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Experimental Study of Aqueous and Mineral Surface Al-Aniline and Al-2-Chloroaniline Complexation

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A thesis submitted to the Faculty of
Graduate Studies and Research in partial
fulfillment of the requirements for the
degree of Master of Science

Department of Earth and Planetary Sciences
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PREFACE

Candidates have the option of including, as part of the thesis, the text of one or more papers submitted or to be submitted for publication, or the clearly-duplicated text of one or more published papers. These texts must be bound as an integral part of the thesis.

If this option is chosen, **connecting texts that provide logical bridges between the different papers are mandatory.** The thesis must be written in such a way that it is more than a mere collection of manuscripts; in other words, results of a series of papers must be integrated.

The thesis must still conform to all other requirements of the "Guidelines for Thesis Preparation". **The thesis must include:** A Table of Contents, an abstract in English and French, an introduction which clearly states the rationale and objectives of the study, a review of the literature, a final conclusion and summary, and a thorough bibliography or reference list.

Additional material must be provided where appropriate (e.g. in appendices) and in sufficient detail to allow clear and precise judgement to be made of the importance and originality of the research reported in the thesis.

In the case of manuscripts co-authored by the candidate and others, **the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent**. Supervisors must attest to the accuracy of such statements at the doctoral oral defense. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to make perfectly clear the responsibilities of all the authors of the co-authored papers.

Note: Professor Fein's contribution to the project involved assistance in planning the experiments and interpreting the results. The idea for the project was his as well.

ABSTRACT

In order to model the transport and fate of aniline and chloroaniline in the subsurface, the geochemical reactions between these contaminants and important metals and minerals surfaces must be quantified.

The thermodynamic stabilities of the aqueous and surface aluminum-aniline and aluminum-2-chloroaniline complexes were investigated at 55°C and 80°C. Solubility and adsorption experiments place quantitative constraints on the thermodynamic properties of these complexes. No evidence was found for stable Al-aniline or Al-2-chloroaniline aqueous complexes. Conversely, the adsorption data provide unequivocal evidence for the presence of two distinct surface Al-aniline and Al-chloroaniline complexes according to the following reactions:

(1) $\mathit{Aniline}^{\circ} + \equiv \mathit{Al(OH)}^{\circ} \leftrightarrow \equiv \mathit{AlOH(Aniline)}^{\circ}$

(2) $\mathit{Aniline}^{\circ} + \equiv \mathit{Al(O)}^{-} \leftrightarrow \equiv \mathit{AlO(Aniline)}^{-}$

(3) $\mathit{Chloroaniline}^{\circ} + \equiv \mathit{Al(OH)}^{\circ} \leftrightarrow \equiv \mathit{AlOH(Chloroaniline)}^{\circ}$

(4) $\mathit{Chloroaniline}^{\circ} + \equiv \mathit{Al(OH_2)}^{+} \leftrightarrow \equiv \mathit{AlOH_2(Chloroaniline)}^{+}$

A constant capacitance model is used to quantify the stability constants for reactions (1) - (4), and the results yield equilibrium constant values of $10^{2.09}$, $10^{2.67}$, $10^{2.87}$ and $10^{2.30}$ respectively. These results indicate that mineral surface complexation can significantly affect total aniline and chloroaniline budgets.

SOMMAIRE

Afin de pouvoir modeller le transport et destin d'aniline et de chloroaniline dans le subsurface, les réactions géochimiques entre ces polluants et d'importants métaux et des surfaces minérales devront être quantifiés.

Les expériences mettent des contraintes sur les propriétés thermodynamiques des complexes Al-aniline aqueuses et de surface. Il n'y avait pas d'evidence de complexes Al-aniline ou Al-2-chloroaniline aqueuses stable. Inversement, les données d'absorption fournissent une preuve sans équivoque, de la présence de deux surfaces distingues de complexe d'Al-aniline. Nous formons les données d'absorption avec les réactions suivantes:

(1) $\mathit{Aniline}^{\circ} + \equiv \mathit{Al(OH)}^{\circ} \leftrightarrow \equiv \mathit{AlOH(Aniline)}^{\circ}$

(2) $\mathit{Aniline}^{\circ} + \equiv \mathit{Al(O)}^{-} \leftrightarrow \equiv \mathit{AlO(Aniline)}^{-}$

(3) $\mathit{Chloroaniline}^{\circ} + \equiv \mathit{Al(OH)}^{\circ} \leftrightarrow \equiv \mathit{AlOH(Chloroaniline)}^{\circ}$

(4) $\mathit{Chloroaniline}^{\circ} + \equiv \mathit{Al(OH_2)}^{+} \leftrightarrow \equiv \mathit{AlOH_2(Chloroaniline)}^{+}$

Nous utilisons un modèle de capacitance constant pour quantifier la stabilité des constants pour les réactions (1)-(4) et les résultats produisent des valeurs d'équilibres constantes de $10^{2.09}$, $10^{2.67}$, $10^{2.87}$ et $10^{2.30}$ respectivement.

Les expériences indiquent que la complexation de surface minérale pourrait avoir un effet significatif sur les budgets totals d'aniline et de chloroaniline.

ACKNOWLEDGMENTS

I am greatly indebted to my supervisor Jeremy B. Fein. I benefited greatly from many fruitful discussions with him over the past three years. I thank Gerard Adams, Jonathan Behar, Sylvain Grégoire, Stephanie Nour, Christopher Paci and Robert Spivock for conducting some of the experiments, as well as Prof. Alfonso Mucci, Jean-François Boily, Peter Wightman and Chris Daughney for many helpful suggestions. The support of friends, Leyla Hoosain, David Palmer, Alger St-Jean, Anne Kosowski, Jason Harrington, Rajib SenGupta, Sandy Archibald, Monique Jeannin, Jim Davies, Olivia Eilers, Andrew Schmidt, and family, Gerry, Roslyn and Garry Yane, was greatly appeciated during this research. I am grateful to Sandra Lalli, Tariq Ahmedali and Glenna Keating for assistance with the atomic absorption spectrophotometer. Funding for this study was provided by an FCAR Nouveaux Chercheurs Grant and a NSERC Operating Grant to J.B.F.

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CHAPTER 1: INTRODUCTION

Aqueous and mineral surface complexation are the dominant chemical controls on the mobility of dissolved metals and organic compounds in groundwater. In order to accurately predict the fate of environmental contaminants, the thermodynamic stabilities of all important surface and aqueous complexes occurring in a system must be known. The relative strength of aqueous metal-organic complexation relative to mineral-surface metal-organic complexation dictates the concentration of the organic molecule in solution. Currently, however, we possess a limited knowledge of the thermodynamic stabilities of many environmentally important aqueous and surface metal-organic complexes. This study focuses on aqueous and mineral surface aluminum-aniline and aluminum-2-chloroaniline complexation.

Aniline and 2-chloroaniline are anthropogenic organic compounds primarily used in the manufacture of polymers, rubbers, pharmaceuticals, and dyes. Both are suspected carcinogens and are highly toxic to aquatic life (Patil and Shinde, 1988; Messner, 1979). Aniline may also be produced by the metabolism of phenylurea and various herbicides (Bartha and Pramer, 1970; Geissbühler, 1969; Herrett, 1969), and can degrade to azo-compounds, which are carcinogenic (Bartha and Pramer, 1967). These contaminants enter the environment by deep well industrial waste injection, from the water discharge from manufacturing plants (Di Corcia and Samperi, 1990; Riggin et al, 1983; Howard, 1991), or by losses during their production, transportation, storage and use (Government of Canada, 1994).

Over 5,300,000 pounds of aniline was released to the environment in 1994, with over 1,600,000 pounds through underground injection alone (U.S. EPA, 1997). Aniline has been found to represent a significant fraction of the water-soluble compounds that are found in coal liquids (Felice, 1982). Biodegradation rates of aniline are high under aerobic conditions (Howard, 1991), although these rates may change significantly if the aniline is adsorbed to a mineral surface.

Chloroanilines can be formed by the microbial decay of herbicides such as phenyl-carbamate and phenylurea (Howard, 1991; Bartha and Pramer, 1967). Chloroaniline has been found in groundwater near a landfill site containing pharmaceutical organic compounds (Holm et al, 1995). Biodegradation of chloroaniline either does not occur or is very slow, and is not expected to be important environmentally (Howard, 1991).

Aqueous aniline and 2-chloroaniline display acid properties according to the following reactions:

$$HAnil^{+} \leftrightarrow H^{+} + Anil^{0} \tag{1}$$

$$HCAnil^{+} \leftrightarrow H^{+} + CAnil^{0} \tag{2}$$

where $Anil^{\circ}$ and $CAnil^{\circ}$ represent deprotonated, neutrally-charged aniline and chloroaniline, respectively. The 25°C pK_a values for these deprotonation reactions are 4.63 and 2.66, respectively (Bolton & Hall, 1967; Bolton & Hall, 1969). Therefore, both molecules are present primarily as neutral species at slightly acidic pH values and higher. Speciation diagrams for these substances are given in Fig. 1. In their neutral states, these organic molecules have an affinity for dissolved metals according to the following aqueous complexation reactions:

$$M^{m+} + Anil^{0} \leftrightarrow M(Anil)^{m+} \qquad (3)$$

$$M^{m+} + CAnil^{0} \leftrightarrow M(CAnil)^{m+} \qquad (4)$$

When a mineral is in contact with an aqueous solution, there are unsatisfied bonds at the mineral-water interface, which create an electric charge associated with the mineral surface. The pH_{pzc} (point of zero charge) of a mineral is the pH at which the surface is uncharged. At any pH other than the pH_{pzc}, there will be an electric field due to the charge of the mineral surface. The electric potential of this field approaches zero as the distance from the mineral surface approaches infinity. Adsorption is classified as either physical or chemical. Physical adsorption is electrostatic attraction between oppositely-charged mineral surfaces and aqueous species. Chemical adsorption involves the formation of a covalent bond between the ion and mineral surface. These reactions tend not to occur between molecules of like charge due to electrostatic repulsion. An important effect of aqueous complexation reactions such as equations (3) and (4) is that they result in the charge of the organic species changing from neutral to positive, radically changing the adsorption behaviour of the organic molecule.

Interactions of aniline and 2-chloroaniline with surface and aqueous aluminum are of interest because of aluminum's reactivity and abundance in the Earth's crust. Very little data exist quantifying the stabilities of metal-aniline aqueous complexes. The stability constants for aniline complexes that have been studied are given only at 25°C, and at a fixed ionic strength of 0.1 molal (Martell & Smith, 1975; Martell & Smith, 1982). Stability constants are only available for aqueous metal-aniline complexes involving Cd^{2+}, Ni^{2+}, Hg^{2+} and Ag^{+} at 25°C, and the associations tend to be weak. Studies have shown that aniline and chloroaniline adsorb onto various clays and soil material with adsorption generally higher under low pH conditions (Howard, 1991; Zachara et al, 1984; Furukawa & Brindley, 1973; Yariv et al, 1969) but theses studies do not address the thermodynamic stabilities of the specific surface species involved in the adsorption reactions. It is essential to quantify the thermodynamic stabilities of aqueous, organic, and mineral surface aniline and chloroaniline complexes in order to accurately model the mobilities of the contaminants in the subsurface. This study uses experiments involving simplified chemical systems to place quantitative constraints on the stabilities of both the aqueous and mineral surface Al-aniline and -chloroaniline complexes.

CHAPTER 2

Experimental Study of Aqueous and Mineral Surface Al-Aniline and Al-2-Chloroaniline Complexation

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ABSTRACT

Aniline and chloroaniline are organic compounds used in the synthesis of rubber and polymers, and both are of great environmental concern. In order to model their transport and fate in the subsurface, the geochemical reactions between these contaminants and important metals and mineral surfaces must be quantified.

The thermodynamic stabilities of the aqueous and surface aluminum-aniline and aluminum-2-chloroaniline complexes were investigated at 55°C and 80°C. Aqueous complexation was studied by measuring the solubility of gibbsite ($Al(OH)_3$) as a function of aniline and chioroaniline concentrations. Aniline and chloroaniline experiments were conducted in pH ranges of 2.7 to 3.0, and 3.1 to 3.7, respectively. Experiments measuring aniline and chloroaniline adsorption onto corundum were conducted as a function of pH, from pH 1.5 to 9.0 at room temperature in a 0.1 molal sodium chloride solution, with starting concentrations of $10^{-3.0}$ and $10^{-3.3}$ molal aniline, $10^{-2.7}$ molal 2-chloroaniline, and 2.72×10^{-3} molal total surface sites.

The experiments place quantitative constraints on the thermodynamic properties of the aqueous and the surface Al-aniline complexes. The solubility data indicate that if Al-aniline or Al-2-chloroaniline aqueous complexes exist, they are not stable enough to significantly affect the solubility of gibbsite under the experimental conditions. Conversely, the

adsorption data provide unequivocal evidence for the presence of two distinct surface Al-aniline and Al-chloroaniline complexes according to the following reactions:

(1) $Aniline^{\circ} + {\equiv}Al(OH)^{\circ} \leftrightarrow {\equiv}AlOH(Aniline)^{\circ}$
(2) $Aniline^{\circ} + {\equiv}Al(O)^{-} \leftrightarrow {\equiv}AlO(Aniline)^{-}$
(3) $Chloroaniline^{\circ} + {\equiv}Al(OH)^{\circ} \leftrightarrow {\equiv}AlOH(Chloroaniline)^{\circ}$
(4) $Chloroaniline^{\circ} + {\equiv}Al(OH_2)^{+} \leftrightarrow {\equiv}AlOH_2(Chloroaniline)^{+}$

We use a constant capacitance model to quantify the stability constants for reactions (1) - (4), and the results yield equilibrium constant values of $10^{2.09}$, $10^{2.67}$, $10^{2.87}$ and $10^{2.30}$ respectively. The experiments indicate that for most contaminated systems, aqueous Al-aniline and Al-chloroaniline complexation does not have a significant effect on aniline speciation in groundwater, but that mineral surface complexation can significantly affect total aniline and chloroaniline budgets.

INTRODUCTION

Aqueous and mineral surface complexation are the dominant chemical controls on the mobilities of dissolved metals and organic compounds in groundwater. In order to accurately predict the fate of environmental contaminants, the thermodynamic stabilities of all important surface and aqueous complexes occurring in a system must be known. The relative strength of aqueous metal-organic complexation relative to mineral-surface metal-organic complexation dictates the concentration of the organic molecule in solution. Currently, however, our knowledge of the thermodynamic stabilities of many environmentally important aqueous and surface metal-organic complexes is limited. This study focuses on aqueous and mineral surface aluminum-aniline and aluminum-2-chloroaniline complexation.

Aniline and 2-chloroaniline are anthropogenic organic compounds primarily used in the manufacture of polymers, rubbers, pharmaceuticals, and dyes. Both are suspected carcinogens and are highly toxic to aquatic life (Patil and Shinde, 1988; Messner, 1979). Aniline may also be produced by the metabolism of phenylurea and various herbicides (Bartha and Pramer, 1970; Geissbühler, 1969; Herrett, 1969). These contaminants enter the environment by deep well industrial waste injection, from the water discharge from manufacturing plants (Di Corcia and Samperi, 1990; Riggin et al, 1983; Howard, 1991), or by losses during their production, transportation, storage and use (Government of Canada, 1994).

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The 25°C pK_a values for the deprotonation of aniline and 2-chloroaniline are 4.63 and 2.66, respectively (Bolton & Hall, 1967; Bolton & Hall, 1969). Both molecules are therefore present primarily as neutral species at slightly acidic pH values and higher. In their neutral states, these organics molecules have an affinity for dissolved metals according to the following aqueous complexation reactions:

$$M^{m+} + Anil^{0} \leftrightarrow M(Anil)^{m+} \qquad (1)$$
$$M^{m+} + CAnil^{0} \leftrightarrow M(CAnil)^{m+} \qquad (2)$$

An important effect of aqueous complexation reactions such as equations (1) and (2) is that they result in the charge of the organic species changing from neutral to positive, radically changing the adsorption behaviour of the organic molecule.

Interactions of aniline and 2-chloroaniline with surface and aqueous aluminum sites were studied because of aluminum's reactivity and abundance in the Earth's crust. Very little data exist quantifying the stabilities of metal-aniline aqueous complexes. The stability constants for aqueous metal-aniline complexes that have been studied are given only at 25°C, and at a fixed ionic strength of 0.1 molal (Martell & Smith, 1975; Martell & Smith, 1982). Stability constants are only available for aqueous metal-aniline complexes Cd^{2+}, Ni^{2+}, Hg^{2+} and Ag^{+} at 25°C, and the associations tend to be weak. Studies have shown that aniline and chloroaniline adsorb onto various clays and soil material with adsorption generally higher under low pH conditions (Howard, 1991; Zachara et al, 1984; Furukawa & Brindley, 1973; Yariv et al, 1969) but theses studies do not address the thermodynamic stabilities of the specific surface species involved in the adsorption reactions. It is essential to quantify the thermodynamic stabilities of aqueous, organic, and mineral surface aniline and chloroaniline complexes in order to accurately model the mobilities of the contaminants in the subsurface. This study uses experiments involving simplified chemical systems to place quantitative constraints on the stabilities of both the aqueous and mineral surface Al-aniline and -chloroaniline complexes. Aqueous complexation experiments were conducted at 55°C and 80°C because the reaction kinetics are faster at elevated temperatures, and to obtain results applicable to deep well injection environments. These results can also be extrapolated 25°C for application to near-surface environments.

EXPERIMENTAL PROCEDURES

Aniline (99.9% pure) and 2-chloroaniline (98%) were obtained from Fischer Scientific and Aldrich Chemical Company, respectively, and were used without further purification. To eliminate the effects of ultrafine-grained particles (Bloom and Weaver, 1982), corundum (99% pure, -100 mesh), obtained from Aldrich Chemical Company and gibbsite (99.4%), purchased from J.T. Baker Inc. were each washed sequentially with 10% nitric acid and 10% sodium hydroxide and rinsed repeatedly with distilled, deionized water until a supernatant pH of 7.5 was reached.

Aqueous Complexation Experiments

Aqueous Al-aniline complexation was studied by measuring the solubility of gibbsite ($Al(OH)_3$) as a function of aniline concentration in nitric acid solutions. Diluting a parent solution of $10^{-0.42}$ molal total aniline, and $10^{-0.45}$ molal total HNO_3 with distilled, deionized water yielded experimental solutions at specific aniline concentrations. This procedure ensures that all experimental solutions have identical aniline:HNO_3 ratios. The ionic strength of the aniline solutions was kept constant at $10^{-2.0}$ molal $NaNO_3$. The starting concentrations for the solubility experiments are given in Tables 1 and 2.

Approximately 25 mL of solution and between 0.35 and 0.55 grams of gibbsite were combined in 125 mL Teflon® bottles. Nitrogen was bubbled through each starting solution for at least 30 minutes to purge the solution of carbon dioxide. The exterior of the bottles was covered with aluminum foil to prevent aniline photodegradation, and each bottle was placed in a constant temperature water bath, maintained either at 80°C ± 1°C or 55°C ± 1°C. Samples were taken periodically until a solubility plateau was attained. Sample solutions were filtered through 0.1 micron cellulose nitrate membranes. The 25°C pH of most samples was measured. All samples were acidified with nitric acid to a pH less than 1.0, and refrigerated for storage until analysis. Total aqueous aluminum concentrations in the samples were determined using flame atomic absorption (AA) spectrophotometry. Gas chromatographic analyses of the starting solutions and the samples were used to verify the starting aniline concentrations, and to verify that the organic did not break down during the course of the experiments. The experimental procedure for Al-chloroaniline experiments was analogous to the one described for the Al-aniline experiments.

For the aniline experiments, a series of experiments was conducted at 55°C and a pH range of approximately 3.3 to 3.7, and two other series at 80°C with pH ranges of 2.7 to 2.9 and 2.9 to 3.0. The pH range for chloroaniline experiments was 3.1 to 3.5 at 80°C and 3.4 to 3.7 at 55°C. These were optimum conditions for measuring the thermodynamic stabilities of the aqueous complexes because at pH values lower than this, the organic molecules exist dominantly in their protonated form and are not likely to form appreciable aqueous metal-organic complexes. At higher pH values, the solubility of gibbsite decreases significantly, making detection with the flame AA impossible.

Surface Complexation Experiments

Adsorption experiments were conducted in Teflon® bottles at room temperature with the bottles wrapped in aluminum foil to maintain darkness. Nitrogen gas was bubbled through a 100 mL aniline or chloroaniline 0.1 molal NaCl solution in the bottles for 30 minutes to purge the system of carbon dioxide. Starting solution compositions for the aniline and chloroaniline experiments are given in Tables 3 to 5. Ten grams of powdered, washed corundum was added to the bottles, and the solution was stirred for 60 minutes with a Teflon®-coated magnetic stirring bar. The relative number of positive, neutral and negative surface sites for corundum in a 0.01 molal NaCl solution was determined by acid/base titrations (Boily & Fein, 1996), and is presented as a speciation diagram in Fig. 2. The total number of surface sites for 10 grams of corundum has been found to be 2.72×10^{-3} molal (Boily & Fein, 1996).

It was determined from kinetic experiments (Fig. 3) that 60 minutes was sufficient for adsorption equilibrium to occur. Each series of experiments was conducted as a function of pH at a fixed aniline:corundum ratio. Aniline experiments were conducted at two different aniline:corundum ratios. The pH of the experimental solutions was adjusted by small additions of either nitric acid or sodium hydroxide. The measured pH reached a plateau after approximately 10 minutes, after which it drifted at a rate of less than 0.002 pH units per minute for the remainder of the experiment. The pH value assigned to an experiment was the average pH value of the pH plateau. The total pH drift at the plateau never exceeded 0.10 pH units. After 60 minutes, samples were extracted from the reaction vessels, filtered through .45 μm cellulose nitrate membranes, and analyzed by high performance liquid chromatography (HPLC) for the final aniline or chloroaniline concentration. Some samples were then acidified to a pH of less than 1.0 and analyzed for total dissolved aluminum using flame AA. The difference between the starting concentration of the organic molecule and the final amount measured by HPLC is the concentration of the organic molecule adsorbed onto the mineral surface. A control experiment at identical conditions but without corundum was conducted. The final aniline concentration measured at the end of this experiment was not significantly different from the starting concentration, demonstrating that aniline is not lost to any route other than mineral surface adsorption during the course of the experiments. Although aqueous Al concentrations for most of the adsorption experiments were below the detection limit of the flame AA (1 ppm total Al), some experimental solutions exhibited aqueous Al concentrations as high as 10 ppm. Measurable aluminum was only found at very low and high pH values. Because aqueous Al-aniline complexations is negligible (see below), it is unlikely that the dissolved Al significantly affected the extent of aniline adsorption observed in the experiments.

RESULTS

Aqueous Complexation Experiments

For all concentrations of aniline or chloroaniline, an increase in aluminum concentration as a function of time is observed until a solubility plateau is reached. The average of the aluminum concentrations at the solubility plateau are compiled in Tables 1 and 2. Some of the 80°C samples were analyzed for aniline and chloroaniline at the solubility plateau, and concentrations measured were equivalent to the initial concentrations. For nearly all experiments, the amount of dissolved aluminum measured is proportional to the aniline or chloroaniline concentrations. However, the solubility experiments were not pH buffered, and the measured aqueous Al concentrations also can be interpreted to increase with decreasing solution pH. The data can not be construed as evidence for or against Al-organic complexation without explicitly calculating the expected gibbsite solubilities, assuming no Al-organic complexation in the experimental solutions.

Solubility plateaus were reached after approximately 20 and 10 days for the 80°C experiments at the lower pH values and the higher pH values, respectively. The 55°C data, however, did not reach steady-state during the course of the experiments. For the chloroaniline experiments, aluminum solubility plateaus were reached after approximately 5 and 8 days for the 80°C and 55°C data, respectively. The inorganic solubility of gibbsite, calculated assuming no Al-aniline aqueous complexation, is given in Tables 4 - 6 along with the measured solubilities. The measured aqueous Al concentrations, in both the aniline and the chloroaniline systems, are not significantly different than the calculated complex-free solubilities, indicating that aqueous Al-aniline and -chloroaniline complexation is not significant under the experimental conditions. The observed increase in Al concentrations with increasing organic concentration is a result of changing pH conditions in the experiments. Solutions with higher concentrations of aniline or chloroaniline are more acidic, and hence exhibit higher gibbsite solubilities than those containing lower organic concentrations.

Surface Complexation Experiments

The concentration of adsorbed aniline is plotted as a function of pH in Figs. 4 and 5 for starting aniline concentrations of $10^{-3.0}$ and $10^{-3.3}$ molal, respectively, with 2.72×10^{-3} molal total number surface sites. For the $10^{-3.0}$ molal starting aniline experiments, adsorption increases with increasing pH at low pH, and reaches a plateau at approximately pH 6.0. The concentration of adsorbed aniline remains fairly constant between pH 6.0 and 9.5, but above pH 9.5, it increases again with increasing pH. The adsorption behaviour up to pH 9.5 indicates the presence of at least one surface species. The additional adsorption observed at pH values greater than 9.5

suggests that another species is stable at high pH. Experiments with $10^{-3.3}$ molal total aniline exhibit a similar pH dependence of adsorption under low pH conditions: increasing adsorption with increasing pH until a plateau is reached at approximately pH 6.5. These experiments were conducted between pH 2.0 and 8.2, and enhanced adsorption relative to the mid-pH adsorption plateau was not observed. The adsorption behaviour of chloroaniline is plotted in Fig. 6. A similar response to that of the aniline experiments is observed: as pH increases in the low to mid-pH range, adsorption reaches a plateau at approximately pH 5.0.

THERMODYNAMIC MODELING

In order to apply the results of these experiments to more complicated systems, it is necessary to determine stability constants for the important complexation reactions. Different stoichiometries and different values of the stability constant for each important aqueous and mineral surface complex yield different expected solubility and adsorption behaviours as functions of pH and concentration of aqueous organic. Comparing these different models to the data enables determination of the stoichiometry and stability constant values for each complex that best fit the experimental data.

Aqueous Complexation Experiments

Because the concentration of dissolved aluminum measured in the solubility experiments was not significantly higher than the calculated concentration, assuming no Al-organic aqueous complexation, we conclude that aqueous complexes are negligible under the experimental conditions. However, the lack of an observed effect can be used to place quantitative constraints on the maximum value for the stability constant of an aqueous Al -aniline and –chloroaniline complex. That is, given the analytical uncertainties associated with the aqueous Al determinations, if the stability constant value was higher, then the experiments would have documented significantly enhanced gibbsite solubilities. These calculations require assumptions concerning the stoichiometry of the important aqueous complexes, and we choose to model the hypothetical complexes with the following reactions:

$$Al^{3+} + Anil^{0} \leftrightarrow AlAnil^{3+} \tag{3}$$
$$Al^{3+} + CAnil^{0} \leftrightarrow AlCAnil^{3+} \tag{4}$$

The stability constants for equilibria (3) and (4) were calculated using mass action, charge balance and mass balance equations. The thermodynamic data for aluminum speciation was taken from Wesolowski and Palmer, 1994, with all other stability constants from Wolery, 1992. The data indicate that the values of these constants for equation (3) must be less than or equal to $10^{-0.93}$ at 80°C and less than $10^{-2.50}$ and $10^{-2.37}$ for equation (4) at 80°C and 55°C, respectively. If the stability constants were higher than this, the enhanced Al concentrations would have been detectable of the flame AA.

Surface Complexation Experiments

Surface complexation effects are modeled using the speciation software FITEQL (Westall, 1982a; Westall, 1982b) with a constant capacitance model for the surface (Schindler & Gamsjäger, 1972). In the aniline-corundum system, the following reactions control the fluid chemistry:

$$HAnil^{+} + \equiv Al(OH_{p})^{p-1} \leftrightarrow \equiv Al(OH_{p})(HAnil)^{p} \qquad (5)$$
$$Anil^{o} + \equiv Al(OH_{q})^{q-1} \leftrightarrow \equiv Al(OH_{q})(Anil)^{q-1} \qquad (6)$$
$$HAnil^{+} \leftrightarrow H^{+} + Anil^{o} \qquad (7)$$
$$\equiv Al(OH)_{2}^{+} \leftrightarrow H^{+} + \equiv Al(OH)^{\circ} \qquad (8)$$
$$\equiv Al(OH)^{\circ} \leftrightarrow H^{+} + \equiv AlO^{-} \qquad (9)$$
$$NaNO_{3} \leftrightarrow Na^{+} + NO_{3}^{-} \qquad (10)$$
$$H_{2}O \leftrightarrow H^{+} + OH^{-} \qquad (11)$$
$$HNO_{3} \leftrightarrow H^{+} + NO_{3}^{-} \qquad (12)$$
$$NaOH \leftrightarrow Na^{+} + OH^{-} \qquad (13)$$

The standard state for the surface is a condition of zero charge and zero surface coverage. Departures from standard state conditions result from the electric field created by the charged mineral surface, and are quantified with the Boltzmann factor (e.g. Parks, 1990):

$$K = K_{(intrinsic)}exp^{(-F\psi/RT)} \qquad (14)$$

where F, ψ, R and T are Faraday's constant, the potential of the electric field, the universal gas constant and absolute temperature, respectively. K and $K_{intrinsic}$ are the values of the equilibrium constant under non-standard state, and standard state conditions, respectively. The standard state for aqueous species is a hypothetical one molal solution that exhibits the behaviour of infinite dilution at the temperature and pressure of interest. Molal activity coefficients are used to quantify changes in activity with respect to the standard state. Activity coefficients of charged species are calculated using the Davies equation (Davies, 1938, and 1962):

$$Log\gamma_i = \frac{-A_\gamma Z_i^2 I^{1/2}}{1+I^{1/2}} - cI \qquad (15)$$

where A_γ = 0.509 at 25°C, I is the ionic strength of the solution, Z is the electronic charge of the ion in question, and c is a constant equal to 0.3. Activity coefficients for all neutral species and H_2O are assumed to be unity. Using these assumptions and standard states, the mass action equations for equilibria (5) through (13) are:

$$K_{(1)} = \frac{(m_{\equiv Al(OH_p)(HAnII)^{p-1}}\gamma_{\equiv Al(OH_p)(HAnII)^{p-1}})}{(m_{HAnII^\circ}\gamma_{HAnII^\circ})(m_{\equiv Al(OH_p)^{p-1}})(\gamma_{\equiv Al(OH_p)^{p-1}})} \qquad (16)$$

$$K_{(2)} = \frac{(m_{\equiv Al(OH_q)(AnII)^{q-1}}\gamma_{\equiv Al(OH_q)(HAnII)^{q-1}})}{(m_{AnII^\circ}\gamma_{AnII^\circ})(m_{\equiv Al(OH_q)^{q-1}})(\gamma_{\equiv Al(OH_q)^{q-1}})} \qquad (17)$$

$$K_{(3)} = \frac{(m_{H^+}\gamma_{H^+})(m_{AnII^\circ}\gamma_{AnII^\circ})}{m_{HAnII^+}\gamma_{HAnII^+}} \qquad (18)$$

$$K_{(4)} = \frac{(m_{\equiv Al(OH)_2^+}\gamma_{\equiv Al(OH)_2^+})}{(m_{\equiv Al(OH)^\circ}\gamma_{\equiv Al(OH)^\circ})(m_{H^+}\gamma_{H^+})} \qquad (19)$$

$$K_{(5)} = \frac{(m_{\equiv Al(OH)^\circ}\gamma_{\equiv Al(OH)^\circ})}{(m_{\equiv Al(O)^-}\gamma_{\equiv Al(O)^-})(m_{H^+}\gamma_{H^+})} \qquad (20)$$

$$K_{(6)} = \frac{(m_{Na^+}\gamma_{Na^+})(m_{NO_3^-}\gamma_{NO_3^-})}{m_{NaNO_3}\gamma_{NaNO_3}} \qquad (21)$$

$$K_{(7)} = (m_{H^+}\gamma_{H^+})(m_{OH^-}\gamma_{OH^-}) \qquad (22)$$

$$K_{(8)} = \frac{(m_{H^+}\gamma_{H^+})(m_{NO_{3^-}}\gamma_{NO_{3^-}})}{m_{HNO_3}\gamma_{HNO_3}} \qquad (23)$$

$$K_{(9)} = \frac{(m_{Na^+}\gamma_{Na^+})(m_{OH^-}\gamma_{OH^-})}{m_{NaOH}\gamma_{NaOH}} \tag{24}$$

where K, m, and γ represent the equilibrium constant, the molality of the species at equilibrium, and its activity coefficient, respectively. Equations (16) through (24) along with the mass balance constraints on total aniline, nitrate, sodium, and surface sites:

$$m_{Total\,aniline} = m_{HAnil^+} + m_{\equiv Al(OH)(Anil)^o} + m_{Anil^o} \tag{25}$$

$$m_{Total\,NO_3} = m_{HNO_3} + m_{NO_3^-} \tag{26}$$

$$m_{Total\,Na} = m_{Na^+} + m_{NaNO_3} + m_{NaOH} \tag{27}$$

$$\begin{aligned} m_{Tot.\,surface\,sites} = {} & m_{\equiv Al(OH)^o} + m_{\equiv Al(OH_2)^+} + m_{\equiv Al(O)^-} + m_{\equiv Al(OH_p)(HAnil)^p} \\ & + m_{\equiv Al(OH_q)(Anil)^{q-1}} \end{aligned} \tag{28}$$

provide quantitative constraints on the speciation and stability of the adsorbed aniline species Known stability constants for reactions (16) through (24) are taken from published data, and are given in Table 6. Equations (16) through (26) represent 13 equations written in terms of 14 unknown parameters: 13 unknown molalities of aqueous or surface species, and the 2 unknown K values. However, because FITEQL solves the system of equations for all data points simultaneously, the system is overdetermined, and a variance factor, V(Y), is calculated within FITEQL that describes the goodness of fit between the data and the reaction or reactions chosen in the model. All possible surface configurations are tested using FITEQL, and based on V(Y) values, this procedure determines the surface species stoichiometries and stability constant values for reactions (5) and/or (6) that best fit the experimental data.

We first consider that the observed adsorption behaviour for the experiments conducted at $10^{-3.0}$ molal total aniline can be modeled using a single adsorption reaction to account for the pH dependence. Sequentially, we attempt to interpret the data with the following equilibria:

$$Ani^{0} + \equiv Al(OH_2)^{+} \leftrightarrow \equiv Al(OH_2)Ani^{+} \qquad (29)$$
$$Ani^{0} + \equiv Al(OH)^{0} \leftrightarrow \equiv Al(OH)Ani^{0} \qquad (30)$$
$$Ani^{0} + \equiv Al(O)^{-} \leftrightarrow \equiv Al(O)Ani^{-} \qquad (31)$$
$$HAni^{+} + \equiv Al(OH)^{0} \leftrightarrow \equiv Al(OH)Ani^{0} \qquad (32)$$

Protonated aniline adsorption onto negative surface sites was not considered, as these species do not coexist to a significant extent under any pH conditions. Similarly, protonated aniline adsorption onto a positive Al site was not considered because under the pH conditions at which the two species coexist, aniline adsorption onto corundum is negligible. FITEQL does not converge for either the $\equiv Al(OH)Ani^{0}$ or the $Al(O)Ani^{-}$ single-species models (equilibria 30, 31), indicating severe misfit between the experimental data and the models; FITEQL does converge for models considering equilibria 29 and 32, but the V(Y) values also indicate severe misfit to the data (Table 7). Much of the misfit of the single-species models is attributable to the enhanced adsorption that occurs at pH values greater than 10.0 (Fig. 4b), with the observed extent of adsorption significantly higher than that predicted by any of the single-species models. This discrepancy is evidence for the presence of an additional surface Al-aniline complex, and we account for the enhanced high pH adsorption by simultaneously considering the formation of two distinct surface aniline species. All possible 2-species models were tested (Table 7), but the best fit to the entire pH dependence of the experimental data is provided by considering reactions (30) and (31) simultaneously. The model that considers these two adsorption reactions yields a variance of 191 with log stability constants of 2.09 and 2.67 for equations (30) and (31) respectively. The model fit to the data depicted in Fig. 4b shows that this 2-species model provides a reasonable fit to all of the data, and that there is no noticeable association between the misfit and pH. In fact, it is not surprising that deprotonated aniline is involved in the adsorption reaction due to coincidence of the onset of adsorption with the deprotonation of aqueous aniline at pH 4.6. Furthermore, the enhanced adsorption observed above pH 9 appears to correspond with the increased concentration of completely deprotonated surface Al sites. Therefore, based both on consideration of the speciation of the mineral-aniline system, and on the FITEQL modeling results, the model most likely to account for the observed aniline adsorption behaviour is one which considers neutrally-charged aniline adsorption onto $\equiv AlOH^{o}$ and $\equiv AlO^{-}$ surface sites.

The data from the set of experiments conducted at $10^{-3.3}$ molal aniline and 2.72×10^{-3} molal total surface sites covers the pH range 2.2 to 8.2. Because the surface Al-aniline species $\equiv Al(O)Anil^{-}$ forms to a significant extent only under high pH conditions, these data do not document the same high pH enhanced adsorption that was observed in the previous experiments, and the data can not be used to further constrain the value of the equilibrium constant for reaction (31). Modeling the system with the single-species model according to equation (30) yields a log K of 2.32 with a variance of 347, in good agreement with the value as constrained by the $10^{-3.0}$ molal total aniline experiments. The model fails to converge when considering equation (31) as a single-species model, or when considering (31) in conjunction with equation (30). These results are compiled in Table 8.

Chloroaniline Experiments

Because the pH range of the chloroaniline experiments is 1.6 to 9.3, negatively-charged mineral surface sites constitute only a small fraction of all receptor sites, and thus are not likely to be involved in the important adsorption reaction(s). The observed adsorption must therefore be due to $HCAnil^{+}$ and/or $CAnil^{o}$ adsorption onto positively charged and/or neutrally-charged Al surface sites. The three adsorption reactions we consider for a single-surface species model are:

$$HCAnil^{+} + \equiv Al(OH)^{o} \leftrightarrow \ \equiv Al(OH)HCAnil^{o} \tag{33}$$
$$CAnil^{o} + \equiv Al(OH)^{o} \leftrightarrow \ \equiv Al(OH)CAnil^{o} \tag{34}$$
$$CAnil^{o} + \equiv Al(OH_2)^{+} \leftrightarrow \ \equiv Al(OH_2)CAnil^{+} \tag{35}$$

$HCAnil^{+}$ adsorption onto a positively-charged, completely protonated surface Al site is not considered due to the lack of significant adsorption observed under the low pH conditions studied. Modeling for these three cases yields log K values of 5.99, 3.22 and 10.12 with variances of 5760, 1006 and 2818 for equations (33), (34) and (35), respectively. The high variances associated with these models suggest that none of the single-species models fit all of the data well, and that a model that incorporates at least two surface complexes must be invoked. We tested all possible species combinations, and find that adsorption of neutrally-charged chloroaniline onto $\equiv Al(OH)^{\circ}$ and $\equiv Al(OH_2)^{+}$ surface sites (Fig. 6) provides the best fit to the experimental data. The variance associated with this model again is relatively high, but association between the misfit and pH does not suggest that the inclusion of an additional Al-aniline surface species could significantly improve the fit of the model to the data. The stability constants and variances for all models are summarized in Table 9.

DISCUSSION

Experiments conducted as a function of pH provide constraints on the stoichiometry of the important surface complexes. Our experimental results indicate that aqueous Al complexation has a negligible effect on aniline and chloroaniline speciation in groundwater. Our results for aniline and chloroaniline adsorption experiments show an increase in adsorption with increasing pH, which is in contrast to results seen in previous studies of aniline adsorption onto soil materials (Zachara et al., 1984; Howard, 1991). The previous studies involved a complex (realistic) mixture of soil organics and mineral surface sites. Out approach has been to isolate specific interactions between aniline and chloroaniline with a distinct type of mineral surface site. Our results are consistent with the previous studies in that they all suggest that partitioning between water and mineral surfaces, although not the only control, exerts a significant effect on aniline and chloroaniline transport in groundwater systems.

To predict the fate of aniline and related compounds, the adsorptive properties of the rock matrix that they contact must be known. The partitioning between water and organic coatings on mineral surfaces can significantly affect the mobility of organic pollutants. To predict the extent of aniline and chloroaniline adsorption onto an organic coating on sediment, the partition coefficient, K_p, must be known. The partition coefficient is defined by the following equation:

$$K_p = \frac{[\textit{aniline adsorbed on organic coatings on sedim ents}]}{[\textit{aniline in water}]} \tag{36}$$

K_p can be calculated from:

$$K_p = f_{oc}\,K_{oc} \tag{37}$$

where f_{oc} is the fraction of organic present in the sediment. Solving equation (37) with log K_{oc} = 1.41 (Howard, 1991) and f_{oc} = 10% yields a value for the partition coefficient of 2.57. Thermodynamic modeling, using this value in conjunction with the adsorption experiment results, indicates that at pH 6, for a system with $10^{-4.0}$ molal total aniline and $10^{-3.0}$ molal total Al mineral surface sites, approximately 18 percent of the aniline adsorbs onto the Al mineral surface sites, 59 percent adsorbs onto organic coating on sediments, and the remaining 23 percent remains in solution. The K_{oc} value for chloroaniline has not been determined, but it is likely that it displays a similar distribution. Although there is considerable uncertainty associated with this calculation due to the large uncertainty in the K_{oc} value, it indicates that the extent of adsorption of aniline onto Al mineral surface sites is significant in the total aniline and chloroaniline budgets and therefore mineral surface aniline complexation must be accurately accounted for in order to determine the mobility of aniline in the subsurface.

CONCLUSIONS

Gibbsite solubility experiments involving aniline and 2-chloroaniline solutions under relatively low pH conditions do not show significantly higher dissolved aluminum concentrations than would be expected assuming that aqueous Al-organic complexation does not occur. We therefore do not find evidence of any important aqueous aluminum-aniline or aluminum-chloroaniline complexes. The experimental data, however, can be used to constrain the maximum thermodynamic stabilities of Al-aniline and Al-chloroaniline aqueous complexes. If complexation does occur, the stability constants for the following reaction:

$$Al^{3+} + Anil^{0} \leftrightarrow Al(Anil)^{3+} \qquad (38)$$

must be lower than $10^{-0.93}$ at 80ºC, and lower than $10^{-2.50}$ and $10^{-2.37}$ at 80°C and 55°C respectively for the following reaction:

$$Al^{3+} + CAnil^{0} \leftrightarrow Al(CAnil)^{3+} \qquad (39)$$

Modeling using these values suggests that even in metal-dominated systems, aqueous Al-organic complexation will not significantly affect aniline or chloroaniline speciation in contaminated aquifers.

The adsorption of aniline and chloroaniline onto corundum (α-Al_2O_3)

over a pH range of 1.5 to 9.0 was measured in 0.1 molal NaCl solutions. The experimental results indicate the presence of two stable aluminum-aniline surface complexes, with values of the stability constants for the reactions:

$$Anil^0 + \equiv Al(OH)^0 \leftrightarrow \equiv AlOH(Anil)^0 \tag{40}$$

$$Anil^0 + \equiv Al(O)^- \leftrightarrow \equiv AlO(Anil)^- \tag{41}$$

of $10^{2.09}$ and $10^{2.67}$ respectively. The chloroaniline adsorption response was also modeled with two surface complexes, with stabilities of $10^{2.87}$ and $10^{2.30}$ for the following reactions:

$$CAnil^0 + \equiv Al(OH)^0 \leftrightarrow \equiv AlOH(CAnil)^0 \tag{42}$$

$$CAnil^0 + \equiv Al(OH)^0 \leftrightarrow \equiv AlOH_2(CAnil)^+ \tag{43}$$

These thermodynamic stabilities suggest that surface complexation can significantly affect the transport of aniline and chloroaniline as these molecules come into contact with aluminum-bearing mineral surfaces.

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TABLES

Table 1: Gibbsite Solubility Data for Al-Aniline Solubility Experiments (80°C), Log Molalities

ID	Aniline	HNO_3	Total Al	Total Al (complex-free)
Y1	-0.42	-0.42	-2.47	-2.79
Y2	-0.60	-0.60	-2.59	-2.80
Y3	-0.78	-0.78	-2.71	-2.83
Y4	-0.96	-0.96	-2.87	-2.90
Y5	-1.14	-1.14	-3.00	-3.24
Y6	-0.46	-0.50	-3.05	-3.16
Y7	-0.60	-0.64	-3.13	-3.17
Y8	-0.89	-0.93	-3.10	-3.23
Y9	-1.14	-1.18	-3.26	-3.47

Table 2: Gibbsite Solubility Data for Aluminum-Chloroaniline Solubility Experiments

55°C

ID	Chloroaniline	HNO_3	Total Al	Total Al (complex-free)
ML1	-1.58	-2.56	-3.75	-3.99
ML2	-1.70	-2.77	-3.84	-4.08
ML3	-1.72	-2.83	-3.98	-4.33
ML4	-1.82	-2.97	-4.09	-4.37
ML5	-2.05	-3.11	-4.18	-4.50

80°C

ID	Chloroaniline	HNO_3	Total Al	Total Al (complex-free)
MR1	-1.58	-2.64	-3.49	-4.99
MR2	-1.70	-2.77	-3.59	-5.07
MR3	-1.72	-2.90	-3.77	-5.32
MR4	-1.82	-3.06	-3.79	-5.52
MR5	-2.05	-3.23	-3.86	-5.56

Table 3: Starting Concentrations for $10^{-3.0}$ molal Aniline Adsorption Experiments

ID	ΣHNO_3	$\Sigma NaOH$	Final pH	Adsorption Concentration (mM)
A24	-2.19	-	2.78	0.043
A23	-2.26	-	3.41	0.014
A21	-2.38	-	4.44	0.054
A22	-2.43	-	4.74	0.056
A20	-2.48	-	5.01	0.166
A19	-2.54	-	5.67	0.206
A41	-2.87	-	6.06	0.231
A17	-2.60	-	6.11	0.176
A18	-2.73	-	7.77	0.187
A15	-2.79	-	7.77	0.182
A16	-2.80	-	8.04	0.164
A8	-	-	8.16	0.220
A13	-	-	8.31	0.217
A14	-	-	8.46	0.182
A38	-	-3.27	9.43	0.222
A40	-	-3.25	9.64	0.231
A39	-	-3.01	10.10	0.292
A35	-	-2.84	10.58	0.354
A36	-	-2.68	10.85	0.300
A27	-	-1.53	10.86	0.319
A29	-	-1.51	11.29	0.271
A33	-	-1.48	11.38	0.386
A28	-	-1.50	11.47	0.294
A32	-	-1.49	11.48	0.277
A31	-	-1.50	11.56	0.257
A30	-	-1.50	11.57	0.262
A34	-	-1.47	11.70	0.357

Experiments conducted at room temperature, $\Sigma NaCl = -1.0$.

Table 4: Starting Concentrations for $10^{-3.3}$ molal Aniline Adsorption

ID	ΣHNO_3	$\Sigma NaOH$	Final pH	Adsorption Concentration (mM)
BW5	-1.77	-	2.16	0.023
BW4	-2.00	-	2.28	0.033
BW6	-2.16	-	2.45	0.055
BW8	-2.36	-	3.20	0.023
BW9	-2.45	-	3.73	0.033
BW19	-2.53	-	4.50	0.065
BL15	-2.63	-	4.57	0.096
BL11	-2.71	-	4.60	0.109
BW17	-2.78	-	5.20	0.094
BL14	-2.75	-	5.25	0.103
B9	-2.79	-	5.35	0.107
BW15	-2.86	-	5.80	0.185
BL13	-2.91	-	6.20	0.174
BL10	-3.01	-	6.70	0.205
BW13	-3.05	-	6.85	0.112
BL12	-3.13	-	7.05	0.124
BW16	-2.97	-	7.27	0.130
BW14	-3.10	-	7.30	0.146
BW18	-3.40	-	7.88	0.146
B6	-	-	7.92	0.185
BW20	-3.71	-	8.20	0.103
B4	-	-3.80	8.52	0.153
B8	-	-2.91	10.50	0.108

Experiments conducted at room temperature, $\Sigma NaCl$ = -1.0.

Table 5: Starting Concentrations for $10^{-2.7}$ molal Chloroaniline Adsorption Experiments

ID	ΣHNO_3	Final pH	Adsorption Concentration (mM)
CN23	-1.47	1.58	0.036
CN22	-1.65	1.75	0.129
CN21	-2.11	2.15	0.249
CN20	-2.41	2.16	0.273
CN18	-2.38	2.19	0.332
CN19	-2.43	2.41	0.370
CN3	-2.41	3.06	0.771
CN13	-2.37	3.25	0.852
CN12	-2.49	3.76	1.154
CN4	-2.53	4.00	0.799
CN1	-2.71	4.21	1.237
CN11	-2.61	4.51	0.943
CN15	-2.65	5.11	1.367
CN14	-2.76	5.70	1.367
CN10	-2.83	6.21	0.988
CN2	-3.01	7.18	1.194
CN8	-3.13	7.62	1.150
CN6	-3.31	7.95	1.152

Experiments conducted at room temperature, $\Sigma NaCl = -1.0$.

Table 6: Stability Constants Used in Thermodynamic Modeling for Adsorption Experiments

Equilibrium	Log K	Source
$HAnil^+ \leftrightarrow H^+ + Anil^0$	4.60	Bolton & Hall (1967)
$HCAnil^+ \leftrightarrow H^+ + CAnil^0$	2.66	Bolton & Hall (1969)
$\equiv Al(OH)_2^+ \leftrightarrow H^+ + \equiv Al(OH)^0$	7.41	Boily and Fein (1996)
$\equiv Al(OH)^0 \leftrightarrow H^+ + \equiv AlO^-$	-10.67	Boily and Fein (1996)
$Na^+ + NO_3^- \leftrightarrow NaNO_3$	-0.6	Martell and Smith (1976)
$H^+ + OH^- \leftrightarrow H_2O$	14.00	Busey & Mesmer (1978)
$H^+ + NO_3^- \leftrightarrow HNO_3$	1.3	Wolery (1992)
$Na^+ + OH^- \leftrightarrow NaOH$	-0.2	Wolery (1992)

Table 7: Surface Speciation Modeling ($10^{-3.00}$ molal total Aniline)

Model	Log K	V(Y)
$\equiv$AlOH(Anil)^{o}	DNC*	-
$\equiv$AlO(Anil)$^{-}$	DNC	-
$\equiv$AlOH(HAnil)$^{+}$	6.61	3215
$\equiv$AlOH$_2$(Anil)$^{+}$	2.27	1631
$\equiv$AlOH$_2$(Anil)$^{+}$, $\equiv$AlOH(HAnil)$^{+}$	DNC	-
$\equiv$AlOH(HAnil)$^{+}$, $\equiv$AlO(Anil)$^{-}$	6.61, 3.18	1728
$\equiv$AlOH(HAnil)$^{+}$, $\equiv$AlOH(Anil)^{o}	5.93, 2.20	423
$\equiv$AlOH(Anil)^{o}, $\equiv$AlO(Anil)$^{-}$	2.09, 2.67	191
$\equiv$AlOH$_2$(Anil)$^{+}$, $\equiv$AlOH(Anil)^{o}	DNC	-
$\equiv$AlOH$_2$(Anil)$^{+}$, $\equiv$AlO(Anil)$^{-}$	2.26, 3.16	953

* DNC = Did not converge, indicating severe misfit to the data

Table 8: Surface Speciation Modeling ($10^{-3.30}$ molal total Aniline)

Model	Log K	V(Y)
$\equiv AlOH(Anil)^{o}$	2.32	347
$\equiv AlO(Anil)^{-}$	2.98	1405
$\equiv AlOH(Anil)^{o}$, $\equiv AlO(Anil)^{-}$	DNC	DNC

DNC: Did not converge

Table 9: Surface Speciation Modeling ($10^{-2.70}$ molal total Chloroaniline)

Model	$\log K_{int}$	V(Y)
$\equiv\mathrm{AlOH(CAnil)}^{\circ}$	3.22	1006
$\equiv\mathrm{AlOH(HCAnil)}^{+}$, $\equiv\mathrm{AlOH_2(CAnil)}^{+}$	DNC	-
$\equiv\mathrm{AlOH(HCAnil)}^{+}$	5.99	5760
$\equiv\mathrm{AlOH_2(CAnil)}^{+}$	2.71	2818
$\equiv\mathrm{AlOH(CAnil)}^{\circ}$, $\equiv\mathrm{AlOH_2(CAnil)}^{+}$	2.87, 2.30	354
$\equiv\mathrm{AlOH(CAnil)}^{\circ}$, $\equiv\mathrm{AlOH(HCAnil)}^{+}$	3.10, 5.54	870

FIGURE CAPTIONS

Figure 1. Speciation diagrams for aniline (a) and chloroaniline (b) in water. The curves represent the fraction of aniline and chloroaniline in protonated and deprotonated form as a function of pH given pK values of 4.63 and 2.66.

Figure 2. The speciation of corundum Al surface sites in a $10^{-1.0}$ molal sodium chloride solution.

Figure 3. Aniline adsorption as a function of duration of the experiment. These experiments involved $10^{-3.0}$ molal total aniline and 2.72 x 10^{-3} molal total surface sites.

Figure 4. Aniline adsorption onto corundum as a function of pH. All experiments from this series were conducted at a fixed initial concentration of $10^{-3.0}$ molal total aniline. The concentration of total surface sites available is $10^{-2.57}$ molal. The triangles represent the concentration of aniline adsorbed onto the mineral surface for each experiment. The solid line is the adsorption predicted by FITEQL for the $\equiv AlOH(Anil)^{\circ}$ -only model (a); and for the best-fitting model that incorporates both the $\equiv AlOH(Anil)^{\circ}$ and $\equiv AlO(Anil)^{-}$ surface species (b).

Figure 5. Aniline adsorption onto corundum as a function of pH. All

experiments from this series were conducted at a fixed initial concentration of $10^{-3.3}$ molal aniline. The concentration of total surface sites available is $10^{-2.57}$ molal. The triangles represent the concentration of aniline adsorbed onto the mineral surface for each experiment. The solid line is the adsorption predicted by FITEQL over the pH range considering only the $\equiv$AlOH(Anil)° surface species.

Figure 6. Chloroaniline adsorption onto corundum as a function of pH. All experiments from this series were conducted at a fixed initial concentration of $10^{-2.7}$ molal chloroaniline. The concentration of total surface sites available is $10^{-2.57}$ molal. The triangles represent the concentration of chloroaniline adsorbed onto the mineral surface for each experiment. The solid line is the adsorption predicted by FITEQL over the pH range considering $\equiv$AlOH(CAnil)° and $\equiv$AlOH$_2$(CAnil)$^+$ as the important surface species.

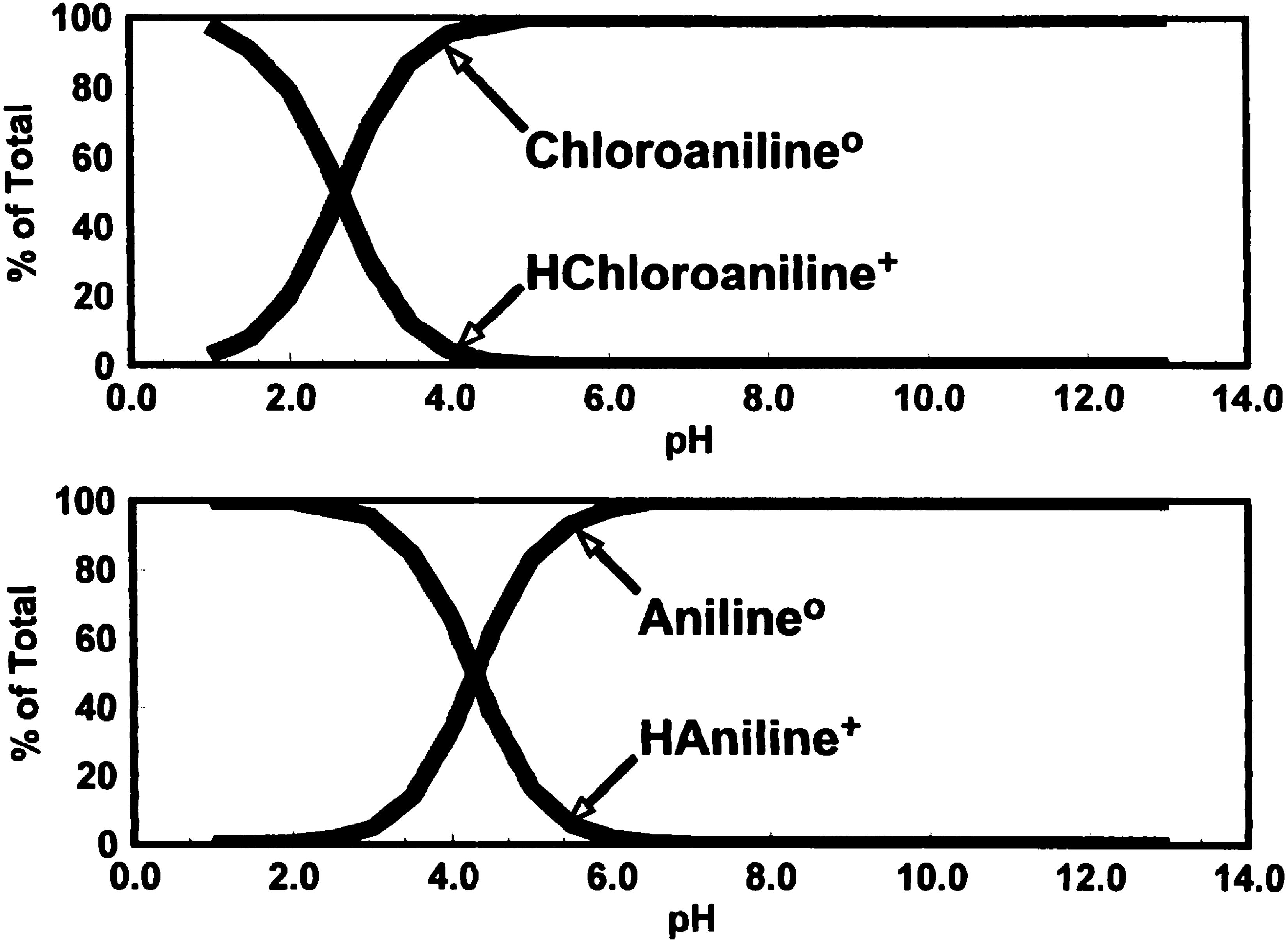


Figure 1
Yane and Fein

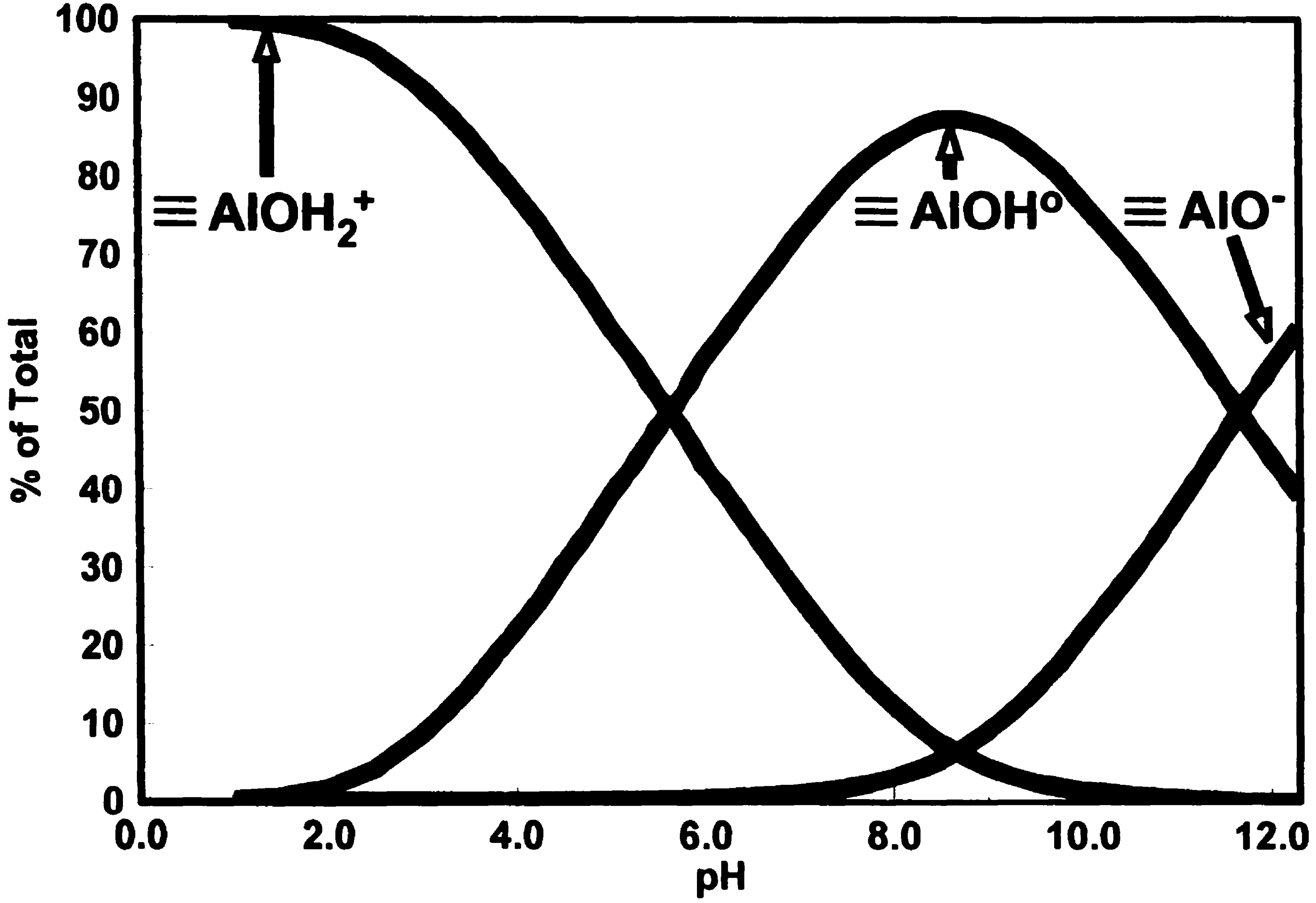


Figure 2
Yane and Fein

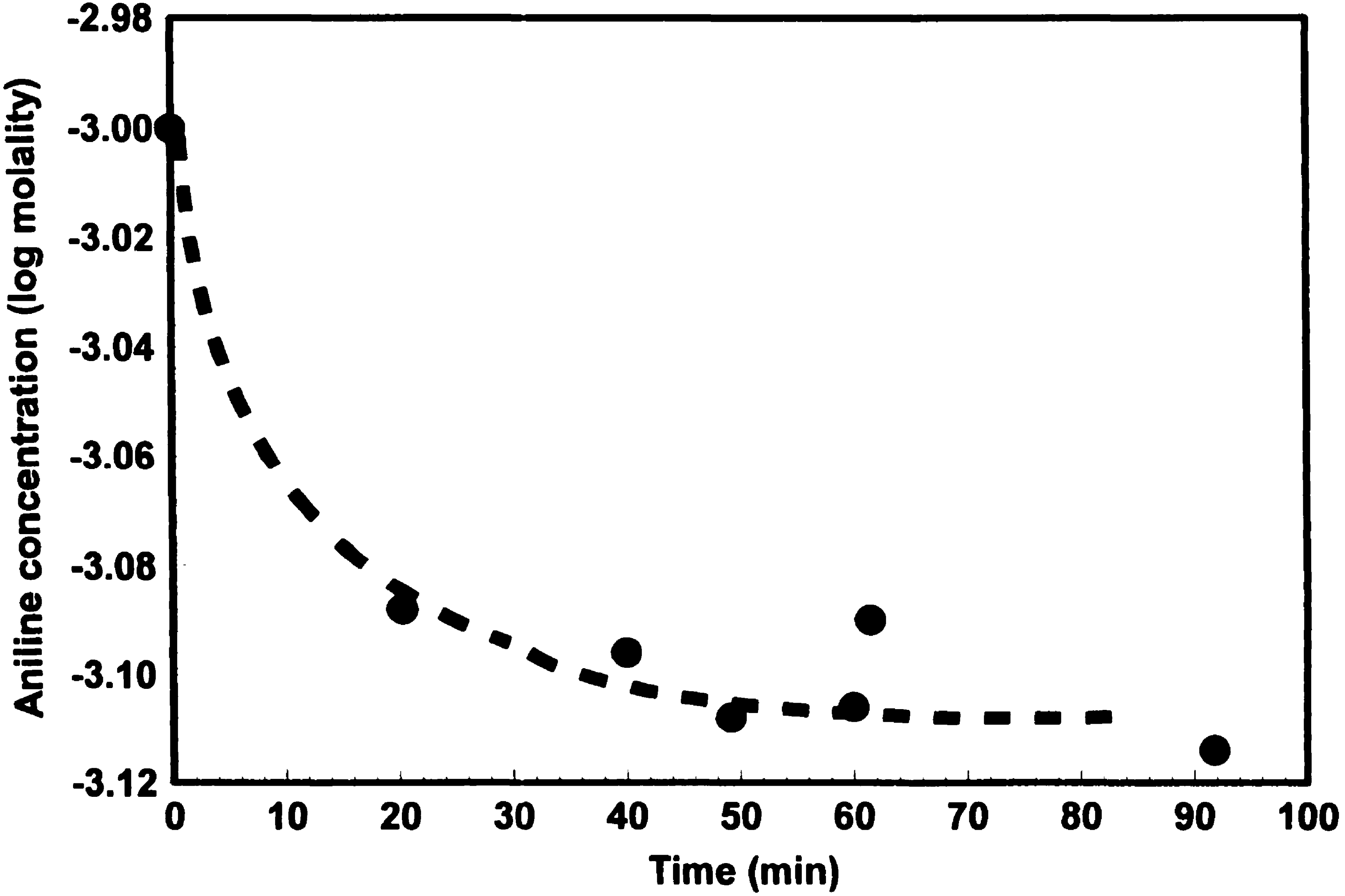


Figure 3
Yane and Fein

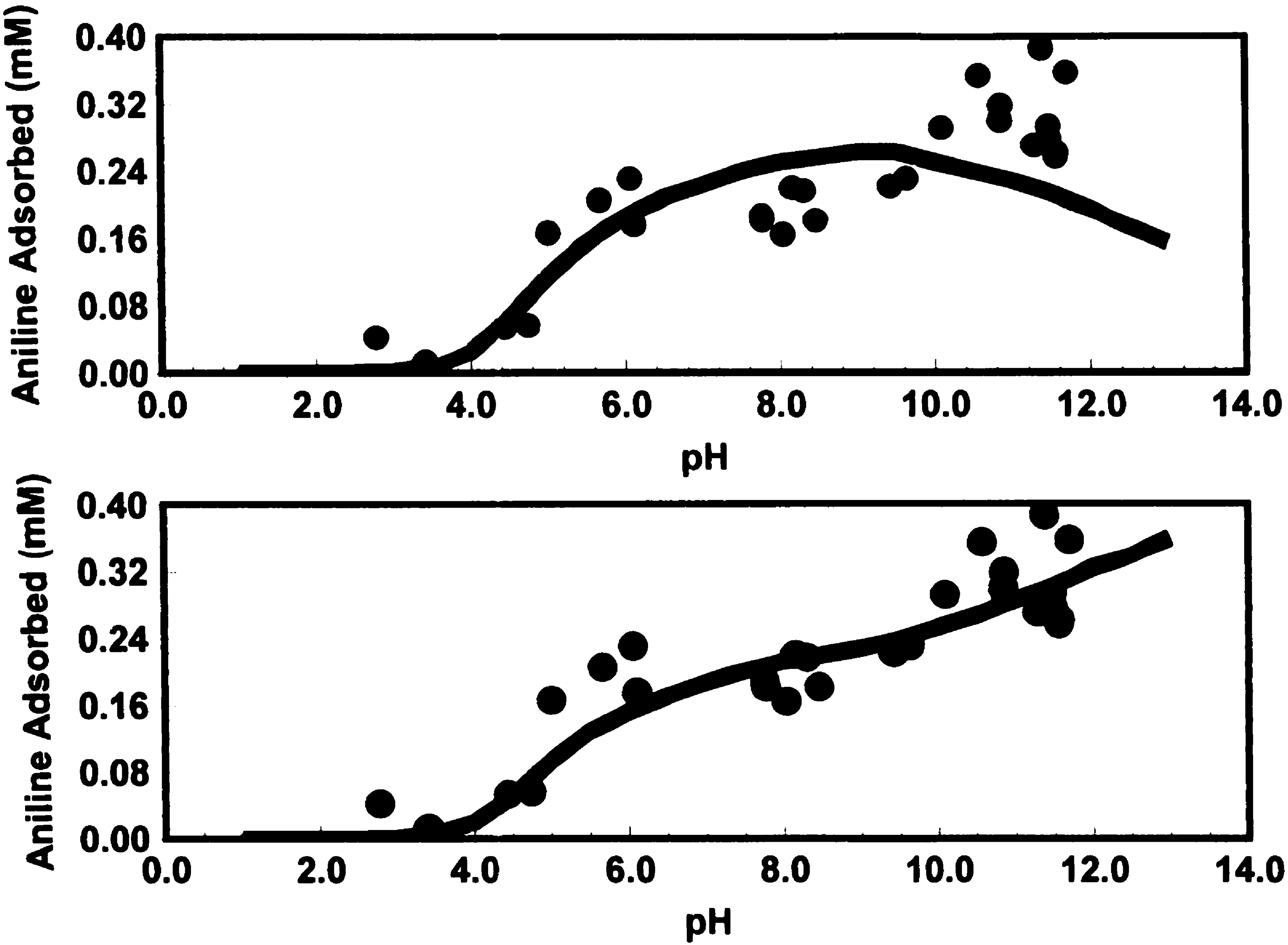


Figure 4
Yane and Fein

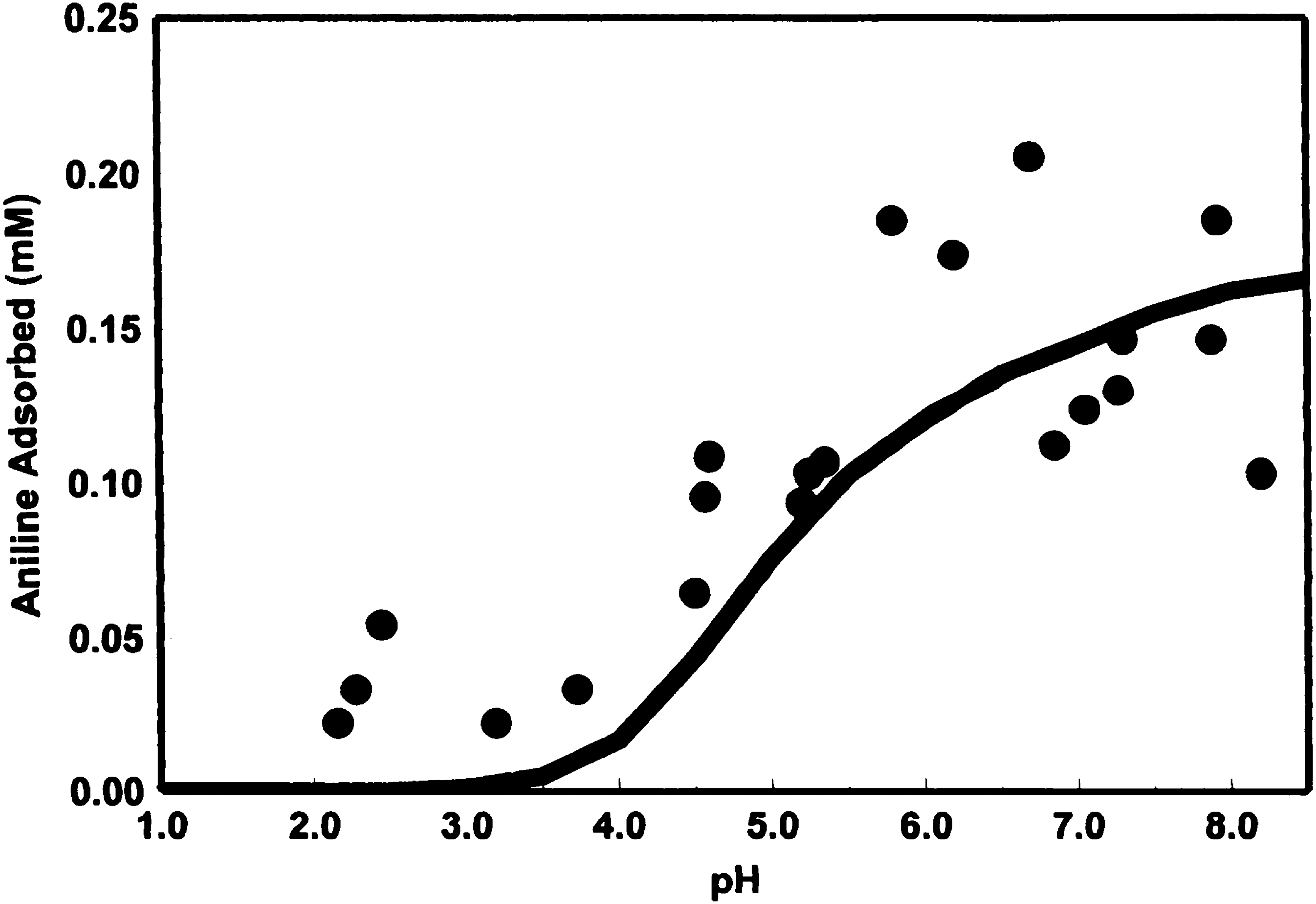


Figure 5
Yane and Fein

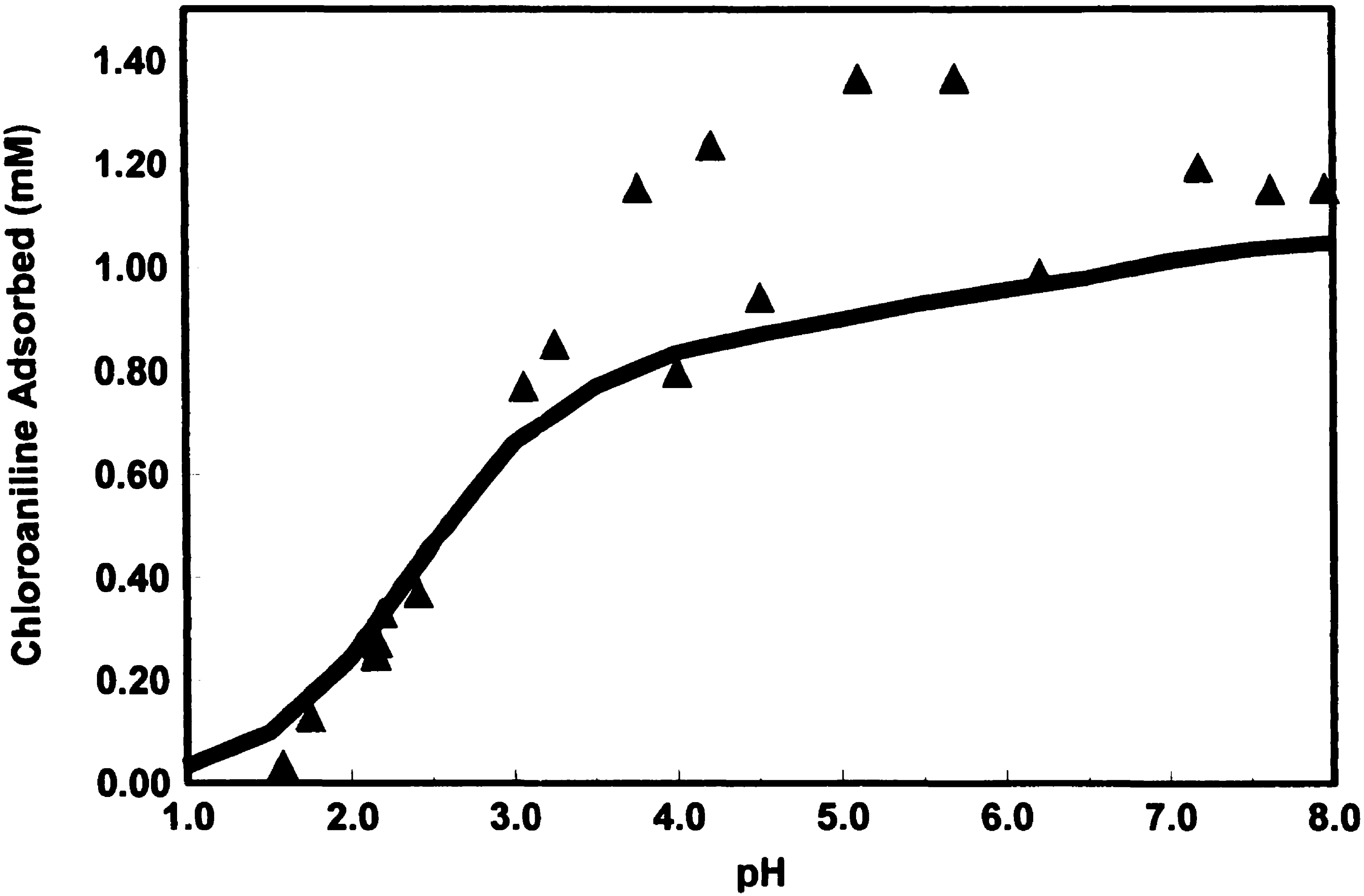


Figure 6
Yane and Fein

CHAPTER 3: CONCLUSIONS

Gibbsite solubility experiments involving aniline and 2-chloroaniline solutions under relatively low pH conditions do not show significantly higher dissolved aluminum concentrations than would be expected assuming that aqueous Al-organic complexation does not occur. We therefore do not find evidence of any important aqueous aluminum-aniline or aluminum-chloroaniline complexes. The experimental data, however, can be used to constrain the maximum thermodynamic stabilities of Al-aniline and Al-chloroaniline aqueous complexes. If complexation does occur, the stability constants for the following reaction:

$$Al^{3+} + Anil^{0} \leftrightarrow Al(Anil)^{3+} \qquad (1)$$

must be lower than $10^{-0.93}$ at 80°C, and lower than $10\text{-}^{2.50}$ and $10^{-2.37}$ at 80°C and 55°C respectively for the following reaction:

$$Al^{3+} + CAnil^{0} \leftrightarrow Al(CAnil)^{3+} \qquad (2)$$

Modeling using these values suggests that even in metal-dominated systems, aqueous Al-organic complexation will not significantly affect aniline or chloroaniline speciation in contaminated aquifers.

The adsorption of aniline and chloroaniline onto corundum (α-Al_2O_3) over a pH range of 1.5 to 9.0 was measured in 0.1 molal NaCl solutions. The experimental results indicate the presence of two stable aluminum-aniline surface complexes, with values of the stability constants for the reactions:

$$Anil^{0} + \equiv Al(OH)^{0} \leftrightarrow \equiv AlOH(Anil)^{0} \qquad (3)$$
$$Anil^{0} + \equiv Al(O)^{-} \leftrightarrow \equiv AlO(Anil)^{-} \qquad (4)$$

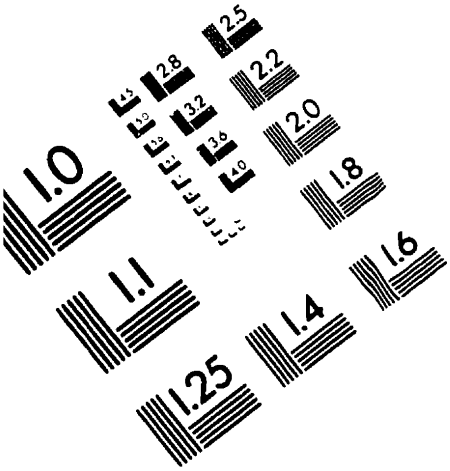
of $10^{2.09}$ and $10^{2.67}$ respectively. The chloroaniline adsorption response was also modeled with two surface complexes, with stabilities of $10^{2.87}$ and $10^{2.30}$ for the following reactions:

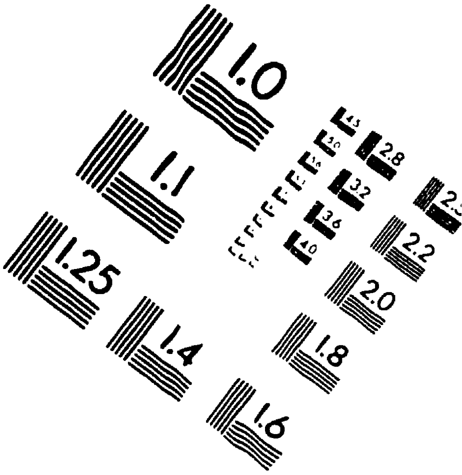
$$CAnil^0 + \equiv Al(OH)^0 \leftrightarrow \equiv AlOH(CAnil)^0 \qquad (5)$$
$$CAnil^0 + \equiv Al(OH)^0 \leftrightarrow \equiv AlOH_2(CAnil)^+ \qquad (6)$$

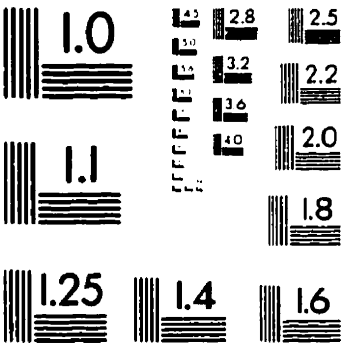
These thermodynamic stabilities suggest that surface complexation can significantly affect the transport of aniline and chloroaniline as these molecules come into contact with aluminum-bearing mineral surfaces.

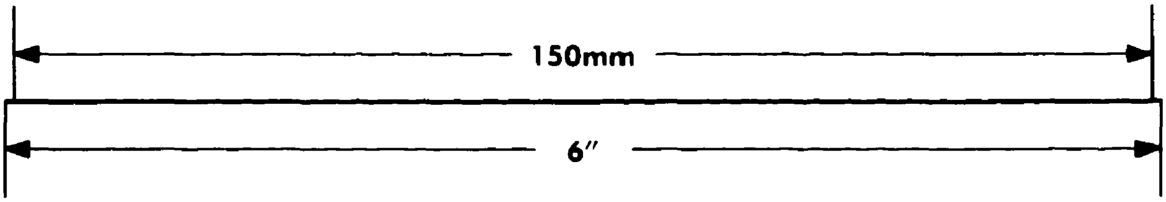
This study quantifies the thermodynamic stabilities of mineral surface aluminum-aniline and -chloroaniline complexes. Additional experiments are needed to quantify the interactions between aniline and related compounds with other aqueous and mineral surface metals of environmental interest, but this study represents a first step toward accurately accounting for their adsorption behaviour in the subsurface.

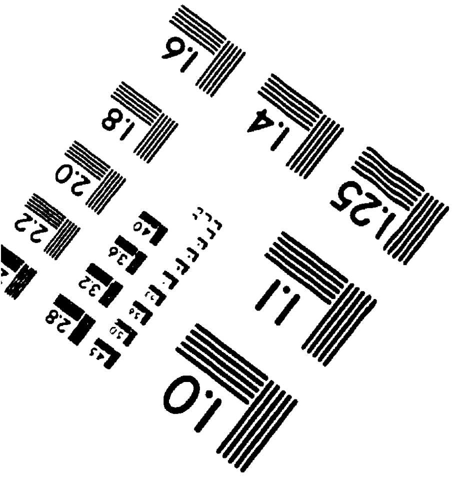
IMAGE EVALUATION TEST TARGET (QA-3)

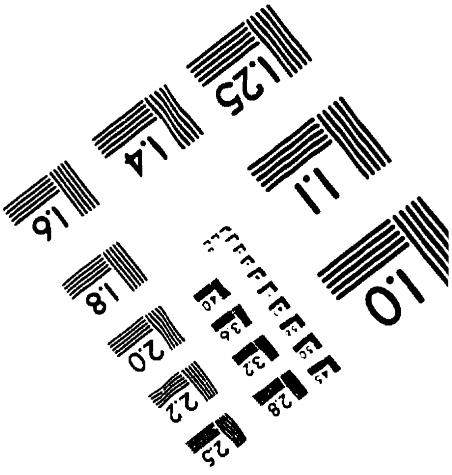












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