.3216	0.1442	0.8146	3.94
	0.1	17.7	5.16	0.4163	0.1761	0.3255	0.1443	0.8195	4.34
	0.05	1.4	5.43	0.4422	0.0892	0.3514	0.0574	1.2531	4.18
Set II	2	94	3.87	0.2629	0.6030	0.1721	0.5712	-0.0548	3.92
	1.5	87.2	3.98	0.2854	0.5276	0.1946	0.4958	0.0600	3.92
	1	76.7	4.16	0.3190	0.4374	0.2282	0.4056	0.2164	3.94
	0.5	59.7	4.45	0.3723	0.2853	0.2815	0.2535	0.5117	3.93
	0.2	35.1	4.86	0.4157	0.1483	0.3249	0.1165	0.9116	3.95
	0.25	41.5	4.75	0.4074	0.1721	0.3166	0.1403	0.8197	3.93
	0.1	18.4	5.14	0.4268	0.0881	0.3360	0.0563	1.2420	3.90
	0.05	1.4	5.43	0.4497	0.0585	0.3589	0.0267	1.5947	3.84
Acidic solution				0.0908	1.1040		1.0722		
Basic solution				0.4573	0.0318	0.3665			
R _{MR} ^h					2.9255				

^a Each set represents individual replicate^b This column present the ratio of buffer solution used^c e.m.f is the electromotive force measured in mV for each solution^d Calculated from Eq [2.4]^e Corrected absorbance calculated using Eq [2.14]^f Calculated using log Eq [2.12]^g Calculated using Eq [2.15]^h Calculated using Eq [2.13]

Table A.5. Experimental data for phenol red indicator in 50% methanol.

	KH ₂ PO ₄ /Na ₂ HPO ₄ ^b	e.m.f ^c	s _p H ^d	Measured Absorbance		Corrected Absorbance ^e		log [PR ⁻]/[HPR] ^f	s _p K _i ^g
				λ_{HPR}^{HPR} (measured)	$\lambda_{PR^-}^{PR^-}$ (measured)	λ_{HPR}^{HPR}	$\lambda_{PR^-}^{PR^-}$		
Set I ^a	4	-51.1	7.56	0.3592	0.0647	0.3189	0.0630	-1.1928	8.76
	2	-67.2	7.84	0.3454	0.1155	0.3051	0.1138	-0.9168	8.75
	1	-83.1	8.11	0.3187	0.1870	0.2784	0.1853	-0.6652	8.77
	0.5	-94.6	8.30	0.2855	0.2921	0.2452	0.2904	-0.4150	8.72
	0.25	-116.7	8.67	0.2233	0.4863	0.1830	0.4846	-0.0655	8.74
	0.2	-111.5	8.59	0.2462	0.4098	0.2059	0.4081	-0.1913	8.78
	0.1	-129.3	8.89	0.1825	0.6030	0.1422	0.6013	0.1377	8.75
	0.05	-132.2	8.94	0.1772	0.6242	0.1369	0.6225	0.1693	8.77
Set II	4	-50.3	7.55	0.3580	0.0637	0.3177	0.0620	-1.1981	8.75
	2	-69.1	7.87	0.3373	0.1210	0.2970	0.1193	-0.8846	8.75
	1	-84	8.12	0.3125	0.1951	0.2722	0.1934	-0.6369	8.76
	0.5	-100.2	8.39	0.2693	0.3322	0.2290	0.3305	-0.3291	8.72
	0.25	-109.2	8.55	0.2470	0.4166	0.2067	0.4149	-0.1859	8.73
	0.2	-95.2	8.31	0.3221	0.2187	0.2818	0.2170	-0.6019	8.91
	0.1	-122.8	8.78	0.2126	0.5317	0.1723	0.5300	-0.0005	8.78
	0.05	-131.5	8.92	0.2090	0.5376	0.1687	0.5359	0.0135	8.91
Acidic solution				0.3769	0.0017	0.3366			
Basic solution				0.0403	1.0382		1.0365		
R_{PR}^h					0.3247				

^a Each set represents individual replicate^b This column present the ratio of buffer solution used^c e.m.f is the electromotive force measured in mV for each solution^d Calculated from Eq [2.4]^e Corrected absorbance calculated using Eq [2.14]^f Calculated using log Eq [2.12]^g Calculated using Eq [2.15]^h Calculated using Eq [2.13]

Table A.6. Experimental data for methyl red indicator in 50% methanol.

	HOAc/NaOAc ^b	e.m.f ^c	s pH ^d	Measured Absorbance		Corrected Absorbance ^e		log [MR ⁻]/[HMR] ^f	s pK _I ^g
				$\lambda_{MR^-}^{MR^-}(measured)$	$\lambda_{HMR}^{HMR}(measured)$	$\lambda_{MR^-}^{MR^-}$	λ_{HMR}^{HMR}		
Set I ^a	2	66.6	5.57	0.3142	0.4671	0.2089	0.4447	0.1024	5.47
	1.5	59.1	5.70	0.3403	0.4140	0.2350	0.3916	0.2088	5.49
	1	48.3	5.88	0.3722	0.3310	0.2669	0.3086	0.3675	5.52
	0.5	31.6	6.17	0.4077	0.2099	0.3024	0.1875	0.6382	5.53
	0.25	14	6.46	0.4350	0.1272	0.3297	0.1048	0.9283	5.54
	0.2	6.9	6.58	0.4458	0.1069	0.3405	0.0845	1.0358	5.55
	0.1	-9	6.85	0.4590	0.0667	0.3537	0.0443	1.3328	5.52
	0.05	-26.3	7.15	0.4596	0.0412	0.3543	0.0188	1.7058	5.44
Set II	2	67	5.57	0.3235	0.4724	0.2182	0.4500	0.1162	5.45
	1.5	59.4	5.70	0.3425	0.4100	0.2372	0.3876	0.2173	5.48
	1	48.6	5.88	0.3686	0.3240	0.2633	0.3016	0.3716	5.51
	0.5	32.1	6.16	0.4191	0.2123	0.3138	0.1899	0.6487	5.51
	0.25	13.9	6.47	0.4447	0.1291	0.3394	0.1067	0.9331	5.53
	0.2	7.5	6.57	0.4472	0.1097	0.3419	0.0873	1.0235	5.55
	0.1	-9.2	6.86	0.4646	0.0667	0.3593	0.0443	1.3396	5.52
	0.05	-25.6	7.13	0.4688	0.0407	0.3635	0.0183	1.7286	5.40
Acidic solution				0.1053	1.0169	0.9945			
Basic solution				0.4743	0.0224	0.3690			
R _{MR} ^h				2.6951					

^a Each set represents individual replicate^b This column present the ratio of buffer solution used^c e.m.f is the electromotive force measured in mV for each solution^d Calculated from Eq [2.4]^e Corrected absorbance calculated using Eq [2.14]^f Calculated using log Eq [2.12]^g Calculated using Eq [2.15]^h Calculated using Eq [2.13]

Table A.7. Experimental data for phenol red indicator in 10% ethanol.

	KH ₂ PO ₄ /Na ₂ HPO ₄ ^b	e.m.f ^c	pH ^d	Measured Absorbance		Corrected Absorbance ^e		log [PR ⁻]/[HPR] ^f	pK _I ^g
				λ_{HPR}^{HPR} (measured)	$\lambda_{PR^-}^{PR^-}$ (measured)	λ_{HPR}^{HPR}	$\lambda_{PR^-}^{PR^-}$		
Set I ^a	4	13.7	6.64	0.3681	0.0388	0.3268	0.0359	-1.4456	8.09
	2	-4.5	6.95	0.3547	0.0759	0.3134	0.0730	-1.1191	8.07
	1	-21.6	7.24	0.3409	0.1326	0.2996	0.1297	-0.8500	8.09
	0.5	-38.9	7.53	0.3067	0.2326	0.2654	0.2297	-0.5491	8.08
	0.25	-43	7.60	0.2995	0.2582	0.2582	0.2553	-0.4913	8.09
	0.2	-29.6	7.38	0.3228	0.1868	0.2815	0.1839	-0.6713	8.05
	0.1	-55.2	7.81	0.2732	0.3446	0.2319	0.3417	-0.3180	8.13
	0.05	-65.6	7.99	0.2387	0.4478	0.1974	0.4449	-0.1335	8.12
Set II	4	12.8	6.66	0.3700	0.0449	0.3287	0.0420	-1.3799	8.04
	2	-4.9	6.96	0.3551	0.0785	0.3138	0.0756	-1.1045	8.06
	1	-20.7	7.23	0.3384	0.1321	0.2971	0.1292	-0.8480	8.07
	0.5	-37	7.50	0.3067	0.2246	0.2654	0.2217	-0.5645	8.07
	0.25	-52.6	7.77	0.2727	0.3327	0.2314	0.3298	-0.3325	8.10
	0.2	-40.4	7.56	0.2997	0.2361	0.2584	0.2332	-0.5309	8.09
	0.1	-68.7	8.04	0.2241	0.4891	0.1828	0.4862	-0.0615	8.10
	0.05	-71.6	8.09	0.2163	0.5123	0.1750	0.5094	-0.0224	8.11
Acidic solution				0.3788	0.0029	0.3375			
Basic solution				0.0413	1.0372		1.0343		
R _{PR} ^h					0.3263				

^a Each set represents individual replicate^b This column present the ratio of buffer solution used^c e.m.f is the electromotive force measured in mV for each solution^d Calculated from Eq [2.4]^e Corrected absorbance calculated using Eq [2.14]^f Calculated using log Eq [2.12]^g Calculated using Eq [2.15]^h Calculated using Eq [2.13]

Table A.8. Experimental data for methyl red indicator in 10% ethanol.

	HOAc/NaOAc ^b	e.m.f ^c	<i>s</i> pH ^d	Measured Absorbance		Corrected Absorbance ^e		log [MR ⁻]/[HMR] ^f	<i>s</i> pK _I ^g
				$\lambda_{MR^-}^{MR^-}$ (measured)	λ_{HMR}^{HMR} (measured)	$\lambda_{MR^-}^{MR^-}$	λ_{HMR}^{HMR}		
Set I ^a	2	120.5	4.84	0.1983	0.6855	0.1263	0.6435	-0.2498	5.09
	1.5	112.9	4.97	0.2248	0.6272	0.1528	0.5852	-0.1258	5.09
	1	102.4	5.14	0.2611	0.5235	0.1891	0.4815	0.0515	5.09
	0.5	85.1	5.44	0.3152	0.3573	0.2432	0.3153	0.3446	5.09
	0.25	60.9	5.85	0.3747	0.1971	0.3027	0.1551	0.7478	5.10
	0.2	67	5.74	0.3633	0.2295	0.2913	0.1875	0.6487	5.09
	0.1	43.8	6.14	0.4017	0.1229	0.3297	0.0809	1.0676	5.07
	0.05	26.2	6.43	0.4141	0.0795	0.3421	0.0375	1.4175	5.02
Set II	2	120.5	4.84	0.1931	0.6858	0.1211	0.6438	-0.2682	5.11
	1.5	113	4.97	0.2236	0.6232	0.1516	0.5812	-0.1262	5.09
	1	102.5	5.14	0.2542	0.5254	0.1822	0.4834	0.0336	5.11
	0.5	85.2	5.44	0.3143	0.3568	0.2423	0.3148	0.3437	5.09
	0.25	60.9	5.85	0.3714	0.1927	0.2994	0.1507	0.7555	5.09
	0.2	67.3	5.74	0.3583	0.2247	0.2863	0.1827	0.6525	5.09
	0.1	44	6.13	0.3956	0.1190	0.3236	0.0770	1.0809	5.05
	0.05	26.6	6.43	0.4070	0.0778	0.3350	0.0358	1.4285	5.00
Acidic solution				0.0720	1.0872		1.0452		
Basic solution				0.4366	0.0420	0.3646			
R_{MR} ^h					2.8667				

^a Each set represents individual replicate^b This column present the ratio of buffer solution used^c e.m.f is the electromotive force measured in mV for each solution^d Calculated from Eq [2.4]^e Corrected absorbance calculated using Eq [2.14]^f Calculated using log Eq [2.12]^g Calculated using Eq [2.15]^h Calculated using Eq [2.13]

Table A.9. Experimental data for phenol red indicator in 30% ethanol.

	$\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ ^b	e.m.f ^c	$s\text{pH}$ ^d	Measured Absorbance		Corrected Absorbance ^e		$\log [\text{PR}^-]/[\text{HPR}]$ ^f	$s\text{pK}_I$ ^g
				$\lambda_{\text{HPR}}^{\text{HPR}}$ (measured)	$\lambda_{\text{PR}^-}^{\text{PR}^-}$ (measured)	$\lambda_{\text{HPR}}^{\text{HPR}}$	$\lambda_{\text{PR}^-}^{\text{PR}^-}$		
Set I ^a	4	-19.5	7.03	0.3727	0.0476	0.3376	0.0433	-1.3685	8.40
	2	-36.1	7.32	0.3564	0.0815	0.3213	0.0772	-1.0958	8.41
	1	-52.2	7.59	0.3377	0.1339	0.3026	0.1296	-0.8448	8.43
	0.5	-68.6	7.86	0.3055	0.2310	0.2704	0.2267	-0.5531	8.42
	0.25	-80.4	8.06	0.2769	0.3161	0.2418	0.3118	-0.3661	8.43
	0.1	-95.1	8.31	0.2385	0.4437	0.2034	0.4394	-0.1420	8.45
	0.05	-100.2	8.40	0.2238	0.4958	0.1887	0.4915	-0.0608	8.46
Set II	4	-20.5	7.05	0.3695	0.0406	0.3344	0.0363	-1.4409	8.49
	2	-36.5	7.32	0.3581	0.0842	0.3230	0.0799	-1.0832	8.40
	1	-50.7	7.56	0.3404	0.1302	0.3053	0.1259	-0.8612	8.42
	0.5	-69	7.87	0.3126	0.2411	0.2775	0.2368	-0.5454	8.42
	0.25	-81.8	8.09	0.2719	0.3262	0.2368	0.3219	-0.3432	8.43
	0.1	-94	8.29	0.2444	0.4297	0.2093	0.4254	-0.1685	8.46
	0.05	-101.6	8.42	0.2147	0.5317	0.1796	0.5274	-0.0087	8.43
Acidic solution				0.3822	0.0043	0.3471			
Basic solution				0.0351	1.0442		1.0399		
R_{PR} ^h					0.3338				

^a Each set represents individual replicate^b This column present the ratio of buffer solution used^c e.m.f is the electromotive force measured in mV for each solution^d Calculated from Eq [2.4]^e Corrected absorbance calculated using Eq [2.14]^f Calculated using log Eq [2.12]^g Calculated using Eq [2.15]^h Calculated using Eq [2.13]

Table A.10. Experimental data for methyl red indicator in 30% ethanol.

	HOAc/NaOAc ^b	e.m.f ^c	<i>s</i> pH ^d	Measured Absorbance		Corrected Absorbance ^e		log [MR ⁻]/[HMR] ^f	<i>s</i> pK _I ^g
				$\lambda_{MR^-}^{MR^-}$ (measured)	λ_{HMR}^{HMR} (measured)	$\lambda_{MR^-}^{MR^-}$	λ_{HMR}^{HMR}		
Set I ^a	2	91.8	5.15	0.2128	0.6760	0.1349	0.6521	-0.2514	5.40
	1.5	84.2	5.28	0.2341	0.6192	0.1562	0.5953	-0.1481	5.43
	1	74	5.45	0.2706	0.5372	0.1927	0.5133	0.0074	5.45
	0.5	56.7	5.75	0.3166	0.3769	0.2387	0.3530	0.2630	5.48
	0.25	32.3	6.16	0.3834	0.2052	0.3055	0.1813	0.6595	5.50
	0.2	38.7	6.05	0.3626	0.2365	0.2847	0.2126	0.5597	5.49
	0.1	15.5	6.44	0.4147	0.1216	0.3368	0.0977	0.9704	5.47
	0.05	-1.6	6.73	0.4294	0.0709	0.3515	0.0470	1.3068	5.42
Set II	2	92.1	5.15	0.2142	0.6858	0.1363	0.6619	-0.2534	5.40
	1.5	84.5	5.28	0.2381	0.6286	0.1602	0.6047	-0.1440	5.42
	1	74	5.45	0.2728	0.5433	0.1949	0.5194	0.0072	5.45
	0.5	57.2	5.74	0.3222	0.3882	0.2443	0.3643	0.2594	5.48
	0.25	32.6	6.15	0.3818	0.2132	0.3039	0.1893	0.6385	5.52
	0.2	38.9	6.05	0.3704	0.2495	0.2925	0.2256	0.5457	5.50
	0.1	15.8	6.44	0.4145	0.1301	0.3366	0.1062	0.9339	5.50
	0.05	-0.9	6.72	0.4305	0.0812	0.3526	0.0573	1.2221	5.50
Acidic solution				0.0779	1.0246	1.0007			
Basic solution				0.4472	0.0239	0.3693			
R_MR^h								2.7097	

^a Each set represents individual replicate^b This column present the ratio of buffer solution used^c e.m.f is the electromotive force measured in mV for each solution^d Calculated from Eq [2.4]^e Corrected absorbance calculated using Eq [2.14]^f Calculated using log Eq [2.12]^g Calculated using Eq [2.15]^h Calculated using Eq [2.13]

Table A.11. Experimental data for phenol red indicator in 50% ethanol.

	$\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ ^b	e.m.f ^c	$s\text{pH}$ ^d	Measured Absorbance		Corrected Absorbance ^e		$\log [\text{PR}^-]/[\text{HPR}]$ ^f	$s\text{pK}_I$ ^g
				$\lambda_{\text{HPR}}^{\text{HPR}}$ (measured)	$\lambda_{\text{PR}^-}^{\text{PR}^-}$ (measured)	$\lambda_{\text{HPR}}^{\text{HPR}}$	$\lambda_{\text{PR}^-}^{\text{PR}^-}$		
Set I ^a	4	-42.5	6.95	0.3674	0.0324	0.3273	0.0322	-1.4881	8.44
	2	-64.5	7.32	0.3566	0.0668	0.3165	0.0666	-1.1579	8.48
	1	-79.8	7.58	0.3462	0.1139	0.3061	0.1137	-0.9111	8.49
	0.5	-90.7	7.77	0.3240	0.1732	0.2839	0.1730	-0.6961	8.46
	0.25	-108.8	8.07	0.2930	0.2940	0.2529	0.2938	-0.4159	8.49
	0.1	-102	7.96	0.2966	0.2465	0.2565	0.2463	-0.4986	8.46
	0.05	-122.6	8.31	0.2979	0.2480	0.2578	0.2478	-0.4982	8.80
Set II	4	-46	7.01	0.3673	0.0408	0.3272	0.0406	-1.3873	8.40
	2	-63	7.30	0.3584	0.0680	0.3183	0.0678	-1.1526	8.45
	1	-80.2	7.59	0.3437	0.1181	0.3036	0.1179	-0.8918	8.48
	0.5	-93.7	7.82	0.3162	0.1956	0.2761	0.1954	-0.6312	8.45
	0.25	-108.1	8.06	0.2870	0.2751	0.2469	0.2749	-0.4344	8.50
	0.1	-121.3	8.28	0.2444	0.3851	0.2043	0.3849	-0.2059	8.49
	0.05	-123.9	8.33	0.2546	0.3935	0.2145	0.3933	-0.2177	8.55
Acidic solution				0.3767	0.0002	0.3366			
Basic solution				0.0401	1.0191		1.0189		
R_{PR} ^h					0.3303				

^a Each set represents individual replicate^b This column present the ratio of buffer solution used^c e.m.f is the electromotive force measured in mV for each solution^d Calculated from Eq [2.4]^e Corrected absorbance calculated using Eq [2.14]^f Calculated using log Eq [2.12]^g Calculated using Eq [2.15]^h Calculated using Eq [2.13]

Table A.12. Experimental data for methyl red indicator in 50% ethanol.

	Measured Absorbance				Corrected Absorbance ^e		log [MR ⁻]/[HMR] ^f	sPK _I ^g	
	HOAc/NaOAc ^b	e.m.f ^c	s _p H ^d	$\lambda_{MR^-}^{MR^-}$ (measured)	λ_{HMR}^{HMR} (measured)	$\lambda_{MR^-}^{MR^-}$			λ_{HMR}^{HMR}
Set I ^a	2	63.5	5.16	0.2608	0.6113	0.1438	0.5730	-0.1649	5.32
	1.5	55.7	5.29	0.2840	0.5651	0.1670	0.5268	-0.0634	5.35
	1	45.5	5.47	0.3068	0.4833	0.1898	0.4450	0.0654	5.40
	0.5	29.8	5.74	0.3568	0.3511	0.2398	0.3128	0.3201	5.41
	0.25	4	6.16	0.4036	0.1969	0.2866	0.1586	0.6925	5.47
	0.2	11.3	6.04	0.3882	0.2206	0.2712	0.1823	0.6080	5.43
	0.1	-11.7	6.42	0.4301	0.1135	0.3131	0.0752	1.0550	5.38
	0.05	-27.4	6.68	0.4454	0.0757	0.3284	0.0374	1.3790	5.32
Set II	2	63.6	5.16	0.2748	0.6228	0.1578	0.5845	-0.1332	5.29
	1.5	56	5.29	0.2794	0.5571	0.1624	0.5188	-0.0689	5.36
	1	45.4	5.47	0.3060	0.4808	0.1890	0.4425	0.0660	5.40
	0.5	29.3	5.74	0.3579	0.3457	0.2409	0.3074	0.3296	5.41
	0.25	4.1	6.16	0.4060	0.1887	0.2890	0.1504	0.7192	5.44
	0.2	11.3	6.04	0.3966	0.2219	0.2796	0.1836	0.6182	5.42
	0.1	-11.2	6.42	0.4336	0.1146	0.3166	0.0763	1.0535	5.37
	0.05	-26.6	6.68	0.4480	0.0724	0.3310	0.0341	1.4226	5.26
Acidic solution				0.1170	0.9719	0.9336			
Basic solution				0.4595	0.0383	0.3425			
R _{MR} ^h				2.7258					

^a Each set represents individual replicate^b This column present the ratio of buffer solution used^c e.m.f is the electromotive force measured in mV for each solution^d Calculated from Eq [2.4]^e Corrected absorbance calculated using Eq [2.14]^f Calculated using log Eq [2.12]^g Calculated using Eq [2.15]^h Calculated using Eq [2.13]

APPENDIX B
Conductance Data for Ca(II), Cd(II), Zn(II) Nitrates and Ca(II) Chlorides in Cosolvents

Table B.1. Conductance of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in alcohol-water mixtures at 25°C.

Methanol											
-----10% Methanol-----				-----30% Methanol-----				-----50% Methanol-----			
Series I		Series II		Series I		Series II		Series I		Series II	
10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ
1.94	106.44	1.94	106.43	1.94	78.49	1.94	78.49	1.94	70.23	1.94	70.33
3.88	105.56	3.88	105.53	3.88	77.80	3.88	77.80	3.88	69.61	3.88	69.68
5.81	104.84	5.81	104.83	5.82	77.31	5.82	77.22	5.82	69.12	5.82	69.08
7.74	104.28	7.74	104.28	7.75	76.87	7.75	76.80	7.75	68.66	7.75	68.64
9.67	103.77	9.67	103.78	9.68	76.33	9.68	76.38	9.68	68.21	9.68	68.19
11.6	103.38	11.6	103.40	11.6	76.08	11.6	76.03	11.6	67.76	11.6	67.74
13.5	102.91	13.5	102.93	13.5	75.62	13.5	75.66	13.5	67.30	13.5	67.36
15.4	102.58	15.4	102.60	15.4	75.36	15.4	75.33	15.4	66.92	15.4	67.03
17.3	102.17	17.3	102.20	17.4	75.06	17.4	75.04	17.4	66.63	17.4	66.67
19.2	101.81	19.2	101.79	19.3	74.79	19.3	74.71	19.3	66.36	19.3	66.40
Ethanol											
-----10% Ethanol-----				-----30% Ethanol-----				-----50% Ethanol-----			
Series I		Series I		Series I		Series I		Series I		Series I	
10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ
1.94	101.64	1.94	101.34	1.94	62.99	1.94	62.91	1.94	50.24	1.94	50.33
3.87	100.86	3.87	100.51	3.88	62.36	3.88	62.36	3.87	49.70	3.87	49.69
5.80	100.17	5.80	99.97	5.81	61.97	5.82	62.04	5.80	49.29	5.81	49.33
7.73	99.65	7.73	99.39	7.74	61.63	7.75	61.68	7.73	48.93	7.73	48.91
9.65	99.17	9.65	98.98	9.67	61.25	9.67	61.28	9.65	48.50	9.66	48.59
11.6	98.80	11.6	98.56	11.6	60.93	11.6	60.95	11.6	48.24	11.6	48.30
13.5	98.41	13.5	98.14	13.5	60.64	13.5	60.66	13.5	47.98	13.5	48.04
15.4	98.02	15.4	97.72	15.4	60.37	15.4	60.39	15.4	47.61	15.4	47.72
17.3	97.67	17.3	97.35	17.3	60.18	17.3	60.13	17.3	47.45	17.3	47.49
19.2	97.31	19.2	96.98	19.2	59.88	19.2	59.89	19.2	47.22	19.2	47.20

Table B.2. Conductance of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in alcohol-water mixtures at 25°C.

Methanol											
-----10% Methanol-----				-----30% Methanol-----				-----50% Methanol-----			
Series I		Series II		Series I		Series II		Series I		Series II	
10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ
2.10	93.01	2.09	92.98	2.10	68.19	2.10	68.19	2.10	61.53	2.10	61.59
4.19	92.22	4.18	92.16	4.20	67.52	4.20	67.49	4.20	60.80	4.20	60.94
6.28	91.46	6.26	91.55	6.29	66.92	6.29	66.97	6.29	60.27	6.29	60.38
8.37	91.00	8.34	91.02	8.38	66.48	8.38	66.52	8.38	59.80	8.38	59.88
10.5	90.48	1.04	90.46	10.5	66.15	10.5	66.17	10.5	59.35	10.5	59.51
12.5	90.08	12.5	90.11	12.5	65.86	12.5	65.81	12.5	58.92	12.6	58.96
14.6	89.68	14.6	89.68	14.6	65.41	14.6	65.50	14.6	58.62	14.6	58.66
16.7	89.23	16.6	89.26	16.7	65.14	16.7	65.22	16.7	58.23	16.7	58.32
18.7	88.84	18.7	88.84	18.8	64.84	18.8	64.91	18.8	57.89	18.8	58.02
20.8	88.49	20.7	88.48	20.8	64.56	20.8	64.58	20.8	57.58	20.8	57.69

Ethanol											
-----10% Ethanol-----				-----30% Ethanol-----				-----50% Ethanol-----			
Series I		Series I		Series I		Series I		Series I		Series I	
10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ
2.10	88.75	2.10	88.75	2.10	54.52	2.10	54.56	2.10	44.16	2.10	44.16
4.19	87.96	4.19	87.93	4.20	53.91	4.20	53.93	4.20	43.56	4.20	43.56
6.28	87.46	6.28	87.40	6.29	53.53	6.29	53.51	6.30	43.07	6.29	43.09
8.36	86.71	8.36	86.66	8.38	53.19	8.38	53.19	8.39	42.71	8.38	42.74
1.04	86.39	1.04	86.35	10.5	52.82	10.5	52.82	10.5	42.31	10.5	42.35
12.5	85.88	12.5	85.85	12.5	52.50	12.5	52.52	12.6	42.15	12.5	42.10
14.6	85.47	14.6	85.45	14.6	52.29	14.6	52.31	14.6	41.83	14.6	41.80
16.6	85.25	16.7	85.23	16.7	52.03	16.7	52.05	16.7	41.43	16.7	41.46
18.7	84.77	18.7	84.80	18.8	51.78	18.8	51.81	18.8	41.28	18.8	41.21
20.7	84.45	20.7	84.44	20.8	51.60	20.8	51.62	20.8	40.93	20.8	40.92

Table B.3. Conductance of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in alcohol-water mixtures at 25°C.

Methanol											
-----10% Methanol-----				-----30% Methanol-----				-----50% Methanol-----			
Series I		Series II		Series I		Series II		Series I		Series II	
10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ
2.10	94.82	2.10	94.84	2.10	68.12	2.10	68.12	2.10	62.09	2.10	62.07
4.19	94.03	4.20	93.96	4.20	67.49	4.20	67.47	4.19	61.46	4.19	61.39
6.28	93.30	6.30	93.19	6.29	66.89	6.30	66.97	6.28	60.89	6.28	60.92
8.37	92.75	8.39	92.61	8.38	66.44	8.39	66.49	8.37	60.53	8.37	60.56
10.5	92.26	10.5	92.21	10.5	66.10	10.5	66.13	10.5	60.24	10.4	60.17
12.5	91.80	12.6	91.81	12.6	65.73	12.6	65.75	12.5	59.91	12.5	59.86
14.6	91.37	14.6	91.34	14.6	65.42	14.6	65.43	14.6	59.55	14.6	59.58
16.7	91.00	16.7	90.95	16.7	65.08	16.7	65.09	16.7	59.24	16.7	59.32
18.7	90.63	18.8	90.62	18.8	64.78	18.8	64.84	18.7	58.95	18.7	58.87
20.8	90.25	20.8	90.27	20.8	64.55	20.8	64.55	20.8	58.69	20.8	58.62
Ethanol											
-----10% Ethanol-----				-----30% Ethanol-----				-----50% Ethanol-----			
Series I		Series I		Series I		Series I		Series I		Series I	
10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ
2.10	87.44	2.10	87.58	2.10	54.20	2.10	54.22	2.10	44.42	2.10	44.44
4.20	86.69	4.19	86.69	4.19	53.62	4.20	53.66	4.20	43.82	4.19	43.86
6.29	86.13	6.28	86.14	6.29	53.15	6.30	53.24	6.30	43.41	6.29	43.40
8.37	85.68	8.37E	85.58	8.37	52.80	8.39	52.84	8.39	43.04	8.37	42.97
10.5	85.16	10.5	85.08	10.5	52.52	10.5	52.52	10.5	42.68	10.5	42.64
12.5	84.75	12.5	84.78	12.5	52.19	12.6	52.25	12.6	42.37	12.5	42.35
14.6	84.35	14.6	84.38	14.6	51.96	14.6	52.00	14.6	41.96	14.6	41.95
16.7	84.01	16.7	84.05	16.7	51.69	16.7	51.71	16.7	41.72	16.7	41.72
18.7	83.66	18.7	83.69	18.7	51.43	18.8	51.49	18.8	41.38	18.7	41.44
20.8	83.35	20.8	83.38	20.8	51.24	20.8	51.23	20.8	41.17	20.8	41.18

Table B.4. Conductance of CaCl₂ in methanol-water mixtures at 25°C.

-----10% Methanol-----				-----30% Methanol-----			
Series I		Series II		Series I		Series II	
10 ⁴ C	Λ	10 ⁴ C	Λ	10 ⁴ C	Λ	10 ⁴ C	Λ
1.99	107.27	1.98	106.78	1.99	75.98	1.99	76.13
3.97	105.06	3.96	105.68	3.97	75.17	3.97	75.38
5.95	104.09	5.94	104.86	5.95	74.53	5.95	74.65
7.92	103.27	7.91	104.12	7.93	74.00	7.93	74.20
9.89	102.62	9.88	103.41	9.90	73.50	9.90	73.66
11.9	102.14	11.8	102.72	11.9	72.86	11.9	73.24
13.8	101.67	13.8	102.04	13.8	72.49	13.8	72.66
15.8	101.22	15.8	101.68	15.8	72.17	15.8	72.32
17.7	100.84	17.7	101.25	17.7	71.71	17.8	71.89
19.7	100.81	19.7	100.78	19.7	71.36	19.7	71.51
-----50% Methanol-----				-----70% Methanol-----			
Series I		Series II		Series I		Series II	
10 ⁴ C	Λ	10 ⁴ C	Λ	10 ⁴ C	Λ	10 ⁴ C	Λ
1.99	65.76	1.98	65.77	1.98	68.42	1.98	68.13
3.97	64.77	3.96	64.83	3.96	67.38	3.97	66.96
5.95	64.08	5.94	64.30	5.93	66.49	5.94	66.16
7.92	63.51	7.91	63.69	7.90	65.73	7.91	65.34
9.89	63.09	9.88	63.15	9.87	65.10	9.88	64.67
11.9	62.58	11.8	62.64	11.8	64.45	11.8	64.07
13.8	62.16	13.8	62.22	13.8	63.92	13.8	63.52
15.8	61.74	15.8	61.79	15.7	63.36	15.8	62.93
17.7	61.36	17.7	61.47	17.7	62.82	17.7	62.43
19.7	60.97	19.7	61.07	19.6	62.34	19.7	61.93

Table B.5. Conductance of CaCl₂ in ethanol-water mixtures at 25°C.

-----10% Ethanol-----				-----30% Ethanol-----			
Series I		Series II		Series I		Series II	
10 ⁴ C	Λ	10 ⁴ C	Λ	10 ⁴ C	Λ	10 ⁴ C	Λ
1.99	97.23	1.98	97.58	1.98	60.24	1.98	60.42
3.97	96.29	3.95	96.62	3.95	59.38	3.95	59.27
5.94	95.38	5.92	95.89	5.92	58.62	5.92	58.72
7.92	94.73	7.89	95.19	7.89	58.20	7.88	58.30
9.89	94.06	9.85	94.60	9.86	57.66	9.84	57.76
11.9	93.48	11.8	93.99	11.8	57.16	11.8	57.25
13.8	92.95	13.8	93.43	13.8	56.74	13.8	56.76
15.8	92.45	15.7	92.90	15.7	56.31	15.7	56.46
17.7	91.96	17.7	92.40	17.7	55.93	17.7	56.02
19.7	91.49	19.6	91.92	19.6	55.59	19.6	55.63
-----50% Ethanol-----				-----70% Ethanol-----			
Series I		Series II		Series I		Series II	
10 ⁴ C	Λ	10 ⁴ C	Λ	10 ⁴ C	Λ	10 ⁴ C	Λ
1.99	47.16	1.99	47.23	1.99	42.38	1.99	42.29
3.97	46.32	3.97	46.44	3.97	41.38	3.97	41.35
5.95	45.70	5.95	45.89	5.95	40.70	5.95	40.60
7.92	45.35	7.93	45.29	7.92	40.13	7.92	40.01
9.90	44.91	9.90	44.95	9.90	39.61	9.89	39.52
11.9	44.63	11.9	44.49	11.9	39.11	11.9	39.04
13.8	44.37	13.8	44.03	13.8	38.70	13.8	38.63
15.8	43.80	15.8	43.94	15.8	38.26	15.8	38.21
17.7	43.37	17.8	43.55	17.7	37.93	17.7	37.83
19.7	42.98	19.7	43.19	19.7	37.58	19.7	37.49

Table B.6. Conductance of CaCl₂ in acetone-water mixtures at 25°C.

-----10% Acetone-----				-----30% Acetone-----			
Series I		Series II		Series I		Series II	
10 ⁴ C	Λ	10 ⁴ C	Λ	10 ⁴ C	Λ	10 ⁴ C	Λ
1.98	110.19	1.98	109.93	1.98	84.33	1.98	85.00
3.96	108.94	3.96	108.78	3.96	82.83	3.96	83.40
5.94	107.88	5.94	107.79	5.94	81.55	5.94	81.92
7.91	107.16	7.91	106.85	7.91	80.45	7.91	80.85
9.88	106.76	9.88	106.22	9.88	79.62	9.88	79.72
11.8	106.11	11.8	105.58	11.8	78.66	11.8	79.00
13.8	105.39	13.8	105.01	13.8	77.71	13.8	78.29
15.8	104.74	15.8	104.35	15.8	77.14	15.8	77.65
17.7	104.21	17.7	103.86	17.7	76.32	17.7	76.88
19.7	103.64	19.7	103.44	19.7	75.83	19.7	76.28
-----50% Acetone-----				-----70% Acetone-----			
Series I		Series II		Series I		Series II	
10 ⁴ C	Λ	10 ⁴ C	Λ	10 ⁴ C	Λ	10 ⁴ C	Λ
1.99	73.07	1.98	73.04	1.99	71.04	1.99	70.89
3.97	71.26	3.96	70.94	3.97	68.59	3.97	68.06
5.95	70.11	5.94	69.53	5.95	66.60	5.95	66.07
7.92	68.92	7.91	68.50	7.92	64.88	7.92	64.37
9.89	67.73	9.88	67.51	9.89	63.58	9.89	63.07
11.9	66.96	11.8	66.61	11.9	62.47	11.9	61.89
13.8	66.21	13.8	65.85	13.8	61.34	13.8	60.99
15.8	65.47	15.8	65.03	15.8	60.44	15.8	59.95
17.7	64.57	17.7	64.41	17.7	59.52	17.7	59.15
19.7	63.91	19.7	63.73	19.7	58.70	19.7	58.31

Figure B.1. Fuoss and Edelson plots based on Eq [3.6]; $\diamond$ Ca (II), $\circ$ Cd (II) and Δ Zn(II) nitrates at 25oC: (a) 10% MeOH, (b) 30% MeOH, (c) 50% MeOH, (d) 10% EtOH, (e) 30% EtOH, (f) 50% EtOH.

Figure B.2. Fuoss and Edelson plots for CaCl_2 based on Eq [3.6]; $\square$ methanol, $\circ$ ethanol, and Δ acetone-water mixtures at 25°C. (a) 10% wt, (b) 30% wt, (c) 50% wt, (d) 70% wt.

LITERATURE CITED

- Abollino, O., M. Aceto, M. Malandrino, C. Sarzanini and E. Mentasti. 2003. Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances. *Water Research*. 37:1619-1627.
- Amrhein, C. and D.L. Suarez. 1991. Sodium-calcium exchange with anion exclusion and weathering corrections. *Soil Sci. Soc. Am. J.* 55:698-706.
- Ananthaswamy, J., B. Sethuram and T. Navaneeth Rao. 1979. Conductometric study of ion-ion and ion-solvent interactions. I. Conductances of silver acetate in 0-50% (w/w) methanol-water mixtures at 35°C. *Bull. Chem. Soc. Jpn.* 52:3076-3079.
- Anderson, D.C., K.W. Brown and J.C. Thomas. 1985. Conductivity of compacted clay soils to water and organic liquids. *Waste Management & Research*. 3:339-349.
- Anderson, J.S. and G. Sposito. 1991. Cesium-adsorption method for measuring accessible structural charge. *Soil Sci. Soc. Am. J.* 55:1569-1576.
- Artiola-Fortuny, J. and W.H. Fuller. 1982. Phenols in municipal solid waste leachates and their attenuation by soil clays. *Soil Sci.* 133:218-227.
- Atkins, P. 1998. Physical Chemistry. 6th edition. W.H. Freeman and Company. New York.
- Barshad, I. 1952. Factors affecting the interlayer expansion of vermiculite and montmorillonite with organic substances. *Soil Sci. Soc. Proceedings*: 176-182.
- Bates, R. G. 1973. Determination of pH: Theory and Practice; Wiley. New York.
- Bedient, P.B., A.M. Asce, N.K. Springer, E. Baca, T.C. Bouvette, S.R. Hutchins and M.B. Tomson. 1983. Groundwater transport from wastewater infiltration. *J. Environ. Sci.* 109:485-501.
- Berkheiser, V. and M.M. Mortland. 1975. Variability in exchange ion position in smectites: dependence on interlayer solvent. *Clays and Clay Minerals*. 23:404-410.
- Bjerrum, N. 1926. Ionic association. I. Influence of ionic association on the activity of ions at moderate degrees of association. *Kgl. Danske Videnskab. Selskab.* 7:1-48.
- Bockris, J. O'M. and A.K.N. Reddy. 1973. Modern Electrochemistry. Vol. 1.

Plenum Press, New York.

Bosch E, and M. Roses. 1988. Ionic equilibria in neutral amphiprotic solvents: variation of electrolyte dissociation constants in *tert*-butyl alcohol with addition of a second solvent. *Anal. Chem.* 60:2008-2013.

Braun, R. D. 1982. Introduction to Chemical Analysis. McGraw-Hill, New York. pp.197-199.

Brindley, G.W., K. Wiewiora and A. Wiewiora. 1969. Intercrystalline swelling of montmorillonite in some water-organic mixtures (Clay-Organic studies XVII). *The American Mineralogist* 54:1635-1644.

Broadwater, T.L., T.J. Murphy and D.F. Evans. 1976. Conductance of binary asymmetric electrolytes in methanol. *J. Phy. Chem.* 80:753-757.

Brown K.W. and J.C. Thomas. 1987. A mechanism by which organic liquids increase the hydraulic conductivity of compacted clay materials. *Soil Sci. Soc. Am. J.* 51:1451-1459.

Brusseau, M. L., A.L. Wood and P.S. Rao. 1991. Influence of organic cosolvents on the sorption kinetics of hydrophobic organic chemicals. *Environ. Sci. Technol.* 25: 903-910.

Doe, H., T. Kitagawa, and K. Sasabe. 1984. Conductometric study of some metal(II) perchlorates in methanol. *J. Phys. Chem.* 88: 3341-3345.

Doe, H., K. Wakamiya, C. Yoshida, H.Ozaki, K.N. Soe and T. Kitagawa. 1987. Potentiometric study of cadmium(II) halide and thiocyanate complexes in methanol. *Inorg. Chem.* 26:2244-2247.

Doe, H., H. Ohe, H. Matoba, A. Ichimura and T. Kitagawa. 1990. Conductometric study of calcium(II), strontium(II), and barium(II) perchlorates in methanol-ethylene glycol mixtures. *Bull. Chem. Soc. Japan.* 63:2785-2789.

Echeverria, J.C., E. Churio, and J.J. Garrido. 2002. Retention mechanisms of Cd on illite. *Clays and Clay Minerals.* 50:614-623.

Elrashidi, M.A. and G.A. O'Connor. 1982. Boron Sorption and desorption in soils. *Soil Sci. Soc. Am. J.* 46:27-31.

Evangelou, V.P. 1998. Soil minerals and surface chemical properties. In *Environmental Soil and Water Chemistry: Principles and Applications*. New York: Wiley. P. 100-224.

- Evers, E.C. and A.G. Knox. 1951. Conductivity studies in methanol. *J. Phys. Chem.* 73:1739-1744.
- Fernandez, F. and R.M. Quigley. 1985. Hydraulic conductivity of natural clays permeated with simple liquid hydrocarbons. *Can. Geotech. J.* 22:205-214.
- Friedman, N.J. and R.A. Plane. 1963. Solvation of copper(II) ion in acetone-water and ethanol-water solutions. *Inorg. Chem.* 2:11-14
- Fuoss, R.M. 1958. Ionic association. III. The equilibrium between ion pairs and free ions. *J. Am. Chem. Soc.* 80:5059-61.
- Fuoss, M.R. and D. Edelson. 1951. Bolaform electrolytes. I. Di-(β -trimethylammonium ethyl) succinate dibromide and related compounds. *J. Phys. Chem.* 73:269-273.
- Fuoss, R.M. and L. Onsager. 1957. Conductance of unassociated electrolytes. *J. Phys. Chem.* 61:668-682.
- Fuoss, R.M. and L. Onsager. 1958. The kinetic term in electrolytic conductance. *J. Phys. Chem.* 62:1339-1340.
- Gaizer, F., H.B. Silber and J. Lázár. 1985. Stability constants of zinc halide complexes in DMSO-water and DMF-water mixtures. *Polyhedron.* 4:1467-1470.
- Ghasemi, J., A. Niazi, M. Kubista and A. Elbergali. 2002. Spectrophotometric determination of acidity constants of 4-(2-pyridylazo) resorcinol in binary methanol-water mixtures. *Analytica Chimica Acta* 455:335-342.
- Green, W. J., G.F. Lee, R.A. Jones and T. Pall. 1983. Interaction of clay soils with water and organic solvents: implications for the disposal of hazardous wastes. *Environ. Sci. Technol.* 17:278-282.
- Handbook of Chemistry and Physics (2003-2004), 84th edition. CRC Press, Boca Raton, Fl.
- Hawes, J.L. and R.L. Kay. 1965. Ionic association of potassium and cesium chlorides in ethanol-water mixtures from conductance measurements at 25°C. *J. Phys. Chem.* 69:2420-2431.
- Hiemenz, P.C. 1986. Principles of Colloid and Surface Chemistry. 2nd edition. Marcel Dekker, INC. New York and Basel.
- Hirsch, D., S. Nir, A. Banin. 1989. Prediction of Cadmium complexation in solution and adsorption to montmorillonite. *Soil Sci. Soc. Am. J.* 53:716-721.
- Israelachvili, J.N. 1987. Solvation forces and liquid structure, as probed by direct

force measurements. *Acc. Chem. Res.* 20:415-421.

Izutsu, K. 2002. Electrochemistry in Nonaqueous Solutions. Wiley-VCH, Weinheim.

Jackson, M.L. 1956. Dispersion of Soil Minerals. *In Soil Chemical Analysis Advanced Course*. 5th print.

Jackson, M.L. 1974. Soil chemical analysis-advanced course. Dept. of Soil Science, Univ. of Wisconsin, Madison, WI.

Janz, G.J. and R.T. Tomkins. 1973. Non-Aqueous Electrolytes Handbook. Volume I. Academic Press, Inc.

Johnston, C.T. and E. Tombácz. 2002. Surface Chemistry of soil minerals. In *Soil Mineralogy with Environmental Applications*. No.7. American Society of Agronomy, Madison, WI.

Kielland, J. 1937. Individual activity coefficients of ions in aqueous solutions. *J. Phys. Chem.* 60:1675-1678.

Kinniburgh, D.G., J.K. Syers and M.L. Jackson. 1975. Specific adsorption of trace amounts of calcium and strontium by hydrous oxides of iron and aluminum. *Soil Sci. Soc. Am. Proc.* 39:464-470.

Kolthof, M. 1953. Acid-base indicators. 2nd edition. The Macmillan Company, New York.

Kolthoff, I.M. 1974. Acid-base equilibria in dipolar aprotic solvents. *Anal. Chem.* 46:1992-2003.

Kosmulski, M. 1990. Effect of n-alcohols on the surface charge density and adsorption of supporting electrolytes on aluminas. *J. Coll. Interf. Sci.* 135:590-593.

Kosmulski, M. 1993. Adsorption of methanol and supporting electrolytes on silica and alumina in mixed solvent systems. *J. Coll. Interf. Sci.* 156:305-310.

Kosmulski, M. 1994. Standard enthalpies of ion adsorption onto oxides from aqueous solutions and mixed solvents. *Colloids Surfaces A: Physicochemical and Engineering Aspects* 83:237-243.

Kosmulski, M. 1995. Oxide/electrolyte interface: electric double layer in mixed solvent systems. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 95:91-100.

- Kosmulski, M. 1996. The effect of the nature of the organic cosolvent on surface charge density of silica in mixed solvents. *J. Coll. Interf. Sci.* 179:128-135.
- Kosmulski, M. 1999. Zeta potentials in nonaqueous media: how to measure and control them. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 159:277-281.
- Kosmulski, M. and E. Matijević. 1992. ζ -potentials of silica in water-alcohol mixtures. *Langmuir*. 8:1060-1064.
- Kunze, G.W. and J.B. Dixon. 1986. Pretreatment for mineralogical analysis. In *Methods of Soil Analysis, Part I. Physical and Mineralogical Methods-Agronomy Monograph no. 9* (2nd edition).
- Lee, W. H.; Wheaton, R. J. 1978. Analysis of conductance data for associated unsymmetrical electrolytes. *J. Phys. Chem.* 82:605-8.
- Lindsay, W.L. 1979. *Chemical Equilibria in Soils*. Wiley & Sons. New York.
- Loeppert, R.H., L.W. Zelazny and B.G. Volk. 1977. Acidic properties of kaolinite in water and acetonitrile. *Soil Sci. Soc. Am. J.* 41:1101-1106.
- Loeppert, R.H., L.W. Zelazny and B.G. Volk. 1979. Titration of pH-dependent sites of kaolinite in water and selected nonaqueous solvents. *Clays and Clay Minerals*. 27: 57-62.
- Martell, A.E. and R.J. Motekaitis. 1992. *Determination and Use of Stability Constants*. 2nd edition. Wiley-VCH.
- McDonald, L.M. 1995. Cosolvent effects on the sorption of Sr, Zn, and Cd to bentonite. Ph.D. thesis, Univ. of Kentucky, Kentucky, U.S.
- Miller, R.M., L.S. Stitzer, J.F. Artiola and W.H. Fuller. 1992. Effect of four alcohols on adsorption and movement of Cd, nickel and zinc through soils. *Chemosphere*. 24:1855-1866.
- Mui K.K. and W.E. McBride. 1974. The stability of some metal complexes in mixed solvents. *Can. J. Chem.* 52:1821-1833.
- Murray, R.S and J. P. Quirk. 1982. The physical swelling of clays in solvents. *Soil Sci. Soc. Am. J.* 46:865-868.
- Mussini, T., A.K. Covington, P. Longhi and S. Rondinini. 1985. Criteria for standardization of pH measurements in organic solvents and water + organic solvent mixtures of moderate to high permittivity. *Pure & Appl. Chem.* 57: 865-876.

- Nancollas, G.H. and M.N. Tomson. 1982. Guidelines for the determination of stability constants. *Pure & Appl. Chem.* 54: 2675-2692.
- Nkedi- Kizza, P., P.S.C. Rao and A.G. Hornsby. 1985. Influence of organic cosolvents on sorption of hydrophobic solvents. *Soil Science*. 108:11-23.
- Olejnik, S., A. M. Posner and J. P. Quirk. 1974. Swelling of montmorillonite in polar organic liquids. *Clays and Clay Minerals*. 22: 361-365.
- Naidu, R., N.S. Bolan, R.S. Kookana, K.G. Tiller. 1994. Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. *Euro. J. Soil Sci.* 45:419-429.
- Nir, S. Specific and non-specific cation adsorption to clays: Solution concentration and surface potentials. *Soil Sci. Soc. Am. J.* 50:52-57.
- Popovytch, O. and R.P.T. Tomkins. 1981. Nonaqueous Solution Chemistry. Wiley & Sons, NY.
- Rao, P.S.C., L.S. Lee and R. Pinal. 1990. Cosolvency and sorption of hydrophobic organic chemicals. *Environ. Sci. Technol.* 24:647-654.
- Reichardt, C. 1988. Solvents and Solvents Effects in Organic Chemistry. 2nd edition. VCH, Weinheim.
- Riley, R.G and J.M. Zachara. 1992. Chemical Contaminants on DOE Land and Selection of Contaminant Mixtures for Subsurface Science Research. US Department of Energy. Office of Energy Research, Subsurface Science Program. Washington, D.C. 20585.
- Rondinini, S., P. Longhi, P.R. Mussini and T. Mussini. 1987. Autoprotolysis constants in nonaqueous solvents and aqueous organic solvent mixtures. *Pure & Appl. Chem.* 59: 1693-1987.
- Rondinini, S., P.R. Mussini, T. Mussini and A. Vertova. 1998. pH measurements in non-aqueous and mixed solvents: predicting pH(PS) of potassium hydrogen phthalate for alcohol-water mixtures. *Pure Appl. Chem.* 70:1419-1422.
- Robert-Baldo, G.M., Morris, R.H. Byrne. 1985. Spectrophotometric Determination of Seawater pH Using Phenol Red. *Anal. Chem.* 57:2564.
- Rosés, M., C. Ràfols and E. Bosch. 1993. Autoprotolysis in aqueous organic solvent mixtures. *Anal. Chem.* 65:2294-2299.
- Salomon, M. 1989. Electrolyte solvation in aprotic solvents. *J. Power Sources*. 26:9-21.

- Sawhney, B.L and R.P. Kozloski. 1984. Organic pollutants in leachates from landfill sites. *J. Environ. Qual.* 13:349-352.
- Schulthess, C.P., and C.P. Huang. 1990. Adsorption of heavy metals by silicon and aluminum oxide surfaces on clay minerals. *Soil Sci. Soc. Am. J.* 54:679-688.
- Shainberg, I., and W.D. Kemper. 1967. Ion exchange equilibria on montmorillonite. *Soil Science.* 103:4-9.
- Shedlovsky. 1932. The electrolytic conductivity of some univalent-univalent electrolytes in water at 25°C. *J. Phys. Chem.* 54:1411-1429.
- Sheets, P.J. and W.H. Fuller. 1986. Transport of cadmium by organic solvents through soils. *Soil Sci. Soc. Am. J.* 50:24-28.
- Smith, R. M. and A.E. Martell. 1976. Critical Stability Constants. Vol. 4: Inorganic Complexes.
- Spivey, H.O. and T. Shedlovsky. 1967. Studies of electrolytic conductance in alcohol-water mixtures. I. Hydraulic acid, sodium chloride, and sodium acetate at 0, 25, and 35° in ethanol-water mixtures. *J. Phy. Chem.* 71:2165-2171.
- Sposito, G. 1980. Derivation of the Freundlich equation for ion exchange reactions in soils. *Soil Sci. Soc. Amer. J.* 44:652-654.
- Sposito, G. 1981. The Thermodynamics of Soil Solutions. Oxford University Press, New York.
- Sposito, G. 1984. The Surface Chemistry of Soils. Oxford University Press, London.
- Sposito G, K. Holtzclaw, L. Charlet, C. Jouany and A.L. Page. 1983. Sodium-calcium and sodium-magnesium exchange on Wyoming bentonite in perchlorate and chloride background ionic media. *Soil. Sci. Soc. Am. J.* 47:51-56.
- Sposito, G., N.T., Skipper, R. Sutton, S. Park. A.K. Soper and J.A. Greathouse. 1999. Surface geochemistry of the clay minerals. *Proc. Natl. Acad. Sci.* 96:3358-3364.
- Stul, M. S., J.B. Uytterhoeven and J. Bock. 1979. The adsorption of n-aliphatic alcohols from dilute aqueous solutions on RNH₃-montmorillonites. II. Interlamellar association of the adsorbate. *Clays and Clay Minerals.* 27:377-386.
- Timmermans, J. 1960. The Physico-Chemical Constants of Binary Systems in Concentrated Solutions. Volume IV. InterScience Publishers, Inc. New York.

- Tobey, S. 1958. The acid dissociation constant of methyl red. A spectrophotometric measurement. *J. Chem. Education*. 35:514-515.
- Undabeytia, T., S. Nir, G. Rytwo, E. Morillo, and C. Maqueda. 1998. Modeling adsorption-desorption processes of Cd on montmorillonite. *Clays and Clay Minerals*. 46:423-428.
- Van Bladel, R. and H.R. Gheyi. 1980. Thermodynamic study of calcium-sodium and calcium-magnesium exchange in calcareous soils. *Soil Sci. Soc. Am. J.* 44:938-942.
- VanBladel, R., H. Halen and P. Cloos. 1993. Calcium-zinc and calcium-cadmium exchange in suspensions of various types of clays. *Clay Minerals*. 28:33-38.
- Xue, Y. and S. J. Traina. 1996a. Cosolvent effect on goethite surface protonation. *Environ. Sci. Technol.* 30:3161-3166.
- Xue, Y. and S. Traina. 1996b. Stability of metal-organic complexes in acetone- and methanol-water mixtures. *Environ. Sci. Technol* 30:3177-3183.
- Yalkowsky, S.H., S.C. Valvani and G.L. Amidon. 1976. Solubility of nonelectrolytes in polar solvents: IV. Nonpolar drugs in mixed solvents. *J. Pharm. Sci.* 65:1488-1494.
- Yamazki, H., R.P. Sperline and H. Freiser. 1992. Spectrophotometric determination of pH and its application to determination of thermodynamic equilibrium constants. *Anal. Chem.* 64:2720-2725.
- Yamazaki, H., R.P. Sperline and H. Freiser. 1993. Spectrophotometric determination of the dissociation constant (pK_a) of arsenous acid. *Analytica Chimica Acta*. 284:379-384.
- Yao, W. and R.H. Byrne. 2001. Spectrophotometric determination of freshwater pH using bromocresol purple and phenol red. *Environ. Sci. Technol.* 35:1197-1201.
- Yeager, E. and A.J. Salkind. 1973. Techniques of Electrochemistry. Vol.2. A Wiley & Sons.
- Zhang, Z.Z. and D.L. Sparks. 1996. Sodium-copper exchange on Wyoming montmorillonite in chloride, perchlorate, nitrate, and sulfate solutions. *Soil Sci. Soc. Am. J.* 60:1750-1757.
- Ziper, C., S. Komarneni and D.E. Baker. 1988. Specific cadmium sorption in relation to the crystal chemistry of clay minerals. *Soil. Sci. Soc. Am. J.* 52:49-53.