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I am submitting herewith a dissertation written by Scott Francis DeMuth entitled "The Transport Dynamics of Zirconium Liquid-Liquid Extraction Based on the Purex Process used for Reprocessing Spent Nuclear Reactor Fuel." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemical Engineering.

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THE TRANSPORT DYNAMICS OF ZIRCONIUM LIQUID-LIQUID EXTRACTION BASED ON THE PUREX PROCESS USED FOR REPROCESSING SPENT NUCLEAR REACTOR FUEL

A Dissertation

Presented for the

Doctor of Philosophy

Degree

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Scott Francis DeMuth

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To my wife Claudia with love.

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ABSTRACT

Fundamental diffusion and chemical reaction theory have been used to model the Purex[1] process solvent extraction of zirconium. Statistical methods have been used to select an appropriate mass transfer model which permits estimation of the complexation reaction rate constants. A non-reacting process was studied in order to characterize the mass transfer coefficients for the contacting vessel used to study the zirconium-Purex process. Zirconium-Purex equilibrium data existing in the literature were used to estimate the metal complex distribution coefficient, and complexation equilibrium constant. The complexation reaction rate constants, and metal complex distribution coefficient, can be used to predict zirconium-Purex mass transfer behavior in most any contacting equipment.

The Purex process utilizes a nitric acid based aqueous phase and a tri-butyl phosphate (TBP)-dodecane organic phase. TBP is the extracting agent in the dodecane diluent. The practical application lies in reprocessing spent nuclear reactor fuel of which zirconium is a fission product. It is necessary to purify recyclable materials (primarily uranium and plutonium), and isolate the waste (fission products and some actinides).

While a good deal of study has been conducted with zirconium in the Purex process since the 1940's, this work usually had one or more of the following limitations, (1) equilibrium only, (2) empirical,

[1]Purex is the acronym for Plutonium-Uranium Extraction.

and/or (3) consideration of diffusion or chemical reaction, but not both combined. This study indicated diffusion and chemical reaction both significantly affect the overall mass transfer rate of zirconium for the specific process conditions and contacting equipment of the study.

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LIST OF SYMBOLS

C = concentration (mass/volume).

$C(0)$ = initial concentration.

C_k = $[NO_3^-]^4[TBP]^2$.

d = diameter.

D^f = diffusion coefficient.

D_s = distribution coefficient (organic concn/aqueous concn).

D_{Zr} = literature reported (overall) distribution coefficient.

D_3 = TBP distribtuion coefficient.

D_4 = $Zr(NO_3)_4 \cdot 2TBP$ distribution coefficient.

k = individual mass transfer coefficient.

k_a = ionization constant.

k_{a4} = $Zr(NO_3)_4 \cdot 2TBP$ aqueous phase mass transfer coefficient.

k_{o4} = $Zr(NO_3)_4 \cdot 2TBP$ organic phase mass transfer coefficient.

K_o = overall mass transfer coefficient.

K_{oa} = aqueous overall mass transfer coefficient.

K_{oo} = organic mass transfer coefficient.

K^f = forward chemical reaction rate constant.

K^b = backward chemical reaction rate constant.

N = moles.

N_{Sc} = Schmidt number (v/D^f).

N_{Sh} = Sherwood number (kd/D^f).

N_{Re} = Reynolds number (wd^2/v).

s = Laplace transform of time.

S = interfacial area.

t = time.

μ = viscosity

ν = kinematic viscosity (μ/ρ).

V = phase volume.

ω = rotational velocity.

ρ = density.

eq = equilibrium conditions.

[ ] = concentration.

Subscripts:

a = aqueous.

j = phase of interest.

o = organic.

1 = Zr^{+4} specie.

2 = NO_3^- specie.

3 = TBP specie.

4 = $Zr(NO_3)_4 \cdot 2TBP$ specie.

Superscripts:

i = interfacial.

* = in equilibrium with bulk concentration of other phase.

Modeling constants:

p = mass transfer coefficient correlation constant.

q = mass transfer coefficient correlation constant.

A_1-A_9= zirconium model constants with regard to time.

f_1-f_5= zirconium model constants with regard to time.

b_o-b_2= zirconium model constants with regard to time.

a_o,a_1= zirconium model constants with regard to time.

Effect levels:

S_1 = 62 cm^2.

S_2 = 79 cm^2.

d_{a1},d_{o1} = 3 cm.

d_{a2},d_{o2} = 6 cm.

V_{a1},V_{o1} = 350 ml.

V_{a2},V_{o2} = 450 ml.

C_{a1} = 1.37×10^{-6} mol/ml.

$C_{a1}/2$ = 0.68×10^{-6} mol/ml.

C_{a2} = 0.0029 mol/ml.

$C_{a2}/2$ = 0.0015 mol/ml.

C_{a3} = 1.13×10^{-6} mol/ml.

$C_{a3}/2$ = 0.57×10^{-6} mol/ml.

1. INTRODUCTION

1.1. Background

Removal of the fission products in spent nuclear reactor fuel is necessary for (1) minimization of fission product neutron poisoning in recycled fuel, (2) minimization of highly radioactive fission products which makes recycled fuel difficult to handle, and (3) careful containment of fission products for disposal. Most methods used for reprocessing spent nuclear fuel are based upon solvent extraction from a nitric acid medium. The most common separation processes are (1) the Redox process which uses methyl isobutyl ketone for extraction and aluminum nitrate as the salting agent, and (2) the Plutonium-Uranium Extraction (Purex) process which uses tri-n-butyl phosphate (TBP) for extraction and nitric acid as the salting agent. Decontamination is achieved by making use of the distribution coefficients, and a multistage cascade, to extract the uranium and plutonium into the TBP loaded organic phase while the fission products remain in the aqueous phase.

The two fission products ruthenium and zirconium complicate satisfactory decontamination during the reprocessing of irradiated fuel by the Purex process. These two highly radioactive fission products can accompany the fissile materials (uranium and plutonium) by extracting into the solvent, and then end up in the low-activity waste streams. The inability to effectively separate uranium and plutonium from ruthenium arises from the diversity of aqueous ruthenium compounds. Zirconium and its daughter product niobium create

difficulties primarily due to reactions with small quantities of radiolytic and hydrolytic degradation products of TBP and the diluent. These reaction products are difficult to back extract, and therefore have a tendency to accumulate in the organic phase which reduces the decontamination factor, and complicates solvent recycle. For these reasons the chemistry and mass transport phenomena of ruthenium and zirconium in nitric acid and organic solvent media are of special interest.

Zirconium has been selected as the specie to be studied for this thesis (rather then ruthenium), primarily due to the availability of a nonradioactive specie. Conditions will be selected which minimize the concentration of hydrolytic zirconium species, and maximize the 4^+ zirconium cation concentration. Careful control of process conditions in an actual reprocessing facility will also limit the radiolytic and hydrolytic species.

1.2. Objectives

The following study is intended to satisfy the thesis requirements for a Ph.D. in Chemical Engineering. The objective has been to make use of well-established fundamental diffusion and chemical reaction principles, to model zirconium solvent extraction for conditions of the Purex solvent extraction process. Statistical methods utilizing a balanced data design were used to develop an overall mass transfer model for the specific process conditions and contacting vessel of this study. Inclusion of only the significant effects in the model simplified the simultaneous solution of the fundamental differential

equations. The statistics allowed reasonable approximations permitting an exact solution to the differential equations.

This study required (1) the characterization of zirconium aqueous chemical behavior for Purex conditions, (2) the selection of appropriate contacting equipment for investigating mass transfer behavior, and (3) development of a mass transfer model for the specific application of this study which can be used for estimating reaction rate constants. Results from this study can provide insight for selection of contacting equipment and optimization of process conditions, and demonstrate an analytical and experimental technique for characterizing other similar species or processes.

1.3. Primary Areas of Investigation

1.3.1. Characterization of Zirconium-Purex Conditions

A critical component for a successful study is the refinement of test conditions. It is important to keep the scope of testing well focused and applicable to real conditions. For these reasons the conditions of this study have been selected as those which would be expected in an actual nuclear fuel reprocessing facility. These conditions are exceptionally important since they define the type of zirconium specie present in aqueous solution.

1.3.2. Selection of Fundamental Mass Transfer Model

Determination of the mass transfer coefficients and reaction rate constants from the data must be done such that a minimum number of constants are regressed. Regressing an excessive number of constants

from a single set of data reduces their credibility. The approach of this study has been to (1) determine the individual mass transfer coefficients for aetic acid transferred from water to isobutanol, and then extrapolate to the zirconium-Purex system, (2) determine the metal complex distribution coefficient and chemical reaction equilibrium constant for the zirconium-Purex system from literature equilibrium data, and (3) regress the forward or reverse reaction rate constant for the zirconium-Purex system from the transient data of this study. Step (1) makes use of a well established and documented correlation relating the Sherwood, Reynolds, and Schmidt numbers. Step (2) requires knowledge of the reaction mechanism and reaction phase. Step (3) will be accomplished by modeling the process conditions of this study with fundamental diffusion and chemical reaction theory.

1.3.3. Selection and Characterization of Contacting Equipment

The stirred cell (Lewis cell) contactor was selected for this study based upon the disadvantages of other contacting devices, the wetted wall contactor (poor mass transfer coefficient model), laminar jet contactor, (short contact time) and single-droplet contactor (limited variation of contact time). Liquid-liquid systems in a Lewis cell have been studied in detail, and several correlations have been developed for predicting the mass transfer coefficients.

1.3.4. Statistical Analysis of Data for Model Simplification

An appropriate overall mass transfer model was selected by determining the significance of each potential model variable. This was accomplished by a half normal plot, which compares the variance due

to a particular effect, to the estimated error assuming data normally distributed. For the case of this study, the measured parameter was the mass transferred over time, and the variable effects are interfacial area, phase volumes, and mass transfer coefficients.

2. LITERATURE SEARCH

2.1. Zirconium in Spent Nuclear Fuel Reprocessing

2.1.1. Concentration and Activity

The zirconium concentration of typical reprocessed commercial fuel, as reported for design conditions of the Barnwell Nuclear Fuel Plant built and owned by Allied-General Nuclear Services at Barnwell, South Carolina, is discussed in the text by Benedict, Pigford, and Levi (1981). Construction of the plant was nearly complete in 1977, when work was halted by President Carter's decision to indefinitely suspend commercial reprocessing in the United States. The plant was designed to reprocess pressurized water reactor (PWR) and boiling water reactor (BWR) fuel.

The primary feed stream was to consist of 1.21 moles/L uranyl nitrate, 2.9 g/L plutonium, and 2.44 M nitric acid. The zirconium composition of PWR fuel with 150 days cooling should be approximately 3.4 Kg Zr/Mg fuel at 9.5×10^5 g U/Mg fuel. Therefore, the concentration of Zr in the HAF feed should have been approximately 1 g/L.

$$\frac{3.4 \text{ Kg-Zr}}{\text{Mg-fuel}} \times \frac{1 \text{ Mg-fuel}}{9.5 \times 10^5 \text{ g-U}} \times \frac{238 \text{ g-U}}{\text{mole-uranyl nitrate}} \times \frac{1.21 \text{ mole-uranyl nitrate}}{\text{L}} = 0.001 \frac{\text{Kg-Zr}}{\text{L}}$$

The radioactive zirconium specie of primary concern in spent fuel is ^{95}Zr. It has a half life of 65 days, and for spent uranium fuel (three-year exposure) from a PWR, its activity at discharge is 1% of the total and at 150 days cooling it is approximately 7% of the total.

2.1.2. Specie Distribution

The reaction kinetics and consequent mass transfer behavior of zirconium for the Purex solvent extraction process can vary substantially due to the tendency to complex, hydrolyze and polymerize, Lo et al. (1983). The existence of polynuclear compounds largely determines the chemical behavior of zirconium in both the aqueous and organic phase. Zirconium by itself exists exclusively in the tetravalent state. It was previously believed that zirconium was extracted only in the form of monomers. However, it is now recognized that certain polynuclear zirconium species can also transfer into the organic phase (Siczek and Steindler, 1978).

In general, the literature agrees that at 3 M HNO_3 or greater, and 0.001 M zirconium or less, $Zr(NO_3)_4 \cdot 2TBP$ will be the dominant extractable specie. Polymerization is minimized with high acid and low zirconium concentration. Hydrolysis is minimized with high acid concentration.

2.1.2.1. Aqueous Phase Monomers. The two most common nitrates of Zr are: (1) zirconyl nitrate, $ZrO(NO_3)_2.2H_2O$, which is formed from dilute nitric acid and (2) the hydrated tetranitrate, $Zr(NO_3)_4.5H_2O$, formed in concentrated nitric acid. The anhydrous nitrate $Zr(NO_3)_4$ and the anhydrous oxy-nitrate $ZrO(NO_3)_2$, can also exist. Solution studies also indicate the possible existence of anionic species $Zr(NO_3)_5^-$ and $Zr(NO_3)_6^{2-}$ (Bailar et al., 1973).

Solovkin (1970 and 1971) determined the primary form of the extractable monomeric species to be $Zr(OH)_i(NO_3)_{4-i}.2TBP$, where $0 \leq i < 4$.

The proposed dominant aqueous species and their reactions are discussed in the text by Baes and Mesmer (1976), and have been utilized by Mailen et al. (1980).

The generalized chemical reaction for the formation of the aqueous metal complex is:

$$Zr(OH)_i^{4-i} + (4-i)NO_3^- + 2TBP = Zr(OH)_i(NO_3)_{4-i} \cdot 2TBP,$$

as proposed by Baes and Mesmer (1976), Mailen et al. (1980), Siczek and Steindler (1978), and Adamskii et al. (1960).

2.1.2.2. Aqueous Phase Polymers. Hydroxyl, oxygen, and polydentate anions preferentially form the bonds making up the bridges of the polymers. Hydrolytic polymerization can occur at low acidity, high metal concentration or high temperature. Some non-extractable polynuclear species at zirconium concentrations greater than 0.01 M form stable complexes not in equilibrium with monomers (Yagodin et al., 1974). These non-extractable, non-equilibrium species are thought to be oxopolymers which never leave the aqueous phase. Some non-extractable polynuclear species are in equilibrium with the monomers and transform into extractable species as the monomers are extracted. It has been determined that zirconium can transfer into the organic phase in the form of hydroxy polymers (Yagodin et al., 1974).

2.1.2.3. Organic Phase. When extracting macro-quantities of hydrolyzed zirconium, polymerization can occur in the organic phase which may prevent back extraction into the aqueous phase during scrubbing (Klyuchnikov et al., 1972). The organic zirconium polymers

are formed by reactions with TBP degradation products and diluent degradation products (Siczek and Steindler, 1978).

Egorov et al. (1960) reported that formation of extractable mono- or di-solvates of zirconium nitrate with TBP depends on the concentration of the free solvent.

2.2. Fundamental Mass Transfer Models

Three well accepted mass transfer models are in use today. These models described in the text by Sherwood, Pigford, and Wilke (1975) are the film model, penetration model and surface renewal model.

2.2.1. Film Theory

The film model which assumes a stagnant film adjacent to the interface, was originally proposed by Nernst (1904), and developed more completely by Whitman (1923), and Lewis and Whitman (1924). The resistance to mass transfer is confined to the film region. This is a steady-state model which gives reliable predictions of the mass transfer rate when simultaneous chemical reaction occurs. An enhancement factor was later developed to define the increased mass transfer due to chemical reaction. The enhancement factor was developed for some of the more complex cases by Van Krevelans (1948).

2.2.2. Penetration Theory

The penetration model was developed by Higbie (1935) to allow for the transient nature of solute diffusion from bubbles to liquid. The most simple version of this model pictures a small fluid element of

uniform concentration in contact with a phase boundary for a fixed length of time.

2.2.3. Surface Renewal Theory

The surface renewal model proposed by Danckwerts (1950, 1951, and 1955) is an extension of the penetration model which allows for a variable contact time. This variable contact time is represented by a probability distribution.

2.3. Mixing Vessels

2.3.1. Wetted-Wall Contactors

Wetted-wall (falling film) columns provide a known contact area for the phases. Studies of gas absorption, vaporization, and distillation in such columns have given mass transfer coefficient values for the gaseous core in reasonable agreement with the Chilton-Colburn analogy. However, correlations for a liquid core are more complex due to distortion of the velocity profiles from drag.

2.3.2. Laminar Jet Contactors

Two types of laminar jet apparatus have been described by Quinn et al. (1961, 1964, and 1965). These apparatus are generally used when short contact times are required.

2.3.3. Stirred-Cell Contactors

The transfer cell with plane interface and individually stirred phases was first introduced by J.B. Lewis (1954). The Lewis cell has been widely adopted for the use of liquid-liquid studies, and more

recently for gas-liquid studies (Davies et al., 1964, and Levenspiel et al., 1974). Most cells of this type have been operated on a transient basis, although a continuous flow type has been described by Olander et al. (1964). An excellent description of the Lewis cell can be found in the text by Laddha and Degaleesan (1978). The transfer cell has many times proved successful for the study of liquid-liquid mass transfer. More recently Mailen et al. (1980) have studied the mass transfer of thorium, zirconium, and uranium with the Lewis cell.

2.3.4. Single-Droplet Contactors

In the single-droplet contactor the mass transfer takes place between the droplets and surrounding continuous phase. The measurement of the individual phase mass transfer coefficients for droplets, is difficult for the majority of systems due to the lack of a convenient method for independently varying the drop velocity. However, this difficulty can be circumvented with systems of very high or very low distribution coefficients, in which the transfer is controlled by one phase (Lo et al., 1983).

2.4. Mass Transfer Coefficient Correlations for Stirred-Cell

2.4.1. Correlation

The earliest well-documented mass transfer studies based on the stirred-cell were done by Lewis (1954). Lewis correlated the individual mass transfer coefficient based on the concept of eddy diffusion from the bulk to the interface. This implied no direct affect on mass transfer due to molecular diffusion.

$$\frac{60k_a}{\nu_a} = 1 + (6.8\times10^{-6})[N_{Re,a} + (\mu_o/\mu_a)N_{Re,o}]^{1.65} .$$

Other experimenters felt the affect of molecular diffusion on the mass transfer coefficient could not be neglected, and therefore included the Schmidt number in the mass transfer coefficient model (McManamey et al., 1961, 1973 and Mayers 1961).

$$N_{Sh,a} = \frac{k_a d_a}{D_a^f} = (\text{constant})(N_{Re,a}N_{Re,o})^{1/2}(N_{Sc,a})^{5/6},$$

$$\frac{60k_a d_a}{\nu_a} = 0.0384\frac{(N_{Re,a})^{0.9}}{(N_{Sc,a})^{0.3}}[1+(\mu_o N_{Re,o})/(\mu_a N_{Re,a})],$$

$$N_{Sh,a} = 0.00316\frac{(N_{Re,a}N_{Re,o})^{0.5}}{(0.6+\mu_o/\mu_a)^{2.4}}(\mu_o/\mu_a)^{1.9}(N_{Sc,a})^{0.8} .$$

Perhaps the best accepted theory considers a Schimdt number dependency to the 1/2 power, in accordance with the surface renewal form of the penetration theory (Bulicka and Prochazka, 1976). The dependency of the Reynolds number affect on the mass transfer coefficient varies from approximately the first to third power depending on experimenter (Brown et al., 1983). That expression can be represented as:

$$N_{Sh,j} = (k_j d/D^f_j) = p(N_{Re,j})^q(N_{Sc,j})^{1/2},$$

where "p" and "q" are constants, and "j" refers to the phase.

2.4.2. Marangoni Effect

The Marangoni effect has been described as random variations of interfacial tension at the interface which result from local concentration variations as mass transfer occurs (Sherwood, Pigford, and Wilke, pg. 186, 1975). The variation of interfacial tension can create local turbulence which increases the mass transfer coefficient, and consequent mass transfer rate. This affect is minimized when the concentration of transfering specie is dilute.

2.5. Test Procedure

2.5.1. Apparatus and Procedures

Procedures dealing with use of a Lewis cell are similar to those used in any contacting vessel. In particular, it is important to carefully control the solution temperature, concentrations, interfacial turbulence, mixing speed, paddle location, and phase volumes. Horner et al. (1980) recommend the initial solutions are pre-equilibrated without the ion of interest (zirconium). This minimizes the transferring of other species once the primary transferring specie is injected into the phase of interest.

2.5.2. Reagent Preparation

There are four reagents of interest for this study, (1) zirconium nitrate, (2) nitric acid, (3) TBP, and (4) the diluent (dodecane). Zaitsev et al. (1972) and Sarsenov et al. (1974) discuss the need for a consistent zirconium starting material if reproducible extractability is required. For the starting zirconium reagent, Zaitsez and Sarenov

recommend zirconium alpha-oxide nitrate which is generated from zirconium alpha-oxide chloride via ion exchange. This approach should maximize zirconium organic extraction products. Mailen et al. (1980) recommends extraction followed by strip to remove inextractables from the feedstock.

Steinberg (1960) recommends preparation of TBP by hydrolyzing organic pyrophosphate impurities with 8 M HCL and washing with 5% Na_2CO_3 and water.

2.5.3. Analytical Requirements

There are basically three different techniques for measuring nonradioactive aqueous zirconium concentrations, (1) colorimetry, (2) mass spectrometry with inductively coupled plasma (ICP) as an ion source, and (3) energy dispersive x-ray fluorescence (XRF). These techniques differ in sensitivity, reliability, difficulty, and cost. While colormetric methods are easily done and inexpensive, Siczek and Steindler (1978) note that some stable polynuclear complexes do not react with colormetric indicators. Gray (1986) reports the mass spectrometry with ICP is very sensitive (0.5 ng/ml Zr) and reproducible, but also time consuming and expensive. In addition, organic analysis requires ashing which can reduce reproducibility. Brooksbank and Stewart (1982) comment that energy dispersive XRF is a multi-element technique used successfully for fission products, unaffected by chemical states and capable of analyzing both aqueous and organic solutions. However, it is expected that XRF is expensive compared to colorimetry.

An alternative to chemical analysis of zirconium is the use of a tracer. There are at least 10 different isotopes of zirconium with half lives for the non-metastable species ranging from 1 minute for Zr^{98} to 10^6 years for Zr^{93}. The species Zr^{95} with a half life of 65 days, and Zr^{97} with a half life of 17 hours are the most commonly used tracers. Both these species are primary beta emitters. An excellent reference for zirconium counting techniques is Steinberg (1960).

2.6. Statistical Methods

To develop a model which accurately predicts behavior of the system studied, it was necessary to ascertain the vessel and process parameters which could potentially affect the overall mass transfer rate. Once the parameters (or effects) had been identified, a systematic determination of their mass transfer significance was conducted. An approach to the systematic determination, similar to this study, was suggested by Levenspiel and Godfrey (1974), and Laurent (1975). The work by Levenspiel and Godfrey, and Laurent has been summarized in the text by Drew et al. (1981). Statistical methods were utilized in this study to ascertain the mass transfer significant effects.

2.6.1. Half Factorial

A Half Factorial design is used to reduce by one-half the number of required samples for a statistical analysis (Anderson and McLean, 1974). This is done in a fashion which maintains a balanced design. When using a Half Factorial design, the number of degrees of freedom

are reduced by one-half, and consequently the information derived from the statistical analysis is less than that of a Full Factorial.

2.6.2. Analysis of Variance

An Analysis of Variance (ANOVA) is commonly used to determine which test parameters significantly affect a process of interest. An F-test is used to determine the significance level of each effect. The subject of ANOVA was developed primarily with the work of Fisher (1918, 1925, and 1935). An excellent text which describes the design of an experiment using an ANOVA is that by Anderson and McLean (1974). Additional information on the topic can be found in many statistics texts, such as the text by Afifi and Azen (1979).

2.6.3. Half Normal Plots

Application of an ANOVA to a half factorial design permits the estimation of the significance of only single effects. Estimation of the significance of interaction effects is not possible with the ANOVA and half factorial design. This is due to the limited degrees of freedom in a half factorial design. If a Half Normal Plot is used, an estimate of the error can be made assuming the data are normally distributed. This will permit estimation of the significance of single and double interaction effects. The assumption of normal distribution can be validated by observing the linearity of data as plotted via the half normal plot. Two sources of information concerning Half Normal Plot analysis are Johnson and Leone (1964), and Daniel (1959).

2.7. Existing Zirconium Models

Most of the past efforts to better understand zirconium solvent extraction have been directed toward characterizing the species and distribution coefficients. Very few models describing transient mass transfer have been proposed. Hughes and Rod (1983) proposed a model for the solvent extraction of metals by organic acids based on the film theory. Their model approached the problem in a fashion similar to this study. They made certain assumptions for their specific case and then developed the mass transfer flux equations. Mailen et al. (1980) developed a kinetic model for the mass transfer of zirconium by the Purex process involving interfacial area and chemical reaction. The same model was used in a similar fashion by Horner et al. (1980) for uranium and thorium.

Hughes and Rod (1983) claim their kinetic model based on the film theory reasonably predicts the mass transfer flux at initial and final conditions for the LIX64N/$CuSO_4$/H_2SO_4 system. The fundamental process they were modeling was:

$$M^{2+} + 2HR = MR_2 + 2H^+,$$

where M^{2+} was the metal ion and HR was the organic acid. The model solutions for their system were quite complex and were not intended intermediate kinetic regimes.

The model of Mailen et al. (1980) applied to uranium, thorium, and zirconium mass transfer made use of the first-order rate equations:

$$\frac{dC_a}{dt} = -\frac{S}{V_a}(K^+)C_a + \frac{S}{V_a}(K^-)C_o, \quad \text{the change in aqueous concn.,}$$

$$\frac{dC_o}{dt} = -\frac{S}{V_o}(K^-)C_o + \frac{S}{V_o}(K^+)C_a, \quad \text{the change in organic concn.,}$$

where $D_s = (K^-)/(K^+)$ at equilibrium.

Upon integration,

$$t = \frac{V_o}{SD_s(K^+)} \ln\{1 - [(D_sC_o)/C_a(t=0)]\}.$$

in terms of changing organic concentration. The author reported the solution equilibria and the plausible extraction equilibria fit the experimental data well.

2.8. Existing Mass Transfer Data

2.8.1. Zirconium Per Purex Conditions

Adamskii et al. (1960) collected equilibrium data which demonstrate the affect of temperature on the zirconium overall distribution coefficient (D_4). Alcock et al. (1957) (1) collected equilibrium data showing the affect of nitric acid and nitrates on D_4 and (2) reported the data of Hesford showing the affect of TBP on D_4. Egorov et al. (1960) collected equilibrium data demonstrating the affect of both HNO_3 and TBP on D_4.

2.8.2. Acetic Acid in Water and Isobutanol

The original work of Lewis (Part II, 1954) dealt with the mass transfer of several different systems, of which acetic acid transfered from water to isobutanol (and the reverse) was included. Lewis reported the distribution coefficient (organic/aqueous) for this system

to be 1.18. The overall aqueous mass transfer coefficients reported are shown in Table 2.1. Lewis reported that during the aqueous to organic mass transfer tests, there appeared to be some degree of interfacial turbulence.

Table 2.1. Lewis' acetic acid mass transfer data.

Direction of Transfer	Reynolds Number Aq	Reynolds Number Org	Acetic Acid Initial Conc. (g/L)	K_{oa} (cm/s)
Aq -> Org	2800	1000	49.8	0.00133
Aq -> Org	2800	1000	52.6	0.00150
Aq -> Org	2800	1500	47.8	0.00183
Aq -> Org	2800	1500	44.8	0.00183
Org -> Aq	3000	1000	48.0	0.00167
Org -> Aq	3000	1000	38.9	0.00167
Org -> Aq	3000	1500	42.8	0.00217
Org -> Aq	3000	1500	45.4	0.00233

3. EXPERIMENTAL

3.1. Stirred-Cell Mixing Vessel

The stirred-cell used for this study (see Figure 3.1), was modeled after that used by Lewis and described in his original paper (Lewis, Part I, 1954). The experiments were carried out in a conventional one liter glass beaker in which each phase was stirred by a central paddle. The paddle size could be independently changed for each phase, which allowed independent control of the Reynolds number for each phase. It was found necessary to use circumferential wall baffles to minimize cavitation. The interfacial area was adjustable by use of central circular disk. The two paddles were adjusted to be the same distance from the interface throughout all experiments.

Various sizes of paddles and sizes of blades on the paddles, were tested in an effort to maximize the rotational velocity operating range without interfacial turbulence. In addition to paddle size, the number and size of wall baffles was investigated to maximize the operating range, see Table 3.1. The conditions selected for optimum operation were 3 cm or 6 cm diameter paddles with vertical blade heights of 0.25 cm. The wall baffle arrangement selected was 4 baffles of 0.25 cm radial height. With these conditions, a rotational velocity of 150 rpms was selected for the experiments. This velocity provided a compromise between time length of experiment and interfacial turbulence. At 150 rpm the interface was flat and well controlled, and each zirconium mass transfer test could be completed in approximately an eight hour day. A slower rotational speed would have provided a

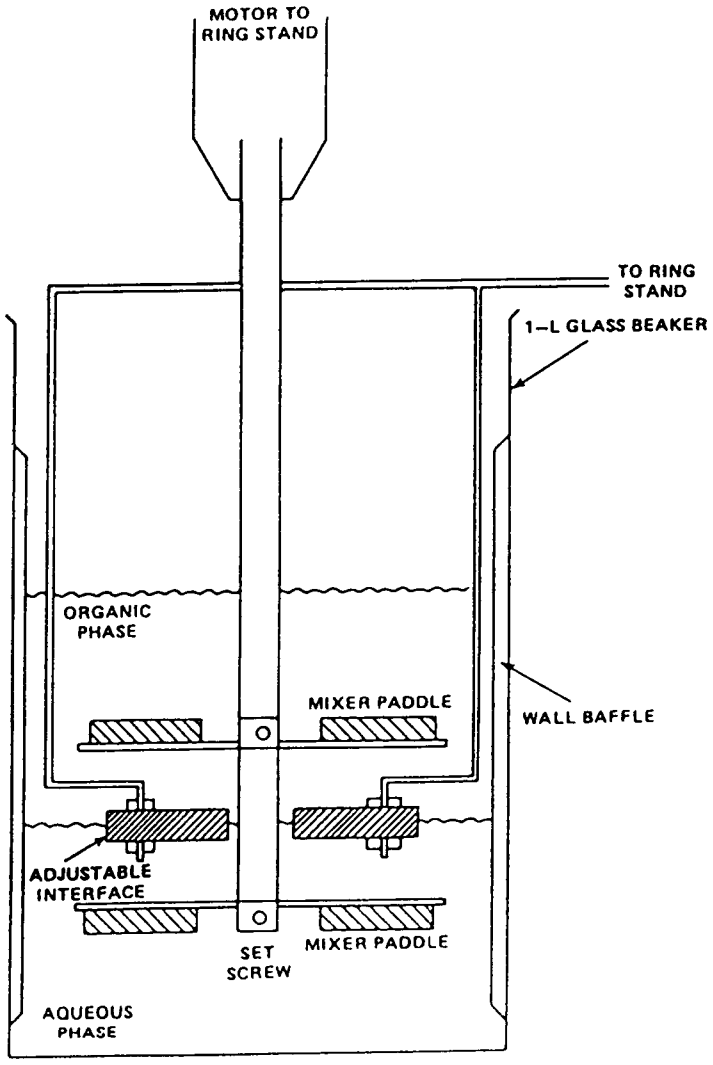


Figure 3.1. Stirred cell.

Table 3.1. Vessel parameters studied.

Item	Sizes and/or Number
Paddle	3.0 cm and 6.0 cm diameter.
Paddle Blades	0.25 cm and 0.50 cm vertical height, 4 blades.
Wall Baffles	0.25 cm and 0.50 cm radial height, 4 and 8 baffles of entire wall length.

more stable interface, but each zirconium mass transfer test would take more time to complete. The mass transfer rate decreased with rotational speed.

Operation of the stirred-cell (see Fig. 3.1) was relatively straight forward. Temperature control was accomplished by placing the entire stirred-cell in a water bath. Once the aqueous and organic phase had equilibrated, the acetic acid or zirconium were injected into the aqueous phase via a calibrated pipet. A known amount of acetic acid or zirconium was introduced into the aqueous phase with a pipet. The samples were then withdrawn from either phase by a pipet of specific volume. Total cumulative sample volume removed during each experiment was not greater than approximately 5% of each phase volume.

The reagents used for the study were of standard laboratory grade. The acetic acid, nitric acid, isobutanol, dodecane, and TBP were laboratory grade at 99.9% purity or better. The zirconium feed stock was purchased from Aldrich Chemical Company (Milwaukee, WI, Product # 25734-6), and guaranteed as $Zr(NO_3)_4$. The zirconium feed stock was

approximately 90 g/L in 13 M nitric acid. The water used was twice deionized.

3.2. Analytical Techniques

The acetic acid concentration was measured by a standard titration method. A conductivity meter was used to measure the pH during the titration, with NaOH the titrant. Both the aqueous and organic (isobutanol) phase were sampled in order to determine the material balance. The organic phase sample was used to determine the overall mass transfer coefficient. Since analytical accuracy was about $\pm$5% of the measurement for either phase, the change in organic concentration could be more accurately measured than the change in aqueous phase concentration.

The zirconium analysis was done by a colorimetric method. The colormetric method used was an established technique which utilized the color reagent Arsenazo III. The reagent Arsenazo III is mixed with the zirconium sample in 9 M HCl. The concentrated HCl tends to reverse any hydrolysis reactions. In addition, the zirconium concentration is kept well below the level at which polymerization occurs. Therefore, this procedure produces a zirconium specie in only the 4^+ cation state. This technique can detect well below 1 ppm zirconium.

The organic zirconium concentration was used to determine the mass transfer rate for each experiment. This was because the overall equilibrium distribution coefficient of zirconium in dodecane/TBP was low (~0.25), such that the change in aqueous concentration was small. In order to analyze the organic zirconium concentration it was first

necessary to back extract the zirconium into an aqueous medium. The Arsenazo III method requires an aqueous medium. Each organic sample collected was 3 ml in volume, and was immediately contacted with 3 ml of 0.01 M HNO_3 for the back extraction. It was determined from a series of tests, that a single back extraction of five minutes vigorus shaking removed 95% or more of the zirconium from the organic phase. An appropriate volume of 0.01 M HNO_3 with back extracted zirconium was then used for the Arsenazo III analysis.

After the Arsenazo III color agent and HCl were added to the zirconium sample, the colored solution was analyzed immediately. This was because low concentrations of HNO_3 present in the zirconium sample would tend to destabilize the color. It was found the color would remain stable for at least five minutes. The final solution was scanned for absorption at 6500 to 7000 A. The peak was approximately 6750 A. The spectrophotometer calibration was found to be constant over at least a four month period.

4. THEORETICAL

4.1. Acetic Acid

4.1.1. Specie of Interest

Acetic acid is a weak electrolyte with a K_a of 1.8×10^{-5} at 25 C (Barrow, pg 418, 1972). Acetic acid, CH_3COOH, forms the ions CH_3COO^- and H^+ in water. The ratio of ionized to non-ionized species can be calculated:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]},$$

where $[CH_3CHOO^-] = [H^+]$,

and then $1.8 \times 10^{-5} = \frac{X^2}{1 - X}$,

$$X = [CH_3COO^-] = 0.004 \text{ M, if } [CH_3COOH] \sim 1 \text{ M} .$$

Based upon the K_a, acetic acid is primarily in the molecular (99.6%) rather than ionized state. This is important since it implies the primary acetic acid specie and diffusion coefficient remain constant during mass transfer.

Dimerization of acetic acid is possible in non-polar solvents, Olander(1980); however, the dipole moment of water and isobutanol are 1.5 and 1.7 debye respectively. Water is known to be polar, so that isobutanol must also be polar also based on dipole moments. Therefore, dimerization of acetic acid in water and isobutanol should be negligible.

4.1.2. Mass Transfer Model

The mass transfer rate of acetic acid from water to isobutanol was used to determine the stirred-cell overall mass transfer coefficient. The overall mass transfer coefficient is determined from the acetic acid mass transfer data, and then it is related to the individual or film mass transfer coefficients. Once the individual film mass transfer coefficients are determined for the acetic acid system, they are extrapolated to the zirconium system via an established correlation for stirred-cells. This correlation relates the Sherwood number, Reynolds number, and Schmidt number. The overall mass transfer coefficient is determined from the acetic acid concentration in the bulk phase.

The overall mass transfer coefficient is defined as:

$$-\frac{V_a}{S}\frac{dC_a}{dt} = K_{oa}(C_a - C_a^*), \qquad (4.1)$$

where

$$D_s = C_o/C_a^*.$$

The material balance for acetic acid introduced into the aqueous phase at time zero, with no acetic acid in the system initially, is:

$$V_a C_a(0) = V_a C_a + V_o C_o.$$

Equation 4.1 combined with the distribution coefficient and material balance can be integrated and solved for the acetic acid concentration in the aqueous or alcohol phase.

Equation 4.1 solved in terms of aqueous acetic acid concentration yields:

$$\frac{dC_a}{dt} = \frac{SK_{oa}}{-V_a}(C_a - C_o/D_s),$$

$$= \frac{SK_{oa}}{-V_a}\{C_a - (1/D_s)(V_a/V_o)[C_a(0) - C_a]\},$$

$$= \frac{SK_{oa}}{-V_a}[(1+A')C_a - AC_a(0)], \qquad (4.2)$$

where, $A' = V_a/(D_s V_o)$.

Rearrangment of Eq. 4.2 in preparation for integration yields;

$$\int \frac{dC_a}{[(1+A')C_a - A'C_a(0)]} = \int \frac{SK_{oa}}{-V_a}\,dt; \quad \text{where } C_a(t=0) = C_a(0),$$

and then upon integration,

$$C_a = \frac{C_a(0)}{(1+A')}(A' + e^{-B't}), \quad \text{where} \quad B' = [(1+A')SK_{oa}]/V_a.$$

K_{oa} can be estimated from the aqueous acetic acid concentration data as follows:

$$K_{oa} = \frac{-V_a}{(1+A')St} \ln\left[\frac{(1+A')C_a - A'C_a(0)}{C_a(0)}\right].$$

To check the solution for C_a at time zero:

$$C_a = \frac{C_a(0)}{(1+A')} [A' + e^{-B'(t=0)}],$$

$$= \frac{C_a(0)}{(1+A')} (A' + 1)$$

$$= C_a(0).$$

To check the solution for C_a at time infinity:

$$C_a = \frac{C_a(0)}{(1+A')} (A' + 0)$$

$$= \frac{A'}{(1+A')} C_a(0) .$$

The material balance at infinite time yields;

$$V_a C_a(0) = V_a C_a + V_o C_o, \quad \text{where} \quad D_s = C_o/C_a,$$

$$V_a C_a(0) = (V_a + V_o D_s) C_a, \quad \text{or}$$

$$C_a = \frac{V_a}{(V_a + V_o D_s)} C_a(0), \quad \text{and dividing by } V_o D_s \text{ yields}$$

$$C_a = \frac{A'}{(1+A')} C_a(0).$$

Equation 4.1 solved in terms of organic acetic acid:

$$\frac{dC_a}{dt} = - \frac{V_o}{V_a} \frac{dC_o}{dt} = \frac{SK_{oa}}{-V_a} (C_a - C_o/D_s).$$

Rearranging yields;

$$\frac{dC_o}{dt} = \frac{SK_{oa}}{V_o}\,[C_a(0) - A''C_o], \quad \text{where} \tag{4.3}$$

$$A'' = (V_o/V_a + 1/D_s).$$

Integration of Eq. 4.3, where $C_o(t=0)=0$, yields;

$$C_o = \frac{C_a(0)}{A''}\,(1 - e^{-B''t}), \quad \text{where} \quad B'' = (A''SK_{oa})/V_o.$$

K_{oa} can be estimated from the organic acetic acid concentration data as follows:

$$K_{oa} = \frac{-V_o}{A''St}\,\ln\left[\frac{C_a(0) - A''C_o}{C_a(0)}\right].$$

To check the solution at time zero:

$$C_o = \frac{C_a(0)}{A''}\,[1 - e^{-B''(t=0)}] = 0.$$

to check the solution at time infinity:

$$C_o = \frac{C_a(0)}{A''}\,(1 - 0).$$

The material balance at infinite time yields:

$$V_aC_a(0) = V_aC_a + V_oC_o, \quad \text{where} \quad D_s = C_o/C_a,$$

$$V_aC_a(0) = (V_a/D_s + V_o)C_o, \quad \text{or}$$

$$C_o = \frac{C_a(0)}{(1/D_s + V_o/V_a)} = \frac{C_a(0)}{A''}, \quad \text{having divided by } V_a.$$

To apply the acetic acid overall mass transfer coefficient to other chemical systems in the same vessel, it is necessary to relate the overall coefficient to the individual coefficients. The overall mass transfer coefficients are related to the individual mass transfer coefficients by consideration of the equilibrium and operating lines. They are defined as follows, and discussed in detail in many mass transfer texts:

$$\frac{-V_a}{S}\frac{dC_a}{dt} = K_{oa}\,(C_a - C_a^*); \quad \text{where} \quad Co/C_a^* = D_s,$$

$$\frac{+V_o}{S}\frac{dC_o}{dt} = K_{oo}\,(C_o^* - C_o); \quad \text{where} \quad Co^*/C_a = D_s,$$

$$\frac{-V_a}{S}\frac{dC_a}{dt} = k_a\,(C_a - C_a^i); \quad \text{where} \quad Co^i/C_a^i = D_s,$$

$$\frac{+V_a}{S}\frac{dC_o}{dt} = k_o\,(C_o^i - C_o).$$

The coefficients are related as,

$$1/K_{oa} = 1/(D_s k_o) + 1/k_a,$$

$$1/K_{oo} = 1/k_o + D_s/k_a.$$

For the acetic acid system of this study, it was concluded the primary resistance to mass transfer was in the organic phase. This allowed the following simplification of the relationship between the overall and individual mass transfer coefficients.

$$k_o = K_{oa}/D_s. \qquad (4.4)$$

The literature review described in Section 2.4.1, presents correlations relating the individual mass transfer coefficient in stirred cells to (1) mixing speed via the Reynolds number and (2) different chemical systems via the Schmidt number. The correlation selected was based on the Penetration or Surface Renewal theory which assumes the mass transfer coefficient is proportional to the square root of the diffusion coefficient of the transferring specie (Bulicka and Prochazka, 1976). The correlation of Bulicka and Prochazka is:

$$N_{Sh,j} = p(N_{Re,j})^{q}(N_{Sc,j})^{1/2}, \tag{4.5}$$

where j is the phase of interest. This is a correlation for the individual, not overall, mass transfer coefficient. The constants (p, q) are specific to the stirred-cell used, and are regressed from the K_{oa} acetic acid data. Equation 4.5 must be rearranged for the regression as follows:

$$k_j = p(D^f_j/d_j)(N_{Re,j})^{q}(N_{Sc,j})^{1/2}, \quad \text{or}$$

$$K_{oa} = pD_s(D^f_a/d_a)(N_{Re,a})^{q}(N_{Sc,a})^{1/2}. \tag{4.6}$$

Linearization of regression coefficients yields:

$$\ln(d_aK_{oa}) = \ln[pD_sD^f_a(N_{Sc,a})^{1/2}] + q[\ln(N_{Re,a})],$$

or

$$Y = \text{intercept} + (\text{slope})X,$$

where

$$Y = \ln(d_a K_{oa}),$$

$$X = \ln(N_{Re,a}),$$

$$q = \text{slope},$$

and

$$p = \{e^{(\text{intercept})}/[D_s D^f_a (N_{Sc,a})^{1/2}]\}.$$

4.2. Zirconium

Based upon variation of the system parameters (1) interfacial area, (2) phase volumes, (3) mass transfer coefficients, and (4) reactant concentrations, it was concluded for the zirconium extraction process of this study, mass transfer is primarily controlled via (I) chemical reaction in the bulk aqueous phase and (II) diffusion of the metal complex in the organic phase. This is particularly true during extraction periods equal to or less than two hours. It is also possible to propose a chemical complexation reaction rate equation including the species Zr^{4+}, NO_3^-, TBP as aqueous phase reactants and $Zr(NO_3)_4 \cdot 2TBP$ as the aqueous phase product. These assumptions are discussed in detail in the Discussion section, and are necessary for the theoretical development of this section.

4.2.1. Species of Interest

The dominant aqueous phase zirconium species have been discussed

by Baes and Mesmer (1976), Mailen et al. (1980) and Siczek and Steindler (1978), as reported in section 2.1.2.1. The work of these researchers indicates that aqueous zirconium concentrations equal to or less than 0.001 M should consist almost entirely of the monomer specie. At nitric acid concentrations equal to or greater than 3 M, zirconium hydrolysis should be negligible. Therefore, the aqueous conditions of this study have been selected as approximately 0.001 M zirconium and 3 M HNO_3. At these conditions, the predominant aqueous species should be Zr^{4+} and $Zr(NO_3)_4 \cdot 2TBP$. The organic conditions have been selected as 30 vol% (1.1 M) TBP in dodecane. This TBP concentration is typical of Purex flowsheets as reported by Benedict, Pigford and Levi (1981). Dodecane was selected as the diluent, rather than a mixed hydrocarbon, to provide reproducibility. It has been concluded, as detailed in the Discussion section, the only significant organic zirconium specie is the metal complex $Zr(NO_3)_4 \cdot 2TBP$.

4.2.2. Diffusion

The diffusional resistance contribution to the overall zirconium mass transfer rate is attributed solely to the organic phase metal complex, $Zr(NO_3)_4.2TBP$. Based upon an aqueous phase complexation reaction, the metal complex enters the organic phase only by diffusion. The following diffusion model is correct by itself. The aqueous metal complex diffusion has been included with no loss of accuracy:

$$+ \frac{V_o}{S} \frac{dC_{o4}}{dt} = k_{o4} \, (C_{o4}^{\,i} - C_{o4}), \tag{4.7}$$

$$= k_{a4} \, (C_{a4} - C_{a4}^{\,i}), \tag{4.8}$$

where

$$C_{o4}{}^{i}/C_{a4}{}^{i} = D_4 .$$

4.2.3. Chemical Reaction

The proposed complexation chemical reaction shown below, is described in section 2.1.2.1:

$$(Zr^{4+}) + 4(NO_3^-) + 2(TBP) \underset{K^b}{\overset{K^f}{<--->}} Zr(NO_3)_4 \cdot 2TBP \ .$$

Mailen (1980) determined the TBP rate dependency with Zr^{+4} and $Zr(OH)^{+3}$ to be approximately two, and the NO_3^- rate dependency with $Zr(OH)^{+3}$ to be approximately 3. Since the rate dependancy TBP and NO_3^- appear to equal the stoichiometry of reaction, it is reasonable to assume the rate dependency for NO_3- with Zr^{4+} to be four.

The reaction rate expression then becomes:

$$-V_a \frac{d[Zr^{4+}]}{dt} = K^f[Zr^{4+}][NO_3^-]^4[TBP]^2 - K^b[Zr(NO_3)_4 \cdot 2TBP] \ .$$

By comparing the initial relative concentrations of the species involved in the reaction, additional simplifications can be made noting that only small amounts of NO_3^- and TBP are consumed by reaction.

[Zr] ~ 0.001 M in the aqueous phase at t=0,

$[NO_3]$ ~ 3.0 M in the aqueous phase at t=0,

[TBP] ~ 1.0 M in the organic phase at t=0.

Therefore,

$[NO_3] \sim [NO_3(t=0)]$ at all time in the aqueous phase, and

$[TBP] \sim [TBP(t=0)]$ at all time in the organic phase.

Since the reactant concentrations profiles in the aqueous phase are assumed flat, and $[TBP]_o \gg [Zr]_a$,

$[TBP]_o/[TBP]_a = D_3$ for the bulk concentrations.

The final chemical reaction expression then becomes,

$$-V_a \frac{dC_{a1}}{dt} = K^f(C_{a1})[C_{a2}(0)]^4[C_{o3}(0)/D_3]^2 - K^b(C_{a4}), \tag{4.9}$$

where $[C_{a2}(0)]$ and $[C_{o3}(0)/D_3]$ are constants.

4.2.4. Distribution Coefficient

The distribution coefficient has been viewed in terms of an aqueous chemical reaction for this study. The equilibrium distribution coefficients reported in the literature do not distinguish between the Zr^{4+} cation and the complexed specie $Zr(NO_3)_4 \cdot 2TBP$. Based on the literature survey, it has been concluded the concentration of the Zr^{4+} cation is essentially zero in the organic phase. The only significant organic zirconium specie is the complex $Zr(NO_3)_4 \cdot 2TBP$.

The following theory produces an expression for D_{Zr} (literature distribution coefficient) in terms of D_4 (true distribution coefficient) and K^f/K^b (reaction equilibrium constant). This expression can be linearized so that a least squares regression can be used to determine D_4 and K^f/K^b from literature equilibrium data.

The distribution coefficient reported in the literature D_{Zr}, should be expressed as:

$$D_{Zr} = \frac{C_{o4}(eq)}{C_{a1}(eq) + C_{a4}(eq)} . \qquad (4.10)$$

Dividing Equation 4.10 by C_{a4} yields:

$$D_{Zr} = \frac{C_{o4}/C_{a4}}{C_{a1}/C_{a4} + C_{a4}/C_{a4}} . \qquad (4.11)$$

Substituting $C_{o4}/C_{a4} = D_4$ into Eq. 4.11, and rearranging yields:

$$\frac{C_{a1}}{C_{a4}} = \frac{D_4}{D_{Zr}} - 1 . \qquad (4.12)$$

Equation 4.12 can be combined with the equilibrium chemical reaction rate expression to allow definition of D_4 and K^f/K^b in terms of D_{Zr}. The chemical reaction at equilibrium can be expressed as:

$$- V_a \frac{dC_{a1}}{dt} = K^f(C_{a1})(C_{a2})^4(C_{o3}/D_3) - K^b(C_{a4}) = 0,$$

rearranging yields;

$$\frac{K^b}{K^f} = \frac{(C_{a1})(C_{a2})^4(C_{o3}/D_3)^2}{(C_{a4})} . \qquad (4.13)$$

Substituting Eq. 4.13 into 4.12 yields:

$$\frac{K^b}{K^f} = (D_4/D_{Zr} - 1)(C_{a2})^4(C_{o3}/D_3)^2,$$

and finally upon rearranging;

$$D_{Zr} = \frac{D_4}{\frac{(K^b/K^f)}{(C_{a2})^4(C_{o3}/D_3)^2} + 1} \quad . \tag{4.14}$$

At a NO_3^- or TBP concentration equal to zero, D_{Zr} equals zero as expected. As NO_3^- or TBP concentration gets large, D_{Zr} approaches D_4 as expected.

The distribution coefficient for TBP (D_3), can be found in the literature and is recorded in Appendix A.1.3. Equation 4.14 can be linearized for the regression as follows:

$$(1/D_{Zr}) = [(K^b/K^f)/D_4](1/C_k) + (1/D_4),$$

where

$$C_k = [C_{a2}(0)]^4[C_{o3}(0)/D_3]^2,$$

and

$$Y = (1/D_{Zr}),$$

$$X = (1/C_k),$$

$$\text{slope} = (K^b/K^f)/D_4,$$

$$\text{intercept} = (1/D_4).$$

4.2.5. Mass Transfer Model

The complete model involves the simultaneous solution of the chemical reaction rate equation and diffusion equations. It is

possible to solve these equations, Eqs. 4.7, 4.8 and 4.9, with use of the material balance and by application of Laplace Transforms. This involves the simultaneous solution of Eqs. 4.7, 4.8 and 4.9. These equations are rearranged in terms of C_{a1} and C_{o4} only.

The chemical reaction expression can be written as:

$$\frac{dC_{a1}}{dt} = \frac{K^b C_{a4}}{V_a} - \frac{K^f C_k C_{a1}}{V_a}, \quad \text{where } C_k = [C_{a2}(0)]^4 [C_{o3}(0)/D_3]^2,$$

$$= A_1 C_{a4} - A_2 C_{a1}, \quad \text{where } A_1 = K^b/V_a, \tag{4.15}$$

$$A_2 = (K^f C_k)/V_a.$$

The diffusion equations can be written as:

$$\frac{dC_{o4}}{dt} = \frac{S}{V_o} k_{o4} (C_{o4}{}^i - C_{o4}), \tag{4.16}$$

$$= \frac{S}{V_o} k_{a4} (C_{a4} - C_{a4}{}^i),$$

$$= A_4 C_{a4} - A_3 C_{o4},$$

where

$$C_{o4}{}^i/C_{a4}{}^i = D_4,$$

$$A_3 = \frac{S}{V_o} k_{o4} \left[1 - \frac{k_{o4}}{V_o(k_{o4} + k_{a4}/D_4)} \right],$$

$$A_4 = \frac{S}{V_o} k_{o4} \left[\frac{k_{a4}}{(k_{o4} + k_{a4}/D_4)} \right].$$

The term C_{a4} can be eliminated from Eqs. 4.15 and 4.16 via the material balance.

$$V_a C_{a1}(0) = V_a C_{a1} + V_a C_{a4} + V_o C_{o4},$$

or

$$C_{a4} = C_{a1}(0) - C_{a1} - (V_o/V_a)C_{o4},$$

and then

$$\frac{dC_{a1}}{dt} = A_1[C_{a1}(0) - C_{a1} - (V_o/V_a)C_{o4}] - A_2 C_{a1},$$

$$= A_1 C_{a1}(0) - A_1 C_{a1} - A_1(V_o/V_a)C_{o4} - A_2 Ca_1,$$

$$= A_5 - A_6 C_{a1} - A_7 C_{o4}, \qquad (4.17)$$

where $A_5 = A_1 C_{a1}(0)$,

$A_6 = (A_1 + A_2)$,

$A_7 = A_1(V_o/V_a)$.

$$\frac{dC_{o4}}{dt} = A_4[C_{a1}(0) - C_{a1} - (V_o/V_a)C_{o4}] - A_3 C_{o4},$$

$$= A_4 C_{a1}(0) - A_3 C_{o4} - A_4(V_o/V_a)C_{o4} - A_4 C_{a1},$$

$$= A_8 - A_4 C_{a1} - A_9 C_{o4}, \qquad (4.18)$$

where $A_8 = A_4 C_{a1}(0)$,

$A_9 = A_3 + A_4(V_o/V_a)$.

It is now possible to Laplace Transform Eqs. 4.17 and 4.18, where:

$$L\{dC/dt\} = sL\{C\} - C(t=0),$$

$$L\{A\} = A/s, \quad \text{where } A = \text{constant}.$$

Noting that $C_{a1}(t=0)=C_{a1}(0)$ and $C_{o4}(t=0)=0$,

$$sL\{C_{a1}\} - C_{a1}(0) = A_5/s - A_6L\{C_{a1}\} - A_7L\{C_{o4}\} \tag{4.19}$$

$$sL\{C_{o4}\} = A_8/s - A_4L\{C_{a1}\} - A_9L\{C_{o4}\} . \tag{4.20}$$

Rearranging Eqs. 4.19 and 4.20 in terms of C_{o4} yields:

$$L\{C_{o4}\} = (1/A_7)[A_5/s - (A_6+s)L\{C_{a1}\}+C_{a1}(\emptyset)],$$

$$L\{C_{o4}\} = [-1/(A_9+s)][A_4L\{C_{a1}\} - A_8/s].$$

Solving for $L\{C_{a1}\}$,

$$(1/A_7)[A_5/s - (A_6+s)L\{C_{a1}\}] = [-1/(A_9+s)][A_4L\{C_{a1}\} - A_8/s],$$

or

$$A_5 - s(A_6+s)L\{C_{a1}\} + sC_{a1}(0) = \frac{-A_7}{(A_9 + s)}[sA_4L\{Ca_1\} - A_8],$$

or

$$(A_9+s)A_5 - s(A_9+s)(A_6+s)L\{C_{a1}\} + s(A_9+s)C_{a1}(0) =$$

$$-sA_4A_7L\{C_{a1}\} + A_7A_8,$$

or

$$s[-s^2 + (-A_6-A_9)s - (-A_4A_7+A_6A_9)]L\{C_{a1}\} =$$

$$-s^2C_{a1}(0) + (-A_5-A_9C_{a1}(0)s - (-A_7A_8+A_5A_9),$$

and finally,

$$L\{C_{a1}\} = \frac{-s^2C_{a1}(0) + [-A_5-A_9\,C_{a1}(0)]s - (-A_7A_8+A_5A_9)}{s[-s^2 + (-A_6-A_9)s - (-A_4A_7+A_6A_9)]},$$

Upon simplification,

$$L\{C_{a1}\} = \frac{f_1s^2 + f_2s + f_3}{s(s^2 + f_4s + f_5)},$$

where $f1 = -C_{a1}(0)$,

$f_2 = (-A_5-A_9)$,

$f_3 = -(-A_7A_8+A_5A_9)$,

$f_4 = (-A_6-A_9)$,

$f_5 = -(-A_4A_7+A_6A_9)$.

The Laplace Transform can be inverse transformed via partial fractions:

$$L\{C_{a1}\} = \frac{f_1s^2 + f_2s + f_3}{s(s+a_o)(s+a_1)} = \frac{b_2}{s} + \frac{b_1}{(s+a_1)} + \frac{b_o}{(s+a_o)}, \qquad (4.21)$$

where $a_o = \{-f_4 + [(f_4)^2 - 4f_5]^{1/2}\}/2$,

$a_1 = \{-f_4 - [(f_4)^2 - 4f_5]^{1/2}\}/2$.

To solve for b_2, multiply both sides of Eq. (4.21) by "s" and set s=0:

$$b_2 = f_3/(a_oa_1).$$

To solve for b_1, multiply both sides of Eq. (4.21) by $(s-a_1)$ and set $s=-a_1$:

$$b_1 = \frac{f_1(-a_1)^2 + f_2(-a_1) + f_3}{-a_1(-a_1+a_0)} .$$

To solve for b_o, multiply both sides of Eq. (4.21) by $(s-a_o)$ and set $s=-a_o$:

$$b_o = \frac{f_1(a_o)^2 + f_2(a_o) + f_3}{a_o(a_o-a_1)} .$$

It is now possible to inverse Laplace Transform Eq. 4.21 to produce the real time solution of C_{a1} as a function of time.

$$C_{a1} = b_2 + b_1e^{-alt} + b_oe^{-aot}. \qquad (4.22)$$

Utilizing the material balance for zirconium, and the diffusion and chemical reaction equations, it is possible to write the solution for both C_{a4} and C_{o4} as a function of time.

Rearranging the chemical reaction equation:

$$dC_{a1}/dt = A_1C_{a4} - A_2C_{a1}, \quad \text{or}$$

$$C_{a4} = (1/A_1)[(dC_{a1}/dt) + A_2C_{a1}],$$

$$dC_{a1}/dt = (-a_1b_1)e^{-alt} - (a_ob_o)e^{-a0t},$$

$$C_{a4} = (1/A_1)[(-alb_1)e^{-alt} - (a_ob_o)e^{-aot} + A_2(b_2 + b_1e^{-alt} + b_oe^{-aot})],$$

and finally,

$$C_{a4} = (1/A_1)[A_2b_2 + b_1(A_2-a_1)e^{-alt} + b_o(A_2-a_o)e^{-aot}]. \qquad (4.23)$$

Utilizing the material balance to solve for C_{o4}:

$$(V_o/V_a)C_{o4} = C_{a1}(0) - C_{a1} - C_{a4},$$

$$= C_{a1}(0) - (b_2 + b_1e^{-alt} + b_oe^{-0t}) -$$

$$(1/A_1)[A_2b_2 + b_1(A_2-a_1)e^{-alt} + b_o(A_2-a_o)e^{-aot}].$$

And upon final rearrangement,

$$C_{o4} = (V_a/V_o)\{[C_{a1}(0) - b_2(1+A_2/A_1)] -$$

$$b_1[1+(A_2-a_1)/A_1]e^{-alt} - b_o[1+(A_2-a_o)/A_1]e^{-aot}\}. \qquad (4.24)$$

A unique expression now exists for each of the existing zirconium species. In order to check the mathematics, Eq. 4.22 should be solved at time zero and time infinity.

At time infinity:

$$C_{a1} = b_2,$$

$$= f_3/(a_oa_1),$$

$$= \frac{f_3}{((f_4)^2 - [(f_4)^2-4f_5]^{1/2})/4} = \frac{A_8A_7 - A_5A_9}{A_4A_7 - A_6A_9}.$$

Continued rearrangement of C_{a1} at infinite time:

$$b_2 = \frac{[A_4C_{a1}(0)]A_1(V_o/V_a) - [A_1C_{a1}(0)][A_3+A_4(V_o/V_a)]}{A_4A_1(V_o/V_a) - (A_1+A_2)[A_3+A_4(V_o/V_a)]},$$

$$b_2 = \frac{A_3 A_1 C_{a1}(0)}{A_1 A_3 - A_2 A_3 - A_2 A_4 (V_o/V_a)},$$

$$b_2 = \frac{\frac{Sk_{o4}}{V_o}\left(\frac{K^b}{V_a}\right) C_{a1}(0)}{\frac{K^b}{V_a}\left(\frac{Ck_{o4}}{V_o}\right) + \frac{K^f C_k}{V_a}\left(\frac{Sk_{o4}}{V_o}\right) + \frac{K^f C_k}{V_a}\left(\frac{Sk_{o4} D_4}{V_a}\right)\frac{V_o}{V_a}},$$

$$= \frac{[(K^b C_{a1}(0)]}{(K^b/V_o) + [(K^f C_k)/V_o] + [(K^f C_k D_4)/V_a]},$$

$$= \frac{K^b C_{a1}(0)}{K^b + K^f C_k + (V_o/V_a) K^f C_k D_4},$$

and finally,

$$C_{a1} = b_2 = C_{a1}(0)/\{1 + [1 + D_4(V_o/V_a)](K_f/K^b)C_k\}. \qquad (4.25)$$

The concentration C_{a1} at time infinity can also be determined from the material balance and chemical reaction expression.

Per the zirconium material balance:

$$C_{a1}(0) = C_{a1} + C_{a4} + (V_o/V_a)C_{o4}.$$

Per the chemical reaction expression at time infinity:

$$(K^f/K^b) = C_{a4}/(C_{a1}C_k).$$

Combining the material balance, distribution coefficient, and reaction rate equation to eliminate C_{a4} and Co_4:

$$C_{a1} = C_{a1} + (K^f/K^b)C_k C_{a1} + D_4(K^f/K^b)C_k C_{a1}(V_o/V_a),$$

$$= [1 + (K^f/K^b)C_k + D_4(K^f/K^b)(V_o/V_a)C_k]C_{a1},$$

$$Ca_1 = C_{a1}(0)/(1 + [1 + D_4(V_o/V_a)](K^f/K^b)C_k). \qquad (4.26)$$

It can be seen that Eq. 4.25 and 4.26 are identical, so that the mathematics of the solution to C_{a1} represented by Eq. 4.22 are correct at infinite time.

Now the mathematics will be checked at time zero. According to Eq. 4.22:

$$C_{a1}(t=0) = b_2 + b_1 + b_o,$$

$$= \frac{f_3}{a_o a_1} + \frac{f_1(a_1)^2 - f_2 a_1 + f_3}{a_1(a_1 - a_o)} + \frac{f_1(a_o)^2 - f_2 a_o + f_3}{a_o(a_o - a_1)},$$

$$= f_1 + f_3\{1/(a_o a_1) - 1/[a_1(a_o - a_1) - 1/[a_o(a_o - a_1)]\},$$

$$= f_1,$$

$$= C_{a1}(0).$$

The equation checks at time zero and time infinity. It is also necessary to check the solutions in the original two differential equations, chemical reaction and diffusion.

For chemical reaction:

$$dC_{a1}/dt = A_1 C_{a4} - A_2 C_{a1}, \quad \text{where}$$

$$dC_{a1}/dt = (-a_1 b_1)e^{-alt} - (a_o b_o)e^{-aot}, \quad \text{and also}$$

$$dC_{a1}/dt = A_1(1/A_1)[A_2 b_2 + b_1(1-a_1)e^{-alt} + b_o(1-a_o)e^{-aot}]$$
$$- (A_2/A_1)(b_2 + b_1 e^{-alt} + b_o e^{-aot}).$$

Combining like terms:

e^{-aot}: $-a_{obo} = b_o(A_2-a_o) - A_2b_o$,

e^{-alt}: $-a_1b_1 = b_1(A_2-a_1) - A_2b_1$,

e^{0}: $0 = A_1(1/A_1)A_2b_2 - A_2b2$.

These equalities indicate that the solutions for C_{a1} and C_{a4} obey the chemical reaction rate equation.

For organic phase diffusion:

$$dC_{o4}/dt = A_4C_{a4} - A_3C_{o4},$$

$$= A_4(1/A_1)[A_2b_2 + b_1(A_2-a_1)e^{-alt} + b_o(A_2-a_o)e^{-aot}]$$
$$- A_3(V_a/V_o)\{C_{a1}(0) - b_2(1+A_2/A_1)$$
$$- b_1[1+(A_2-a_1)/A_1]e^{-alt} - b_o[1+(A_2-ao)/A_1]e^{-aot}\},$$

Per the overall solution:

$$dC_{o4}/dt = (V_a/V_o)a_1b_1[1 + (A_2-a_1)/A_1]e^{-alt} +$$
$$(V_a/V_o)a_ob_o[1 + (A_2-a_o)/A_1]e^{-aot}, \text{ per } C_{o4} \text{ solution}$$

Combining like terms:

e^{0}: $(A_4/A_1)A_2b_2 - A_3(V_a/V_o)C_{a1}(0) + A_3b_2(1+A_2/A_2) = 0$,

e^{-al}: $(V_a/V_o)a_1b_1[1+(A_2-a_1)/A_1] = (A_4/A_1)b_1(A_2-a_1)$
$+ A_3(V_a/V_o)b_1[1+(A_2-a_1)/A_1]$.

e^{-al}: $(V_a/V_o)a_ob_o[1+(A_2-a_o)/A_1] = (A_4/A_1)b_o(A_2-a_o)$
$+ A_3(V_a/V_o)b_o[1+(A_2-a_o)/A_1]$.

These solutions are most easily solved by plugging in actual values to check the equality. This has been done in the Appendix A.3.10.

4.3. Statistical Analysis

The experimental procedure for developing the overall zirconium mass transfer model is shown in Figure 4.1. If interfacial area has a significant affect on mass transfer, then the process is at least partially controlled by diffusion. Determining if the aqueous mixer diameter or organic mixer diameter significantly affects mass transfer will indicate in which phase or phases the significant diffusion occurs. The mixer diameter can be related to the Reynolds number and then mass transfer coefficient. If interfacial area does not significantly affect the mass transfer, than the process has to be entirely chemical reaction controlled. If the process is at least partially diffusion controlled, the significance of chemical reaction can be ascertained by variation of the reactant concentrations Zr^{4+}, NO_3^-, and TBP.

4.3.1. Half Factorial Design

The design of an experiment for which statistical methods are to be used for determining significant effects requires careful selection of the test conditions for each sample. Since each experiment has a cost associated with it, the total number of samples should be no more than necessary. For this reason, a 1/2 factorial has been selected as the experimental design. The parameters to be tested are those which affect diffusion and chemical reaction, and can be manipulated via the test vessel or process conditions. These parameters are (1)

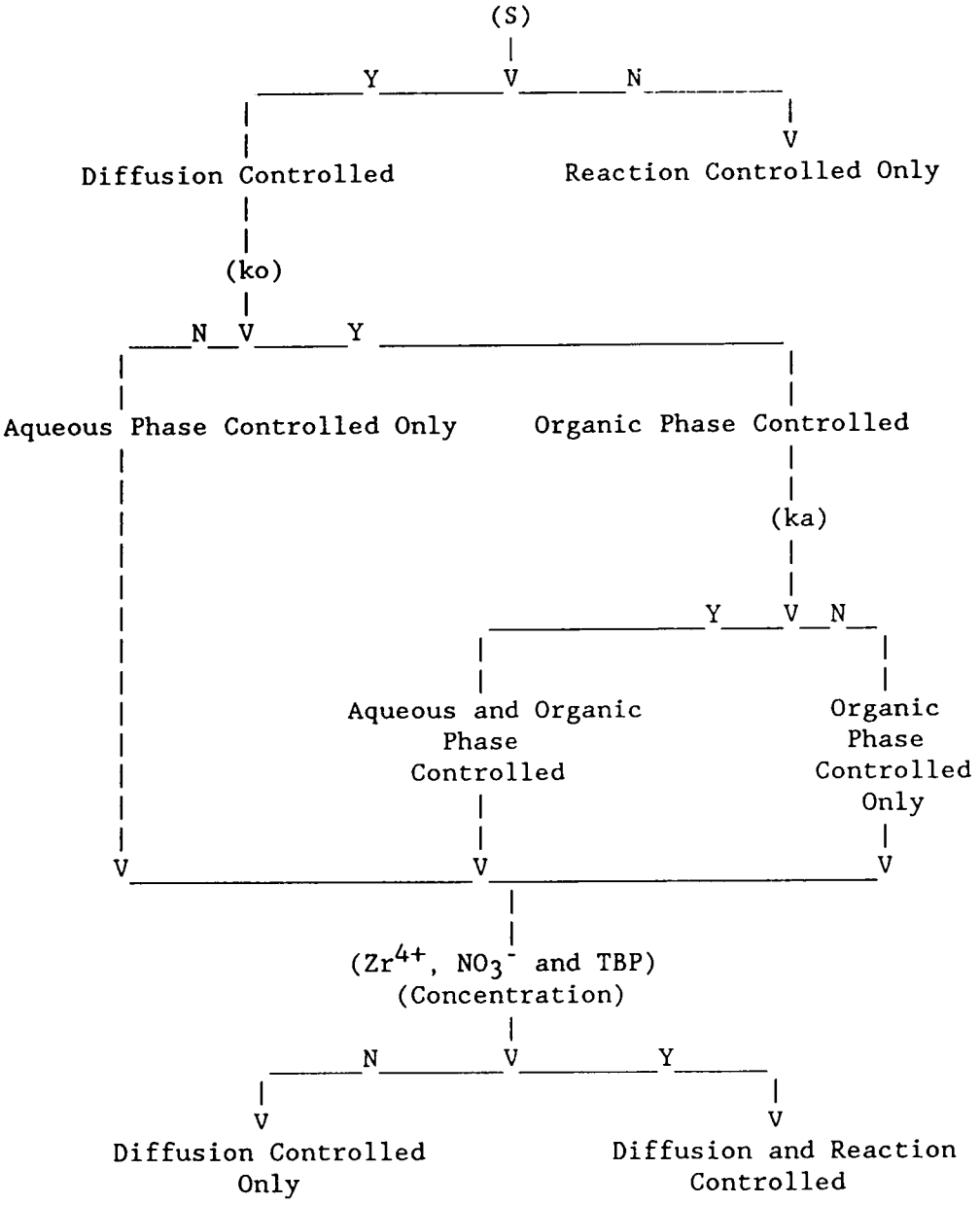


Fig. 4.1. Plan for selecting mass transfer model.

interfacial area S, (2,3) volume of each phase V_a and V_o, and (4,5) mass transfer coefficient of each phase as defined by the mixer diameter d_a and d_o. Table 4.1 shows the 1/2 factorial design as applied to the parameters of this study.

The experimental scheme shown in Table 4.1 is based on a 2x2x2x2x2 or 2^5 design, (area)x(aqueous volume)x(organic volume)x(aqueous mass transfer coefficient)x(organic mass transfer coefficient). This design requires $2^5/2$ or 16 samples. The data of interest per statistical analysis will be the sum-of-squares for each parameter. The sum-of-squares is defined as the sum of the squared difference between the measured and mean value. This will give a relative indication how much each parameter affects the mass transfer rate. The greater the

Table 4.1. Required samples for 1/2 factorial.

		$d_{a1}.d_{o1}$	$d_{a2}.d_{o1}$	$d_{a1}.d_{o2}$	$d_{a2}.d_{o2}$
S_1	V_{a1},V_{o1}	X	0	0	X
S_1	V_{a2},V_{o1}	0	X	X	0
S_1	V_{a1},V_{o2}	0	X	X	0
S_1	V_{a2},V_{o2}	X	0	0	X
S_2	V_{a1},V_{o1}	0	X	X	0
S_2	V_{a2},V_{o1}	X	0	0	X
S_2	V_{a1},V_{o2}	X	0	0	X
S_2	V_{a2},V_{o2}	0	X	X	0

Note: "X" indicates a data point will be collected at these conditions, "0" indicates a data point will not be collected.

sum-of-squares, the more data variation is accounted for by that particular parameter.

There are a number of statistical tests which were considered for data analysis. The Analysis of Variance (ANOVA) is limited to only single effects due to the 1/2 factorial design which has only half the degrees of freedom as a full factorial. The 1/2 Normal Plot is shown in the results section, and can handle double interaction effects of a 1/2 factorial design. The ANOVA and 1/2 Normal Plot are statistical tests and indicate significance at a particular confidence level.

4.3.2. Half Normal Plot

The half normal plot is based upon estimating the data error assuming the data normally distributed. The error is estimated at one standard deviation, which corresponds to the approximate 67% confidence interval. For a set of n data points, only the upper (0.33 n-1) effects have potential for significance. This approach allows the use of "degrees of freedom" consumed by the ANOVA error estimate to be used for double interaction effects, i.e., SxVa, SxVo, etc. See Appendix A.2.3 for a detailed example.

5. RESULTS

5.1. Acetic Acid Transfered from Water to Isobutanol

5.1.1. Acetic Acid Distribution Coefficient

To model mass transfer behavior of acetic acid in water and isobutanol, it was necessary to determine the distribution (or partition) coefficient. The original data are in Appendix A.2.1, and plotted in Fig. 5.1. The regression analysis determined the distribution coefficient to be 1.28 with an R^2 of 0.998 for six data points.

5.1.2. Acetic Acid Mass Transfer Data

The aqueous phase acetic acid overall mass transfer coefficients were measured at two distinct interfacial areas, phase volumes, and mixer diameters (i.e. Reynolds numbers). These conditions were 62 and 79 cm^2 for the interfacial area, 350 and 450 ml for the volumes, 3 and 6 cm for the mixer diameters. The detailed data from each of these 16 tests are shown in Appendix A.2.2. Table 5.1 displays the average overall aqueous phase mass transfer coefficient for each of the 16 tests. The conditions at which tests were not conducted are shown by an "X" in the table. An example of a single test is shown in Figure 5.2. The conditions can be interpreted as S_1=62 cm^2, S_2=79 cm^2, (V_{a1} and V_{o1})=350 ml, (V_{a2} and V_{o2})=450 ml, (d_{a1} and d_{o1})=3 cm, and (d_{a2} and d_{o2})=6 cm. The curve shown in Figure 5.2 represents the predicted concentrations based on the average K_{oa} determined from data collected at 30, 45 and 60 minutes into this test.

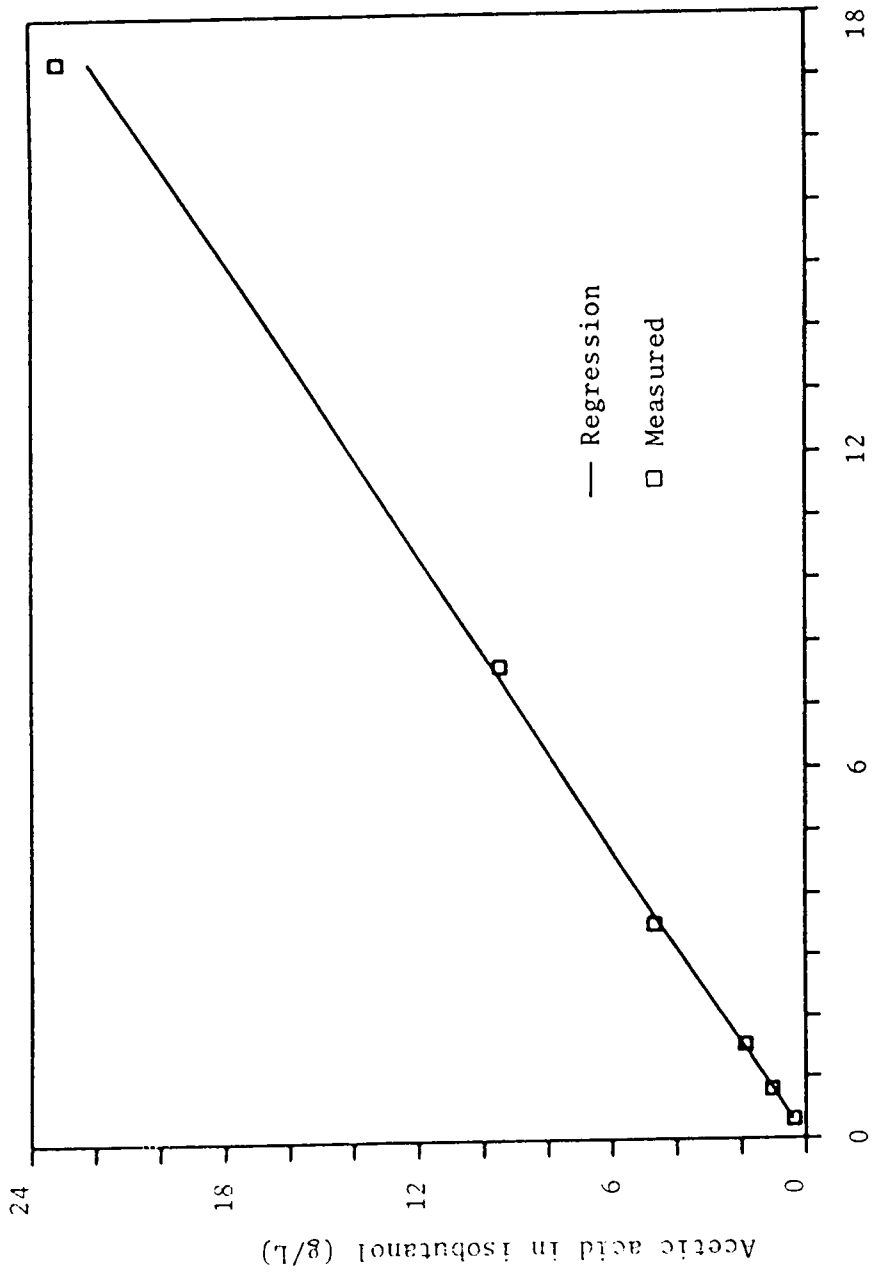


Figure 5.1. Distribution coefficient, acetic acid in water and isobutanol.

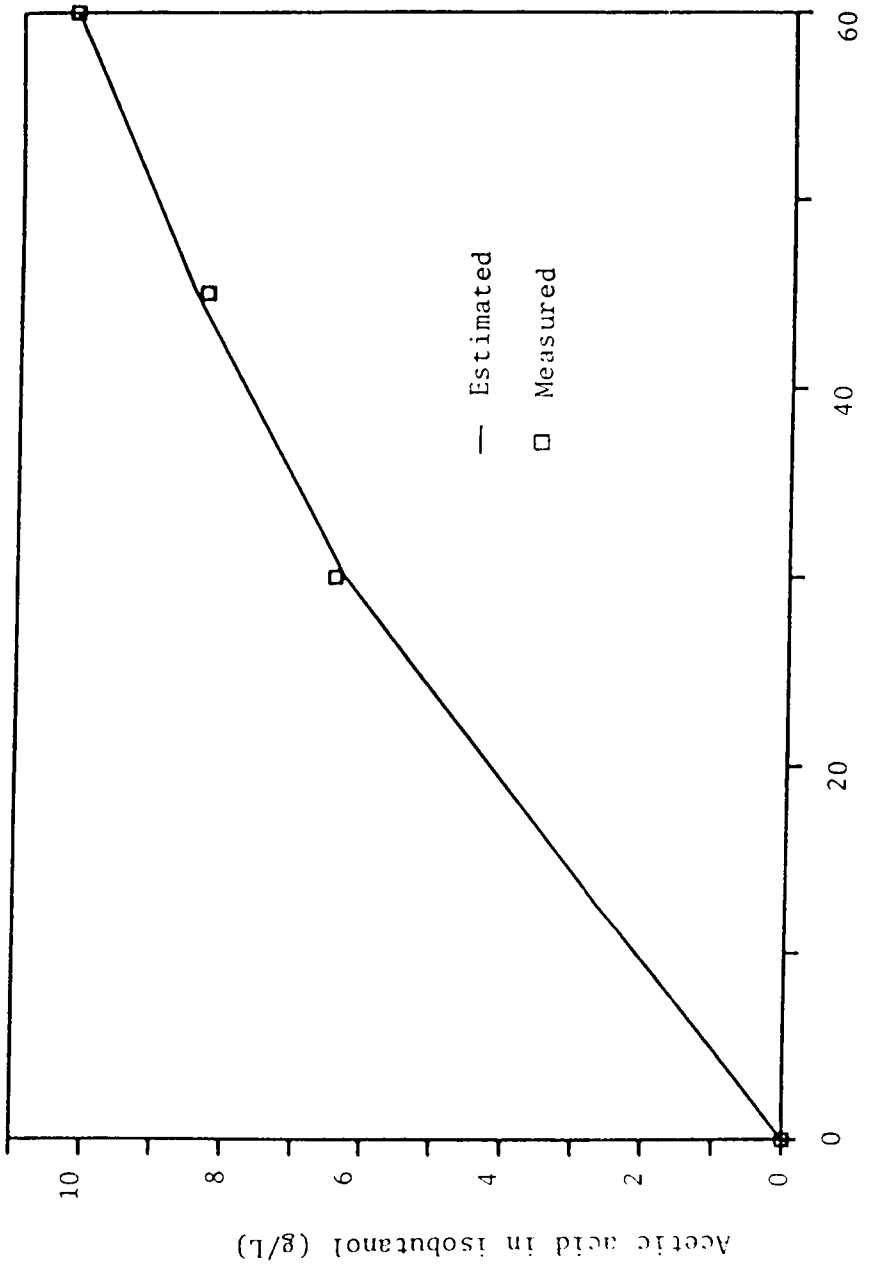


Figure 5.2. Acetic acid in water and isobutanol, test Acid19.

5.1.3. Acetic Acid Data Analysis

Acetic acid data analysis consisted of two primary efforts. First, it was necessary to ascertain which process variables had the greatest affect on the acetic acid mass transfer rate. Second, it was necessary to relate the individual mass transfer coefficient to the overall mass transfer coefficient.

5.1.3.1. Half normal plot. The Half Normal Plot was used to ascertain which of the process and/or system parameters had the greatest affect on the acetic acid mass transfer rate. Figure 5.3 shows the results of the Half Normal Plot. The Half Normal Plot was prepared from the least-square-means of the data set shown in Table 5.1.

Table 5.1. Acetic acid aqueous phase overall mass transfer coefficient.

		Overall Mass Transfer Coefficient (cm/s)			
	Phase	Mixer Diameter			
Area	Volume	d_{a1},d_{o1}	d_{a2},d_{o1}	d_{a1},d_{o2}	d_{a2},d_{o2}
S_1	V_{a1},V_{o1}	0.000036	X	X	0.000956
	V_{a2},V_{o1}	X	0.000604	0.000925	X
	V_{a1},V_{o2}	X	0.000215	0.000771	X
	V_{a2},V_{o2}	0.000057	X	X	0.001151
S_2	V_{a1},V_{o1}	X	0.000083	0.000878	X
	V_{a2},V_{o1}	0.000092	X	X	0.001019
	V_{a1},V_{o2}	0.000034	X	X	0.000774
	V_{a2},V_{o2}	X	0.001055	0.000872	X

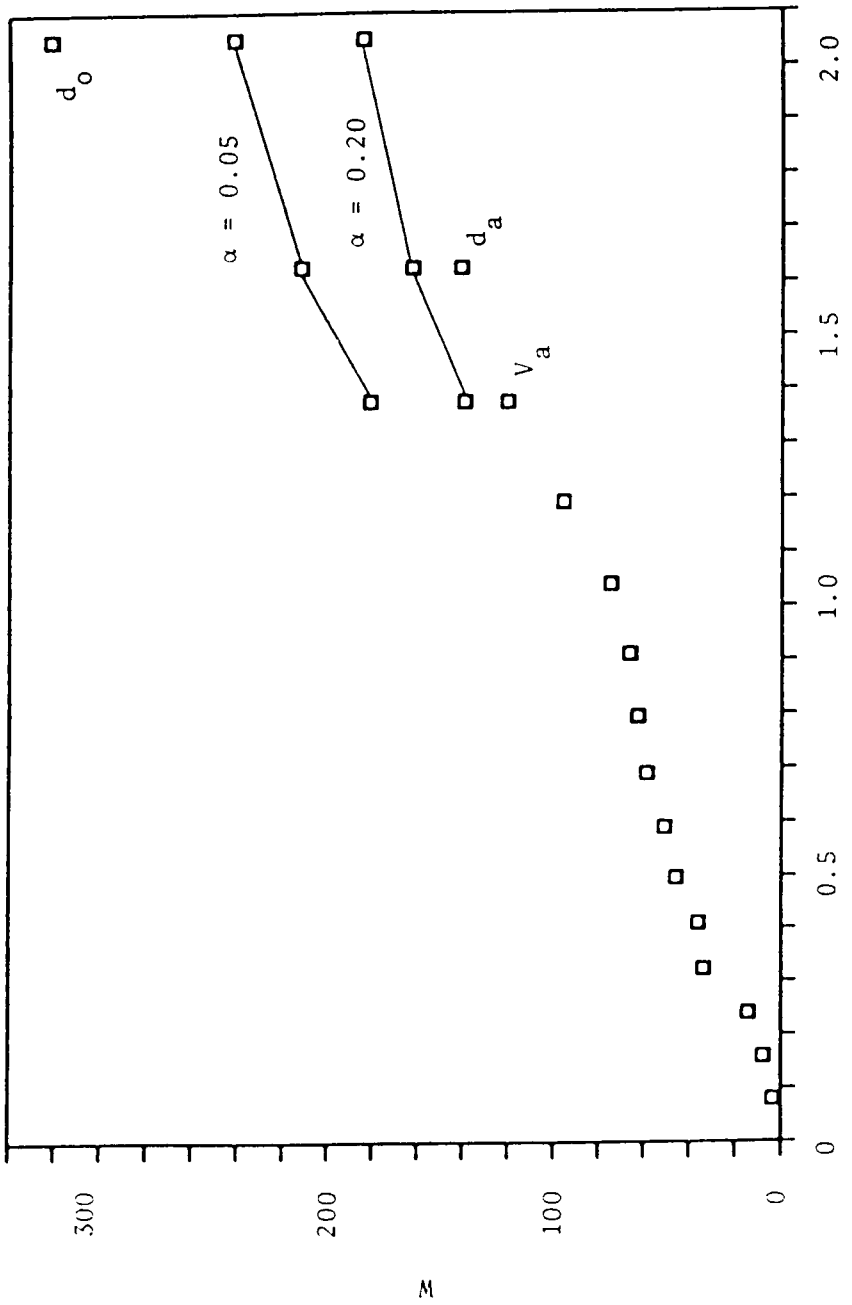


Figure 5.3. Half normal plot, acetic acid test.

The least-square-mean is the expected value of a class (effect of interest), for a balanced design with all covariates (other effects) at their mean value, see Searle et al. (1980). The details of preparing the Half Normal Plot can be found in Appendix A.2.3. Figure 5.3 demonstrates clearly the organic mass transfer coefficient has the greatest affect on the acetic acid mass transfer rate. In fact, the organic mass transfer coefficient has a significant affect on the acetic acid mass transfer rate at the 0.05 significance level. This implies five out of one hundred tests would not detect signficance.

5.1.3.2. Mass transfer coefficient correlation. The physical properties of the acetic acid, water, and isobutanol system are shown in Table 5.2. The diffusion coefficients were estimated via the Wilke-Chang correlation. Viscosities were obtained from the data based correlation published in Reid, Prausnitz and Sherwood (1977). These properties were required to correlate the individual mass transfer coefficient.

It was determined from the Half Normal Plot, the primary resistance to acetic acid mass transfer was in the isobutanol phase. This allowed simplification of the individual mass transfer coefficient correlation. The correlation used to relate the individual and overall mass transfer coefficient is based on the surface renewal form of the penetration theory, and proposed by Bulicka and Prochazka (1976). The surface renewal form predicts the individual mass transfer coefficient is related to the Schmidt number to the one half power.

Table 5.2. Acetic acid, water, and isobutanol properties.

Property	Value at 25°C
Water:	
viscosity (g/cm-s) -	0.008906
density (g/cm^3) -	1.00
mole wt. (g/gmole) -	18.00
association factor -	2.6
Isobutanol:	
viscosity (g/cm-s) -	0.01706
denisty (g/cm^3) -	0.80
mole wt. (g/gmole) -	74.12
association factor -	1.25
Acetic acid:	
diffusion coefficient;	
water (cm^2/s) -	0.0000014
isobutanol (cm^2/s) -	0.0000010

The correlation shown below as Eq. (5.1), relates the Sherwood number to the Reynolds and Schmidt number. The constants "p" and "q" have

$$N_{Shj} = p(N_{Rej})^q(N_{Scj})^{1/2}$$

or

$$k_j = p(D^f/d_j)(N_{Rej})^q(N_{Scj})^{1/2}. \qquad (5.1)$$

been determined from the acetic acid overall mass transfer coefficients via a linear regression. Since the resistance to mass transfer was found to be primarily in the organic phase,

$$1/K_{oa} = 1/(D_s\ k_o).$$

This regression is detailed in Appendix A.2.4, the constants were found to be p = 0.0000934 and q = 1.38. The regression correlation in terms of Sherwood and Reynolds numbers is shown in Figure 5.4. The mass transfer coefficient units per the above correlation are cm/s. The final expression can be written as:

$$k_j = 0.0000934(D^f/d_j)(N_{Rej})^{1.38}(N_{Scj})^{1/2}, \qquad (5.2)$$

where k_j(cm/s), D^f(cm^2/s), d_j(cm).

Using Equation 5.2, the ratio of acetic acid isobutanol individual mass transfer coefficient to aqueous mass transfer coefficient (k_a/k_o) is calculated to be 2.5.

5.2 Zirconium Transfered from Water Plus Nitric Acid to TBP Plus Dodecane.

5.2.1. Metal Complex Distribution Coefficient and Complexation Equalibrium Constant

The zirconium distribution coefficient for the complexed specie, and the equilibrium constant for the complexation reaction, were calculated from data existing in the literature. The distribution coefficent D_4, and equilibrium constant (K^f/K^b), were linearly regressed from the data as shown in the Theoretical section, Eq. (4.14). The data utilized are listed in Appendix A.1.1 along with their references. The regression was performed over a nitric acid concentration range of approximately 2 M (0.002 mol/ml) to 4 M (0.004 mol/ml), and TBP concentration range of 10 vol % (0.37 M or 0.00037 mol/ml) to 25 vol % (0.92 M or 0.00092 mol/ml). These conditions were similar to those of this study.

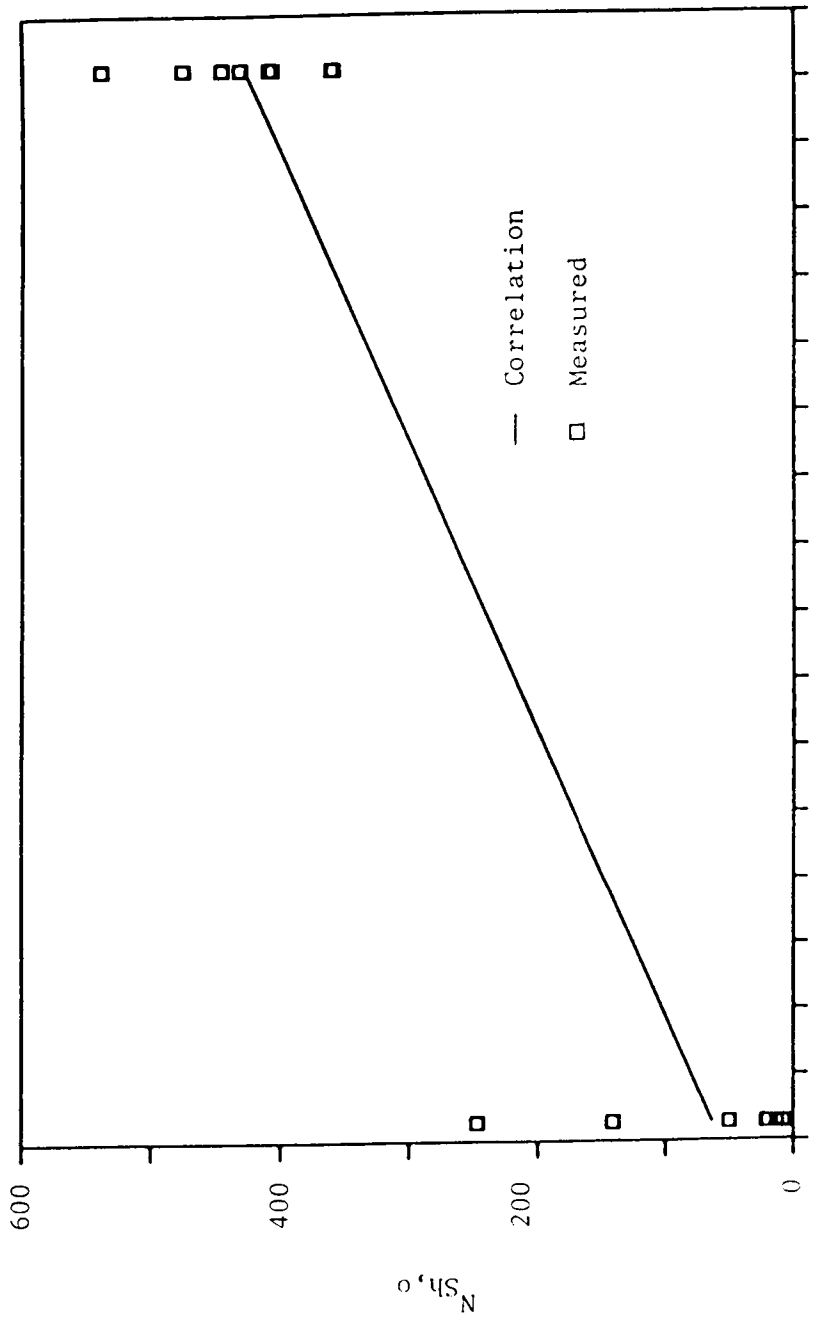


Figure 5.4. Individual mass transfer coefficient correlation for stirred cell.

Figure 5.5 shows the result of the linear regression for the determination of D_4 and (K^f/K^b), for the zirconium complex $Zr(NO_3)_4 \cdot 2TBP$ as detailed in Section 4.2.4. Based on Equation 4.14, it was determined that:

$$(1/D_{Zr}) = \frac{(1.1x10^{-22})}{[NO_3^-(0)]^4(TBP)^2} + 2.87, \qquad (5.3)$$

where units of NO_3^- and TBP concentration are mole/ml,

and D_4=0.35,

(K^f/K^b)=[1/(3.69x10^{-23})](mole/ml)^6,

and units of K^f are [(mole/s)(ml/mole)^7] and K^b are (ml/s).

Several equilbrium tests were conducted during this study to validate the Equation 5.3. Two of these equilibrium tests are shown in Figure 5.5. The details of this regression are reported in Appendix A.3.1.

5.2.2. Zirconium Mass Transfer Data

The zirconium mass transfer data collected are reported in terms of colormetric peak height, shown in Appendix A.3.2. Each test consisted of organic phase zirconium samples collected at two, four and six hours. In general, at six hours the zirconium had reached about 2/3 of its organic equilibrium concentration. The total mass of zirconium accumulated in the organic phase at each of the time intervals is listed in Tables 5.3 and 5.4, in units of (g).

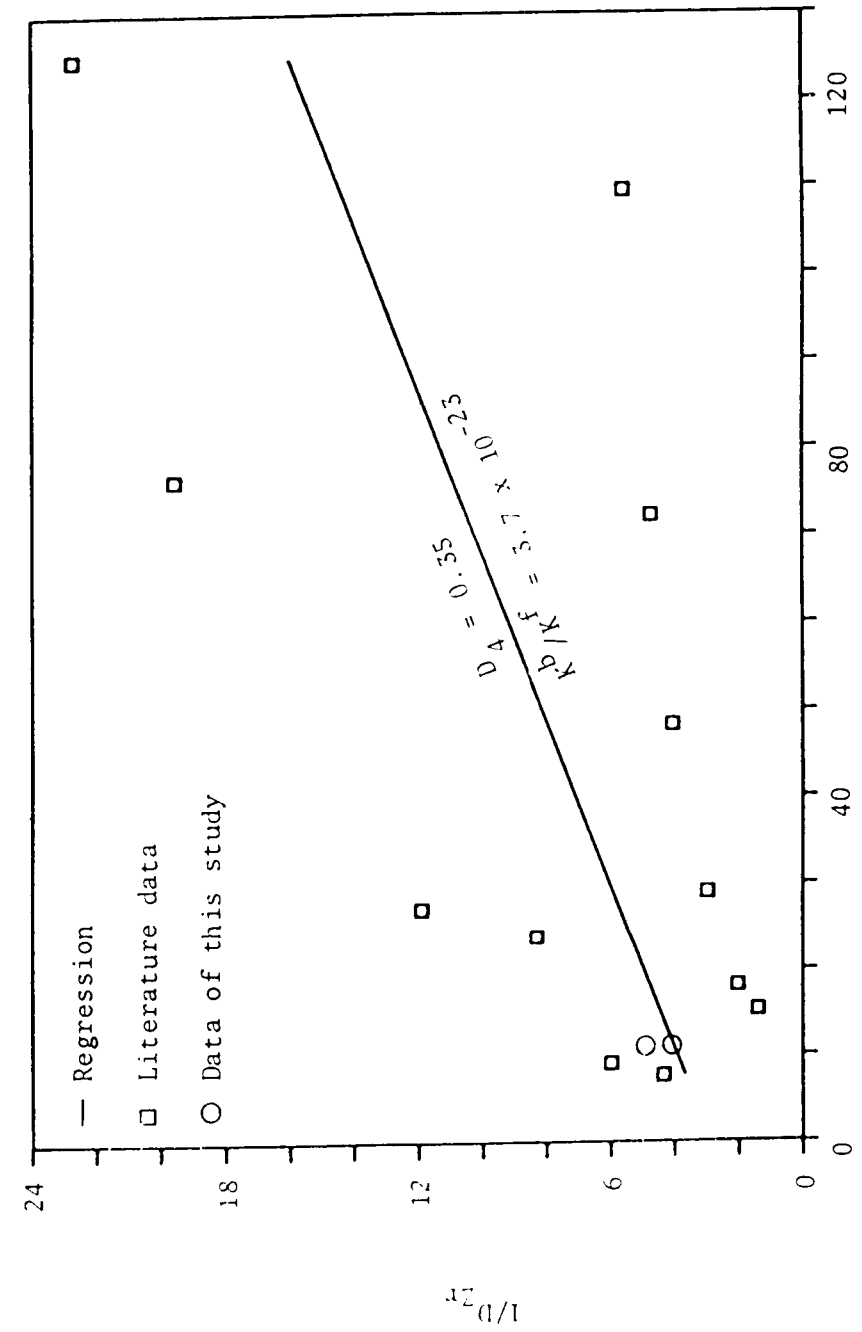


Figure 5.5. Zirconium metal complex distribution coefficient.

Table 5.3. Accumulated zirconium in organic phase for interfacial area, phase volume, and mixer diameter changes.

Area	Phase Volume	Hr	Mass Transfered (g x 10^5) Zr Specified by Mixer Diameter d_{a1}, d_{o1}	d_{a2}, d_{o1}	d_{a1}, d_{o2}	d_{a2}, d_{o2}
S_1	V_{a1}, V_{o1}	2	46	X	X	271
		4	88			403
		6	140			570
	V_{a2}, V_{o1}	2	X	130	147	X
		4		243	269	
		6		321	356	
	V_{a1}, V_{o2}	2	X	75	139	X
		4		115	252	
		6		166	337	
	V_{a2}, V_{o2}	2	66	X	X	250
		4	115			454
		6	166			607
S_2	V_{a1}, V_{o1}	2	X	177	389	X
		4		306	531	
		6		423	619	
	V_{a2}, V_{o1}	2	137	X	X	280
		4	268			445
		6	281			612
	V_{a1}, V_{o2}	2	76	X	X	319
		4	145			520
		6	206			632
	V_{a2}, V_{o2}	2	X	194	240	X
		4		373	421	
		6		410	532	

Note: Numerical values are accumulated zirconium (g x 10^5) in the organic phase.

Table 5.4. Accumulated zirconium in organic phase for concentration changes.

Conditions	Time(hr)	Zr g x 10^5
$S_2, V_{a1}, V_{o1}, d_{a2}, d_{o2}, C_{a1}, C_{a2}, C_{o3}$	2	399
	4	510
	6	629
$S_2, V_{a1}, V_{o1}, d_{a2}, d_{o2}, (C_{a1}/2), C_{a2}, C_{o3}$	2	133
	4	173
	6	240
$S_2, V_{a1}, V_{o1}, d_{a2}, d_{o2}, C_{a1}, (C_{a2}/2), C_{o3}$	2	70
	4	113
	6	133
$S_2, V_{a1}, V_{o1}, d_{a2}, d_{o2}, C_{a1}, C_{a2}, (C_{o3}/2)$	2	136
	4	187
	6	216

5.2.3. Zirconium Data Analysis

5.2.3.1. Half normal plots and concentration affect. The interfacial area, phase volume, and mixer diameter effects which most significantly affected mass transfer were determined via a Half Normal Plot applied to the balanced data of Table 5.3. Details of the Half Normal Plot analysis are recorded in the Appendix A.3.3. The Half Normal Plots for the zirconium accumulated in the organic phase at two, four and six hours are shown as Figures 5.6, 5.7 and 5.8 respectively. Effects which lie above the significance curves are significant at that level. The results of these plots for the four most significant effects have been summarized in Table 5.5. It can be seen the variation of interfacial area and organic mixer diameter (organic mass transfer coefficient) were the most significant effects, while the aqueous mixer diameter and the (aqueous volume)-(organic mixer diameter) interaction were significant to a lessor degree. The relative significance of these four effects can be judged by the sum-of-squares shown in Table 5.6.

The affect of Zr^{4+}, NO_3^-, and TBP concentration on the mass transfer rate was demonstrated by single tests, rather than a statistical experimental design such as Table 5.3. Figure 5.9 shows the affect of these concentrations on zirconium accumulated in the organic phase. Figure 5.10 compares the organic phase metal complex individual mass transfer coefficient calculated from the zirconium data assuming instantaneous chemical reaction (i.e. equilibrium), with the predicted mass transfer coefficient estimated by Equation 5.2. Appendix A.3.9 details the model for instantaneous reaction.

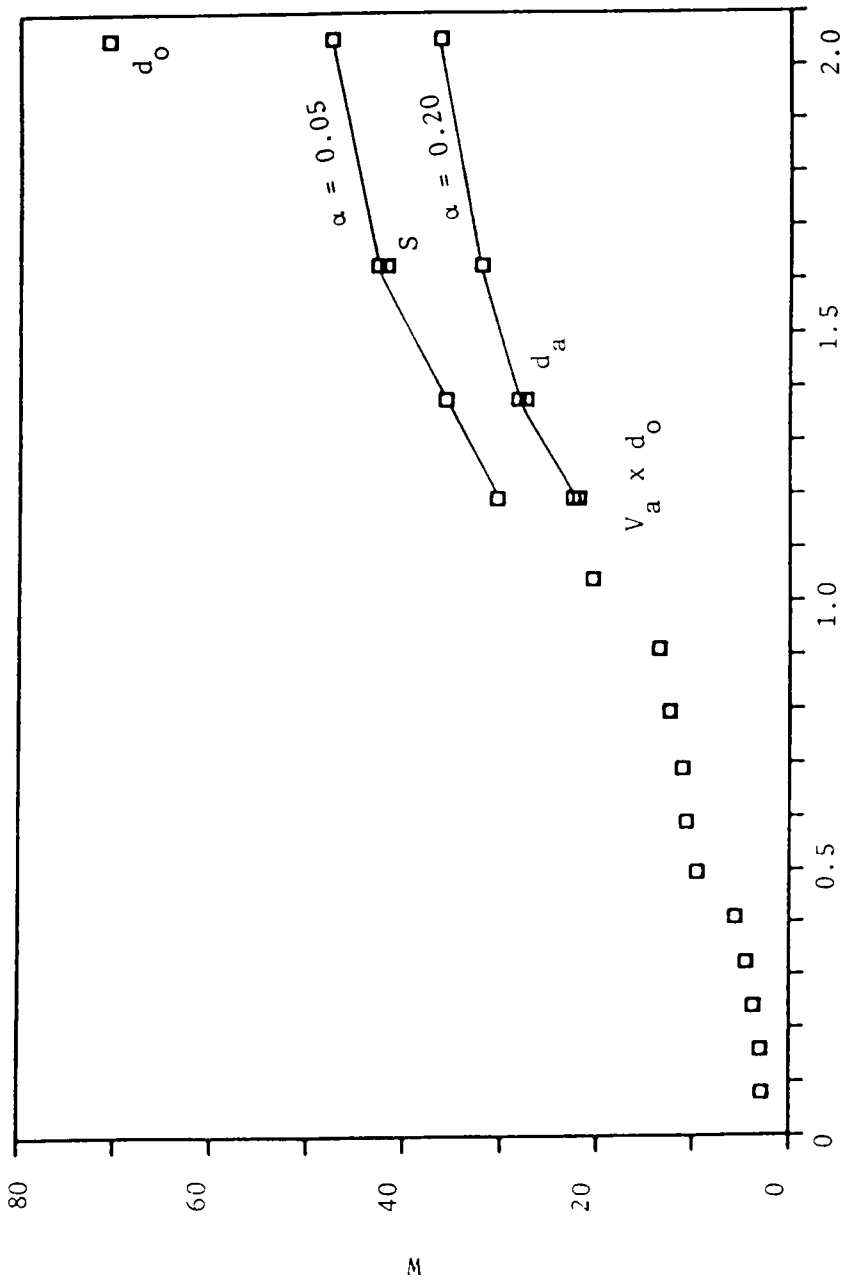


Figure 5.6. Half normal plot, zirconium test at two hours.

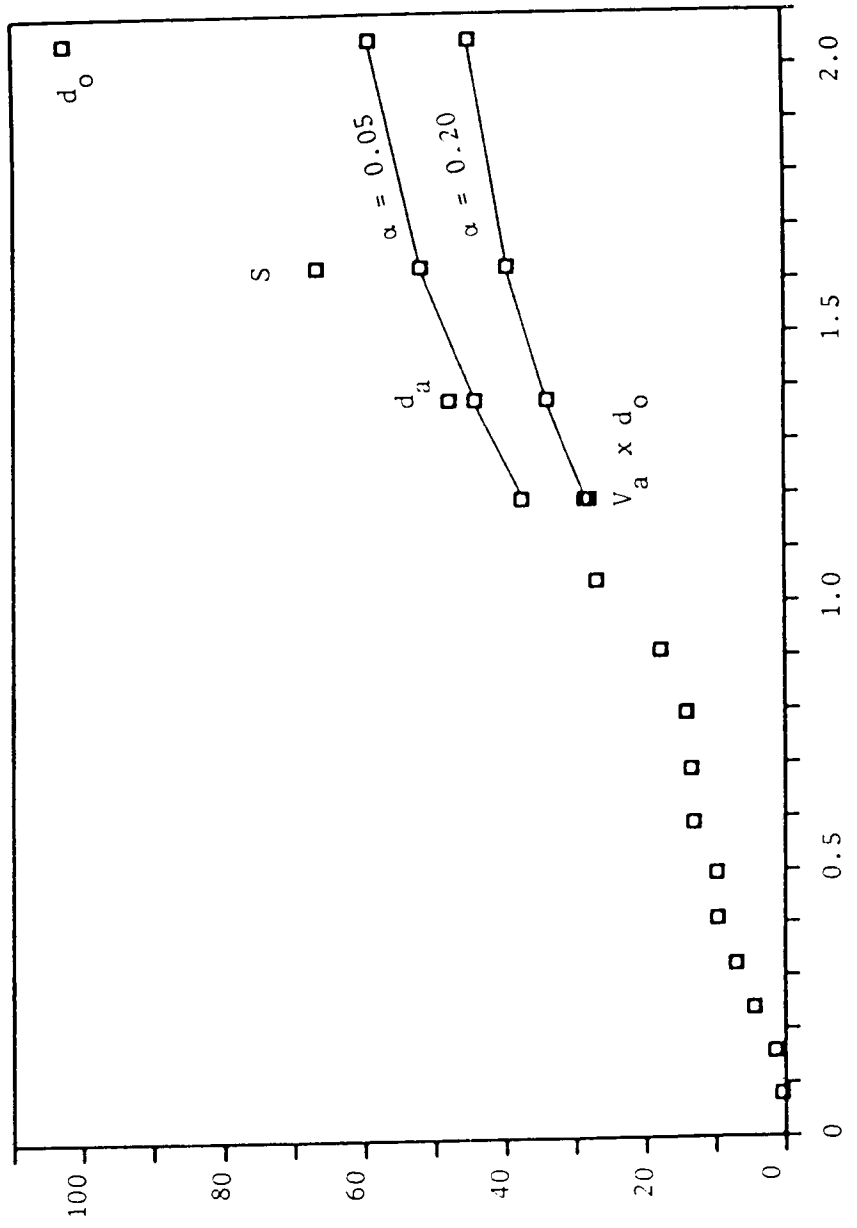


Figure 5.7. Half normal plot, zirconium test at four hours.

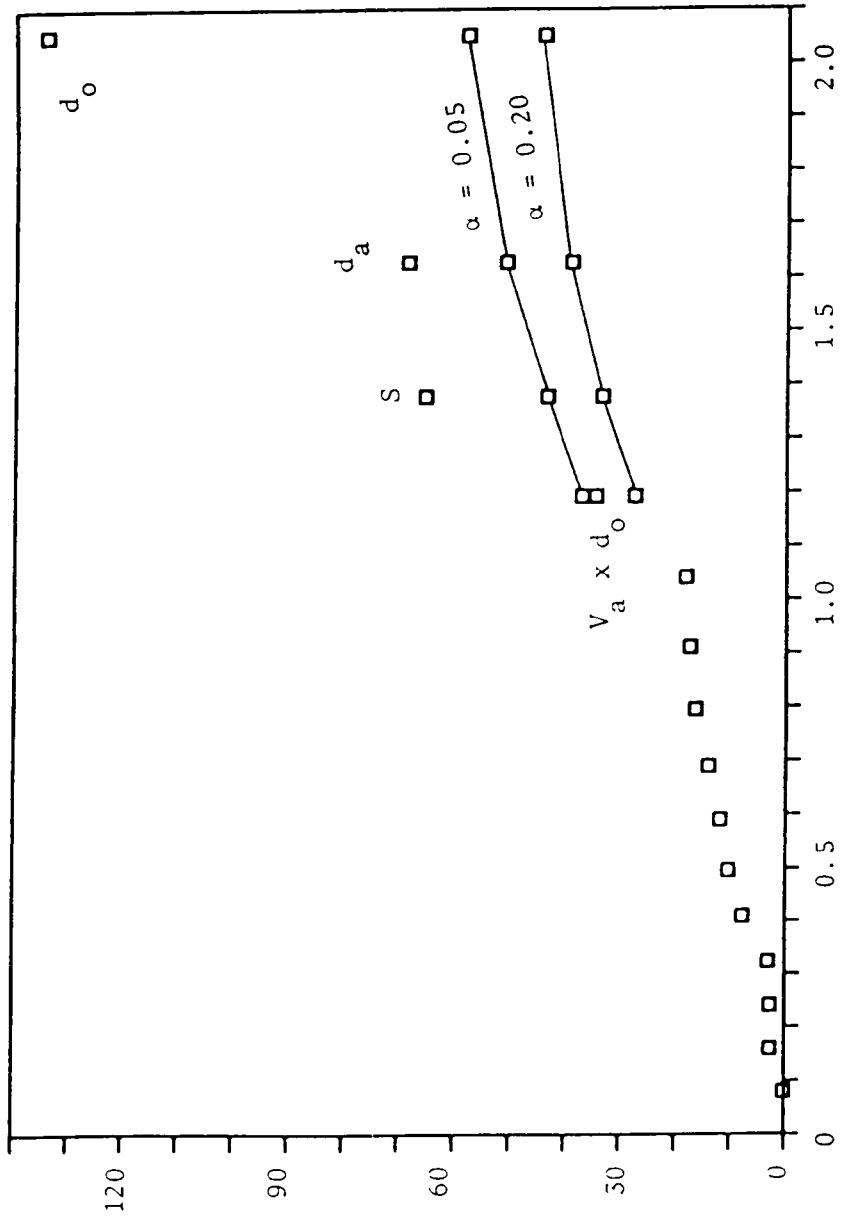


Figure 5.8. Half normal plot, zirconium test at six hours.

Table 5.5. Suumary of zirconium half normal plots.

	Time(hr)					
	2		4		6	
	Significance Level					
Affect	0.05	0.20	0.05	0.20	0.05	0.20
d_o	Yes	Yes	Yes	Yes	Yes	Yes
S	No	Yes	Yes	Yes	Yes	Yes
d_a	No	No	Yes	Yes	Yes	Yes
V_a*d_o	No	No	No	No	No	Yes

Note: Yes indicates affect was significant at particular level.

Table 5.6. Sum-of-squares for zirconium mass transfer data.

	Time(hr)		
	2	4	6
Affect	(Sum-of-the Squares)x10^{12}		
d_o	80372	168510	289444
S	29584	71556	69169
d_a	12996	37056	76176
V_a*d_o	7832	13340	5402

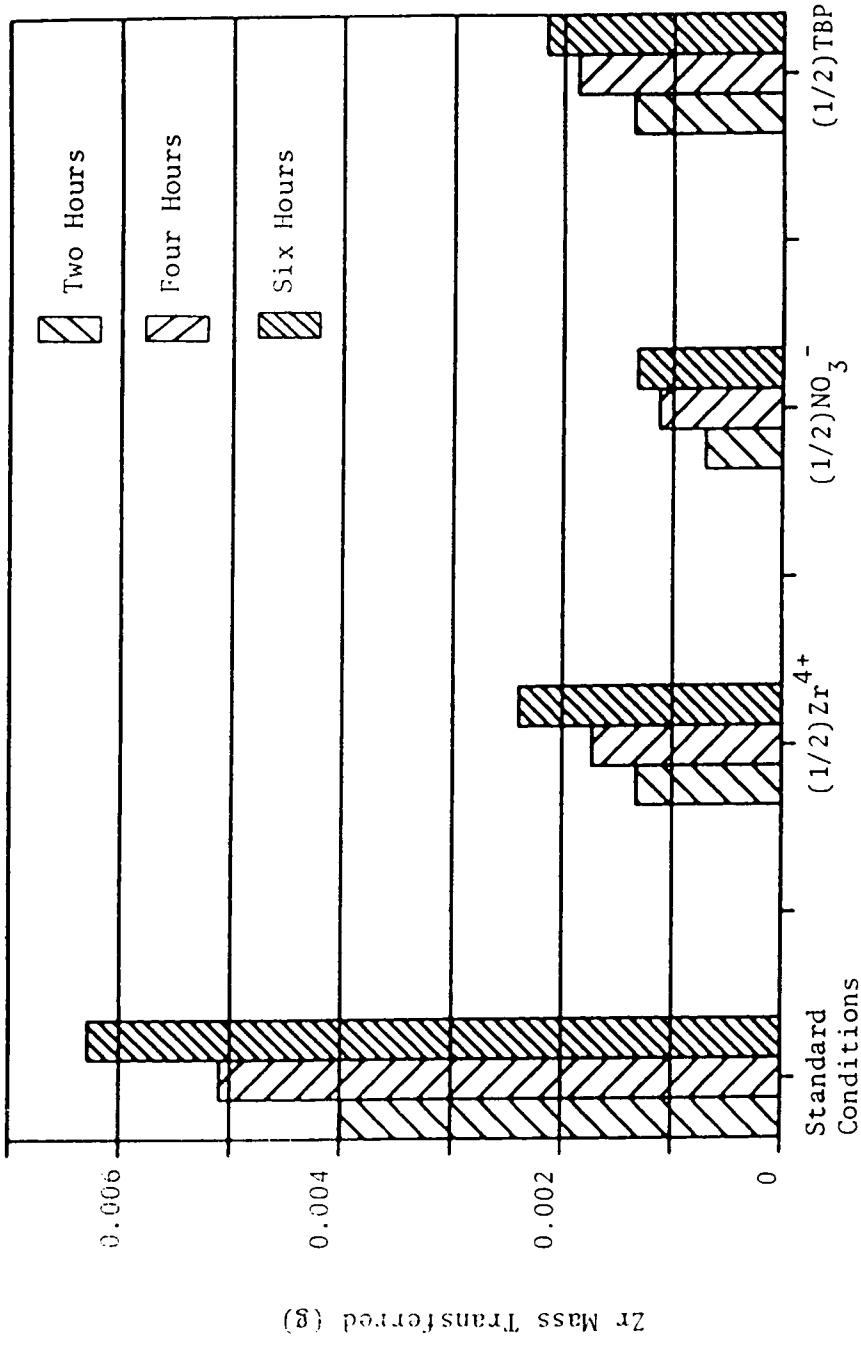


Figure 5.9. Concentration affect on mass transferred.

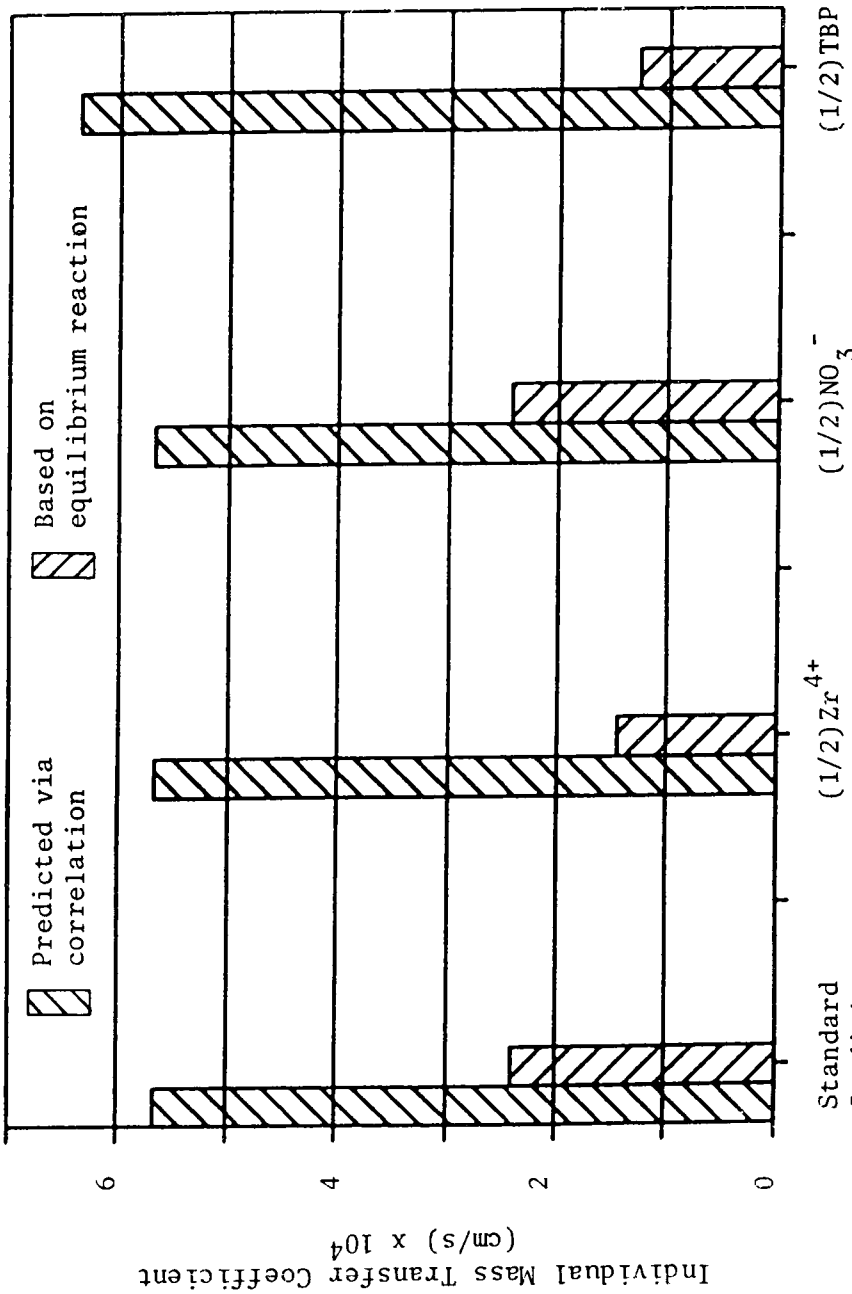


Figure 5.10. Concentration affect on mass transfer coefficient assuming equilibrium reaction.

5.2.3.2. Diffusion and mass transfer coefficients. To regress from data the forward complexation reaction rate constant, it was necessary to estimate the metal complex individual mass transfer coefficients. These mass transfer coefficients were estimated via the Sherwood - Reynolds - Schmidt number correlation of Equation 5.2. It was necessary to determine diffusion coefficients in order calculate a mass transfer coefficient for the zirconium system. The aqueous diffusion coefficients were estimated via the Wilke-Chang correlation, and TBP-dodecane diffusion coefficients were estimated via Lusis-Ratcliff correlation per Reid, Prausnitz and Sherwood (1977). Appendix A.3.4 shows the details of the diffusion coefficient calculations. Diffusion coefficients for the important species are shown in Table 5.7.

Once the diffusion coefficients had been estimated, the mass transfer coefficients could be calculated per Equation 5.2. Table 5.8 displays the mass transfer coefficients of the important species. Appendix A.3.5 details the calculations used to estimate the individual mass transfer coefficients for the zirconium-Purex system of this study.

5.2.3.3. Regression. To perform a regression analysis from balanced data, it was decided to include data involving the change of each variable included in the overall model. These variables were (1) interfacial area, (2) aqueous phase volume, (3) organic phase volume, (4) aqueous mass transfer coefficient, (5) organic mass transfer coefficient, (6) Zr^{4+} initial aqueous concentration, (7) NO_3^- initial

Table 5.7. Diffusion coefficients.

Specie	Diffusion Coefficient (cm^2/s) Phase aqueous	Phase 30 vol% TBP in dodecane
TBP	0.00000508	0.00000625
$Zr(NO_3)_4.2TBP$	0.00000289	0.00000468

Table 5.8. Individual mass transfer coefficients.

Specie	Individual Mass Transfer Coefficient (cm/s) 3 M HNO_3 aqueous		30 vol% TBP in dodecane	
	Mixer Diameter(cm) 3	6	3	6
TBP	0.000335	0.001135	---	---
$Zr(NO_3)_4.2TBP$	0.000254	0.000860	0.000167	0.000567
$Zr(NO_3)_4.2TBP$	---	---	0.000188*	0.000636*

* - 15 vol% TBP in dodecane.

aqueous concentration and (8) TBP initial organic concentration. This involved nine data sets including the standard conditions from which the conditions were varied. For reasons detailed in the Discussion section, only data at two hours were included in the regression. Table 5.9 indicates which data sets were included.

The purpose of the regression analysis was to determine K^f based upon aprior estimation of D_4, K^f/K^b, and k_{o4}. A weighted regression analysis was used, and is discribed in Appendix A.3.6. The results of the regression yielded,

$$K^f = 6.5 \times 10^{21} \ [(\text{mole/s})(\text{ml/mole})^7],$$

with an average error of 24% of the predicted value, and 1.1×10^{-14} $(\text{mole/ml})^2$ variance, for the organic $Zr(NO_3)_4.2TBP$ concentration.

5.2.3.5. Model results. The organic phase metal complex concentration data used for regression, along with predicted concentrations for all aqueous and organic zirconium species based on Equations 4.22, 4.23 and 4.24, are shown Figures 5.11 through 5.19. Figure 5.11 shows the concentration over time for the three zirconium species ($[Zr^{4+}]_a$,$[Zr(NO_3)_4 \cdot 2TBP]_a$, and $[Zr(NO_3)_4 \cdot 2TBP]_o$) at standard conditions of (S_2,V_{a1},V_{o1},k_{a2},k_{o2},C_{a1},C_{a2},C_{o3}). Figures 5.12 through 5.14 display the concentration versus time for the three zirconium species when standard conditions are altered by decreasing the initial concentrations of Ca1, Ca2, and Co3, by one half.

Figure 5.15 shows the zirconium concentration profiles and measured data for the interfacial area change from 79 cm^2 to 62 cm^2.

Table 5.9. Data included for K^f regression.

Area	Phase Volume	Data Sets Included in Regression d_{a1}, d_{o1}	d_{a2}, d_{o1}	d_{a1}, d_{o2}	d_{a2}, d_{o2}
S_1	V_{a1}, V_{o1}	X	X	X	1
	V_{a2}, V_{o1}	X	X	X	X
	V_{a1}, V_{o2}	X	X	X	X
	V_{a2}, V_{o2}	X	X	X	X
S_2	V_{a1}, V_{o1}	X	2	3	4
	V_{a2}, V_{o1}	X	X	X	5
	V_{a1}, V_{o2}	X	X	X	6
	V_{a2}, V_{o2}	X	X	X	X
	$S_2, V_{a1}, V_{o1}, d_{a2}, d_{o2}, (C_{a1}/2), C_{a2}, C_{o3}$				7
	$S_2, V_{a1}, V_{o1}, d_{a2}, d_{o2}, C_{a1}, (C_{a2}/2), C_{o3}$				8
	$S_2, V_{a1}, V_{o1}, d_{a2}, d_{o2}, C_{a1}, C_{a2}, (C_{o3}/2)$				9

Note: Numerical values indicate one of nine data sets included in regression.

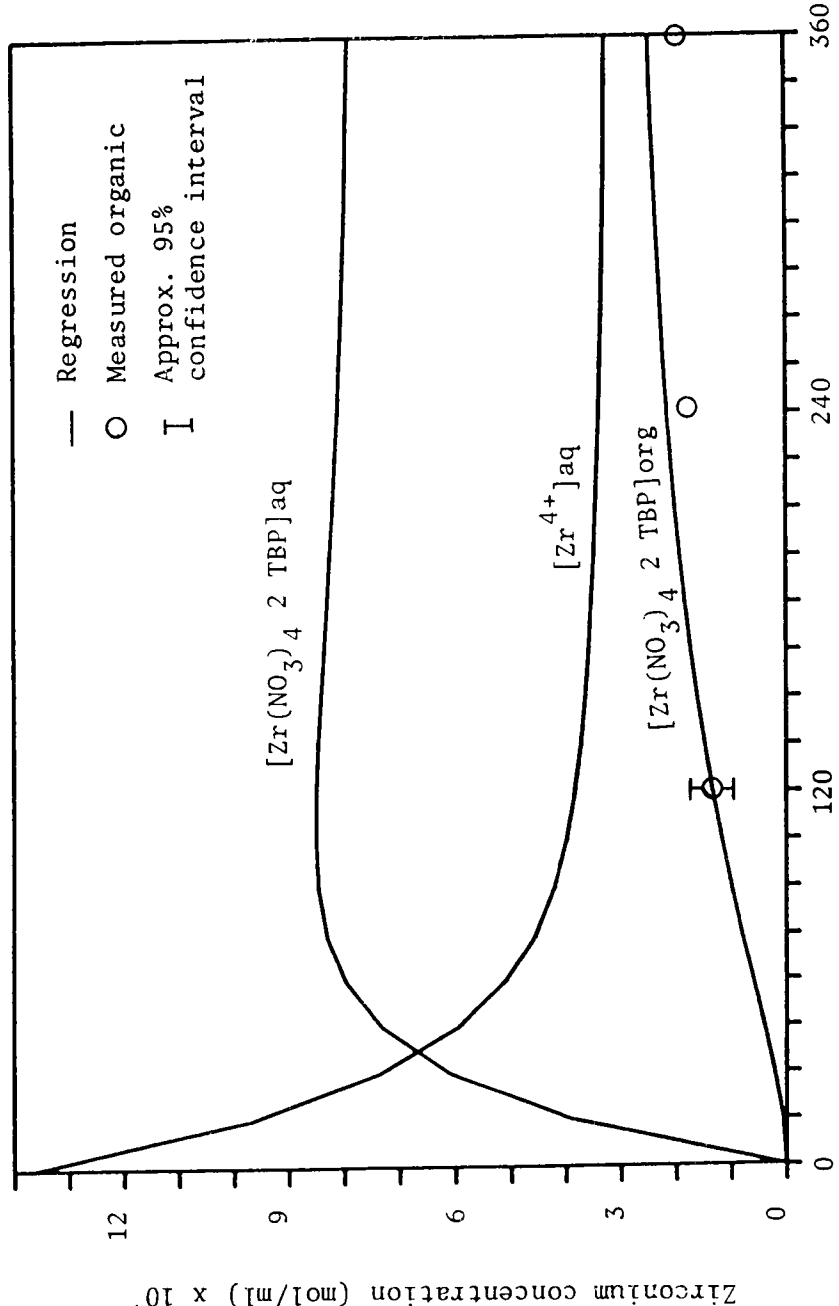


Figure 5.11. Zirconium concentration for S_2, V_{a1}, V_{o1}, d_{a2}, d_{o2}, C_{a1}, C_{a2}, C_{o3}.

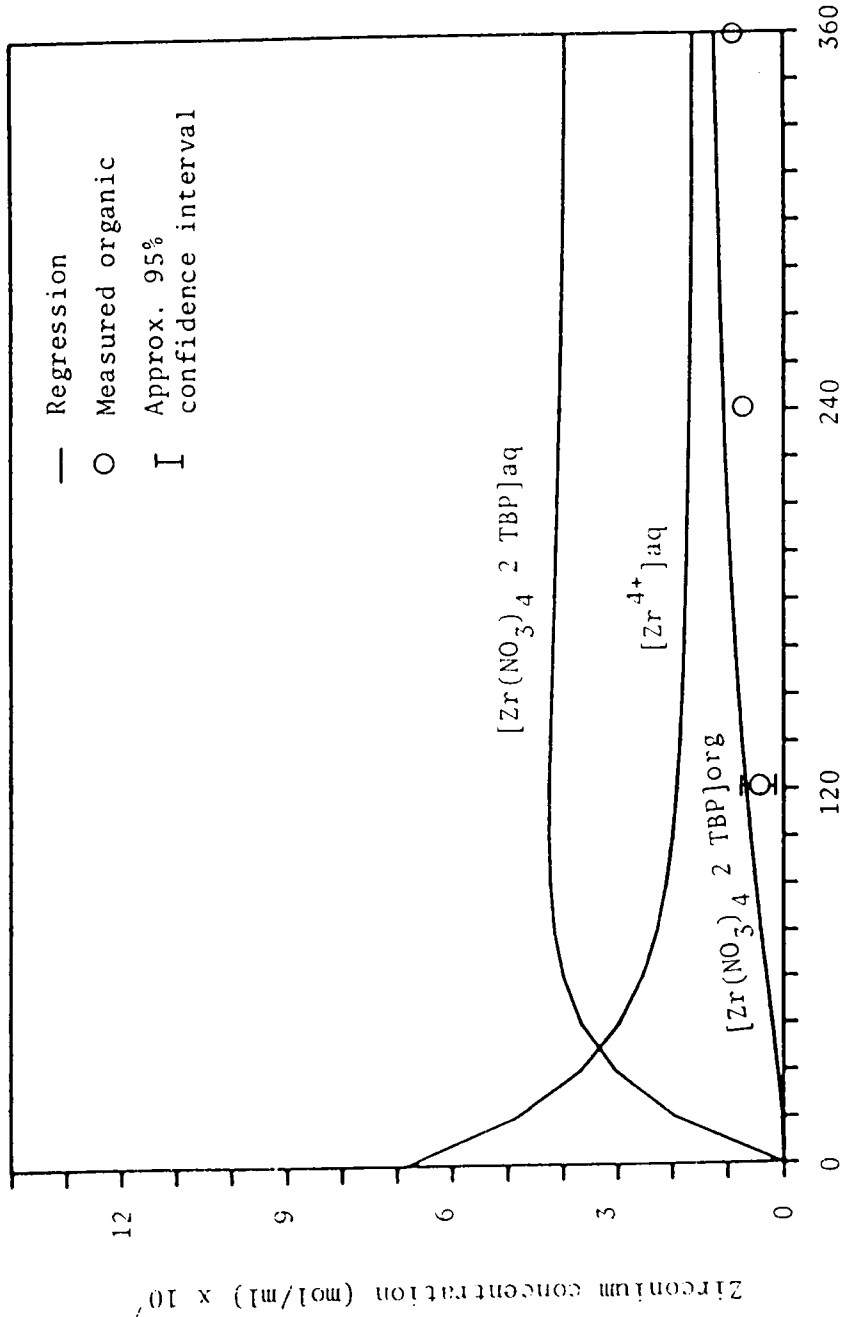


Figure 5.12. Zirconium concentration for S_2, V_{a1}, V_{o1}, d_{a2}, d_{o2}, $C_{a1/2}$, C_{a2}, C_{o3}.

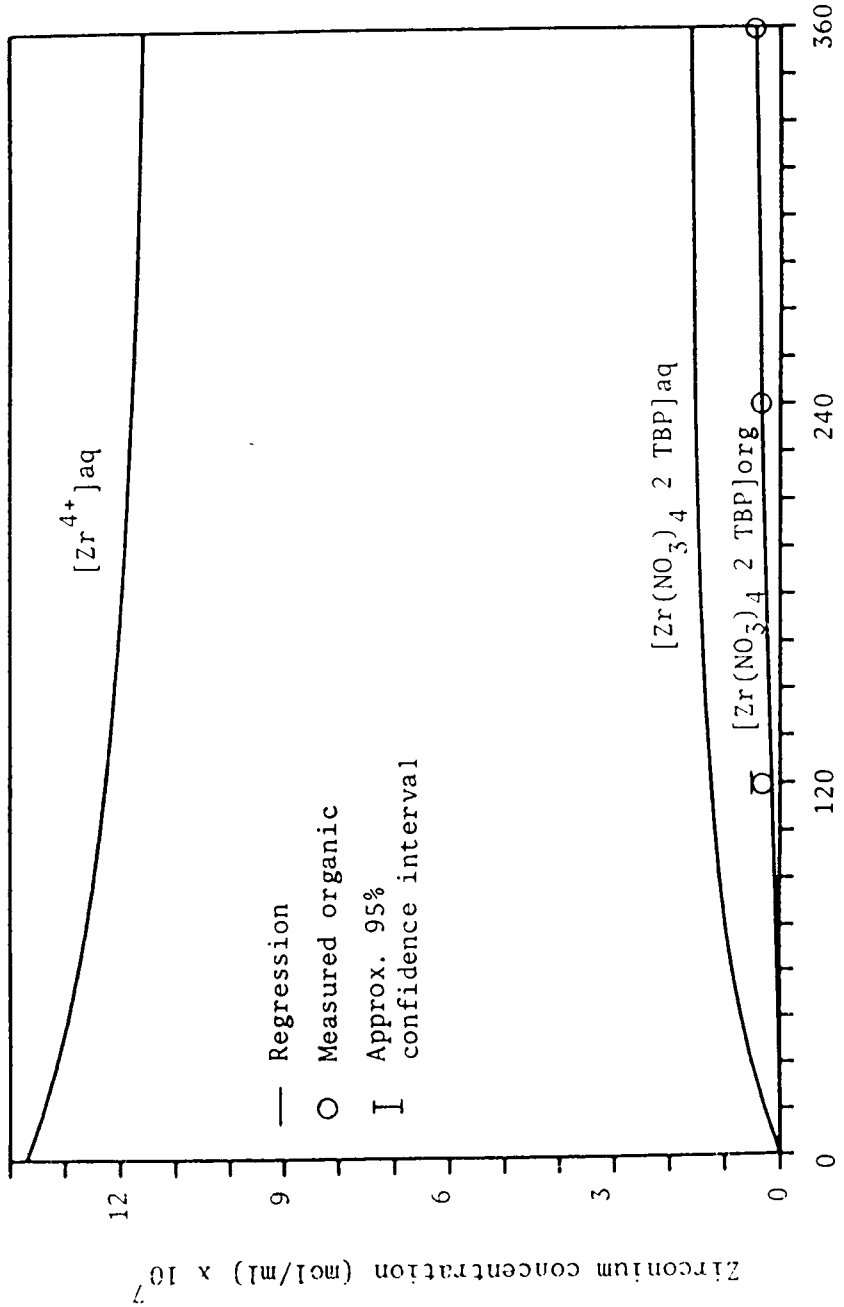


Figure 5.13. Zirconium concentration for S_2, V_{a1}, V_{o1}, d_{a2}, d_{o2}, C_{a1}, $C_{a2/2}$, C_{o3}.

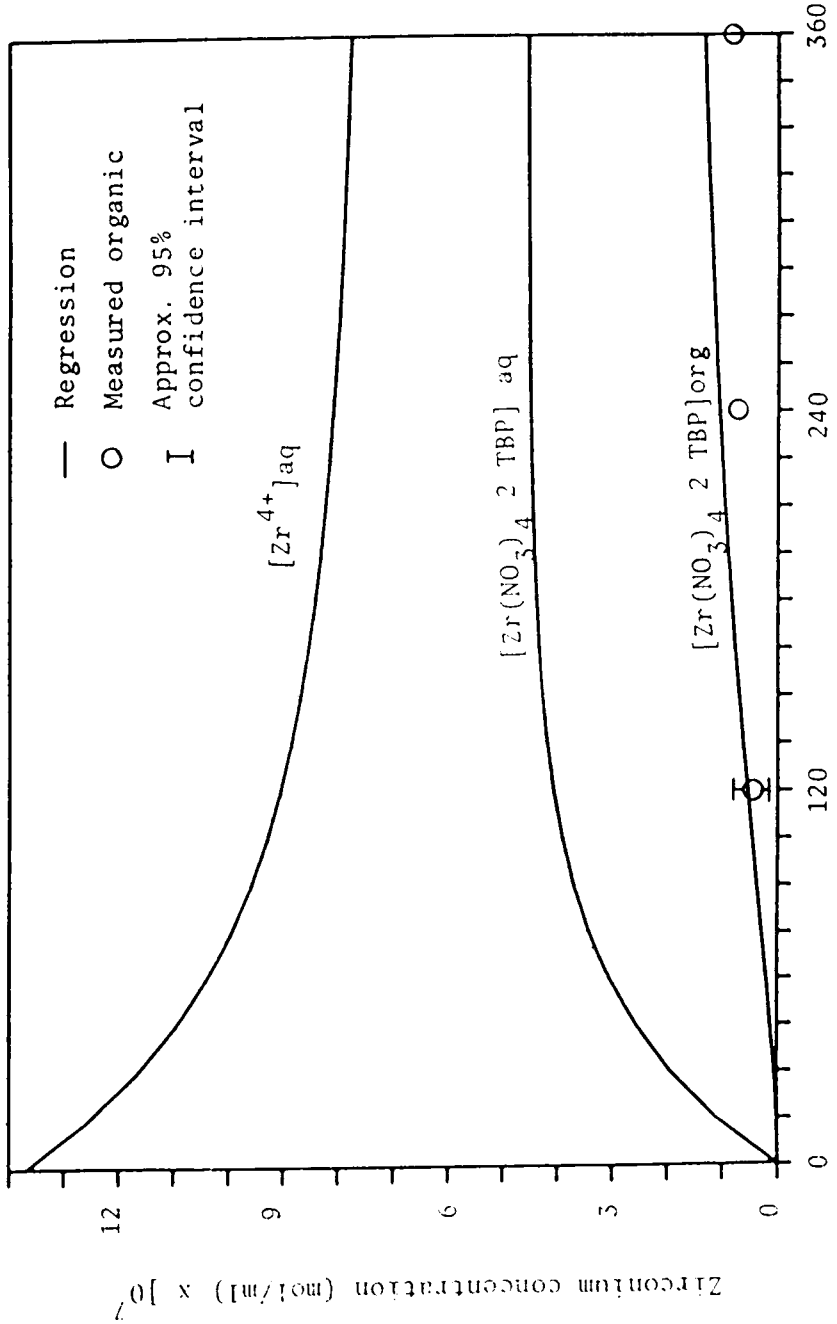


Figure 5.14. Zirconium concentration for S_2, V_{a1}, V_{o1}, d_{a2}, d_{o2}, C_{a1}, C_{a2}, $C_{o3/2}$.

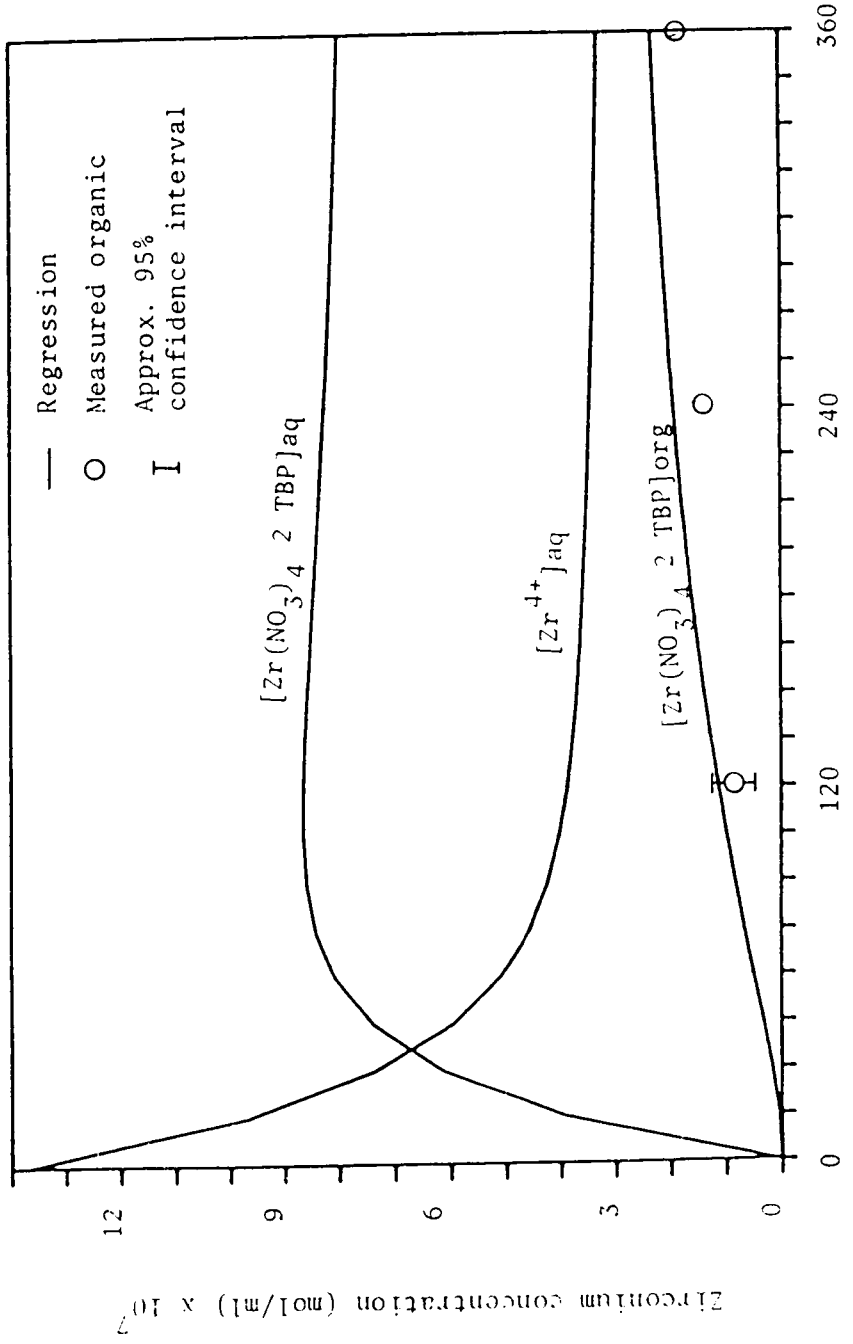


Figure 5.15. Zirconium concentration for S_1, V_{a1}, V_{o1}, d_{a2}, d_{o2}, C_{a1}, C_{a2}, C_{o3}.

Figures 5.16 through 5.19 show the predicted and measured organic metal complex concentration versus time profile. These figures represents the conditions of maximum phase volumes (Figures 5.16 for aqueous and 5.17 for organic), and minimum mass transfer coefficients (Figures 5.18 for aqueous and 5.19 for organic), with otherwise standard conditions.

In Figure 5.11 through 5.19, the approximate 95% confidence interval as described in Appendix A.3.8 is shown for each organic phase metal complex concentration measured at two hours.

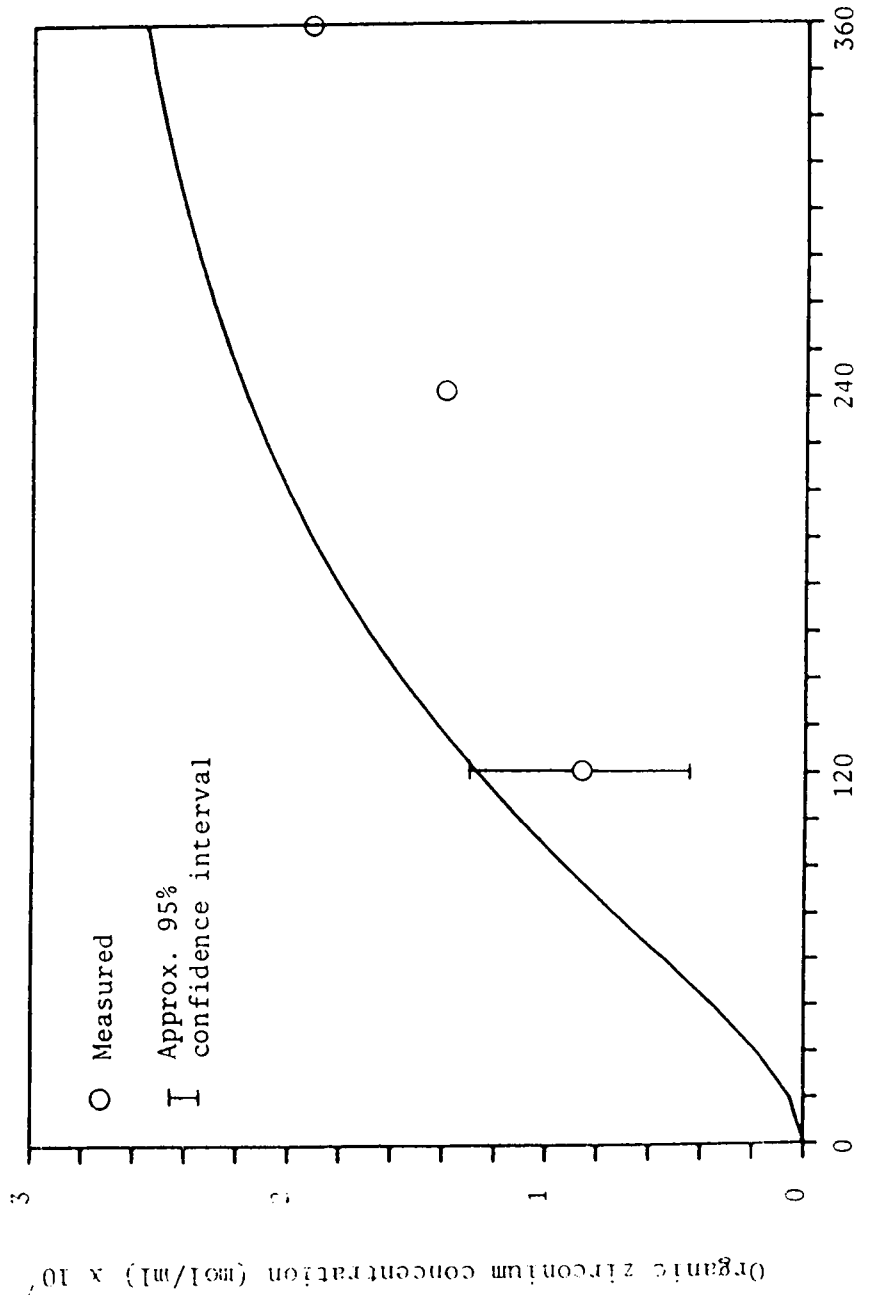


Figure 5.16. Zirconium concentration for S_2, V_{a2}, V_{o1}, d_{a2}, d_{o2}, C_{a1}, C_{a2}, C_{o3}.

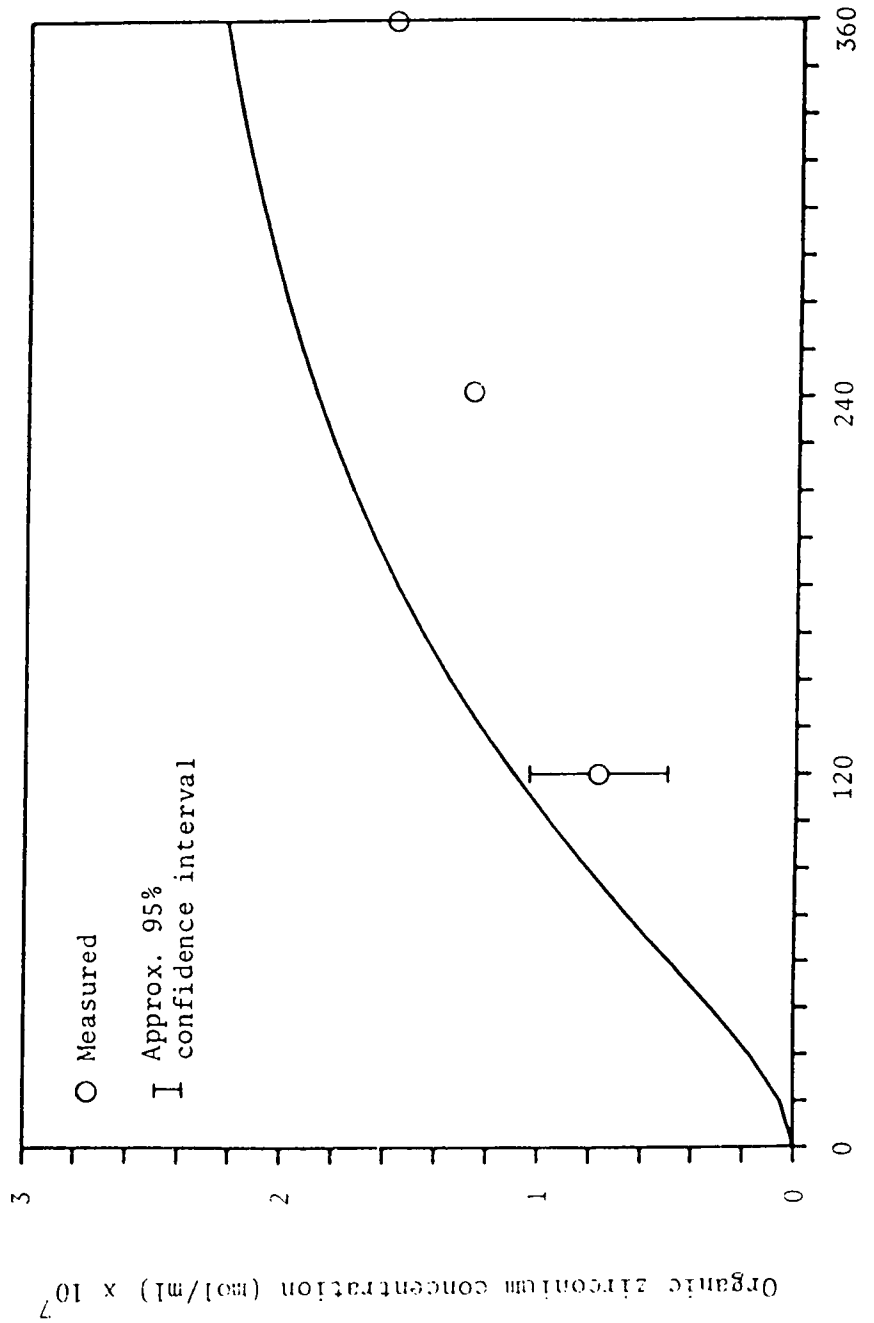


Figure 5.17. Zirconium concentration for S_2, V_{a1}, V_{o2}, d_{a2}, d_{o2}, C_{a1}, C_{a2}, C_{o3}.

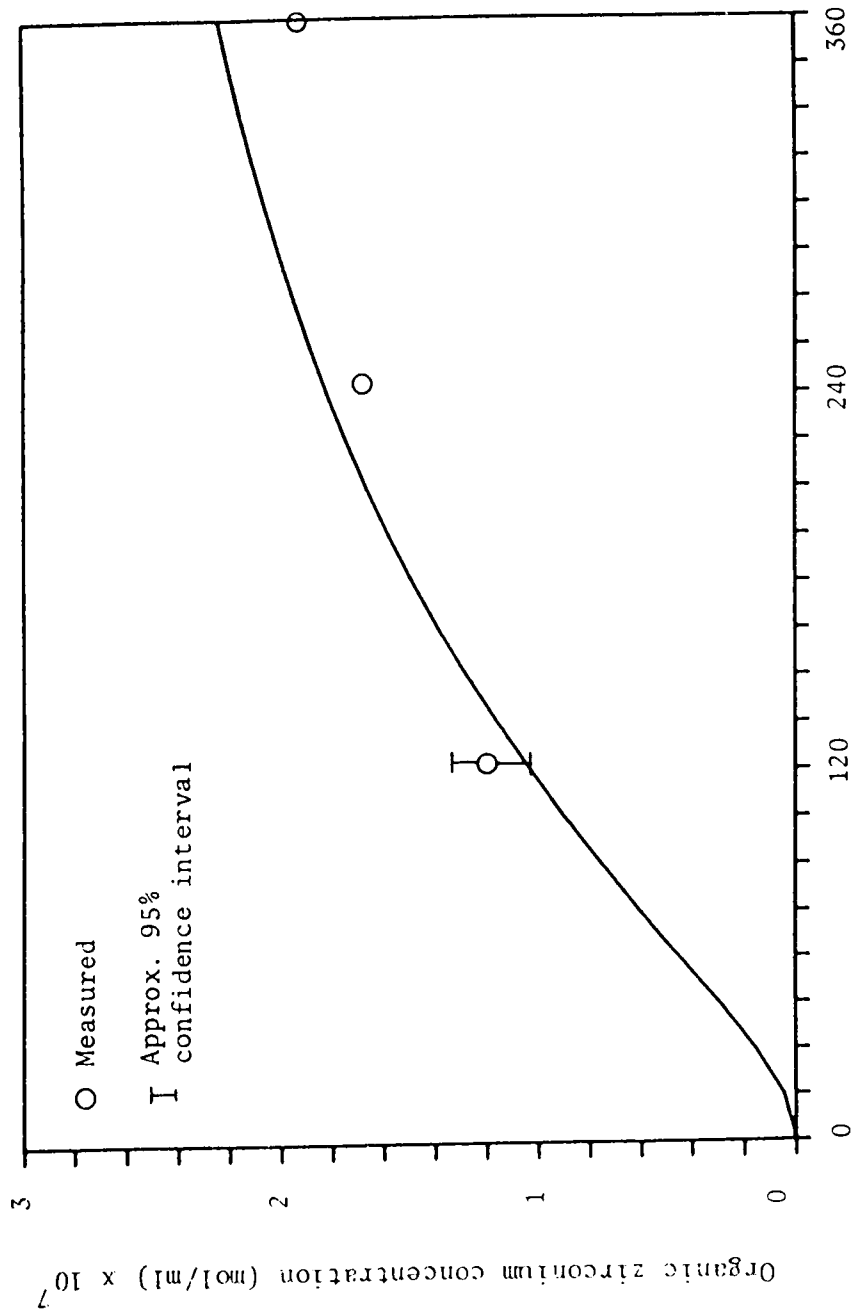


Figure 5.18. Zirconium concentration for S_2, V_{a1}, V_{o1}, d_{a1}, d_{o2}, C_{a1}, C_{a2}, C_{o3}.

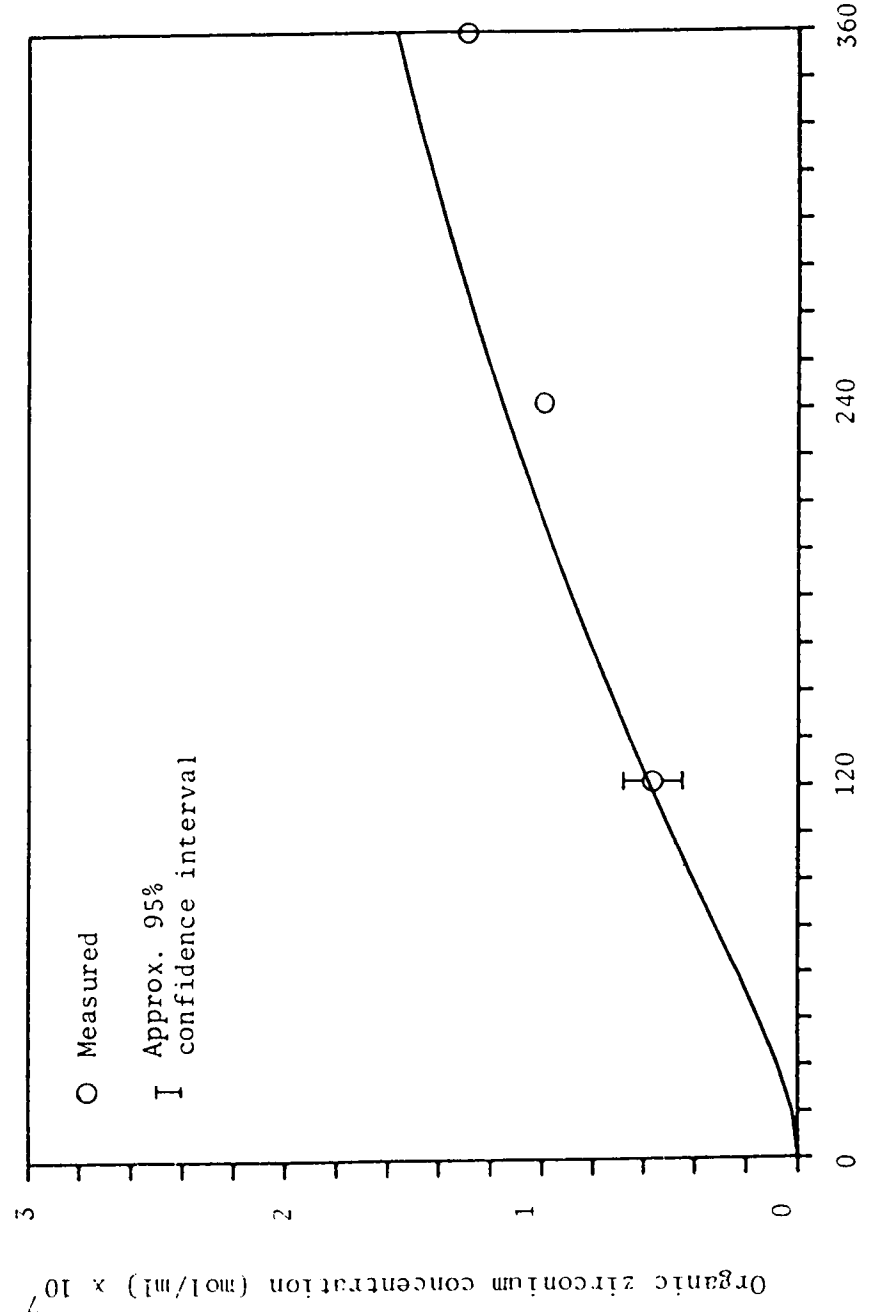


Figure 5.19. Zirconium concentration for S_2, V_{a1}, V_{o1}, d_{a2}, d_{o1}, C_{a1}, C_{a2}, C_{o3}.

6. DISCUSSION

6.1. Species and Mechanisms Involving Zirconium Mass Transfer

Characterization of zirconium-Purex mass transfer behavior requires knowledge of which parameters have potential for affecting the mass transfer. These parameters concern both diffusion and chemical reaction. Mass transfer without reaction is characterized by the distribution coefficient and mass transfer coefficients. Chemical reaction is characterized by the forward and reverse rate constants. The mass transfer coefficient is dependent on the contacting vessel and process conditions, while the distribution coefficient and reaction rate constants are dependent on only the process conditions. The determination of distribution coefficients and reaction rate constants will allow design calculations for any contacting vessel with known mass transfer coefficients.

It would not be reliable to determine all four parameters affecting mass transfer (i.e. mass transfer coefficient, distribution coefficient, forward reaction rate constant, and reverse reaction rate constant) from the transient zirconium data of this study. These constants are best determined from a combination of (1) non reacting, non zirconium-Purex mass transfer data, (2) literature equilibrium zirconium-Purex data, and (3) zirconium-Purex mass transfer data of this study. The vessel mass transfer coefficients (k) were characterized via the Sherwood, Reynolds and Schmidt numbers by using a non reacting, non zirconium system, i.e. acetic acid transfering from

water to isobutanol. The zirconium metal complex distribution coefficient (D_4) and reaction equilibrium constant (K^f/K^b) were regressed from zirconium-Purex equilibrium data found in the literature. The forward reaction rate constant was regressed from the zirconium mass transfer data of this study. The reverse reaction rate constant was then directly calculated from the equlibrium constant and forward rate constant.

Critical to the determination of the metal complex distribution coefficient and reaction rate constants, was the prior knowledge of where the chemical reaction occured. It was necessary to know in which phase the reaction occured, and whether the reaction occured in the bulk, film, or both. Initially it was thought the phase volume affect on mass transfer would distinguish the phase of reaction; however, the statistics indicated phase volume had no significant affect on the mass transfer rate. Consequently, it was necessary to use the literature for ascertaining the phase of chemical reaction.

The low ionization ($K_a = 1x10^{-4}$) of HNO_3 in TBP-dodecane (Marcus & Kertes, pg 679), indicates very little NO_3^- would be available as a reactant in the organic phase. The low ionization (essentially unionized) of the similar metal complex $UO_2(NO_3)_2.2TBP$ in TBP-dodecane (Marcus & Kertes, pg 704), indicates the uranium metal cation is essentially nonexistant in the organic phase. These two facts support the assumption the reaction occurs in the aqueous phase. A true metal complex does exist in the TBP-dodecane phase, as determined by infrared measurements of the TBP oxygen-phosphorus bond length decrease in the presence on metal salts (Marcus & Kertes, pg. 699, 1969).

The following discussion addresses each of the species present in the zirconium-Purex process, and their diffusional resistance contribution to the overall mass transfer model.

$\underline{Zr^{4+}\ specie}$. Reaction occurs in the aqueous phase in which Zr^{4+} is introduced initially. Based upon the low ionization of $UO_2(NO_3)_2 \cdot 2TBP$ in TBP, it is concluded Zr^{4+} is not soluable in the organic phase. Based on results of the Half Normal Plot discussed later in this section, the aqueous diffusional resistance to Zr^{4+} has an insignificant affect on the overall mass transfer rate.

$\underline{NO_3^-\ specie}$. The NO_3^- specie exists in the reacting phase at a concentration several orders of magnitude greater than the initial Zr^{4+} concentration. Therefore, the aqueous diffusional resistance to NO_3^- should have an insignificant affect on the overall mass transfer rate.

TBP specie. The organic phase concentration of TBP is several orders of magnitude greater than the initial Zr^{4+} concentration. Therefore, the organic phase diffusional resistance to TBP should have an insignificant affect on the overall mass transfer rate. The aqueous phase TBP concentration is initially approximately equal to the Zr^{4+} concentration. According to the Half Normal Plots discussed later in this section, the aqueous diffusional resistance increases with time. The Half Normal Plots indicate negigible aqueous phase diffusional resistance at two hours, and significant aqueous phase diffusional resistance at four and six hours. This assumption permits the simultaneous solution to the defining differential equations for time two hours or less. Without this simplification, a numerical solution would be required.

$\underline{Zr(NO_3)_4.2TBP\ specie}$. It has been concluded from the half normal plots the organic phase diffusional resistance is clearly more significant than the aqueous phase resistance, as demonstrated by the estimated mass transfer coeffcients of Table 5.8. However, diffusional resistance in both phases has been included in the final model since it (1) does not hinder the differential equations simultaneous solution and (2) does not significantly affect the K^f value regressed. This provides a model with greater applicability to other contacting vessels or process systems.

The final model developed for determining the forward reaction rate constant K^f, is based on the following fundamental differential equations defining the chemical reaction and diffusion.

The final model selected for the zirconium mass transfer from nitric acid to TBP/dodecane, is applicable to the stirred-cell and test conditions of this study at two hours or less into each test. The model is based on the following chemical reaction rate, diffusion rate, and material balance equations, as described in Section 4.2.5.

Chemical reaction:

$$-V_a \frac{dC_{a1}}{dt} = K^f(C_{a1})[C_{a2}(t=0)]^4[C_{o3}(t=0)/D_3]^2 - K^b(C_{a4}) ,$$

Diffusion:

$$-V_o \frac{dC_{o4}}{dt} = k_{o4}(C_{o4}{}^i - C_{o4}),$$

$$-V_o \frac{dC_{o4}}{dt} = k_{a4}(C_{a4} - C_{a4}^{i}),$$

$$C_{o4}^{i}/C_{a4}^{i} = D_4.$$

Material balance:

$$V_a C_{a1}(t=0) = V_a C_{a1} + V_a Ca_4 + V_o C_{o4}.$$

The final solution to the above differential equations has the following form, where the solution constants are discussed in the Section 4.2.5.

$$C_{a1} = b_2 + b_1 e^{-alt} + b_o e^{-aot},$$

$$C_{a4} = (1/A_1)[A_2 b_2 + b_1(A_2 - a_1)e^{-alt} + b_o(A_2 - a_o)e^{-aot},$$

$$C_{o4} = (V_a/V_o)[C_{a1}(t=0) - C_{a1} - C_{a4}).$$

6.2. Acetic Acid in Water and Isobutanol

6.2.1. Dissociation and Dimerization

This subject is discussed in Section 4.1.1. It is noted that acetic acid is a weak electrolyte with a Ka of 1.8×10^{-5}. Consequently, over 99% of the aqueous acetic acid is in the molecular form, and can be treated as a single specie. Dimerization is negigible since both water and isobutanol are polar, see section 4.1.1.

6.2.2. Distribution Coefficient

The distribution coefficient for acetic acid in water and isobutanol was measured at six different concentrations (25 C), and via a linear regression was determined to be 1.28 with an R^2 (correlation coefficient) of 0.998. The R^2 value indicated an excellent fit to the data, which in turn demonstrated the distribution coefficient as constant over the range of test conditions. The acetic acid distribution coefficient was reported as 1.18 by Lewis, see Section 2.8.2.

6.2.3. Mass Transfer Data

The acetic acid mass transfer data was used to estimate the individual mass transfer coefficient for the zirconium-Purex system. This was accomplished by measuring the overall mass transfer coefficient for the acetic acid system, and extrapolating via an established correlation to the zirconium-Purex system. The extrapolation was accomplished by considering the relationship between the Sherwood, Reynolds and Schmidt numbers. The primary complication was relating the overall and individual mass transfer coefficients; however, this was simplified when the data was analyzed and the process was determined to be primarily organic phase diffusion controlled.

The Half Normal Plot, Figure 5.3 of Section 5.1.3.1, was used to determine the primary resistance to acetic acid mass transfer was in the organic phase. It is clearly evident the organic mixer diameter had a much greater affect on the overall aqueous phase mass transfer coefficient, than the aqueous mixer diameter. It is not claimed that

the aqueous mixer diameter had no affect on the overall aqueous phase mass transfer coefficient. It is claimed the organic mixer effect was significantly greater than the aqueous mixer effect, and hence the overall effect can be reasonably approximated as due to the organic mixer only. The aqueous to organic individual mass transfer coefficient ratio (k_a/k_o) was 2.5, which supports the conclusion that primary diffusional resistance lies in the organic phase.

The correlation used to relate the Sherwood, Reynolds and Schmidt numbers was applicable only for the individual mass transfer coefficient, based on the Sherwood number definition. The acetic acid mass transfer data was based on the bulk phase concentrations, and consequently only the overall mass transfer coefficient could be calculated. It was necessary to relate the overall and individual mass transfer coefficients for the acetic acid data. This step was simplified by the determination that mass transfer resistance occurred primarily in the organic phase. Upon this assumption, the overall and individual mass transfer coefficients were directly related via,

$$1/K_{oa} = 1/(D_s k_o).$$

The data of Lewis indicated $K_{oa}(N_{Re},\text{organic}=2800) = 0.00183$ cm/s. The data of this study indicated $K_{oa}(N_{Re},\text{organic}= 2800)=0.000519$ cm/s. The data of this study yielded mass transfer coefficients about 3.5 times smaller than those of Lewis. This is not surprising since vessel parameters such as mixer design (number and size of blades), wall baffle design (number and size of blades), and distance from mixer to interface were not necessarily similar. Additionally, Lewis noted some

degree of interfacial turbulence during his testing, of which none appeared to occur during this study. The interfacial turbulence would have enhanced Lewis' mass transfer coefficient.

6.2.4. Marangoni Effect

Affects on mass transfer due to the Marangoni effect are discussed in Section 2.4.3. It is important to demonstrate the acetic acid data collected for this study was not significantly influenced by the Marangoni effect. A technique for ascertaining the significance of the Marangoni effect is the comparison of mass transfer coefficients for mass transfer in opposite directions. The Marangoni effect tends to increase or decrease the mass transfer rate in only one direction.

Based on the data from Lewis (Part II, 1954), for acetic acid transfer from water to isobutanol, K_{oa}(aqueous) = 0.00150 cm/s at N_{Re},average = 2000. For transfer from isobutanol to water, K_{oa}(organic) = 0.00167 cm/s at N_{Re},average = 2000. The difference between K_{oa}(aqueous) and K_{oa}(organic) at N_{Re} = 2000, is 10% of K_{oa}(organic). It can be seen the difference between K_{oa}(aqueous) and K_{oa}(organic) is small enough to not be of great concern.

Lewis' test was performed over a range of acetic acid and Reynolds number similar to this study, see Table 6.1. Based on Lewis' data, the Marangoni effect for conditions of this study does not appear significant.

Table 6.1. Acetic acid test conditions related to Marangoni effect.

Experimentor	N_{Re} Range	Acetic Acid Concn. Range
Lewis	1000-3000	35-55 g/L at t=0
This Study	1000-10,000	30 g/L at t=0

6.2.5. Individual Mass Transfer Coefficient Correlation

As claimed in Section 6.1.3, the primary resistance to mass transfer occurs in the isobutanol phase, and consequently the overall mass transfer coefficient can be directly related to the individual mass transfer coefficient. For the organic mixer diameter of 3 cm, K_{oa}(3 cm) = 0.000271 cm/s $\pm$ 0.000369 cm/s. For the organic mixer diameter of 6 cm, K_{oa}(6 cm) = 0.000918 cm/s $\pm$ 0.000126 cm/s. These values are obtained from the data of Table 5.1, where the uncertainties equal one standard deviation of the eight data points. The 3 cm average consists of data from (d_{a1},d_{o1}) and (d_{a2},d_{o1}) conditions. The 6 cm average consists of data from (d_{a1},d_{o2}) and (d_{a2},d_{o2}) conditions. The average for these two conditions was then used to determine the constant for Equation 5.2, as demonstrated by Figure 5.4.

The individual mass transfer coefficients for both mixer diameters was determined via the distribution coefficient,

$$k_o = K_{oa}/D_s,$$

to be ko(3 cm) = 0.000212 cm/s $\pm$ 0.000288 cm/s, and ko(6 cm) = 0.000717 cm/s $\pm$ 0.000098 cm/s at one standard deviation uncertainty. Relating these values to a t-distribution for 8 data points and the 95 % confidence level yields,

$$ko\ (3\ cm) = 0.000212 \pm 2.365(0.000288)/(8)^{1/2},$$

$$= 0.000212\ cm/s \pm 0.000241\ cm/s,$$

$$ko\ (6\ cm) = 0.000717 \pm 2.365(0.000098)/(8)^{1/2},$$

$$= 0.000717 \pm 0.000082.$$

where the t-statistic is 2.365 for (n-1) degress of freedom, and n=(number of data points).

The regression analysis, see Appendix A.2.4, yielded the following expression for the individual mass transfer coefficient for the stiired-cell used in this study,

$$k_j = 0.0000934(D^f/d_j)(N_{Rej})^{1.38}(N_{Scj})^{1/2}$$

where j is the phase of interest. Estimation of the above correlation uncertainty for systems other than acetic acid in water and isobutanol is not practical, since correlation with various Schmidt numbers was not conducted. In addition, uncertainties due to estimated diffusion coefficient estimation should be included, and these are not known.

6.3. Zirconium Data

6.3.1. Metal Complex Distribution Coefficient and Complexation Reaction Constant

The metal complex distribution coefficient (D_4), and reaction equilibrium constant (K^f/K^b), were calculated from literature data rather than collecting equilibrium data during this study. The final equation and its development, relating the metal complex distribution coefficient (D_4), reaction equilibrium constant (K^f/K^b) and overall distribution coefficient (D_{Zr}) are detailed in Section 4.2.4. The regression is shown in Figure 5.5. It can be observed from Figure 5.5 that the data forms two apparent lines. The data was chosen from literature to be balanced with respect to HNO_3 and TBP. Six data points including HNO_3 variations and six data points with TBP variation were utilized. The range of variation was selected to best cover the test conditions of this study. The HNO_3 data covered the range of 2 M to 4 M, and was collected by Adamskii and Alcock (see Appendix A.1.1) at 20 C to 23 C, and 20 vol% TBP in mixed hydrocarbon diluent. The TBP data covered the range of 10 vol% to 25 vol% in xylene, and was collected by Egorov at 20 C, and 3 M HNO_3.

The two apparent lines of Figure 5.5 represent the (1) HNO_3 varied data and (2) TBP varied data. The slight temperature, diluent and experimentor differences probably account for the two distinct lines. The essential criterea for evaluating the regression is comparison of the predicted value for the overall distribution coefficient, with a measured value for conditions of this study. The predicted value of D_{Zr} at $[NO_3^-(t=0)]_{aq}$=2.9M and $[TBP(t=0)]_{aq}$=0.3g/L is D_{Zr}=0.248. The

measured value of D_{Zr} during this study, at $[NO_3^-(T=0)]_{aq}$=2.9M and $[TBP(t=0)]_{aq}$=0.3g/L, was D_{Zr}=0.20 to 0.25. The close comparison indicated the regression was acceptable for the process conditions of this study.

The literature indicates D_{Zr} is a function of the aqueous zirconium concentration; however, the theroretical model developed for this study (based on aqueous phase reaction) does not allow for dependance on the zirconium concentration. The literature indicates this dependence becomes insignificant as the zirconium concentration approaches infinite dilution. It is true that as the aqueous zirconium concentration increases, zirconium polymers begin to form, each with their own organic solubility. As a result of this polymerization, D_{Zr} would depend on the aqueous zirconium concentration. In addition, the D_{Zr} of this study makes use of concentrations, rather than activity coefficients. Irregardless of the reason for D_{Zr} dependence on zirconium concentration, this study was performed at conditions of zirconium infinite dilution. At infinite dilution literature data indicated D_{Zr} independence on zirconium concentration, just as the model developed for this study requires. In addition, there are important process conditions in actual fuel reprocessing where zirconium exists at infinite dilution (typical scrub cycle).

6.3.2. Half Normal Plot and Reaction Effect

The Half Normal plot results, Figures 5.6 through 5.8, indicate the most significant affect on the mass transfer rate, not including concentrations, was the organic phase mass transfer coefficient. The

second greatest effect (not including concentrations) was the interfacial area, and the third greatest effect (not including concentrations) was the aqueous phase mass transfer coefficient. The plots did not indicate any other parameter (phase volumes), or parameter interaction effects, were particularly significant. By definition, only the four most significant effects can be significant via a Half Normal plot analysis.

The Half Normal plot results, and sum-of-squares shown in Tables 5.5 and 5.6, indicate the organic mass transfer coefficient is clearly the most significant effect (not including concentrations). The interfacial area is also significant as would be expected if any mass transfer coefficients were significant. As noted from Tables 5.5 and 5.6, the aquoeus mass transfer coefficient has minimal significance until four to six hours into a test. At six hours into a test the aquoeus mass transfer coefficient becomes as significant as the interfacial area.

Figure 5.9 shows that chemical reaction does occur; however, it does not establish whether or not it is instantaneous. This figure demonstrates reactant concentrations significantly affect the mass transfer rate; however, an instantaneous reaction could possibly accomplish this by changing the interfacial metal complex concentration. Changing the interfacial metal complex concentration would change the diffusional mass transfer rate.

Figure 5.10 presents evidence the chemical reaction is not instantaneous. This figure compares the predicted metal complex mass transfer coefficient calculated via the correlation developed during

acetic acid tests, with the same mass transfer coefficient reqressed from the zirconium mass transfer data assuming an instantaneous (or equilbrium) reaction. Two aspects of Figure 5.10 indicate the reaction is not instantaneous: (1) The zirconium regressed k_{o4} based on an instantaneous reaction is approximately 1/2 the predicted k_{o4} based on the acetic acid correlation. Either the acetic acid correlation predicts a k_{o4} greater than actuality, or an additional resistance exists during mass transfer, namely chemical reaction. (2) The zirconium regressed k_{o4}'s at reduced reactant concentrations are in general less than the zirconium regressed k_{o4}'s at higher reactant concentrations. This indicates reducing reactant concentrations increases the overall resistance, as explained by non equilibrium chemical reaction. It should be noted contrary to (2) above, when reactant NO_3^- concentration was decreased, k_{o4} did not decrease; however, its calculated effect is more susceptible to the estimated reaction power dependency of four, than TBP at two, or zirconium at one.

The final evidence of non equilibrium reaction is the regressed optimum value of K^f and K^b from the data of this study. Figure 5.11 clearly indicates non equilibrium chemical reaction at equal to or less than two hours.

6.3.3. Estimation of Metal Complex Individual Mass Transfer Coefficient

Calculation of the $Zr(NO_3)_4.2TBP$ individual mass transfer coefficient via the correlation developed from the acetic acid data (Equation 5.2), required an estimate of these diffusion coefficient in

both aqueous and organic phase. Estimation of the diffusion coefficients was done with the Wilke-Chang correlation for the aqueous phase, and Lusis-Ratcliff correlation for the organic phase, see Reid, Prausnitz and Sherwood (pgs. 567 and 572). To use these correlations it was necessary to estimate the molal volume at normal boiling point for both $Zr(NO_3)_4.2TBP$ and TBP. The molal volume at normal boiling point was estimated by additive methods for the constituent atoms. The constituent atom molal volumes at normal boiling point were estimated by the Tyn and Calus method from the critical volumes, see Reid, Prausnitz and Sherwood (pg. 59). It was necessary to interpolate the Zr critical volume from known critical volumes of similar elements listed in Table 3-306, pg. 3-229 of Perry and Chilton. Appendix A.3.4 details the critical volume interpolation. Appendix A.3.5 presents the individual mass transfer coefficient calculations.

6.3.4. Regression Analysis for K^f

Determination of K^f required the simultaneous solution of differential Equations 4.15 and 4.16. The affect of TBP diffusional resistance had to be neglected, otherwise a numerical solution was required. Since the sum-of-squares and Half Normal plots indicated aqueous phase diffusional resistance was negligible at two hours or less, and the inital aqueous phase TBP concentration was approximately equal to the zirconium cation concentration, it was felt appropriate to neglect TBP diffusional resistance for data collected at two hours or less. Also, the TBP aqueous phase individual mass transfer coefficient was at least two times greater than the metal complex organic phase

individual mass transfer coefficient (see Table 5.8), which further supported the assumption of negigible TBP diffusional resistance.

The data used for the regression analysis of K^f was balanced with regard to each model parameter, i.e. S, V_a, V_o, d_a, do, C_{a1}, C_{a2}, and C_{o3}. The combined data used for regression reflected parameter level changes of S, V_a, V_o, d_a, d_o, $C_{a1}(t=0)$, $C_{a2}(t=0)$ and $C_{o3}(t=0)$. Table 5.9 shows the conditions of each data point. Only the data at two hours was used for the regression. Each data point used for the regression is shown with the model prediction in Figures 5.11 through 5.19.

Due to the range of measured organic phase zirconium concentrations, a weighted sum-of-squares regression analysis was selected to estimate K^f, see Appendix A.3.6. The measured organic phase zirconium concentrations spanned an order of magnitude; consequently, it was felt the variance of a weighted sum-of-squares would be more constant throughout the data, rather than a non weighted sum-of-squares. Similar variance throughout the data is essential for an unbiased regression.

6.3.5 Data Uncertainty

The data uncertainty was estimated using a typical uncertainty anaysis, with a perturbation technique for estimating partial derivatives, see Appendix A.3.8. Due to the high degree of model non linearity with regard to the regression coefficient K^f, the perturbation technique was required for estimating partial derivatives. Confidence intervals for each data point included in the K^f regression

are shown in Figures 5.11 through 5.19. They were calculated as two time the standard error of estimate, or approximate 95% confidence interval. The average absolute percent difference between the predicted and measured organic metal complex concentration was 24% for all data used in the regression.

6.3.6. Existing Literature Models

The only literature based well-developed transient model for zirconium-Purex mass transfer is that of Mailen, et. al. (1980). Their model takes the form of a reversible reaction dependent on phase volume and interfacial area. This model is shown below:

$$-\frac{dC_{a1}}{dt} = \frac{S}{V_a}(K^+)C_{a1} - \frac{S}{V_o}(K^-)C_{o4} \ .$$

The forward reaction rate was reported as $K^+ = 0.00015$ cm/s. The forward reaction rate constant of this study was reported as $K^f = 1.6 \times 10^{21}$ [(mole/s)(ml/mole)^7]. The reaction rate expression for this study is:

$$-\frac{dC_{a1}}{dt} = \frac{K^f}{V_a}C_{a1}(C_{a2})^4(C_{o3}/D_3)^2 - \frac{K^b}{V_a}C_{a4}.$$

The forward reaction rate constant for each model can be related by:

$$S(K^+) = K^f(C_{a2})^4(C_{o3}/D_3)^2, \quad \text{or}$$

$$K^+ = (K^f/S)[Ca_2(t=0)]^4[C_{o3}(t=0)/D_3]^2.$$

Mailen's forward rate constant, and the equivalent forward rate constant of this study are shown in Table 6.2. The close comparison is interesting.

Table 6.2 Comparison of reaction rate constants.

K^*(cm/s)		
Mailen	This Study	
	$S=62\ cm^2$	$S=79\ cm^2$
0.0015	0.0023	0.0018

Note:

$K^* = K^+$, and

$K^* = (K^f/S)[Ca_2(t=0)]^4[C_{o3}(t=0)/D_3]^2$.

7. CONCLUSIONS

7.1. Overall Mass Transfer Characteristics

It can be concluded for the stirred-cell and process conditions of this study, both chemical reaction and diffusional resistance significantly affect the zirconium mass transfer rate.

Based upon low ionization values for HNO_3 in the organic phase, and low ionization values for similar metal complexes in the organic phase, the reaction occurs predominantly in the aqueous phase.

Due to the TBP loading of the aqueous phase at initial test conditions, the TBP diffusional resistance does not significantly affect the mass transfer rate at early test times. According to the Half Normal plots, and estimated mass transfer coefficients, the metal complex primary diffusional resistance lies in the organic phase at all test times.

The average error of the predicted versus measured organic metal complex concentration was 24% for the regression data. The assumptions of (1) negligible aqueous phase diffusional resistance at two hours or less, and (2) aqueous phase chemical reaction, were combined such that a non numerical solution to the defining differential equations was possible.

The fundamental constants derived from literature, and similar constants this study, were within reasonable agreement. The D_{Zr}=0.248 derived from literature data compares well with D_{Zr}=0.20-0.25 measured during this study. The $(K^{f}Ck/S)$=0.0030-0.0040 cm/s measured during this study compared well with K^{+}=0.0015 cm/s determined by Mailen

(1980). Mailen's reaction constant K^+ depended partially on diffusional resistance, which may explain the lower value.

7.2. Fundamental Constants

The fundamental constants determined from this study include D_4, K^f and K^b. These constants are applicable to any contacting vessel with similar process conditions. The distribution coefficient of the metal complex D_4, reflects its solubility in the organic phase. It has been determined for the range of HNO_3 from 2 M to 4 M, and range of TBP from 10 vol% to 30 vol%. The reaction equilibrium constant (K^f/K^b) specifies the ratio of zirocnium cation to zrconium complex in the aqueous phase. It has been determined for the same range of conditions as D_4. All three fundamental parameters, D_4, K^f, and K^b were determined at conditions of infinite zirconium dilution.

The conditions of this study are similar to a typical scrub bank during nuclear fuel reporocessing, except that much of the TBP would be complexed with uranium and plutonium. This implies that TBP diffusional resistance would be significant due to low concentrations of free TBP. However, modern contacting equipment in reprocessing facilities include mixer-settlers or centrifugal contactors which have high (interfacial area)/(phase volume) ratios. In this case the mass transfer rate would likely be completely reaction controlled.

7.3. Applicability

Modern reprocessing facility designers promote the use of mixer-settlers or centrifugal contactors for most solvent extraction

processes. Their short residence time reduces hydrolytic and radiolytic solvent degradation, and their compact size reduces capital costs. An example of process conditions for a well mixed vessel with high interfacial area can be found in Treybal, 1980 (Illustration 10.7, pg. 525). From this Illustration the (interfacial area)/(phase volume) ratio can be calculated for the well mixed vessel. Based on the vessel of Treybal's Illustration 10.7, the (interfacial area/phase volume) ratio is 1000 times greater for the well mixed vessel than the stirred-cell of this study. Since diffusion is proportional to the (interfacial area)/(phase volume) ratio, chemical reaction would probably completely control mass transfer in a well mixed vessel.

The chemical reaction controlled mass transfer model, with instantaneous diffusion, is shown below for application in well-mixed contactor.

$$-V_a \frac{dC_{a1}}{dt} = K^f(C_{a1})[C_{a2}(t=0)]^4[C_{o3}(t=0)/D_3]^2 - K^b(C_{a4}),$$

$$V_aC_{a1}(t=0) + V_oC_{o4}(t=0) = V_aC_{a1} + V_aC_{a4} + V_oC_{o4},$$

$$C_{o4}/C_{a4} = D_4.$$

These three equations can be substituted into the expression for a steady-state mixed flow reactor shown as Equation 13, pg. 103 of Levenspiel, 1972.

Upon substitution into Levenspiel's Equation 13:

$$t = \frac{C_{a1}(t=0) - C_{a1}}{-r},$$

$$= [C_{a1}(t=0)-C_{a1}]/[K^f C_{a1}(C_{a2})^4(C_{o3}/D_3)^2-K^b C_{a4}].$$

For an ideal extraction stage based on a Purex type flowsheet, the amount of zirconium transfered to the organic phase is of interest. If only C_{a1} enters the ideal stage, the quantity is $C_{o4}/C_{a1}(t=0)$ is a measure of conversion into the organic phase.

Based upon the above assumptions where $C_k = (C_{a2})^4(C_{o3}/D_3)^2$, $V_r=V_o/V_a$, $C_{a1}(t=0)=C_{a1}^o$:

$$t = \frac{(1/D_4+V_r)C_{o4}}{K^f C_k C_{a1}^o - [K^f C_k(1/D_4+V_r)+(K^b/D_4)]C_{o4}},$$

or,

$$\frac{C_{o4}}{C_{a1}^o} = \frac{t(K^f/C_k)}{t[K^f C_k(1/D_4+V_r)+(K^b/D_4)] + (1/D_4+V_r)}.$$

For a small mixer-settler where t=10 s, and process conditions similar to this study (C_{a2} = 0.0029 mol/ml and C_{o3}/D_3 = 1.13 x10^{-6} mol/ml) with V_r=1:

$$\frac{C_{o4}}{C_{a1}^o} = \frac{(10)(0.14)}{10[0.14(2.86+1)+(0.17)] + (2.86+1)},$$

$$= 0.13.$$

For conditions where the TBP is 50% loaded in the organic phase with uranium and plutonium:

$$C_{o3}/D_3 = (1.13/2) \times 10^{-6} \text{ mol/ml},$$

and then,

$$\frac{C_{o4}}{C_{a1}^{o}} = \frac{(10)(0.036)}{10[0.036(2.86+1)+(0.17)] + (2.86+1)},$$

$$= 0.05.$$

Units are

$$K^f/K^b = 2.7 \times 10^{2}{}_{2} \text{ (mole)}^{-6},$$

$$K^f = 1.6 \times 10^{21} \text{ [(mole/s)(ml/mole)}^{7}\text{]},$$

$$K^b = 0.059 \text{ (ml/s)},$$

$$D_4 = 0.35.$$

This model claims extraction of zirconium in an ideal stage with process conditions of 30 vol % TBP in the organic and 3.5 M HNO_3 in the aqueous feed, will be 13% for a 10 s mixing residence time. If the TBP is assumed 50% loaded with other species (or only 15 vol% TBP available for extraction), then extraction is reduced to 5%.

For an ideal scrub stage based on a Purex type flowsheet, similar calculations could be performed.

8. RECOMMENDATIONS

8.1. Additional Zirconium Efforts

Additonal zirconium efforts could begin with application of the reaction controlled model of Section 7.3 to a well mixed contacting vessel. This could be done with a mixer settler or centrifugal contactor. By varying the flow to such vessels, the residence time and consequent extent of chemical reaction can be investigated. Measurement of the organic metal complex concentration can be compared to the model prediction. It would not be necessary to know the mass transfer cefficient since the process should be entirely reaction controlled. However, determination of the mass transfer coefficients can be used to calculate the film thickness and consequent significance of the film reaction.

A complete model could be developed assuming an aqueous phase reaction. This model would possibly involve the film and bulk reaction control, TBP diffusional control, NO_3^- diffusional control, and metal complex diffusional control. This model would very likely require a numerical solution.

It would be advantageous to investigate further the phase of reaction. Existing evidence is indirect so that direct measurements of the zirconium species in each phase would be valuable.

Determination of the fundamental constants D_4 and K^f/K^b based upon the use of activity coefficients rather than concentrations would be interesting. Howvever, during such work it would be critical to carefully control the cation specie.

8.2. Non zirconium species.

Due to the preponderance of existing uranium data, it would be worth while to repeat this study for uranium. Determination of D_4 and K^f/K^b could be done from the large selection of equilibrium data in the literature. It is also possible that applicable transient data exists in the literature, such that even K^f and K^b could be determined without performing any experiments.

The statistical procedure used for this study could be applied to a wide range of species and processes. With solvent extraction being critical to nuclear fuel reprocessing, such efforts would yield fundamental constants not presently available for any of the reprocessing species.

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APPENDIXES

A.1. Data from Literature

A.1.1. Zirconium Overall Distribution Coefficient

The following data sets were collected from literature, and reflect the most appropriate equilibrium data as related to this study. Table A.1 shows the affect of temperature and nitric acid concentration on the overall distribution coefficient for tracer zirconium concentrations, with 20 vol% TBP in saturated hydrocarbons. Table A.2 displays the affect of nitric acid concentration on the overall distribution coefficient for tracer zirconium concentrations, with 19 vol% TBP in kerosene at 20 to 23 C. Table A.3 displays the affect of nitric acid and TBP concentration on the overall distribution coefficient for tracer zirconium concentrations, with TBP in xylene at 20 C.

A.1.2. Nitric Acid Distribution Coefficient

The overall distribution coefficient (ionized plus unionized) for nitric acid in 30 vol% TBP was found to be approximately 0.2 (organic/aqueous) for 3 M HNO_3, per Figures 9C9 and 9C11 of Marcus & Kertes, and Figure 10.16 of Benedict, Pigford & Levi. This was with a dodecane or kerosene diluent at 25 to 55 C.

A.1.3. TBP Distribution Coefficient

The TBP solubility in water, for 30 vol% TBP in dodecane was reported as approximately 0.3 g/L per Table 10.14 of Benedict, Pigford & Levi.

Table A.1. Adamskii's data for the affect of temperature on D_{Zr}.

Temperature (C)	Aqueous Nitric Acid Conc. (M)	Zr Distribution Coeff. (org/aq)
23	0.36	0.0068
	0.50	0.0089
	0.60	0.011
	1.04	0.019
	1.94	0.044
	2.84	0.084
	3.74	0.167
	5.70	0.58
	6.35	0.98
	7.28	1.80
	9.00	4.70
	10.80	9.10
40	0.40	0.0040
	0.66	0.0084
	1.10	0.019
	2.00	0.053
	2.90	0.121
	3.80	0.238
	5.58	0.64
70	0.24	0.0009
	0.36	0.0050
	0.58	0.012
	1.00	0.040
	1.82	0.099
	2.66	0.200
	3.50	0.38
	5.40	0.78

Conditions: (Zr^{95} tracer, 20 vol % TBP in saturated hydrocarbons).

Table A.2. Alcock's data for the HNO_3 affect on D_{Zr}.

Aqueous Nitric Acid Conc. (M)	Zr Distribution Coeff. (org/aq)
0.98	0.015
2.02	0.045
2.25	0.051
3.01	0.120
4.01	0.23
4.96	0.49
5.19	0.53
6.04	0.90
6.94	1.37
7.98	2.37
8.03	2.02
9.10	4.4
10.2	8.2
10.5	9.8
11.2	11.4
12.2	40
13.1	134

Conditions: (Zr^{95} tracer, 20 - 23 C, 19 vol % TBP in kerosene).

Table A.3. Egorov's data for the affect of HNO_3 and TBP on D_{Zr}.

Aqueous Nitric Acid Conc. (M)	Organic TBP Conc. (M)	Zr Distribution Coeff. (org/aq)
3.02	0.323	0.178
3.02	0.398	0.211
3.06	0.474	0.246
3.04	0.620	0.335
3.07	0.769	0.490
2.98	0.890	0.710
4.08	0.186	0.525
4.09	0.237	0.670
4.02	0.282	0.844
4.02	0.364	1.38
4.10	0.446	2.07
4.10	0.525	3.00
4.98	0.141	0.845
4.95	0.211	1.26
4.92	0.275	1.67
5.04	0.305	2.14
4.98	0.343	2.92
4.95	0.384	3.98

Cnditions: (Zr^{95} tracer at 10^{-5} M, 20 C, Xylene diluent).

A.2. Acetic Acid Original Data

A.2.1. Distribution Coefficient

Table A.4 lists the complete set of measurements made in determining the acetic acid distribution in water-isobutanol. Each phase, water and isobutanol, consisted of 100 ml of solution. Contact was made at a controlled temperature of 25 C, in a shaking device for approximately one hour. It was determined that equilibrium was established by comparing timed tests.

Table A.4. Complete data for Acetic Acid distribution in Water-Isobutanol.

Sample No.	Initial Aqueous			Final Aqueous		
	sample (ml)	titrant (ml)	(conc)	sample (ml)	titrant (ml)	(conc)
1	1	6.74	0.1	2	5.76	0.1
2	2	5.70	0.1	5	6.34	0.1
3	5	6.84	0.1	10	5.87	0.1
4	10	5.70	0.1	25	6.38	0.1
5	5	6.18	0.025	5	2.66	0.025
6	50	5.70	0.1	50	2.58	0.1

NaOH was the titrant used to neutralize acetic acid sample.

A.2.2. Mass Transfer Data

The pertinent data used to calculate each acetic acid overall mass transfer coefficient of Table 5.1 are presented in the following Lotus printouts, Figures A.1 through A.16. The Lotus program used to calculate the overall mass transfer coefficient, based on the model of Section 4.1.2, is presented in Figure A.17 for test ACID15. Table A.5 displays the relation between each test title and the test conditions.

Table A.5. Acetic acid test title versus test conditions.

Area	Phase Volume	Test Title d_{a1},d_{o1}	d_{a2},d_{o1}	d_{a1},d_{o2}	d_{a2},d_{o2}
S_1	V_{a1},V_{o1}	Acid15	X	X	Acid9
	V_{a2},V_{o1}	X	Acid13	Acid7	X
	V_{a1},V_{o2}	X	Acid14	Acid8	X
	V_{a2},V_{o2}	Acid16	X	X	Acid10
S_2	V_{a1},V_{o1}	X	Acid2	Acid3	X
	V_{a2},V_{o1}	Acid6	X	X	Acid11
	V_{a1},V_{o2}	Acid17	X	X	Acid12
	V_{a2},V_{o2}	X	Acid18	Acid19	X

Figures A.18 through A.21 display the measured and predicted acetic acid concentration in isobutanol with time, for selected tests Acid15, Acid9, Acid10 and Acid18 respectively. The predicted acetic acid concentration was based on the overall mass transfer coefficient averaged from measurements at 30, 45 and 60 minutes.

Test Date: 02/01/89
ACID2

Test Conditions:

1. aqueous phase volume (ml) =	350.00
2. organic phase volume (ml) =	350.00
3. NaOH titrant concn. (N):	
aqueous	0.10
organic	0.01
4. interfacial area (cm^2) =	79.00
5. mixing speed (rpm) =	150.00
6. temperature (C) =	25.00
7. paddle diameter (cm):	
aqueous	6.00
organic	3.00
8. regression partition coeff. (org.aq) =	1.28
9. sample size (ml):	
aqueous	2.00
organic	1.00
10.acetic acid solute;	
i. feed sample volume (ml) =	10.00
ii. sample concn. (M) =	17.40
11.final titrant (ml);	
i. aqueous =	8.05
ii. organic =	2.94

Data Parameters:

1. water;	
i. VISB =	658.25
ii. VISTO =	283.16
iii. density (g/cc) =	1.00
iv. mole wt (g/mole) =	18.00
v. association parameter z =	2.60
2. isobutanol;	
i. VISB =	1193.10
ii. VISTO =	343.85
iii. density (g/cc) =	0.80
iv. mole wt (g/mole) =	74.12
v. association parameter z =	1.25
3. acetis acid;	
i. molal volume (ml/mole) =	64.10
ii. mole wt (g/mole) =	60.05

Figure A.1. Acetic acid test Acid2.

Calculations:

1. initial acid conc. in water;
   - i. final aqueous (g/L) = 24.17
   - ii. final organic (g/L) = 1.77
   - iii. inital aq (g/L), for Koa calc = 29.03
   - iii. inital aqueous (g/L), feed based = 29.03
   - iv. initial and final material balance (%) = 11.88
   - v. initial aqueous - final based (g/L) = 25.58

2. viscosity (g/cm-s);
   - i. water = 0.008906
   - ii. isobutanol = 0.017055

3. diffusion coefficient, acetic acid in;
   - i. water (cm^2/s)x100 = 0.001395
   - ii. isobutanol (cm^2/s)x100 = 0.001025

4. Reynolds number (w=rps);
   - i. water = 10084
   - ii. isobutanol = 1058

time (s)	LOG [time(s)]	base (ml)	Co(g/L) measured	Ca(g/L) org based	Koa calc (cm/s)	Ca(g/L) calc	Error %
1800	3.26	---	0.98	28.04	0.000086	28.07	-0.1
2700	3.43	---	1.43	27.60	0.000084	27.62	-0.1
3600	3.56	---	1.77	27.26	0.000079	27.17	0.3
				measured			
4500	3.65	7.63	---	22.91	0.000260	23.24	-1.4
5400	3.73	7.41	---	22.25	0.000248	22.35	-0.5
8000	3.90	7.03	---	21.11	0.000207	20.19	4.4

A aq = 1.797991
A org = 1.760270

		Aq & Org ave
Koa average aq (cm/s) =	0.000238	0.000160
Koa average og (cm/s) =	0.000083	

Base (ml)	Time (s)	Cbo (M) meas	Cbo(g/L) meas	Cba(g/L) org based
1.64	1800	0.0164	0.98	28.04
2.38	2700	0.0238	1.43	27.60
2.94	3600	0.0294	1.77	27.26

Figure A.1. (continued).

Test Date: 02/01/89
ACID3

Test Conditions:

1. aqueous phase volume (ml) =	350.00
2. organic phase volume (ml) =	350.00
3. NaOH titrant concn. (N):	
aqueous	0.10
organic	0.01
4. interfacial area (cm^2) =	79.00
5. mixing speed (rpm) =	150.00
6. temperature (C) =	25.00
7. paddle diameter (cm):	
aqueous	3.00
organic	6.00
8. regression partition coeff. (org.aq) =	1.28
9. sample size (ml):	
aqueous	2.00
organic	1.00
10.acetic acid solute;	
i. feed sample volume (ml) =	10.00
ii. sample concn. (M) =	17.40
11.final titrant (ml);	
i. aqueous =	5.81
ii. organic =	18.90

Data Parameters:

1. water;	
i. VISB =	658.25
ii. VISTO =	283.16
iii. density (g/cc) =	1.00
iv. mole wt (g/mole) =	18.00
v. association parameter z =	2.60
2. isobutanol;	
i. VISB =	1193.10
ii. VISTO =	343.85
iii. density (g/cc) =	0.80
iv. mole wt (g/mole) =	74.12
v. association parameter z =	1.25
3. acetis acid;	
i. molal volume (ml/mole) =	64.10
ii. mole wt (g/mole) =	60.05

Figure A.2. Acetic acid test Acid3.

Calculations:

1. initial acid conc. in water;
   - i. final aqueous (g/L) = 17.45
   - ii. final organic (g/L) = 11.35
   - iii. inital aq (g/L), for Koa calc = 29.03
   - iii. inital aqueous (g/L), feed based = 29.03
   - iv. initial and final material balance (%) = 2.17
   - v. initial aqueous - final based (g/L) = 28.40

2. viscosity (g/cm-s);
   - i. water = 0.008906
   - ii. isobutanol = 0.017055

3. diffusion coefficient, acetic acid in;
   - i. water (cm^2/s)x100 = 0.001395
   - ii. isobutanol (cm^2/s)x100 = 0.001025

4. Reynolds number (w=rps);
   - i. water = 2521
   - ii. isobutanol = 4232

time (s)	LOG [time(s)]	base (ml)	Co(g/L) measured	Ca(g/L) org based	Koa calc (cm/s)	Ca(g/L) calc	Error %
1800	3.26	---	8.36	20.67	0.000988	21.33	-3.2
2700	3.43	---	9.73	19.30	0.000831	18.96	1.7
3600	3.56	---	11.35	17.68	0.000815	17.23	2.5
				measured			
1800	3.26	7.03	---	21.11	0.000920	21.31	-0.9
2700	3.43	6.42	---	19.28	0.000840	18.94	1.8
3600	3.56	5.81	---	17.45	0.000854	17.22	1.3

A aq = 1.797991
A org = 1.760270

Aq & Org ave

Koa average aq (cm/s) = 0.000871
Koa average og (cm/s) = 0.000878
0.000875

Base (ml)	Time (s)	Cbo (M) meas	Cbo(g/L) meas	Cba(g/L) org based
13.92	1800	0.1392	8.36	20.67
16.20	2700	0.1620	9.73	19.30
18.90	3600	0.1890	11.35	17.68

Figure A.2. (continued).

Test Date: 02/10/89
ACID6

Test Conditions:

1. aqueous phase volume (ml) =	450.00
2. organic phase volume (ml) =	350.00
3. NaOH titrant concn. (N):	
aqueous	0.10
organic	0.01
4. interfacial area (cm^2) =	79.00
5. mixing speed (rpm) =	150.00
6. temperature (C) =	25.00
7. paddle diameter (cm):	
aqueous	3.00
organic	3.00
8. regression partition coeff. (org.aq) =	1.28
9. sample size (ml):	
aqueous	1.00
organic	2.00
10.acetic acid solute;	
i. feed sample volume (ml) =	12.86
ii. sample concn. (M) =	17.40
11.final titrant (ml);	
i. aqueous =	4.50
ii. organic =	5.90

Data Parameters:

1. water;	
i. VISB =	658.25
ii. VISTO =	283.16
iii. density (g/cc) =	1.00
iv. mole wt (g/mole) =	18.00
v. association parameter z =	2.60
2. isobutanol;	
i. VISB =	1193.10
ii. VISTO =	343.85
iii. density (g/cc) =	0.80
iv. mole wt (g/mole) =	74.12
v. association parameter z =	1.25
3. acetis acid;	
i. molal volume (ml/mole) =	64.10
ii. mole wt (g/mole) =	60.05

Figure A.3. Acetic acid test Acid6.

Calculations:

1. initial acid conc. in water;
   - i. final aqueous (g/L) = 27.02
   - ii. final organic (g/L) = 1.77
   - iii. inital aq (g/L), for Koa calc = 29.03
   - iii. inital aqueous (g/L), feed based = 29.03
   - iv. initial and final material balance (%) = 3.51
   - v. initial aqueous - final based (g/L) = 28.01

2. viscosity (g/cm-s);
   - i. water = 0.008906
   - ii. isobutanol = 0.017055

3. diffusion coefficient, acetic acid in;
   - i. water (cm^2/s)x100 = 0.001395
   - ii. isobutanol (cm^2/s)x100 = 0.001025

4. Reynolds number (w=rps);
   - i. water = 2521
   - ii. isobutanol = 1058

time (s)	LOG [time(s)]	base (ml)	Co(g/L) measured	Ca(g/L) org based	Koa calc (cm/s)	Ca(g/L) calc	Error %
1800	3.26	---	1.17	27.87	0.000101	27.97	-0.4
2700	3.43	---	1.66	27.37	0.000098	27.46	-0.3
3600	3.56	---	1.77	27.26	0.000078	26.96	1.1
			measured				
3600	3.56	4.50	---	27.02	0.000095	26.99	---

A aq = 2.025993
A org = 1.542707

Aq & Org ave
0.000094

Koa average aq (cm/s) = 0.000095
Koa average og (cm/s) = 0.000092

Base (ml)	Time (s)	Cbo (M) meas	Cbo(g/L) meas	Cba(g/L) org based
3.88	1800	0.0194	1.17	27.87
5.52	2700	0.0276	1.66	27.37
5.90	3600	0.0295	1.77	27.26

Figure A.3. (continued).

Test Date: 02/21/89
ACID7

Test Conditions:

1. aqueous phase volume (ml) =	450.00
2. organic phase volume (ml) =	350.00
3. NaOH titrant concn. (N):	
aqueous	0.01
organic	0.01
4. interfacial area (cm^2) =	62.00
5. mixing speed (rpm) =	150.00
6. temperature (C) =	25.00
7. paddle diameter (cm):	
aqueous	3.00
organic	6.00
8. regression partition coeff. (org.aq) =	1.28
9. sample size (ml):	
aqueous	1.00
organic	1.00
10.acetic acid solute;	
i. feed sample volume (ml) =	12.86
ii. sample concn. (M) =	17.40
11.final titrant (ml);	
i. aqueous =	36.00
ii. organic =	18.20

Data Parameters:

1. water;	
i. VISB =	658.25
ii. VISTO =	283.16
iii. density (g/cc) =	1.00
iv. mole wt (g/mole) =	18.00
v. association parameter z =	2.60
2. isobutanol;	
i. VISB =	1193.10
ii. VISTO =	343.85
iii. density (g/cc) =	0.80
iv. mole wt (g/mole) =	74.12
v. association parameter z =	1.25
3. acetis acid;	
i. molal volume (ml/mole) =	64.10
ii. mole wt (g/mole) =	60.05

Figure A.4. Acetic acid test Acid7.

Calculations:

1. initial acid conc. in water;
   - i. final aqueous (g/L) = 21.62
   - ii. final organic (g/L) = 10.93
   - iii. inital aq (g/L), for Koa calc = 29.03
   - iii. inital aqueous (g/L), feed based = 29.03
   - iv. initial and final material balance (%) = -2.42
   - v. initial aqueous - final based (g/L) = 29.73

2. viscosity (g/cm-s);
   - i. water = 0.008906
   - ii. isobutanol = 0.017055

3. diffusion coefficient, acetic acid in;
   - i. water (cm^2/s)x100 = 0.001395
   - ii. isobutanol (cm^2/s)x100 = 0.001025

4. Reynolds number (w=rps);
   - i. water = 2521
   - ii. isobutanol = 4232

time (s)	LOG [time(s)]	base (ml)	Co(g/L) measured	Ca(g/L) org based	Koa calc (cm/s)	Ca(g/L) calc	Error %
1800	3.26	---	7.22	21.81	0.000983	22.15	-1.5
2700	3.43	---	9.20	19.83	0.000909	19.72	0.6
3600	3.56	---	10.93	18.10	0.000883	17.78	1.8
				measured			
3600	3.56	36.00	---	21.62	0.000545	21.51	---

A aq = 2.025993
A org = 1.542707

		Aq & Org ave
Koa average aq (cm/s) =	0.000545	0.000735
Koa average og (cm/s) =	0.000925	

Base (ml)	Time (s)	Cbo (M) meas	Cbo(g/L) meas	Cba(g/L) org based
12.02	1800	0.1202	7.22	21.81
15.32	2700	0.1532	9.20	19.83
18.20	3600	0.1820	10.93	18.10

Figure A.4. (continued).

Test Date: 02/22/89
ACID8

Test Conditions:

1. aqueous phase volume (ml) =	350.00
2. organic phase volume (ml) =	450.00
3. NaOH titrant concn. (N):	
aqueous	0.01
organic	0.01
4. interfacial area (cm^2) =	62.00
5. mixing speed (rpm) =	150.00
6. temperature (C) =	25.00
7. paddle diameter (cm):	
aqueous	3.00
organic	6.00
8. regression partition coeff. (org.aq) =	1.28
9. sample size (ml):	
aqueous	1.00
organic	1.00
10.acetic acid solute;	
i. feed sample volume (ml) =	10.00
ii. sample concn. (M) =	17.40
11.final titrant (ml);	
i. aqueous =	35.65
ii. organic =	11.84

Data Parameters:

1. water;	
i. VISB =	658.25
ii. VISTO =	283.16
iii. density (g/cc) =	1.00
iv. mole wt (g/mole) =	18.00
v. association parameter z =	2.60
2. isobutanol;	
i. VISB =	1193.10
ii. VISTO =	343.85
iii. density (g/cc) =	0.80
iv. mole wt (g/mole) =	74.12
v. association parameter z =	1.25
3. acetis acid;	
i. molal volume (ml/mole) =	64.10
ii. mole wt (g/mole) =	60.05

Figure A.5. Acetic acid test Acid8.

Calculations:

1. initial acid conc. in water;
   - i. final aqueous (g/L) = 21.41
   - ii. final organic (g/L) = 7.11
   - iii. inital aq (g/L), for Koa calc = 29.03
   - iii. inital aqueous (g/L), feed based = 29.03
   - iv. initial and final material balance (%) = -3.70
   - v. initial aqueous - final based (g/L) = 30.10

2. viscosity (g/cm-s);
   - i. water = 0.008906
   - ii. isobutanol = 0.017055

3. diffusion coefficient, acetic acid in;
   - i. water (cm^2/s)x100 = 0.001395
   - ii. isobutanol (cm^2/s)x100 = 0.001025

4. Reynolds number (w=rps);
   - i. water = 2521
   - ii. isobutanol = 4232

time (s)	LOG [time(s)]	base (ml)	Co(g/L) measured	Ca(g/L) org based	Koa calc (cm/s)	Ca(g/L) calc	Error %
1800	3.26	---	4.59	24.44	0.000769	24.43	0.0
2700	3.43	---	6.82	22.20	0.000860	22.72	-2.3
3600	3.56	---	7.11	21.91	0.000684	21.32	2.7
				measured			
3600	3.56	35.65	---	21.41	0.000698	21.31	---

A aq = 1.620659
A org = 2.039991

Aq & Org ave

Koa average aq (cm/s) = 0.000698
Koa average og (cm/s) = 0.000771
0.000734

Base (ml)	Time (s)	Cbo (M) meas	Cbo(g/L) meas	Cba(g/L) org based
7.64	1800	0.0764	4.59	24.44
11.36	2700	0.1136	6.82	22.20
11.84	3600	0.1184	7.11	21.91

Figure A.5. (continued).

Test Date: 02/22/89
ACID9

Test Conditions:

1. aqueous phase volume (ml) =	350.00
2. organic phase volume (ml) =	350.00
3. NaOH titrant concn. (N):	
aqueous	0.01
organic	0.01
4. interfacial area (cm^2) =	62.00
5. mixing speed (rpm) =	150.00
6. temperature (C) =	25.00
7. paddle diameter (cm):	
aqueous	6.00
organic	6.00
8. regression partition coeff. (org.aq) =	1.28
9. sample size (ml):	
aqueous	1.00
organic	1.00
10.acetic acid solute;	
i. feed sample volume (ml) =	10.00
ii. sample concn. (M) =	17.40
11.final titrant (ml);	
i. aqueous =	28.65
ii. organic =	17.10

Data Parameters:

1. water;	
i. VISB =	658.25
ii. VISTO =	283.16
iii. density (g/cc) =	1.00
iv. mole wt (g/mole) =	18.00
v. association parameter z =	2.60
2. isobutanol;	
i. VISB =	1193.10
ii. VISTO =	343.85
iii. density (g/cc) =	0.80
iv. mole wt (g/mole) =	74.12
v. association parameter z =	1.25
3. acetis acid;	
i. molal volume (ml/mole) =	64.10
ii. mole wt (g/mole) =	60.05

Figure A.6. Acetic acid test Acid9.

Calculations:

1. initial acid conc. in water;
   - i. final aqueous (g/L) = 17.20
   - ii. final organic (g/L) = 10.27
   - iii. inital aq (g/L), for Koa calc = 29.03
   - iii. inital aqueous (g/L), feed based = 29.03
   - iv. initial and final material balance (%) = 6.66
   - v. initial aqueous - final based (g/L) = 27.09

2. viscosity (g/cm-s);
   - i. water = 0.008906
   - ii. isobutanol = 0.017055

3. diffusion coefficient, acetic acid in;
   - i. water (cm^2/s)x100 = 0.001395
   - ii. isobutanol (cm^2/s)x100 = 0.001025

4. Reynolds number (w=rps);
   - i. water = 10084
   - ii. isobutanol = 4232

time (s)	LOG [time(s)]	base (ml)	Co(g/L) measured	Ca(g/L) org based	Koa calc (cm/s)	Ca(g/L) calc	Error %
1800	3.26	---	7.37	21.65	0.001056	22.18	-2.4
2700	3.43	---	9.04	19.99	0.000943	19.91	0.4
3600	3.56	---	10.27	18.76	0.000868	18.17	3.1
				measured			
3600	3.56	28.65	---	17.20	0.001134	17.09	---

A aq = 1.797991
A org = 1.760270

Aq & Org ave

Koa average aq (cm/s) = 0.001134
Koa average og (cm/s) = 0.000956 0.001045

Base (ml)	Time (s)	Cbo (M) meas	Cbo(g/L) meas	Cba(g/L) org based
12.28	1800	0.1228	7.37	21.65
15.05	2700	0.1505	9.04	19.99
17.10	3600	0.1710	10.27	18.76

Figure A.6. (continued).

Test Date: 02/23/89
ACID10

Test Conditions:

1. aqueous phase volume (ml) =	450.00
2. organic phase volume (ml) =	450.00
3. NaOH titrant concn. (N):	
aqueous	0.01
organic	0.01
4. interfacial area (cm^2) =	62.00
5. mixing speed (rpm) =	150.00
6. temperature (C) =	25.00
7. paddle diameter (cm):	
aqueous	6.00
organic	6.00
8. regression partition coeff. (org.aq) =	1.28
9. sample size (ml):	
aqueous	1.00
organic	1.00
10. acetic acid solute;	
i. feed sample volume (ml) =	12.86
ii. sample concn. (M) =	17.40
11. final titrant (ml);	
i. aqueous =	33.65
ii. organic =	17.35

Data Parameters:

1. water;	
i. VISB =	658.25
ii. VISTO =	283.16
iii. density (g/cc) =	1.00
iv. mole wt (g/mole) =	18.00
v. association parameter z =	2.60
2. isobutanol;	
i. VISB =	1193.10
ii. VISTO =	343.85
iii. density (g/cc) =	0.80
iv. mole wt (g/mole) =	74.12
v. association parameter z =	1.25
3. acetis acid;	
i. molal volume (ml/mole) =	64.10
ii. mole wt (g/mole) =	60.05

Figure A.7. Acetic acid test Acid10.

Calculations:

1. initial acid conc. in water;
   - i. final aqueous (g/L) = 20.21
   - ii. final organic (g/L) = 10.42
   - iii. inital aq (g/L), for Koa calc = 29.03
   - iii. inital aqueous (g/L), feed based = 29.03
   - iv. initial and final material balance (%) = -4.03
   - v. initial aqueous - final based (g/L) = 30.20

2. viscosity (g/cm-s);
   - i. water = 0.008906
   - ii. isobutanol = 0.017055

3. diffusion coefficient, acetic acid in;
   - i. water (cm^2/s)x100 = 0.001395
   - ii. isobutanol (cm^2/s)x100 = 0.001025

4. Reynolds number (w=rps);
   - i. water = 10084
   - ii. isobutanol = 4232

time (s)	LOG [time(s)]	base (ml)	Co(g/L) measured	Ca(g/L) org based	Koa calc (cm/s)	Ca(g/L) calc	Error %
1800	3.26	---	6.22	22.82	0.001083	22.52	1.3
2700	3.43	---	9.10	19.93	0.001226	20.30	-1.9
3600	3.56	---	10.42	18.61	0.001144	18.57	0.2
				measured			
3600	3.56	33.65	---	20.21	0.000883	20.10	---

A aq = 1.797994
A org = 1.760266

		Aq & Org ave
Koa average aq (cm/s) =	0.000883	0.001017
Koa average og (cm/s) =	0.001151	

Base (ml)	Time (s)	Cbo (M) meas	Cbo(g/L) meas	Cba(g/L) org based
10.35	1800	0.1035	6.22	22.82
15.16	2700	0.1516	9.10	19.93
17.35	3600	0.1735	10.42	18.61

Figure A.7. (continued).

Test Date: 02/24/89
ACID11

Test Conditions:

1. aqueous phase volume (ml) =	450.00
2. organic phase volume (ml) =	350.00
3. NaOH titrant concn. (N):	
aqueous	0.01
organic	0.01
4. interfacial area (cm^2) =	79.00
5. mixing speed (rpm) =	150.00
6. temperature (C) =	25.00
7. paddle diameter (cm):	
aqueous	6.00
organic	6.00
8. regression partition coeff. (org.aq) =	1.28
9. sample size (ml):	
aqueous	1.00
organic	1.00
10.acetic acid solute;	
i. feed sample volume (ml) =	12.86
ii. sample concn. (M) =	17.40
11.final titrant (ml);	
i. aqueous =	31.00
ii. organic =	21.20

Data Parameters:

1. water;	
i. VISB =	658.25
ii. VISTO =	283.16
iii. density (g/cc) =	1.00
iv. mole wt (g/mole) =	18.00
v. association parameter z =	2.60
2. isobutanol;	
i. VISB =	1193.10
ii. VISTO =	343.85
iii. density (g/cc) =	0.80
iv. mole wt (g/mole) =	74.12
v. association parameter z =	1.25
3. acetis acid;	
i. molal volume (ml/mole) =	64.10
ii. mole wt (g/mole) =	60.05

Figure A.8. Acetic acid test Acid11.

Calculations:

1. initial acid conc. in water;
   - i. final aqueous (g/L) = 18.62
   - ii. final organic (g/L) = 12.73
   - iii. inital aq (g/L), for Koa calc = 29.03
   - iii. inital aqueous (g/L), feed based = 29.03
   - iv. initial and final material balance (%) = 3.00
   - v. initial aqueous - final based (g/L) = 28.16

2. viscosity (g/cm-s);
   - i. water = 0.008906
   - ii. isobutanol = 0.017055

3. diffusion coefficient, acetic acid in;
   - i. water (cm^2/s)x100 = 0.001395
   - ii. isobutanol (cm^2/s)x100 = 0.001025

4. Reynolds number (w=rps);
   - i. water = 10084
   - ii. isobutanol = 4232

time (s)	LOG [time(s)]	base (ml)	Co(g/L) measured	Ca(g/L) org based	Koa calc (cm/s)	Ca(g/L) calc	Error %
1800	3.26	---	9.16	19.87	0.001064	20.14	-1.4
2700	3.43	---	12.09	16.94	0.001093	17.43	-2.9
3600	3.56	---	12.73	16.30	0.000900	15.45	5.2
				measured			
3600	3.56	31.00	---	18.62	0.000699	18.49	---

A aq = 2.025993
A org = 1.542707

Koa average aq (cm/s) = 0.000699
Koa average og (cm/s) = 0.001019

Aq & Org ave 0.000859

Base (ml)	Time (s)	Cbo (M) meas	Cbo(g/L) meas	Cba(g/L) org based
15.26	1800	0.1526	9.16	19.87
20.13	2700	0.2013	12.09	16.94
21.20	3600	0.2120	12.73	16.30

Figure A.8. (continued).

Test Date: 02/24/89
ACID12

Test Conditions:

1. aqueous phase volume (ml) =	350.00
2. organic phase volume (ml) =	450.00
3. NaOH titrant concn. (N):	
aqueous	0.01
organic	0.01
4. interfacial area (cm^2) =	79.00
5. mixing speed (rpm) =	150.00
6. temperature (C) =	25.00
7. paddle diameter (cm):	
aqueous	6.00
organic	6.00
8. regression partition coeff. (org.aq) =	1.28
9. sample size (ml):	
aqueous	1.00
organic	1.00
10.acetic acid solute;	
i. feed sample volume (ml) =	10.00
ii. sample concn. (M) =	17.40
11.final titrant (ml);	
i. aqueous =	32.80
ii. organic =	14.10

Data Parameters:

1. water;	
i. VISB =	658.25
ii. VISTO =	283.16
iii. density (g/cc) =	1.00
iv. mole wt (g/mole) =	18.00
v. association parameter z =	2.60
2. isobutanol;	
i. VISB =	1193.10
ii. VISTO =	343.85
iii. density (g/cc) =	0.80
iv. mole wt (g/mole) =	74.12
v. association parameter z =	1.25
3. acetis acid;	
i. molal volume (ml/mole) =	64.10
ii. mole wt (g/mole) =	60.05

Figure A.9. Acetic acid test Acid12.

Calculations:

1. initial acid conc. in water;
   - i. final aqueous (g/L) = 19.70
   - ii. final organic (g/L) = 8.47
   - iii. inital aq (g/L), for Koa calc = 29.03
   - iii. inital aqueous (g/L), feed based = 29.03
   - iv. initial and final material balance (%) = -3.79
   - v. initial aqueous - final based (g/L) = 30.13

2. viscosity (g/cm-s);
   - i. water = 0.008906
   - ii. isobutanol = 0.017055

3. diffusion coefficient, acetic acid in;
   - i. water (cm^2/s)x100 = 0.001395
   - ii. isobutanol (cm^2/s)x100 = 0.001025

4. Reynolds number (w=rps);
   - i. water = 10084
   - ii. isobutanol = 4232

time (s)	LOG [time(s)]	base (ml)	Co(g/L) measured	Ca(g/L) org based	Koa calc (cm/s)	Ca(g/L) calc	Error %
1800	3.26	---	5.80	23.22	0.000812	23.43	-0.9
2700	3.43	---	7.72	21.30	0.000809	21.53	-1.0
3600	3.56	---	8.47	20.56	0.000701	20.04	2.5
				measured			
3600	3.56	32.80	---	19.70	0.000751	19.59	---

A aq = 1.620659
A org = 2.039991

Aq & Org ave

Koa average aq (cm/s) = 0.000751
Koa average og (cm/s) = 0.000774
0.000762

Base (ml)	Time (s)	Cbo (M) meas	Cbo(g/L) meas	Cba(g/L) org based
9.66	1800	0.0966	5.80	23.22
12.86	2700	0.1286	7.72	21.30
14.10	3600	0.1410	8.47	20.56

Figure A.9. (continued).

Test Date: 03/01/89
ACID13

Test Conditions:

1. aqueous phase volume (ml) =	450.00
2. organic phase volume (ml) =	350.00
3. NaOH titrant concn. (N):	
aqueous	0.01
organic	0.01
4. interfacial area (cm^2) =	62.00
5. mixing speed (rpm) =	150.00
6. temperature (C) =	25.00
7. paddle diameter (cm):	
aqueous	6.00
organic	3.00
8. regression partition coeff. (org.aq) =	1.28
9. sample size (ml):	
aqueous	1.00
organic	1.00
10.acetic acid solute;	
i. feed sample volume (ml) =	12.86
ii. sample concn. (M) =	17.40
11.final titrant (ml);	
i. aqueous =	38.70
ii. organic =	14.84

Data Parameters:

1. water;	
i. VISB =	658.25
ii. VISTO =	283.16
iii. density (g/cc) =	1.00
iv. mole wt (g/mole) =	18.00
v. association parameter z =	2.60
2. isobutanol;	
i. VISB =	1193.10
ii. VISTO =	343.85
iii. density (g/cc) =	0.80
iv. mole wt (g/mole) =	74.12
v. association parameter z =	1.25
3. acetis acid;	
i. molal volume (ml/mole) =	64.10
ii. mole wt (g/mole) =	60.05

Figure A.10. Acetic acid test Acid13.

Calculations:

1. initial acid conc. in water;
   - i. final aqueous (g/L) = 23.24
   - ii. final organic (g/L) = 8.91
   - iii. inital aq (g/L), for Koa calc = 29.03
   - iii. inital aqueous (g/L), feed based = 29.03
   - iv. initial and final material balance (%) = -2.58
   - v. initial aqueous - final based (g/L) = 29.78

2. viscosity (g/cm-s);
   - i. water = 0.008906
   - ii. isobutanol = 0.017055

3. diffusion coefficient, acetic acid in;
   - i. water (cm^2/s)x100 = 0.001395
   - ii. isobutanol (cm^2/s)x100 = 0.001025

4. Reynolds number (w=rps);
   - i. water = 10084
   - ii. isobutanol = 1058

time (s)	LOG [time(s)]	base (ml)	Co(g/L) measured	Ca(g/L) org based	Koa calc (cm/s)	Ca(g/L) calc	Error %
1800	3.26	---	4.50	24.53	0.000555	24.19	1.4
2700	3.43	---	6.80	22.23	0.000607	22.26	-0.1
3600	3.56	---	8.91	20.12	0.000652	20.59	-2.3
				measured			
3600	3.56	38.70	---	23.24	0.000399	23.15	---

A aq = 2.025993
A org = 1.542707

Aq & Org ave

Koa average aq (cm/s) = 0.000399 0.000502
Koa average og (cm/s) = 0.000604

Base (ml)	Time (s)	Cbo (M) meas	Cbo(g/L) meas	Cba(g/L) org based
7.49	1800	0.0749	4.50	24.53
11.32	2700	0.1132	6.80	22.23
14.84	3600	0.1484	8.91	20.12

Figure A.10. (continued).

Test Date: 03/01/89
ACID14

Test Conditions:

1. aqueous phase volume (ml) =	350.00
2. organic phase volume (ml) =	450.00
3. NaOH titrant concn. (N):	
aqueous	0.01
organic	0.01
4. interfacial area (cm^2) =	62.00
5. mixing speed (rpm) =	150.00
6. temperature (C) =	25.00
7. paddle diameter (cm):	
aqueous	6.00
organic	3.00
8. regression partition coeff. (org.aq) =	1.28
9. sample size (ml):	
aqueous	1.00
organic	1.00
10.acetic acid solute;	
i. feed sample volume (ml) =	10.00
ii. sample concn. (M) =	17.40
11.final titrant (ml);	
i. aqueous =	44.55
ii. organic =	4.54

Data Parameters:

1. water;	
i. VISB =	658.25
ii. VISTO =	283.16
iii. density (g/cc) =	1.00
iv. mole wt (g/mole) =	18.00
v. association parameter z =	2.60
2. isobutanol;	
i. VISB =	1193.10
ii. VISTO =	343.85
iii. density (g/cc) =	0.80
iv. mole wt (g/mole) =	74.12
v. association parameter z =	1.25
3. acetis acid;	
i. molal volume (ml/mole) =	64.10
ii. mole wt (g/mole) =	60.05

Figure A.11. Acetic acid test Acid14.

Calculations:

1. initial acid conc. in water;
   - i. final aqueous (g/L) = 26.75
   - ii. final organic (g/L) = 2.73
   - iii. inital aq (g/L), for Koa calc = 29.03
   - iii. inital aqueous (g/L), feed based = 29.03
   - iv. initial and final material balance (%) = -2.76
   - v. initial aqueous - final based (g/L) = 29.83

2. viscosity (g/cm-s);
   - i. water = 0.008906
   - ii. isobutanol = 0.017055

3. diffusion coefficient, acetic acid in;
   - i. water (cm^2/s)x100 = 0.001395
   - ii. isobutanol (cm^2/s)x100 = 0.001025

4. Reynolds number (w=rps);
   - i. water = 10084
   - ii. isobutanol = 1058

time (s)	LOG [time(s)]	base (ml)	Co(g/L) measured	Ca(g/L) org based	Koa calc (cm/s)	Ca(g/L) calc	Error %
1800	3.26	---	1.57	27.45	0.000231	27.56	-0.4
2700	3.43	---	2.04	26.99	0.000203	26.88	0.4
3600	3.56	---	2.73	26.30	0.000210	26.24	0.2
				measured			
3600	3.56	44.55	---	26.75	0.000161	26.71	---

A aq = 1.620659
A org = 2.039991

Aq & Org ave

Koa average aq (cm/s) = 0.000161
Koa average og (cm/s) = 0.000215 0.000188

Base (ml)	Time (s)	Cbo (M) meas	Cbo(g/L) meas	Cba(g/L) org based
2.62	1800	0.0262	1.57	27.45
3.39	2700	0.0339	2.04	26.99
4.54	3600	0.0454	2.73	26.30

Figure A.11. (continued).

Test Date: 03/01/89
ACID15

Test Conditions:

1. aqueous phase volume (ml) =	350.00
2. organic phase volume (ml) =	350.00
3. NaOH titrant concn. (N):	
aqueous	0.01
organic	0.01
4. interfacial area (cm^2) =	62.00
5. mixing speed (rpm) =	150.00
6. temperature (C) =	25.00
7. paddle diameter (cm):	
aqueous	3.00
organic	3.00
8. regression partition coeff. (org.aq) =	1.28
9. sample size (ml):	
aqueous	1.00
organic	1.00
10.acetic acid solute;	
i. feed sample volume (ml) =	10.00
ii. sample concn. (M) =	17.40
11.final titrant (ml);	
i. aqueous =	44.60
ii. organic =	0.97

Data Parameters:

1. water;	
i. VISB =	658.25
ii. VISTO =	283.16
iii. density (g/cc) =	1.00
iv. mole wt (g/mole) =	18.00
v. association parameter z =	2.60
2. isobutanol;	
i. VISB =	1193.10
ii. VISTO =	343.85
iii. density (g/cc) =	0.80
iv. mole wt (g/mole) =	74.12
v. association parameter z =	1.25
3. acetis acid;	
i. molal volume (ml/mole) =	64.10
ii. mole wt (g/mole) =	60.05

Figure A.12. Acetic acid test Acidl5.

Calculations:

1. initial acid conc. in water;
   - i. final aqueous (g/L) = 26.78
   - ii. final organic (g/L) = 0.58
   - iii. inital aq (g/L), for Koa calc = 29.03
   - iii. inital aqueous (g/L), feed based = 29.03
   - iv. initial and final material balance (%) = 7.04
   - v. initial aqueous - final based (g/L) = 26.98

2. viscosity (g/cm-s);
   - i. water = 0.008906
   - ii. isobutanol = 0.017055

3. diffusion coefficient, acetic acid in;
   - i. water (cm^2/s)x100 = 0.001395
   - ii. isobutanol (cm^2/s)x100 = 0.001025

4. Reynolds number (w=rps);
   - i. water = 2521
   - ii. isobutanol = 1058

time (s)	LOG [time(s)]	base (ml)	Co(g/L) measured	Ca(g/L) org based	Koa calc (cm/s)	Ca(g/L) calc	Error %
1800	3.26	---	0.36	28.66	0.000039	28.69	-0.1
2700	3.43	---	0.53	28.50	0.000038	28.52	-0.1
3600	3.56	---	0.58	28.45	0.000031	28.36	0.3
				measured			
3600	3.56	44.60	---	26.78	0.000130	26.74	---

A aq = 1.797991
A org = 1.760270

Aq & Org ave

Koa average aq (cm/s) = 0.000130 0.000083
Koa average og (cm/s) = 0.000036

Base (ml)	Time (s)	Cbo (M) meas	Cbo(g/L) meas	Cba(g/L) org based
0.60	1800	0.0060	0.36	28.66
0.88	2700	0.0088	0.53	28.50
0.97	3600	0.0097	0.58	28.45

Figure A.12. (continued).

Test Date: 03/02/89
ACID16

Test Conditions:

1. aqueous phase volume (ml) =	450.00
2. organic phase volume (ml) =	450.00
3. NaOH titrant concn. (N):	
aqueous	0.01
organic	0.01
4. interfacial area (cm^2) =	62.00
5. mixing speed (rpm) =	150.00
6. temperature (C) =	25.00
7. paddle diameter (cm):	
aqueous	3.00
organic	3.00
8. regression partition coeff. (org.aq) =	1.28
9. sample size (ml):	
aqueous	1.00
organic	1.00
10.acetic acid solute;	
i. feed sample volume (ml) =	12.86
ii. sample concn. (M) =	17.40
11.final titrant (ml);	
i. aqueous =	44.60
ii. organic =	1.61

Data Parameters:

1. water;	
i. VISB =	658.25
ii. VISTO =	283.16
iii. density (g/cc) =	1.00
iv. mole wt (g/mole) =	18.00
v. association parameter z =	2.60
2. isobutanol;	
i. VISB =	1193.10
ii. VISTO =	343.85
iii. density (g/cc) =	0.80
iv. mole wt (g/mole) =	74.12
v. association parameter z =	1.25
3. acetis acid;	
i. molal volume (ml/mole) =	64.10
ii. mole wt (g/mole) =	60.05

Figure A.13. Acetic acid test Acidl6.

Calculations:

1. initial acid conc. in water;
   - i. final aqueous (g/L) = 26.78
   - ii. final organic (g/L) = 0.96
   - iii. inital aq (g/L), for Koa calc = 29.03
   - iii. inital aqueous (g/L), feed based = 29.03
   - iv. initial and final material balance (%) = 5.75
   - v. initial aqueous - final based (g/L) = 27.36

2. viscosity (g/cm-s);
   - i. water = 0.008906
   - ii. isobutanol = 0.017055

3. diffusion coefficient, acetic acid in;
   - i. water (cm^2/s)x100 = 0.001395
   - ii. isobutanol (cm^2/s)x100 = 0.001025

4. Reynolds number (w=rps);
   - i. water = 2521
   - ii. isobutanol = 1058

time (s)	LOG [time(s)]	base (ml)	Co(g/L) measured	Ca(g/L) org based	Koa calc (cm/s)	Ca(g/L) calc	Error %
1800	3.26	---	0.34	28.69	0.000048	28.62	0.2
2700	3.43	---	0.59	28.44	0.000056	28.42	0.1
3600	3.56	---	0.96	28.07	0.000068	28.22	-0.5
				measured			
3600	3.56	44.60	---	26.78	0.000168	26.74	---

A aq = 1.797994
A org = 1.760266

		Aq & Org ave
Koa average aq (cm/s) =	0.000168	0.000113
Koa average og (cm/s) =	0.000057	

Base (ml)	Time (s)	Cbo (M) meas	Cbo(g/L) meas	Cba(g/L) org based
0.57	1800	0.0057	0.34	28.69
0.99	2700	0.0099	0.59	28.44
1.61	3600	0.0161	0.96	28.07

Figure A.13. (continued).

Test Date: 03/02/89
ACID17

Test Conditions:

1. aqueous phase volume (ml) =	350.00
2. organic phase volume (ml) =	450.00
3. NaOH titrant concn. (N):	
aqueous	0.01
organic	0.01
4. interfacial area (cm^2) =	79.00
5. mixing speed (rpm) =	150.00
6. temperature (C) =	25.00
7. paddle diameter (cm):	
aqueous	3.00
organic	3.00
8. regression partition coeff. (org.aq) =	1.28
9. sample size (ml):	
aqueous	1.00
organic	1.00
10.acetic acid solute;	
i. feed sample volume (ml) =	10.00
ii. sample concn. (M) =	17.40
11.final titrant (ml);	
i. aqueous =	47.00
ii. organic =	1.20

Data Parameters:

1. water;	
i. VISB =	658.25
ii. VISTO =	283.16
iii. density (g/cc) =	1.00
iv. mole wt (g/mole) =	18.00
v. association parameter z =	2.60
2. isobutanol;	
i. VISB =	1193.10
ii. VISTO =	343.85
iii. density (g/cc) =	0.80
iv. mole wt (g/mole) =	74.12
v. association parameter z =	1.25
3. acetis acid;	
i. molal volume (ml/mole) =	64.10
ii. mole wt (g/mole) =	60.05

Figure A.14. Acetic acid test Acid17.

Calculations:

1. initial acid conc. in water;
   - i. final aqueous (g/L) = 28.22
   - ii. final organic (g/L) = 0.72
   - iii. inital aq (g/L), for Koa calc = 29.03
   - iii. inital aqueous (g/L), feed based = 29.03
   - iv. initial and final material balance (%) = 0.97
   - v. initial aqueous - final based (g/L) = 28.74

2. viscosity (g/cm-s);
   - i. water = 0.008906
   - ii. isobutanol = 0.017055

3. diffusion coefficient, acetic acid in;
   - i. water (cm^2/s)x100 = 0.001395
   - ii. isobutanol (cm^2/s)x100 = 0.001025

4. Reynolds number (w=rps);
   - i. water = 2521
   - ii. isobutanol = 1058

time (s)	LOG [time(s)]	base (ml)	Co(g/L) measured	Ca(g/L) org based	Koa calc (cm/s)	Ca(g/L) calc	Error %
1800	3.26	---	0.26	28.77	0.000028	28.71	0.2
2700	3.43	---	0.47	28.56	0.000034	28.56	-0.0
3600	3.56	---	0.72	28.30	0.000040	28.41	-0.4
				measured			
3600	3.56	47.00	---	28.22	0.000042	28.21	---

A aq = 1.620659
A org = 2.039991

Aq & Org ave

Koa average aq (cm/s) = 0.000042 0.000038
Koa average og (cm/s) = 0.000034

Base (ml)	Time (s)	Cbo (M) meas	Cbo(g/L) meas	Cba(g/L) org based
0.43	1800	0.0043	0.26	28.77
0.78	2700	0.0078	0.47	28.56
1.20	3600	0.0120	0.72	28.30

Figure A.14. (continued).

Test Date: 03/02/89
ACID18

Test Conditions:

1. aqueous phase volume (ml) =	450.00
2. organic phase volume (ml) =	450.00
3. NaOH titrant concn. (N):	
aqueous	0.01
organic	0.01
4. interfacial area (cm^2) =	79.00
5. mixing speed (rpm) =	150.00
6. temperature (C) =	25.00
7. paddle diameter (cm):	
aqueous	6.00
organic	3.00
8. regression partition coeff. (org.aq) =	1.28
9. sample size (ml):	
aqueous	1.00
organic	1.00
10.acetic acid solute;	
i. feed sample volume (ml) =	12.86
ii. sample concn. (M) =	17.40
11.final titrant (ml);	
i. aqueous =	30.00
ii. organic =	18.46

Data Parameters:

1. water;	
i. VISB =	658.25
ii. VISTO =	283.16
iii. density (g/cc) =	1.00
iv. mole wt (g/mole) =	18.00
v. association parameter z =	2.60
2. isobutanol;	
i. VISB =	1193.10
ii. VISTO =	343.85
iii. density (g/cc) =	0.80
iv. mole wt (g/mole) =	74.12
v. association parameter z =	1.25
3. acetis acid;	
i. molal volume (ml/mole) =	64.10
ii. mole wt (g/mole) =	60.05

Figure A.15. Acetic acid test Acid18.

Calculations:

1. initial acid conc. in water;
   - i. final aqueous (g/L) = 18.02
   - ii. final organic (g/L) = 11.09
   - iii. inital aq (g/L), for Koa calc = 29.03
   - iii. inital aqueous (g/L), feed based = 29.03
   - iv. initial and final material balance (%) = 1.15
   - v. initial aqueous - final based (g/L) = 28.70

2. viscosity (g/cm-s);
   - i. water = 0.008906
   - ii. isobutanol = 0.017055

3. diffusion coefficient, acetic acid in;
   - i. water (cm^2/s)x100 = 0.001395
   - ii. isobutanol (cm^2/s)x100 = 0.001025

4. Reynolds number (w=rps);
   - i. water = 10084
   - ii. isobutanol = 1058

time (s)	LOG [time(s)]	base (ml)	Co(g/L) measured	Ca(g/L) org based	Koa calc (cm/s)	Ca(g/L) calc	Error %
1800	3.26	---	7.81	21.22	0.001152	21.71	-2.3
2700	3.43	---	9.39	19.64	0.001010	19.38	1.3
3600	3.56	---	11.09	17.95	0.001002	17.64	1.7
				measured			
3600	3.56	30.00	---	18.02	0.000999	17.90	---

A aq = 1.797994
A org = 1.760266

		Aq & Org ave
Koa average aq (cm/s) =	0.000999	0.001027
Koa average og (cm/s) =	0.001055	

Base (ml)	Time (s)	Cbo (M) meas	Cbo(g/L) meas	Cba(g/L) org based
13.00	1800	0.1300	7.81	21.22
15.64	2700	0.1564	9.39	19.64
18.46	3600	0.1846	11.09	17.95

Figure A.15. (continued).

Test Date: 03/02/89
ACID19

Test Conditions:

1. aqueous phase volume (ml) =	450.00
2. organic phase volume (ml) =	450.00
3. NaOH titrant concn. (N):	
aqueous	0.01
organic	0.01
4. interfacial area (cm^2) =	79.00
5. mixing speed (rpm) =	150.00
6. temperature (C) =	25.00
7. paddle diameter (cm):	
aqueous	3.00
organic	6.00
8. regression partition coeff. (org.aq) =	1.28
9. sample size (ml):	
aqueous	1.00
organic	1.00
10.acetic acid solute;	
i. feed sample volume (ml) =	12.86
ii. sample concn. (M) =	17.40
11.final titrant (ml);	
i. aqueous =	32.20
ii. organic =	17.06

Data Parameters:

1. water;	
i. VISB =	658.25
ii. VISTO =	283.16
iii. density (g/cc) =	1.00
iv. mole wt (g/mole) =	18.00
v. association parameter z =	2.60
2. isobutanol;	
i. VISB =	1193.10
ii. VISTO =	343.85
iii. density (g/cc) =	0.80
iv. mole wt (g/mole) =	74.12
v. association parameter z =	1.25
3. acetis acid;	
i. molal volume (ml/mole) =	64.10
ii. mole wt (g/mole) =	60.05

Figure A.16. Acetic acid test Acid19.

Calculations:

1. initial acid conc. in water;
   - i. final aqueous (g/L) = 19.34
   - ii. final organic (g/L) = 10.24
   - iii. inital aq (g/L), for Koa calc = 29.03
   - iii. inital aqueous (g/L), feed based = 29.03
   - iv. initial and final material balance (%) = -0.48
   - v. initial aqueous - final based (g/L) = 29.17

2. viscosity (g/cm-s);
   - i. water = 0.008906
   - ii. isobutanol = 0.017055

3. diffusion coefficient, acetic acid in;
   - i. water (cm^2/s)x100 = 0.001395
   - ii. isobutanol (cm^2/s)x100 = 0.001025

4. Reynolds number (w=rps);
   - i. water = 2521
   - ii. isobutanol = 4232

time (s)	LOG [time(s)]	base (ml)	Co(g/L) measured	Ca(g/L) org based	Koa calc (cm/s)	Ca(g/L) calc	Error %
1800	3.26	---	6.49	22.55	0.000898	22.69	-0.6
2700	3.43	---	8.36	20.67	0.000847	20.50	0.8
3600	3.56	---	10.24	18.79	0.000872	18.79	0.0
				measured			
3600	3.56	32.20	---	19.34	0.000802	19.22	---

A aq = 1.797994
A org = 1.760266

		Aq & Org ave
Koa average aq (cm/s) =	0.000802	0.000837
Koa average og (cm/s) =	0.000872	

Base (ml)	Time (s)	Cbo (M) meas	Cbo(g/L) meas	Cba(g/L) org based
10.80	1800	0.1080	6.49	22.55
13.92	2700	0.1392	8.36	20.67
17.06	3600	0.1706	10.24	18.79

Figure A.16. (continued).

```
A1: 'Test Date: 03/02/89
A2: 'ACID19
A4: 'Test Conditions:
B6: '1. aqueous phase volume (ml) =
H6: (F2) 450
B7: '2. organic phase volume (ml) =
H7: (F2) 450
B8: '3. NaOH titrant concn. (N):
B9: '     aqueous
H9: (F2) 0.01
B10: '     organic
H10: (F2) 0.01
B11: '4. interfacial area (cm^2) =
H11: (F2) 79
B12: '5. mixing speed (rpm) =
H12: (F2) 150
B13: '6. temperature (C) =
H13: (F2) 25
B14: '7. paddle diameter (cm):
H14: (F2) '
B15: '     aqueous
H15: (F2) 3
B16: '     organic
H16: (F2) 6
B17: '8. regression partition coeff. (org.aq) =
H17: (F2) 1.28
B18: '9. sample size (ml):
H18: (F2) '
B19: '     aqueous
H19: (F2) 1
B20: '     organic
H20: (F2) 1
B21: '10.acetic acid solute;
C22: 'i.  feed sample volume (ml) =
H22: (F2) 12.86
C23: 'ii. sample concn. (M) =
H23: (F2) 17.4
B24: '11.final titrant (ml);
C25: 'i.  aqueous =
H25: (F2) 6.44/0.2
C26: 'ii. organic =
H26: (F2) 8.53/0.5
A29: 'Data Parameters:
B30: '1. water;
C31: 'i.   VISB =
H31: (F2) 658.25
C32: 'ii.  VISTO =
```

Figure A.17. Acetic acid test Acid19, Lotus program.

```
H32: (F2) 283.16
C33: 'iii. density (g/cc) =
H33: (F2) 0.998
C34: 'iv.  mole wt (g/mole) =
H34: (F2) 18
C35: 'v.   association parameter z =
H35: (F2) 2.6
B37: '2. isobutanol;
C38: 'i.   VISB =
H38: (F2) 1193.1
C39: 'ii.  VISTO =
H39: (F2) 343.85
C40: 'iii. density (g/cc) =
H40: (F2) 0.802
C41: 'iv.  mole wt (g/mole) =
H41: (F2) 74.123
C42: 'v.   association parameter z =
H42: (F2) 1.25
B44: '3. acetis acid;
C45: 'i.   molal volume (ml/mole) =
H45: (F2) 64.1
C46: 'ii.  mole wt (g/mole) =
H46: (F2) 60.052
A61: 'Calculations:
A63: '1.  initial acid conc. in water;
B64: 'i.   final aqueous (g/L) =
H64: (F2) +H46*($H$9*$H$25/$H$19)
B65: 'ii.  final organic (g/L) =
H65: (F2) +H46*($H$10*$H$26/$H$20)
B66: 'iii. inital aq (g/L), for Koa calc =
H66: (F2) +H67
A67: '
B67: 'iii. inital aqueous (g/L), feed based =
H67: (F2) +H46*$H$23*$H$22/($H$6+$H$22)
B68: 'iv.  initial and final material balance (%) =
H68: (F2) 100*(H67-H69)/H67
B69: 'v.   initial aqueous - final based (g/L) =
H69: (F2) (H64*(H6+H22/2)+H65*(H7+H22/2))/(H6+H22)
A71: '2.  viscosity (g/cm-s);
B72: 'i.  water =
H72: 0.01*@EXP($H$31*(1/($H$13+273)-1/$H$32))
B73: 'ii. isobutanol =
H73: 0.01*@EXP($H$38*(1/($H$13+273)-1/$H$39))
A75: '3.  diffusion coefficient, acetic acid in;
B76: 'i.  water (cm^2/s)x100 =
H76: ((0.000000074)*($H$13+273)*($H$35*$H$34)^0.5)/(100*$H$72*
     ($H$45)^0.6)*100
```

Figure A.17. (continued-2).

```
B77: 'ii. isobutanol (cm^2/s)x100 =
H77: ((0.000000074)*($H$13+273)*($H$42*$H$41)^0.5)/(100*$H$73*
     ($H$45)^0.6)*100
A79: '4.  Reynolds number (w=rps);
B80: 'i.   water =
H80: (F0) +$H$33*($H$12/60)*($H$15)^2/$H$72
B81: 'ii.  isobutanol =
H81: (F0) +$H$40*($H$12/60)*($H$16)^2/$H$73
A82: '-------------------------------------------------
A83: '    time
B83: '   LOG
C83: '   base
D83: ' Co(g/L)
E83: ' Ca(g/L)
F83: ' Koa calc
G83: ' Ca(g/L)
H83: '   Error
A84: '     (s)
B84: '[time(s)]
C84: '   (ml)
D84: 'measured
E84: 'org based
F84: '  (cm/s)
G84: '   calc
H84: '      %
A86: 1800
B86: (F2) @LOG(A86)
C86: (F2) '    ---
D86: (F2) +E101
E86: (F2) +F101
F86: (-$H$7/($H$11*$C$93))*(1/$A86)*@LN(($H$66-$C$93*$D86)/$H$66)
G86: (F2) +$H$66-($H$66/$C$93)*(1-@EXP(-$H$11*$C$93*$E$96*$A86/$H$7))
H86: (F1) 100*(E86-G86)/E86
A87: 2700
B87: (F2) @LOG(A87)
C87: (F2) '    ---
D87: (F2) +E102
E87: (F2) +F102
F87: (-$H$7/($H$11*$C$93))*(1/$A87)*@LN(($H$66-$C$93*$D87)/$H$66)
G87: (F2) +$H$66-($H$66/$C$93)*(1-@EXP(-$H$11*$C$93*$E$96*$A87/$H$7))
H87: (F1) 100*(E87-G87)/E87
A88: 3600
B88: (F2) @LOG(A88)
C88: (F2) '    ---
D88: (F2) +E103
E88: (F2) +F103
F88: (-$H$7/($H$11*$C$93))*(1/$A88)*@LN(($H$66-$C$93*$D88)/$H$66)
```

Figure A.17. (continued-3).

```
G88: (F2) +$H$66-($H$66/$C$93)*(1-@EXP(-$H$11*$C$93*$E$96*$A88/$H$7))
H88: (F1) 100*(E88-G88)/E88
E89: (F2) 'measured
A90: 3600
B90: (F2) @LOG(A90)
C90: (F2) 6.44/0.2
D90: (F2) '      ---
E90: (F2) +$H$46*$H$9*$C90/$H$19
F90:-(($H$6+0.75*$H$22)/($H$11*$C$92*$A90))*@LN(($C$92*$E90-
     $H$66/$H$17)/(($C$92-1/$H$17)*$H$66))
G90: (F2)(1/$C$92)*($H$66/$H$17+($C$92-1/$H$17)*$H$66*@EXP(-$H$11
     *$C$92*$E$95*$A90/($H$6+0.075*$H$22)))
H90: (F1) '      ---
B92: 'A aq  =
C92: 1+($H$6+0.75*$H$22)/($H$17*$H$7)
B93: 'A org =
C93: ($H$7/($H$6+0.75*$H$22)+1/$H$17)
B94: '
E94: '
G94: 'Aq & Org ave
B95: 'Koa average aq (cm/s) =
E95: +F90
G95: (E95+E96)/2
B96: 'Koa average og (cm/s) =
E96: (F86+F87+F88)/3
A97: '-------------------------------------------------
B99: '    Base
C99: '    Time
D99: ' Cbo (M)
E99: 'Cbo(g/L)
F99: 'Cba(g/L)
B100: '    (ml)
C100: '     (s)
D100: '  meas
E100: '  meas
F100: 'org based
B101: (F2) 5.4/0.5
C101: 1800
D101: (F4) +$H$10*($B101/1000)*($H$7/$H$20)/($H$7/1000)
E101: (F2) +$H$46*D101
F101: (F2) +$H$66-E101
B102: (F2) 6.96/0.5
C102: 2700
D102: (F4) +$H$10*($B102/1000)*($H$7/$H$20)/($H$7/1000)
E102: (F2) +$H$46*D102
```

Figure A.17. (continued-4).

```
F102: (F2) +$H$66-E102
B103: (F2) 8.53/0.5
C103: 3600
D103: (F4) +$H$10*($B103/1000)*($H$7/$H$20)/($H$7/1000)
E103: (F2) +$H$46*D103
F103: (F2) +$H$66-E103
```

Figure A.17. (continued-5).

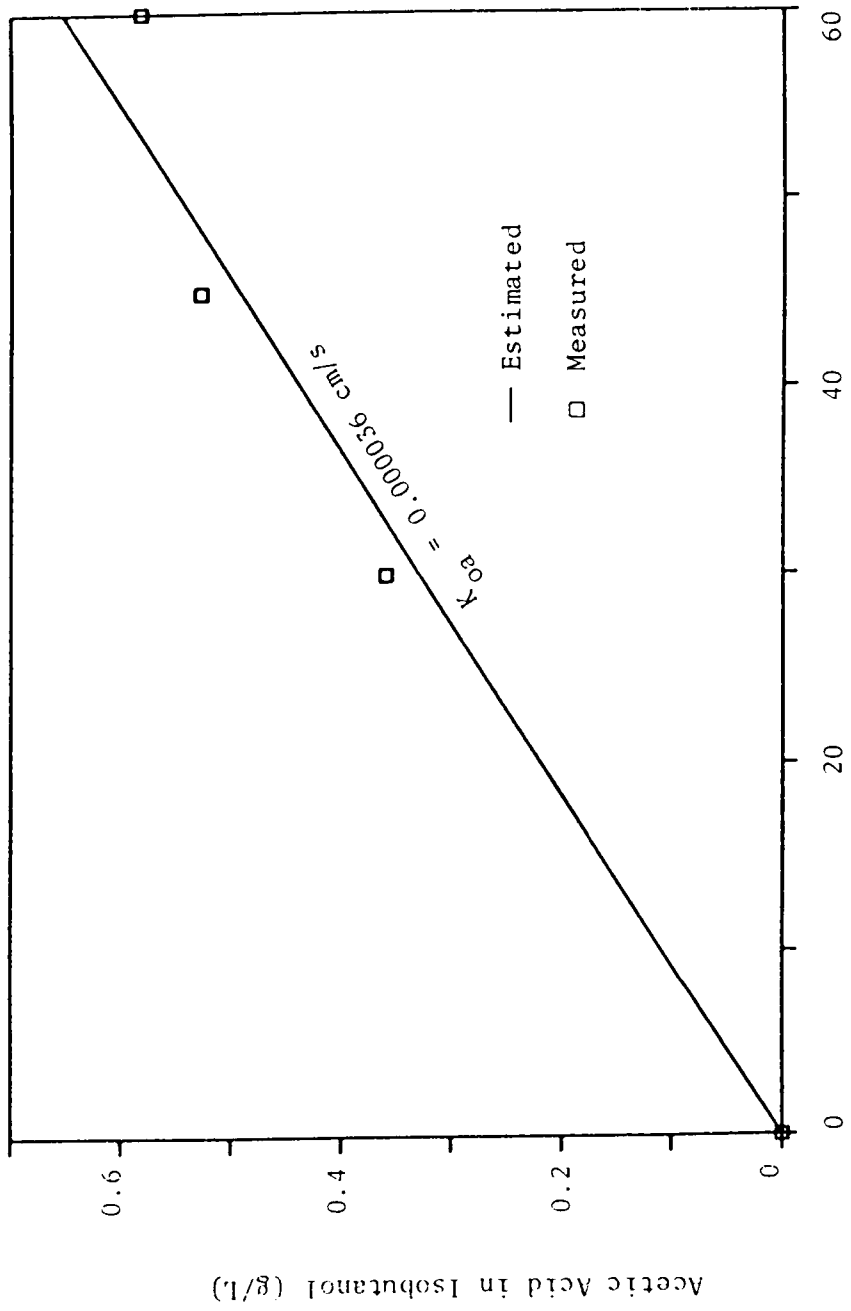


Figure A.18. Acetic acid in water and isobutanol, test Acid15.

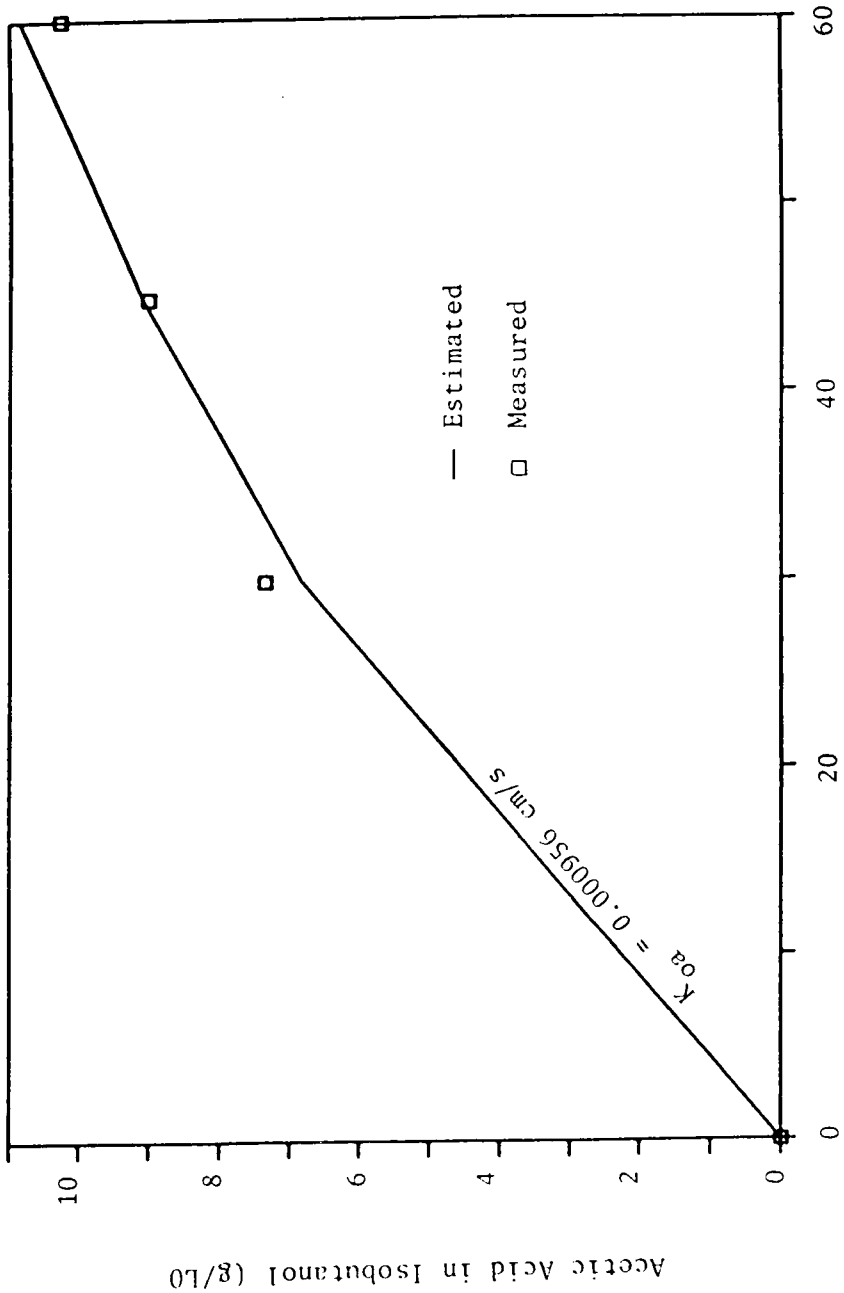


Figure A.19. Acetic acid in water and isobutanol, test Acid9.

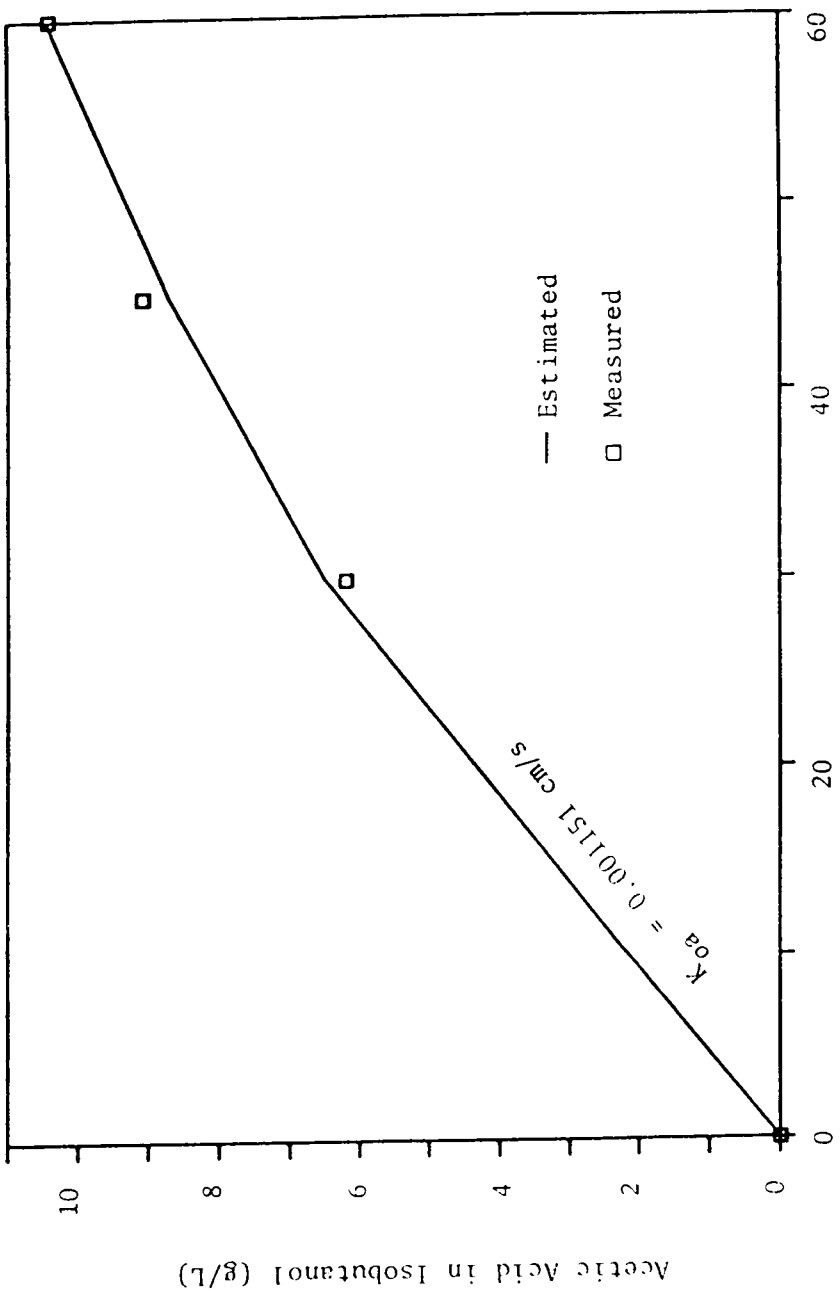


Figure A.20. Acetic acid in water and isobutanol, test Acid10.

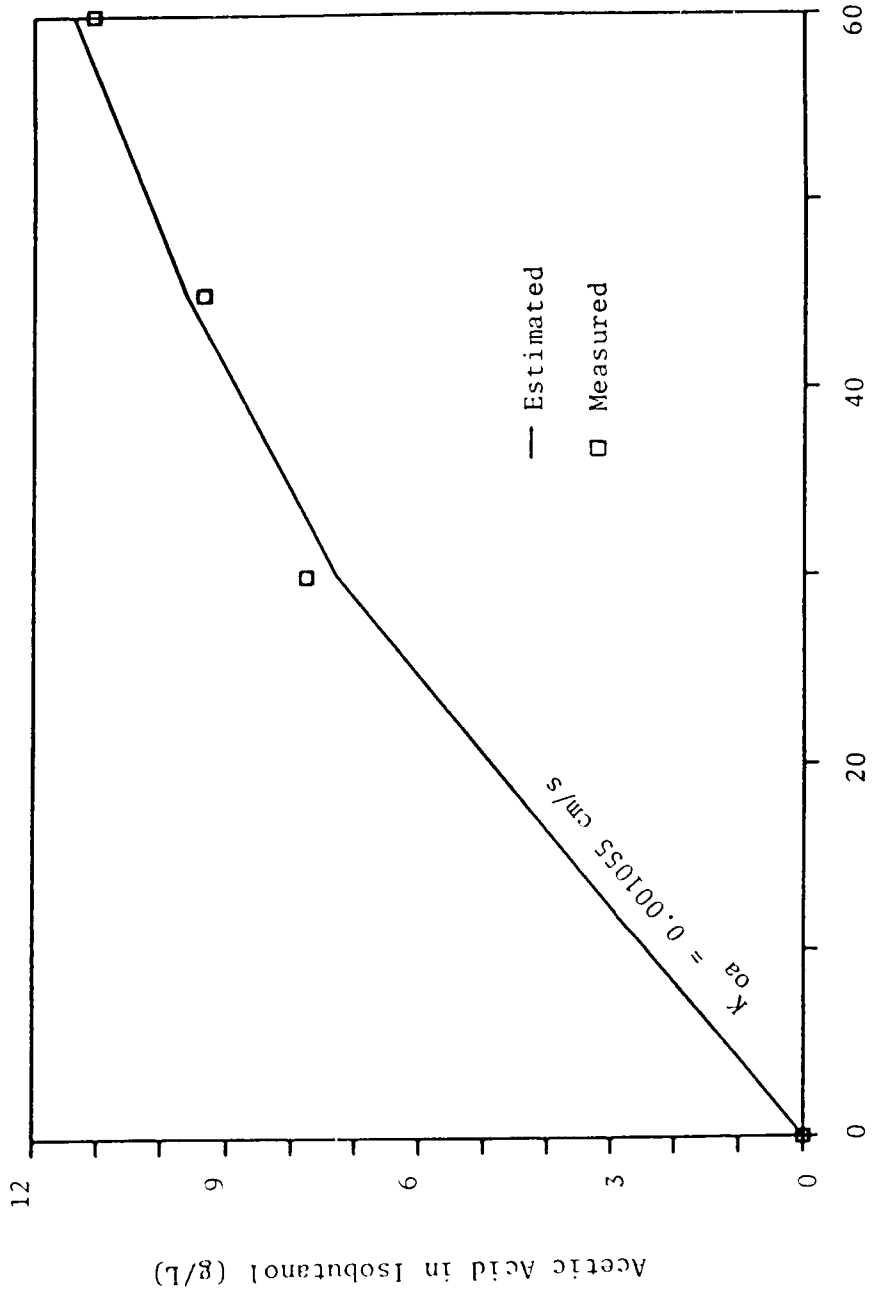


Figure A.21. Acetic acid in water and isobutanol, test Acid18.

A.2.3. Half Normal Plot

A Half Normal plot was prepared for the data of Table 5.1. This plot is shown in Figure 5.3. The plot was prepared by first determining the least-square-means, as described in the SAS User's Guide: Statistics, 1982 edition, pg 177. Table A.6 displays the sum-of-squares for the effects which are potentially components of the mass transfer model. Table A.7 lists the acetic acid least-squares-means (LSMEANS) in desending order, along with the required statistics for generating the Half Normal plot. The Least-Square-Means have similar ordering as the sum-of-squares.

Table A.6. Sum-of-squares for acetic acid effects.

Effects	Sum-of-Squares
d_o	1657656
d_a	320922
V_a	233772
V_a*d_a	147456
d_a*d_o	90000
V_o*d_o	71289
$S*V_o$	63756
V_a*d_o	55696
V_a*V_o	42025
$S*V_a$	34040
$S*d_o$	21170
V_o*d_a	18496
S	3249
$S*d_a$	992
V_o	210

Table A.7. Data for acetic acid half normal plot.

Parameter	LSMEANS	W	Z(15)	Ci(0.05)	Ci(0.20)
d_o	582	322	2.05	3.23	2.47
	610				
d_a	454	142	1.63	2.84	2.18
	737				
V_a	475	121	1.38	2.43	1.87
	717				
V_a*d_a	429	96	1.19	2.07	1.53
	521				
	479				
	954				
d_a*d_o	57	75	1.04		
	851				
	491				
	984				
V_o*d_o	204	67	0.91		
	981				
	344				
	855				
$S*V_o$	641	63	0.79		
	522				
	543				
	677				

Table A.7. Data for acetic acid half normal plot (continued).

Parameter	LSMEANS	W	Z(15)	Ci(0.05)	Ci(0.20)
V_a*d_o	94	59	0.69		
	856				
	454				
	980				
V_a*V_o	523	51	0.59		
	427				
	662				
	772				
$S*V_a$	507	46	0.50		
	656				
	443				
	777				
$S*d_o$	223	36	0.41		
	940				
	325				
	896				
V_o*d_a	429	34	0.32		
	521				
	479				
	954				
S	582	14	0.24		
	610				
$S*d_a$	432	8	0.16		
	731				
	476				
	744				
V_o	592	4	0.08		
	599				

The W-factor is determined by averaging the least-square-means as follows:

single affect -

$$W=ABS[LSMEAN(1) - LSMEAN(2)]/2,$$

where ABS is absolute value,

interaction affect -

$$W=ABS\{[LSMEAN(1)+LSMEAN(2)] - [LSMEAN(3)+LSMEAN(4)]\}/4.$$

The Z(15) component is the weighting factor for 15 degrees of freedom. Ci(0.05) and Ci(0.20) are the critical factors for determining the significance at the corresponding values of 0.05 and 0.20.

Since the data is assumed normally distributed, the W-factor at the eleventh most significant effect should represent the error at one standard deviation, for a data set with 15 degrees of freedom. As a matter of definition for this discussion, the fifteen most significant W-value corresponds to the most significant effect. This W(11)-value is mutliplied by the critical factors Ci to obtain the significance limit in terms of a W-factor. The critical W(11)*Ci values, shown in Table A.8, must be less than the actual corresponding W-value for significance. This analysis assumes every parameter with a W-value less than or equal to W(11) is not significant. See Section 4.3 for a discription of the Half Normal plot analysis.

Table A.8. Half normal plot signifcance values.

Parameter	W	W(11)*Ci(0.05)	W(11)*Ci(0.20)
d_o	322	242	185
d_a	142	213	163
V_a	120	182	140
V_a*d_a	96	155	115

The half normal plot is based upon an estimate of the error via the eleventh most significant effect. This error can also be estimated via a linear regression as follows,

$$SE = \frac{W(i)*Z(i,14)}{[Z(i,14)]^2},$$

where Z(i,14) is the weighting factor for 14 degrees of freedom, SE is the standard error, and i goes from 1 to 10 based on 16 orginal data points. Parameters more significant than the tenth W(10,14) are neglected. If the data is normally distributed, SE will equal W(11). The Z(i,14) values are listed in Table A.9.

Table A.9 Values of Z(i,14) for SE calculation.

Parameter	Z(i,14)
V_o*d_o	0.997
$S*V_o$	0.864
V_a*d_o	0.745
V_a*V_o	0.635
$S*V_a$	0.533
$S*d_o$	0.437
V_o*d_a	0.345
S	0.256
$S*d_a$	0.169
V_o	0.084

The SE calculated via the linear regression was 75.15, which is compared to the W(11) value of 75. The close correspondance of W(11) and SE indicates the data was normally distributed to a high degree, and the Half Normal plot is a legitimate technique for ascertaining parameter significance.

A.2.4. Individual Mass Transfer Coefficient Correlation

The correlation used to relate the Sherwood, Reynolds and Schmidt number, which allow prediction of the individual mass transfer coefficient, is discussed in Section 4.1.2. This correlation, Equation 4.6 was programed via Lotus for a linear regression. The Lotus worksheet is shown in Figure A.22, and corresponding program steps in Figure A.23. Two K_{oa} values were used for the regression, the average of the eight values of Table 5.1 at the 3 cm organic mixer diameter, and the average of the eight values of Table 5.1 at the 6 cm organic mixer diameter. These values were 0.000271 cm/s and 0.000918 cm/s respectively. The regression form is discussed in detail in section 4.1.2. The final regression yielded the correlation constants 0.0000934 and 1.38, shown in Equation 5.2.

ACETIC ACID MASS TRANSFER CORRELATION OF OVERALL AND INDIVIDUAL ,ASS TRANSFER COEFFICIENT

			Da	Ds
NSc,o	2075	2075	0.000013	1.28
			Do	
NRe,o	4232	1058	0.000010	
do	6	3	1/Koa=1/(Dsko)	
Koa,meas	0.000918	0.000272	ko = Koa/Ds	
ko,meas	0.000717	0.000213		
ko,calc	0.000717	0.000212		

ko = a(Df/d)(NRe,o)^b(NSc,o)^0.5 NSh,o=[(ko)(do)/Df,o]

ln(ko) = ln[a(NSc,o)^0.5] + bln(NRe,o)

y= ln[(d)ko] slope= (y1-y2)/(x1-x2)

x= ln(NRe,o) intercept= y1-(slope)x1

slope= b b=slope

intercept= ln[a(Df)(NSc,o)^0.5] a=[e^(intercept)]/[Df(NSc,o)^0.5]

y1	y2	x1	x2	slope	intercept	b	a
-5.44814	-7.35795	8.350429	6.964135	1.377640	-16.9520	1.38	9.53E-05

NRe,o	Koa(cm/s)	ko(cm/s)	do(cm)	NSh,o	ko-pred	NSh-pred
1058	0.000036	0.000028	3	8.44	0.000212	64
1058	0.000057	0.000044	3	13.36	0.000212	64
1058	0.000092	0.000071	3	21.56	0.000212	64
1058	0.000034	0.000026	3	7.97	0.000212	64
1058	0.000604	0.000471	3	141.56	0.000212	64
1058	0.000215	0.000167	3	50.39	0.000212	64
1058	0.000083	0.000064	3	19.45	0.000212	64
1058	0.001055	0.000824	3	247.27	0.000212	64
4232	0.000925	0.000722	6	433.59	0.000717	430
4232	0.000771	0.000602	6	361.41	0.000717	430
4232	0.000878	0.000685	6	411.56	0.000717	430
4232	0.000872	0.000681	6	408.75	0.000717	430
4232	0.000956	0.000746	6	448.13	0.000717	430
4232	0.001151	0.000899	6	539.53	0.000717	430
4232	0.001019	0.000796	6	477.66	0.000717	430
4232	0.000774	0.000604	6	362.81	0.000717	430

Figure A.22. Lotus worksheet, mass transfer coefficient correlation regression.

```
A1: 'ACETIC ACID MASS TRANSFER CORRELATION OF OVERALL AND
A2: 'INDIVIDUAL ,ASS TRANSFER COEFFICIENT
G3: '    Da
H3: '     Ds
A4: 'NSc,o
C4: 2075
E4: 2075
G4: 0.000013
H4: 1.28
G5: '    Do
A6: 'NRe,o
C6: 4232
E6: 1058
G6: (F6) 0.00001
A8: '   do
C8: 6
E8: 3
G8: '1/Koa=1/(Dsko)
A10: 'Koa,meas
C10: (F6) (B34+B35+B36+B37+B38+B39+B40+B41)/8
E10: (F6) (B26+B27+B28+B29+B30+B31+B32+B33)/8
G10: 'ko = Koa/Ds
A11: 'ko,meas
C11: (F6) +C10/$H$4
E11: (F6) +E10/$H$4
A12: 'ko,calc
C12: (F6) +$H$23*($G$6/C8)*(C6)^$G$23*(C4)^0.5
E12: (F6) +$H$23*($G$6/E8)*(E6)^$G$23*(E4)^0.5
A14: '  ko = a(Df/d)(NRe,o)^b(NSc,o)^0.5
F14: 'NSh,o=[(ko)(do)/Df,o]
A15: '  ln(ko) = ln[a(NSc,o)^0.5] + bln(NRe,o)
A17: '  y= ln[(d)ko]
E17: 'slope= (y1-y2)/(x1-x2)
A18: '  x= ln(NRe,o)
E18: 'intercept= y1-(slope)x1
A19: '  slope= b
E19: 'b=slope
A20: '  intercept= ln[a(Df)(NSc,o)^0.5]
E20: 'a=[e^(intercept)]/[Df(NSc,o)^0.5]
A22: '   y1
B22: '   y2
C22: '   x1
D22: '   x2
E22: '   slope
F22: 'intercept
G22: '     b
H22: '   a
```

Figure A.23. Lotus program, mass transfer coefficient correlation regression.

```
A23: @LN(C8*C11)
B23: @LN(E8*E11)
C23: @LN(C6)
D23: @LN(E6)
E23: (A23-B23)/(C23-D23)
F23: +A23-E23*C23
G23: (F2) +E23
H23: (S2) @EXP(F23)/(G6*C4^0.5)
A25: '   NRe,o
B25: 'Koa(cm/s)
C25: ' ko(cm/s)
D25: '  do(cm)
E25: '   NSh,o
F25: ' ko-pred
G25: 'NSh-pred
A26: +$E$6
B26: 0.000036
C26: +B26/$H$4
D26: 3
E26: (F2) +C26*D26/$G$6
F26: +$E$12
G26: (F0) +F26*D26/$G$6
A27: +$E$6
B27: 0.000057
C27: +B27/$H$4
D27: 3
E27: (F2) +C27*D27/$G$6
F27: +$E$12
G27: (F0) +F27*D27/$G$6
A28: +$E$6
B28: 0.000092
C28: +B28/$H$4
D28: 3
E28: (F2) +C28*D28/$G$6
F28: +$E$12
G28: (F0) +F28*D28/$G$6
A29: +$E$6
B29: 0.000034
C29: +B29/$H$4
D29: 3
E29: (F2) +C29*D29/$G$6
F29: +$E$12
G29: (F0) +F29*D29/$G$6
A30: +$E$6
B30: 0.000604
C30: +B30/$H$4
D30: 3
```

Figure A.23. (continued-2).

```
E30: (F2) +C30*D30/$G$6
F30: +$E$12
G30: (F0) +F30*D30/$G$6
A31: +$E$6
B31: 0.000215
C31: +B31/$H$4
D31: 3
E31: (F2) +C31*D31/$G$6
F31: +$E$12
G31: (F0) +F31*D31/$G$6
A32: +$E$6
B32: 0.000083
C32: +B32/$H$4
D32: 3
E32: (F2) +C32*D32/$G$6
F32: +$E$12
G32: (F0) +F32*D32/$G$6
A33: +$E$6
B33: 0.001055
C33: +B33/$H$4
D33: 3
E33: (F2) +C33*D33/$G$6
F33: +$E$12
G33: (F0) +F33*D33/$G$6
A34: +$C$6
B34: 0.000925
C34: +B34/$H$4
D34: 6
E34: (F2) +C34*D34/$G$6
F34: +$C$12
G34: (F0) +F34*D34/$G$6
A35: +$C$6
B35: 0.000771
C35: +B35/$H$4
D35: 6
E35: (F2) +C35*D35/$G$6
F35: +$C$12
G35: (F0) +F35*D35/$G$6
A36: +$C$6
B36: 0.000878
C36: +B36/$H$4
D36: 6
E36: (F2) +C36*D36/$G$6
F36: +$C$12
G36: (F0) +F36*D36/$G$6
A37: +$C$6
B37: 0.000872
```

Figure A.23. (continued-3).

```
C37: +B37/$H$4
D37: 6
E37: (F2) +C37*D37/$G$6
F37: +$C$12
G37: (F0) +F37*D37/$G$6
A38: +$C$6
B38: 0.000956
C38: +B38/$H$4
D38: 6
E38: (F2) +C38*D38/$G$6
F38: +$C$12
G38: (F0) +F38*D38/$G$6
A39: +$C$6
B39: 0.001151
C39: +B39/$H$4
D39: 6
E39: (F2) +C39*D39/$G$6
F39: +$C$12
G39: (F0) +F39*D39/$G$6
A40: +$C$6
B40: 0.001019
C40: +B40/$H$4
D40: 6
E40: (F2) +C40*D40/$G$6
F40: +$C$12
G40: (F0) +F40*D40/$G$6
A41: +$C$6
B41: 0.000774
C41: +B41/$H$4
D41: 6
E41: (F2) +C41*D41/$G$6
F41: +$C$12
G41: (F0) +F41*D41/$G$6
```

Figure A.23. (continued-4).

A.3. Zirconium Original Data

A.3.1. Metal Complex Distribution Coefficient and Complexation Equilibrium Constant

The regression analysis form used to determine the metal complex distribution coefficient and reaction equilibrium constant is detailed in Section 4.2.4. The data used for the regression was selected from literature, which is summarized in Appendix A.1.1. Figure A.24 shows the regression results as accomplished via the Lotus program presented in Figure A.25. The aqueous TBP concentration was linearly extraploted from the aqueous solubility reported for 30 vol% organic in Appendix A.1.3. Figures A.26 and A.27 show the effect of HNO_3 and TBP on the overall distribution coefficient as predicted by the regression. Both plots approach the constant value of D_4 with increasing HNO_3 or TBP concentrations.

CALCULATION OF D4 (METAL COMPLEX) AND Kf/Kb (REACTION EQUILIBRIUM CONSTANT)

Tracer Zr at 23 C.

$Y = aX + b,$

$(1/Dzr) = [(Kb/Kf)/D4](1/Ck) + (1/D4)$

$Y = 1/Dzr,$
$X = 1/Ck,$
$a = (Kb/Kf)/D4,$
$b = 1/D4.$

$Ck = ([Ca2]^4)x([Ca3]^2)$

HNO3 (mole/cc)	TBP(g/L)	Dzr	TBP (mole/cc)	Y	X	Dzr,calc	Ycalc
0.00194	0.20	0.044	7.52E-07	22.72727	1.2E+23	0.062215	16.07323
0.00225	0.19	0.051	7.14E-07	19.60784	7.6E+22	0.091293	10.95371
0.00284	0.20	0.084	7.52E-07	11.90476	2.7E+22	0.174182	5.741114
0.00301	0.19	0.120	7.14E-07	8.333333	2.4E+22	0.185506	5.390638
0.00374	0.20	0.167	7.52E-07	5.988023	9.0E+21	0.261680	3.821455
0.00401	0.19	0.230	7.14E-07	4.347826	7.6E+21	0.272706	3.666949
0.00302	0.09	0.178	3.31E-07	5.617977	1.1E+23	0.069162	14.45871
0.00302	0.11	0.211	4.08E-07	4.739336	7.2E+22	0.095228	10.50100
0.00306	0.13	0.246	4.86E-07	4.065040	4.8E+22	0.125428	7.972688
0.00304	0.17	0.335	6.36E-07	2.985074	2.9E+22	0.168639	5.929802
0.00307	0.21	0.490	7.88E-07	2.040816	1.8E+22	0.209180	4.780552
0.00298	0.24	0.710	9.13E-07	1.408450	1.5E+22	0.223419	4.475887

Regression Output:

		D4	Kb/Kf
Constant	2.865235	0.349011	3.69E-23
Std Err of Y Est	5.684979		
R Squared	0.378317		
No. of Observations	12		Dzr(30% TBP)
Degrees of Freedom	10		(2.9 M HNO3)
			0.247749
X Coefficient(s)	1.1E-22		
Std Err of Coef.	4.3E-23		

Figure A.24. Lotus worksheet, metal complex regression analysis.

```
A1: 'CALCULATION OF D4 (METAL COMPLEX) AND Kf/Kb (REACTION
A2: 'EQUILIBRIUM CONSTANT)
A4: 'Tracer Zr at 23 C.
F4: 'Y = aX + b,
F5: '
A6: '(1/Dzr) = [(Kb/Kf)/D4](1/Ck) + (1/D4)
F6: 'Y = 1/Dzr,
F7: 'X = 1/Ck,
A8: 'Ck = ([Ca2]^4)x([Ca3]^2)
F8: 'a = (Kb/Kf)/D4,
F9: 'b = 1/D4.
A11: '  HNO3
B11: 'TBP(g/L)
C11: '    Dzr
D11: '   TBP
E11: '   Y
F11: '   X
G11: 'Dzr,calc
H11: '   Ycalc
A12: '(mole/cc)
D12: '(mole/cc)
A13: 1.94/1000
B13: (F2) 0.2
C13: (F3) 0.044
D13: (S2) +B13/(1000*266)
E13: 1/C13
F13: 1/($A13^4*$D13^2)
G13: +$F$31/($G$31/(A13^4*(D13)^2)+1)
H13: 1/G13
A14: 2.25/1000
B14: (F2) 0.19
C14: (F3) 0.051
D14: (S2) +B14/(1000*266)
E14: 1/C14
F14: 1/($A14^4*$D14^2)
G14: +$F$31/($G$31/(A14^4*(D14)^2)+1)
H14: 1/G14
A15: 2.84/1000
B15: (F2) 0.2
C15: (F3) 0.084
D15: (S2) +B15/(1000*266)
E15: 1/C15
F15: 1/($A15^4*$D15^2)
G15: +$F$31/($G$31/(A15^4*(D15)^2)+1)
H15: 1/G15
A16: 3.01/1000
B16: (F2) 0.19
```

Figure A.25. Lotus program, metal complex regression analysis.

```
C16: (F3) 0.12
D16: (S2) +B16/(1000*266)
E16: 1/C16
F16: 1/($A16^4*$D16^2)
G16: +$F$31/($G$31/(A16^4*(D16)^2)+1)
H16: 1/G16
A17: 3.74/1000
B17: (F2) 0.2
C17: (F3) 0.167
D17: (S2) +B17/(1000*266)
E17: 1/C17
F17: 1/($A17^4*$D17^2)
G17: +$F$31/($G$31/(A17^4*(D17)^2)+1)
H17: 1/G17
A18: 4.01/1000
B18: (F2) 0.19
C18: (F3) 0.23
D18: (S2) +B18/(1000*266)
E18: 1/C18
F18: 1/($A18^4*$D18^2)
G18: +$F$31/($G$31/(A18^4*(D18)^2)+1)
H18: 1/G18
A19: 0.00302
B19: (F2) 0.3*323/1100
C19: 0.178
D19: (S2) +B19/(1000*266)
E19: 1/C19
F19: 1/($A19^4*$D19^2)
G19: +$F$31/($G$31/(A19^4*(D19)^2)+1)
H19: 1/G19
A20: 0.00302
B20: (F2) 0.3*398/1100
C20: 0.211
D20: (S2) +B20/(1000*266)
E20: 1/C20
F20: 1/($A20^4*$D20^2)
G20: +$F$31/($G$31/(A20^4*(D20)^2)+1)
H20: 1/G20
A21: 0.00306
B21: (F2) 0.3*474/1100
C21: 0.246
D21: (S2) +B21/(1000*266)
E21: 1/C21
F21: 1/($A21^4*$D21^2)
G21: +$F$31/($G$31/(A21^4*(D21)^2)+1)
H21: 1/G21
A22: 0.00304
```

Figure A.25. (continued-2).

```
 B22: (F2) 0.3*620/1100
C22: 0.335
D22: (S2) +B22/(1000*266)
E22: 1/C22
F22: 1/($A22^4*$D22^2)
G22: +$F$31/($G$31/(A22^4*(D22)^2)+1)
H22: 1/G22
A23: 0.00307
B23: (F2) 0.3*769/1100
C23: (F3) 0.49
D23: (S2) +B23/(1000*266)
E23: 1/C23
F23: 1/($A23^4*$D23^2)
G23: +$F$31/($G$31/(A23^4*(D23)^2)+1)
H23: 1/G23
A24: 0.00298
B24: (F2) 0.3*890/1100
C24: (F3) 0.71
D24: (S2) +B24/(1000*266)
E24: 1/C24
F24: 1/($A24^4*$D24^2)
G24: +$F$31/($G$31/(A24^4*(D24)^2)+1)
H24: 1/G24
C28: '
B29: 'Regression Output:
A30: 'Constant
D30: 2.8652359657
F30: '   D4
G30: '  Kb/Kf
A31: 'Std Err of Y Est
D31: 5.6849790713
F31: 1/D30
G31: (S2) +C36*F31
A32: 'R Squared
D32: 0.3783172619
A33: 'No. of Observations
D33: 12
G33: 'Dzr(30% TBP)
A34: 'Degrees of Freedom
D34: 10
G34: '(2.9 M HNO3)
G35: +$F$31/($G$31/((0.0029)^4*(0.00000113)^2)+1)
A36: 'X Coefficient(s)
C36: 1.0576467E-22
A37: 'Std Err of Coef.
C37: 4.2874289E-23
```

Figure A.25. (continued-3).

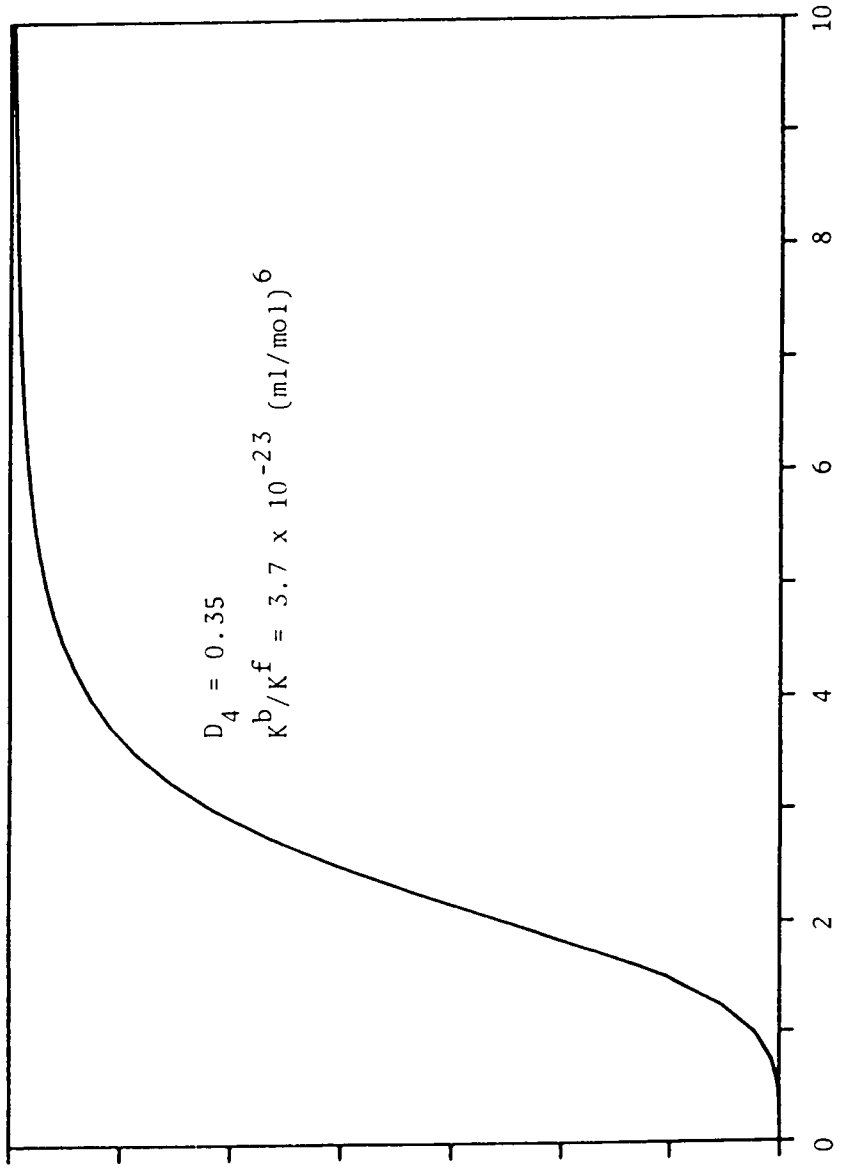


Figure A.26. Estimated D_{Zr} versus HNO_3 concentration.

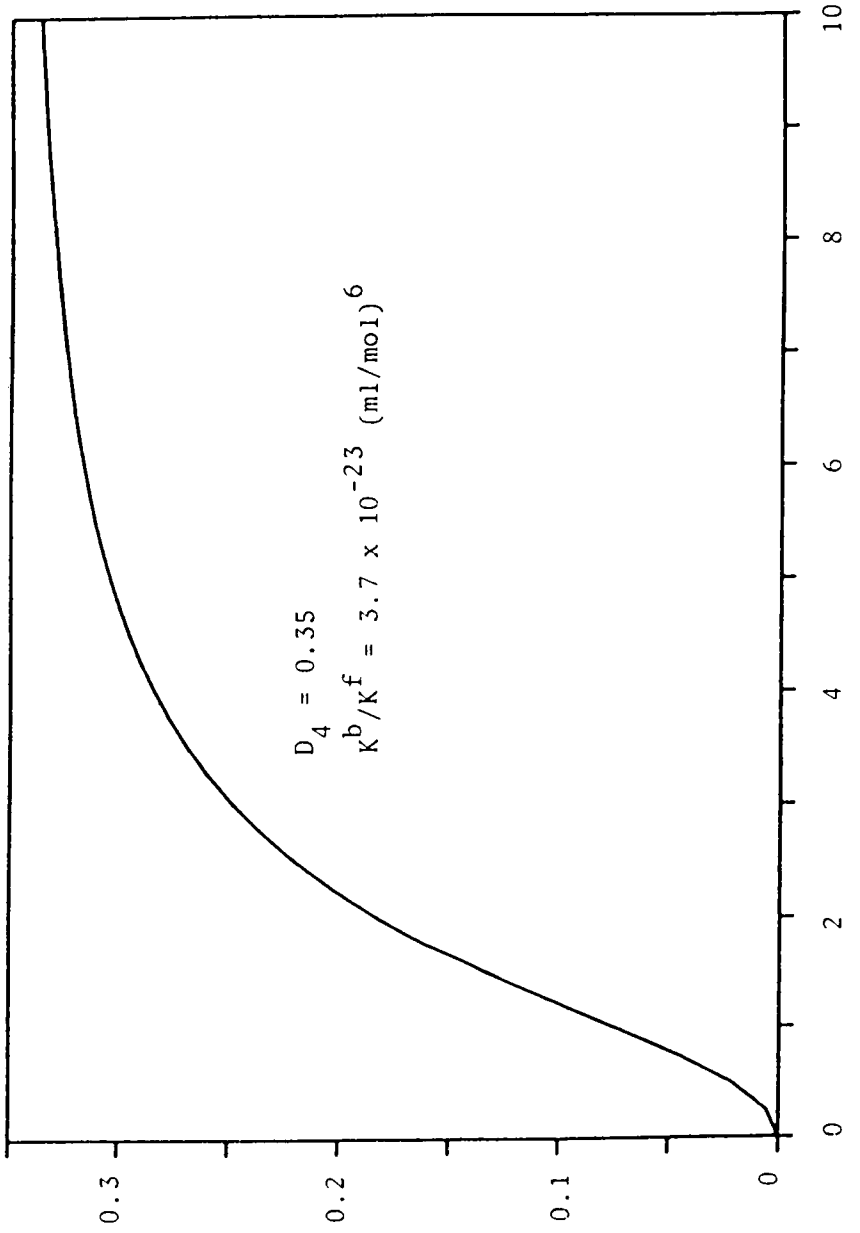


Figure A.27. Estimated D_{Zr} versus TBP concentration.

A.3.2. Mass Transfer Data

Tables A.10 and A.11 display the volume of zirconium sample collected and corresponding colormetric peak. An example Lotus worksheet Figure A.28, and corresponding program Figure A.29, demonstrate how the zirconium data was logged and analyzed via a spectrophotmetric calibration curve. All significant conditions are listed. A similar listing was generated for each of the twenty zirconium tests conducted.

Table A.10. Zirconium colormetric peak heights.

Area	Phase Volume	(Peak Height)/(Sample Size-ml) $d_{a1}.d_{o1}$	$d_{a2}.d_{o1}$	$d_{a1}.d_{o2}$	$d_{a2}.d_{o2}$	Hr
S_1	V_{a1},V_{o1}	650/1.00	X	X	3575/1.00	2
		1225/1.00			2800/0.50	4
		1950/1.00			2375/0.30	6
	V_{a2},V_{o1}	X	2650/1.50	2050/1.00	X	2
			1700/0.50	2800/0.75		4
			2225/0.50	2475/0.50		6
	V_{a1},V_{o2}	X	825/1.00	1500/1.00	X	2
			1250/1.00	2725/0.50		4
			1800/1.00	1825/0.50		6
	V_{a2},V_{o2}	1425/2.00	X	X	2700/1.00	2
		1250/1.00			2450/0.50	4
		1800/1.00			3150/0.50	6
S_2	V_{a1},V_{o1}	X	1475/0.60	2700/0.50	X	2
			2125/0.50	2950/0.40		4
			2350/0.40	2150/0.25		6
	V_{a2},V_{o1}	1900/1.00	X	X	1950/0.50	2
		1875/0.50			2475/0.40	4
		1575/0.40			2550/0.30	6
	V_{a1},V_{o2}	1650/2.00	X	X	1900/0.55	2
		2350/1.50			2250/0.40	4
		2225/1.00			2050/0.30	6
	V_{a2},V_{o2}	X	2100/1.00	1300/0.50	X	2
			1625/0.40	2275/0.50		4
			1325/0.30	2300/0.40		6

Table A.11. Zirconium colormetric peak heights, for concentration changes.

Conditions	(Peak Height)/(Sample Volume-ml)	Hr
$S_2, V_{a1}, V_{o1}, d_{a2}, d_{o2}$ C_{a1}, C_{a2}, C_{o3} (standard)	3925/0.75	2
	2125/0.30	4
	1750/0.20	6
$S_2, V_{a1}, V_{o1}, d_{a2}, d_{o2}$ $(C_{a1}/2), C_{a2}, C_{o3}$	1850/1.00	2
	2400/1.00	4
	2500/0.75	6
$S_2, V_{a1}, V_{o1}, d_{a2}, d_{o2}$ $C_{a1}, (C_{a2}/2), C_{o3}$	975/1.00	2
	1575/1.00	4
	1850/1.00	6
$S_2, V_{a1}, V_{o1}, d_{a2}, d_{o2}$ $C_{a1}, C_{a2}, (C_{o3}/2)$	1425/0.75	2
	1950/0.75	4
	2250/0.75	6

Test Date: 12/12/88
ZR1

Test Conditions:

1. Aqueous phase volume (cc).	350
2. Organic phase volume (cc).	350
3. Interfacial area (cm^2).	62
4. Mixing speed (rpm).	150
5. Temperature (C).	25
6. Paddle diameter, aq/org (cm).	6/6
7. Zr partition coeff. (org.aq).	0.24
8. TBP aq solubility at initially 3.5 M HNO3 (g/L);	0.3
TBP mole wt.,	266
TBP aqueous concentration at t0, (mole/cc).	1.13E-06
9. Zr in aqueous phase at t0, (g/L);	0.1250
Zr in aqueous phase at t0, (mole/cc),	1.37E-06
Zr mole wt (g/mole).	91.22
10.Zr(NO3)4.2TBP mole wt (g/mole);	871
ko, film [Zr(NO3)4.2TBP] (cm/s).	0.000567
ka, film [Zr(NO3)4.2TBP] (cm/s).	0.000860
11.HNO3 conc. at t0, (M);	3.5
NO3,1- distribution coefficient (O/A),	0.2
NO3,1- concentration (mole/cc) at t(f).	0.0029

Time (s)	Time (hr)	Org Based C4a(g/L) measure	C4o(g/L) measure
0	0	0.124968	0
7200	2	0.117236	0.007732
14400	4	0.113444	0.011524
21600	6	0.108686	0.016281

Figure A.28. Lotus worksheet, zirconium test ZR1 concentration calculations.

Calibration Data (Arsenazo III based):

Standard - Conc. = 10 mg/L Zr
Dilution= 25 ml of HNO3

Sample #	Vol Stand (ml)	Zr (ug/ml)	Peak Height	Zr calc (ug/ml)	Error (%)	slope	intercept
6	1.5	0.6	0.6	0.6	0	1.379310	-0.22758
5	1	0.4	0.455	0.4	0	0.930232	-0.02325
4	0.5	0.2	0.24	0.197447	1.276276	0.825825	-0.00075
3	0.375	0.15	0.185	0.152027	-1.35135	0.825825	-0.00075
2	0.25	0.1	0.125	0.102477	-2.47747	0.825825	-0.00075
1	0.125	0.05	0.06	0.048798	2.402402	0.825825	-0.00075
0	0	0	0	-0.00075	---	0.825825	-0.00075

Regression Output:

Constant	-0.00075
Std Err of Y Est	0.002501
R Squared	0.999249
No. of Observations	5
Degrees of Freedom	3
X Coefficient(s)	0.825825
Std Err of Coef.	0.013068

Mass Transfer Data (Arsenazo III based):

Sample #	Time (min)	Peak Height	Sample Volume (ml)	Aqueous chart Zr meas (ug/L)	Aqueous Sample Zr meas (g/L)
Feed	0	0.1825	0.03	0.149962	0.124968

Dilution = 25 ml HNO3

Sample #	Time (min)	Peak Height	Sample Volume (ml)	Organic chart Zr meas (ug/L)	Organic Sample Zr meas (g/L)	DZr (%)	Org based aqueous Sample Zr meas (g/L)
00	0	0	0	0	0	0.0	0.124968
01	120	0.3575	1	0.309302	0.007732	27.5	0.117236
02	240	0.28	0.5	0.230480	0.011524	42.3	0.113444
03	360	0.2375	0.3	0.195382	0.016281	62.4	0.108686

Figure A.28. (continued).

```
A1: 'Test Date: 12/12/88
A2: 'ZR1
A4: 'Test Conditions:
B6: '1. Aqueous phase volume (cc).
H6: 350
B7: '2. Organic phase volume (cc).
H7: 350
B8: '3. Interfacial area (cm^2).
H8: 62
B9: '4. Mixing speed (rpm).
H9: 150
B10: '5. Temperature (C).
H10: 25
B11: '6. Paddle diameter, aq/org (cm).
H11: '     6/6
B12: '7. Zr partition coeff. (org.aq).
H12: 0.24
B13: '8. TBP aq solubility at initially 3.5 M HNO3 (g/L);
H13: 0.3
B14: '     TBP mole wt.,
H14: 266
B15: '     TBP aqueous concentration at t0, (mole/cc).
H15: (S2) +H13/(1000*H14)
B16: '9. Zr in aqueous phase at t0, (g/L);
H16: (F4) +F68
B17: '      Zr in aqueous phase at t0, (mole/cc),
H17: (S2) +H16/(1000*H18)
B18: '      Zr mole wt (g/mole).
H18: 91.22
B19: '10.Zr(NO3)4.2TBP mole wt (g/mole);
H19: 871
B20: '      ko, film [Zr(NO3)4.2TBP] (cm/s).
H20: 0.000567
B21: '      ka, film [Zr(NO3)4.2TBP] (cm/s).
H21: (F6) 0.00086
B22: '11.HNO3 conc. at t0, (M);
H22: 3.5
B23: '      NO3,1- distribution coefficient (O/A),
H23: 0.2
A24: '
B24: '      NO3,1- concentration (mole/cc) at t(f).
H24: (F4) 0.001*H22/(1+H23)
A25: '---------------------------------------------------
A27: '
B27: '
C27: 'Org Based
D27: '
```

Figure A.29. Lotus program, zirconium test ZR1 concentration calculations.

```
A28: '    Time
B28: '    Time
C28: ' C4a(g/L)
D28: ' C4o(g/L)
A29: '     (s)
B29: '    (hr)
C29: ' measure
D29: ' measure
A30: 60*B76
B30: (F0) +A30/3600
C30: +H76
D30: +F76
A31: 7200
B31: (F0) +A31/3600
C31: +H77
D31: +F77
A32: 60*B78
B32: (F0) +A32/3600
C32: +H78
D32: +F78
A33: 21600
B33: (F0) +A33/3600
C33: +H79
D33: +F79
A34: '
D34: '
A35: '-----------------------------------------------------------
A36: 'Calibration Data (Arsenazo III based):
G36: '
A38: 'Standard -
C38: 'Conc. =
D38: 10
E38: 'mg/L Zr
C39: 'Dilution=
D39: 25
E39: 'ml of HNO3
A41: 'Sample #
B41: 'Vol Stand
C41: '   Zr
D41: '  Peak
E41: ' Zr calc
F41: '  Error
G41: '
H41: '
B42: '  (ml)
C42: ' (ug/ml)
D42: ' Height
```

Figure A.29. (continued-2).

```
E42: ' (ug/ml)
F42: '   (%)
G42: '  slope
H42: 'intercept
A43: +A44+1
B43: 1.5
C43: +$D$38*B43/$D$39
D43: 0.6
E43: (+G43*D43+H43)
F43: 100*(C43-E43)/C43
G43: (C43-C44)/(D43-D44)
H43: (D43*C44-D44*C43)/(D43-D44)
A44: +A45+1
B44: 1
C44: +$D$38*B44/$D$39
D44: 0.455
E44: (+G44*D44+H44)
F44: 100*(C44-E44)/C44
G44: (C44-C45)/(D44-D45)
H44: (D44*C45-D45*C44)/(D44-D45)
A45: +A46+1
B45: 0.5
C45: +$D$38*B45/$D$39
D45: 0.24
E45: (+$C$58*D45+$D$52)
F45: 100*(C45-E45)/C45
G45: +$C$58
H45: +$D$52
A46: +A47+1
B46: 0.375
C46: +$D$38*B46/$D$39
D46: 0.185
E46: (+$C$58*D46+$D$52)
F46: 100*(C46-E46)/C46
G46: +$C$58
H46: +$D$52
A47: +A48+1
B47: 0.25
C47: +$D$38*B47/$D$39
D47: 0.125
E47: (+$C$58*D47+$D$52)
F47: 100*(C47-E47)/C47
G47: +$C$58
H47: +$D$52
A48: +A49+1
B48: 0.125
C48: +$D$38*B48/$D$39
```

Figure A.29. (continued-3).

```
D48: 0.06
E48: (+$C$58*D48+$D$52)
F48: 100*(C48-E48)/C48
G48: +$C$58
H48: +$D$52
A49: 0
B49: 0
C49: +$D$38*B49/$D$39
D49: 0
E49: (+$C$58*D49+$D$52)
F49: '   ---
G49: +$C$58
H49: +$D$52
B51: 'Regression Output:
G51: '
A52: 'Constant
D52: -0.0007507508
F52: '
G52: '
A53: 'Std Err of Y Est
D53: 0.0025012509
G53: '
A54: 'R Squared
D54: 0.9992492492
A55: 'No. of Observations
D55: 5
A56: 'Degrees of Freedom
D56: 3
A58: 'X Coefficient(s)
C58: 0.8258258258
A59: 'Std Err of Coef.
C59: 0.0130688931
A61: '---------------------------------------------------
A62: 'Mass Transfer Data (Arsenazo III based):
E64: ' Aqueous
F64: ' Aqueous
G64: '
A65: '
D65: '  Sample
E65: '  chart
F65: ' Sample
G65: '
A66: 'Sample #
B66: '   Time
C66: '   Peak
D66: '  Volume
E66: ' Zr meas
```

Figure A.29. (continued-4).

```
F66: ' Zr meas
G66: '
B67: '   (min)
C67: '  Height
D67: '   (ml)
E67: '  (ug/L)
F67: '  (g/L)
G67: '
A68: 'Feed
B68: 0
C68: 0.1825
D68: 0.03
E68: +$G$47*C68+$H$47
F68: +E68*($E$70/D68)/1000
G68: '
C70: 'Dilution  =
E70: 25
F70: 'ml HNO3
H71: 'Org based
D72: '
E72: ' Organic
F72: ' Organic
G72: '
H72: ' aqueous
D73: ' Sample
E73: '  chart
F73: ' Sample
H73: ' Sample
A74: 'Sample #
B74: '  Time
C74: '  Peak
D74: ' Volume
E74: ' Zr meas
F74: ' Zr meas
G74: '     DZr
H74: ' Zr meas
B75: '  (min)
C75: ' Height
D75: '  (ml)
E75: '  (ug/L)
F75: '  (g/L)
G75: '     (%)
H75: '  (g/L)
A76: 'OO
B76: 0
C76: 0
D76: 0
```

Figure A.29. (continued-5).

```
E76: 0
F76: 0
G76: (F1) 100*(F76/H76)/$H$12
H76: +$F$68
A77: 'O1
B77: 120
C77: 0.3575
D77: 1
E77: +$G$44*C77+$H$44
F77: +E77*($E$70/D77)/1000
G77: (F1) 100*(F77/H77)/$H$12
H77: +$F$68-($H$7/$H$6)*F77
A78: 'O2
B78: 240
C78: 0.28
D78: 0.5
E78: +$G$47*C78+$H$47
F78: +E78*($E$70/D78)/1000
G78: (F1) 100*(F78/H78)/$H$12
H78: +$F$68-($H$7/$H$6)*F78
A79: 'O3
B79: 360
C79: 0.2375
D79: 0.3
E79: +$G$47*C79+$H$47
F79: +E79*($E$70/D79)/1000
G79: (F1) 100*(F79/H79)/$H$12
H79: +$F$68-($H$7/$H$6)*F79
```

Figure A.29. (continued-6).

A.3.3. Half normal plots

The zirconium half normal plots were prepared in a fashion identical to the acetic acid data, Appendix A.2.3. The W-factors for the data at two, four and six hours are shown in Table A.12. The

Table A.12 W-factors for zirconium data.

Parameter	W-factor 2 hr	4 hr	6 hr
d_o	71	103	135
S	43	67	66
d_a	29	48	69
V_a*d_o	22	29	18*
V_a*V_o	21*	27*	35
V_o	14	10	17
$S*d_a$	13	13	14
V_o*d_a	11	18	3
$S*V_a$	11	14	18
$S*d_o$	10	1	1
$S*V_o$	6	2	3
V_a*d_a	5	7	8
$Vo*d_o$	4	10	11
V_a	3	14	12
d_a*d_o	3	5	3
error (SE)	15	18	18

* - W(11)

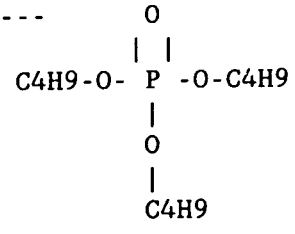
standard error was the W(11) factor esitmated via the linear regression as described in Appendix A.2.3. Factors such as Z-15 and Z-14 were indentical for the acetic acid and zirconium Half Normal plot analysis.

A.3.4. Diffusion Coefficient Estimation

Diffusion coefficients for the zirconium-Purex system were calculated via Lotus worksheet Figure A.30, which details the structural contributions used to estimate molal volumes at normal boiling point. The corresponding Lotus program is Figure A.31. The regression to estimate molar volume for the zirconium cation is shown in Figure A.32. Properties required for the Wilke-Chang or Lusis-Ratcliff correlations, such as density, viscosity, etc., are calulated for mixed solutions.

Diffusion Coefficient Estimation:

TBP;



C12 H27 O4 P

Structural contribution to molar volume at boiling point -

	cc/gmole	#	cume
C	14.8	12	177.6
H	3.7	27	277.5
O	7.4	4	307.1
P	27	1	334.1

NO3;

Structural contribution to molar volume at boiling point -

	cc/gmole	#	cume
N	15.6	1	15.6
O	7.4	3	37.8

Zr, Zr(NO3)4.2TBP, UO2, UO2(NO3)2.2TBP, NO3, TBP, O;

Structural contribution to molar volume at boiling point -

	cc/gmole	mole wt	Pred	Regression Output:	
P	27	31	28.14331	Constant	24.83908
S	25.6	32	28.24989	Std Err of Y Est	3.538298
Ti	35.7	48	29.95530	R Squared	0.585094
V	32	51	30.27506	No. of Observations	10
Cr	27.4	52	30.38165	Degrees of Freedom	8
Ge	34.5	73	32.62		
As	30.5	75	32.83317	X Coefficient(s)	0.106587
Sn	42.3	119	37.52304	Std Err of Coef.	0.031733
Sb	34.2	122	37.84280		
I	37	127	38.37574		
Zr	?	91	34.53858		
U	?	238	50.20699		

average % error = 8.571138

Figure A.30. Lotus worksheet, diffusion coefficient estimation.

	Zr	UO2	NO3	TBP	Zr(NO3)4 .2TBP	UO2(NO3)2 .2TBP	O
Volume: (cc/gmole)	34.53858	65.00699	37.8	334.1	853.9385	823.6069	7.4

Wilke-Chang

D(aq): (cm^2/s)	1.98E-05	1.36E-05	1.88E-05	5.08E-06	2.89E-06	2.96E-06
D(org) (cm^2/s)	2.44E-05	1.67E-05	2.31E-05	6.25E-06	3.56E-06	3.64E-06

Lusis-Ratcliff/Zr(NO3)4.2TBP

	TBP	Dodecane	30% TBP
D(org) (cm^2/s)	1.62E-06	4.37E-06	4.68E-06

UO2(NO3)2.2TBP

D(org) (cm^2/s)	1.63E-06	4.41E-06	4.72E-06

PROPERTIES OF HNO3 AND TBP;

25 C

	H2O	HNO3	TBP	Dodecane
Mole wt:	18	63	266	170
Assoc:	2.6	1	1	1
Density:	1	1.78	0.972	0.76
Viscos: (cp)	0.890684	1.47	3.2	1.148166

	HNO3(M) 3	TBP(V%) 30
Mole Wt.	20.53088	194.9048
Viscos: (cp)	0.953674	1.506271
Assoc:	2.510013	1
Density:	1.09514	0.8236
H2O(M):	50.34111	---
Dodec(M):	---	3.129411
TBP(M):	---	1.096240

Figure A.30. (continued).

```
A1: 'Diffusion Coefficient Estimation:
A4: 'TBP;
A5: '---
B5: 'O
A6: '         |
B6: ' |
A7: ' C4H9-O-
B7: 'P -O-C4H9
B8: '|
B9: 'O
B10: '|
B11: 'C4H9
A13: 'C12 H27 O4 P
A15: 'Structural contribution to molar volume at boiling point -
B17: ' cc/gmole
C17: '        #
D17: '    cume
A18: '    C
B18: 14.8
C18: 12
D18: +C18*B18
A19: '    H
B19: 3.7
C19: 27
D19: +C19*B19+D18
A20: '    O
B20: 7.4
C20: 4
D20: +C20*B20+D19
A21: '    P
B21: 27
C21: 1
D21: +C21*B21+D20
A24: 'NO3;
A25: '---
A26: 'Structural contribution to molar volume at boiling point -
B28: ' cc/gmole
C28: '        #
D28: '    cume
A29: '    N
B29: 15.6
C29: 1
D29: +C29*B29
A30: '    O
B30: 7.4
C30: 3
D30: +C30*B30+D29
```

Figure A.31. Lotus program, diffusion coefficient estimation.

```
A33: 'Zr, Zr(NO3)4.2TBP, UO2, UO2(NO3)2.2TBP, NO3, TBP, O;
A34: '-------------------------------------------------
A35: 'Structural contribution to molar volume at boiling point -
B37: ' cc/gmole
C37: '  mole wt
D37: '    Pred
F37: 'Regression Output:
A38: '     P
B38: 27
C38: 31
D38: +$G$44*C38+$H$38
E38: 'Constant
H38: 24.839087838
A39: '     S
B39: 25.6
C39: 32
D39: +$G$44*C39+$H$38
E39: 'Std Err of Y Est
H39: 3.5382986039
A40: '    Ti
B40: 35.7
C40: 48
D40: +$G$44*C40+$H$38
E40: 'R Squared
H40: 0.5850947983
A41: '     V
B41: 32
C41: 51
D41: +$G$44*C41+$H$38
E41: 'No. of Observations
H41: 10
A42: '    Cr
B42: 27.4
C42: 52
D42: +$G$44*C42+$H$38
E42: 'Degrees of Freedom
H42: 8
A43: '    Ge
B43: 34.5
C43: 73
D43: +$G$44*C43+$H$38
A44: '    As
B44: 30.5
C44: 75
D44: +$G$44*C44+$H$38
E44: 'X Coefficient(s)
G44: 0.1065878378
```

Figure A.31. (continued-2).

```
A45: '    Sn
B45: 42.3
C45: 119
D45: +$G$44*C45+$H$38
E45: 'Std Err of Coef.
G45: 0.0317339388
A46: '    Sb
B46: 34.2
C46: 122
D46: +$G$44*C46+$H$38
A47: '     I
B47: 37
C47: 127
D47: +$G$44*C47+$H$38
A48: '    Zr
B48: '      ?
C48: 91
D48: +$G$44*C48+$H$38
A49: '     U
B49: '      ?
C49: 238
D49: +$G$44*C49+$H$38
A50: 'average % error =
C50: +J48
F58: 'Zr(NO3)4
G58: 'UO2(NO3)2
B59: '    Zr
C59: '   UO2
D59: '    NO3
E59: '    TBP
F59: '  .2TBP
G59: '  .2TBP
H59: '      O
A60: 'Volume:
B60: +$D$48
C60: +$D$49+2*H60
D60: +$D$30
E60: +$D$21
F60: +B60+4*(D60)+2*(E60)
G60: +C60+2*(H60)+2*(D60)+2*(E60)
H60: +$B$30
A61: '(cc/gmole)
C62: 'Wilke-Chang
A63: 'D(aq):
B63: (S2) (0.000000074)*(($B$94*$B$91)^0.5)*298/($B$92*B60^0.6)
C63: (S2) (0.000000074)*(($B$94*$B$91)^0.5)*298/($B$92*C60^0.6)
D63: (S2) (0.000000074)*(($B$94*$B$91)^0.5)*298/($B$92*D60^0.6)
```

Figure A.31. (continued-3).

```
E63: (S2) (0.000000074)*(($B$94*$B$91)^0.5)*298/($B$92*E60^0.6)
F63: (S2) (0.000000074)*(($B$94*$B$91)^0.5)*298/($B$92*F60^0.6)
G63: (S2) (0.000000074)*(($B$94*$B$91)^0.5)*298/($B$92*G60^0.6)
H63: '
A64: '(cm^2/s)
A65: 'D(org)
B65: (S2) (0.000000074)*(($C$94*$C$91)^0.5)*298/($C$92*B60^0.6)
C65: (S2) (0.000000074)*(($C$94*$C$91)^0.5)*298/($C$92*C60^0.6)
D65: (S2) (0.000000074)*(($C$94*$C$91)^0.5)*298/($C$92*D60^0.6)
E65: (S2) (0.000000074)*(($C$94*$C$91)^0.5)*298/($C$92*E60^0.6)
F65: (S2) (0.000000074)*(($C$94*$C$91)^0.5)*298/($C$92*F60^0.6)
G65: (S2) (0.000000074)*(($C$94*$C$91)^0.5)*298/($C$92*G60^0.6)
A66: '(cm^2/s)
B68: 'Lusis-Ratcliff/Zr(NO3)4.2TBP
A69: '
B69: '   TBP
C69: ' Dodecane
D69: ' 30% TBP
A70: 'D(org)
B70: (S2)((0.0000000852)*(298)/($D$85*$E$60^0.33333))*(1.4*
     ($E$60/$F$60)^0.33333+$E$60/$F$60)
C70: (S2)((0.0000000852)*(298)/($E$85*$I$60^0.33333))*(1.4*
     ($I$60/$F$60)^0.33333+$I$60/$F$60)
D70: (S2)($C$98/($C$97+$C$98))*$B70*$D$85^0.8+($C$97/
     ($C$97+$C$98))*$C70*$E$85^0.8
A71: '(cm^2/s)
C73: 'UO2(NO3)2.2TBP
A74: 'D(org)
B74: (S2)((0.0000000852)*(298)/($D$85*$E$60^0.33333))*(1.4*
     ($E$60/$F$60)^0.33333+$E$60/$G$60)
C74: (S2)((0.0000000852)*(298)/($E$85*$I$60^0.33333))*(1.4*
     ($I$60/$F$60)^0.33333+$I$60/$G$60)
D74: (S2)($C$98/($C$97+$C$98))*$B74*$D$85^0.8+($C$97/
     ($C$97+$C$98))*$C74*$E$85^0.8
A75: '(cm^2/s)
B75: (S2) '
A78: 'PROPERTIES OF HNO3 AND TBP;
A79: '-------------------------
C80: '25 C
B81: '     H2O
C81: '    HNO3
D81: '     TBP
E81: 'Dodecane
```

Figure A.31. (continued-4).

```
A82: 'Mole wt:
B82: 18
C82: 63
D82: 266
E82: 170
A83: 'Assoc:
B83: 2.6
C83: 1
D83: 1
E83: 1
A84: 'Density:
B84: 1
C84: 1.78
D84: 0.972
E84: 0.76
A85: 'Viscos:
B85: @EXP(658.25*(1/298-1/283.16))
C85: 1.47
D85: 3.2
E85: @EXP(631.63*(1/298-1/318.78))
A86: '(cp)
B88: ' HNO3(M)
C88: ' TBP(V%)
E88: '
B89: 3
C89: 30
E89: '
B90: '--------
C90: '--------
A91: 'Mole Wt.
B91: +$B$89/($B$96+$B$89)*C82+$B$96/($B$96+$B$89)*B82
C91: +C98/(C97+C98)*D82+C97/(C97+C98)*E82
A92: 'Viscos:
B92: 0.1*10^(0.9527+0.0089*B89)
C92: 0.1*10^((C89/100)*(1.345+0.36*C89/100)+(1-C89/100)*@LOG(10*E85))
A93: '(cp)
A94: 'Assoc:
B94: +$B$89/($B$96+$B$89)*C83+$B$96/($B$96+$B$89)*B83
C94: 1
A95: 'Density:
B95: 0.99704+0.0327*B89
C95: 0.972*(C89/100)+(1-C89/100)*E84
A96: 'H2O(M):
B96: (1/B82)*(1000*B95-B89*C82)
C96: '   ---
A97: 'Dodec(M):
B97: '   ---
```

Figure A.31. (continued-5).

```
C97: 1000*(1-C89/100)*E84/E82
A98: 'TBP(M):
B98: '    ---
C98: 1000*(C89/100)*D84/D82
```

Figure A.31. (continued-6).

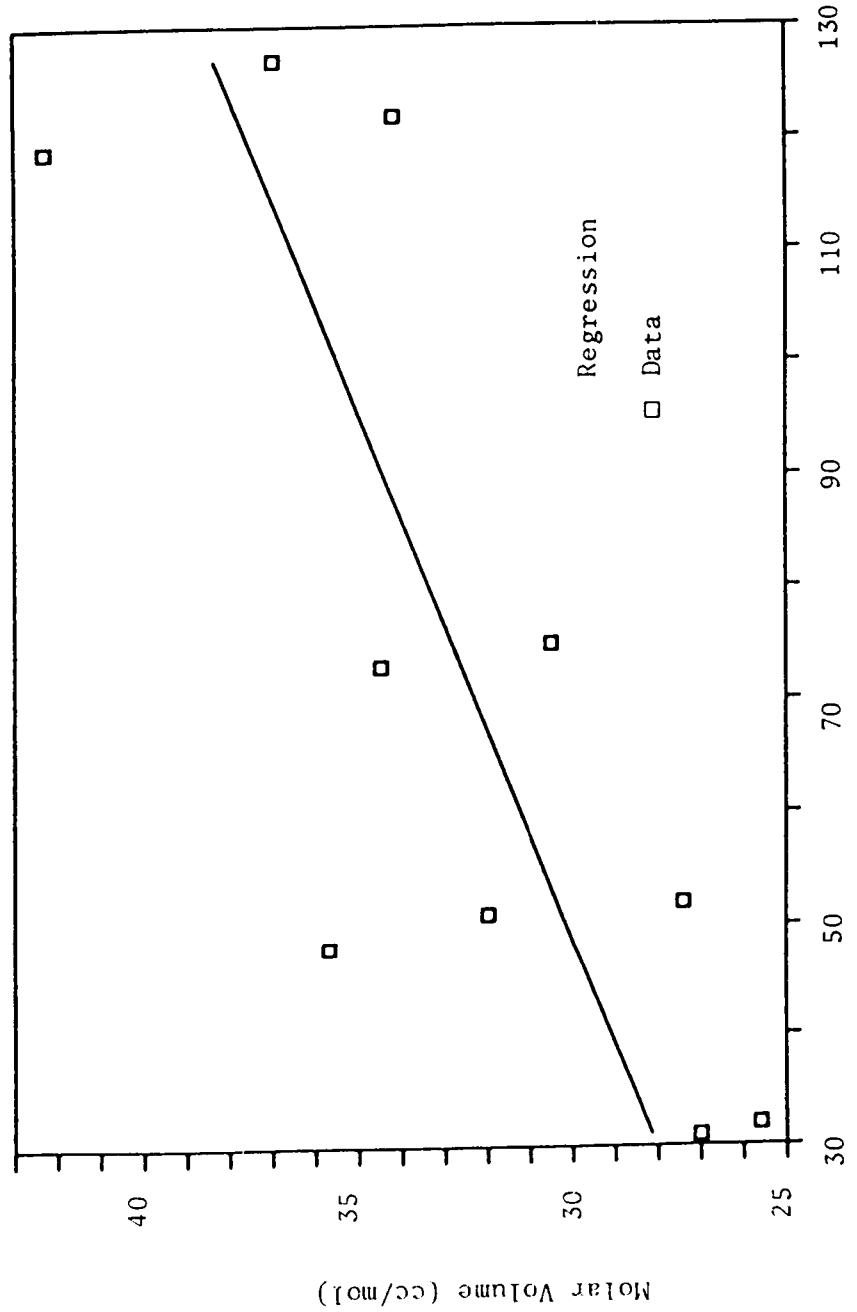


Figure A.32. Molar volume of pure elements.

A.3.5. Individual Mass Transfer Coefficient Estimation

Figure A.33 shows the Lotus worksheet, and Figure A.34 the Lotus program used to calculate the individual mass transfer coefficients. Table A.13 lists the properties and conditions required to estimate the individual mass transfer coefficient.

Table A.13. Zr-Purex estimated individual mass transfer coefficients.

Parameter	Value							
Specie	TBP		Zr*		Zr*		Zr*	
Phase	aq		aq		org		org	
Acid or TBP	3M		3M		30%		15%	
#(rpm)	150		150		150		150	
#(g/cc)	1.095		1.095		0.824		0.792	
#(g/cm-s)	0.0095		0.0095		0.0151		0.0129	
$D^f(cm^2/s)x10^6$	2.90		5.08		4.70		4.80	
N_{Sc}	2992		1714		3899		3393	
d(cm)	3	6	3	6	3	6	3	6
N_{Re}	2584	10335	2593	10374	1228	4911	1381	5526
$k(cm/s)x10^6$	335	1135	254	860	167	567	188	636

* - metal complex.

MASS TRANSFER COEFFICIENT CORRELATION
BASED UPON SURFACE RENEWAL THEORY

Zr(NO3)4.2TBP
3.5 M HNO3
30% TBP

1/Koa = 1/(Dsko)

kd/Df = (constant)(NRe^z)(NSc^0.5),
NRE = (d^2)W/V,
NSC = V/Df.

rpm	Df,o (cm^2/s)	NSc,o	NRe,o	Yo (g/cc)	d(cm)	Uo (gm/cm-s)
150	4.70E-06	3899	4911	0.824	6	0.0151

power	constant	ko(cm/s)
1.38	9.34E-05	0.000567

Figure A.33. Lotus worksheet, mass transfer coefficient estimation.

```
A1: 'MASS TRANSFER COEFFICIENT CORRELATION
A2: 'BASED UPON SURFACE RENEWAL THEORY
F3: 'Zr(NO3)4.2TBP
A4: '1/Koa = 1/(Dsko)
F4: '3.5 M HNO3
F5: '30% TBP
A6: 'kd/Df = (constant)(NRe^z)(NSc^0.5),
A7: 'NRE = (d^2)W/V,
A8: 'NSC = V/Df.
A10: '
B10: '   Df,o
E10: '    Yo
G10: '    Uo
A11: '     rpm
B11: '(cm^2/s)
C11: '   NSc,o
D11: '   NRe,o
E11: '  (g/cc)
F11: '   d(cm)
G11: '(gm/cm-s)
A12: 150
B12: (S2) 0.0000047
C12: (F0) (G12/E12)/B12
D12: (F0) +F12^2*(A12/60)*E12/G12
E12: 0.824
F12: 6
G12: 0.0151
A14: '   power
B14: 'constant
D14: 'ko(cm/s)
A15: (F2) 1.38
B15: (S2) 0.0000934
D15: (F6) +B15*(B12/F12)*D12^A15*C12^0.5
A17: '
E18: '
H18: '
E19: '
H19: '
E20: '
G20: '
H20: '
E21: '
G21: '
```

Figure A.34. Lotus program, mass transfer coefficient estimation.

A.3.6. Regression Analysis for K^f

The data included in the regression analysis are shown in Table 5.9. A Basic program was written to calculate the weighted least-square error based on the value of K^f, shown in Figure A.35. A K^f value was guessed, weighted sum-of-squares calculated, and new K^f guessed to find the least weighted sum-of-squares. The weighted error (WE) was determined as follows:

$$WE = \sum_{i=1}^{18} (([C_{o4}(predict)-C_{o4}(calc)]/C_{o4}(calc))^2)^{1/2}.$$

The least sum-of-squares occurred for,

$K^f = 1.6 \times 10^{21}$ [(mole/s)(ml/mole)^7].

```
100 REM  PROGRAM NAME "NLREG"
110 REM
120 REM  THE MODEL TO BE CURVE FIT EMPLOYS THREE PRIMARY EQUATIONS:
130 REM    (1) REACTION IN THE AQUEOUS PHASE;
140 REM    (2) PRODUCT DIFFUSION IN AQUEOUS AND ORGANIC PHASE;
150 REM    (3) MATERIAL BALANCE.
160 REM
170 REM  REQUIRED INPUT VARIABLES:
180 REM    (1) PRODUCT AQUEOUS AND ORGANIC MASS TRANSFER COEFICIENT;
190 REM    (2) AQUEOUS AND ORGANIC PHASE VOLUMES;
200 REM    (3) INTERFACIAL AREA;
210 REM    (4) INITIAL AQUEOUS HNO3 CONCENTRATION;
220 REM    (5) INITIAL ORGANIC TBP CONCENTRATION;
230 REM    (6) INITIAL AQUEOUS Zr CONCENTRATION;
240 REM    (7) MEASURED PRODUCT CONCENTRATION IN ORGANIC
250 REM        PHASE WITH TIME.
260 REM
270 REM  REQUIRED INPUT CONSTANTS:
280 REM    (1) Zr(NO3)4.2TBP DISTRIBUTION COEFFICIENT;
290 REM    (2) TBP DISTRIBUTION COEFFICIENT.
295 REM    (3) NO3- DISTRIBUTION COEFFICENT
300 REM
310 REM  THE METHOD OF CURVE FIT IS MINIMIZATION OF WEIGHTED RESIDUALS.
1050 REM THE PROGRAM IS WRITTEN IN GW-BASIC, 1/89, SFD.
1060 DIM S(75),VA(75),VO(75),KA(75),KO(75),CA1(75),CA2(75),
         CO3(75),CO4(75),T(75)
1100 J=0
1101 ER0=0
1105 REM
1110 REM
1113 REM DATA RECALL
1114 REM
1115 CLS:INPUT"Do you wish to create a data file (Y/N) ?";F$
1125 IF F$="n" OR F$="N" THEN GOTO 1150
1130 GOSUB 5000:REM  FILE CREATION
1140 REM
1150 CLS:INPUT"Name of data file to be recovered #:###.DAT = ?";Z$
1160 GOSUB 6000:REM  FILE RECOVERY
1161 ER0=ER
1170 REM
1171 IF J>0 THEN GOTO 1300
1180 CLS:INPUT"Change any data (Y/N) ?";C$
1190 IF C$="n" OR C$="N" THEN GOTO 1230
1200 GOSUB 4000
1210 REM
1220 REM
1230 CLS:INPUT"Print data (Y/N) ?";P$
```

Figure A.35. Basic program, regression analysis.

```
1240 IF P$="n" OR P$="N" THEN GOTO 1300
1250 GOSUB 8000
1280 REM
1290 REM
1295 REM
1300 FOR I=1 TO NDP
1310 IF S(I)=1 THEN S(I)=62:GOTO 1330
1320 S(I)=79
1330 IF VA(I)=1 THEN VA(I)=350:GOTO 1350
1340 VA(I)=450
1350 IF VO(I)=1 THEN VO(I)=350:GOTO 1370
1360 VO(I)=450
1370 IF KA(I)=1 THEN KA(I)=.000254:GOTO 1390
1380 KA(I)=.00086
1390 IF KO(I)=1 THEN KO(I)=.000167:GOTO 1410
1400 KO(I)=.000567
1410 IF CA1(I)=1 THEN CA1(I)=6.85E-07:GOTO 1430
1420 CA1(I)=1.37E-06
1430 IF CA2(I)=1 THEN CA2(I)=.00175:GOTO 1450
1440 CA2(I)=.0035
1450 IF CO3(I)=1 THEN CO3(I)=.00055:GOTO 1465
1460 CO3(I)=.0011
1465 CO4(I)=(.00001)*(CO4(I)/VO(I))*(1/91.22)
1466 IF T(I)=1 THEN T(I)=7200:GOTO 1470
1467 IF T(I)=2 THEN T(I)=14400:GOTO 1470
1468 T(I)=21600
1470 NEXT I
1480 REM
1490 REM
1500 D2=.2
1510 D3=975
1520 REM
1530 REM
1900 REM
1910 REM
1920 REM
1930 IF J>0 THEN GOTO 2020
2000 CLS:INPUT "D4 = ?";D4
2010 INPUT "(Kb/Kf) = ";KBKF
2020 INPUT "Kf = ";KF
2030 REM
2040 REM
2050 REM
3000 KB=KBKF*KF
3005 ER=0
3006 VAR=0
3007 PER=0
```

Figure A.35. (continued-2).

```
3010 FOR I=1 TO NDP
3020 A1=KB/VA(I)
3030 CA2(I)=CA2(I)/(1+D2)
3040 CO3(I)=D3*CO3(I)/(1+D3)
3050 CK=(CA2(I)^4)*(CO3(I)/D3)^2
3060 A2=(KF*CK)/VA(I)
3070 A3=(S(I)*KO(I)/VO(I))*(1-KO(I)/(KA(I)/D4+KO(I)))
3080 A4=S(I)*KO(I)*KA(I)/(VO(I)*(KA(I)/D4+KO(I)))
3090 A5=A1*CA1(I)
3100 A6=A1+A2
3110 A7=A1*VO(I)/VA(I)
3120 A8=A4*CA1(I)
3130 A9=A3+A4*VO(I)/VA(I)
3140 F1=CA1(I)
3150 F2=A5+A9*CA1(I)
3160 F3=A5*A9-A7*A8
3170 F4=A6+A9
3180 F5=A6*A9-A4*A7
3190 AA0=(F4+(F4^2-4*F5)^.5)/2
3200 AA1=(F4-(F4^2-4*F5)^.5)/2
3210 B2=F3/(AA0*AA1)
3220 B1=(F1*AA1^2-F2*AA1+F3)/(AA1*(AA1-AA0))
3230 B0=(F1*AA0^2-F2*AA0+F3)/(AA0*(AA0-AA1))
3240 REM
3250 CC1=CA1(I)-B2*(1+A2/A1)
3260 CC2=B1*(1+(A2-AA1)/A1)*EXP(-AA1*T(I))
3270 CC3=B0*(1+(A2-AA0)/A1)*EXP(-AA0*T(I))
3280 CCO4=(VA(I)/VO(I))*(CC1-CC2-CC3)
3290 REM
3300 ER=ER+((CO4(I)-CCO4)/CCO4)^2
3301 PER=PER+100*ABS((CO4(I)-CCO4)/CCO4)/NDP
3305 VAR=VAR+(CCO4-CO4(I))^2
3310 NEXT I
3320 REM
3325 DIFF=ER-ER0
3330 REM
3340 PRINT:PRINT "D4 = ";D4
3350 PRINT "(Kb/Kf) = ";KBKF
3360 PRINT "Kf = ";KF
3370 PRINT:PRINT "ERROR0 = ";ER0,"ERROR1 = ";ER
3375 PRINT:PRINT "Difference = ";DIFF
3440 LPRINT:LPRINT "D4 = ";D4
3450 LPRINT "(Kb/Kf) = ";KBKF
3460 LPRINT "Kf = ";KF
3465 LPRINT "Variance = ";VAR
3470 LPRINT:LPRINT "ERROR0 = ";ER0,"ERROR1 = ";ER
3471 LPRINT:LPRINT "WEIGHTED SUM-OF-SQUARES = ";ER
```

Figure A.35. (continued-3).

```
3472 LPRINT:LPRINT "AVERAGE PERCENT ERROR = ";PER
3480 PRINT"Type CONTINUE":STOP
3490 J=J+1
3500 GOTO 1160
3900 REM
3910 REM
4000 CLS:INPUT"Save changes (Y/N) ?";S$
4010 IF S$="n" OR S$="N" THEN GOTO 4100
4020 OPEN Z$ FOR OUTPUT AS #1
4030 REM
4100 CLS:INPUT"Data set # to be changed =";II
4180 PRINT"S(";II;") = ":INPUT S(II)
4190 PRINT"Va(";II;") = ":INPUT VA(II)
4200 PRINT"Vo(";II;") = ":INPUT VO(II)
4210 PRINT"ka(";II;") = ":INPUT KA(II)
4220 PRINT"ko(";II;") = ":INPUT KO(II)
4230 PRINT"CZr(0),aq(";II;") = ":INPUT CA1(II)
4240 PRINT"CNO3(0),aq(";II;") = ":INPUT CA2(II)
4250 PRINT"CTBP(0),org(";II;") = ":INPUT CO3(II)
4255 PRINT"CZr(NO3)4.2TBP,org[g/L](";II;") = ":INPUT CO4(II)
4260 PRINT"t(";II;") = ":INPUT T(II)
4300 IF S$="n" OR S$="N" THEN GOTO 4500
4310 PRINT #1,NDP
4320 PRINT #1,DAT$
4330 FOR I=1 TO NDP
4340 PRINT #1,S(I),VA(I),VO(I),KA(I),KO(I),CA1(I),CA2(I),CO3(I),
          CO4(I),T(I)
4350 NEXT I
4360 CLOSE #1
4500 RETURN
5000 REM
5010 REM
5020 REM
5030 REM DATA
5040 REM
5044 CLS:INPUT"Filename #:###.DAT = ";Z$
5045 OPEN Z$ FOR OUTPUT AS #1
5050 CLS:INPUT"Number of data sets = ";NDP
5055 REM
5066 CLS:INPUT"Data set description = ?";DAT$
5067 PRINT #1,NDP
5068 PRINT #1,DAT$
5070 FOR I=1 TO NDP
5080 PRINT"S(";I;") = ":INPUT S(I)
5090 PRINT"Va(";I;") = ":INPUT VA(I)
5100 PRINT"Vo(";I;") = ":INPUT VO(I)
5110 PRINT"ka(";I;") = ":INPUT KA(I)
5120 PRINT"ko(";I;") = ":INPUT KO(I)
```

Figure A.35. (continued-4).

```
5130 PRINT"CZr(0),aq(";I;") = ":INPUT CA1(I)
5140 PRINT"CNO3(0),aq(";I;") = ":INPUT CA2(I)
5150 PRINT"CTBP(0),org(";I;") = ":INPUT CO3(I)
5155 PRINT"CZr(NO3)4.2TBP,org[g/L](";I;") = ":INPUT CO4(I)
5160 PRINT"t(";I;") = ":INPUT T(I)
5170 PRINT #1,S(I),VA(I),VO(I),KA(I),KO(I),CA1(I),CA2(I),CO3(I),
          CO4(I),T(I)
5200 NEXT I
5400 CLOSE #1
5900 RETURN
6000 REM
6010 REM
6020 REM
6030 REM DATA RCOVERY
6040 REM
6050 OPEN Z$ FOR INPUT AS #1
6060 INPUT #1,NDP
6065 INPUT #1,DAT$
6070 FOR I=1 TO NDP
6080 INPUT #1,S(I),VA(I),VO(I),KA(I),KO(I),CA1(I),CA2(I),CO3(I),
          CO4(I),T(I)
6090 NEXT I
6100 CLOSE #1
6200 RETURN
7000 REM
7010 REM
7020 REM
7030 REM  DATA FILE LISTING
7040 REM
7060 LPRINT:LPRINT"Filename = ";Z$
7065 LPRINT:LPRINT"Number of data sets = ";NDP
7070 LPRINT:LPRINT DAT$
7080 LPRINT:LPRINT "TBP distribution coefficient (O/A) = ";D3
7085 LPRINT:LPRINT "NO3- distribution coefficient (O/A) = ";D2
7090 LPRINT:LPRINT"Zr(NO3)4.2TBP distribution coefficient (O/A) = ";D4
7100 LPRINT:LPRINT "WEIGHTED SUM-OF-SQUARES ";ERR
7101 LPRINT:LPRINT "PERCENT ERROR = ";PER
7900 RETURN
7950 REM
7960 REM
8000 LPRINT:LPRINT DAT$
8010 FOR I=1 TO NDP
8020 LPRINT S(I);" ";VA(I);" ";VO(I);" ";KA(I);" ";KO(I);" ";CA1(I);"
         ";CA2(I);" ";CO3(I);" ";CO4(I);" ";T(I)
8030 NEXT I
8040 RETURN
```

Figure A.35. (continued-5).

A.3.7. Film Thickness for Metal Complex

The aqueous phase film thickness for the metal complex can be estimated from the diffusion and mass transfer coefficient based on the Film theory.

$$x_o = D^f_{a4}/k_{a4},$$

$$= (2.9 \times 10^{-6}\ cm^2/s)/(0.000254\ cm/s),$$

$$= 0.011\ cm \text{ for 3 cm mixer, maximum thickness.}$$

The height of liquid for the least volume tested was 4.5 cm, therefore the aqueous film volume was 0.24% of the total aqueous volume. For TBP the aqueous film volume was 0.33% of total aqueous volume.

A.3.8. Data Uncertainty

An error propagation analysis was performed which related the measured concentration variance to the predicted concentration variance. It is based on the concept that the variance of a general function of variables involves the square of the partial derivative of the function with respect to each variable, (Volk, pg. 154, 1969). For this study the dependent variable was the predicted organic zirconium concentration, and the independent variables were the measured organic concentrations used for the K^f regression. The predicted value ($\hat{c}_{o4}$), is based on the value of K_f regressed from the nine measured organic zirconium concentrations (from two hours test time), and listed in Table 5.9. Consequently, the predicted value $\hat{c}_{o4}$ is a complex function of the nine data points as related by the mass transfer model and regression method.

The predicted concentration variance for the jth data point is defined as:

$$\sigma^2(\hat{c}_{o4,j}) = \sum_{i=1}^{n} (\partial \hat{c}_{o4,j}/\partial C_{o4,i})\sigma^2(C_{o4,j}), \qquad A.1$$

where σ^2 is the variance and n the number of independent variables (regression data points).

The variance of each data point used for the regression, was calculated as:

$$\sigma^2(\hat{c}_{o4,j}) = \frac{\hat{c}_{o4,j}}{(n-1)} \sum_{i=1}^{n} [(\hat{c}_{o4,i} - C_{o4,i})/\hat{c}_{o4,i}]. \qquad A.2$$

The partial derivative of Equation A.1 was determined by approximating the relationship between dependent and independent variables as a Taylor's series. If the higher order terms of the Taylor's series are neglected, the partial derivatives can be approximated at differences. This is acceptable as long as the variance of each dependent variable is not large, i.e. slope of partial derivative is approximately linear over the range of variance.

The approximated partial derivatives become:

$$(\partial \hat{c}_{o4,} / \partial C_{o4,i}) = \{[\hat{c}_{o4,j}(1) - \hat{c}_{o4,j}(2)]/[C_{o4,i}(1) - C_{o4,i}(2)]\} ,$$

where $\hat{c}_{o4,j}(1)$ is the predicted value based upon K^f determined from $C_{o4,i}(1)$ values as measured, and $\hat{c}_{o4,j}(2)$ is the predicted value based upon K^f determined from $C_{o4,i}(2)$ which are measured values perturbed by 10% (increased).

The final 95% confidence interval was estimated as two standard errors, where one standard error equals the square root of the variance. Figure A.36 shows the details of this analysis. The measured values $C_{o4,i}$ are under the column MEASURED. The predicted values based on non perturbed measured values are under the column OPTIMUM PREDICTED. The predicted values for each perturbed measured value are under the columns Y1 through Y9. The value $[\hat{c}_{o4,j}(1) - \hat{c}_{o4,j}(2)]$ are under the DIFF columns. The variance of each measured value per Equation A.2 is under the "Variance" column. The final variance for each predicted value is under "Var" column, as calculated per Equation A.1. The measured value $C_{o4,i}$ is represented by Y1 through Y9 in Figure A.36.

per Equation A.1. The measured value $C_{o4,i}$ is represented by Y1 through Y9 in Figure A.36.

			Weighted SS/(n-1) mole/ml	J* = {[DIFF/(amt pert)]^2}Var			
PERTURBATION = 10%			0.077987				
Kf	1.60	1.61	1.63	1.65	1.60	1.60	1.62
UNITS OF	(mole/ml)x10^8						
	OPTIMUM	Y1	Y2	Y3	Y4	Y5	Y6
MEASURED	PREDICTED	PREDICT	PREDICT	PREDICT	PREDICT	PREDICT	PREDICT
8.49	11.45	11.47	11.51	11.54	11.45	11.45	11.49
5.54	5.83	5.84	5.86	5.88	5.83	5.83	5.85
12.18	10.43	10.45	10.48	10.51	10.43	10.43	10.46
8.77	12.82	12.85	12.90	12.95	12.82	12.82	12.87
7.77	11.18	11.20	11.23	11.27	11.18	11.18	11.22
12.50	13.54	13.57	13.61	13.65	13.54	13.54	13.59
4.17	6.77	6.78	6.80	6.83	6.77	6.77	6.79
2.19	1.62	1.63	1.64	1.65	1.62	1.62	1.63
4.26	5.55	5.57	5.60	5.64	5.55	5.55	5.58
UNITS OF	(mole/ml)						
	Variance	DIFF	DIFF	DIFF	DIFF	DIFF	DIFF
	1.02E-15	2.00E-10	6.00E-10	9.00E-10	0.00E+00	0.00E+00	4.00E-10
	2.65E-16	1.00E-10	3.00E-10	5.00E-10	0.00E+00	0.00E+00	2.00E-10
	8.48E-16	2.00E-10	5.00E-10	8.00E-10	0.00E+00	0.00E+00	3.00E-10
	1.28E-15	3.00E-10	8.00E-10	1.30E-09	0.00E+00	0.00E+00	5.00E-10
	9.75E-16	2.00E-10	5.00E-10	9.00E-10	0.00E+00	0.00E+00	4.00E-10
	1.43E-15	3.00E-10	7.00E-10	1.10E-09	0.00E+00	0.00E+00	5.00E-10
	3.57E-16	1.00E-10	3.00E-10	6.00E-10	0.00E+00	0.00E+00	2.00E-10
	2.05E-17	1.00E-10	2.00E-10	3.00E-10	0.00E+00	0.00E+00	1.00E-10
	2.40E-16	2.00E-10	5.00E-10	9.00E-10	0.00E+00	0.00E+00	3.00E-10
J*	Y1	5.67E-19	5.11E-18	1.15E-18	0.00E+00	0.00E+00	2.27E-18
	Y2	8.64E-20	7.77E-19	2.16E-18	0.00E+00	0.00E+00	3.45E-19
	Y3	2.29E-19	1.43E-18	3.66E-18	0.00E+00	0.00E+00	5.15E-19
	Y4	1.50E-18	1.07E-17	2.82E-17	0.00E+00	0.00E+00	4.17E-18
	Y5	6.46E-19	4.04E-18	1.31E-17	0.00E+00	0.00E+00	2.58E-18
	Y6	8.24E-19	4.48E-18	1.11E-17	0.00E+00	0.00E+00	2.29E-18
	Y7	2.06E-19	1.85E-18	7.40E-18	0.00E+00	0.00E+00	8.22E-19
	Y8	4.27E-20	1.71E-19	3.84E-19	0.00E+00	0.00E+00	4.27E-20
	Y9	5.29E-19	3.31E-18	1.07E-17	0.00E+00	0.00E+00	1.19E-18

Figure A.36. Lotus worksheet, confidence interval.

1.60	1.82	1.63

Y7 PREDICT	Y8 PREDICT	Y9 PREDICTED
11.45	11.81	11.51
5.83	6.02	5.86
10.43	10.76	10.48
12.82	13.34	12.90
11.18	11.53	11.23
13.54	13.95	13.61
6.77	6.97	6.80
1.62	1.75	1.64
5.55	5.91	5.60

DIFF	DIFF	DIFF					
0.00E+00	3.60E-09	6.00E-10					
0.00E+00	1.90E-09	3.00E-10					
0.00E+00	3.30E-09	5.00E-10					
0.00E+00	5.20E-09	8.00E-10					
0.00E+00	3.50E-09	5.00E-10					
0.00E+00	4.10E-09	7.00E-10					
0.00E+00	2.00E-09	3.00E-10				standard	percent
0.00E+00	1.30E-09	2.00E-10			(mole/ml)	error	at two
0.00E+00	3.60E-09	5.00E-10				of	standard
				Var	Pred	estimate	errors
0.00E+00	1.84E-16	5.11E-18	2.08E-16		1.14E-07	1.44E-08	25.21
0.00E+00	3.12E-17	7.77E-19	3.53E-17		5.83E-08	5.94E-09	20.39
0.00E+00	6.23E-17	1.43E-18	6.95E-17		1.04E-07	8.34E-09	15.99
0.00E+00	4.51E-16	1.07E-17	5.06E-16		1.28E-07	2.25E-08	35.08
0.00E+00	1.98E-16	4.04E-18	2.22E-16		1.12E-07	1.49E-08	26.66
0.00E+00	1.54E-16	4.48E-18	1.77E-16		1.35E-07	1.33E-08	19.65
0.00E+00	8.22E-17	1.85E-18	9.43E-17		6.77E-08	9.71E-09	28.70
0.00E+00	7.21E-18	1.71E-19	8.02E-18		1.62E-08	2.83E-09	34.97
0.00E+00	1.72E-16	3.31E-18	1.91E-16		5.55E-08	1.38E-08	49.75
					ave		28.49

Figure A.36. (continued).

```
D32: 'Weighted
D33: (F2) 'SS/(n-1)
D34: 'mole/ml
E34: (F2) 'J* = {[DIFF/(amt pert)]^2}Var
A35: 'PERTURBATION = 10%
D35: (F6) 0.623893/8
A37: '   Kf
B37: (F2) 1.6
C37: (F2) 1.61
D37: (F2) 1.63
E37: (F2) 1.65
F37: (F2) 1.6
G37: (F2) 1.6
H37: (F2) 1.62
A38: 'UNITS OF (mole/ml)x10^8
B39: ' OPTIMUM
C39: '   Y1
D39: '   Y2
E39: '   Y3
F39: '   Y4
G39: '   Y5
H39: '   Y6
A40: 'MEASURED
B40: 'PREDICTED
C40: ' PREDICT
D40: ' PREDICT
E40: ' PREDICT
F40: ' PREDICT
G40: ' PREDICT
H40: ' PREDICT
A41: (F2) 12.73
B41: (F2) 11.45
C41: (F2) 11.47
D41: (F2) 11.51
E41: (F2) 11.54
F41: (F2) 11.45
G41: (F2) 11.45
H41: (F2) 11.49
A42: (F2) 5.54
B42: (F2) 5.83
C42: (F2) 5.84
D42: (F2) 5.86
E42: (F2) 5.88
F42: (F2) 5.83
G42: (F2) 5.83
H42: (F2) 5.85
A43: (F2) 12.18
```

Figure A.37. Lotus program, confidence interval.

B43: (F2) 10.43
C43: (F2) 10.45
D43: (F2) 10.48
E43: (F2) 10.51
F43: (F2) 10.43
G43: (F2) 10.43
H43: (F2) 10.46
A44: (F2) 8.77
B44: (F2) 12.82
C44: (F2) 12.85
D44: (F2) 12.9
E44: (F2) 12.95
F44: (F2) 12.82
G44: (F2) 12.82
H44: (F2) 12.87
A45: (F2) 7.77
B45: (F2) 11.18
C45: (F2) 11.2
D45: (F2) 11.23
E45: (F2) 11.27
F45: (F2) 11.18
G45: (F2) 11.18
H45: (F2) 11.22
A46: (F2) 12.5
B46: (F2) 13.54
C46: (F2) 13.57
D46: (F2) 13.61
E46: (F2) 13.65
F46: (F2) 13.54
G46: (F2) 13.54
H46: (F2) 13.59
A47: (F2) 4.17
B47: (F2) 6.77
C47: (F2) 6.78
D47: (F2) 6.8
E47: (F2) 6.83
F47: (F2) 6.77
G47: (F2) 6.77
H47: (F2) 6.79
A48: (F2) 2.19
B48: (F2) 1.62
C48: (F2) 1.63
D48: (F2) 1.64
E48: (F2) 1.65
F48: (F2) 1.62
G48: (F2) 1.62
H48: (F2) 1.63

Figure A.37. (continue-2).

```
A49: (F2) 4.26
B49: (F2) 5.55
C49: (F2) 5.57
D49: (F2) 5.6
E49: (F2) 5.64
F49: (F2) 5.55
G49: (F2) 5.55
H49: (F2) 5.58
A50: (F2) 'UNITS OF (mole/ml)
B51: (F2) 'Variance
C51: (F2) '    DIFF
D51: (F2) '    DIFF
E51: (F2) '    DIFF
F51: (F2) '    DIFF
G51: (F2) '    DIFF
H51: (F2) '    DIFF
B52: (S2) (B41/10^8)^2*$D$35
C52: (S2) -($B9-C41)/10^8
D52: (S2) -($B9-D41)/10^8
E52: (S2) -($B9-E41)/10^8
F52: (S2) -($B9-F41)/10^8
G52: (S2) -($B9-G41)/10^8
H52: (S2) -($B9-H41)/10^8
B53: (S2) (B42/10^8)^2*$D$35
C53: (S2) -($B10-C42)/10^8
D53: (S2) -($B10-D42)/10^8
E53: (S2) -($B10-E42)/10^8
F53: (S2) -($B10-F42)/10^8
G53: (S2) -($B10-G42)/10^8
H53: (S2) -($B10-H42)/10^8
B54: (S2) (B43/10^8)^2*$D$35
C54: (S2) -($B11-C43)/10^8
D54: (S2) -($B11-D43)/10^8
E54: (S2) -($B11-E43)/10^8
F54: (S2) -($B11-F43)/10^8
G54: (S2) -($B11-G43)/10^8
H54: (S2) -($B11-H43)/10^8
B55: (S2) (B44/10^8)^2*$D$35
C55: (S2) -($B12-C44)/10^8
D55: (S2) -($B12-D44)/10^8
E55: (S2) -($B12-E44)/10^8
F55: (S2) -($B12-F44)/10^8
G55: (S2) -($B12-G44)/10^8
H55: (S2) -($B12-H44)/10^8
B56: (S2) (B45/10^8)^2*$D$35
C56: (S2) -($B13-C45)/10^8
D56: (S2) -($B13-D45)/10^8
```

Figure A.37. (continue-3).

```
E56: (S2) -($B13-E45)/10^8
F56: (S2) -($B13-F45)/10^8
G56: (S2) -($B13-G45)/10^8
H56: (S2) -($B13-H45)/10^8
B57: (S2) (B46/10^8)^2*$D$35
C57: (S2) -($B14-C46)/10^8
D57: (S2) -($B14-D46)/10^8
E57: (S2) -($B14-E46)/10^8
F57: (S2) -($B14-F46)/10^8
G57: (S2) -($B14-G46)/10^8
H57: (S2) -($B14-H46)/10^8
B58: (S2) (B47/10^8)^2*$D$35
C58: (S2) -($B15-C47)/10^8
D58: (S2) -($B15-D47)/10^8
E58: (S2) -($B15-E47)/10^8
F58: (S2) -($B15-F47)/10^8
G58: (S2) -($B15-G47)/10^8
H58: (S2) -($B15-H47)/10^8
B59: (S2) (B48/10^8)^2*$D$35
C59: (S2) -($B16-C48)/10^8
D59: (S2) -($B16-D48)/10^8
E59: (S2) -($B16-E48)/10^8
F59: (S2) -($B16-F48)/10^8
G59: (S2) -($B16-G48)/10^8
H59: (S2) -($B16-H48)/10^8
B60: (S2) (B49/10^8)^2*$D$35
C60: (S2) -($B17-C49)/10^8
D60: (S2) -($B17-D49)/10^8
E60: (S2) -($B17-E49)/10^8
F60: (S2) -($B17-F49)/10^8
G60: (S2) -($B17-G49)/10^8
H60: (S2) -($B17-H49)/10^8
A62: '   J*
B62: '   Y1
C62: (S2) +$B52*(C52/(0.1*$A41/10^8))^2
D62: (S2) +$B52*(D52/(0.1*$A41/10^8))^2
E62: (S2) +$B52*(E52/(0.1*$A41/10^8))^2
F62: (S2) +$B52*(F52/(0.1*$A41/10^8))^2
G62: (S2) +$B52*(G52/(0.1*$A41/10^8))^2
H62: (S2) +$B52*(H52/(0.1*$A41/10^8))^2
B63: '   Y2
C63: (S2) +$B53*(C53/(0.1*$A42/10^8))^2
D63: (S2) +$B53*(D53/(0.1*$A42/10^8))^2
E63: (S2) +$B53*(E53/(0.1*$A42/10^8))^2
F63: (S2) +$B53*(F53/(0.1*$A42/10^8))^2
G63: (S2) +$B53*(G53/(0.1*$A42/10^8))^2
H63: (S2) +$B53*(H53/(0.1*$A42/10^8))^2
```

Figure A.37. (continue-4).

```
B64: '   Y3
C64: (S2) +$B54*(C54/(0.1*$A43/10^8))^2
D64: (S2) +$B54*(D54/(0.1*$A43/10^8))^2
E64: (S2) +$B54*(E54/(0.1*$A43/10^8))^2
F64: (S2) +$B54*(F54/(0.1*$A43/10^8))^2
G64: (S2) +$B54*(G54/(0.1*$A43/10^8))^2
H64: (S2) +$B54*(H54/(0.1*$A43/10^8))^2
B65: '   Y4
C65: (S2) +$B55*(C55/(0.1*$A44/10^8))^2
D65: (S2) +$B55*(D55/(0.1*$A44/10^8))^2
E65: (S2) +$B55*(E55/(0.1*$A44/10^8))^2
F65: (S2) +$B55*(F55/(0.1*$A44/10^8))^2
G65: (S2) +$B55*(G55/(0.1*$A44/10^8))^2
H65: (S2) +$B55*(H55/(0.1*$A44/10^8))^2
B66: '   Y5
C66: (S2) +$B56*(C56/(0.1*$A45/10^8))^2
D66: (S2) +$B56*(D56/(0.1*$A45/10^8))^2
E66: (S2) +$B56*(E56/(0.1*$A45/10^8))^2
F66: (S2) +$B56*(F56/(0.1*$A45/10^8))^2
G66: (S2) +$B56*(G56/(0.1*$A45/10^8))^2
H66: (S2) +$B56*(H56/(0.1*$A45/10^8))^2
B67: '   Y6
C67: (S2) +$B57*(C57/(0.1*$A46/10^8))^2
D67: (S2) +$B57*(D57/(0.1*$A46/10^8))^2
E67: (S2) +$B57*(E57/(0.1*$A46/10^8))^2
F67: (S2) +$B57*(F57/(0.1*$A46/10^8))^2
G67: (S2) +$B57*(G57/(0.1*$A46/10^8))^2
H67: (S2) +$B57*(H57/(0.1*$A46/10^8))^2
B68: '   Y7
C68: (S2) +$B58*(C58/(0.1*$A47/10^8))^2
D68: (S2) +$B58*(D58/(0.1*$A47/10^8))^2
E68: (S2) +$B58*(E58/(0.1*$A47/10^8))^2
F68: (S2) +$B58*(F58/(0.1*$A47/10^8))^2
G68: (S2) +$B58*(G58/(0.1*$A47/10^8))^2
H68: (S2) +$B58*(H58/(0.1*$A47/10^8))^2
B69: '   Y8
C69: (S2) +$B59*(C59/(0.1*$A48/10^8))^2
D69: (S2) +$B59*(D59/(0.1*$A48/10^8))^2
E69: (S2) +$B59*(E59/(0.1*$A48/10^8))^2
F69: (S2) +$B59*(F59/(0.1*$A48/10^8))^2
G69: (S2) +$B59*(G59/(0.1*$A48/10^8))^2
H69: (S2) +$B59*(H59/(0.1*$A48/10^8))^2
B70: '   Y9
C70: (S2) +$B60*(C60/(0.1*$A49/10^8))^2
D70: (S2) +$B60*(D60/(0.1*$A49/10^8))^2
E70: (S2) +$B60*(E60/(0.1*$A49/10^8))^2
F70: (S2) +$B60*(F60/(0.1*$A49/10^8))^2
```

Figure A.37. (continue-5).

```
G70: (S2) +$B60*(G60/(0.1*$A49/10^8))^2
H70: (S2) +$B60*(H60/(0.1*$A49/10^8))^2
I37: (F2) 1.6
J37: (F2) 1.82
K37: (F2) 1.63
I39: '   Y7
J39: '   Y8
K39: '   Y9
I40: ' PREDICT
J40: ' PREDICT
K40: 'PREDICTED
I41: (F2) 11.45
J41: (F2) 11.81
K41: (F2) 11.51
I42: (F2) 5.83
J42: (F2) 6.02
K42: (F2) 5.86
I43: (F2) 10.43
J43: (F2) 10.76
K43: (F2) 10.48
I44: (F2) 12.82
J44: (F2) 13.34
K44: (F2) 12.9
I45: (F2) 11.18
J45: (F2) 11.53
K45: (F2) 11.23
I46: (F2) 13.54
J46: (F2) 13.95
K46: (F2) 13.61
I47: (F2) 6.77
J47: (F2) 6.97
K47: (F2) 6.8
I48: (F2) 1.62
J48: (F2) 1.75
K48: (F2) 1.64
I49: (F2) 5.55
J49: (F2) 5.91
K49: (F2) 5.6
I51: (F2) '    DIFF
J51: (F2) '    DIFF
K51: (F2) '    DIFF
I52: (S2) -($B9-I41)/10^8
J52: (S2) -($B9-J41)/10^8
K52: (S2) -($B9-K41)/10^8
I53: (S2) -($B10-I42)/10^8
J53: (S2) -($B10-J42)/10^8
K53: (S2) -($B10-K42)/10^8
```

Figure A.37. (continue-6).

```
I54: (S2) -($B11-I43)/10^8
J54: (S2) -($B11-J43)/10^8
K54: (S2) -($B11-K43)/10^8
I55: (S2) -($B12-I44)/10^8
J55: (S2) -($B12-J44)/10^8
K55: (S2) -($B12-K44)/10^8
I56: (S2) -($B13-I45)/10^8
J56: (S2) -($B13-J45)/10^8
K56: (S2) -($B13-K45)/10^8
I57: (S2) -($B14-I46)/10^8
J57: (S2) -($B14-J46)/10^8
K57: (S2) -($B14-K46)/10^8
I58: (S2) -($B15-I47)/10^8
J58: (S2) -($B15-J47)/10^8
K58: (S2) -($B15-K47)/10^8
N58: 'standard
O58: ' percent
I59: (S2) -($B16-I48)/10^8
J59: (S2) -($B16-J48)/10^8
K59: (S2) -($B16-K48)/10^8
M59: '(mole/ml)
N59: '  error
O59: ' at two
I60: (S2) -($B17-I49)/10^8
J60: (S2) -($B17-J49)/10^8
K60: (S2) -($B17-K49)/10^8
N60: '   of
O60: 'standard
L61: '   Var
M61: '   Pred
N61: ' estimate
O61: '  errors
I62: (S2) +$B52*(I52/(0.1*$A41/10^8))^2
J62: (S2) +$B52*(J52/(0.1*$A41/10^8))^2
K62: (S2) +$B52*(K52/(0.1*$A41/10^8))^2
L62: (S2) +C62+D62+E62+F62+G62+H62+I62+J62+K62
M62: (S2) +$B41/10^8
N62: (S2) +L62^0.5
O62: (F2) 200*N62/M62
I63: (S2) +$B53*(I53/(0.1*$A42/10^8))^2
J63: (S2) +$B53*(J53/(0.1*$A42/10^8))^2
K63: (S2) +$B53*(K53/(0.1*$A42/10^8))^2
L63: (S2) +C63+D63+E63+F63+G63+H63+I63+J63+K63
M63: (S2) +$B42/10^8
N63: (S2) +L63^0.5
O63: (F2) 200*N63/M63
I64: (S2) +$B54*(I54/(0.1*$A43/10^8))^2
```

Figure A.37. (continue-7).

```
J64: (S2) +$B54*(J54/(0.1*$A43/10^8))^2
K64: (S2) +$B54*(K54/(0.1*$A43/10^8))^2
L64: (S2) +C64+D64+E64+F64+G64+H64+I64+J64+K64
M64: (S2) +$B43/10^8
N64: (S2) +L64^0.5
O64: (F2) 200*N64/M64
I65: (S2) +$B55*(I55/(0.1*$A44/10^8))^2
J65: (S2) +$B55*(J55/(0.1*$A44/10^8))^2
K65: (S2) +$B55*(K55/(0.1*$A44/10^8))^2
L65: (S2) +C65+D65+E65+F65+G65+H65+I65+J65+K65
M65: (S2) +$B44/10^8
N65: (S2) +L65^0.5
O65: (F2) 200*N65/M65
I66: (S2) +$B56*(I56/(0.1*$A45/10^8))^2
J66: (S2) +$B56*(J56/(0.1*$A45/10^8))^2
K66: (S2) +$B56*(K56/(0.1*$A45/10^8))^2
L66: (S2) +C66+D66+E66+F66+G66+H66+I66+J66+K66
M66: (S2) +$B45/10^8
N66: (S2) +L66^0.5
O66: (F2) 200*N66/M66
I67: (S2) +$B57*(I57/(0.1*$A46/10^8))^2
J67: (S2) +$B57*(J57/(0.1*$A46/10^8))^2
K67: (S2) +$B57*(K57/(0.1*$A46/10^8))^2
L67: (S2) +C67+D67+E67+F67+G67+H67+I67+J67+K67
M67: (S2) +$B46/10^8
N67: (S2) +L67^0.5
O67: (F2) 200*N67/M67
I68: (S2) +$B58*(I58/(0.1*$A47/10^8))^2
J68: (S2) +$B58*(J58/(0.1*$A47/10^8))^2
K68: (S2) +$B58*(K58/(0.1*$A47/10^8))^2
L68: (S2) +C68+D68+E68+F68+G68+H68+I68+J68+K68
M68: (S2) +$B47/10^8
N68: (S2) +L68^0.5
O68: (F2) 200*N68/M68
I69: (S2) +$B59*(I59/(0.1*$A48/10^8))^2
J69: (S2) +$B59*(J59/(0.1*$A48/10^8))^2
K69: (S2) +$B59*(K59/(0.1*$A48/10^8))^2
L69: (S2) +C69+D69+E69+F69+G69+H69+I69+J69+K69
M69: (S2) +$B48/10^8
N69: (S2) +L69^0.5
O69: (F2) 200*N69/M69
I70: (S2) +$B60*(I60/(0.1*$A49/10^8))^2
J70: (S2) +$B60*(J60/(0.1*$A49/10^8))^2
K70: (S2) +$B60*(K60/(0.1*$A49/10^8))^2
L70: (S2) +C70+D70+E70+F70+G70+H70+I70+J70+K70
M70: (S2) +$B49/10^8
N70: (S2) +L70^0.5
```

Figure A.37. (continue-8).

```
O70: (F2) 200*N70/M70
M71: '    ave
O71: (F2) (O62+O63+O64+O65+O66+O67+O68+O69+O70)/9
```

Figure A.37. (continue-9).

A.3.9. Instantaneous Diffusion or Instantaneous Reaction

The model selected for the zirconium system of this study, presented in Section 4.2.5, can be simplified by assuming instantaneous diffusion or reaction.

Assuming instantaneous diffusion implies diffusional resistance has no significant affect on the overall mass transfer rate. This model can be developed as follows.

$$-V_a \frac{dC_{a1}}{dt} = K^f(C_{a1})[C_{a2}(t=0)]^4[C_{o3}(t=0)/D_3]^2 - K^b(C_{a4}),$$

$$V_a[C_{a1}(t=0)] = V_aC_{a1} + V_aC_{a4} + V_oC_{o4},$$

$$C_{o4}/C_{a4} = D_4.$$

These three equations (with three unknowns C_{a1}, C_{a4} and C_{o4}) can be simultaneously solved for any of the three existing zirconium species.

Assuming instantaneous chemical reaction occurs, or equilibrium reaction, the model can be developed as follows.

$$-\frac{V_o}{S} \frac{dC_{o4}}{dt} = k_{o4}(C_{o4,i} - C_{o4}),$$

$$-\frac{V_o}{S} \frac{dC_{o4}}{dt} = k_{a4}(C_{a4} - C_{a4,i}).$$

$$\frac{K^f}{K^b} = \frac{(C_{a4})}{(C_{a1})[C_{a2}(t=0)]^4[C_{o3}(t=0)/D_3]^2},$$

$$V_a[C_{a1}(t=0)] = V_aC_{a1} + V_aC_{a4} + V_oC_{o4},$$

$$C_{o4,i}/C_{a4,i} = D_4.$$

These five equations (with five unknowns C_{a1}, C_{a4}, $C_{a4,i}$, C_{o4} and $C_{o4,i}$) can be simultaneously solved for any of the three existing zirconium species.

A.3.10. Model Solution Check

The model solution used for regression, Equation 4.24, was checked at infinite time and found correct. At intitial time, due to the model complexity, the solution was checked by substitution of actual values. The terms to be checked, are those for e^{0}, e^{-aot} and e^{-alt}, and are discussed in Section 4.2.5. The coefficient for these terms were calculated via Lotus worksheet A.38 and program A.39. The coefficients should each be zero. The results as shown are,

e^{0} coefficient = -4.4×10^{-26},

e^{-aot} coefficient = 0,

e^{-alt} coefficient = -3.6×10^{-11}.

These coefficients are all zero within computer roundoff error. This validates the model solution at initial time.

CHECK ON SOLUTION FOR MODEL AND ZIRCONIUM PLOT ROUTINE

Standard Conditions
Assume values: Concn(mole/cc)

Va	Vo	Ca2(0)	Co3(0)/D3	Kf/Kb	Kf	D4	ko4
350	350	0.002900	1.13E-06	2.71E+22	1.60E+21	0.35	0.000567

S	Ca1(0)	Kb	Ck	ka4
79	1.37E-06	0.059040	9.00E-23	0.000862
				0.003036

A1	A2	A3	A4	A5	A6	A7	A8
1.69E-04	4.11E-04	1.04E-04	3.63E-05	2.31E-10	5.80E-04	1.69E-04	4.98E-11

A9	f1	f2	f3	f4	f5	a0	a1
1.40E-04	1.37E-06	4.23E-10	2.4E-14	0.000720	7.53E-08	5.94E-04	0.000126 +/- 4.80E-08

bo	b1	b2
9.22E-07	1.29E-07	3.19E-07

Zero terms:

(A4/A1)A2b2 =	2.8E-11
-A3(Va/Vo)Ca1(0)=	-1.4E-10
A3b2(1+A2/A1)=	1.1E-10
(Vo/Va)	
sum	-2.9E-26

e(-a1*t) terms:

(Va/Vo)a1b1[1+(A2-a1)/A1]	4.4E-11
(Va/Vo)A3b1[1+(A2-a1)/A1]	3.6E-11
(A4/A1)b1(A2-a1)	7.9E-12
SUM	4.8E-27

Time(min)	Time(s)	Ca1	Ca4	Co4
0	0	1.37E-06	0	0.00E+00
15	900	9.75E-07	3.89E-07	6.72E-09
30	1800	7.38E-07	6.09E-07	2.21E-08
45	2700	5.96E-07	7.32E-07	4.13E-08
60	3600	5.10E-07	7.99E-07	6.16E-08
75	4500	4.56E-07	8.33E-07	8.16E-08
90	5400	4.22E-07	8.48E-07	1.01E-07
105	6300	3.99E-07	8.53E-07	1.18E-07
120	7200	3.84E-07	8.52E-07	1.34E-07
135	8100	3.73E-07	8.48E-07	1.49E-07
150	9000	3.65E-07	8.43E-07	1.62E-07
165	9900	3.59E-07	8.38E-07	1.74E-07
180	10800	3.54E-07	8.32E-07	1.84E-07
195	11700	3.49E-07	8.27E-07	1.94E-07
210	12600	3.46E-07	8.22E-07	2.02E-07
225	13500	3.43E-07	8.18E-07	2.09E-07
240	14400	3.40E-07	8.14E-07	2.16E-07
255	15300	3.38E-07	8.10E-07	2.22E-07
270	16200	3.36E-07	8.07E-07	2.28E-07
285	17100	3.34E-07	8.04E-07	2.32E-07
300	18000	3.32E-07	8.01E-07	2.37E-07
315	18900	3.31E-07	7.99E-07	2.40E-07
330	19800	3.30E-07	7.96E-07	2.44E-07
345	20700	3.29E-07	7.95E-07	2.47E-07
360	21600	3.28E-07	7.93E-07	2.50E-07

Figure A.38. Lotus worksheet, solution check.

```
e(-ao*t) terms:
(Va/Vo)aobo[1+(A2-ao)/A1]
-4.4E-11

(Va/Vo)A3bo[1+(A2-ao)/A1]
-7.7E-12

(A4/A1)bo(A2-ao)
-3.6E-11

SUM
-3.5E-25
```

Figure A.38. (continued).

```
A1: 'CHECK ON SOLUTION FOR MODEL AND ZIRCONIUM PLOT ROUTINE
A3: 'Standard Conditions
A4: 'Assume values:
C4: 'Concn(mole/cc)
A6: '      Va
B6: '      Vo
C6: '  Ca2(0)
D6: 'Co3(0)/D3
E6: '  Kf/Kb
F6: '   Kf
G6: '     D4
H6: '   ko4
A7: (F0) 350
B7: (F0) 350
C7: (F6) 0.0029
D7: (S2) (3/2)*0.000000752
E7: (S2) 1/3.6900000E-23
F7: (S2) 1.6000000E+21
G7: (F2) 0.349
H7: (F6) 0.000567
A9: (S2) '      S
B9: (S2) '  Ca1(0)
C9: (S2) '     Kb
D9: (S2) '   Ck
H9: (S2) '   ka4
A10: (F0) 79
B10: (S2) 0.00137/1000
C10: (F6) +F7/E7
D10: (S2) +C7^4*D7^2
H10: (F6) 1.52*H7
H11: (F6) +H10/G7+H7
A13: (S2) '    A1
B13: (S2) '    A2
C13: (S2) '    A3
D13: (S2) '    A4
E13: (S2) '    A5
F13: (S2) '    A6
G13: (S2) '    A7
H13: (S2) '    A8
A14: (S2) +C10/A7
B14: (S2) +F7*D10/A7
C14: (S2) (A10*H7/B7)*(1-H7/H11)
D14: (S2) (A10*H7/B7)*H10/H11
E14: (S2) +A14*B10
F14: (S2) +A14+B14
G14: (S2) +A14*(B7/A7)
H14: (S2) +D14*B10
```

Figure A.39. Lotus program, solution check.

```
A17: (S2) '    A9
B17: (S2) '    f1
C17: (S2) '    f2
D17: (S2) '    f3
E17: (S2) '    f4
F17: (S2) '    f5
G17: (S2) '    a0
H17: (S2) '    a1
A18: (S2) +C14+D14*(B7/A7)
B18: (S2) +B10
C18: (S2) +E14+A18*B10
D18: (G) (-G14*H14+E14*A18)
E18: (G) +F14+A18
F18: (S2) (-D14*G14+F14*A18)
G18: (S2) (E18+(E18^2-4*F18)^0.5)/2
H18: (G) (E18-(E18^2-4*F18)^0.5)/2
H19: (S2) '   +/-
H20: (S2) 0.000000048
A21: (S2) '    bo
B21: (S2) '    b1
C21: (S2) '    b2
D21: (S2) 'Time(min)
E21: (S2) ' Time(s)
F21: (S2) '   Ca1
G21: (S2) '   Ca4
H21: (S2) '   Co4
A22: (S2) (B18*G18^2-C18*G18+D18)/(G18*(G18-H18))
B22: (S2) (B18*H18^2-C18*H18+D18)/(H18*(H18-G18))
C22: (S2) +D18/(G18*H18)
D22: (F0) 0
E22: (F0) +D22*60
F22: (S2) +$C$22+$B$22*@EXP(-$H$18*E22)+$A$22*@EXP(-$G$18*E22)
G22: (G) 0
H22: (S2) 0
D23: (F0) (D22+15)
E23: (F0) +D23*60
F23: (S2) +$C$22+$B$22*@EXP(-$H$18*E23)+$A$22*@EXP(-$G$18*E23)
G23: (S2) (1/$A$14)*($K23+$B$14*$F23)
H23: (S2) ($A$7/$B$7)*($B$10-$F23-$G23)
A24: 'Zero terms:
D24: (F0) (D23+15)
E24: (F0) +D24*60
F24: (S2) +$C$22+$B$22*@EXP(-$H$18*E24)+$A$22*@EXP(-$G$18*E24)
G24: (S2) (1/$A$14)*($K24+$B$14*$F24)
H24: (S2) ($A$7/$B$7)*($B$10-$F24-$G24)
A25: '(A4/A1)A2b2 =
C25: (D14/A14)*B14*C22
```

Figure A.39. (continued-2).

```
D25: (F0) (D24+15)
E25: (F0) +D25*60
F25: (S2) +$C$22+$B$22*@EXP(-$H$18*E25)+$A$22*@EXP(-$G$18*E25)
G25: (S2) (1/$A$14)*($K25+$B$14*$F25)
H25: (S2) ($A$7/$B$7)*($B$10-$F25-$G25)
D26: (F0) (D25+15)
E26: (F0) +D26*60
F26: (S2) +$C$22+$B$22*@EXP(-$H$18*E26)+$A$22*@EXP(-$G$18*E26)
G26: (S2) (1/$A$14)*($K26+$B$14*$F26)
H26: (S2) ($A$7/$B$7)*($B$10-$F26-$G26)
A27: '-A3(Va/Vo)Ca1(0)=
C27: -C14*(A7/B7)*B10
D27: (F0) (D26+15)
E27: (F0) +D27*60
F27: (S2) +$C$22+$B$22*@EXP(-$H$18*E27)+$A$22*@EXP(-$G$18*E27)
G27: (S2) (1/$A$14)*($K27+$B$14*$F27)
H27: (S2) ($A$7/$B$7)*($B$10-$F27-$G27)
D28: (F0) (D27+15)
E28: (F0) +D28*60
F28: (S2) +$C$22+$B$22*@EXP(-$H$18*E28)+$A$22*@EXP(-$G$18*E28)
G28: (S2) (1/$A$14)*($K28+$B$14*$F28)
H28: (S2) ($A$7/$B$7)*($B$10-$F28-$G28)
A29: 'A3b2(1+A2/A1)=
C29: +C14*C22*(1+B14/A14)*(A7/B7)
D29: (F0) (D28+15)
E29: (F0) +D29*60
F29: (S2) +$C$22+$B$22*@EXP(-$H$18*E29)+$A$22*@EXP(-$G$18*E29)
G29: (S2) (1/$A$14)*($K29+$B$14*$F29)
H29: (S2) ($A$7/$B$7)*($B$10-$F29-$G29)
A30: '    (Vo/Va)
D30: (F0) (D29+15)
E30: (F0) +D30*60
F30: (S2) +$C$22+$B$22*@EXP(-$H$18*E30)+$A$22*@EXP(-$G$18*E30)
G30: (S2) (1/$A$14)*($K30+$B$14*$F30)
H30: (S2) ($A$7/$B$7)*($B$10-$F30-$G30)
A31: '    sum
C31: +C25+C27+C29
D31: (F0) (D30+15)
E31: (F0) +D31*60
F31: (S2) +$C$22+$B$22*@EXP(-$H$18*E31)+$A$22*@EXP(-$G$18*E31)
G31: (S2) (1/$A$14)*($K31+$B$14*$F31)
H31: (S2) ($A$7/$B$7)*($B$10-$F31-$G31)
D32: (F0) (D31+15)
E32: (F0) +D32*60
F32: (S2) +$C$22+$B$22*@EXP(-$H$18*E32)+$A$22*@EXP(-$G$18*E32)
G32: (S2) (1/$A$14)*($K32+$B$14*$F32)
H32: (S2) ($A$7/$B$7)*($B$10-$F32-$G32)
```

Figure A.39. (continued-3).

```
D33: (F0) (D32+15)
E33: (F0) +D33*60
F33: (S2) +$C$22+$B$22*@EXP(-$H$18*E33)+$A$22*@EXP(-$G$18*E33)
G33: (S2) (1/$A$14)*($K33+$B$14*$F33)
H33: (S2) ($A$7/$B$7)*($B$10-$F33-$G33)
D34: (F0) (D33+15)
E34: (F0) +D34*60
F34: (S2) +$C$22+$B$22*@EXP(-$H$18*E34)+$A$22*@EXP(-$G$18*E34)
G34: (S2) (1/$A$14)*($K34+$B$14*$F34)
H34: (S2) ($A$7/$B$7)*($B$10-$F34-$G34)
A35: 'e(-a1*t) terms:
D35: (F0) (D34+15)
E35: (F0) +D35*60
F35: (S2) +$C$22+$B$22*@EXP(-$H$18*E35)+$A$22*@EXP(-$G$18*E35)
G35: (S2) (1/$A$14)*($K35+$B$14*$F35)
H35: (S2) ($A$7/$B$7)*($B$10-$F35-$G35)
A36: '(Va/Vo)a1b1[1+(A2-a1)/A1]
D36: (F0) (D35+15)
E36: (F0) +D36*60
F36: (S2) +$C$22+$B$22*@EXP(-$H$18*E36)+$A$22*@EXP(-$G$18*E36)
G36: (S2) (1/$A$14)*($K36+$B$14*$F36)
H36: (S2) ($A$7/$B$7)*($B$10-$F36-$G36)
A37: ($A$7/$B$7)*$H$18*$B$22*(1+($B$14-$H$18)/$A$14)
D37: (F0) (D36+15)
E37: (F0) +D37*60
F37: (S2) +$C$22+$B$22*@EXP(-$H$18*E37)+$A$22*@EXP(-$G$18*E37)
G37: (S2) (1/$A$14)*($K37+$B$14*$F37)
H37: (S2) ($A$7/$B$7)*($B$10-$F37-$G37)
D38: (F0) (D37+15)
E38: (F0) +D38*60
F38: (S2) +$C$22+$B$22*@EXP(-$H$18*E38)+$A$22*@EXP(-$G$18*E38)
G38: (S2) (1/$A$14)*($K38+$B$14*$F38)
H38: (S2) ($A$7/$B$7)*($B$10-$F38-$G38)
A39: '(Va/Vo)A3b1[1+(A2-a1)/A1]
D39: (F0) (D38+15)
E39: (F0) +D39*60
F39: (S2) +$C$22+$B$22*@EXP(-$H$18*E39)+$A$22*@EXP(-$G$18*E39)
G39: (S2) (1/$A$14)*($K39+$B$14*$F39)
H39: (S2) ($A$7/$B$7)*($B$10-$F39-$G39)
A40: ($A$7/$B$7)*$C$14*$B$22*(1+($B$14-$H$18)/$A$14)
D40: (F0) (D39+15)
E40: (F0) +D40*60
F40: (S2) +$C$22+$B$22*@EXP(-$H$18*E40)+$A$22*@EXP(-$G$18*E40)
G40: (S2) (1/$A$14)*($K40+$B$14*$F40)
H40: (S2) ($A$7/$B$7)*($B$10-$F40-$G40)
D41: (F0) (D40+15)
E41: (F0) +D41*60
```

Figure A.39. (continued-4).

```
F41: (S2) +$C$22+$B$22*@EXP(-$H$18*E41)+$A$22*@EXP(-$G$18*E41)
G41: (S2) (1/$A$14)*($K41+$B$14*$F41)
H41: (S2) ($A$7/$B$7)*($B$10-$F41-$G41)
A42: '(A4/A1)b1(A2-a1)
D42: (F0) (D41+15)
E42: (F0) +D42*60
F42: (S2) +$C$22+$B$22*@EXP(-$H$18*E42)+$A$22*@EXP(-$G$18*E42)
G42: (S2) (1/$A$14)*($K42+$B$14*$F42)
H42: (S2) ($A$7/$B$7)*($B$10-$F42-$G42)
A43: ($D$14/$A$14)*$B$22*($B$14-$H$18)
D43: (F0) (D42+15)
E43: (F0) +D43*60
F43: (S2) +$C$22+$B$22*@EXP(-$H$18*E43)+$A$22*@EXP(-$G$18*E43)
G43: (S2) (1/$A$14)*($K43+$B$14*$F43)
H43: (S2) ($A$7/$B$7)*($B$10-$F43-$G43)
D44: (F0) (D43+15)
E44: (F0) +D44*60
F44: (S2) +$C$22+$B$22*@EXP(-$H$18*E44)+$A$22*@EXP(-$G$18*E44)
G44: (S2) (1/$A$14)*($K44+$B$14*$F44)
H44: (S2) ($A$7/$B$7)*($B$10-$F44-$G44)
A45: 'SUM
D45: (F0) (D44+15)
E45: (F0) +D45*60
F45: (S2) +$C$22+$B$22*@EXP(-$H$18*E45)+$A$22*@EXP(-$G$18*E45)
G45: (S2) (1/$A$14)*($K45+$B$14*$F45)
H45: (S2) ($A$7/$B$7)*($B$10-$F45-$G45)
A46: +A37-A40-A43
D46: (F0) (D45+15)
E46: (F0) +D46*60
F46: (S2) +$C$22+$B$22*@EXP(-$H$18*E46)+$A$22*@EXP(-$G$18*E46)
G46: (S2) (1/$A$14)*($K46+$B$14*$F46)
H46: (S2) ($A$7/$B$7)*($B$10-$F46-$G46)
A49: 'e(-ao*t) terms:
A50: '(Va/Vo)aobo[1+(A2-ao)/A1]
A51: ($A$7/$B$7)*$G$18*$A$22*(1+($B$14-$G$18)/$A$14)
A53: '(Va/Vo)A3bo[1+(A2-ao)/A1]
A54: ($A$7/$B$7)*$C$14*$A$22*(1+($B$14-$G$18)/$A$14)
A56: '(A4/A1)bo(A2-ao)
A57: ($D$14/$A$14)*$A$22*($B$14-$G$18)
A59: 'SUM
A60: +A51-A54-A57
```

Figure A.39. (continued-5).

VITA

Scott DeMuth was born 1955 in Minneapolis, Minnesota. He attended Richfield High School in a suburb of Minneapolis. Under graduate studies occurred first at Gustavus Adolphus College and second the University of Minnesota, finishing a Bachelor of Chemical Engineering in 1980. In 1980 he began woking for Union Carbide Nuclear Division at the Oak Ridge Gaseous Diffusion Plant. Work efforts were concentrated on process development for the Gaseous Centrifuge Enrichment Plant. A Master of Science in Chemical Engineering was received in 1985 while going to school part time at the University of Tennessee. In 1985 work efforts were redirected to nuclear fuel reprocessing at the Oak Ridge National Laboratory.