Capillary Electrophoretic Separations of Metal Ions

Elena Hofman

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CAPILLARY ELECTROPHORETIC SEPARATIONS OF METAL IONS

by

Elena Hofman

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
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Elena Hofman
CAPILLARY ELECTROPHORETIC SEPARATIONS OF METAL IONS

Elena Hofman, M.S.

Western Michigan University, 2003

Transition-metal (Zn(II), Co(II), Ni(II) and Cu(II)) ion separation was studied using 8-hydroxyquinoline-5-sulfonic acid and 2-methyl-8-hydroxyquinoline ligands with surfactants (cationic and anionic) by capillary electrophoresis under a variety of conditions (like pH, ionic strength, voltage and ion, ligand and surfactant amounts) and has debuted a clear separation mechanism. With cationic surfactants, ligands compete with capillary surface silanols for the metal ions; with anionic surfactants, ligands, silanols and micelles compete.

An empirical parameter, $K_e$, (electrophoretic-mobilities based) rationalizing the separation was proposed, experimentally analyzed and supported; it provides a silanol group per cm$^2$ value of the capillary surface, an equilibrium constant for the exchange of metal ions between the micelles and the complexes, and a quantitative and fundamental understanding of the electropherograms and separation mechanisms.

Capillary pretreatment with low cationic amounts makes constant, reproducible concentrations of surface silanol groups that, with ligands, exchange ions with mobile phase complexes (resulting in different mobilities for different ion complexes) and that, with anionic surfactants above critical micelle concentration, exchange ions with micelles (resulting in different migrations for different ion complexes).
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CHAPTER I

INTRODUCTION

Selective separation of metal ions from a variety of complex matrices is a challenging and important problem for detection and remediation. Selective separation of metal ions on an analytical scale is essential for addressing a variety of environmental problems. The work described in this thesis addresses the analytical separation of transition metal ions by capillary electrophoresis (CE) employing surfactant molecular assemblies. Studies were performed under a variety of conditions to gain a fundamental understanding of electrically driven separation of metal ions in the presence of organized molecular assemblies.

Several recent publications have employed CE for the detection and separation of metal ions. [3, 13, 15, 29] Metal ion separations by CE have many advantages over HPLC:

1. Separation can be achieved in shorter period of time.
2. CE requires only microliters of samples and mobile phase, thus minimizing disposal volumes.
3. CE provides high efficiency and resolution. [1, 2]
4. Separations can be readily controlled using different parameters like pH, applied voltage and ionic strength. [3]

The separation principle of metal ions by the CE system is based on the complexation equilibria between the injected metal ions and a ligand in an electrophoretic buffer resulting in different electrophoretic mobilities for different metal ion complexes. The best selectivity in metal ion separation is obtained by complexing the metal ions with a chelating ligand. Both complexation kinetics and equilibrium will influence efficiency and selectivity of separation. [3-8, 30]

A chelating ligand like ethylenediaminetetraacetic acid (EDTA), which forms very stable anionic complexes with different metals, has been employed. [9-11] Several studies of the separation of EDTA metal complexes were performed at a low pH range. The metal ions Pb$^{2+}$,
Cu$^{2+}$, Ni$^{2+}$, Zn$^{2+}$ and Fe$^{2+}$ were separated at pH 4.0 in the presence of the cationic surfactant hexadecyltrimethylammonium bromide (HTAB) which was added to reduce electroosmotic flow (EOF) with UV detection at 200 nm. [9] However, separation selectivity among Pb$^{2+}$, Cu$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$ was very small. Only Fe$^{2+}$ was separated significantly from the other three metals. A more successful separation of Pb$^{2+}$, Cu$^{2+}$, Cr$^{2+}$ and Fe$^{2+}$ was achieved in the pH range 4.0-6.0 in the presence of the cationic surfactant tetradecyltrimethylammonium bromide (TTAB) in the mobile phase with UV detection at 270 nm. [10] EDTA complexes of the transition metals were separated in the moderate pH range (5.5-7.0) in the presence of the cationic surfactant cetyltrimethylammonium bromide (CTAB) at a detection wavelength of 240 nm. [11] EDTA complexes have very small differences in the stability constants of closely related metal ions, like transition metal ions, resulting in poor selectivities among these metal ions.

CE separations of transition metals with a ligand like 4-(2-pyridylazo)resorcinol (PAR) were achieved at a high pH range (8.0-9.2). Saitoh’s work describes separation between transition metal-PAR complexes in the presence of sodium dodecyl sulfate (SDS) at pH 9.2. No baseline separation was obtained between Ni(II), Zn(II), Cd(II) and Fe(II). [12]

Timerbaev achieved better separation of metal-PAR complexes. Co(III), Cu(II), Ni(II), Fe(III) and Zn(II) were separated at pH 8.0 in the presence of SDS in the mobile phase employing a detection wavelength of 254 nm. However, metal ions like Fe(III) and Zn(II) still did not have a baseline separation. [13] Separations of PAR complexes were done only in the presence of SDS. Metal ions, which formed unstable PAR complexes like Mn(II), alkaline earth metal ions, La(III), Zr(IV), Sn(IV) and U(VI) had broad asymmetrical peak shapes or did not give any peaks under the experimental conditions. [4] Separation selectivity of PAR anionic complexes was highly dependent on the background electrolyte, in particular cations present in the medium.

The 8-hydroxyquinoline ligand family has not been investigated in detail for CE separations of metal ions. These ligands could provide baseline separation of different metal ion families due to their significantly different stability constants. [16] Separations reported in literature with 8-hydroxyquinoline-5-sulfonic acid (HQS) were achieved only in a high pH range (8.9-9.5) [26]
with a boric acid buffer as the electrophoretic buffer in the presence of cationic and anionic surfactants [14, 15] at a detection wavelength of 254 nm. These separations did not provide baseline separation of all transition metal ions. The studies reported in literature only dealt with obtaining separations; the fundamental mechanisms of separations were not investigated.

A major objective of the work discussed below was to obtain separation of the transition metal ions Cu(II), Ni(II), Co(II) and Zn(II) using the 8-hydroxyquinoline ligand family and to discern the separation mechanism in the presence of cationic and anionic surfactants below and above their critical micelle concentrations (cmc). The separation of the transition metal ions Cu(II), Ni(II), Co(II) and Zn(II) by CE is challenging as they have similar ionic radii and tend to form 1:2 metal ligand complexes with many ligands. These often, as indicated in literature reports, lead to complexes with similar electrophoretic mobilities and incomplete separations. [14] The 8-hydroxyquinoline family has significant differences in stability constants for the transition metal ions which could be exploited for their separations. [16] It was successfully demonstrated their baseline separations in the presence of cationic and anionic surfactants using HPLC [17] where the competing metal ion complexation equilibria in the mobile and stationary phases result in different retention times and baseline separation.

The specific objectives of the work described here are:

1. Determine optimum conditions for the CE separation of Co(II), Ni(II), Cu(II) and Zn(II) with HQS and 2-methyl-8-hydroxyquinoline (HMeQ) in the presence of cationic surfactants such as octyltrimethylammonium bromide (OTAB), cetyltrimethylammonium nitrate (CTAN) and the anionic surfactant SDS.

2. Examine the influence of pH, ligand concentration, surfactant concentration, applied voltage and ionic strength on separations.

3. Discern the fundamental mechanism of separation and the role of surfactant assemblies in mediating these separations.

The role of molecular surfactant assemblies, like micelles and adsorbed surfactant monolayers in mediating metal ion separations, is a major focus of research in our group as this is
important for environmentally friendly ways of detecting and remediating toxic wastes. It is also important from a fundamental viewpoint, as little information is available in literature on the role of surfactants in mediating metal ion separations. Therefore, this work focused on: (a) obtaining transition metal ion separation with HQS and HMeQ with the cationic surfactants OTAB and CTAN under submicellar conditions and with the anionic surfactant SDS under micellar conditions and (b) discerning both the role of surfactants adsorbed and the role of micelles in mediating metal ion separation.
CHAPTER II

EXPERIMENTAL

Instruments

**CE System**

CE experiments were performed with a Beckman P/ACE MDQ instrument with on-column UV-visible detection. The detection wavelength was selected by employing various 5 nm band pass filters. The detection wavelength in this study was 254 nm. Data collection and analysis was performed with 32 Karat software running under the Windows operating system. Separations were performed with a fused-silica capillary of 57 cm total length/50 cm effective length, 75 µm I.D., 375 µm O.D.

**UV-Visible Spectrophotometer**

UV-visible absorbance spectra of the ligand and complexes were recorded with a Hewlett-Packard HP 8453 spectrophotometer. A 1 cm path length quartz cell was used. Spectra of concentrated solutions were recorded with a 1 mm path length quartz cell.

**pH Meter**

An ACCUMET® Basic Model AB15 pH meter with an ORION® ROSS combination glass electrode was used to measure pH. Standard buffer solutions obtained from Fisher Scientific were used for electrode calibration.
Reagents

**Metal Ion Solutions**

Solutions of Co(II), Cu(II), Ni(II) and Zn(II) were prepared from nitrate salts (Aldrich Chemical Company) for separation with HQS and from perchlorate salts (Aldrich Chemical Company) for separation with 8-hydroxyquinaldine in $1 \times 10^{-3}$ HNO$_3$.

**Ligands**

**HQS**

HQS was obtained from the Aldrich Chemical Company with a purity of 98%. It was recrystallized from ethanol-water (90:10) to achieve higher purity before it was used in metal ion separation. A saturated solution of the ligand was prepared at room temperature by dissolving HQS in the ethanol-water solution. This solution was heated and more HQS was added to reach saturation. When the solution was allowed to cool, crystals formed and separated from the liquid. They were collected by filtration and air-dried. The purity of the recrystallized ligand was determined to be higher than 99.5% from the amount of Cu(II) complexed.

**HMeQ**

HMeQ (98%) was obtained from the Aldrich Chemical Company and purified by recrystallization. HMeQ was dissolved in 100 ml of ethanol at room temperature until the solution was saturated. The solution was then boiled and more ligand was added. When the solution cooled, freshly formed white crystals were collected by filtration and air-dried. The purity of the recrystallized ligand was determined to be higher than 99.5% from the amount of Cu(II) complexed.
Surfactants

SDS

SDS (Figure 1), 99% pure, was obtained from Fluka and it was recrystallized to a higher purity before being used. A 65 g portion of SDS was dissolved in 130 ml of water. This solution was heated to 70-80°C and then filtrated. 200 ml of ethanol was added to the solution. The precipitated SDS crystals were collected by filtration and air-dried.

OTAB

OTAB (Figure 2), 98% pure, was obtained from Fluka.

CTAN

CTAN (Figure 3) was prepared in the laboratory from CTAB (98%). 15 g of CTAB (Fluka) was dissolved in 50 ml of methanol and 10 ml of water. To precipitate bromide as AgBr, AgNO₃ was added to the solution. The mixture was heated to 40°C and then filtered. The filtrate was concentrated to obtain CTAN as a white powder and dried under a vacuum at room temperature. [19]

Buffers

Types

Succinic, phosphoric and boric acid buffers of constant ionic strength were used as electrophoretic buffers. [33]

NaClO₄ and NaNO₃

NaClO₄ (Aldrich) and NaNO₃ (Aldrich) 99% pure were used as supporting electrolytes to adjust the ionic strengths of electrophoretic run buffers. All solutions were prepared in deionized water.
Figure 1. SDS Micelle, cmc = 1.4x10^{-4} M, Molecular Weight = 288.38 g/mole
Aggregation Number: 40
Figure 2. OTAB, cmc = 0.269 M, Molecular Weight = 252.24 g/mole
Figure 3. CTAN, Aggregation Number: 50
Separation Procedure

Metal ions were separated by injecting either metal complexes or metal ions into the electrophoretic buffers with ligand present. Fresh capillaries were conditioned by washing with methanol (5 minutes), water (5 minutes), 0.1 M NaOH (10 minutes) and water (5 minutes). The capillary was rinsed with $1 \times 10^{-5}$ M of EDTA at the end of each separation run (2 minutes) followed by 0.1 M NaOH (2 minutes) and water (2 minutes). Electroosmotic flow was determined from the migration time of acetone for each experimental condition.

Voltage Dependence

Resolution and peak shapes can be influenced by voltage. Performing the experiment at voltages higher than 25 kV is not recommended because it will lead to Joule heating of the mobile phase which will result in bubble formation which will interfere with optical detection. If the voltage is low, the analyte migration time can be too long. The optimal voltage range is 15-25 kV.

Sample Preparation for Oncolumn Complex Formation Method

**Ligand: HQS**

The concentration of HQS in the electrophoretic buffer was $5 \times 10^{-4}$ M and metal nitrates of concentration $1.25 \times 10^{-4}$ M in $1 \times 10^{-3}$ M HNO$_3$ were injected for 5 s.

**Ligand: HMeQ**

Metal perchlorates of concentration $1 \times 10^{-3}$ M in $1 \times 10^{-3}$ HNO$_3$ were injected for 10 s. The concentration of HMeQ in the electrophoretic buffer containing an appropriate concentration of SDS was $3 \times 10^{-3}$ M.

Sample Preparation for Precolumn Complex Formation Method

Complexes for separations where the metals were injected as their complexes formed from
9x10^{-5} M metal nitrates in 1x10^{-4} M HNO_3 and 9.8x10^{-4} M HQS. Complexes were formed in a succinate buffer at pH 5.7. Complexes were injected for 10 s. This experiment was not performed for HMeQ.

**Mobile Phase Preparation**

**Ligand: HQS**

**Precolumn Complex Formation.** These experiments were conducted in the pH range 5.7-6.7 (succinic acid buffer) and 6.2-7.5 (phosphate buffer) at various ionic strengths adjusted with NaNO_3.

**Oncolumn Complex Formation.** Mobile phase containing 5x10^{-4} M ligand with a pH range 5.6-6.2 was obtained with a succinate buffer at an ionic strength of 0.02 M.

**Ligand: HMeQ**

**Precolumn Complex Formation.** Only oncolumn complex formation experiments were conducted since the precolumn complex often leads to precipitation.

**Oncolumn Complex Formation.** Precipitation during the oncolumn complexation experiment was avoided by injecting low metal concentrations (1x10^{-3} M) into the electrophoretic buffer containing the ligand with a concentration range 1x10^{-3} - 3x10^{-3} M. Injection time is only 10 s. These experiments were performed in the pH range 9.0-9.7 employing a borate buffer and adjusting the ionic strength with NaClO_4.

**Surfactant**

**OTAB, Ligand: HQS.** The capillary was conditioned before each experiment and rinsed with 2x10^{-3} M OTAB (2 minutes) every three runs.
CTAN, Ligand HQS. The capillary was conditioned with $1 \times 10^{-5}$ M CTAN (2 minutes) before each run.

SDS, Ligand: HQS. Mobile phase contained 0.05 M SDS. Also, in the precolumn complex formation method, metal complexes were formed in a $2 \times 10^{-3}$ M SDS solution.

SDS, Ligand: HMeQ. The mobile phase contained $2.5 \times 10^{-2}$ M SDS.

Neutral Marker
EOF was determined for each experimental condition (pH, surfactant concentration, applied voltage and ionic strength) by injecting 0.1 ml acetone in 2 ml H$_2$O.

Injection Time
Most CE experiments (precolumn complex formation in the case of HQS and all HMeQ experiments) were conducted with an injection time of 10 s. Metals in the oncolumn complex formation experiments (ligand HQS) were injected for 5 s.
CHAPTER III

RESULTS AND DISCUSSION

General Discussion

Detection

UV-vis detection was used in all separations. The hydrated metal ions Co(II), Ni(II), Cu(II) and Zn(II) have very low absorbance values in the UV region making their direct detection difficult. However, their complexes with HQS and HMeQ have strong absorbance values at 254 nm. UV-vis spectra are shown on Figures 4 and 5 for different ligand:metal ratios.

Identification of Metal Ions

The identity of metal ions in a separation mixture was established by comparing their migration times in a mixture to migration times obtained by individual injections of each metal complex or metal ion for precolumn and oncolumn formation experiments respectively.

Data Treatment

All mobilities in CE are defined as velocity (cm/s) per unit field strength (V/cm) and therefore are measured in units of cm$^2$/Vs.

Electrophoretic mobility, $\mu$, is: [20, 25, 27]

\[ \mu = \mu_{\text{app}} - \mu_{\text{cof}} \]  

(1)
Figure 4. UV-vis Spectra for Ligand (HQS):Metal Complexes.
Ligand:Metal Ratio: 10
1 = Ligand, 2 = Zn(II), 3 = Co(II), 4 = Cu(II), 5 = Ni(II)
Figure 5. UV-vis Spectra for Ligand (HQS):Metal Complexes.
Ligand:Metal Ratio: 5
1 = Ligand, 2 = Zn(II), 3 = Co(II), 4 = Cu(II), 5 = Ni(II)
Apparent mobility, $\mu_{\text{app}}$, and electroosmotic mobility, $\mu_{\text{eof}}$, are calculated using Equations 2 and 3.

\[
\mu_{\text{app}} = \frac{L_d \times L_t}{V \times t} \tag{2}
\]

\[
\mu_{\text{eof}} = \frac{L_d \times L_t}{V \times t_o} \tag{3}
\]

where:

- $L_d$ = capillary length to detector, cm
- $L_t$ = total capillary length, cm
- $t_o$ = migration time of a neutral molecule, s
- $t$ = migration time of the charged analyte, s
- $V$ = applied voltage, V

The distribution constant, $D$, can be calculated using the general chromatographic relation, Equation 4.

\[
D = \frac{t - t_o}{t_o} \tag{4}
\]

The dynamic radii of the complexes, $R$, were calculated using an Einsteinian equation, Equation 5. They are slightly higher than geometric radii due to their solvation. [21]

\[
\frac{q}{R} = 6\pi\eta\mu \tag{5}
\]

where:

- $q = z \times 1.6 \times 10^{-19}$ coulomb ($z =$ charge of the metal ion)
- $\eta$ = viscosity
- $\eta$ of H$_2$O at $25^\circ$C = $8.95 \times 10^{-3}$ poise = $8.95 \times 10^{-4}$ SI units (Nm$^2$s)
The zeta potential ($\zeta$), which is the characteristic of the charge and the potential distribution at the capillary wall interface, and the electrophoretic buffer were calculated according to Smoluchowski's Equation, Equation 6. [24,28]

$$\zeta = \frac{v \times \eta \times L}{\varepsilon_0 \times E \times V} = \frac{\eta \times \mu_{\text{eof}}}{\varepsilon_0 \times E}$$  

(6)

where:  
- $v$ = velocity, $\text{cm} / \text{s}$, $= L / t$  
- $\varepsilon_0$ = permittivity of the vacuum, $8.854 \times 10^{-12}$ $\text{F} \cdot \text{m}^{-1}$  
- $E$ = relative permittivity (or dielectric constant), unit-less ($\text{H}_2\text{O} = 80$)  
- $\varepsilon_0 \times E = \varepsilon^1 = 8.854 \times 10^{-12} \times 79$ $\text{F} \cdot \text{m}^{-1}$ (Appendix B)

**Metal Ion Separation in the Absence of Surfactants**

In the blank experiment, separation of Co(II), Zn(II), Ni(II) and Cu(II) was performed without surfactant present in the system. Experimental data is shown on Figures 6 and 7 at pH of 5.82 and 5.77 respectively.

Table 1 summarizes electrophoretic mobilities, which were calculated based on data from the precolumn complex formation experiment and the oncolumn complex formation experiment.

The electropherograms show that in the absence of surfactants the separation was incomplete and the peaks are asymmetrical. Precolumn and oncolumn complex formation yielded anionic 1:2 metal:ligand complexes except in the case of Co(II) which formed a 1:3 metal:ligand complex in precolumn complexation. The similarities of electrophoretic mobilities and broad asymmetric peaks resulted in poor separation. (Table 1) The separation was performed in the presence of anionic and cationic surfactants to obtain complete baseline separation of the metal ions. This approach is based on the successful separation of these metal ions by HPLC on a reverse phase column using the 8-hydroxyquinoline family of ligands and anionic and cationic surfactants. [17] This work clearly demonstrated that the organized microenvironment of the surfactant mediated the complete separation of Co(II), Ni(II), Cu(II) and Zn(II).
Figure 6. Sample Preparation by Precolumn Complex Formation Method
Mobile Phase: Succinate Buffer, pH 5.82, I = 0.05 M
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II)
Figure 7. Sample Preparation by Oncolumn Complex Formation Method
Mobile Phase: Succinate Buffer, pH 5.77, $I = 0.02$ M
1 = Zn(II), 2 = Co(II), 3 = Cu(II), 4 = Ni(II)
Table 1

Metal Ion Separation in the Absence of Surfactants

<table>
<thead>
<tr>
<th></th>
<th>Zn(II)</th>
<th>Co(II)</th>
<th>Ni(II)</th>
<th>Cu(II)</th>
<th>Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1:2 Complex)</td>
<td>(1:3 Complex)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precolumn Complex Formation (pH 5.82)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrophoretic Mobility, $\mu$ (cm$^2$/Vs)</td>
<td>-2.0x10$^{-4}$ ±0.1x10$^{-4}$</td>
<td>-2.0x10$^{-4}$ ±0.1x10$^{-4}$</td>
<td>-2.2x10$^{-4}$ ±0.1x10$^{-4}$</td>
<td>-2.4x10$^{-4}$ ±0.1x10$^{-4}$</td>
<td>-3.1x10$^{-4}$ ±0.1x10$^{-4}$</td>
</tr>
<tr>
<td>Oncolumn Complex Formation (pH 5.77)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrophoretic Mobility, $\mu$ (cm$^2$/Vs)</td>
<td>-2.7x10$^{-4}$ ±0.1x10$^{-4}$</td>
<td>-3.3x10$^{-4}$ ±0.1x10$^{-4}$</td>
<td>-3.7x10$^{-4}$ ±0.1x10$^{-4}$</td>
<td>-3.3x10$^{-4}$ ±0.1x10$^{-4}$</td>
<td></td>
</tr>
</tbody>
</table>

Note: All are 1:2 metal:ligand complexes except in the case of Co(II) which also formed a 1:3 metal:ligand complex (precolumn complex formation).
**Metal Ion Separation in Organized Microenvironments**

In order to improve separation between metal ions which have similar charge and size, as in the case with Co(II), Ni(II), Zn(II) and Cu(II), surfactant (cationic and anionic) mediated capillary chromatography was used.

**Metal Ion Separation with Cationic Surfactant**

**Precolumn Complex Formation**

A metal ion solution was added to an excess of ligand before the experiment. The optimum ligand:metal ratio was in the range 9-11 for the formation of metal complexes. An equilibrium is established between metal complexes and metal free ions, with most of the metal present in the complex form. Complex formation equilibrium is shown in Figure 8. Successful metal ion separation in the presence of cationic surfactant was achieved at concentrations of the surfactant below its cmc.

Low submicellar concentration of a cationic surfactant is necessary to obtain a reproducible concentration of SiO⁻ groups on the surface of the capillary wall. (Figure 9) This is important in order to obtain a reproducible baseline separation of Co(II), Ni(II), Cu(II) and Zn(II). The concentration of SiO⁻ groups in the absence of a cationic surfactant could have large variables and Si-O-Si groups may also be present, resulting in poor resolution of the metal ions. Concentration of a cationic surfactant at and above its cmc results in a monolayer formation [21, 27] blocking the SiO⁻ groups necessary for the generation of EOF and separation. A very high concentration of a cationic surfactant would lead to bilayer formation and reversal of the EOF. These concentrations of cationic surfactants did not yield baseline separations of metal ions.

pH, ligand:metal ratio and ionic strength were varied to obtain optimum separation of Zn(II), Ni(II), Co(II) and Cu(II) and to understand the mechanism of their separation.
Figure 8. Metal Complex Formation Equilibrium for HQS
Figure 9. Adsorption of \((\text{CH}_3)_3\text{N}^+\text{R}\) on the Capillary Wall at Very Low Concentration of Silanol Groups. R is Octyl (OTAB) and Hexadecyl (CTAN).
**pH Dependence**

Choices of buffer and pH strongly influence separation parameters like selectivity of metal complexes and resolution. EOF is a function of SiO⁻ groups on the capillary wall and hence pH of the mobile phase. The extent of complexation depends on the ligand:metal ratio and pH.

Equilibrium for 1:2 metal:ligand complexes can be described in general by:

\[
M^{2+} + 2HL^- \leftrightarrow ML_2 + 2H^+ \quad (7)
\]

where: \( M = \text{metal} \)

With increasing pH less free metal ions and more complexes are present in the solution. The optimum pH range is a function of \( pK_a \) values of the ligand. Therefore, for HQS (\( pK_1 = 2.04 \), \( pK_2 = 4.19 \), \( pK_3 = 8.48 \)) metal complexation pH used should be greater than the \( pK_2 \) value of the ligand. (Figure 10)

It was determined that baseline separation of metal ions could not be achieved below pH 5.7 due to insufficient concentration of SiO⁻ groups on the capillary wall.

Differences in electrophoretic mobilities of metal ligand complexes result from distribution equilibria between SiO⁻ on capillary wall and complexes in the mobile phase for separation with OTAB and CTAN. In the case of SDS, it results from distribution equilibria between SiO⁻ on the capillary and complexes in the micellar mobile phase.

Stability constants of the metal complexes are shown in Table 2. [16]

Four different buffer systems (succinate, phosphate, tris and borate) were used for the pH dependence experiments. However, only experiments with succinic and phosphoric acid buffers as an electrophoretic gave reproducible results. Electropherograms did not show any metal peaks, or peaks were not reproducible, in experiments with tris-buffer as the electrophoretic buffer. When a borate buffer was used, separation was achieved but metal peaks were very broad.
Ligand: 8-hydroxyquinoline-5-sulfonic acid hydrate

Figure 10. HQS, Molecular Weight = 225.23 g/mole
<table>
<thead>
<tr>
<th>Log Stability Constant (Ligand: HQS)</th>
<th>Co(II)</th>
<th>Zn(II)</th>
<th>Cu(II)</th>
<th>Ni(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_1$</td>
<td>8.11</td>
<td>7.54</td>
<td>11.92</td>
<td>9.02</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>6.95</td>
<td>6.78</td>
<td>9.95</td>
<td>7.75</td>
</tr>
<tr>
<td>$\beta$</td>
<td>15.06</td>
<td>14.32</td>
<td>21.87</td>
<td>16.77</td>
</tr>
<tr>
<td>$\beta_3$</td>
<td>5.36</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta'$</td>
<td>20.42</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Metal ion separation in the presence of the cationic surfactant OTAB were successful in the succinate and phosphate buffer environments. A succinate buffer was used as the electrophoretic buffer in the pH range 5.7-6.7. Calculation of the fraction of species, shown in Figure 11 and Appendix A, indicate that Cu, Zn, Ni and Co are present as their 1:2 metal:ligand complexes and Co also forms 1:3 complex. The electropherogram in Figure 12 indicates peaks for 1:2 and 1:3 metal:ligand complexes for Co(II). The 1:2 complex has a faster migration time than the 1:3 complex as could be expected based on their charge-to-size ratio (q/r, Equation 6). This also indicates that the equilibrium between the 1:2 and 1:3 complex is slow compared to that between the 1:1 and the 1:2 complex, which is fast. Experimental data shows that separation is better in the presence of a surfactant (Figure 12) than in its absence (Figure 6).

Electrophoretic mobilities and logs of distribution constants were calculated from the experimental data (Figure 12 and Appendix C) and are summarized in Tables 3 and 4 respectively. Equations 1-4 were used for these calculations.

A distribution constant (Table 4) is an important parameter in chromatography which characterizes the distribution of an analyte between the mobile and stationary phases. The distribution constant was calculated from the experimental migration times of the ionic species and neutral marker using Equation 4.

Figure 13 shows the log of the distribution constant vs. pH.

The slopes of log D vs. pH (Table 5) do not follow values expected from complex formations (Equations 8-10) or dissociation equilibria which would be +2 and -2 respectively for 1:2 metal:ligand complexes.

We propose the mechanism (Equations 11-14) for separation based on the hypothesis of interaction between the capillary surface silanol groups and ML$_2^{2-}$ complexes in the mobile phase. Here, $K_2$ is the acid dissociation constant of the silanol group.

\[
M^{2+} + 2HL^{-} \rightleftharpoons ML_2^{2-} + 2H^+ \quad (8)
\]
Figure 11. Fraction Calculations. pH 3.5-7.2
Figure 12. pH Dependence. Metal-HQS Complexes at Different pH.
Succinate Buffer, pH = 5.75, I = 0.05 M, Applied Voltage = 15 kV
Capillary Pretreated with 2x10^{-3} M OTAB
1 = Ligand, 2 = Zn(II), Co(II) (1:2 Complex), 3 = Ni(II), 4 = Cu(II),
5 = Co (II) (1:3 Complex)
<table>
<thead>
<tr>
<th>pH</th>
<th>$\mu_{\text{Zn(II) + Co(II)}}$ (cm$^2$/Vs)</th>
<th>$\mu_{\text{Ni(II)}}$ (cm$^2$/Vs)</th>
<th>$\mu_{\text{Cu(II)}}$ (cm$^2$/Vs)</th>
<th>$\mu_{\text{Co(II)}}$ (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.75</td>
<td>$-2.36 \times 10^{-4}$ ± $1.21 \times 10^{-5}$</td>
<td>$-2.46 \times 10^{-4}$ ± $1.25 \times 10^{-5}$</td>
<td>$-2.84 \times 10^{-4}$ ± $1.44 \times 10^{-5}$</td>
<td>$-3.46 \times 10^{-4}$ ± $1.62 \times 10^{-5}$</td>
</tr>
<tr>
<td>5.9</td>
<td>$-2.29 \times 10^{-4}$ ± $1.14 \times 10^{-5}$</td>
<td>$-2.44 \times 10^{-4}$ ± $1.24 \times 10^{-5}$</td>
<td>$-2.76 \times 10^{-4}$ ± $1.42 \times 10^{-5}$</td>
<td>$-3.37 \times 10^{-4}$ ± $1.60 \times 10^{-5}$</td>
</tr>
<tr>
<td>6.1</td>
<td>$-2.27 \times 10^{-4}$ ± $1.14 \times 10^{-5}$</td>
<td>$-2.47 \times 10^{-4}$ ± $1.25 \times 10^{-5}$</td>
<td>$-2.74 \times 10^{-4}$ ± $1.42 \times 10^{-5}$</td>
<td>$-3.34 \times 10^{-4}$ ± $1.61 \times 10^{-5}$</td>
</tr>
<tr>
<td>6.3</td>
<td>$-2.23 \times 10^{-4}$ ± $1.13 \times 10^{-5}$</td>
<td>$-2.44 \times 10^{-4}$ ± $1.25 \times 10^{-5}$</td>
<td>$-2.66 \times 10^{-4}$ ± $1.32 \times 10^{-5}$</td>
<td>$-3.27 \times 10^{-4}$ ± $1.52 \times 10^{-5}$</td>
</tr>
<tr>
<td>6.5</td>
<td>$-2.19 \times 10^{-4}$ ± $1.13 \times 10^{-5}$</td>
<td>$-2.45 \times 10^{-4}$ ± $1.25 \times 10^{-5}$</td>
<td>$-2.63 \times 10^{-4}$ ± $1.3 \times 10^{-5}$</td>
<td>$-3.23 \times 10^{-4}$ ± $1.51 \times 10^{-5}$</td>
</tr>
<tr>
<td>6.7</td>
<td>$-2.19 \times 10^{-4}$ ± $1.13 \times 10^{-5}$</td>
<td>$-2.62 \times 10^{-4}$ ± $1.3 \times 10^{-5}$</td>
<td>$-3.19 \times 10^{-4}$ ± $1.51 \times 10^{-5}$</td>
<td></td>
</tr>
</tbody>
</table>
Table 4
Log D vs. pH (Succinate Buffer, OTAB)

<table>
<thead>
<tr>
<th>pH</th>
<th>Log D (Zn(II) + Co(II))</th>
<th>Log D (Ni(II))</th>
<th>Log D (Cu(II))</th>
<th>Log D (Co(II))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.75</td>
<td>0.04586 ±0.00230</td>
<td>0.083 ±0.004</td>
<td>0.2362 ±0.0119</td>
<td>0.5294 ±0.0265</td>
</tr>
<tr>
<td>5.9</td>
<td>0.01851 ±0.000911</td>
<td>0.078 ±0.004</td>
<td>0.204 ±0.0102</td>
<td>0.4842 ±0.0243</td>
</tr>
<tr>
<td>6.1</td>
<td>0.0109 ±0.00090</td>
<td>0.0894 ±0.004</td>
<td>0.1956 ±0.0099</td>
<td>0.4662 ±0.0232</td>
</tr>
<tr>
<td>6.3</td>
<td>-0.0064 ±0.00029</td>
<td>0.0784 ±0.004</td>
<td>0.1655 ±0.0099</td>
<td>0.4294 ±0.0228</td>
</tr>
<tr>
<td>6.5</td>
<td>-0.0220 ±0.0011</td>
<td>0.0806 ±0.004</td>
<td>0.1541 ±0.0077</td>
<td>0.4140 ±0.0202</td>
</tr>
<tr>
<td>6.7</td>
<td>-0.0220 ±0.0011</td>
<td></td>
<td>0.1495 ±0.0074</td>
<td>0.3939 ±0.0200</td>
</tr>
</tbody>
</table>
Figure 13. pH Dependence. Log D vs. pH
<table>
<thead>
<tr>
<th></th>
<th>Zn(II), Co(II)</th>
<th>Ni(II)</th>
<th>Cu(II)</th>
<th>Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1:2 Complex)</td>
<td>(1:3 Complex)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slope</td>
<td>-0.0702 ±0.0035</td>
<td>-0.0023 ±0.0001</td>
<td>-0.09 ±0.0045</td>
<td>0.0013 ±0.0065</td>
</tr>
<tr>
<td>Intercept</td>
<td>0.4397 ±0.0220</td>
<td>0.096 ±0.0048</td>
<td>0.743 ±0.03715</td>
<td>0.2876 ±0.0144</td>
</tr>
</tbody>
</table>
\[ K = \frac{[ML^2\cdot] \times [H^+]^2}{[M^{2+}] \times [HL^-]^2} \]  \hspace{1cm} (9)

\[ \log K = \log D - 2pH - 2\log [HL^-] \]  \hspace{1cm} (10)

\[
\begin{array}{c}
\text{Si-OH} \\
\downarrow
\end{array}
\begin{array}{c}
\text{K}_2 \\
\Rightarrow
\end{array}
\begin{array}{c}
\text{Si-O}^- \\
\downarrow
\end{array}
\begin{array}{c}
\text{Si-OH} \\
\end{array}
\Rightarrow
\begin{array}{c}
\text{Si-O}^- + 2H^+ \\
\end{array}
\hspace{1cm} (11)

\[
\begin{array}{c}
\text{Si-O}^- \\
\downarrow
\end{array}
\begin{array}{c}
\end{array}
\begin{array}{c}
\Rightarrow
\end{array}
\begin{array}{c}
\text{Si-O}^- + \text{ML}^2\cdot \\
\downarrow
\end{array}
\begin{array}{c}
\text{Si-O}^- \\
\end{array}
\Rightarrow
\begin{array}{c}
\text{M + 2L}^2\cdot \\
\end{array}
\hspace{1cm} (12)

Overall equilibrium is the sum of (11) and (12):

\[
\begin{array}{c}
\text{Si-OH} \\
\downarrow
\end{array}
\begin{array}{c}
\text{K}_\text{Si} \\
\Rightarrow
\end{array}
\begin{array}{c}
\text{Si-O}^- \\
\downarrow
\end{array}
\begin{array}{c}
\text{Si-OH} \\
\end{array}
\Rightarrow
\begin{array}{c}
\text{M + 2H}^+ + 2\text{L}^2\cdot \\
\end{array}
\hspace{1cm} (13)

\[ \mu \propto K_\text{Si} [\text{SiO}^-] \]  \hspace{1cm} (14)

This mechanism indicates that the exchange of metal ions between the metal complexes in the mobile phase and surface silanol groups results in differences in electrophoretic mobilities of the metal ions. We propose a new empirical parameter, \( K_e \), with respect to: (a) the electrophoretic mobility of the metal ion; (b) the concentration of the free metal ion; (c) the metal complex stability, \( \beta \); and (d) the acid dissociation constant, \( K_a \), of HQS.
This empirical parameter is related to the distribution constant of the metal ion determined from the electropherograms, and the acid dissociation constant, $K_2$, of the silanol groups.

\[
K_e = \frac{\mu}{\beta K_a^2 [M^{2+}]} \tag{15}
\]

The distribution constant, $D$, is defined in Equation 17 and is calculated from the mobilities of the anionic complex and acetone (EOF marker), Equation 4.

\[
K_e = \frac{K_2 \times D \times [HL^-]^2}{[(SiO^-)_2] \times [H^+]^2} \tag{16}
\]

Equation 18 can be derived for pH dependence based on the mechanism and the derivation of $K_e$ and $D$.

\[
\log K_e - \log D - 2 \log [HL^-] = \frac{\log K_2 + 2pH}{[(SiO^-)_2]} \tag{18}
\]

The values of $K_e$ calculated using Equation 18 are displayed in Table 6.
Table 6
Log $K_e$ vs. pH (Succinate Buffer, OTAB)

<table>
<thead>
<tr>
<th>pH</th>
<th>Log $K_e$ (\text{Zn(II) + Co(II)})</th>
<th>Log $K_e$ (\text{Ni(II)})</th>
<th>Log $K_e$ (\text{Cu(II)})</th>
<th>Log $K_e$ (\text{Co(II)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.75</td>
<td>6.01</td>
<td>3.32</td>
<td>6.07</td>
<td>6.38</td>
</tr>
<tr>
<td>5.9</td>
<td>6.39</td>
<td>3.68</td>
<td>6.46</td>
<td>6.85</td>
</tr>
<tr>
<td>6.1</td>
<td>6.78</td>
<td>4.06</td>
<td>6.86</td>
<td>7.36</td>
</tr>
<tr>
<td>6.3</td>
<td>7.17</td>
<td>4.44</td>
<td>7.24</td>
<td>7.87</td>
</tr>
<tr>
<td>6.5</td>
<td>7.37</td>
<td>4.63</td>
<td>7.43</td>
<td>8.14</td>
</tr>
<tr>
<td>6.7</td>
<td>7.75</td>
<td></td>
<td>7.83</td>
<td>8.68</td>
</tr>
</tbody>
</table>
Equation 18 clearly indicates that the plot of the quantity on the left hand side vs. pH should yield a slope of 2 for 1:2 metal:ligand complexes.

The plot in Figure 14 clearly indicates slopes close to +2 for Ni(II), Cu(II) and Zn(II). In the case of Co(II) the slopes for calculations based on the slower migration time is between 2 and 3 indicating the presence of both 1:2 and 1:3 complexes. The slope for Co(II) with a faster migration time is close to 2 and this line lies very close to Zn(II); it is not displayed for the sake of clarity.

Silanol groups per cm$^2$ can be derived based on Equation 19 and intercept values. Comparisons of experimental [SiO]$^2_2$ values with theoretical [SiO]$^2_2$ values, which is equal to $5.9 \times 10^{15}$ groups/cm$^2$ [22], show that these values are reasonably close.

\[
\frac{K_2}{[(SiO^2)^2]} = \frac{10^\text{intercept} \times N_A}{N_A} \tag{19}
\]

where: \(N_A = \text{Avogadro's number} \ (6.022 \times 10^{23} \ \text{mol}^{-1})\)

A phosphate buffer was also used in the pH range 6.2-7.3. 1:2 metal:ligand complexes are present for Ni(II), Cu(II) and Zn(II) and both 1:2 and 1:3 metal:ligand complexes are present for Co(II). (Figure 11) Experimental data are presented in Figure 15 and Appendix C. It is evident that the migration of Ni(II) gets slower as pH increases and eventually has migration times between the times of Cu(II) and Co(II).

Electrophoretic mobilities and log $K_\varepsilon$ were calculated from experimental data and are summarized in Tables 7 and 8 respectively.

Plots of log D vs. pH again have slopes that do not provide any information on the equalibria contributing to the separation of complexes. The plot of log $K_\varepsilon$ in Figure 16, Equation 18 and log $K_\varepsilon$ vs. pH does provide the correct slopes as predicted by the mechanism.

Slopes for Figure 16 and Table 11 indicate the presence of 1:2 complexes for Zn(II), Cu(II) and both 1:2 and 1:3 complexes for Co(II).
Figure 14. pH Dependence. Log $K_e - \log D - 2\log [HL^-]$ vs. pH
Figure 15. pH Dependence. Metal-HQS Complexes at Different pH. Phosphate Buffer, pH 6.98, Capillary Pretreated with 2x10^{-3} M OTAB
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
<table>
<thead>
<tr>
<th>pH</th>
<th>( \mu \text{ Zn(II)+Co(II)} ) (cm(^2)/Vs)</th>
<th>( \mu \text{ Ni(II)} ) (cm(^2)/Vs)</th>
<th>( \mu \text{ Cu(II)} ) (cm(^2)/Vs)</th>
<th>( \mu \text{ Co(II)} ) (cm(^2)/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.23</td>
<td>-2.43x10(^{-4}) ±1.1x10(^{-5})</td>
<td>-2.77x10(^{-4}) ±1.2x10(^{-5})</td>
<td>-2.86x10(^{-4}) ±1.3x10(^{-5})</td>
<td>-3.49x10(^{-4}) ±1.6x10(^{-5})</td>
</tr>
<tr>
<td>6.43</td>
<td>-2.52x10(^{-4}) ±1.1x10(^{-5})</td>
<td>-2.86x10(^{-4}) ±1.2x10(^{-5})</td>
<td>-2.93x10(^{-4}) ±1.4x10(^{-5})</td>
<td>-3.55x10(^{-4}) ±1.6x10(^{-5})</td>
</tr>
<tr>
<td>6.73</td>
<td>-2.59x10(^{-4}) ±1.1x10(^{-5})</td>
<td>-2.98x10(^{-4}) ±1.4x10(^{-5})</td>
<td>-3.59x10(^{-4}) ±1.7x10(^{-5})</td>
<td></td>
</tr>
<tr>
<td>6.98</td>
<td>-2.65x10(^{-4}) ±1.1x10(^{-5})</td>
<td>-3.00x10(^{-4}) ±1.4x10(^{-5})</td>
<td>-3.6x10(^{-4}) ±1.7x10(^{-5})</td>
<td></td>
</tr>
<tr>
<td>7.28</td>
<td>-2.70x10(^{-4}) ±1.2x10(^{-5})</td>
<td>-2.97x10(^{-4}) ±1.4x10(^{-5})</td>
<td>-3.55x10(^{-4}) ±1.7x10(^{-5})</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>Log $K_e$ Zn(II), Co(II) (1:2 Complex)</td>
<td>Log $K_e$ Ni(II)</td>
<td>Log $K_e$ Cu(II)</td>
<td>Log $K_e$ Co(II) (1:3 Complex)</td>
</tr>
<tr>
<td>-----</td>
<td>-------------------------------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>6.23</td>
<td>6.81</td>
<td>4.11</td>
<td>6.87</td>
<td>7.37</td>
</tr>
<tr>
<td>6.43</td>
<td>7.22</td>
<td>4.50</td>
<td>7.28</td>
<td>7.91</td>
</tr>
<tr>
<td>6.73</td>
<td>7.83</td>
<td>7.95</td>
<td>8.73</td>
<td></td>
</tr>
<tr>
<td>6.98</td>
<td>8.41</td>
<td>8.47</td>
<td>9.57</td>
<td></td>
</tr>
<tr>
<td>7.28</td>
<td>8.99</td>
<td>9.03</td>
<td>10.39</td>
<td></td>
</tr>
</tbody>
</table>
Figure 16. pH Dependence. $\log K_e - \log D - 2\log [HL']$ vs. pH. pH 6.2-7.3
Silanol groups per cm² (Table 12) calculated from the intercept values using Equation 19 are similar to the theoretical value.

Metal ion separations were also performed with the cationic surfactant CTAN to examine the effect of surfactant alkyl chain length. The cmc of CTAN is 1 × 10⁻⁴ M which is much lower than the cmc of OTAB (0.269 M). Therefore, a much smaller concentration of CTAN is needed to form micelles. However, metal ion separation was better at a sub-micellar condition as in the case of OTAB. The capillary was conditioned with 1 × 10⁻⁵ M of surfactant by rinsing it before each run. As OTAB experiments have shown, precolumn complex formation is better for metal ion separation in the presence of the cationic surfactant than the oncolumn complex formation method. Thus, only the precolumn complex formation method was used in CTAN experiments.

Metal ion separation was carried out with CTAN in the pH range 6.12-7.28. (Figure 17) Electrophoretic mobilities and log $K_c$ are presented in Tables 9 and 10.

The data treatment based on log $K_c$ vs. pH (Figures 14, 18 and Table 11) indicates that this method is applicable to the separation of metal ions in the presence of CTAN. According to the slope, values (1:2 metal complexes in the case of Zn(II), Co(II), Ni(II) and Cu(II) and 1:3 complex in the case of Co(II)) were formed. Slopes are consistent with values that were calculated based on data from the pH dependence experiments in the presence of another cationic surfactant, OTAB. A meaningful separation mechanism is discerned not from a plot of log $D$ vs. pH, but from the plot of log $K_c$ vs. pH in both cases. This demonstrates the value of the parameter $K_c$ to understanding electrophoretic separations.

Silanol groups/cm² were calculated from experimental intercept values. (Figures 14 and 18 and Table 12)

Table 12 indicates agreement between the experimental values of silanol groups/cm² from the intercept and the theoretical value 5.9 × 10¹⁵. (Appendix B) Significant low and high deviations from this value are also observed with Co(II)(1:3). A complex always yields much higher values. The proposed mechanism and the $K_c$ provide a molecular-level understanding of the separation of metal ions.
Figure 17.  

pH Dependence. Phosphate Buffer, pH 6.66  
Capillary Pretreated with 1x10^{-5} M CTAN  
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
<table>
<thead>
<tr>
<th>pH</th>
<th>μ Zn(II) (cm²/Vs)</th>
<th>μ Ni(II) (cm²/Vs)</th>
<th>μ Cu(II) (cm²/Vs)</th>
<th>μ Co(II) (cm²/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.23</td>
<td>-2.24x10⁴±1.1x10⁵</td>
<td>-2.42x10⁴±1.2x10⁵</td>
<td>-2.69x10⁴±1.3x10⁵</td>
<td>-3.35x10⁴±1.6x10⁵</td>
</tr>
<tr>
<td>6.4</td>
<td>-2.47x10⁴±1.2x10⁵</td>
<td>-2.65x10⁴±1.3x10⁵</td>
<td>-2.86x10⁴±1.4x10⁵</td>
<td>-3.49x10⁴±1.7x10⁵</td>
</tr>
<tr>
<td>6.66</td>
<td>-2.33x10⁴±1.1x10⁵</td>
<td>-2.71x10⁴±1.3x10⁵</td>
<td>-2.71x10⁴±1.3x10⁵</td>
<td>-3.33x10⁴±1.6x10⁵</td>
</tr>
<tr>
<td>6.92</td>
<td>-2.37x10⁴±1.1x10⁵</td>
<td>-2.78x10⁴±1.3x10⁵</td>
<td>-2.71x10⁴±1.3x10⁵</td>
<td>-3.33x10⁴±1.6x10⁵</td>
</tr>
<tr>
<td>7.12</td>
<td>-2.38x10⁴±1.1x10⁵</td>
<td>-2.86x10⁴±1.4x10⁵</td>
<td>-2.71x10⁴±1.3x10⁵</td>
<td>-3.32x10⁴±1.6x10⁵</td>
</tr>
<tr>
<td>pH</td>
<td>Log $K_e$ Zn(II)</td>
<td>Log $K_e$ Ni(II)</td>
<td>Log $K_e$ Cu(II)</td>
<td>Log $K_e$ Co(II)</td>
</tr>
<tr>
<td>----</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>6.23</td>
<td>6.93</td>
<td>4.19</td>
<td>6.97</td>
<td>7.46</td>
</tr>
<tr>
<td>6.4</td>
<td>7.35</td>
<td>4.60</td>
<td>7.39</td>
<td>8.00</td>
</tr>
<tr>
<td>6.66</td>
<td>7.92</td>
<td>5.19</td>
<td>7.96</td>
<td>8.80</td>
</tr>
<tr>
<td>6.92</td>
<td>8.31</td>
<td>5.58</td>
<td>8.35</td>
<td>9.36</td>
</tr>
<tr>
<td>7.12</td>
<td>8.69</td>
<td>5.97</td>
<td>8.74</td>
<td>9.92</td>
</tr>
</tbody>
</table>
Figure 18. pH Dependence. Log $K_e - \log D - 2 \log [HL^-]$ vs. pH
Phosphate Buffer, Capillary Pretreated with CTAN
Table 11
Log $K_e = \log D - 2 \log [H^+]$ vs. pH

<table>
<thead>
<tr>
<th></th>
<th>Zn(II), Co(II)</th>
<th>Ni(II)</th>
<th>Cu(II)</th>
<th>Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1:2 Complex)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slope</td>
<td>$1.8828 \pm 0.0941$</td>
<td>$1.7839 \pm 0.0892$</td>
<td>$1.8828 \pm 0.0941$</td>
<td>$2.4944 \pm 0.1247$</td>
</tr>
<tr>
<td>Intercept</td>
<td>$1.1381 \pm 0.0569$</td>
<td>$-0.9253 \pm 0.0463$</td>
<td>$1.1381 \pm 0.0569$</td>
<td>$-2.3621 \pm 0.1181$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Phosphate Buffer, pH 6.2-7.3, OTAB
| Slope         | $2.0915 \pm 0.1046$ |            | $2.0915 \pm 0.1046$ | $2.938 \pm 0.1469$ |
| Intercept     | $-0.3137 \pm 0.0157$ |            | $-0.3137 \pm 0.0157$ | $-5.3914 \pm 0.2696$ |
|              |                |            |            |            |
| Phosphate Buffer, pH 6.2-7.2, CTAN
<p>| Slope         | $2.014 \pm 0.1007$ | $1.8343 \pm 0.0917$ | $2.014 \pm 0.1007$ | $2.8195 \pm 0.1410$ |
| Intercept     | $0.3061 \pm 0.0153$ | $-1.2519 \pm 0.0626$ | $0.3061 \pm 0.0153$ | $-4.5215 \pm 0.2261$ |</p>
<table>
<thead>
<tr>
<th>Silanol Groups/cm²</th>
<th>Zn(II), Co(II)</th>
<th>Ni(II)</th>
<th>Cu(II)</th>
<th>Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>(1:2 Complex)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Succinate Buffer, pH 5.7-6.7, OTAB</td>
<td>5.51x10¹³ ±2.75x10¹²</td>
<td>6.38x10¹⁵ ±3.19x10¹⁴</td>
<td>5.51x10¹³ ±2.75x10¹²</td>
<td>1.75x10¹⁷ ±8.75x10¹⁵</td>
</tr>
<tr>
<td>[(SiO₂)₂]</td>
<td>9.85x10¹⁴ ±4.92x10¹³</td>
<td>9.85x10¹⁴ ±4.92x10¹³</td>
<td>1.18x10²⁰ ±5.90x10¹⁸</td>
<td></td>
</tr>
<tr>
<td>Phosphate Buffer, pH 6.2-7.3, OTAB</td>
<td>1.24x10¹⁵ ±6.2x10¹³</td>
<td>8.54x10¹⁵ ±4.1x10¹³</td>
<td>1.24x10¹⁵ ±6.2x10¹³</td>
<td>1.67x10¹⁹ ±8.2x10¹³</td>
</tr>
<tr>
<td>Phosphate Buffer, pH 6.2-7.2, CTAN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

50
Ligand Dependence

The proposed mechanism was further examined by varying ligand concentrations. These experiments were conducted by maintaining a constant metal ion concentration and varying the ligand concentration when the complexes were prepared for injection. The ligand-to-metal ratio was varied from 5-11. Ligand ([HQS] = 7.4x10^-4 - 9.8x10^-4 M) dependency experiments were conducted using a succinate buffer (Figure 19) and a phosphate buffer in the presence of OTAB.

Electrophoretic mobilities and log Ke values were calculated from experimental data and are summarized in Tables 13 and 14.

Log D vs. log [HQS] has slopes less than 1 and do not indicate the separation mechanism. However, the plot of log Ke - log D - 2pH (Equation 18) vs. log [HQS] clearly has slopes close to 2 for 1:2 complexes and slopes between 2 and 3 for Co(II), indicating both 1:2 and 1:3 complexes.

Silanol groups/cm\(^2\) were calculated from intercept values (Figure 20) using Equation 19. They reasonably agree with the theoretical value of 5.9x10\(^{15}\) M with deviation to the lower and higher values also observed.

A ligand dependence experiment was also performed using a phosphate buffer as the electrophoretic buffer at pH 6.2. The electropherograms of metal ion separation in the presence of OTAB are shown in Figure 21 and Appendix C for the different ligand concentrations.

Electrophoretic mobilities and Ke were calculated from experimental data. (Tables 15 and 16)

Log D vs. log [HQS] again does not provide information on the separation mechanism while log Ke - log D - 2pH vs. log [HQS] (Figure 22) has slopes 2 and 3 which indicate the formation of a 1:2 complex for Cu(II) and Zn(II) and both 1:2 and 1:3 complexes for Co(II).

The ligand:metal ratio of the metal complex for metal ion separation in the presence of CTAN was varied in the range 6-10 with an excess of ligand to examine the influence of ligand concentration on separation. Concentration of the metals was constant. Experimental data are presented in Figure 23 and Appendix C.
Figure 19. Separation of Metal-HQS Complexes
Succinate Buffer, pH = 6.2, Ligand Concentration: 8.3x10^{-4} M
Capillary Pretreated with 2x10^{-3} M OTAB
1 = Ligand, Zn(II)+Co(II), 2 = Ni(II), 3 = Cu(II), 4 = Co(II)
Table 13

Electrophoretic Mobilities vs. Ligand (Succinate Buffer, pH 6.2, OTAB)

<table>
<thead>
<tr>
<th>Ligand (HQS)</th>
<th>µ Zn(II) + Co(II)</th>
<th>µ Ni(II)</th>
<th>µ Cu(II)</th>
<th>µ Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (M)</td>
<td>(cm²/Vs)</td>
<td>(cm²/Vs)</td>
<td>(cm²/Vs)</td>
<td>(1:3 Complex) (cm²/Vs)</td>
</tr>
<tr>
<td>9.8x10⁻⁴</td>
<td>-2.46x10⁻⁴</td>
<td>-2.67x10⁻⁴</td>
<td>-2.83x10⁻⁴</td>
<td>-3.42x10⁻⁴</td>
</tr>
<tr>
<td>±1.1x10⁻⁵</td>
<td>±1.3x10⁻⁵</td>
<td>±1.5x10⁻⁵</td>
<td>±1.7x10⁻⁵</td>
<td>±1.7x10⁻⁵</td>
</tr>
<tr>
<td>9.2x10⁻⁴</td>
<td>-2.38x10⁻⁴</td>
<td>-2.57x10⁻⁴</td>
<td>-2.77x10⁻⁴</td>
<td>-3.35x10⁻⁴</td>
</tr>
<tr>
<td>±1.0x10⁻⁵</td>
<td>±1.2x10⁻⁵</td>
<td>±1.5x10⁻⁵</td>
<td>±1.6x10⁻⁵</td>
<td>±1.6x10⁻⁵</td>
</tr>
<tr>
<td>8.3x10⁻⁴</td>
<td>-2.40x10⁻⁴</td>
<td>-2.62x10⁻⁴</td>
<td>-2.81x10⁻⁴</td>
<td>-3.40x10⁻⁴</td>
</tr>
<tr>
<td>±1.0x10⁻⁵</td>
<td>±1.2x10⁻⁵</td>
<td>±1.5x10⁻⁵</td>
<td>±1.6x10⁻⁵</td>
<td>±1.6x10⁻⁵</td>
</tr>
<tr>
<td>7.4x10⁻⁴</td>
<td>-2.31x10⁻⁴</td>
<td>-2.55x10⁻⁴</td>
<td>-2.74x10⁻⁴</td>
<td>-3.33x10⁻⁴</td>
</tr>
<tr>
<td>±9x10⁻⁶</td>
<td>±1.2x10⁻⁵</td>
<td>±1.4x10⁻⁵</td>
<td>±1.6x10⁻⁵</td>
<td>±1.6x10⁻⁵</td>
</tr>
</tbody>
</table>
Table 14  
Log $K_c$ vs. Ligand (Sucinate Buffer, pH 6.2, OTAB)

<table>
<thead>
<tr>
<th>Log Ligand</th>
<th>Log $K_c$ Zn(II), Co(II)</th>
<th>Log $K_c$ Ni(II)</th>
<th>Log $K_c$ Cu(II)</th>
<th>Log $K_c$ Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (M)</td>
<td>(1:2 Complex)</td>
<td></td>
<td></td>
<td>(1:3 Complex)</td>
</tr>
<tr>
<td>-3.00877</td>
<td>6.82</td>
<td>4.10</td>
<td>6.87</td>
<td>7.37</td>
</tr>
<tr>
<td>-3.03621</td>
<td>6.75</td>
<td>4.03</td>
<td>6.81</td>
<td>7.28</td>
</tr>
<tr>
<td>-3.08197</td>
<td>6.66</td>
<td>3.94</td>
<td>6.72</td>
<td>7.17</td>
</tr>
<tr>
<td>-3.13312</td>
<td>6.55</td>
<td>3.84</td>
<td>6.61</td>
<td>7.03</td>
</tr>
</tbody>
</table>
Figure 20. Ligand Dependence. Log $K_e$ - Log D - 2pH vs. Log [HQS]
Succinate Buffer, pH 6.2, OTAB
Figure 21. Ligand Dependence Electropherograms
Phosphate Buffer, pH = 6.2, OTAB, [HQS] = 8.3x10^{-4} M
1 = Ligand, 2 = Zn(II), 3 = Co(II), 4 = Ni(II), 5 = Cu(II), 6 = Co(II)
Table 15

Electrophoretic Mobilities vs. Ligand (Phosphate Buffer, pH 6.2, OTAB)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$\mu$ Zn(II) (cm$^2$/Vs)</th>
<th>$\mu$ Co(II) (cm$^2$/Vs)</th>
<th>$\mu$ Ni(II) (cm$^2$/Vs)</th>
<th>$\mu$ Cu(II) (cm$^2$/Vs)</th>
<th>$\mu$ Co(II) (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (M)</td>
<td>$-2.04 \times 10^{-4}$</td>
<td>$-2.11 \times 10^{-4}$</td>
<td>$-2.39 \times 10^{-4}$</td>
<td>$-2.49 \times 10^{-4}$</td>
<td>$-3.11 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$\pm 9 \times 10^{-6}$</td>
<td>$\pm 9 \times 10^{-6}$</td>
<td>$\pm 1.2 \times 10^{-5}$</td>
<td>$\pm 1.5 \times 10^{-5}$</td>
<td>$\pm 1.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>$9.2 \times 10^{-4}$</td>
<td>$-2.00 \times 10^{-4}$</td>
<td>$-2.06 \times 10^{-4}$</td>
<td>$-2.34 \times 10^{-4}$</td>
<td>$-2.44 \times 10^{-4}$</td>
<td>$-3.13 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$\pm 9 \times 10^{-6}$</td>
<td>$\pm 9 \times 10^{-6}$</td>
<td>$\pm 1.2 \times 10^{-5}$</td>
<td>$\pm 1.5 \times 10^{-5}$</td>
<td>$\pm 1.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>$8.3 \times 10^{-4}$</td>
<td>$-2.12 \times 10^{-4}$</td>
<td>$-2.10 \times 10^{-4}$</td>
<td>$-2.39 \times 10^{-4}$</td>
<td>$-2.56 \times 10^{-4}$</td>
<td>$-3.18 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$\pm 9 \times 10^{-6}$</td>
<td>$\pm 9 \times 10^{-6}$</td>
<td>$\pm 1.2 \times 10^{-5}$</td>
<td>$\pm 1.5 \times 10^{-5}$</td>
<td>$\pm 1.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>$7.4 \times 10^{-4}$</td>
<td>$-2.20 \times 10^{-4}$</td>
<td>$-2.27 \times 10^{-4}$</td>
<td>$-2.52 \times 10^{-4}$</td>
<td>$-2.68 \times 10^{-4}$</td>
<td>$-3.30 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$\pm 1.0 \times 10^{-5}$</td>
<td>$\pm 1.0 \times 10^{-5}$</td>
<td>$\pm 1.5 \times 10^{-5}$</td>
<td>$\pm 1.6 \times 10^{-5}$</td>
<td>$\pm 1.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>Ligand Concentration (M)</td>
<td>Log $K_c$ Zn(II)</td>
<td>Log $K_c$ Co(II)</td>
<td>Log $K_c$ Ni(II)</td>
<td>Log $K_c$ Cu(II)</td>
<td>Log $K_c$ Co(II)</td>
</tr>
<tr>
<td>--------------------------</td>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>-3.00877</td>
<td>6.74</td>
<td>7.15</td>
<td>4.05</td>
<td>6.81</td>
<td>7.32</td>
</tr>
<tr>
<td>-3.03621</td>
<td>6.67</td>
<td>7.07</td>
<td>3.99</td>
<td>6.75</td>
<td>7.20</td>
</tr>
<tr>
<td>-3.08197</td>
<td>6.61</td>
<td>6.98</td>
<td>3.91</td>
<td>6.68</td>
<td>7.15</td>
</tr>
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<td>-3.13312</td>
<td>6.53</td>
<td>6.87</td>
<td>3.83</td>
<td>6.60</td>
<td>7.03</td>
</tr>
</tbody>
</table>
Figure 22. Ligand Dependence. Log $K_e$ - Log D - 2pH vs. Log [HQS].
Phosphate Buffer, pH 6.2, Capillary Pretreated with 2x10^{-3} M OTAB
Figure 23. Ligand Dependence (Concentration: $7.4 \times 10^{-4}$ M)
Phosphate Buffer, pH 6.2, CTAN
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Electrophoretic mobilities and log $K_e$ were calculated from experimental data. Results are summarized in Tables 17 and 18.

Experimental plots are presented in Figure 24. Slopes and intercepts are summarized in Table 19.

Data analysis using $K_e$ (Table 19) clearly indicates the formation of 1:2 metal:ligand complexes for metal ions except Co(II) which yields a 1:3 complex as well. Data analysis for all metal ions supports the proposed mechanism and analysis using $K_e$.

Reasonable agreement between calculated and theoretical values of silanol groups/cm$^2$ is observed with several intercepts. Deviations to the lower and higher values of the silanol group concentration are also observed. Experimental values of silanol groups/cm$^2$ in Tables 12 and 20 support the mechanism in which the silanol groups exchange metal ions with the ligand in the mobile phase.

**Surfactant Dependence**

To determine the role of a surfactant in metal ion separation, the capillary was conditioned with different concentrations of the cationic surfactant, CTAN, before the separation. Concentration of the surfactant was varied from values below to values above the cmc of the surfactant. Experimental data is presented in Figure 25.

Concentration of the surfactant that was used for capillary conditioning was varied from 0 M to $8 \times 10^{-3}$ M. Separations of the metal ions were only obtained at a CTAN concentration at or below its cmc. Separations at lower surfactant concentration values, $1 \times 10^{-5}$ M (Figure 17), were better than at higher surfactant concentration values, $6 \times 10^{-5}$ M (Figure 25). Also, separations were poor above cmc due to the formation of a monolayer and eventually a bilayer of CTAN on the capillary walls. However, data was used for all concentrations of the surfactant in our calculations.

Calculated electrophoretic mobilities and log $K_e$ are summarized in Tables 21 and 22. Log $K_e$ was plotted vs. the log concentration of the surfactant. (Figure 26)
Table 17
Electrophoretic Mobilities vs. Ligand (Phosphate Buffer, pH 6.2, CTAN)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$\mu$ Zn(II) (cm$^2$/Vs)</th>
<th>$\mu$ Ni(II) (cm$^2$/Vs)</th>
<th>$\mu$ Cu(II) (cm$^2$/Vs)</th>
<th>$\mu$ Co(II) (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (M) (cm$^2$/Vs)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.8x10^{-4}</td>
<td>-2.19x10^{-4} ±1.1x10^{-5}</td>
<td>-2.45x10^{-4} ±1.2x10^{-5}</td>
<td>-2.63x10^{-4} ±1.3x10^{-5}</td>
<td>-3.29x10^{-4} ±1.6x10^{-5}</td>
</tr>
<tr>
<td>8.3x10^{-4}</td>
<td>-2.15x10^{-4} ±1.1x10^{-5}</td>
<td>-2.37x10^{-4} ±1.1x10^{-5}</td>
<td>-2.59x10^{-4} ±1.2x10^{-5}</td>
<td>-3.27x10^{-4} ±1.6x10^{-5}</td>
</tr>
<tr>
<td>7.4x10^{-4}</td>
<td>-2.07x10^{-4} ±1.0x10^{-5}</td>
<td>-2.32x10^{-4} ±1.1x10^{-5}</td>
<td>-2.52x10^{-4} ±1.2x10^{-5}</td>
<td>-3.17x10^{-4} ±1.5x10^{-5}</td>
</tr>
<tr>
<td>6.6x10^{-4}</td>
<td>-2.22x10^{-4} ±1.1x10^{-5}</td>
<td>-2.44x10^{-4} ±1.2x10^{-5}</td>
<td>-2.66x10^{-4} ±1.3x10^{-5}</td>
<td>-3.32x10^{-4} ±1.6x10^{-5}</td>
</tr>
<tr>
<td>5.5x10^{-4}</td>
<td>-2.09x10^{-4} ±1.1x10^{-5}</td>
<td>-2.35x10^{-4} ±1.1x10^{-5}</td>
<td>-2.55x10^{-4} ±1.2x10^{-5}</td>
<td>-3.19x10^{-4} ±1.2x10^{-5}</td>
</tr>
<tr>
<td>Ligand Concentration (M)</td>
<td>Log $K_\varepsilon$ Zn(II)</td>
<td>Log $K_\varepsilon$ Ni(II)</td>
<td>Log $K_\varepsilon$ Cu(II)</td>
<td>Log $K_\varepsilon$ Co(II)</td>
</tr>
<tr>
<td>-------------------------</td>
<td>--------------------------</td>
<td>----------------------------</td>
<td>---------------------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>$9.8 \times 10^{-4}$</td>
<td>6.77</td>
<td>4.06</td>
<td>6.84</td>
<td>7.35</td>
</tr>
<tr>
<td>$8.3 \times 10^{-4}$</td>
<td>6.62</td>
<td>3.91</td>
<td>6.69</td>
<td>7.16</td>
</tr>
<tr>
<td>$7.4 \times 10^{-4}$</td>
<td>6.50</td>
<td>3.80</td>
<td>6.57</td>
<td>7.01</td>
</tr>
<tr>
<td>$6.6 \times 10^{-4}$</td>
<td>6.44</td>
<td>3.74</td>
<td>6.50</td>
<td>6.92</td>
</tr>
<tr>
<td>$5.5 \times 10^{-4}$</td>
<td>6.26</td>
<td>3.57</td>
<td>6.33</td>
<td>6.70</td>
</tr>
</tbody>
</table>
Figure 24. Ligand Dependence. Log $K_e$ - Log D - 2pH vs. Log [HQS]
<table>
<thead>
<tr>
<th></th>
<th>Zn(II), Co(II)</th>
<th>Ni (II)</th>
<th>Cu(II)</th>
<th>Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>(1:2 Complex)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Succinate Buffer, pH 6.2, OTAB</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slope</td>
<td>1.8687 ±0.0934</td>
<td>1.7281 ±0.0864</td>
<td>1.8687 ±0.0934</td>
<td>2.3576 ±0.1179</td>
</tr>
<tr>
<td>Intercept</td>
<td>-0.1292 ±0.0065</td>
<td>-3.2575 ±0.1629</td>
<td>-0.1292 ±0.0065</td>
<td>1.5677 ±0.0784</td>
</tr>
<tr>
<td>Phosphate Buffer, pH 6.2, OTAB</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slope</td>
<td>2.8609 ±0.1430</td>
<td>2.1519 ±0.1076</td>
<td>2.4493 ±0.1224</td>
<td>3.1244 ±0.1562</td>
</tr>
<tr>
<td>Intercept</td>
<td>3.3975 ±0.1700</td>
<td>-1.9539 ±0.0977</td>
<td>1.6692 ±0.0835</td>
<td>3.929 ±0.1964</td>
</tr>
<tr>
<td>Phosphate Buffer, pH 6.2, CTAN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slope</td>
<td>1.9682 ±0.0984</td>
<td>1.8272 ±0.0914</td>
<td>1.9682 ±0.0984</td>
<td>2.4415 ±0.1221</td>
</tr>
<tr>
<td>Intercept</td>
<td>0.1628 ±0.0081</td>
<td>-2.9691 ±0.1485</td>
<td>0.1628 ±0.0081</td>
<td>1.8076 ±0.0904</td>
</tr>
<tr>
<td></td>
<td>Zn(II), Co(II)</td>
<td>Ni(II)</td>
<td>Cu(II)</td>
<td>Co(II)</td>
</tr>
<tr>
<td>---------------------</td>
<td>----------------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td><strong>Silanol Groups/cm²</strong></td>
<td>(1:2 Complex)</td>
<td>(1:3 Complex)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Succinate Buffer, pH 6.2, OTAB</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([(\text{SiO})_2])</td>
<td>1.02x10^{15}</td>
<td>1.37x10^{18}</td>
<td>1.02x10^{15}</td>
<td>4.84x10^{14}</td>
</tr>
<tr>
<td>±5.10x10^{13}</td>
<td>±6.85x10^{16}</td>
<td>±5.10x10^{13}</td>
<td>±5.10x10^{13}</td>
<td>±2.42x10^{13}</td>
</tr>
<tr>
<td><strong>Phosphate Buffer, pH 6.2, OTAB</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([(\text{SiO})_2])</td>
<td>3.03x10^{11}</td>
<td>6.8x10^{16}</td>
<td>1.62x10^{13}</td>
<td>8.93x10^{11}</td>
</tr>
<tr>
<td>±5.10x10^{10}</td>
<td>±3.4x10^{15}</td>
<td>±8.10x10^{11}</td>
<td>±8.10x10^{11}</td>
<td>±4.47x10^{10}</td>
</tr>
<tr>
<td><strong>Phosphate Buffer, pH 6.2, CTAN</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([(\text{SiO})_2])</td>
<td>4.66x10^{15}</td>
<td>7.06x10^{17}</td>
<td>4.66x10^{15}</td>
<td>4.19x10^{14}</td>
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<tr>
<td>±2.3x10^{14}</td>
<td>±3.5x10^{16}</td>
<td>±2.3x10^{14}</td>
<td>±2.0x10^{13}</td>
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</tr>
</tbody>
</table>
Figure 25.  Surfactant Dependence (Concentration: 6.0x10^{-5} M)  
Mobile Phase: Phosphoric Buffer, pH 6.2  
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Table 21

Electrophoretic Mobilities vs. CTAN (Phosphate Buffer, pH 6.2)

<table>
<thead>
<tr>
<th>CTAN</th>
<th>μ Zn(II) (cm²/Vs)</th>
<th>μ Ni(II) (cm²/Vs)</th>
<th>μ Cu(II) (cm²/Vs)</th>
<th>μ Co(II) (cm²/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-2.58x10⁻⁴ ±1.2x10⁻⁵</td>
<td>-3.14x10⁻⁴ ±1.5x10⁻⁵</td>
<td>-3.14x10⁻⁴ ±1.5x10⁻⁵</td>
<td>-3.84x10⁻⁴ ±1.9x10⁻⁵</td>
</tr>
<tr>
<td>1.2x10⁵</td>
<td>-3.54x10⁻⁴ ±1.7x10⁻⁵</td>
<td>-3.84x10⁻⁴ ±1.9x10⁻⁵</td>
<td>-3.99x10⁻⁴ ±1.9x10⁻⁵</td>
<td>-4.63x10⁻⁴ ±2.3x10⁻⁵</td>
</tr>
<tr>
<td>3.0x10⁵</td>
<td>-2.15x10⁻⁴ ±1.0x10⁻⁵</td>
<td>-2.47x10⁻⁴ ±1.2x10⁻⁵</td>
<td>-2.59x10⁻⁴ ±1.3x10⁻⁵</td>
<td>-3.20x10⁻⁴ ±1.6x10⁻⁵</td>
</tr>
<tr>
<td>6.0x10⁵</td>
<td>-2.47x10⁻⁴ ±1.2x10⁻⁵</td>
<td>-2.70x10⁻⁴ ±1.3x10⁻⁵</td>
<td>-2.9x10⁻⁴ ±1.4x10⁻⁵</td>
<td>-3.44x10⁻⁴ ±1.7x10⁻⁵</td>
</tr>
<tr>
<td>1.0x10⁴</td>
<td>-2.48x10⁻⁴ ±1.2x10⁻⁵</td>
<td>-2.73x10⁻⁴ ±1.3x10⁻⁵</td>
<td>-2.91x10⁻⁴ ±1.4x10⁻⁵</td>
<td>-3.44x10⁻⁴ ±1.7x10⁻⁵</td>
</tr>
<tr>
<td>2.0x10⁴</td>
<td>-2.56x10⁻⁴ ±1.2x10⁻⁵</td>
<td>-2.82x10⁻⁴ ±1.4x10⁻⁵</td>
<td>-2.99x10⁻⁴ ±1.4x10⁻⁵</td>
<td>-3.53x10⁻⁴ ±1.7x10⁻⁵</td>
</tr>
<tr>
<td>3.0x10⁴</td>
<td>-2.95x10⁻⁴ ±1.4x10⁻⁵</td>
<td>-3.18x10⁻⁴ ±1.5x10⁻⁵</td>
<td>-3.39x10⁻⁴ ±1.7x10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>4.0x10⁴</td>
<td>-2.71x10⁻⁴ ±1.3x10⁻⁵</td>
<td>-2.98x10⁻⁴ ±1.5x10⁻⁵</td>
<td>-3.19x10⁻⁴ ±1.6x10⁻⁵</td>
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<tr>
<td>5.0x10⁴</td>
<td>-2.95x10⁻⁴ ±1.4x10⁻⁵</td>
<td>-3.23x10⁻⁴ ±1.6x10⁻⁵</td>
<td>-3.42x10⁻⁴ ±1.7x10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>8.0x10⁴</td>
<td>-2.85x10⁻⁴ ±1.4x10⁻⁵</td>
<td>-3.15x10⁻⁴ ±1.5x10⁻⁵</td>
<td>-3.32x10⁻⁴ ±1.6x10⁻⁵</td>
<td>-4.04x10⁻⁴ ±2.01x10⁻⁵</td>
</tr>
<tr>
<td>1.5x10³</td>
<td>-3.53x10⁻⁴ ±1.7x10⁻⁵</td>
<td>-3.92x10⁻⁴ ±1.9x10⁻⁵</td>
<td>-4.08x10⁻⁴ ±2.0x10⁻⁵</td>
<td></td>
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<tr>
<td>3.0x10³</td>
<td>-2.96x10⁻⁴ ±1.4x10⁻⁵</td>
<td>-3.2x10⁻⁴ ±1.6x10⁻⁵</td>
<td>-3.37x10⁻⁴ ±1.6x10⁻⁵</td>
<td>-4.07x10⁻⁴ ±2.0x10⁻⁵</td>
</tr>
</tbody>
</table>

68
Table 21–Continued

<table>
<thead>
<tr>
<th>CTAN</th>
<th>$\mu$ Zn(II) (cm$^2$/Vs)</th>
<th>$\mu$ Ni(II) (cm$^2$/Vs)</th>
<th>$\mu$ Cu(II) (cm$^2$/Vs)</th>
<th>$\mu$ Co(II) (cm$^2$/Vs)</th>
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<tbody>
<tr>
<td>5.0x10^{-3}</td>
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<td>-3.15x10^{-4}</td>
<td>-3.15x10^{-4}</td>
<td>-3.85x10^{-4}</td>
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<td>±1.4x10^{-5}</td>
<td>±1.6x10^{-5}</td>
<td>±1.6x10^{-5}</td>
<td>±1.9x10^{-5}</td>
</tr>
<tr>
<td>6.0x10^{-3}</td>
<td>-3.22x10^{-4}</td>
<td>-3.42x10^{-4}</td>
<td>-3.72x10^{-4}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±1.6x10^{-5}</td>
<td>±1.7x10^{-5}</td>
<td>±1.8x10^{-5}</td>
<td></td>
</tr>
<tr>
<td>7.0x10^{-3}</td>
<td>-2.36x10^{-4}</td>
<td>-2.60x10^{-4}</td>
<td>-2.84x10^{-4}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±1.2x10^{-5}</td>
<td>±1.3x10^{-5}</td>
<td>±1.4x10^{-5}</td>
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</tr>
<tr>
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</tr>
<tr>
<td></td>
<td>±1.3x10^{-5}</td>
<td>±1.4x10^{-5}</td>
<td>±1.5x10^{-5}</td>
<td>±1.9x10^{-5}</td>
</tr>
</tbody>
</table>
Table 22
Log $K_\text{e}$ vs. CTAN

<table>
<thead>
<tr>
<th>CTAN</th>
<th>Log $K_\text{e}$ Zn(II)</th>
<th>Log $K_\text{e}$ Ni(II)</th>
<th>Log $K_\text{e}$ Cu(II)</th>
<th>Log $K_\text{e}$ Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.84</td>
<td>4.10</td>
<td>6.91</td>
<td>7.33</td>
</tr>
<tr>
<td>$1.2 \times 10^{-5}$</td>
<td>6.98</td>
<td>4.23</td>
<td>7.00</td>
<td>7.43</td>
</tr>
<tr>
<td>$3.0 \times 10^{-5}$</td>
<td>6.76</td>
<td>4.02</td>
<td>6.81</td>
<td>7.24</td>
</tr>
<tr>
<td>$6.0 \times 10^{-5}$</td>
<td>6.82</td>
<td>4.08</td>
<td>6.85</td>
<td>7.29</td>
</tr>
<tr>
<td>$1.0 \times 10^{-4}$</td>
<td>6.82</td>
<td>4.08</td>
<td>6.86</td>
<td>7.29</td>
</tr>
<tr>
<td>$2.0 \times 10^{-4}$</td>
<td>6.84</td>
<td>4.09</td>
<td>6.87</td>
<td>7.31</td>
</tr>
<tr>
<td>$3.0 \times 10^{-4}$</td>
<td>6.90</td>
<td>4.15</td>
<td>6.92</td>
<td>7.36</td>
</tr>
<tr>
<td>$4.0 \times 10^{-4}$</td>
<td>6.86</td>
<td>4.11</td>
<td>6.89</td>
<td>7.33</td>
</tr>
<tr>
<td>$5.0 \times 10^{-4}$</td>
<td>6.90</td>
<td>4.15</td>
<td>6.93</td>
<td>7.36</td>
</tr>
<tr>
<td>$8.0 \times 10^{-4}$</td>
<td>6.88</td>
<td>4.14</td>
<td>6.92</td>
<td>7.35</td>
</tr>
<tr>
<td>$1.5 \times 10^{-3}$</td>
<td>6.98</td>
<td>4.23</td>
<td>7.01</td>
<td>7.44</td>
</tr>
<tr>
<td>$3.0 \times 10^{-3}$</td>
<td>6.90</td>
<td>4.17</td>
<td>6.92</td>
<td>7.36</td>
</tr>
<tr>
<td>$5.0 \times 10^{-3}$</td>
<td>6.84</td>
<td>4.10</td>
<td>6.92</td>
<td>7.33</td>
</tr>
<tr>
<td>$6.0 \times 10^{-3}$</td>
<td>6.94</td>
<td>4.19</td>
<td>6.95</td>
<td>7.40</td>
</tr>
<tr>
<td>$7.0 \times 10^{-3}$</td>
<td>6.80</td>
<td>4.06</td>
<td>6.83</td>
<td>7.28</td>
</tr>
<tr>
<td>$8.0 \times 10^{-3}$</td>
<td>6.85</td>
<td>4.11</td>
<td>6.88</td>
<td>7.32</td>
</tr>
</tbody>
</table>
Figure 26. Surfactant Dependence. Phosphate Buffer, pH 6.2, CTAN
Table 22 and Figure 26 shows that $K_e$ is independent of surfactant concentration. This conforms to the proposed mechanism (Equations 11, 12 and 13) and clearly shows that negatively charged silanol groups of the capillary walls drive the separation in the case of a cationic surfactant. At high concentrations of cationic surfactants, monolayer and bilayer formations neutralize these groups resulting in poor separation.

Voltage Dependence

One important factor for CE separation is applied voltage which influences ion migration time. Data is presented in Figure 27 for an applied voltage of 22 kV which is in comparison with Figure 83 (Appendix C) at 18 kV, which clearly indicates shorter migration times.

Calculated electrophoretic mobilities, zeta potentials and ionic radii are presented in Tables 23 and 24. Rates of ion movement in the electric field depend on a zeta potential. Zeta potentials were calculated using Equation 6 based on electroosmotic mobilities at different applied voltages.

Zeta potential is reasonably constant in the voltage range 15-25 kV. Zeta potential is only sensitive to ionic strength. (Table 23) Electrophoretic mobilities for the anionic complexes change almost a factor of 2 at this voltage range. (Table 23) This can be due to a decrease in the ionic radii (Table 24) corresponding to the deformation of the solvation sphere at higher voltages. [24]

Ionic Strength Dependence

Separation of the complexes improved and migration times increased at higher ionic strengths. In the current experiment, metal ion separation was performed at five different ionic strengths. Ionic strength of the phosphoric buffer was kept constant at 0.01 M. Different amounts of NaNO$_3$ were added to the mobile phase. The capillary was pretreated with $1 \times 10^{-5}$ M of CTAN. Experimental data is presented on Figures 28 and 29.

Electrophoretic mobilities, zeta potential and ionic radii were calculated based on experimental data. (Table 25 and Appendix C)
Figure 27. Voltage Dependence (22 kV)
Mobile Phase: Phosphate Buffer, pH 6.2, I = 0.05
Capillary Pretreated with 1x10^-5 M CTAN
1 = Ligand+Zn(II), 2 = Co(II) (1:2), 3 = Ni(II), 4 = Cu(II), 5 = Co(II) (1:3)
<table>
<thead>
<tr>
<th>Voltage (kV)</th>
<th>ζ (mV)</th>
<th>µ Zn(II) (cm²/Vs)</th>
<th>µ Co(II) (cm²/Vs)</th>
<th>µ Ni(II) (cm²/Vs)</th>
<th>µ Cu(II) (cm²/Vs)</th>
<th>µ Co(II) (cm²/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>-53.465</td>
<td>-1.99x10⁻⁴</td>
<td>-2.05x10⁻⁴</td>
<td>-2.20x10⁻⁴</td>
<td>-2.42x10⁻⁴</td>
<td>-3.03x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>±2.6</td>
<td>±1.0x10⁻⁵</td>
<td>±1.0x10⁻⁵</td>
<td>±1.1x10⁻⁵</td>
<td>±1.2x10⁻⁵</td>
<td>±1.6x10⁻⁵</td>
</tr>
<tr>
<td>18</td>
<td>-56.314</td>
<td>-2.77x10⁻⁴</td>
<td>-2.81x10⁻⁴</td>
<td>-3.01x10⁻⁴</td>
<td>-3.28x10⁻⁴</td>
<td>-4.02x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>±2.4</td>
<td>±1.4x10⁻⁵</td>
<td>±1.4x10⁻⁵</td>
<td>±1.4x10⁻⁵</td>
<td>±1.6x10⁻⁵</td>
<td>±1.9x10⁻⁵</td>
</tr>
<tr>
<td>22</td>
<td>-58.241</td>
<td>-3.70x10⁻⁴</td>
<td>-3.73x10⁻⁴</td>
<td>-3.84x10⁻⁴</td>
<td>-4.31x10⁻⁴</td>
<td>-5.28x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>±2.9</td>
<td>±1.9x10⁻⁵</td>
<td>±1.9x10⁻⁵</td>
<td>±1.9x10⁻⁵</td>
<td>±2.1x10⁻⁵</td>
<td>±2.6x10⁻⁵</td>
</tr>
<tr>
<td>25</td>
<td>-59.254</td>
<td>-4.26x10⁻⁴</td>
<td>-4.26x10⁻⁴</td>
<td>-4.42x10⁻⁴</td>
<td>-4.89x10⁻⁴</td>
<td>-6.23x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>±2.9</td>
<td>±2.1x10⁻⁵</td>
<td>±2.1x10⁻⁵</td>
<td>±2.2x10⁻⁵</td>
<td>±2.4x10⁻⁵</td>
<td>±3.1x10⁻⁵</td>
</tr>
</tbody>
</table>
Table 24
Ionic Radii vs. Voltage (Phosphate Buffer, pH 6.2, CTAN)

<table>
<thead>
<tr>
<th>Voltage (kV)</th>
<th>R Zn(II) (Å)</th>
<th>R Ni(II) (Å)</th>
<th>R Cu(II) (Å)</th>
<th>R Co(II) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>9.57 ±0.47</td>
<td>9.31 ±0.46</td>
<td>8.67 ±0.44</td>
<td>11.82 ±0.52</td>
</tr>
<tr>
<td>18</td>
<td>6.89 ±0.34</td>
<td>6.80 ±0.34</td>
<td>6.34 ±0.34</td>
<td>8.72 ±0.44</td>
</tr>
<tr>
<td>22</td>
<td>5.15 ±0.26</td>
<td>5.11 ±0.26</td>
<td>4.97 ±0.25</td>
<td>6.64 ±0.33</td>
</tr>
<tr>
<td>25</td>
<td>4.48 ±0.22</td>
<td>4.48 ±0.22</td>
<td>4.32 ±0.22</td>
<td>8.86 ±0.44</td>
</tr>
</tbody>
</table>
Figure 28. Ionic Strength Dependence. $I = 0.01 \text{ M, CTAN}$

$1 = \text{Ligand + Zn(II)}, 2 = \text{Co(II)}, 3 = \text{Ni(II)}, 4 = \text{Cu(II)}, 5 = \text{Co(II)}$
Figure 29. Ionic Strength Dependence. $I = 0.09 \text{ M}$, CTAN
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
<table>
<thead>
<tr>
<th>I (M)</th>
<th>$\zeta$ (mV)</th>
<th>$\mu$ Zn(II)</th>
<th>$\mu$ Ni(II)</th>
<th>$\mu$ Cu(II)</th>
<th>$\mu$ Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>-86.941</td>
<td>-2.69x10^{-4}</td>
<td>-2.90x10^{-4}</td>
<td>-3.24x10^{-4}</td>
<td>-3.90x10^{-4}</td>
</tr>
<tr>
<td></td>
<td>±4.347</td>
<td>±1.3x10^{-5}</td>
<td>±1.4x10^{-5}</td>
<td>±1.6x10^{-5}</td>
<td>±1.9x10^{-5}</td>
</tr>
<tr>
<td>0.03</td>
<td>-67.405</td>
<td>-2.45x10^{-4}</td>
<td>-2.66x10^{-4}</td>
<td>-2.93x10^{-4}</td>
<td>-3.66x10^{-4}</td>
</tr>
<tr>
<td></td>
<td>±3.370</td>
<td>±1.2x10^{-5}</td>
<td>±1.3x10^{-5}</td>
<td>±1.4x10^{-5}</td>
<td>±1.8x10^{-5}</td>
</tr>
<tr>
<td>0.05</td>
<td>-59.056</td>
<td>-2.34x10^{-4}</td>
<td>-2.50x10^{-4}</td>
<td>-2.78x10^{-4}</td>
<td>-3.43x10^{-4}</td>
</tr>
<tr>
<td></td>
<td>±2.953</td>
<td>±1.2x10^{-5}</td>
<td>±1.3x10^{-5}</td>
<td>±1.4x10^{-5}</td>
<td>±1.7x10^{-5}</td>
</tr>
<tr>
<td>0.07</td>
<td>-54.034</td>
<td>-2.31x10^{-4}</td>
<td>-2.46x10^{-4}</td>
<td>-2.71x10^{-4}</td>
<td>-3.32x10^{-4}</td>
</tr>
<tr>
<td></td>
<td>±2.702</td>
<td>±1.2x10^{-5}</td>
<td>±1.2x10^{-5}</td>
<td>±1.3x10^{-5}</td>
<td>±1.7x10^{-5}</td>
</tr>
<tr>
<td>0.09</td>
<td>-43.814</td>
<td>-1.63x10^{-4}</td>
<td>-1.74x10^{-4}</td>
<td>-2.01x10^{-4}</td>
<td>-2.61x10^{-4}</td>
</tr>
<tr>
<td></td>
<td>±2.191</td>
<td>±8x10^{-6}</td>
<td>±8x10^{-6}</td>
<td>±1.0x10^{-5}</td>
<td>±1.3x10^{-5}</td>
</tr>
</tbody>
</table>
By definition, the arrangement of negative charges on the surface of the capillary and the positive charges in the liquid phase is referred to as the electrical double layer at the interface. [24] Calculated zeta potential decreases as ionic strength increases, consistent with a double-layer theory. Similarly, thickness of the electrical double layer at the capillary wall-electrophoretic buffer interface decreases with the increase of ionic strength. This behavior is analogous to that of the electrical double layer at the electrode-electrolyte interface. This indicates that changes in the apparent ionic mobilities with ionic strength are due to a change in electroosmotic mobility caused by a change in the thickness of the electrical double layer and a change in the electrophoretic mobility.

The $\mu_{ep}$ of anionic complexes quadratically depend on $I^{1/2}$ as indicated by equations in Table 26 and the plot in Figure 30. At low values a linear relationship between $\mu_{ep}$ and $I^{1/2}$ is observed as predicted by Onsager’s equation. Deviations occur at high I values.

The deviation is better accounted for by Pitts’ equation. (Equation 20) The constants $a_0$, $a_1$ and $a_2$ for Pitts’ equation fit experimental $\mu_{ep}$ values with $I^{1/2}$ which were determined by multiple regression. These values are listed in Table 27 and the plot of:

$$\mu_{ep} \quad \text{vs.} \quad \frac{I^{1/2}}{(1+a_2 I^{1/2})}$$

is shown in Figure 31.

Pitts’ equation is based on Onsager’s equation for equivalent conductivity as ionic conductivity depends on ionic mobility. As a result, the constant, $a_0$, in Pitts’ equation corresponds to electrophoretic mobility at infinite dilution and $a_1$ is the Onsager slope that accounts for the influence of ionic strength on electrophoretic mobility.

$$\mu_{ep} = \frac{a_0 - a_1(I^{1/2})}{(1 + a_2 I^{1/2})} \quad \text{(20)}$$

where: $a_0 = \text{mobility at infinite dilution}$
$a_1 = \text{Onsager slope}$
$a_2 = \text{constant obtained from the fitting}$
Table 26
Metal Ion Mobility Dependence on Square Root of Ionic Strength

<table>
<thead>
<tr>
<th>Metal</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(II)</td>
<td>$y = 2.8 \times 10^{-3} I - 7 \times 10^{-4} I^{1/2} - 2 \times 10^{-4}$</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>$y = 3.0 \times 10^{-3} I - 7 \times 10^{-4} I^{1/2} - 2 \times 10^{-4}$</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>$y = 2.6 \times 10^{-3} I - 5 \times 10^{-4} I^{1/2} - 2 \times 10^{-4}$</td>
</tr>
<tr>
<td>Co(II)</td>
<td>$y = 3.2 \times 10^{-3} I - 7 \times 10^{-4} I^{1/2} - 3 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Figure 30. Ionic Strength Dependence. Electrophoretic Mobilities.
<table>
<thead>
<tr>
<th></th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(II)</td>
<td>-2.7x10^{-4}</td>
<td>-5.20x10^{-5}</td>
<td>-2.85566</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>-2.9x10^{-4}</td>
<td>-6.10x10^{-5}</td>
<td>-2.82007</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>-3.3x10^{-4}</td>
<td>-8.12x10^{-5}</td>
<td>-2.69393</td>
</tr>
<tr>
<td>Co(II)</td>
<td>-4.0x10^{-4}</td>
<td>-2.23x10^{-3}</td>
<td>-2.68138</td>
</tr>
</tbody>
</table>
Figure 31. Ionic Strength Dependence. Pitts’ Plot
Figure 31 for Zn\textsuperscript{2+} shows the fit of the experimental electrophoretic mobility values with Equation 20.

Pitts' equation is a modification of the Debye-Hickel-Onsager equation which states that $\mu = \mu_0 - a_1 \times I^{1/2}$ and generally applies at very low ionic strengths with appropriately infinite dilution. At high ionic strengths, like the one employed in the experiment, Pitts' equation more appropriately accounts for the influence of ionic strength on electrophoretic mobility. Pitts' equation empirically takes into account non-ideal variations at high ionic strengths caused by large derivation of activity coefficients from unity.

**Oncolumn Complex Formation**

Oncolumn complex formation was achieved by injecting metals into the electrophoretic buffer with the ligand. Transition metal complexes can be formed rapidly except in the case of Ni(II). This results in broad peaks for Ni(II). The order of migration of metal ions differs from that of precolumn complex formation, with Ni(II) having the longest retention time. This can be rationalized by its slow complexation kinetics.\[19, 31\] The other important differences with precolumn complex formation are that only a 1:2 complex was observed for Co(II) which could not be separated from Zn(II). Metal ion separation with oncolumn complex formation was not as good as precolumn complex formation. Typical separation by oncolumn complex formation after rinsing the capillary with 2x10\textsuperscript{-3} M OTAB is shown on Figure 32.

Electrophoretic mobilities and log $K_e$ were calculated from experimental data and summarized in Tables 28 and 29.

The plot of log D vs. pH does not provide any important information about metal complex formation equilibria. However, calculations based on the proposed mechanism and $K_e$ clearly indicate the formation of 1:2 complexes for all 4 metals. (Figure 33, Table 30)

Experimental data shows that the proposed mechanism is consistent not only for precolumn complex formation but also for oncolumn complex formation.
Figure 32. pH Dependence. Succinate Buffer, pH 5.68, OTAB
1 = Zn(II), 2 = Co(II), 3 = Cu(II), 4 = Ni(II)
<table>
<thead>
<tr>
<th>pH</th>
<th>μ Zn(II) (cm²/Vs)</th>
<th>μ Ni(II) (cm²/Vs)</th>
<th>μ Cu(II) (cm²/Vs)</th>
<th>μ Co(II) (cm²/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.56</td>
<td>-2.11 x 10⁻⁴ ± 1.1 x 10⁻⁵</td>
<td>-3.14 x 10⁻⁴ ± 1.5 x 10⁻⁵</td>
<td>-2.60 x 10⁻⁴ ± 1.3 x 10⁻⁵</td>
<td>-2.11 x 10⁻⁴ ± 1.1 x 10⁻⁵</td>
</tr>
<tr>
<td>5.68</td>
<td>-2.24 x 10⁻⁴ ± 1.1 x 10⁻⁵</td>
<td>-3.23 x 10⁻⁴ ± 1.6 x 10⁻⁵</td>
<td>-2.63 x 10⁻⁴ ± 1.3 x 10⁻⁵</td>
<td>-2.26 x 10⁻⁴ ± 1.1 x 10⁻⁵</td>
</tr>
<tr>
<td>5.78</td>
<td>-2.20 x 10⁻⁴ ± 1.1 x 10⁻⁵</td>
<td>-3.22 x 10⁻⁴ ± 1.6 x 10⁻⁵</td>
<td>-2.66 x 10⁻⁴ ± 1.3 x 10⁻⁵</td>
<td>-2.22 x 10⁻⁴ ± 1.1 x 10⁻⁵</td>
</tr>
<tr>
<td>5.87</td>
<td>-2.29 x 10⁻⁴ ± 1.1 x 10⁻⁵</td>
<td>-3.29 x 10⁻⁴ ± 1.7 x 10⁻⁵</td>
<td>-2.66 x 10⁻⁴ ± 1.3 x 10⁻⁵</td>
<td>-2.31 x 10⁻⁴ ± 1.1 x 10⁻⁵</td>
</tr>
<tr>
<td>5.97</td>
<td>-2.31 x 10⁻⁴ ± 1.1 x 10⁻⁵</td>
<td>-3.31 x 10⁻⁴ ± 1.7 x 10⁻⁵</td>
<td>-2.61 x 10⁻⁴ ± 1.3 x 10⁻⁵</td>
<td>-2.31 x 10⁻⁴ ± 1.1 x 10⁻⁵</td>
</tr>
<tr>
<td>pH</td>
<td>Log $K_e$ Zn(II)</td>
<td>Log $K_e$ Ni(II)</td>
<td>Log $K_e$ Cu(II)</td>
<td>Log $K_e$ Co(II)</td>
</tr>
<tr>
<td>-----</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>5.56</td>
<td>5.43</td>
<td>2.92</td>
<td>5.40</td>
<td>5.59</td>
</tr>
<tr>
<td>5.68</td>
<td>5.65</td>
<td>3.11</td>
<td>5.69</td>
<td>5.81</td>
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<td>5.78</td>
<td>5.84</td>
<td>3.29</td>
<td>5.90</td>
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<tr>
<td>5.87</td>
<td>6.05</td>
<td>3.48</td>
<td>6.10</td>
<td>6.30</td>
</tr>
<tr>
<td>5.97</td>
<td>6.26</td>
<td>3.67</td>
<td>6.28</td>
<td>6.54</td>
</tr>
</tbody>
</table>
Figure 33. pH Dependence. On-column Complex Formation.
Log $K_e - \log D - 2\log [HL]$
Table 30

Log $K_e$ − Log $D$ − 2log [HL] vs. pH (On-column Complex Formation)

<table>
<thead>
<tr>
<th></th>
<th>Zn(II)</th>
<th>Co(II)</th>
<th>Cu(II)</th>
<th>Ni(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>2.2165 ± 0.1108</td>
<td>2.2165 ± 0.1108</td>
<td>2.1513 ± 0.1076</td>
<td>1.6302 ± 0.0081</td>
</tr>
<tr>
<td>Intercept</td>
<td>-6.7243 ± 0.3362</td>
<td>-6.7243 ± 0.3362</td>
<td>-6.6654 ± 0.3332</td>
<td>-6.4898 ± 0.3245</td>
</tr>
</tbody>
</table>
Metal Ion Separation with Anionic Surfactant

Metal ion separations were also performed in the presence of the anionic surfactant SDS. Experiments in the presence of SDS avoid such cationic surfactant problems as adsorption of the surfactant by the negatively charged capillary walls. Therefore, it is possible to have a high concentration of the surfactant during the experiment. In our set of experiments we added 0.05 M of SDS to the mobile phase, which is much higher than the cmc of SDS (0.02 M). Therefore, SDS micelles are present in the mobile phase. Our proposed mechanism for SDS is based on the competition between the negatively charged silanol groups of the capillary walls and the negatively charged surfactant for the positively charged metal ions. (Equation 21)

\[
K_{\text{micelle}} \quad (21)
\]

\[
\text{Micelle} + ML_2^{2-} \ \Leftrightarrow \ \text{MicelleM} + 2L^{2-}
\]

\[
K_{\text{SiM}} \quad (22)
\]

\[
\text{MicelleM} + (\text{SiO})_2 \ \Leftrightarrow \ (\text{SiO})_2 \ M + \text{Micelle}
\]

Based on this relationship \( K_{\text{micelle}} \) can be defined:

\[
K_{\text{micelle}} = \frac{[\text{MicelleM}] [L^{2-}]^2}{[\text{Micelle}] [ML^{2-}]^2} \quad (23)
\]

\[
K_{\text{SiM}} = \frac{[(\text{SiO})_2M] [\text{Micelle}]}{[\text{MicelleM}] [(\text{SiO})_2]} \quad (24)
\]
\[ K_{\text{SiM}} \frac{K_{\text{micelle}}}{[\text{ML}_2^2]} = \frac{[\text{SiO}_2^2M][L^2]}{[(\text{SiO})_2][\text{L}^2]} \]  

(25)

\[ K_{\text{SiM}} \frac{K_{\text{micelle}}}{[\text{ML}_2^2]} = \frac{[\text{SiO}_2^2][\text{H}^+]}{[(\text{SiO})_2][\text{H}^+]} \]  

(26)

\[ K_{\text{SiM}} \frac{D K_a^2}{[\text{HL}^-]^2} = \frac{[\text{HL}^-]^2}{[(\text{SiO})_2][\text{H}^+]} \]  

(27)

\[ \frac{K_a^2}{K_{\text{micelle}}[(\text{SiO})_2][\text{H}^+]} = \frac{\log K_e}{\log \text{ice}_{\text{ne}}[(\text{SiO})_2] + \log D + 2\log [\text{HL}^-] + 2 \text{pH}} \]  

(30)

The empirical parameter \( K_e \) is related to \( K_{\text{SiM}} \). (Equation 28)

\[ K_e = \frac{K_{\text{SiM}}}{K_a^2} \]  

(28)

\[ K_{\text{SiM}} = \frac{M}{\beta K_a^2} \]  

(29)

An intercept can be used to calculate \( K_{\text{micelle}} \) using the theoretical value of \([(\text{SiO})_2]\) which is \(5.9 \times 10^{15}\) groups/cm\(^2\).

\[ \text{Intercept} = \frac{\log K_2 N_A}{[(\text{SiO})_2]} \]  

(31)
Pre-column Complex Formation

pH Dependence

Succinate and phosphate buffers were used as the main electrophoretic buffers in the current experiment. The experimental pH range is 5.75-7.2. The metal ions form an anionic complex with the HQS ligand and the separation in the presence of SDS depends on the competition for the metal ion between the silanol groups and the ligand. The separation results are presented on Figure 34 and Appendix C.

Electrophoretic mobilities and log $K_e$ are summarized in Tables 31 and 32.

The slope of log D vs. pH does not provide useful information on the separation mechanism. However, the slope of log $K_e - \log D - 2\log [HL^-]$ vs. pH (Figure 35) indicates the formation of 1:2 complexes for all metals with the exception of Co(II) which in addition forms a 1:3 complex. The definition of $K_e$ for both cationic and anionic surfactant-mediated separations provides a means to discern the mechanism of separations. $K_{micelle}$ was calculated from the intercept and from using the theoretical value for silanol groups per cm$^2$.

A second buffer, which was used as an electrophoretic buffer in the SDS experiment, was a phosphoric acid buffer. Experimental conditions are the same as previous experiments except pH was in the range 6.2-7.28. Data is presented in Figure 36.

Electrophoretic mobilities and log $K_e$ were calculated from experimental data and are summarized in Tables 33 and 34.

Plots based on the calculated data are presented in Figure 37. While the plot of log D vs. pH does not indicate the mechanism of separation, the plot of log $K_e - \log D - 2[HL^-]$ vs. pH shows that 1:2 metal:ligand complexes of Co(II), Zn(II), Ni(II) and Cu(II) are formed. In the case of Co(II), a 1:3 metal:ligand complex is also formed. A summary of the slopes and intercept values is given in Table 35. Slope values are consistent for metal ion separation in the succinate and phosphate buffer environments in the presence of SDS. $K_{micelle}$ was calculated based on the experimental intercept values (Table 36) and theoretical values for silanol groups per cm$^2$ ($5.9 \times 10^{15}$). (Equation 31)
Figure 34. pH Dependence. Succinate Buffer, pH 5.98, $I = 0.01$ M, 0.05 M SDS

1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Table 31
Electrophoretic Mobilities vs. pH (Succinate Buffer)

<table>
<thead>
<tr>
<th>pH</th>
<th>$\mu_{Zn(II)}$ (cm$^2$/Vs)</th>
<th>$\mu_{Ni(II)}$ (cm$^2$/Vs)</th>
<th>$\mu_{Cu(II)}$ (cm$^2$/Vs)</th>
<th>$\mu_{Co(II)}$ (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.75</td>
<td>$-2.72 \times 10^{-4}$</td>
<td>$-2.76 \times 10^{-4}$</td>
<td>$-3.18 \times 10^{-4}$</td>
<td>$-3.82 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$\pm 1.3 \times 10^{-5}$</td>
<td>$\pm 1.3 \times 10^{-5}$</td>
<td>$\pm 1.5 \times 10^{-5}$</td>
<td>$\pm 1.9 \times 10^{-5}$</td>
</tr>
<tr>
<td>5.98</td>
<td>$-2.56 \times 10^{-4}$</td>
<td>$-2.71 \times 10^{-4}$</td>
<td>$-3.01 \times 10^{-4}$</td>
<td>$-3.63 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
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<td>$\pm 1.3 \times 10^{-5}$</td>
<td>$\pm 1.5 \times 10^{-5}$</td>
<td>$\pm 1.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>6.17</td>
<td>$-2.44 \times 10^{-4}$</td>
<td>$-2.68 \times 10^{-4}$</td>
<td>$-2.89 \times 10^{-4}$</td>
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<td>$\pm 1.4 \times 10^{-5}$</td>
<td>$\pm 1.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>6.37</td>
<td>$-2.28 \times 10^{-4}$</td>
<td>$-2.52 \times 10^{-4}$</td>
<td>$-2.76 \times 10^{-4}$</td>
<td>$-3.37 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$\pm 1.1 \times 10^{-5}$</td>
<td>$\pm 1.2 \times 10^{-5}$</td>
<td>$\pm 1.3 \times 10^{-5}$</td>
<td>$\pm 1.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>6.5</td>
<td>$-2.29 \times 10^{-4}$</td>
<td>$-2.59 \times 10^{-4}$</td>
<td>$-2.74 \times 10^{-4}$</td>
<td>$-3.34 \times 10^{-4}$</td>
</tr>
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<td></td>
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<td>$\pm 1.2 \times 10^{-5}$</td>
<td>$\pm 1.3 \times 10^{-5}$</td>
<td>$\pm 1.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>6.7</td>
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<td>$-2.37 \times 10^{-4}$</td>
<td>$-2.55 \times 10^{-4}$</td>
<td>$-3.15 \times 10^{-4}$</td>
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<td>$\pm 1.2 \times 10^{-5}$</td>
<td>$\pm 1.5 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Table 32

Log $K_a$ vs. pH (Succinate Buffer)

<table>
<thead>
<tr>
<th>pH</th>
<th>Log $K_a$ Zn(II)</th>
<th>Log $K_a$ Ni(II)</th>
<th>Log $K_a$ Cu(II)</th>
<th>Log $K_a$ Co(II)</th>
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</thead>
<tbody>
<tr>
<td>5.75</td>
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<td>3.37</td>
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<td>5.98</td>
<td>6.44</td>
<td>3.73</td>
<td>6.50</td>
<td>6.88</td>
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<tr>
<td>6.17</td>
<td>6.82</td>
<td>4.10</td>
<td>6.88</td>
<td>7.38</td>
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<tr>
<td>6.37</td>
<td>7.18</td>
<td>4.45</td>
<td>7.26</td>
<td>7.89</td>
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<tr>
<td>6.5</td>
<td>7.38</td>
<td>4.66</td>
<td>7.45</td>
<td>8.15</td>
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<tr>
<td>6.7</td>
<td>7.74</td>
<td>5.01</td>
<td>7.81</td>
<td>8.68</td>
</tr>
</tbody>
</table>
Figure 35.  Log $K_e$ - Log $D$ - 2log [HL$^-$] vs. pH. $I = 0.01$ M, 0.05 M SDS
Figure 36. pH Dependence. Phosphate Buffer, pH 6.22, I = 0.01 M
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Table 33
Electrophoretic Mobilities vs. pH (Succinate Buffer)

<table>
<thead>
<tr>
<th>pH</th>
<th>$\mu$ Zn(II)</th>
<th>$\mu$ Ni(II)</th>
<th>$\mu$ Cu(II)</th>
<th>$\mu$ Co(II)</th>
</tr>
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<tbody>
<tr>
<td>6.2</td>
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<td>$-2.79 \times 10^{-4}$</td>
<td>$-3.02 \times 10^{-4}$</td>
<td>$-3.64 \times 10^{-4}$</td>
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<td>$\pm 1.3 \times 10^{-5}$</td>
<td>$\pm 1.5 \times 10^{-5}$</td>
<td>$\pm 1.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>6.4</td>
<td>$-2.48 \times 10^{-4}$</td>
<td>$-2.73 \times 10^{-4}$</td>
<td>$-2.84 \times 10^{-4}$</td>
<td>$-3.45 \times 10^{-4}$</td>
</tr>
<tr>
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<td>$\pm 1.3 \times 10^{-5}$</td>
<td>$\pm 1.4 \times 10^{-5}$</td>
<td>$\pm 1.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>6.7</td>
<td>$-2.33 \times 10^{-4}$</td>
<td>$-2.77 \times 10^{-4}$</td>
<td>$-3.38 \times 10^{-4}$</td>
<td>$\pm 1.1 \times 10^{-5}$</td>
</tr>
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<td></td>
<td>$\pm 1.3 \times 10^{-5}$</td>
<td>$\pm 1.3 \times 10^{-5}$</td>
<td>$\pm 1.6 \times 10^{-5}$</td>
<td>$\pm 1.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>7.0</td>
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<td>$-2.78 \times 10^{-4}$</td>
<td>$-3.39 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$\pm 1.1 \times 10^{-5}$</td>
<td>$\pm 1.4 \times 10^{-5}$</td>
<td>$\pm 1.3 \times 10^{-5}$</td>
<td>$\pm 1.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>7.28</td>
<td>$-2.40 \times 10^{-4}$</td>
<td>$-3.03 \times 10^{-4}$</td>
<td>$-2.72 \times 10^{-4}$</td>
<td>$-3.32 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$\pm 1.2 \times 10^{-5}$</td>
<td>$\pm 1.5 \times 10^{-5}$</td>
<td>$\pm 1.3 \times 10^{-5}$</td>
<td>$\pm 1.6 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Table 34
Log $K_a$ vs. pH (Succinate Buffer)

<table>
<thead>
<tr>
<th>pH</th>
<th>$\text{Log } K_a \text{ Zn(II)}$</th>
<th>$\text{Log } K_a \text{ Ni(II)}$</th>
<th>$\text{Log } K_a \text{ Cu (II)}$</th>
<th>$\text{Log } K_a \text{ Co(II)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.2</td>
<td>6.84</td>
<td>4.12</td>
<td>6.90</td>
<td>7.39</td>
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<tr>
<td>6.4</td>
<td>7.22</td>
<td>4.49</td>
<td>7.27</td>
<td>7.90</td>
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<td>6.7</td>
<td>7.78</td>
<td>7.85</td>
<td>8.71</td>
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</tr>
<tr>
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<td>8.43</td>
<td>9.54</td>
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<td>7.28</td>
<td>8.93</td>
<td>6.25</td>
<td>8.99</td>
<td>10.36</td>
</tr>
</tbody>
</table>
Figure 37. pH Dependence. Log $K_e - \log D - 2\log [HL']$ vs. pH
Table 35
Log $K_e$ - Log D - 2log [HL] vs. pH

<table>
<thead>
<tr>
<th></th>
<th>Zn(II)</th>
<th>Ni(II)</th>
<th>Cu(II)</th>
<th>Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Succinate Buffer, pH 5.7-6.7, SDS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slope</td>
<td>2.0037 ±0.1001</td>
<td>1.8688 ±0.0934</td>
<td>2.0037 ±0.1001</td>
<td>2.6212 ±0.1311</td>
</tr>
<tr>
<td>Intercept</td>
<td>0.5214 ±0.0261</td>
<td>-1.3438 ±0.0672</td>
<td>0.5214 ±0.0261</td>
<td>-2.9621 ±0.1481</td>
</tr>
<tr>
<td><strong>Phosphate Buffer, pH 6.2-7.3, SDS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slope</td>
<td>2.0555 ±0.1028</td>
<td>1.9483 ±0.0974</td>
<td>2.0555 ±0.1028</td>
<td>2.8742 ±0.1437</td>
</tr>
<tr>
<td>Intercept</td>
<td>0.1532 ±0.0077</td>
<td>-1.9009 ±0.0950</td>
<td>0.1532 ±0.0077</td>
<td>-4.6365 ±0.2318</td>
</tr>
<tr>
<td>$K_{\text{micelle}}$ with:</td>
<td>Zn(II), Co(II)</td>
<td>Ni(II)</td>
<td>Cu(II)</td>
<td>Co(II)</td>
</tr>
<tr>
<td>-------------------------</td>
<td>----------------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td></td>
<td>(1:2 Complex)</td>
<td></td>
<td></td>
<td>(1:3 Complex)</td>
</tr>
<tr>
<td>Succinate Buffer pH 5.7-6.7</td>
<td>3.079x10$^7$</td>
<td>2.257x10$^9$</td>
<td>3.079x10$^7$</td>
<td>9.374x10$^{10}$</td>
</tr>
<tr>
<td></td>
<td>$\pm 1.54x10^6$</td>
<td>$\pm 1.128x10^8$</td>
<td>$\pm 1.54x10^6$</td>
<td>$\pm 4.687x10^9$</td>
</tr>
<tr>
<td>Phosphate Buffer pH 6.2-7.3</td>
<td>7.188x10$^7$</td>
<td>8.141x10$^9$</td>
<td>7.188x10$^7$</td>
<td>4.429x10$^{12}$</td>
</tr>
<tr>
<td></td>
<td>$\pm 3.594x10^6$</td>
<td>$\pm 4.071x10^8$</td>
<td>$\pm 3.594x10^6$</td>
<td>$\pm 2.215x10^{11}$</td>
</tr>
</tbody>
</table>
Table 36 indicates that $K_{\text{micelle}}$ values are such that the competition for the metal ion between SDS micelles and ligand molecules (Equation 25) is significant. This competition and the competition with surface silanol groups results in different electrophoretic mobilities and metal ion separations. $K_{\text{micelle}}$ exhibits a large variation between metal ions which most likely is due to an indirect evaluation of this constant from the intercept of log $K_c$. The order of magnitude of $K_{\text{micelle}}$ is more significant than its value derived from the plot. We may conclude that $K_{\text{micelle}}$ has a lower limit of $10^7$ which is significant enough to establish equilibrium. (Equation 25)

Dynamic radii (Equation 5) were calculated based on experimental data and were compared with dynamic radii calculated from metal ion separations in the presence of cationic surfactants. Data is summarized in Table 37.

Dynamic radii of all metal complexes are in the range 6-9 Å. (Table 37) Radii experiments with cationic and anionic surfactants are in a similar range.

**Ligand Dependence**

Separations were carried out at a constant pH and at a varying ligand concentration to support the proposed mechanism. In this experiment the metal ion concentration was held constant and the ligand concentration was varied in the range $4.6 \times 10^{-4}$-$9.8 \times 10^{-4}$ M. Concentrations of the ligand were always much higher than the metal concentrations to ensure complete complexation of metal ions. Succinic and phosphoric acid buffers were used as electrophoretic buffers. Experimental data are shown in Figure 38 and Appendix C.

Electrophoretic mobilities and log $K_c$ calculated from experimental data are shown in Tables 38 and 39.

Experimental plots are shown in Figure 39.

Slopes indicate the formation of 1:2 metal:ligand complexes for all metals and of 1:3 metal:ligand complexes for Co(II). $K_{\text{micelle}}$ was calculated based on intercept values. (Table 43) $K_{\text{micelle}}$ has an estimated lower limit of $10^7$ (more accuracy is hard to determine from these experiments) except for the 1:3 complex of Co(II). The 1:3 complex of Co(II) exhibits a much larger variation between pH dependence (Table 35) and ligand dependence (Table 39). This may be attributable to slow equilibrium between the 1:2 and 1:3 complexes of Co(II).
### Table 37
Dynamic Radii vs. pH

<table>
<thead>
<tr>
<th>Buffer</th>
<th>Surfactant</th>
<th>R Zn(II) (Å)</th>
<th>R Ni(II) (Å)</th>
<th>R Cu(II) (Å)</th>
<th>R Co(II) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH Dependence</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Succinate</td>
<td>OTAB</td>
<td>8.47 ±0.44</td>
<td>7.78 ±0.38</td>
<td>7.05 ±0.34</td>
<td>8.58 ±0.47</td>
</tr>
<tr>
<td>Phosphate</td>
<td>OTAB</td>
<td>7.41 ±0.37</td>
<td>6.78 ±0.34</td>
<td>6.47 ±0.31</td>
<td>8.05 ±0.41</td>
</tr>
<tr>
<td>Phosphate</td>
<td>CTAN</td>
<td>8.09 ±0.40</td>
<td>7.13 ±0.35</td>
<td>6.98 ±0.35</td>
<td>8.51 ±0.42</td>
</tr>
<tr>
<td>Succinate</td>
<td>SDS</td>
<td>8.01 ±0.40</td>
<td>7.34 ±0.36</td>
<td>6.71 ±0.33</td>
<td>8.28 ±0.41</td>
</tr>
<tr>
<td>Phosphate</td>
<td>SDS</td>
<td>7.88 ±0.39</td>
<td>6.67 ±0.33</td>
<td>6.76 ±0.33</td>
<td>8.34 ±0.41</td>
</tr>
<tr>
<td>Ligand Dependence</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Succinate</td>
<td>OTAB</td>
<td>7.99 ±0.40</td>
<td>7.33 ±0.33</td>
<td>6.84 ±0.29</td>
<td>8.48 ±0.46</td>
</tr>
<tr>
<td>Phosphate</td>
<td>OTAB</td>
<td>9.13 ±0.52</td>
<td>7.92 ±0.41</td>
<td>7.51 ±0.37</td>
<td>8.99 ±0.51</td>
</tr>
</tbody>
</table>


Figure 38. Ligand Dependence (Concentration: $6.64 \times 10^{-4}$ M)
Mobile Phase: Succinate Buffer, pH 6.2, $I = 0.01$ M, 0.05 M SDS
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Table 38
Electrophoretic Mobilities vs. Ligand

<table>
<thead>
<tr>
<th>Ligand</th>
<th>( \mu ) Zn(II)</th>
<th>( \mu ) Ni(II)</th>
<th>( \mu ) Cu(II)</th>
<th>( \mu ) Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cm(^2)/Vs)</td>
<td>(cm(^2)/Vs)</td>
<td>(cm(^2)/Vs)</td>
<td>(cm(^2)/Vs)</td>
</tr>
<tr>
<td>9.8(\times 10^{-4})</td>
<td>-1.65(\times 10^{-4})</td>
<td>-1.86(\times 10^{-4})</td>
<td>-2.09(\times 10^{-4})</td>
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<tr>
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<td>(\pm 8\times 10^{-6})</td>
<td>(\pm 9\times 10^{-6})</td>
<td>(\pm 1.0\times 10^{-5})</td>
<td>(\pm 1.3\times 10^{-5})</td>
</tr>
<tr>
<td>8.28(\times 10^{-4})</td>
<td>-1.59(\times 10^{-4})</td>
<td>-1.79(\times 10^{-4})</td>
<td>-2.05(\times 10^{-4})</td>
<td>-2.66(\times 10^{-4})</td>
</tr>
<tr>
<td></td>
<td>(\pm 8\times 10^{-6})</td>
<td>(\pm 9\times 10^{-6})</td>
<td>(\pm 1.0\times 10^{-5})</td>
<td>(\pm 1.3\times 10^{-5})</td>
</tr>
<tr>
<td>7.36(\times 10^{-4})</td>
<td>-1.58(\times 10^{-4})</td>
<td>-1.74(\times 10^{-4})</td>
<td>-2.04(\times 10^{-4})</td>
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<td>(\pm 1.0\times 10^{-5})</td>
<td>(\pm 1.3\times 10^{-5})</td>
</tr>
<tr>
<td>6.64(\times 10^{-4})</td>
<td>-1.54(\times 10^{-4})</td>
<td>-1.72(\times 10^{-4})</td>
<td>-2.03(\times 10^{-4})</td>
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<tr>
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<td>(\pm 8\times 10^{-6})</td>
<td>(\pm 8\times 10^{-6})</td>
<td>(\pm 1.0\times 10^{-5})</td>
<td>(\pm 1.3\times 10^{-5})</td>
</tr>
<tr>
<td>5.52(\times 10^{-4})</td>
<td>-1.52(\times 10^{-4})</td>
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</tr>
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<td></td>
<td>(\pm 7\times 10^{-6})</td>
<td>(\pm 8\times 10^{-6})</td>
<td>(\pm 1.0\times 10^{-5})</td>
<td>(\pm 1.3\times 10^{-5})</td>
</tr>
<tr>
<td>4.6(\times 10^{-4})</td>
<td>-1.49(\times 10^{-4})</td>
<td>-1.72(\times 10^{-4})</td>
<td>-2.03(\times 10^{-4})</td>
<td>-2.67(\times 10^{-4})</td>
</tr>
<tr>
<td></td>
<td>(\pm 7\times 10^{-6})</td>
<td>(\pm 8\times 10^{-6})</td>
<td>(\pm 1.0\times 10^{-5})</td>
<td>(\pm 1.3\times 10^{-5})</td>
</tr>
<tr>
<td>Concentration (M)</td>
<td>Log $K_e$ Zn(II)</td>
<td>Log $K_e$ Ni(II)</td>
<td>Log $K_e$ Cu(II)</td>
<td>Log $K_e$ Co(II)</td>
</tr>
<tr>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>9.8x10^{-4}</td>
<td>6.65</td>
<td>3.94</td>
<td>6.74</td>
<td>7.26</td>
</tr>
<tr>
<td>8.28x10^{-4}</td>
<td>6.48</td>
<td>3.78</td>
<td>6.58</td>
<td>7.07</td>
</tr>
<tr>
<td>7.36x10^{-4}</td>
<td>6.38</td>
<td>3.67</td>
<td>6.48</td>
<td>6.94</td>
</tr>
<tr>
<td>6.64x10^{-4}</td>
<td>6.28</td>
<td>3.58</td>
<td>6.39</td>
<td>6.82</td>
</tr>
<tr>
<td>5.52x10^{-4}</td>
<td>6.12</td>
<td>3.44</td>
<td>6.22</td>
<td>6.63</td>
</tr>
<tr>
<td>4.6x10^{-4}</td>
<td>5.96</td>
<td>3.29</td>
<td>6.07</td>
<td>6.44</td>
</tr>
</tbody>
</table>
Figure 39. Ligand Dependence. Log $K_e - \log D - 2pH$
The ligand dependence experiment was performed using a phosphoric acid buffer as an electrophoretic buffer. Experimental pH is 6.2. Data is shown in Figure 40 and Appendix C.

Electrophoretic mobilities and log $K_e$ factors are presented in Tables 40 and 41. Experimental plots are shown in Figure 41 and Appendix C.

Data analysis (Table 42) shows that metal ion separation processes, and metal complex formation in particular, can be described by the proposed mechanism. It indicates a formation of a 1:2 complex of Co(II), Ni(II), Zn(II) and Cu(II) and a 1:3 complex of Co(II) when data analysis based on the distribution constant fails. This data analysis is independent from the buffer environment. Experiments were done in the succinate and phosphate buffers and the data is consistent. $K_{\text{micelle}}$ was calculated based on the intercept values. (Table 43)

Table 43 clearly indicates that calculated $K_{\text{micelle}}$ for all metal ions in succinate and phosphate buffer environments agree with each other.

**Voltage Dependence**

Current experiments show metal ion separation dependence on applied voltage. Migrations times of the metal ions become shorter with increases in voltage from 15-25 kV. Experimental data is presented in Figure 42 and Appendix C.

Calculated electrophoretic mobilities and zeta potentials are presented in Table 44. The zeta potential is, as expected, reasonably constant with applied voltage as previously determined with CTAN experiments. (Table 23) The difference in the zeta potentials in Tables 25 and 44 is due to ionic strength differences. The zeta potential at higher ionic strength (Table 25) is lower than at lower ionic strength (Table 44) since the surface charge density on the capillary wall is lower at a higher ionic strength compared to a lower ionic strength. [24] In the case of CTAN, electrophoretic mobilities for the anionic complex change by almost a factor of 2 between 15-25 kV. This again could be attributed to a decrease in ionic radii (Table 45) due to the determination of the solvation sphere at higher voltages. [24]
Figure 40. Ligand Dependence (Concentration $6.64 \times 10^{-4} \text{ M}$)
Phosphate Buffer, pH 6.2, $I = 0.01 \text{ M}$
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
<table>
<thead>
<tr>
<th>Ligand Concentration (M)</th>
<th>( \mu \text{ Zn (II)} ) (cm(^2)/Vs)</th>
<th>( \mu \text{ Ni(II)} ) (cm(^2)/Vs)</th>
<th>( \mu \text{ Cu(II)} ) (cm(^2)/Vs)</th>
<th>( \mu \text{ Co(II)} ) (cm(^2)/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.8x10(^{-4})</td>
<td>-2.21x10(^{-4})</td>
<td>-2.44x10(^{-4})</td>
<td>-2.66x10(^{-4})</td>
<td>-3.28x10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>( \pm 1.1x10^{-5} )</td>
<td>( \pm 1.2x10^{-5} )</td>
<td>( \pm 1.3x10^{-5} )</td>
<td>( \pm 1.6x10^{-5} )</td>
</tr>
<tr>
<td>8.28x10(^{-4})</td>
<td>-2.14x10(^{-4})</td>
<td>-2.4x10(^{-4})</td>
<td>-2.6x10(^{-4})</td>
<td>-3.21x10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>( \pm 1.0x10^{-5} )</td>
<td>( \pm 1.2x10^{-5} )</td>
<td>( \pm 1.3x10^{-5} )</td>
<td>( \pm 1.6x10^{-5} )</td>
</tr>
<tr>
<td>7.36x10(^{-4})</td>
<td>-2.13x10(^{-4})</td>
<td>-2.33x10(^{-4})</td>
<td>-2.6x10(^{-4})</td>
<td>-3.19x10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>( \pm 1.0x10^{-5} )</td>
<td>( \pm 1.1x10^{-5} )</td>
<td>( \pm 1.3x10^{-5} )</td>
<td>( \pm 1.6x10^{-5} )</td>
</tr>
<tr>
<td>6.64x10(^{-4})</td>
<td>-2.09x10(^{-4})</td>
<td>-2.35x10(^{-4})</td>
<td>-2.56x10(^{-4})</td>
<td>-3.18x10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>( \pm 1.0x10^{-5} )</td>
<td>( \pm 1.1x10^{-5} )</td>
<td>( \pm 1.3x10^{-5} )</td>
<td>( \pm 1.6x10^{-5} )</td>
</tr>
<tr>
<td>4.6x10(^{-4})</td>
<td>-2.12x10(^{-4})</td>
<td>-2.35x10(^{-4})</td>
<td>-2.61x10(^{-4})</td>
<td>-3.22x10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>( \pm 1.0x10^{-5} )</td>
<td>( \pm 1.1x10^{-5} )</td>
<td>( \pm 1.3x10^{-5} )</td>
<td>( \pm 1.6x10^{-5} )</td>
</tr>
</tbody>
</table>
Table 41
Log $K_e$ vs. Ligand

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Log $K_e$ Zn(II)</th>
<th>Log $K_e$ Ni(II)</th>
<th>Log $K_e$ Cu(II)</th>
<th>Log $K_e$ Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.8x10^{-4}</td>
<td>6.77</td>
<td>4.06</td>
<td>6.84</td>
<td>6.35</td>
</tr>
<tr>
<td>8.28x10^{-4}</td>
<td>6.61</td>
<td>3.91</td>
<td>6.69</td>
<td>7.15</td>
</tr>
<tr>
<td>7.36x10^{-4}</td>
<td>6.51</td>
<td>3.80</td>
<td>6.58</td>
<td>7.02</td>
</tr>
<tr>
<td>6.64x10^{-4}</td>
<td>6.41</td>
<td>3.72</td>
<td>6.49</td>
<td>6.90</td>
</tr>
<tr>
<td>5.52x10^{-4}</td>
<td>6.30</td>
<td>3.61</td>
<td>6.42</td>
<td>6.72</td>
</tr>
<tr>
<td>4.6x10^{-4}</td>
<td>6.11</td>
<td>3.43</td>
<td>6.18</td>
<td>6.52</td>
</tr>
</tbody>
</table>
Figure 41. Ligand Dependence. Log $K_c$ - Log $D$ - 2pH
Table 42

Log $K_e$ - Log D - 2pH (pH 6.2, SDS)

<table>
<thead>
<tr>
<th>Buffer</th>
<th>Zn(II)</th>
<th>Ni(II)</th>
<th>Cu(II)</th>
<th>Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>Succinate</td>
<td>1.9815 ±0.0991</td>
<td>1.8463 ±0.0923</td>
<td>1.9815 ±0.0991</td>
</tr>
<tr>
<td></td>
<td>Phosphate</td>
<td>1.7828 ±0.0891</td>
<td>1.8675 ±0.0934</td>
<td>1.7828 ±0.0891</td>
</tr>
<tr>
<td>Intercept</td>
<td>Succinate</td>
<td>0.3145 ±0.0157</td>
<td>-2.8197 ±0.1410</td>
<td>0.3145 ±0.0157</td>
</tr>
<tr>
<td></td>
<td>Phosphate</td>
<td>-0.1572 ±0.0079</td>
<td>-2.6162 ±0.1308</td>
<td>-0.1572 ±0.0079</td>
</tr>
</tbody>
</table>
Table 43

\(K_{\text{micelle}}\) (pH 6.2, SDS)

<table>
<thead>
<tr>
<th>Buffer</th>
<th>Zn(II), Co(II)</th>
<th>Ni(II)</th>
<th>Cu(II)</th>
<th>Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1:2 Complex)</td>
<td>(1:3 Complex)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(K_{\text{micelle}})</td>
<td>Succinate</td>
<td>4.958x10^7</td>
<td>6.753x10^{10}</td>
<td>4.958x10^7</td>
</tr>
<tr>
<td></td>
<td>±2.479x10^6</td>
<td>±3.377x10^9</td>
<td>±2.479x10^6</td>
<td>±3.293x10^4</td>
</tr>
<tr>
<td>(K_{\text{micelle}})</td>
<td>Phosphate</td>
<td>1.47x10^8</td>
<td>4.227x10^{10}</td>
<td>1.47x10^8</td>
</tr>
<tr>
<td></td>
<td>±7.35x10^6</td>
<td>±2.113x10^9</td>
<td>±7.35x10^6</td>
<td>±1.901x10^4</td>
</tr>
</tbody>
</table>
Figure 42. Voltage Dependence (22 kV), Succinate Buffer, pH 6.2, I = 0.01 M
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Table 44

Zeta Potential and Electrophoretic Mobilities vs. Voltage (I = 0.01 M)

<table>
<thead>
<tr>
<th>Voltage (kV)</th>
<th>ζ (mV)</th>
<th>μ Zn(II) (cm²/Vs)</th>
<th>μ Ni(II) (cm²/Vs)</th>
<th>μ Cu(II) (cm²/Vs)</th>
<th>μ Co(II) (cm²/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>-69 ±3.2</td>
<td>-2.13x10⁻⁴</td>
<td>-2.3x10⁻⁴</td>
<td>-2.56x10⁻⁴</td>
<td>-3.17x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±1.0x10⁻⁵</td>
<td>±1.1x10⁻⁵</td>
<td>±1.2x10⁻⁵</td>
<td>±1.5x10⁻⁵</td>
</tr>
<tr>
<td>18</td>
<td>-70 ±3.5</td>
<td>-2.57x10⁻⁴</td>
<td>-2.79x10⁻⁴</td>
<td>-3.1x10⁻⁴</td>
<td>-3.85x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±1.2x10⁻⁵</td>
<td>±1.3x10⁻⁵</td>
<td>±1.5x10⁻⁵</td>
<td>±1.9x10⁻⁵</td>
</tr>
<tr>
<td>22</td>
<td>-71 ±3.5</td>
<td>-3.14x10⁻⁴</td>
<td>-3.41x10⁻⁴</td>
<td>-3.81x10⁻⁴</td>
<td>-4.75x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±1.5x10⁻⁵</td>
<td>±1.7x10⁻⁵</td>
<td>±1.9x10⁻⁵</td>
<td>±2.3x10⁻⁵</td>
</tr>
<tr>
<td>25</td>
<td>-71 ±3.5</td>
<td>-3.54x10⁻⁴</td>
<td>-3.87x10⁻⁴</td>
<td>-4.35x10⁻⁴</td>
<td>-5.45x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±1.7x10⁻⁵</td>
<td>±1.9x10⁻⁵</td>
<td>±2.1x10⁻⁵</td>
<td>±2.7x10⁻⁵</td>
</tr>
</tbody>
</table>
Table 45
Ionic Radii vs. Voltage (Succinate Buffer, pH 6.2, SDS)

<table>
<thead>
<tr>
<th>Voltage (kV)</th>
<th>$R_{\text{Zn(II)}}$ (Å)</th>
<th>$R_{\text{Ni(II)}}$ (Å)</th>
<th>$R_{\text{Cu(II)}}$ (Å)</th>
<th>$R_{\text{Co(II)}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>8.97 ±0.45</td>
<td>8.28 ±0.41</td>
<td>7.46 ±0.37</td>
<td>9.04 ±0.45</td>
</tr>
<tr>
<td>18</td>
<td>7.43 ±0.37</td>
<td>6.83 ±0.34</td>
<td>6.15 ±0.31</td>
<td>7.43 ±0.37</td>
</tr>
<tr>
<td>22</td>
<td>6.08 ±0.30</td>
<td>5.59 ±0.26</td>
<td>5.00 ±0.25</td>
<td>6.02 ±0.30</td>
</tr>
<tr>
<td>25</td>
<td>5.39 ±0.27</td>
<td>4.93 ±0.25</td>
<td>4.39 ±0.22</td>
<td>5.25 ±0.26</td>
</tr>
</tbody>
</table>
**Surfactant Dependence**

The proposed mechanism of metal ion separation in the presence of an anionic surfactant is based on the competition between negatively charged silanol groups of the capillary walls and negatively charged anionic micelle for the possession of the positively charged metal cation. (Equations 21-30) Surfactant dependence experiments were performed to understand the participation of the micelle in the metal ion separation. In the case of the anionic surfactant we are not dealing with problems like the adsorption of the surfactant by the negatively charged capillary walls as we were with the cationic surfactant experiments. Therefore, concentration of the surfactant used can be much higher than its cmc. To determine the participation of the surfactant in metal ion separation, the experiment was performed in the presence of 0.01-0.05 M of SDS in the mobile phase. Experimental data is presented in Figure 43 and Appendix C.

Electrophoretic mobilities are summarized in Table 46. Log $K_e$ values are in Table 47.

Electrophoretic mobilities of the anionic complexes and log $K_e$ do not significantly change with an increasing concentration of the surfactant which is consistent with the proposed mechanism.

**Oncolumn Complex Formation**

Another way of sample introduction is oncolumn complex formation. For this method, a metal sample was injected into the mobile phase which contained a ligand and a surfactant which resulted in complex formation in the capillary. As indicated in Figure 44 and Appendix C, separation of the transition metal ions could be achieved but was not as good as when the complexes were injected. Separations using oncolumn complex formation in the presence of SDS is, however, much better than in the presence of OTAB and CTAN.

Calculated electrophoretic mobilities and log $K_e$ are presented in Tables 48 and 49.

Comparisons between the plot of log D vs. pH and plot of log $K_e$ with respect to log D and [HL⁻] (Figure 45) illustrate that the new parameter $K_e$ can better describe metal complex formation than the traditional method based on distribution constant calculations. Slope and intercept values of the plots are presented in Table 50.
Figure 43. Surfactant Dependence
Mobile Phase: Succinate Buffer, pH 5.75, I = 0.01 M, 0.04 M SDS
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Table 46
Electrophoretic Mobilities vs. Surfactant

<table>
<thead>
<tr>
<th>Surfactant Concentration (M)</th>
<th>μ Zn(II) (cm²/Vs)</th>
<th>μ Ni(II) (cm²/Vs)</th>
<th>μ Cu(II) (cm²/Vs)</th>
<th>μ Co(II) (cm²/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.015</td>
<td>-2.24x10⁻⁴ ±1.1x10⁻⁵</td>
<td>-2.69x10⁻⁴ ±1.3x10⁻⁵</td>
<td>-2.89x10⁻⁴ ±1.4x10⁻⁵</td>
<td>-3.49x10⁻⁴ ±1.7x10⁻⁵</td>
</tr>
<tr>
<td>0.025</td>
<td>-2.37x10⁻⁴ ±1.1x10⁻⁵</td>
<td>-2.55x10⁻⁴ ±1.2x10⁻⁵</td>
<td>-2.82x10⁻⁴ ±1.4x10⁻⁵</td>
<td>-3.42x10⁻⁴ ±1.7x10⁻⁵</td>
</tr>
<tr>
<td>0.030</td>
<td>-2.41x10⁻⁴ ±1.2x10⁻⁵</td>
<td>-2.55x10⁻⁴ ±1.2x10⁻⁵</td>
<td>-2.86x10⁻⁴ ±1.4x10⁻⁵</td>
<td>-3.46x10⁻⁴ ±1.7x10⁻⁵</td>
</tr>
<tr>
<td>0.04</td>
<td>-2.30x10⁻⁴ ±1.1x10⁻⁵</td>
<td>-2.38x10⁻⁴ ±1.2x10⁻⁵</td>
<td>-2.76x10⁻⁴ ±1.3x10⁻⁵</td>
<td>-3.36x10⁻⁴ ±1.6x10⁻⁵</td>
</tr>
<tr>
<td>0.05</td>
<td>-2.13x10⁻⁴ ±1.0x10⁻⁵</td>
<td>-2.18x10⁻⁴ ±1.0x10⁻⁵</td>
<td>-2.62x10⁻⁴ ±1.3x10⁻⁵</td>
<td>-3.23x10⁻⁴ ±1.6x10⁻⁵</td>
</tr>
</tbody>
</table>
Table 47
Log $K_e$ vs. Surfactant

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Log $K_e$ Zn(II)</th>
<th>Log $K_e$ Ni(II)</th>
<th>Log $K_e$ Cu(II)</th>
<th>Log $K_e$ Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.015</td>
<td>5.99</td>
<td>3.35</td>
<td>6.08</td>
<td>6.38</td>
</tr>
<tr>
<td>0.025</td>
<td>6.02</td>
<td>3.33</td>
<td>6.07</td>
<td>6.37</td>
</tr>
<tr>
<td>0.030</td>
<td>6.02</td>
<td>3.33</td>
<td>6.07</td>
<td>6.38</td>
</tr>
<tr>
<td>0.04</td>
<td>6.00</td>
<td>3.30</td>
<td>6.06</td>
<td>6.36</td>
</tr>
<tr>
<td>0.05</td>
<td>5.97</td>
<td>3.26</td>
<td>6.03</td>
<td>6.34</td>
</tr>
</tbody>
</table>
Figure 44. On-column Complex Formation. Succinic Buffer, pH 5.87, I = 0.02 M
1 = Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II)
<table>
<thead>
<tr>
<th>pH</th>
<th>$\mu$ Zn(II) (cm$^2$/Vs)</th>
<th>$\mu$ Ni(II) (cm$^2$/Vs)</th>
<th>$\mu$ Cu(II) (cm$^2$/Vs)</th>
<th>$\mu$ Co(II) (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.63</td>
<td>$-2.79 \times 10^{-4}$</td>
<td>$-3.65 \times 10^{-4}$</td>
<td>$-3.22 \times 10^{-4}$</td>
<td>$-2.85 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$\pm 1.4 \times 10^{-5}$</td>
<td>$\pm 1.8 \times 10^{-5}$</td>
<td>$\pm 1.6 \times 10^{-5}$</td>
<td>$\pm 1.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>5.75</td>
<td>$-2.74 \times 10^{-4}$</td>
<td>$-3.64 \times 10^{-4}$</td>
<td>$-3.10 \times 10^{-4}$</td>
<td>$-2.81 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$\pm 1.3 \times 10^{-5}$</td>
<td>$\pm 1.8 \times 10^{-5}$</td>
<td>$\pm 1.5 \times 10^{-5}$</td>
<td>$\pm 1.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>5.87</td>
<td>$-2.63 \times 10^{-4}$</td>
<td>$-3.64 \times 10^{-4}$</td>
<td>$-3.02 \times 10^{-4}$</td>
<td>$-2.82 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$\pm 1.3 \times 10^{-5}$</td>
<td>$\pm 1.8 \times 10^{-5}$</td>
<td>$\pm 1.5 \times 10^{-5}$</td>
<td>$\pm 1.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>6.03</td>
<td>$-2.68 \times 10^{-4}$</td>
<td>$-3.68 \times 10^{-4}$</td>
<td>$-2.96 \times 10^{-4}$</td>
<td>$-2.88 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$\pm 1.3 \times 10^{-5}$</td>
<td>$\pm 1.8 \times 10^{-5}$</td>
<td>$\pm 1.4 \times 10^{-5}$</td>
<td>$\pm 1.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>6.12</td>
<td>$-2.66 \times 10^{-4}$</td>
<td>$-3.66 \times 10^{-4}$</td>
<td>$-2.91 \times 10^{-4}$</td>
<td>$-2.86 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$\pm 1.3 \times 10^{-5}$</td>
<td>$\pm 1.8 \times 10^{-5}$</td>
<td>$\pm 1.4 \times 10^{-5}$</td>
<td>$\pm 1.4 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Table 49
Log $K_e$ – Oncolumn Complex Formation

<table>
<thead>
<tr>
<th>pH</th>
<th>Log $K_e$ Zn(II)</th>
<th>Log $K_e$ Ni(II)</th>
<th>Log $K_e$ Cu(II)</th>
<th>Log $K_e$ Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.63</td>
<td>5.55</td>
<td>2.99</td>
<td>5.58</td>
<td>5.67</td>
</tr>
<tr>
<td>5.75</td>
<td>5.94</td>
<td>3.34</td>
<td>5.76</td>
<td>6.14</td>
</tr>
<tr>
<td>5.87</td>
<td>6.12</td>
<td>3.53</td>
<td>6.16</td>
<td>6.38</td>
</tr>
<tr>
<td>6.03</td>
<td>6.32</td>
<td>3.72</td>
<td>6.35</td>
<td>6.64</td>
</tr>
<tr>
<td>6.12</td>
<td>6.51</td>
<td>3.90</td>
<td>6.54</td>
<td>6.89</td>
</tr>
</tbody>
</table>
Figure 45. Oncolumn Complex Formation. Log $K_e - \log D - 2\log [HL]\cdot$
Table 50
Slopes and Intercepts – Log D and Log K_e – Log D – 2 Log [HL']

<table>
<thead>
<tr>
<th></th>
<th>Zn(II)</th>
<th>Ni(II)</th>
<th>Cu(II)</th>
<th>Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log D</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slope</td>
<td>-0.0764 ±0.0038</td>
<td>0.0185 ±0.0009</td>
<td>-0.1923 ±0.0096</td>
<td>0.0261 ±0.0013</td>
</tr>
<tr>
<td>Intercept</td>
<td>0.4379 ±0.0219</td>
<td>0.1942 ±0.0097</td>
<td>1.2281 ±0.0614</td>
<td>0.2876 ±0.01438</td>
</tr>
</tbody>
</table>

|       |              |              |              |              |
| Log K_e – Log D – 2[HL'] |              |              |              |              |
| Slope | 1.8926 ±0.0946 | 1.7133 ±0.0857 | 2.1816 ±0.1091 | 2.2605 ±0.1130 |
| Intercept | -5.0297 ±0.2514 | -6.8828 ±0.3441 | -6.8487 ±0.3424 | -6.9774 ±0.3489 |
As Table 50 shows, slopes of log D vs. pH do not provide information on the separation mechanism. On the other hand, slopes of the proposed mechanism clearly indicate a 1:2 metal complex formation; based on this information we believe that the proposed mechanism can be applied to oncolumn metal complex formation.

**Ligand: HMeQ**

Metal ion separation experiments were done using a neutral ligand, 8-hydroxyquinaldine or HMeQ, as a chelating ligand.

Separations of the transition metals using HMeQ as a ligand were achieved in a high pH range (9.0-9.7) using a boric acid buffer as an electrophoretic buffer in the mobile phase. Experiments at lower pH values were unsuccessful due to the high pKa values of the ligand. (Figure 46) Calculations of the fraction of the metal-ligand species using stability constants [16] in Table 51 indicate that Co(II), Cu(II), Ni(II) and Zn(II) form neutral 1:2 complexes with a HMeQ ligand. The complex structure is shown in Figure 47.

Fraction calculations are presented in Figure 48. Detailed derivations of the equations are shown in Appendix A.

Concentration of the ligand was varied in the range 1x10^{-3}-3x10^{-3} M. (Figure 49) Concentration of the metals was constant, 1x10^{-3} M. According to the fraction calculations at the given ligand concentrations, all metals form 1:2 complexes.

Unlike HQS, the precapillary complex formation with HMeQ did not yield reproducible electropherograms due to the poor solubility of the complex formed. Formation of the complex on the capillary in the presence of SDS yielded reproducible electropherograms. The oncolumn complex formation was only successful in the presence of SDS and was unsuccessful in the presence of OTAB and CTAN. The complex precipitated in the presence of cationic surfactants and these experiments were not pursued.

As in the case of the HQS ligand, metal ion separations in the presence of SDS is based on the competition between negatively charged micelle and negatively charged silanol groups of the capillary walls for the positively charged metal ion. In order to understand the metal ion separation mechanism with HMeQ the influence of ionic strength and ligand and surfactant concentrations on the separation were also investigated.
Figure 46. HMeQ

$$pK_1 = 5.61$$
$$pK_2 = 10.16$$
Table 51
Stability Constants – HMeQ Complexes

<table>
<thead>
<tr>
<th>Log of</th>
<th>Co(II)</th>
<th>Zn(II)</th>
<th>Cu(II)</th>
<th>Ni(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_1$</td>
<td>9.63</td>
<td>9.92</td>
<td>12.48</td>
<td>9.41</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>8.87</td>
<td>11.52</td>
<td>8.35</td>
<td></td>
</tr>
<tr>
<td>$\beta$</td>
<td>18.50</td>
<td>18.72</td>
<td>24.00</td>
<td>17.76</td>
</tr>
</tbody>
</table>
\[ M^{2+} + 2HL^- \leftrightarrow ML_2 + 2H^+ \]

Figure 47. Structure of Metal HMeQ Complex
Figure 48. Fractions of the Species Co(II). pH 8.8-10.0
Figure 49. Fractions Calculations – Ni(II)
Ligand Concentrations: $1 \times 10^{-3}$-$3 \times 10^{-3}$ M. pH 9.5
**pH Dependence**

pH dependence was studied in the range 9.2-9.7. Data for the pH dependence experiment is presented in Figure 50 and Appendix C.

As we can see from the electropherograms, migration times of the metal ions are in accordance with their stability constants (Table 51), with Co(II) having the shortest migration time and Cu(II) having the longest migration time. The Ni(II) complex however is an exception to this trend and may be the result of its slow complexation kinetics. [19, 31] By comparison, the order of migration for on-column complex formation for HQS is Zn(II), Co(II), Cu(II) and Ni(II) with a much poorer separation between Zn(II) and Co(II). The Co(II) only yielded 1:2 metal:ligand complexes with HMeQ while it formed both 1:2 and 1:3 metal:ligand complexes with HQS.

Electrophoretic mobilities, ionic radii, distribution constants and $K_e$ parameters were calculated from experimental data and are summarized in Tables 52-54.

Dynamic radii for HMeQ metal complexes (Table 53) are smaller than dynamic radii for the HQS-metal complexes. (Table 37) This most likely is due to the difference between the neutral complexes of HMeQ and the anionic complexes of HQS.

To determine if the mechanism proposed for HQS complexes is valid for HMeQ complexes, log $K_e$ (Table 55) was corrected with respect to the distribution constant and [HL−] concentration and was plotted vs. pH. (Equation 32)

$$\log K_e = \log K_{micelle} [(SiO)_2] + \log D + 2\log [HL^-] + 2 \text{pH} \quad (32)$$

This plot is presented in Figure 51.

Slopes and intercepts in Figure 51 are summarized in Table 55.

As shown by the plot, the slope indicates consistency with the proposed mechanism involving interaction between negatively charged silanol groups and positively charged metal ions and 1:2 complex formation as in Equations 25 and 26.

The influence of SDS concentration on the metal ion separation was investigated to further support the separation mechanism proposed.
Figure 50.  pH Dependence.  pH 9.7, 0.025 M SDS
0 = Peak from Electrophoretic Buffer
1 = Co(II), 2 = Zn(II), 3 = Cu(II), 4 = Ni(II)
### Table 52

Electrophoretic Mobilities vs. pH

<table>
<thead>
<tr>
<th>pH</th>
<th>$\mu$ Co(II) (cm$^2$/Vs)</th>
<th>$\mu$ Zn(II) (cm$^2$/Vs)</th>
<th>$\mu$ Cu(II) (cm$^2$/Vs)</th>
<th>$\mu$ Ni(II) (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.2</td>
<td>-3.19x10$^{-4}$</td>
<td>-3.60x10$^{-4}$</td>
<td>-3.81x10$^{-4}$</td>
<td>-3.92x10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>±1.5x10$^{-5}$</td>
<td>±1.8x10$^{-5}$</td>
<td>±1.9x10$^{-5}$</td>
<td>±1.9x10$^{-5}$</td>
</tr>
<tr>
<td>9.5</td>
<td>-3.31x10$^{-4}$</td>
<td>-3.67x10$^{-4}$</td>
<td>-3.93x10$^{-4}$</td>
<td>-3.99x10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>±1.6x10$^{-5}$</td>
<td>±1.8x10$^{-5}$</td>
<td>±1.9x10$^{-5}$</td>
<td>±1.9x10$^{-5}$</td>
</tr>
<tr>
<td>9.7</td>
<td>-3.46x10$^{-4}$</td>
<td>-3.76x10$^{-4}$</td>
<td>-3.96x10$^{-4}$</td>
<td>-4.06x10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>±1.7x10$^{-5}$</td>
<td>±1.8x10$^{-5}$</td>
<td>±1.9x10$^{-5}$</td>
<td>±2.0x10$^{-5}$</td>
</tr>
</tbody>
</table>
Table 53

Ionic Radii vs. pH

<table>
<thead>
<tr>
<th>pH</th>
<th>R Co(II) (Å)</th>
<th>R Zn(II) (Å)</th>
<th>R Cu(II) (Å)</th>
<th>R Ni(II) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.2</td>
<td>5.97 ±0.29</td>
<td>5.29 ±0.26</td>
<td>5.00 ±0.25</td>
<td>4.86 ±0.24</td>
</tr>
<tr>
<td>9.5</td>
<td>5.77 ±0.29</td>
<td>5.19 ±0.26</td>
<td>4.85 ±0.24</td>
<td>4.78 ±0.24</td>
</tr>
<tr>
<td>9.7</td>
<td>5.51 ±0.27</td>
<td>5.07 ±0.25</td>
<td>4.82 ±0.24</td>
<td>4.70 ±0.24</td>
</tr>
<tr>
<td>pH</td>
<td>$\text{Log } K_e \text{ Co(II)}$</td>
<td>$\text{Log } K_e \text{ Zn(II)}$</td>
<td>$\text{Log } K_e \text{ Cu(II)}$</td>
<td>$\text{Log } K_e \text{ Ni(II)}$</td>
</tr>
<tr>
<td>-----</td>
<td>-------------------------------</td>
<td>-------------------------------</td>
<td>-------------------------------</td>
<td>-------------------------------</td>
</tr>
</tbody>
</table>
Figure 51. \( \log K_e - \log D - 2\log [HL^+] \) vs. pH for HMeQ Complexation
\( I = 0.03 \text{ M}, 0.025 \text{ M SDS} \)
Table 55
Slopes and Intercepts – ($\log K_e - \log D - 2\log [HL^-]$)

<table>
<thead>
<tr>
<th></th>
<th>Co(II)</th>
<th>Zn(II)</th>
<th>Cu(II)</th>
<th>Ni(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>2.0335 ±0.1017</td>
<td>2.0074 ±0.1004</td>
<td>2.0074 ±0.1004</td>
<td>2.0074 ±0.1004</td>
</tr>
<tr>
<td>Intercept</td>
<td>-2.9822 ±0.1491</td>
<td>-0.7079 ±0.0354</td>
<td>-0.7079 ±0.0354</td>
<td>-0.7079 ±0.0354</td>
</tr>
</tbody>
</table>
Surfactant Dependence

Separation of metal ions was performed at different concentrations of surfactant in the mobile phase. Concentration of the surfactant was varied from 0.01-0.04 M. We intentionally kept the concentration of the surfactant much higher than cmc in order for SDS micelles to compete with negatively charged silanol groups for positively charged metal ions.

Electrophoretic mobilities and $K_e$ parameters were calculated from experimental data and based on the mechanism equations. Results are summarized in Tables 56-58 which indicate the independence of electrophoretic mobilities, $K_e$ and ionic radii on the concentration of SDS, as expected from the mechanism.
Table 56
Electrophoretic Mobilities vs. Surfactant

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>μ Co(II) (cm²/Vs)</th>
<th>μ Zn(II) (cm²/Vs)</th>
<th>μ Cu(II) (cm²/Vs)</th>
<th>μ Ni(II) (cm²/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (M)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>-2.32x10⁻⁴ ±1.1x10⁻⁵</td>
<td>-2.93x10⁻⁴ ±1.4x10⁻⁵</td>
<td>-3.04x10⁻⁴ ±1.5x10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>0.025</td>
<td>-2.69x10⁻⁴ ±1.3x10⁻⁵</td>
<td>-2.98x10⁻⁴ ±1.4x10⁻⁵</td>
<td>-3.20x10⁻⁴ ±1.6x10⁻⁵</td>
<td>-3.23x10⁻⁴ ±1.6x10⁻⁵</td>
</tr>
<tr>
<td>0.04</td>
<td>-2.85x10⁻⁴ ±1.4x10⁻⁵</td>
<td>-3.05x10⁻⁴ ±1.5x10⁻⁵</td>
<td>-3.22x10⁻⁴ ±1.6x10⁻⁵</td>
<td>-3.26x10⁻⁴ ±1.6x10⁻⁵</td>
</tr>
</tbody>
</table>
Table 57

Ionic Radii vs. Surfactant

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>R Co(II) (Å)</th>
<th>R Zn(II) (Å)</th>
<th>R Cu(II) (Å)</th>
<th>R Ni(II) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (M)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>8.22 ±0.41</td>
<td>6.52 ±0.32</td>
<td>6.27 ±0.31</td>
<td></td>
</tr>
<tr>
<td>0.025</td>
<td>7.10 ±0.35</td>
<td>6.41 ±0.32</td>
<td>5.96 ±0.29</td>
<td>5.91 ±0.29</td>
</tr>
<tr>
<td>0.04</td>
<td>6.69 ±0.33</td>
<td>6.25 ±0.31</td>
<td>5.92 ±0.29</td>
<td>5.86 ±0.29</td>
</tr>
<tr>
<td>Concentration (M)</td>
<td>Log $K_e$ Co(II)</td>
<td>Log $K_e$ Zn(II)</td>
<td>Log $K_e$ Cu(II)</td>
<td>Log $K_e$ Ni(II)</td>
</tr>
<tr>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>0.01</td>
<td>13.15</td>
<td>13.25</td>
<td>13.27</td>
<td></td>
</tr>
<tr>
<td>0.025</td>
<td>11.21</td>
<td>13.26</td>
<td>13.29</td>
<td>13.29</td>
</tr>
<tr>
<td>0.04</td>
<td>11.24</td>
<td>13.27</td>
<td>13.29</td>
<td>13.30</td>
</tr>
</tbody>
</table>
CHAPTER IV

CONCLUSIONS

Separation of transition metal ions Co(II), Ni(II), Cu(II) and Zn(II) in the presence of the ligands HQS and HMeQ with cationic surfactants OTAB and CTAN and the anionic surfactant SDS were investigated by CE under a variety of conditions like pH, ligand concentration, applied voltage and ionic strength. The significant results are:

1. Separation of metal ion complexes in the presence of a small concentration of cationic surfactants adsorbed on the surface of the capillary is due to the exchange of the metal ion between the metal complexes in the mobile phase and the surface silanol groups. This leads to a difference in the electrophoretic mobilities of the metal complexes and their separation.

2. The separation in the presence of anionic surfactants result from the competition for the metal ion between the anionic micelles and the surface silanol groups leading to a difference in electrophoretic mobilities. This additional competition for the metal ion by the anionic micelles causes a further decrease in the mobilities of the metal ion complexes in the presence of anionic micelles compared to the cationic surfactant layers on the capillary walls.

3. A new empirical parameter, $K_e$, has been proposed to understand these separation mechanisms. This parameter is related to electrophoretic mobilities and hence the concentrations of the ligand and pH. Analysis of the electropherograms in terms of $K_e$ provides the expected dependencies on the concentration of ligand and pH.

4. The speciation of the metal complexes can be clearly discerned from this parameter.

5. The parameter $K_e$ also yields the concentration of surface silanol groups and the equilibrium constant for the exchange of the metal ion between the metal complexes and the anionic micelles. This equilibrium constant was determined for the first time and has fundamental significance for metal ion complex formation and dissociation studies as well as separations based
on these with anionic micelles.

6. Dynamic radii of the metal complexes were determined from electrophoretic mobilities and agree with those calculated from the geometry of the complexes.

7. A limited number of separations where the ionic strength and the applied voltages were varied could be rationalized based on the separation mechanism proposed in the presence of the cationic surfactants and anionic micelles.

8. This work has provided valuable fundamental insights into the separation of metal ions in the presence of ligands and surfactants by CE that have not been previously reported in the literature.
CHAPTER V

FUTURE DIRECTIONS

This research has provided valuable fundamental information on the mechanism of metal ion separations mediated by surfactant assemblies. A significant result of the work is the empirical parameter $K_e$ which enables an analysis of the electropherograms and an understanding of the separation mechanisms. The following directions for future work are suggested:

1. Verify the validity of the parameter $K_e$ with other metal ions and ligand systems to establish the generality of its applications.

2. Investigate metal ion separations in the presence of ligands that self-assemble to form micelles.

3. Nanoparticles like Au and Si have well-defined sizes and can be appropriately derivatized with functional groups to render their surfaces positive or negative. They thus become micelle mimetic systems, which do not have the monomer-micelle equilibrium encountered with the conventional and chelating surfactants. The behavior of these nanoparticles in an electrical field in the absence and presence of metal ions would provide valuable fundamental information on their behavior in an electric field and on their usefulness for the separation and detection of metal ions. This would have great practical significance, as usually nanomolar concentrations of nanoparticles are sufficient to achieve significant perturbations in the equilibria as well as measurable signals for detection. This would also provide another way to test the parameter $K_e$. 

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REFERENCES


References—Continued


Appendix A

Species Fraction Derivation
The total species fraction equation is described by:

\[ [H_2L]_t = [H_2L] + [HL^-] + [L^{2-}] \]  \hspace{1cm} (33)

Therefore, the fractions of \([H_2L], [HL^-]\) and \([L^{2-}]\) are:

\[
\frac{a_{[H_2L]}}{[H_2L]_t} = \frac{[H_2L]}{[H_2L]_t} \]  \hspace{1cm} (34)

\[
\frac{a_{[HL^-]}}{[H_2L]_t} = \frac{[HL^-]}{[H_2L]_t} \]  \hspace{1cm} (35)

\[
\frac{a_{[L^{2-}]}{[H_2L]_t} = \frac{[L^{2-}]}{[H_2L]_t} \]  \hspace{1cm} (36)

Dissociation equilibria of the ligand can be described by:

\[ K_{a1} \]

\[ H_2L \leftrightarrow HL^- + H^+ \]  \hspace{1cm} (37)

\[ K_{a2} \]

\[ HL^- \leftrightarrow L^{2-} + H^+ \]  \hspace{1cm} (38)

\[ K_{a1} \text{ and } K_{a2}, \text{ acid dissociation constants, can be expressed by:} \]

\[ K_{a1} = \frac{[HL^-] \times [H^+]}{[H_2L]_t} \]  \hspace{1cm} (39)
K_{a2} = \frac{[L^2^-] \times [H^+]}{[HL^-]} \quad (40)

Substituting Equations 39 and 40 into Equations 34-36 gives:

\[
a_{[H_2L]} = \frac{1}{1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1} \times K_{a2}}{[H^+]^2}} \quad (41)
\]

\[
a_{[HL^-]} = \frac{K_{a1}}{[H^+]^2} \quad (42)
\]

\[
a_{[L^2^-]} = \frac{K_{a1} \times K_{a2}}{[H^+]^2} \quad (43)
\]

Equations 44-47 describe the equalibria of metal complex formation.

\[
\beta_1 \quad (44)
\]

\[M^{2+} + L^{2-} \rightleftharpoons ML^-\]
The overall equilibrium is:

\[ \beta_2 \quad \text{ML} + L^{2-} \iff \text{ML}_2^{2-} \]  

where the overall stability constant, \( \beta \), equals:

\[ \beta = \beta_1 \times \beta_2 \]  

The fraction of metal species are given by Equations 49-55.

\[ [\text{ML}_2^{2-}] = \beta \times [\text{M}^{2+}] \times [L^{2-}]^2 \]  

Equations 53-56 can be derived from Equations 47 and 50-52.
\[ a_{[M^{2+}]} = \frac{1}{1 + \beta_1 \times [L^2] + \beta_1 \times \beta_2 \times [L^2]^2} \]  

(53)

\[ a_{[ML]} = \frac{\beta_1 \times [L^2]}{1 + \beta_1 \times [L^2] + \beta_1 \times \beta_2 \times [L^2]^2} \]  

(54)

\[ a_{[ML_2^{2-}]} = \frac{\beta_1 \times \beta_2 \times [L^2]^2}{1 + \beta_1 \times [L^2] + \beta_1 \times \beta_2 \times [L^2]^2} \]  

(55)

For Co(II) 1:3 complex, the overall stability constant, \( \beta = \beta_1 \times \beta_2 \times \beta_3 \).

\[ a_{[ML_3^{3-}]} = \frac{\beta_1 \times \beta_2 \times \beta_3 \times [L^2]^3}{1 + \beta_1 \times [L^2] + \beta_1 \times \beta_2 \times [L^2]^2 + \beta_1 \times \beta_2 \times \beta_3 \times [L^2]^3} \]  

(56)

Fractions of the ligand (HQS) and metal species are presented in Figures 52-55.

Fractions of the ligand (HMeQ) and metal species are presented in Figures 56-59.
Figure 52. Fraction Calculations. pH 3.5-7.2. Ligand: HQS.
Figure 53. Fraction Calculations. pH 3.5-7.2. Zn(II).
Figure 54. Fraction Calculations. pH 3.5-7.2. Cu(II).
Figure 55. Fraction Calculations. pH 3.5-7.2. Ni(II).
Figure 56. Fraction Calculations. pH 8.8-10.0. Ligand: HMeQ.
Figure 57. Fraction Calculations. pH 8.8-10.0. Co(II).
Figure 58. Fraction Calculations. pH 8.8-10.0. Zn(II).
Figure 59. Fraction Calculations. pH 8.8-10.0. Cu(II).
Appendix B

Data Treatment
Zeta Potential Calculations

The zeta potential [24] was calculated according to Equation 57:

\[
\zeta = \frac{v \times \eta \times L_e}{E_0 \times \varepsilon \times V}
\]  

(57)

\[v = L_{ef}t\]  

(58)

where:  
- \(L_{ef}\) = effective length of the capillary, m  
- \(s\) = migration time of the species, s  
- \(v\) = velocity, ms\(^{-1}\)

\[\varepsilon' = \varepsilon \times E_0 = 8.854 \times 10^{-12} \times 79 \text{ F m}^{-1}\]  

(59)

where:  
- \(\varepsilon\) = dielectric constant, unit-less  
- \(E_0\) = conversion factor, 8.854 \times 10^{-12}, \text{ F m}^{-1}
Silanol Group Concentration

\[ \text{Si}--\text{O}--\text{Si}--\text{O}--\text{Si} \]

\[ \text{Si} \quad \text{Si} \quad \text{O} \quad \text{O} \]

\[ \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \]

\[ (\text{SiO})_2^- \]

\[ \text{O}^- \]

Figure 60. Surface of the Capillary

Capillary surface area, S, equals:

\[ S = \pi d \times l = 3.14 \times 75 \times 10^{-4} \, \text{cm} \times 50 \, \text{cm} = 1.18 \, \text{cm}^2 = 1.18 \times 10^{14} \, \text{nm}^2 \]  \hspace{1cm} (60)

where:

- \( d \) = diameter of the capillary (75 \( \mu \text{m} \))
- \( l \) = length of the capillary, cm

OH groups per \( \text{nm}^2 \), \( n \), is approximately 50 per \( \text{nm}^2 \).

\[ [(\text{SiO})_2^-] = S \times n = 1.18 \times 10^{14} \, \text{nm}^2 \times 50 = 5.9 \times 10^{15} \]  \hspace{1cm} (61)

\( \log 5.9 \times 10^{15} = 15.77 \)
Appendix C

Experimental Data

(Electropherograms)
Figure 61. Sample Preparation by Precolumn Complex Formation Method
Absent Surfactant
Mobile Phase: Phosphate Buffer, pH 6.45, I = 0.01 M, Ligand: HQS
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 62. pH Dependence. Metal-HQS Complexes at Different pH.
Succinate Buffer, pH 5.66, I = 0.05 M, 2x10⁻³ M OTAB
1 = Ligand, 2 = Zn(II), Co(II) (1:2 Complex), 3 = Ni(II), 4 = Cu(II)
5 = Co(II) (1:3 Complex)
Figure 63. pH Dependence. Metal-HQS Complexes at Different pH.
Succinate Buffer, pH 5.90, I = 0.05 M, 2x10⁻³ M OTAB
1 = Ligand, 2 = Zn(II), Co(II) (1:2 Complex), 3 = Ni(II), 4 = Cu(II)
5 = Co(II) (1:3 Complex)
Figure 64. pH Dependence. Metal-HQS Complexes at Different pH.
Succinate Buffer, pH 6.10, I = 0.05 M, 2x10^{-3} M OTAB
1 = Ligand, 2 = Zn(II), Co(II) (1:2 Complex), 3 = Ni(II), 4 = Cu(II)
5 = Co(II) (1:3 Complex)
Figure 65. pH Dependence. Metal-HQS Complexes at Different pH. Succinate Buffer, pH 6.30. I = 0.05 M, 2x10^{-3} M OTAB
1 = Ligand, 2 = Zn(II), Co(II) (1:2 Complex), 3 = Ni(II), 4 = Cu(II)
5 = Co(II) (1:3 Complex)
Figure 66. pH Dependence. Metal-HQS Complexes at Different pH.
Succinate Buffer, pH 6.50, I = 0.05 M, 2x10^{-3} M OTAB
1 = Ligand, 2 = Zn(II), Co(II) (1:2 Complex), 3 = Ni(II), 4 = Cu(II)
5 = Co(II) (1:3 Complex)
Figure 67. pH Dependence. Metal-HQS Complexes at Different pH. 
Succinate Buffer, pH 6.70, I = 0.05 M, 2x10^-3 M OTAB
1 = Ligand, 2 = Zn(II), Co(II) (1:2 Complex), 3 = Ni(II), 4 = Cu(II)
5 = Co(II) (1:3 Complex)
Figure 68. pH Dependence. Metal-HQS Complexes at Different pH.
Phosphate Buffer, pH 6.23, I = 0.05 M, 2x10⁻³ M OTAB
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 69. pH Dependence. Metal-HQS Complexes at Different pH.
Phosphate Buffer, pH 6.43, I = 0.05 M, 2x10⁻³ M OTAB
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 70. pH Dependence. Metal-HQS Complexes at Different pH.
Phosphate Buffer, pH 6.73, I = 0.05 M, 2x10^{-3} M OTAB
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 71. pH Dependence. Metal-HQS Complexes at Different pH.
Phosphate Buffer, pH 7.28, I = 0.05 M, 2x10^{-3} M OTAB
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 72. Ligand Dependence (Concentration: $9.8 \times 10^{-4}$ M). Metal-HQS Complexes. Succinate Buffer, pH 6.2, $I = 0.05$ M, $2 \times 10^{-3}$ M OTAB
1 = Ligand, Zn(II)+Co(II), 2 = Ni(II), 3 = Cu(II), 4 = Co(II)
Figure 73. Ligand Dependence (Concentrations: 9.2x10^{-4} M). Metal-HQS Complexes. Succinate Buffer, pH 6.2, I = 0.05 M, 2x10^{-3} M OTAB
1 = Ligand, Zn(II)+Co(II), 2 = Ni(II), 3 = Cu(II), 4 = Co(II)
Figure 74. Ligand Dependence (Concentrations: $7.4 \times 10^{-4}$ M). Metal-HQS Complexes. Succinate Buffer, pH 6.2, $I = 0.05$ M, $2 \times 10^{-3}$ M OTAB
1 Ligand, Zn(II)+Co(II), 2 = Ni(II), 3 = Cu(II), 4 = Co(II)
Figure 75. Ligand Dependence. Metal-HQS Complexes. $[\text{HQS}] = 9.8 \times 10^{-4}$ M Phosphate Buffer, pH 6.2, $I = 0.05$ M, $2 \times 10^{-3}$ M OTAB
1 = Ligand, 2 = Zn(II), 3 = Co(II), 4 = Ni(II), 5 = Cu(II), 6 = Co(II)
Figure 76. Ligand Dependence. Metal-HQS Complexes. [HQS] = 9.2x10^-4 M Phosphate Buffer, pH 6.2, I = 0.05 M, 2x10^-3 M OTAB
1 = Ligand, 2 = Zn(II), 3 = Co(II), 4 = Ni(II), 5 = Cu(II), 6 = Co(II)
Figure 77. Ligand Dependence. Metal-HQS Complexes. [HQS] = 7.4x10^{-4} M Phosphate Buffer, pH 6.2, I = 0.05 M, 2x10^{-3} M OTAB
1 = Ligand, 2 = Zn(II), 3 = Co(II), 4 = Ni(II), 5 = Cu(II), 6 = Co(II)
Figure 78. Oncolumn Metal Ion Separation
Succinate Buffer, pH 5.56, I = 0.02 M, 2x10^{-3} M OTAB
1 = Zn(II), 2 = Co(II), 3 = Cu(II), 4 = Ni(II)
Figure 79. Oncolumn Metal Ion Separation
Succinate Buffer, pH 5.78, I = 0.02 M, 2x10^{-3} M OTAB
1 = Zn(II), 2 = Co(II), 3 = Cu(II), 4 = Ni(II)
Figure 80. Oncolumn Metal Ion Separation
Succinate Buffer, pH 5.87, I = 0.02, 2x10^{-3} M OTAB
1 = Zn(II), 2 = Co(II), 3 = Cu(II), 4 = Ni(II)
Figure 81.  Oncolumn Metal Ion Separation
Succinate Buffer, pH 5.97, I = 0.02 M, 2x10^{-3} M OTAB
1 = Zn(II), 2 = Co(II), 3 = Cu(II), 4 = Ni(II)
Figure 82. Voltage Dependence (15 kV)
Phosphate Buffer, pH 6.2, I = 0.05 M, 1x10^{-5} M CTAN
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 83. Voltage Dependence (18 kV)
Phosphate Buffer, pH 6.2, I = 0.05 M, 1x10^-5 M CTAN
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 84. Voltage Dependence (25 kV)
Phosphate Buffer, pH 6.2, I = 0.05 M, 1x10⁻⁵ M CTAN
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 85. Ionic Strength Dependence
Phosphate Buffer, pH 6.2, I = 0.03 M, 1x10⁻⁵ M CTAN
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 86. Ionic Strength Dependence
Phosphate Buffer, pH 6.2, I = 0.05 M, 1x10^{-5} M CTAN
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 87. Ionic Strength Dependence
Phosphate Buffer, pH 6.2, I = 0.07 M, 1x10^{-5} M CTAN
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 88. pH Dependence
Phosphate Buffer, pH 6.23, I = 0.05 M, 1x10^-5 M CTAN
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 89. pH Dependence

Phosphate Buffer, pH 6.4, I = 0.05 M, 1x10^{-5} M CTAN
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 90. pH Dependence
Phosphate Buffer, pH 6.92, I = 0.05 M, 1x10^{-5} M CTAN
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 91. pH Dependence
Phosphate Buffer, pH 7.12, I = 0.05 M, 1x10^{-5} M CTAN
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 92.  Ligand Dependence (Concentration: $9.8 \times 10^{-4}$ M)  
$\text{pH 6.2, } I = 0.05 \text{ M, } 1 \times 10^{-5} \text{ M CTAN}$  
$1 = \text{Ligand, } 2 = \text{Zn(II)+Co(II), } 3 = \text{Ni(II), } 4 = \text{Cu(II), } 5 = \text{Co(II)}$
Figure 93. Ligand Dependence (Concentration $8.3 \times 10^{-4}$ M)
pH 6.2, $I = 0.05$ M, $1 \times 10^{-5}$ M CTAN
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 94. Ligand Dependence (Concentration: $6.6 \times 10^{-4}$ M)

pH 6.2, $I = 0.05$ M, $1 \times 10^{-5}$ M CTAN

1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 95. Ligand Dependence (Concentration: $5.5 \times 10^{-4}$ M)

pH 6.2, $I = 0.05$ M, $1 \times 10^{-5}$ M CTAN

1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 96. Surfactant Dependence (Concentration: 0 M CTAN)
Phosphate Buffer, pH 6.2
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 97.  Surfactant Dependence (Concentration: $1.2 \times 10^{-5}$ M CTAN)
Phosphate Buffer, pH 6.2
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 98. Surfactant Dependence (Concentration: $3.0 \times 10^{-5}$ M CTAN)
Phosphate Buffer, pH 6.2
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 99. Surfactant Dependence (Concentration: $1.0 \times 10^{-4}$ M CTAN)
Phosphate Buffer, pH 6.2
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 100. Surfactant Dependence (Concentration: 2.0x10^{-4} M CTAN)
Phosphate Buffer, pH 6.2
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 101. pH Dependence. Succinate Buffer, pH 5.75, I = 0.01 M, 0.05 M SDS
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 102. pH Dependence. Succinate Buffer, pH 6.17, I = 0.01 M, 0.05 M SDS
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 103. pH Dependence. Succinate Buffer, pH 6.37, $I = 0.01$ M, 0.05 M SDS
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 104. pH Dependence. Succinate Buffer, pH 6.5, I = 0.01 M, 0.05 M SDS
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 105. pH Dependence. Succinate Buffer, pH 6.7, I = 0.01 M, 0.05 M SDS
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 106. pH Dependence. Phosphate Buffer, pH 6.4, $I = 0.01 \text{ M}$, $0.05 \text{ M SDS}$
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 107. pH Dependence. Phosphate Buffer, pH 6.7, $I = 0.01$ M, 0.05 M SDS
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 108. pH Dependence. Phosphate Buffer, pH 7.0, I = 0.01 M, 0.05 M SDS
1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 109. pH Dependence. Phosphate Buffer, pH 7.28, $I = 0.01 \text{ M}, 0.05 \text{ M SDS}$

1 = Ligand+Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 110. Ligand Dependence (Concentration: $9.8 \times 10^{-4}$ M)
Succinate Buffer, pH 6.2, $I = 0.01$ M, 0.05 M SDS
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 111. Ligand Dependence (Concentration: $8.28 \times 10^{-4}$ M)
Succinate Buffer, pH 6.2, $I = 0.01$ M, 0.05 M SDS
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 112. Ligand Dependence (Concentration: $7.36 \times 10^{-4}$ M)
Succinate Buffer, pH 6.2, $I = 0.01$ M, 0.05 M SDS
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 113. Ligand Dependence (Concentration: $5.52 \times 10^{-4}$ M)
Succinate Buffer, pH 6.2, $I = 0.01$ M, 0.05 M SDS
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 114. Ligand Dependence (Concentration: $4.6 \times 10^{-4}$ M)
Succinate Buffer, pH 6.2, $I = 0.01$ M, 0.05 M SDS
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 115. Ligand Dependence (Concentration: $9.8 \times 10^{-4}$ M) 
Phosphate Buffer, pH 6.2, I = 0.01 M, 0.05 M SDS 
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 116. Ligand Dependence (Concentration: $8.28 \times 10^{-4}$ M)
Phosphate Buffer, pH 6.2, $I = 0.01$ M, 0.05 M SDS
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 117. Ligand Dependence (Concentration: $7.36 \times 10^{-4}$ M)
Phosphate Buffer, pH 6.2, $I = 0.01$ M, 0.05 M SDS
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 118. Ligand Dependence (Concentration: $4.6 \times 10^{-4}$ M)
Phosphate Buffer, pH 6.2, $I = 0.01$ M, $0.05$ M SDS
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 119. Voltage Dependence (15 kV)
Succinate Buffer, pH 6.2, I = 0.01 M, 0.05 M SDS
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 120. Voltage Dependence (18 kV)
Succinate Buffer, pH 6.2, I = 0.01 M, 0.05 M SDS
1 = Ligand, 2=Zn(II)+Co(II), 3=Ni(II), 4=Cu(II), 5=Co(II)
Figure 121. Voltage Dependence (25 kV)
Succinate Buffer, pH 6.2, I = 0.01 M, 0.05 M SDS
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 122  Surfactant Dependence
Succinate Buffer, pH 5.75, I = 0.01, 0.05 M SDS
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 123  Surfactant Dependence
Succinate Buffer, pH 5.75, $I = 0.01$, 0.025 M SDS
1 = Ligand, 2 = Zn(II)+ Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 124. Surfactant Dependence
Succinate Buffer, pH 5.75, I = 0.01, 0.03 M SDS
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 125  Surfactant Dependence
Succinate Buffer, pH 5.75, I = 0.01, 0.05 M SDS
1 = Ligand, 2 = Zn(II)+Co(II), 3 = Ni(II), 4 = Cu(II), 5 = Co(II)
Figure 126. Oncolumn Complex Formation
Succinate Buffer, pH 5.63, I = 0.02 M, 0.05 M SDS
1 = Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II)
Figure 127. Oncolumn Complex Formation
Succinate Buffer, pH 5.75, I = 0.02 M, 0.05 M SDS
1 = Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II)
Figure 128. Oncolumn Complex Formation
Succinate Buffer, pH 6.03, I = 0.02 M, 0.05 M SDS
1 = Zn(II), 2 = Co(II), 3 = Ni(II), 4 = Cu(II)
Figure 129. Oncolumn Complex Formation
Succinate Buffer, pH 6.12, $I = 0.02$ M, 0.05 M SDS
$1 = \text{Zn(II)}, 2 = \text{Co(II)}, 3 = \text{Ni(II)}, 4 = \text{Cu(II)}$
Figure 130. pH Dependence. Oncolumn Complex Formation. Borate Buffer, pH 9.2, 0.025 M SDS
0 = Peak from Electrophoretic Buffer
1 = Co(II), 2 = Zn(II), 3 = Cu(II), 4 = Ni(II)
Figure 131. pH Dependence. Oncolumn Complex Formation. Borate Buffer, pH 9.5, 0.025 M SDS
0 = Peak from Electrophoretic Buffer
1 = Co(II), 2 = Zn(II), 3 = Cu(II), 4 = Ni(II)
BIBLIOGRAPHY


