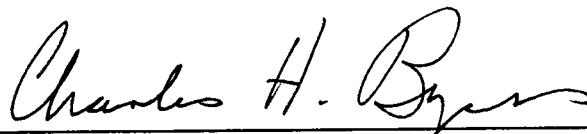


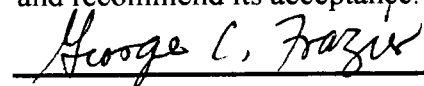
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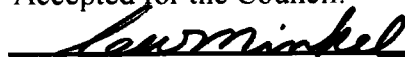
Charles H. Byers, Major Professor

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Accepted for the Council:



Associate Vice Chancellor and Dean
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AN INVESTIGATION INTO THE HYDROLYSIS AND CONDENSATION REACTIONS OF
ZIRCONIUM (IV) BUTOXIDES

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Jason Tylor Zielke
August 1997

DEDICATION

This thesis is dedicated to my parents Ernest and Frances Zielke, my “little” sisters, Megan and Lisa Zielke, my Grandma Alma Jean and Grandpa Howard Miller and Grandma Betty Zielke as well as my lifelong friends along the way. Thank you for the love, support and encouragement that you have provided.

ACKNOWLEDGMENTS

There are many people to whom I am indebted in earning this degree. The first that I would like to mention are my head research advisor, Charles H. Byers and my immediate supervisor at Oak Ridge National Laboratory, Michael Z-C. Hu. I am also very grateful to those that have consented to serve on my thesis committee, Professors Fred Weber and George Frazier.

There are also a few others that I would like to mention. I am very grateful to Michael T. Harris, my former research advisor, for the opportunity to work at Oak Ridge National Laboratory as well as his assistance in this project. I would also like to mention Amit Singhal, a postdoctoral researcher at ORNL, who gave me invaluable assistance in the area of small angle X-ray scattering. Finally, I would like to thank Dr. J.S. Lin for his accommodating me in the Small Angle X-Ray Scattering Facility at ORNL.

ABSTRACT

The sol-gel process permits the careful control of the size and morphology of materials during the earliest stages of production (Hench and West, 1990). Some of the current applications are development of advanced materials for structural, electrical and optical purposes. One of the important methods of preparing these high-purity materials is the synthesis of metal oxide gels and particles from metal alkoxides.

The hydrolysis and condensation reactions of the zirconium alkoxides are extremely vital to the sol-gel process, since the alkoxides react to form the respective oxide powders and gels. However, a rapid mixing technique must be used to study these reactions because they can be nearly completed within a few seconds. Monitoring these reactions within a millisecond time regime allows one to control the morphology, size, and uniformity of the resulting particles. Two instrumental analyses that can be combined with the rapid mixing technique are Fourier Transform Infrared Spectroscopy (FTIR) and small-angle X-ray scattering (SAXS). FTIR was used in studying soluble-species reaction kinetics. The aggregation kinetics of the polymeric clusters and particles forming in time were studied using the SAXS technique. Key parameters such as mixing time, base and water concentrations, alkoxide concentrations, and alkoxide-to-water ratios were fully investigated to control the powder synthesis. These experimental results can be used to verify and determine model parameters for reaction and aggregative kinetics.

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1. INTRODUCTION

Sol-gel processing has gained a significant level of interest in the past years for the production of advanced materials. A sol is defined as a dispersion of colloidal particles in solution and a gel is a series of interconnected, rigid networks with submicrometer pores and length scales greater than 1 micrometer. One of the main advantages of the sol-gel process is that it allows the careful control of the size and morphology of materials during the earliest stages of production, so that high-purity materials can be developed to fulfill specific demands (Hench and West, 1990). The most popular precursors described in the literature are either aqueous inorganic salts or metal organic compounds.

Some of the current applications of this process involve the development of a new generation of advanced materials for structural, electrical, optical and optoelectronic uses. Also, the development of ceramics that possess higher purity, strength and homogeneity is of major industrial interest. Due to their viscous properties, they are also easily used in the development of thin films from such techniques as dip-coating, spraying and spin coating (Klein, 1988). In order for these monoliths to be used in industrial applications, subsequent processes like aging, drying, stabilization, and densification must be employed. These processes, in turn, depend upon the morphology and structure of the resultant gels. Therefore, it is necessary that fundamental studies into the chemistry and physics during the earliest stages of these systems be performed in order that these processes be optimized for industrial uses.

For the purpose of this study, the synthesis of oxide gels from zirconium alkoxide precursors will be investigated. The main objective of this research is to experimentally determine the hydrolysis, condensation and gelation kinetic parameters of zirconium butoxides in the presence of OH^- . All chemical reaction data reported from FTIR spectroscopy will be considered to be first order in substrate concentration, $[\text{Zr-O-R}]$ according to the following equation:

$$-r_{\text{ZrOR}} = K_H [\text{Zr-O-R}] \quad (1.1)$$

where units for the rate are given in $\text{mol}\cdot\text{sec}^{-1}$ and K_H is the hydrolysis rate constant to be computed from the data. We shall see in the chapter entitled, ANALYSIS, the justification for this assumption.

1.1 Background

Metal alkoxides are popular metal-oxide ceramic precursors due to the purity of the starting materials, the low temperature at which the reactions occur, the ease of the reactions and their reactivity towards water. It is vital that there exists a correlation between the physics and chemistry of these parameters and the sol-gel derived materials.

There are essentially two governing reactions involved in the metal alkoxide method, hydrolysis and condensation. The relative rates at which these reactions occur determine the structure and morphology of the gels; therefore, it is necessary to

understand the kinetics of hydrolysis and condensation. For experimental purposes, these reactions must be carried out in a non-aqueous environment like ethyl alcohol, since the transition metal alkoxides react instantaneously with water to form undesired precipitation products (Livage, Henry and Sanchez, 1988). In order to control this instantaneous precipitation, the concentration of alkoxide can either be very much larger than the concentration of water, or a catalyst such as acid or base can be added that slows down the hydrolysis and condensation reactions. Therefore, such parameters as $[\text{alkoxide}]/[\text{water}]$ ratios, water concentration, pH and temperature must be investigated to elucidate the early stage chemistry and physics (Yoldas, 1986). In order for the size and morphology to be consistently reproduced, the kinetics of these reactions must be understood in detail; that is, the soluble species consumption kinetics due to hydrolysis as well as the gelation or aggregation kinetics from condensation.

1.2 Literature Survey

Metal alkoxides are extensively used in the ceramics industry. However, the level at which they can be used remains limited, due to the difficulties associated with studying the early stages. Zirconium alkoxide reacts vigorously with water to form either a precipitate or a gel depending upon several parameters like temperature, alkoxide concentration, presence of an inhibitor and temperature. The chemistry that controls the resultant morphology often occurs within 1 second. For industrial purposes the reactivity of these precursors poses a problem that must be simplified. For example, in industrial

coating processes the hydrolysis and condensation chemistry must be controlled within this time frame if the deposited film is to meet specified criteria (Klein, 1988). In this study zirconia gels were formed by zirconium n-butoxide hydrolysis and OH^- was used as an inhibitor. In previous efforts there have been several problems in the elucidation of hydrolysis chemistry of metal alkoxides (Budd, 1985). First of all, the hydrolysis is very fast and without the aid of an in-situ method at very small reaction times, all products are reported as time-averaged concentrations (Hartel and Berglund, 1986; Blanchard, 1995). Secondly, since hydrolysis competes with condensation so that there is a simultaneous burst of hydrolyzed monomers as well as condensed products, it is very difficult to accurately determine the hydrolysis rate coefficients, K_H . Finally, the possibility that hydrolysis is reversible has been neglected, based upon the assumption that adding enough water ensures complete hydrolysis before significant condensation occurs. (Sanchez and McCormick, 1992)

Alcoholic systems of tetraethoxsilane $[\text{Si}(\text{OR})_4]$, where $\text{R}=\text{C}_2\text{H}_5$ have been exhaustively studied. (Brinker, 1990). In fact, most of the work on metal alkoxides has emphasized these systems. To a lesser extent, titanium alkoxide solutions in alcohol have also been studied. Growth models have been predicted and experimentally verified at long times for both silica and titania systems (Zukoski, 1992; Harris, 1988 and 1992). Recently, however, Harris and coworkers have submitted some results to be published for the hydrolysis and condensation mechanisms of zirconium alkoxides at early stages wherein the inhibitor used was H^+ (Singhal, 1997).

In 1952, Bradley (1952) published a series of papers that dealt with several

aspects of group IV metal alkoxides (Ti, Zr, etc.). However, most of the literature emphasizes the titanium group IV metal alkoxides. (Barringer and Bowen, 1985). There have been very few studies on the initial stages of the reactions involving the hydrolysis and condensation pathways of zirconium alkoxides. Recently Kumazawa and co-workers used zirconium tetrabutoxides to prepare ZrO_2 particles by controlled hydrolysis (Kumazawa, 1994). These researchers studied the same systems as this current study, however, at much longer times. They studied the relationship between particle size, initial zirconium tetrabutoxides, reaction temperature and reaction time. Nevertheless, experimental results are still lacking in the literature to verify the growth mechanisms that result in zirconia gels rather than particles. Yoldas has studied the properties and parameters that affect zirconium oxides formed by alkoxide hydrolysis and condensation mechanisms (Yoldas, 1986). Singhal and coworkers have recently investigated the zirconia gelation systems using an inorganic acid as an inhibitor to hydrolysis (Singhal, 1996). There have been a few spectroscopic studies on the Group IV alkoxides with an emphasis on the structural aspects of these species, but not at the earliest stages of hydrolysis and condensation (Guilment, 1996).

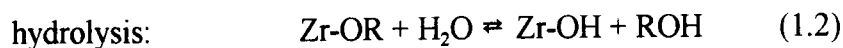
Guilment and co-workers suggested that as the $[water]/[alkoxide]$ increased, there would be a greater tendency for the reactants to form a precipitate. There is, in fact, a more complete removal of -OR groups as this ratio increases. One reason for instantaneous precipitation is that at such high hydrolysis ratios, the -OR groups are nearly completely removed from the molecular structure. In order for there to be solubility in ethanol, it is necessary that there still remain a few residual OR groups in solution that have not been

completely hydrolyzed (Livage, 1988). In general, localized condensation occurs once the water/alkoxide ratio exceeds a critical concentration. Consequently, there will be phase separation as evidenced by the appearance of a milk-colored solution. The introduction of base or acid into the systems helps to prevent the localized condensations and thus maintain a clear solution at the earliest stages. Smit has stated that as this hydrolysis ratio decreases, less zirconium alkoxides will become hydroxolated (Smit, 1987).

It is seen from a literature survey that data has not been published for the earliest stages of hydrolysis and condensation of zirconium butoxides using base as an inhibitor. One of the chief aims of this study is to provide a database as well as a preliminary mechanism for the nucleation and growth of alkoxide processes. With the aid of a method developed in our research group, it is now possible to study the early stages of these reactions. The rapid mixing technique has been successfully used for systems that are catalyzed by H^+ (Singhal and coworkers, 1997), but not for systems wherein base is used as the catalyst. This thesis will report the data and conclusions that were found in this study of zirconium butoxides in base performed at the Oak Ridge National Laboratory in Oak Ridge, Tennessee. Chapter 2 entitled METHODS will discuss in detail the experiments that were performed. The ANALYSIS, Chapter 3, will give both the results and the analyses from the experiments performed. Finally, Chapter 4 will give the summary and recommendations from these experiments.

1.3 Chemistry and Theoretical Background

The chemistry involved in the sol-gel process is based on inorganic polymerization (Bradley, 1952; Brinker, 1990; Livage, 1988). The precursors for these polymers are generally metallo-organic compounds like the metal alkoxides, $M(OR)_n$ (Blanchard, 1995). Starting from molecular precursors, an oxide network is obtained via a series of hydroxylation and condensation reactions:

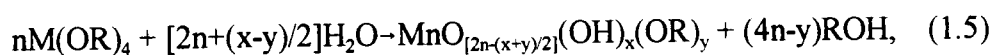


where R represents an alkyl group and M signifies the metal of interest. For the systems of interest in this study, M will be zirconium and -R will be a butoxy group, $R=C_4H_9$. Barringer has proposed that hydrolysis and condensation are not simultaneous reactions, therefore, not competitive, and that the mechanisms can be analyzed in a mechanistic approach (Barringer, 1985). That is, hydrolysis and condensation are essentially a series of initiation and propagation steps, wherein hydrolysis is the initiation step followed by condensation. According to Barringer, the hydrolysis reaction is the rate limiting step, wherein 3 of the 4 -OR groups are readily eliminated. The fourth alkoxy group is often very difficult to remove, and it sometimes is never removed due to steric hindrance as well as solvent effects.

Transition metal alkoxides are fairly electropositive and their oxidation state is usually smaller than other metal alkoxides (Bradley, 1952). The result is that they will readily react with nucleophilic agents so as to increase their coordination (Livage, 1988). During hydrolysis, a hydroxyl ion becomes attached to the metal atom, thus leading to the formation of hydroxylated M-OH groups. Depending upon the amount of water and catalyst present, hydrolysis may or may not go to completion. It is possible that only a few of the -OR ligands will be replaced by -OH groups so that the metal is only partially hydrolyzed. Two partially hydrolyzed molecules can link together in a condensation reaction. Condensation is a process that liberates a small molecule such as water or alcohol en route to the formation of polymer (Brinker, 1990).

There are essentially three mechanisms for condensation. Olation is a condensation process in which a hydroxy bridge is formed between two metal centers, HO-Zr-OH. This is an S_N reaction wherein the hydroxy group is the nucleophile and H_2O is the leaving group. An S_N reaction is one in which a "nucleus loving" reagent, one that is electron deficient, attacks an atom such that a substitution occurs and there is a departing leaving group so that overall charge on the species is conserved (Miller, 1992). Consequently the rate at which olation occurs is related to the lability of the aquo ligand ($-OH_2$) which depends on size, electronegativity and the electronic configuration of M. Oxolation (1.3) is a condensation reaction in which an oxo bridge, M-O-M, is formed between two metal centers via nucleophile addition and the leaving group is R-OH (Yoldas, 1986). Nucleophilic addition occurs whenever an electron rich nucleophile attacks an electron-deficient area of a molecule. After coordination and charge transfer a

leaving group will exit to accomodate the addition. The third condensation mechanism is a water elimination mechanism called alcoxolation, (1.4). Livage, et al. (1988) have proposed that alcoxolation is the predominant mechanism for the condensation process. Whenever the preferred coordination of the metal is satisfied, the condensation will proceed via nucleophilic substitution (S_n) and it will proceed via nucleophilic addition (A_n) whenever the preferred coordination is not satisfied. An overall hydrolytic polycondensation that takes into account the variability of the alkoxide (M-OR), hydroxide (M-OH) and oxide, (M-O-M) has been established by Day, et al,



where n is the number of Zr atoms in the polymer and x and y are the numbers of OH and OR groups in the molecule (Day, 1992).

Hydrolysis, condensation and alcoholysis can each be described by the following three step process (Livage, 1988):

1. Nucleophilic addition of negatively charged OH groups to positively charged metal atom M.
2. Proton transfer within the transition state complex from the entering ligand (XOH) towards a negatively charged oxygen of an adjacent alkoxy group.
3. Departure of the protonated (R-OH) species.

From these three steps, it is clear that the reactions depend upon the relative partial charge distribution. The following conditions must, therefore, be fulfilled.

$$\delta(M) > 0,$$

$$\delta(OR) < \delta(H), \text{ and}$$

$$\delta(\text{ROH}) > 0$$

The rate limiting step for the overall reaction occurs whenever these criteria are not fulfilled. It is necessary that the partial charge of the various species in the reactants, transition state complexes and intermediate products be computed (Harris, 1992)

In order to elucidate the difficulties of these reactions, Livage proposed a model called the Partial Charge Model (PCM). The PCM describes the chemistry of these reactions in terms of the chemical moieties that are present at any given time and the localized charges associated with them. PCM also allows one to qualitatively predict the reaction scheme for the hydrolysis and condensation reactions based upon the electronegativity of the attacking and leaving groups.

Since water has a very high dielectric constant, it contributes to the dissociation of the ionic species and it behaves as a sigma donor thus acting as a good nucleophile. The driving forces for these nucleophilic reactions to take place are the low electronegativity of the metal organic precursors as well as the desire for the d^0 transition metals to increase their coordination numbers by accepting lone pairs of electrons from the nucleophilic ligands. The basis for the model is the principle of "electronegativity equalization" (Sanderson, 1951) which states: "when atoms of different electronegativity combine, they adjust to the same intermediate electronegativity in the compound". The following criteria are proposed in the development of the PCM.

- a. There is a linear relationship between electronegativity and charge.

$$\chi_i = \chi_i^o + \eta_i \delta_i \quad (1.6)$$

b. The following equation determines the hardness:

$$\eta_i = k\sqrt{\chi_i^o} \quad (1.7)$$

where $k=1.36$.

c. Charge is conserved

$$Z = \sum p_i \delta_i \quad (1.8)$$

where p_i corresponds to the stoichiometry of atom i .

Upon solving and combining Eqs. 1.6 to 1.8, it is seen that the mean electronegativity of a molecule is given by

$$\bar{\chi} = \frac{\sum_i p_i \sqrt{\chi_i^o} + 1.36Z}{\sum_i (p_i / \sqrt{\chi_i^o})} \quad (1.9)$$

The partial charge distribution on some group G is given by

$$\delta(G) = S(G)(\bar{\chi} - \chi^o(G)) \quad (1.10)$$

where $S(G)$, is defined as the softness of the group.

$$S(G) = \frac{\sum_i (p_i / \sqrt{\chi_i^o})}{1.36} \quad (1.11)$$

This model has been used to predict the relative rates of hydrolysis, and helps to clarify why the partial charge of

$$\delta(\text{Zr}(\text{OR})_4) > \delta(\text{Ti}(\text{OR})_4) > \delta(\text{Si}(\text{OR})_4).$$

The hydrolysis rates of zirconium are fastest in this series, as it is the most electropositive of the metal ligands.

The model has also been used to study the effect of acid and base catalyst on the hydrolysis and condensation reactions. The theoretical predictions of polymeric growth from the PCM agree with the experimental results. The model suggests that H^+ catalyzed condensation processes are directed towards the end of chains rather than the middle, whereas OH^- catalyzed condensation is directed towards the middle of chains. The net result of these two mechanisms is that either more extended, less highly branched polymers or more compact highly branched polymers will be formed, respectively (Brinker, 1990).

The number of bonds that a monomer can form is called the functionality, f . Whenever $f > 2$, polymers may form three dimensional cross linked structures. The polymerization of zirconium and titanium alkoxides, for example, may lead to this complex branching since the fully hydrolyzed monomer, $[\text{M}(\text{OH})_4]$ is tetra functional. However, under certain reaction conditions such as variations in water concentration and different acid or base concentrations, fewer than four ligands will be capable of

condensation. This implies that little branching will occur. To further elucidate the trends for either cross linked or linear polymers, experimental work must be performed using small angle x-ray scattering. From equations 1.2 to 1.5 it is readily verified that the cumulative ratio, $([H_2O]_0 - [H_2O]) / \{4([M-OR]_0 - [M-OR])\}$, is equal to unity whenever there is hydrolysis without condensation. The symbol $[]_0$ denotes the initial concentration of either water or the M-OR ligand. Whenever condensation is also occurring the cumulative ratio is less than unity and it approaches 0.5 when condensation is much more rapid than hydrolysis. Depending upon factors such as pH, reagent concentration and temperature, the hydrolysis and condensation reactions can result in the formation of gels, flocculated precipitates, or powders.

The aggregation or growth mechanisms for colloidal particles are rooted in the theory of classical colloidal stability. They are a function of the total interaction potential, V_t . The foundational theory that accounts for the competitive forces involved in the total potential is the DLVO (Derjaguin, Landau, Verwey and Overbeek) theory. The DLVO theory describes stability of colloidal particles as a function of the overall forces that are present in a system: the attractive van der Waals, the electrostatic repulsive and the solvation interaction potential (Look and Zukoski, 1992). This competition determines the stability or instability of colloidal systems. The attractive van der Waals forces between particles is principally manifested in flocculation. Flocculation is defined as the process wherein two or more dispersed particles cluster together to form an aggregate such that the kinetic properties of each particle are combined with that of the cluster. The particles are held together by attractive van der

Waals forces. The forces that compete with flocculation are electrostatic repulsive forces due to ions in solution. Since the interaction of particle formation is a function of the potential energy in a system, it is helpful to define an energy barrier, wherein repulsive potential energy is defined as positive and attractive potential is negative. Both the attractive and repulsive forces decrease as a function of distance between the bodies involved in the interactions. The random phenomena that describe the relative collisions of colloidal particles in solution independent of the interparticle forces is called Brownian motion. Since collisions cause aggregation, the contributions from this diffusion must also be considered in the development of an aggregation model. In the absence of repulsive barriers, von Smouchowski provided the mathematical framework for the kinetics of coagulation (von Smoluchowski, 1916). Von Smoluchowski's methodology was to consider an individual particle and to calculate the number of particles diffusing towards it, according to classical Fick's Law.

Several aggregation models currently exist in the literature for describing gelation phenomena. Since condensation is not a reversible process, bonds form randomly. Consequently polymer formation is governed by Brownian diffusion as well as interparticle and intermolecular forces, and are not able to convert to equilibrium configurations. Fractal structures are formed whenever a monomer forms bonds at random. Most of our current knowledge about fractal aggregation currently exists in computer simulation models, as it is nearly impossible to experimentally isolate these mechanisms with the clarity that computer simulations yield (Martin and Hurd, 1987). Some of the current models that describe aggregation processes are the Witten & Sander

model or simply referred to as diffusion-limited aggregation (DLA) (Witten & Sander, 1981), the Percolation model wherein it is assumed that the reactivity of all the functional groups on a monomer is likely probable and that bonds form between polymers and not within them (Brinker, 1990), and the reaction-limited-aggregation model (RLA), where growth occurs strictly by condensation of monomers with clusters or by condensation of clusters with other clusters (Meakin, 1983). In DLA, particles traverse by random walks and irreversibly collide with immobile clusters. To this point, all DLA computer simulations have either admitted the effect of Brownian motion or the effect of chemical processes that govern the motion of the polymeric species. In most DLA characterized systems, the diffusing polymers grow according to their sticking probability. Recently, results have been reported wherein the aggregative growth was due to both DLA and RLA (Khatouri, 1995). It is not the focus of this study, however, to simulate any of these growth processes with computer models, but to use the results of current models to describe the growth that occurs during the gelation.

A mass fractal follows a pattern such that the mass of the fractal increases with its radius according to $m \sim r^3$, so its density ($\rho \sim m/r^3$) decreases as the object gets larger. This is directly opposite to moities that exhibit conventional Euclidian geometry. A tree is an example of a mass fractal. The number of bonds that a monomer can form is called its functionality, f . For $f > 2$, the linkage of chains can be cross linked to form a 3-D structures that demonstrate this very complex branching (Brinker, 1990).

The chemistry and kinetics of transition metal alkoxides is order of magnitudes faster than the silica system. Whereas in the silica systems kinetics can be studied on a

minute or hour time scale, the zirconia and titania systems must be studied on a millisecond to second time scale, since these react much more readily with atmospheric water. It is therefore necessary that an in-situ reaction scheme be employed that allows for analyses to be performed in a millisecond time regime. The method of choice is called continuous rapid mixing (Kustin, 1969). Combined with other instrumental analyses as Fourier Transform Infrared Spectroscopy (FTIR) and Small Angle X-ray Scattering (SAXS), these reactions can be fully investigated systematically. Parameters useful for the modeling of reaction and aggregative kinetics will be established from these experimental results. The main focus of this research is to experimentally determine parameters that affect the hydrolysis, condensation and gelation kinetics. Combining the results of these experimental analyses it may be possible to establish an overall kinetic model that will account for both the soluble species reaction kinetics as well as the kinetics of aggregation due to the condensation and diffusion processes.

2. METHODS

2.1 Experimental

2.1.1 Apparatus and Materials Used

This section describes the equipment and materials used in this research project as well as the explicit details as to how the items were set up and the procedures of how each experiment was performed.

Technical grade zirconium butoxides in 80% butanol was obtained from Aldrich Chemical Company. Also, 200 proof reagent grade absolute ethanol from Aaper Alcohol and Chemical Co, and volumetric titration grade tetramethyl ammonium hydroxide, $(\text{CH}_3)_4\text{NH}_4\text{OH}$, obtained from Aldrich, were used. All water used in this study was doubly de-ionized, so that the conductivity was measured as $18 \text{ mmhos}\cdot\text{cm}^{-1}$. All solvents were used in the experiments as received, no further modifications or purifications were performed. All glassware was cleaned by soaking in $2 \text{ M H}_2\text{SO}_4$, followed by thorough rinsing with distilled water and dried in air at 180°C . Before using, the glassware was rinsed with dry ethanol. The reactant concentrations used in the studies are reported in Table 2-1. Since the ethanol and alkoxides readily absorb moisture from the air, special care was taken to prevent excess exposure of the solutions to the atmosphere.

Due to the extreme lability of zirconium alkoxide systems toward hydrolysis, it

Table 2-1: Reactant Concentrations (mol/l)

Experiment	$[\text{Zr}(\text{OC}_4\text{H}_9)_4]$ (M)	$[\text{H}_2\text{O}]$ (M)	$[\text{OH}^-]$ (M)
A	0.1	1.1	0.01
B	0.1	1.1	0.005
C	0.1	1.1	0.0025
D	0.1	0.55	0.01
E	0.1	0.55	0.005
F	0.1	0.55	0.0025

was necessary to study these reactions using a continuous-rapid-mixing technique so that information could be gained about the earliest stages of hydrolysis and condensation.

2.1.1.1 Peristaltic Pump

The vehicle used to perform the rapid mixing experiments was an Ismatec peristaltic pump (MV-GE). In order for there to be sufficient pressure to cause flow, silicon tubing was used in the pump. However, Teflon tubing was used whenever possible to minimize potential reactions that may occur between the solution and the tube wall. The rapid mixing continuous flow experiments were performed by mixing an equal flow rate of zirconium butoxide/ethanol and H₂O/HCl/ethanol reactants in a mixing tee. The maximum achievable volumetric flow rate with the pump was $Q=2.9 \text{ cm}^3/\text{s}$. However, all experiments were performed at a flow rate of 1.5-1.8 cm³/s, as the silicon tubing would frequently burst at the highest flow rate, due to the rapid material breakdown from the pump heads. The volumetric flow rate in a peristaltic pump is independent of the length and volume of the tubing as the applied pressure in the pump is the driving force for flow. However, the time of reaction does change with volume of tubing, since it is defined in these experiments as the time of residence of the fluid in the reaction coordinate:

$$\tau = \frac{V}{Q} \quad (2.1)$$

where V =volume of reactor (cm^3) and Q =volumetric flow rate (cm^3/s) so that the units of τ are given in seconds. Since the time of reaction depends upon V and Q , one can either change the volume or change the flow rate to achieve different reaction times. It is important to note that once V and Q are fixed, the time of mixing is independent of how long the reactants flow. For example, if the V and Q are fixed so that a residence time of, say, 1 second is defined in the reactor, then 10 seconds of flowing will give the same residence time that 2 hours would give.

The point of origin for the reaction coordinate is taken to be the mixing tee, where the two solvent streams are mixed in a 1:1 fashion. The concentration of the stock solutions are immediately cut in half once they mix in the tee. For example, the stock solutions of 0.2 M Zr butoxides and 2.2 M $\text{H}_2\text{O}/0.01$ M OH^- would instantly become 0.1 M Zr, 1.1 M $\text{H}_2\text{O}/0.005$ M OH^- , respectively. In this investigation, all conditions are reported at the 1:1 mixed concentrations. The volume of the mixing tee in which reaction occurred was experimentally determined as 0.1 cm^3 . The total volume of the tee was measured to be 0.3 cm^3 , but since the reaction only occurs in 1/3 of the tee, this value of 0.1 cm^3 was taken to be the actual mixing volume. This volume was determined by taring a tee on an analytical scale and then weighing again after filling with distilled water. The volume was then calculated by taking the density of water to be 1.0 g/cm^3 . To create the static reaction times, it was necessary to compute the relative volumes of tubing that would accommodate the $Q=1.7 \text{ cm}^3/\text{s}$. The volume of interest began with the mixing tee, 0.1 cm^3 , and continued until the point of observation where a detector read

the signals. Silicon tubing was used for the pump so that continuous flow could be ensured. Teflon tubing acquired from Cole-Parmer was used as the pipeline from the reactants to the silicon tubing of the pump, then from the pump to the mixing tee. Finally, it was used again for the reaction coordinate. The diameter of the Teflon tubing for the pre-reaction regimes was 1/16" ID. The actual mixing, however, occurred at an ID of 1/32". The reaction coordinate was normally 1/16" ID as this was the easiest tubing size to accommodate in terms of geometric demands from the analytical instruments. Since all experiments were performed at the same flow rates, it is assumed that the calculated Reynolds number is a good indication that thorough mixing is obtained in this turbulent regime. The Reynolds number was calculated using ethanol as the basis since the volume of ethanol is so much larger than either water or alkoxide. The calculated Reynolds number was $N_{re} > 2900$ for all experiments. The transition regime from laminar to turbulent is about 2000 for circular pipes (Perry, 1972). This ensured that mixing was in the turbulent regime so that radial gradients of temperature, concentration and flow were negligible. Once the volume of the fittings, mixing tee, and appropriate flow-cell were measure, a least volume was calculated as that volume that would occur if the point of observation were as close as is mechanically possible. From this, the best time can be calculated as the shortest residence time possible,

$$T_{best} = \frac{V_{best}}{Q} \quad (2.2).$$

Figure 2-1 gives the schematic setup for the experiments from the stock solutions to the point of observation. The points of observation for this study were either a manufactured flow-through cell from Spectra-Tech or a homemade flattened quartz capillary.

2.1.1.2 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR is an analytical instrument that detects the vibrational and rotational modes of the ligands of interest and yields the result as either absorbance or transmission on the ordinate and wavenumbers (cm^{-1}) on the abscissa. Infrared signals arise from minute vibrations that naturally occur within molecules. The individual atoms are modeled as balls connected by springs. The resultant spectra are useful in providing such information as molecular structure, symmetry and concentration. The infrared spectra can be used as fingerprints both to identify and monitor a particular species. By monitoring the relative detected intensity at these characteristic fingerprint regions, it is possible to determine the concentration of a given species in the sample of interest. A Fourier Transform Infrared spectrophotometer was used to determine the relative concentrations of the reactant species as the reaction progressed.

The first step in determining the concentration of the species of interest was to establish a frame of reference to which the reactants could be compared. This was accomplished by establishing a standard curve for each of the reactants of interest for the fingerprint regions. Figures 2-2 and 2-3 are examples of the appropriately labeled solvent subtracted fingerprint regions. Meanwhile, Figures 2-4 and 2-5 illustrate the typical standard curves for these reactants. It was discovered that the 34°C and the 23°C

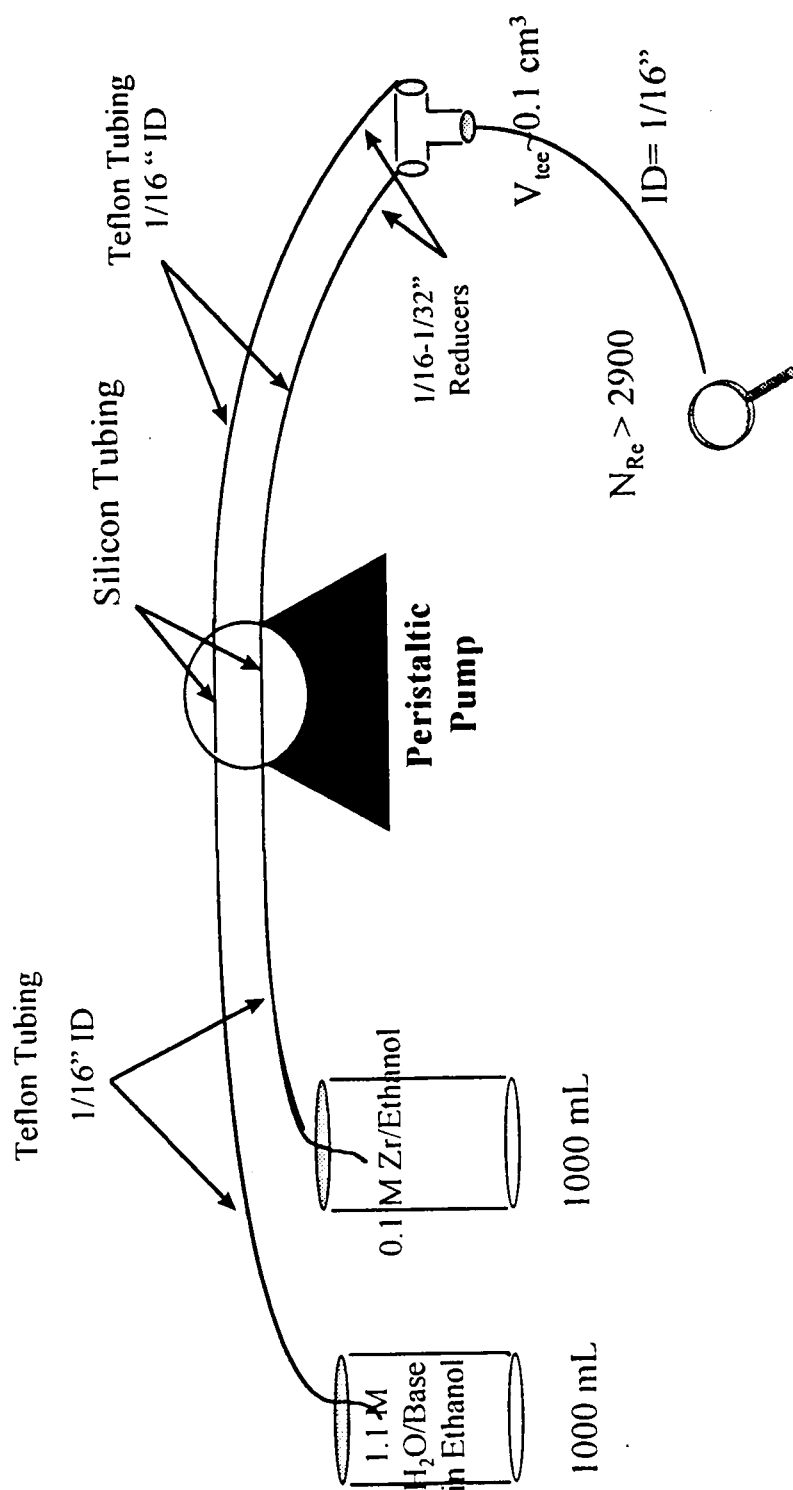


Figure 2-1: Schematic setup for flow-through experiments

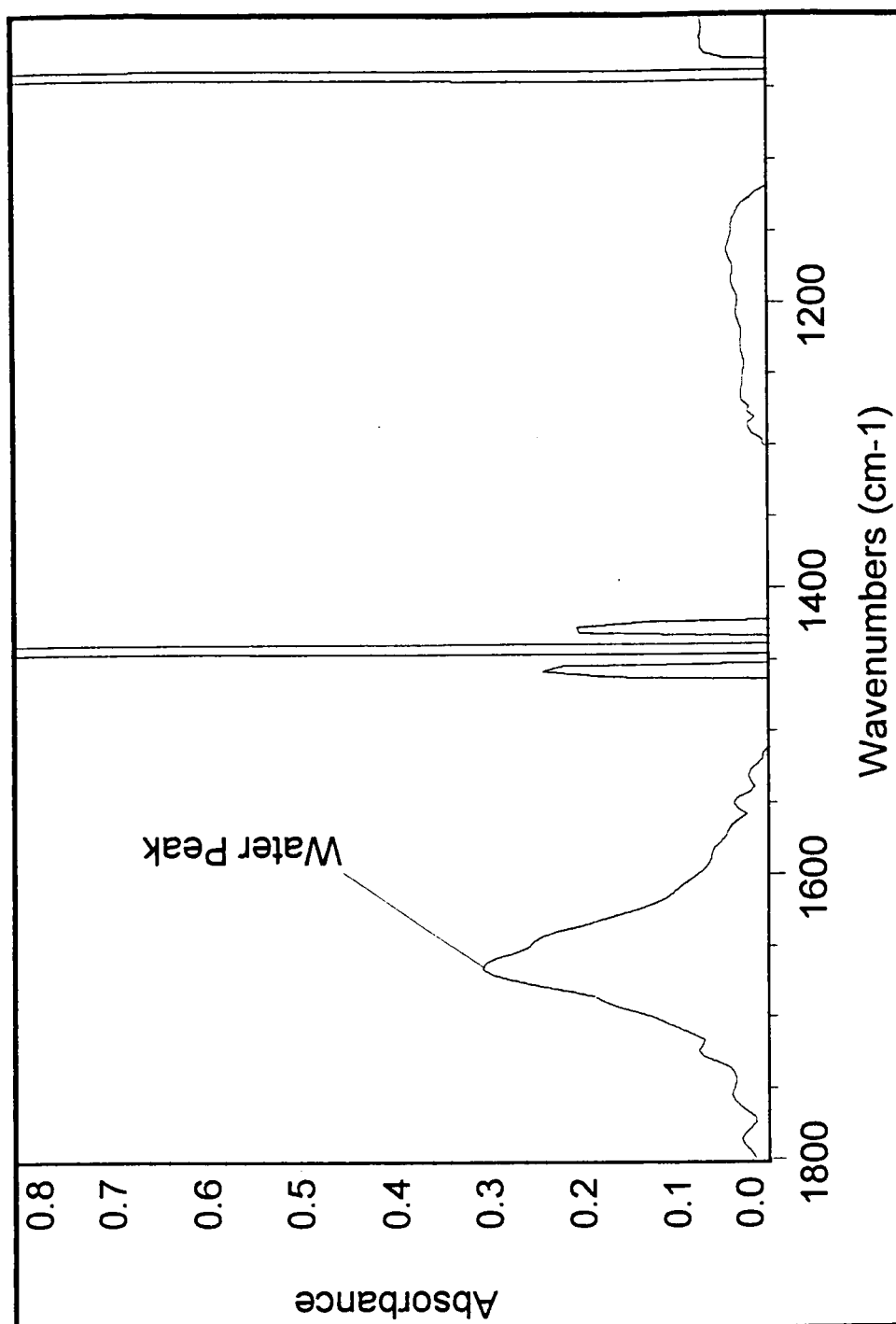


Figure 2-2: Solvent subtracted spectra of water fingerprint region where $[\text{H}_2\text{O}] = 1.1 \text{ M}$

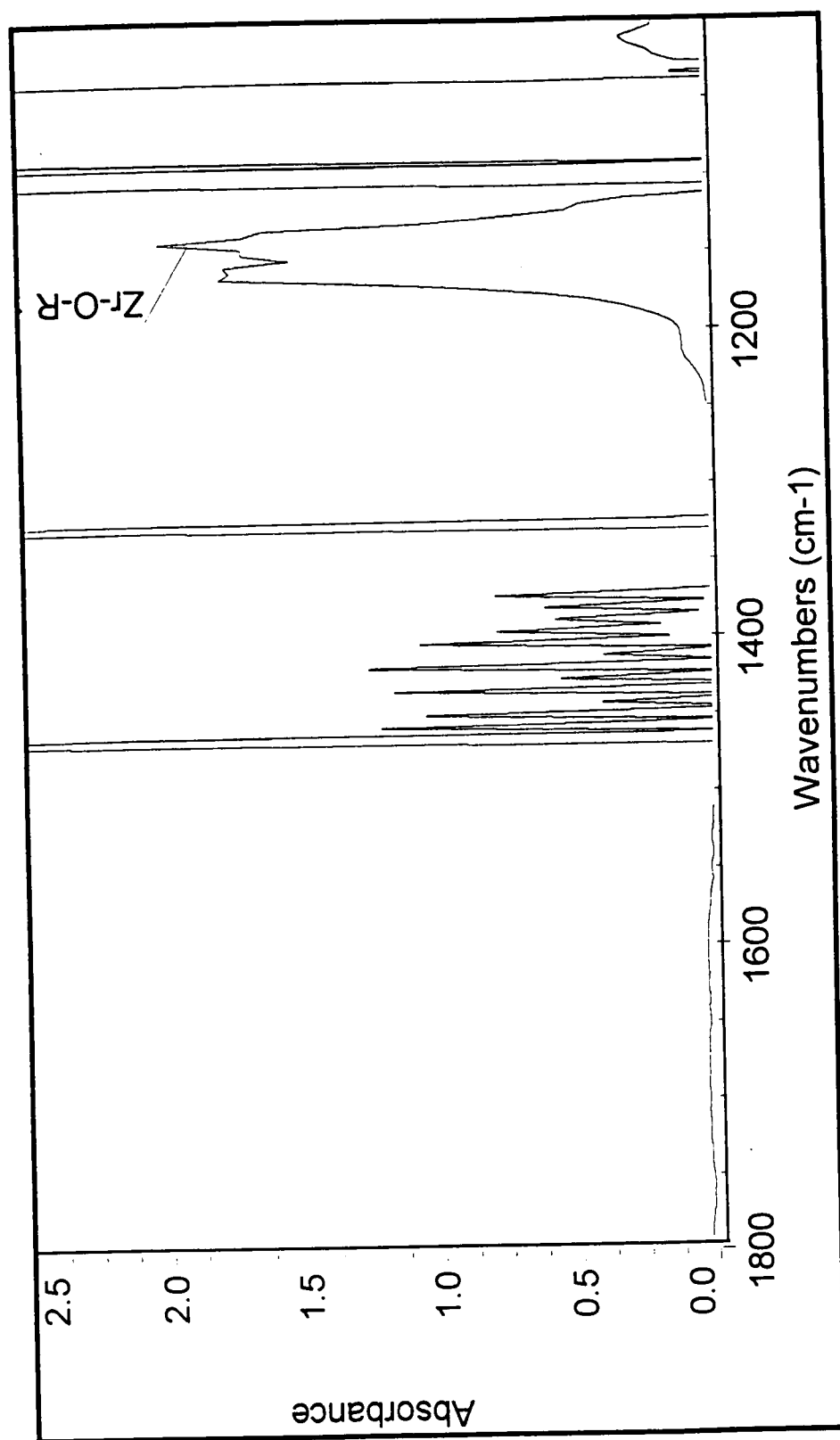


Figure 2-3: Solvent subtracted spectra of Zr-OR fingerprint region where $[Zr]=0.1$ M

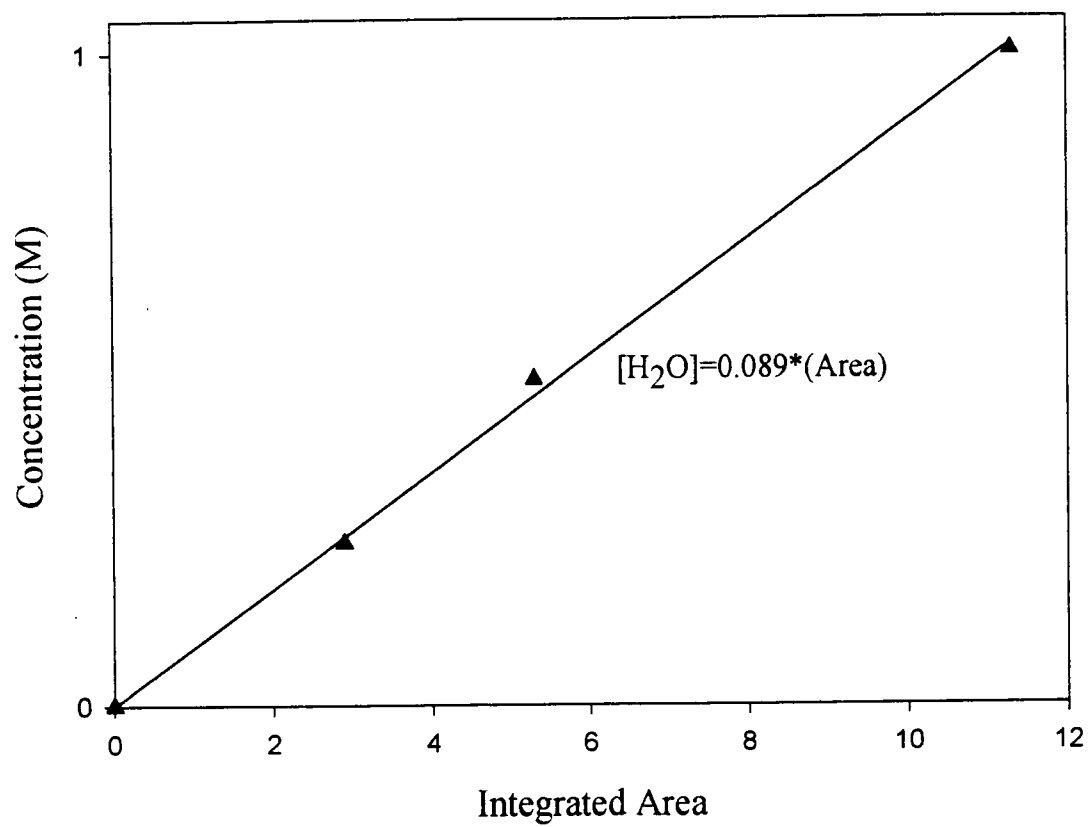


Figure 2-4: H₂O Standard Curve for Region 1685-1619 cm⁻¹

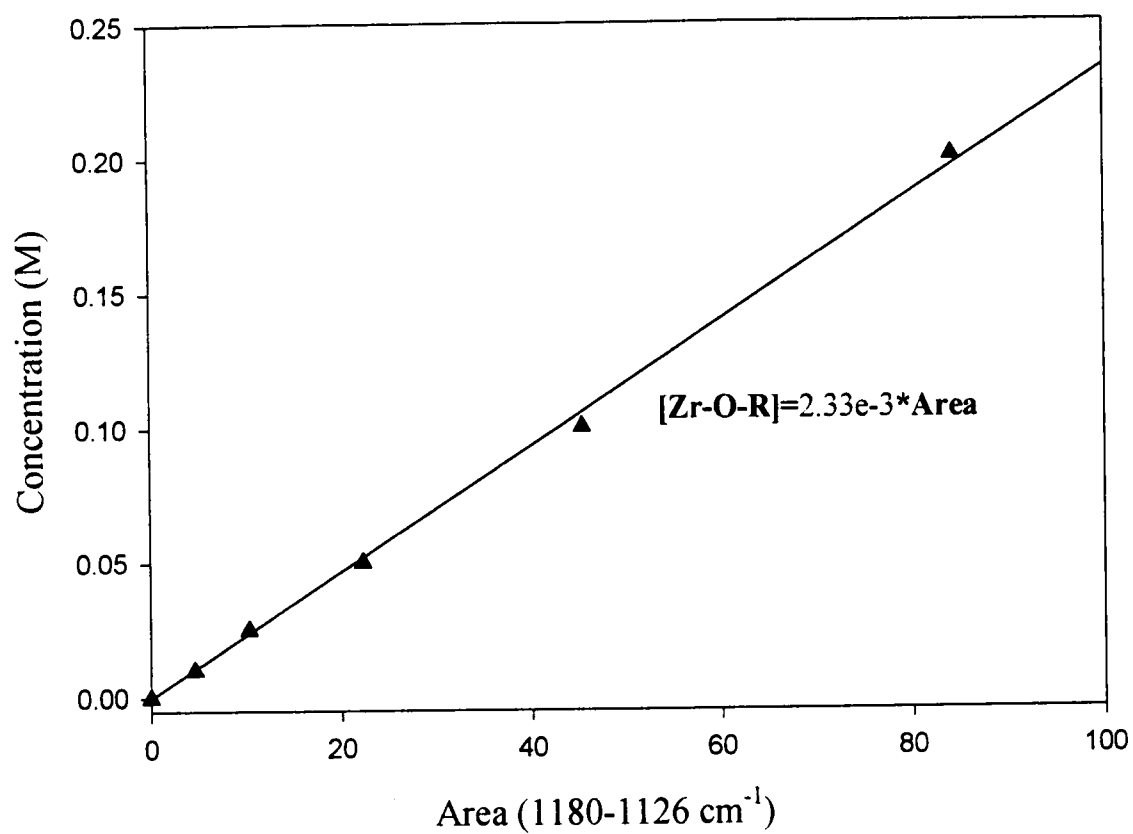


Figure 2-5: Standard Curve for Zirconium Butoxides

standard curves had about the same slope for the linearly regressed data whereas the 10°C standard curves had a lower linearly regressed slope. This phenomenon was due to the fact that the colder temperatures slowed down the rotational and vibrational movements of the molecules, thus, the measured intensity was less. An experimental technique that was useful in resolving the associated fingerprint regions was the solvent subtraction technique. This technique is extremely useful for organic solvents since they demonstrate very high absorption. With solvent subtraction, the background is taken to be the sample cell containing ethanol. This background is then subtracted from all sample spectra. This method was used successfully in this investigation. In order to further eliminate any background interference from either temperature or fluid flow phenomena, the individual backgrounds were taken at the same temperature and flow rates as the experimental conditions. Using the linear regression lines from the standard curves, the concentrations were calculated as a function of the integrated areas for the fingerprint regions. $[H_2O]_0$ and $[Zr-O-R]_0$, the initial concentration of the species at $t=0$, were taken to be the extrapolated values from the standard curves whenever only the reactants of interest were present in the reactor.

All FTIR experiments were performed on a Nicolet 560 Spectrophotometer with a liquid nitrogen-cooled MCT detector at a spectral resolution of 8 cm^{-1} . The spectrophotometer was controlled with OMNIC software provided by Nicolet on a PC computer with a Windows 3.1 platform. Although changing samples did not require the sample chamber to be opened, it was necessary to open the chamber to change the reactor volume so that discrete reaction times could be obtained. In order to reduce the

risk of affecting the spectra with moisture, the sample chamber was opened as little as possible. The experimental procedure was to perform experiments A through F at a given reactor volume before changing the tubing. Between each set of experiments, the process was thoroughly rinsed with ethanol for at least 30 seconds so that the next experiment would not be contaminated by the proceeding one. A process line of vaporized liquid nitrogen or gaseous N_2 was provided at a pressure of 10-20 psia. This helped to provide an inert atmosphere wherein the effects of water moisture were essentially negligible at the resolution used in the experiments. The sample chamber on the FTIR had a clear window so that leaking problems were immediately detected in the process line. In the case of a leak, the sample chamber was thoroughly cleaned and purged with N_2 for several hours before it was used again. A reference standard of 1.5 micron polystyrene film with a known spectra was used to determine the effect of atmosphere on the output. Once this spectra was taken, it was matched against a library of spectra found in the accompanying software package for the spectrophotometer. For all experiments, the statistical library search matched the polystyrene reference with 95 % accuracy. The output spectrum from the FTIR was recorded in Absorbance (arbitrary units) versus Wavenumbers (cm^{-1}) on the abscissa.

The cell windows were made from ZnSe, a material that has very negligible absorbance in the mid-IR regions ($4000 - 400\ cm^{-1}$). The window had a radius of 18 mm and a width of 2 mm. In order to accommodate flow, one window was placed upon the other separated by a grooved aluminum or Teflon spacer. The groove helped to minimize the volume between the windows to ensure a continuous reaction pathway and

minimize back- mixing in the reactor as flow would circulate without it. The typical slit width between the windows was 100 microns. From trial and error it was found that this was the optimum width. For smaller distances, pressure buildup occurred which caused leaking. At greater distances, the spectral distinction of alkoxides became worse and worse. This phenomenon is due to Beer's law which states that absorbance is directly proportional to path width as well as concentration. For greater distances, the instrument had difficulties in discriminating solvent background from sample as there was "infinite absorption". However, at the optimum width the background noise due to the solvent was virtually eliminated via the solvent subtraction technique. Other than leaking problems, there was not an experimental limit on how small this separation could be.

Different reaction temperatures were also studied so that activation energies and rate constants could be determined. For experiments wherein the temperature was not ambient, thermocouples were used to monitor the process conditions at the inlet and outlet of the flow-through cell. That is, a thermocouple was placed immediately before mixing and one was placed immediately after the sample cell. The average of these two temperatures was taken to be the reaction temperature. The temperature sources that were used in the experiments were water baths maintained at 5 °C and 40 °C. The actual experimental temperatures were 10 °C, 23 °C and 34 °C, respectively. To ensure that localized temperature gradients were minimized, the reaction flasks were incubated in the baths for at least thirty minutes. The temperature drop between the two thermocouples was much smaller than that between the water bath and the first thermocouple. In other words, heat loss was due more to surface area convection to the

atmosphere than to the relative heats of reaction that may occur.

2.1.1.3 Small Angle X-Ray Scattering

Small Angle X-Ray scattering (SAXS) was used to establish a preliminary data base of the relative size of primary particles as well as structural transitions during the condensation reactions.

2.1.1.3.a Apparatus: The small angle X-ray scattering (SAXS) experiments for this research were conducted on the 10-m SAXS instrument at Oak Ridge National Laboratory (Hendricks, 1978). The instrument was equipped with two gate valves and a vacuum pump so that operating pressures were about 10^{-6} Torr. One gate valve was placed between the power source and the sample chamber and the other was placed between the sample chamber and the detector. Consequently, it was possible to control the pressure throughout the 10-meter SAXS instrument. The X-ray source was a 12-kW Rigaku rotating anode generator operated at 40 kV and 100 mA with a copper target and a graphite crystal monochromator. A pinhole collimator and a 20 x 20 cm² dimensional position-sensitive counter of 64 x 64 channels were also used. In order to absorb X-rays close to the zero scattering angle so that the detector was not burned, a 1-cm diameter lead beam stop was used. The sample-to-detector distance was set at either 1.069 or 5.069 m.

Several preliminary corrections were performed before collecting data. The sample scattering was corrected for detector sensitivity, dark current and background solvent. The sensitivity run was performed by closing the gate valve between the X-ray source and the sample chamber and inserting Fe-55, an isotope that emits X-rays, into the

sample holder. Collection time on the detector using the Fe-55 as the X-ray source lasted about 3-4 hours. Extreme precaution was taken when handling this sample so that the body was not exposed to the radioactive side of the Fe-55. This sample was immediately placed into its radiation proof safe after usage in order to comply with health physics safety standards. In order to determine the relative effect of scattering from cosmic sources and other substantial radiation sources, such as the nearby Neutron Scattering Facility, a dark current correction was also performed. To measure the dark current, both gate valves were closed so that the detector would only detect cosmic radiation. Collection time on the dark current usually took about 1-2 hours. The third correction was to account for background solvent. Although the other two corrections could be performed at any time during the experiments, it was necessary to correct for background before data collection, because the scattering was dependent upon both the solvent and the local morphologies of the flow-through cell. Therefore, all solvent corrections were measured in the same reactor as that in which the actual data were measured. It was also necessary to measure the transmission coefficient of the scattering materials so that the intensity would be measured with respect to this value:

$$T_m = \frac{(I_{gcs} - I_{dc}) - 0.686 (I_s - I_{dc})}{(I_{gc} - I_{dc}) - 0.686 (I_{mt} - I_{dc})} \quad (2.3)$$

where I_{gcs} is the measured intensity of glassy carbon and sample (glassy carbon being an automated filter that has a characteristic scattering intensity), I_{dc} is the counts from the dark current, I_s is the sample scattering intensity, I_{gc} is the measured intensity from glassy

carbon alone, and I_{mt} is the measured count rate in Hz of the empty beam. From the transmission, the thickness of the capillary was calculated. Typical values for the thickness of the capillaries were 0.8-1.1 mm.

The sample holder was constructed from aluminum and it was used to hold a homemade flattened glass capillary. These flow-through reactors were made by melting 2.0 mm diameter quartz capillaries between two graphite blocks that contained fixed grooves at $\sim 600^\circ\text{C}$ for 1 hour. Once these capillaries were flattened, they were carefully glued in an aluminum holder with Du Pont® 2-Ton epoxy and left to dry. This was a very difficult technique to learn, due to the fragility of the glass capillaries and the demands of the process. Leaking and bursting would frequently occur during the experiments. Whenever a capillary did burst, it was necessary to correct for solvent background again, as each capillary had different local porous morphology on the Angstrom length scale. Although it was extremely difficult to master this technique, once it was learned, the capillaries made an excellent flow-through setup for these experiments.

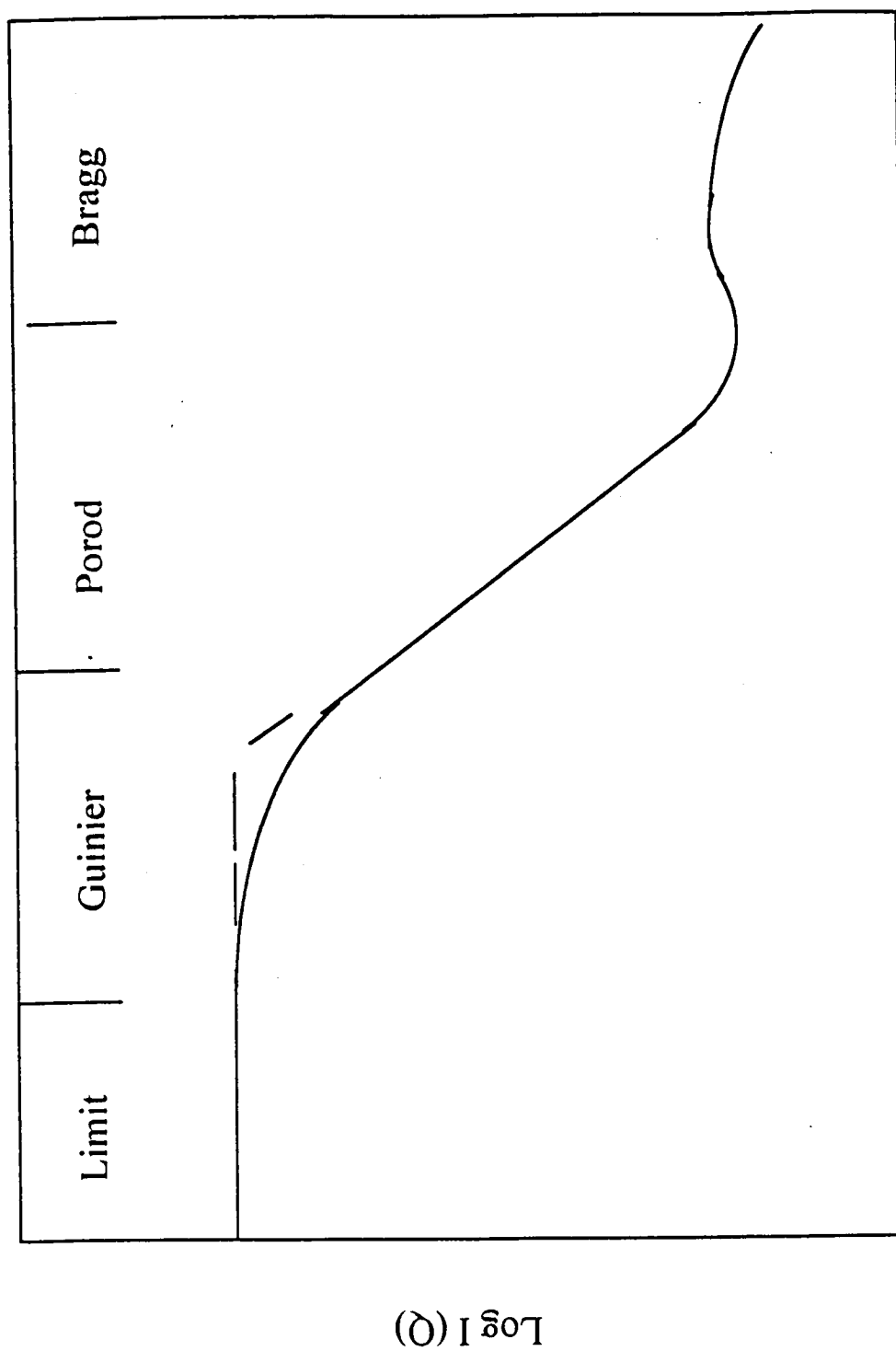
2.1.1.3.b Theory of SAXS: The theory of small angle X-ray scattering has been worked out in detail by Guinier (Guinier, 1953). With SAXS it is possible to investigate structures on length scales from ~ 5 to $1000 \text{ \AA}$. Small angle X-ray scattering arises from the electron density differences between a particle and the medium in which the particle is embedded. The scattering depends on the number of particles, the electron contrast between particle and the medium, and the size of the particles themselves,

$$I(q) = I_e(q) N_p (\Delta \rho v)^2 \exp(-q^2 R_g^2 / 3) \quad (2.4)$$

where v is the volume of the particle, N_p is the number of particles per unit volume, R_g is the radius of gyration, I_e is the scattering from a single electron, $\Delta \rho$ is the electron density difference between the particle and the medium, and q is the scattered wave vector, $q = 4\pi \sin(\theta / \lambda)$, where 2θ is the scattering angle and λ is the wavelength of the incident X-rays. The wavelength of the X-ray was $\lambda = 1.54 \text{ \AA}$, which is considerably smaller than the size of the particles being detected.

Whenever an incident X-ray beam bombards a particle, the angular dependence of the scattered intensity is measured. Figure 2-6 shows a schematic small-angle-scattering curve from a typical dilute macromolecular solution (Keefer, 1984). The Bragg region is characterized by large scattering angles. Information from this region is useful in studying interatomic spacings. The Guinier region is characterized by small scattering angles. The Porod region occurs at intermediate angles. The Guinier and Porod regions are the two areas of interest for these studies.

The radius of gyration is defined as the weight average radius of the particle. The R_g values can be found from the scattering data by means of a Guinier plot. Plotting $\ln I$ vs Q^2 gives a straight line with a slope $R_g^2/3$. This works for data in the range $QR_g < 1.3$. The zero angle scattering intensity, $I(0)$ is obtained by extrapolation of Guinier's law to



$\text{Log } (Q)$

Figure 2-6 Schematic Small-Angle X-ray Curves

$Q=0$. $I(0)$ gives useful information about the number of particles and electrons in each particle:

$$I(0) = I_e(0) N_p (\Delta \rho v)^2 \quad (2.5).$$

Equations 2.4 and 2.5 hold primarily for monodisperse systems, but for systems with a wide range of polydispersity the following hold (Guinier, 1955):

$$R_g^2 = \frac{\sum M_i R_i^2}{\sum M_i} \quad (2.6)$$

$$I(0) = I_e(0) \sum_{i=1}^N N_{p,i} (\Delta \rho_i v_i)^2 \quad (2.7).$$

Figure 2.7 gives a linear regression of scattered raw data for a Guinier plot. The experimental conditions in this plot are 0.1 M Z, 1.1 M H₂O, and 0.01 M OH⁻. Whenever there is curvature in the Guinier plot, a polydisperse system is being observed. Guinier data exhibits a bias towards the largest particle size as these bulkier species dominate the data at low Q , whereas smaller particles dominate the data at high Q . Most of the relevant information about the structure of the particle occurs for $0.1 < qA < 20$, where A is defined as the diameter of the particle, or the largest distance that can be scanned between two discrete points in a particle. The inequalities represent the extremes as either high or low Q values. A compromise that is commonly used in dealing with this bias is referred to as the resolution criterion (Schmidt, 1996). Although R_g is a

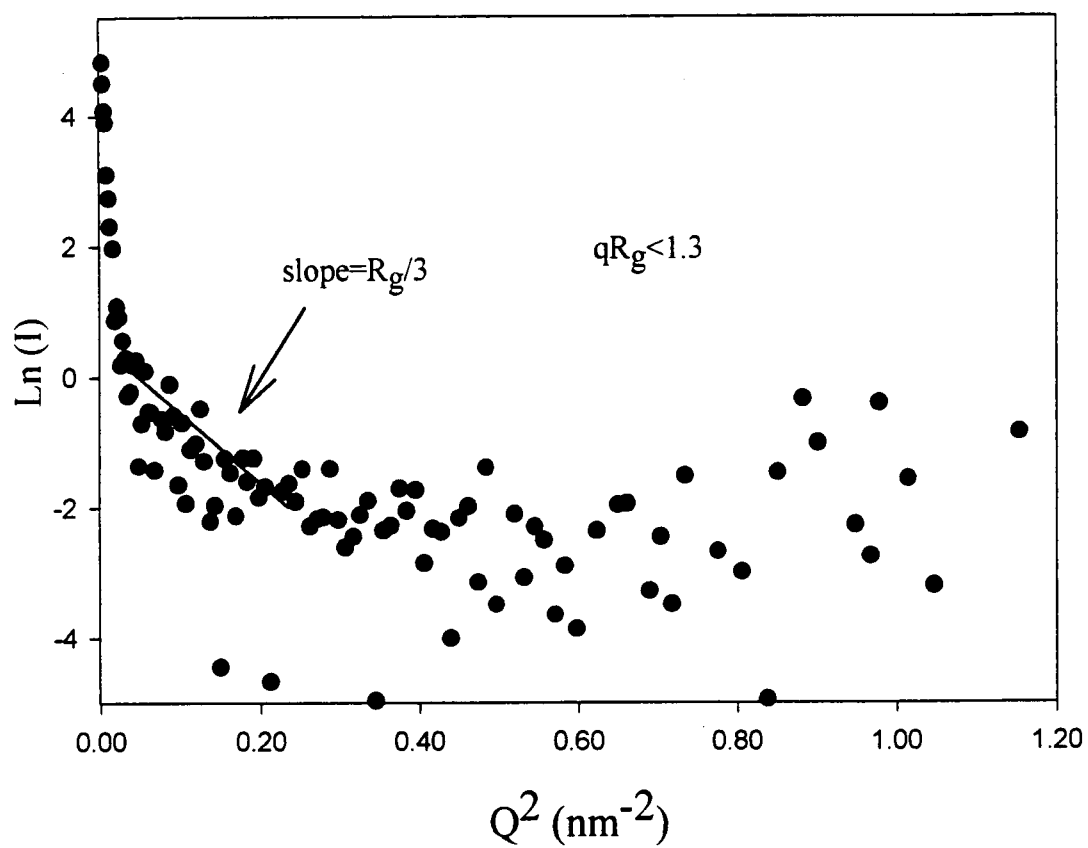


Figure 2-7: Guinier Plot for 0.1 M Zr-OR, 1.1 M H_2O , 0.01 M OH^-

parameter that intuitively relates the size of a particle to its spatial extensions, the radius of gyration is useful in characterizing certain geometries. For example, the radius of a sphere is given by

$$R_s = \sqrt{\left(\frac{5}{3}\right)} R_g \quad (2.10)$$

whereas long rods are characterized by

$$L \approx \sqrt{(12)} R_g \quad (2.11).$$

Scattering at intermediate angles ($R_g \gg Q^{-1} \gg A$) can be characterized by the Porod Law, wherein the data can be modeled as a power law:

$$I \propto Q^{-D_f} \quad (2.12)$$

where $-D_f$ is the slope of the regressed line from the data. Whenever $0 \leq D_f \leq 3$, the system is characterized by mass fractals, D_f (Hurd 1987). The Porod region is useful in monitoring the structural stages that occur during the polymeric gelation process. Figure 2-8 is an example of data taken in the Porod region for experimental conditions of 0.1 M Zr, 1.1 M H_2O and 0.01 M OH^- taken at 23°C. The linearly regressed slope gives the value for the fractal dimension. From fractal dimension analyses it is possible to predict the structure as well as the growth mechanisms for the metal alkoxide polymeric clusters and species (Brinker, 1990). With the aid of computer simulations, quantitative models can be predicted. However, the fractal dimensions were used in this study to qualitatively predict growth patterns upon the basis of current simulation models.

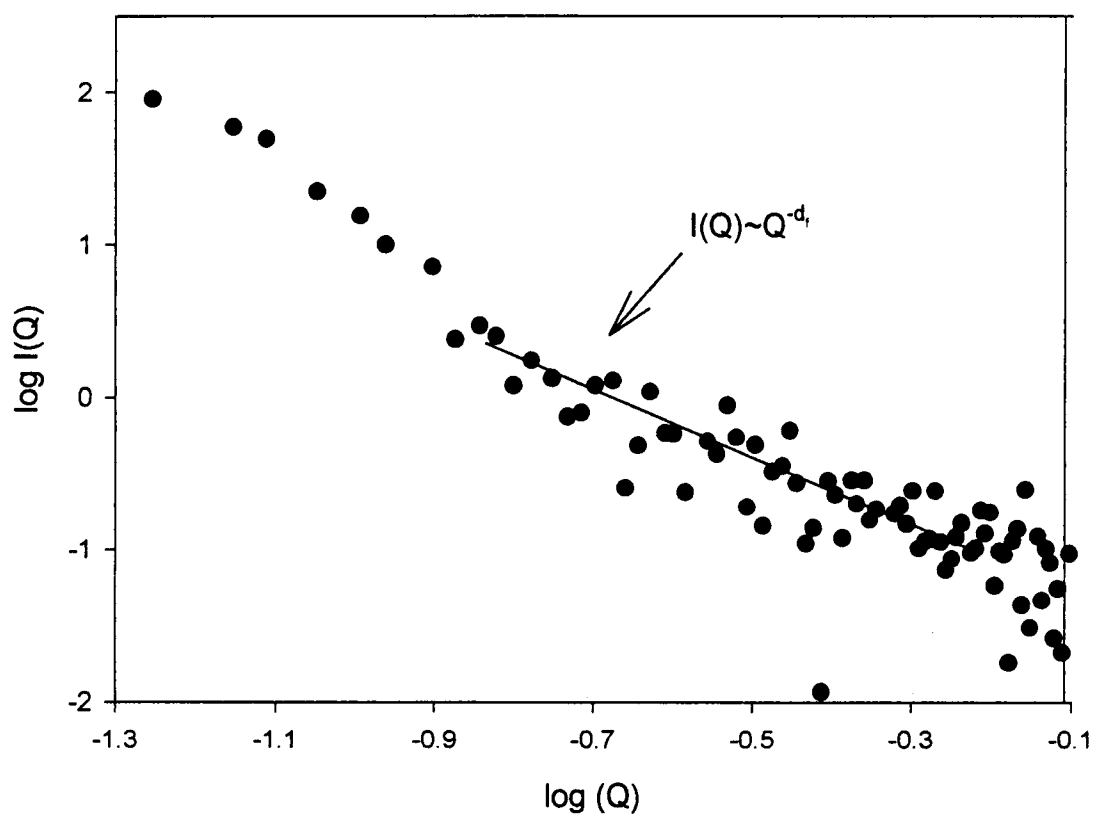


Figure 2-8: Porod Plot for polymeric growth in the system
0.1 M Zr-OR, 1.1 M H₂O, 0.001 M OH⁻¹ in ethanol

There were three main issues that were investigated in this research using the SAXS technique. These are size (R_g -radius of gyration), structure (D_f -fractal dimension) and growth kinetics (dR_g/dt) of the condensation products that are formed during the hydrolytic condensation of metal alkoxides. The primary importance of R_g is to establish the initial size of the metal alkoxide in solution. It is then possible to know whether the metal alkoxide exists as a monomer, trimer, tetramer or other. The shape of an overall kinetic curve is a function of the overall interaction potentials between the aggregating clusters and the rate of the condensation reaction.

2.2 Summary

Using a rapid-mixing technique in combination with FTIR spectroscopy and SAXS, a study was performed to elucidate the early-stage chemistry and reaction phenomena of the hydrolysis and condensation of zirconium butoxides in ethanol. The following chapter entitled ANALYSIS gives both the results from these experiments and the analyses from the data.

3. ANALYSIS

3.1 Introduction

Fourier transform infrared spectroscopy and small-angle X-ray scattering experiments were performed to study the early stage kinetics of the hydrolysis and condensation of zirconium (IV) butoxides in ethanol. FTIR spectroscopy was used to investigate the associated reaction kinetics for hydrolysis and condensation. Meanwhile, SAXS was used to study growth kinetics and early stage structural transitions.

It has been verified in the literature that hydrolysis and condensation are not reversible reactions (Barringer, 1985). The reactions are, however, overlapping. That is, hydrolysis does not go to completion before condensation begins. In this study it was determined that they occur simultaneously. Nevertheless, the dominant mechanism in the earliest stages is indeed hydrolysis. In fact, the majority of hydrolysis readily occurs within 1 second. It is evidenced, too, from the experimental data that the early stages of condensation begin to occur within this time scale. This was the primary time frame of interest in this study for quantitative analysis, although several data points were collected for longer times. To elucidate the physics and chemistry for this region implies that one can control the resultant morphology of the product gels or powders of interest. These studies were performed using the rapid-mixing-technique. The earliest time that was studied was 100 msec.

3.2 Hydrolysis and Condensation Rate Data

Hydrolysis and condensation are facile reactions in the presence of water, due to their low electronegativity and desire to increase coordination by accepting electrons that want to occupy the outer d^0 shells. This makes them susceptible to nucleophilic attack from hydroxo groups. Upon the addition of a strong base, the hydrolysis of metal alkoxide is slowed down significantly. That is, the hydroxo group behaves as an inhibitor to hydrolysis. Bases that do not strongly dissociate into OH^- groups do very little to slow down the reaction. In this case, hydrolysis would proceed as if no inhibitor were present. For example, a few attempts were initially made to perform these experiments with ammonium hydroxide. It was discovered that the reactions immediately precipitated making in-situ experiments nearly impossible to perform with this particular base. Eventually tetramethyl ammonium hydroxide was used as the base since it has a very high dissociation constant. Although much of the hydrolysis is completed within 1 second, condensation continues for minutes, hours or days depending upon the $[\text{OH}^-]$. Inhibitor concentrations were selected for this study that yielded powders and gels. However, due to experimental limitations, analytical techniques were only used on the systems that formed gels. Instantaneous precipitation was used as a guideline for the amount of base that must be added so that it would be possible to perform the experiments. FTIR experiments were used to study the relative reaction kinetics of hydrolysis and condensation, whereas SAXS was used to determine relative size and growth information as the reaction proceeded through the condensation

pathways.

Experimental results and analyses will be given in this chapter to elucidate the kinetics of the very complex hydrolysis and condensation reactions of zirconium butoxides in ethanol. The experimental setup, the materials used, as well as the detailed procedures for combining FTIR and SAXS with rapid mixing have been thoroughly discussed in Chapter 2, entitled METHODS.

3.2.1 FTIR Results

Figure 3-1 is an example of a solvent subtracted spectra for 0.1 M Zr, 0.01 M OH⁻ and 1.1 M H₂O taken at 100 milliseconds and 25°C. Spectra like these were used to monitor the concentration of both water and alkoxide as the reaction progressed. In all cases A-F (where data sets A through F are described in Table 2-1 on page 18) it was observed that the intensity of the Zr-O-R area, ~1120-1180 cm⁻¹, dropped significantly within 1 second, whereas the intensity of the water region, 1620-1660 cm⁻¹ either changed very little or actually grew in size after the initial concentration decay. Cases A-C were performed at three different reaction temperatures 10°C, 23°C and 34°C, whereas Cases D, E and F were performed at laboratory temperature, 23°C. The appropriately labeled Figures 3-2 through 3-7 show the percent of Zr-O-R groups that remain as the hydrolytic condensation proceeds for the different experimental conditions. In Figures 3-8 through 3-13 the percent of water remaining in time is graphically illustrated for the appropriately labeled reaction conditions. The effects that the OH⁻ groups have upon the rate of hydrolysis at fixed temperatures are seen in Figures 3-14 through 3-16.

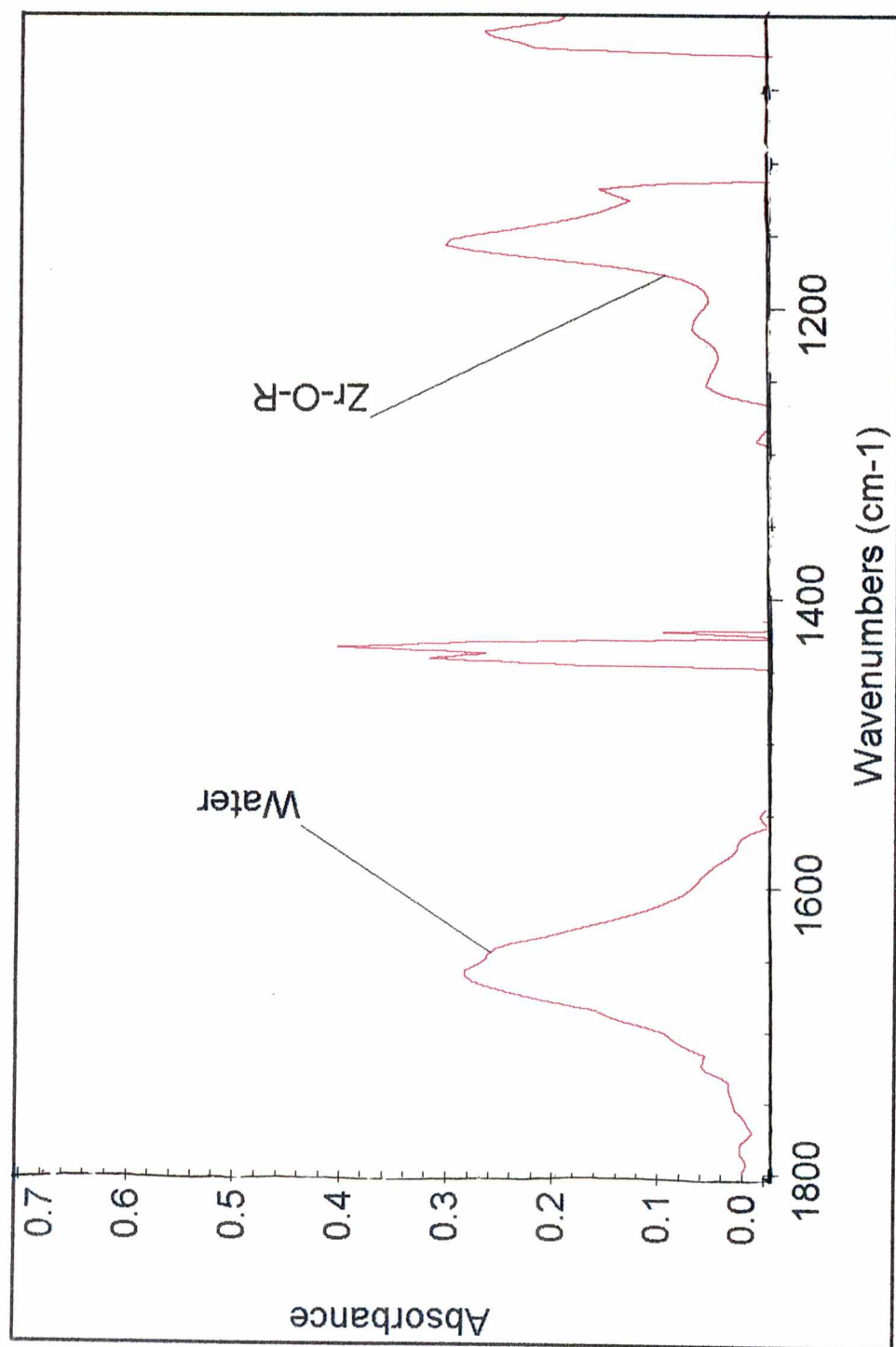


Figure 3-1: Solvent Subtracted FTIR Spectra of 0.1 M Zr (IV) Butoxides, 0.01 M OH⁻, and 1.1 M H₂O in Ethanol and Water at 100 milliseconds and 25 C

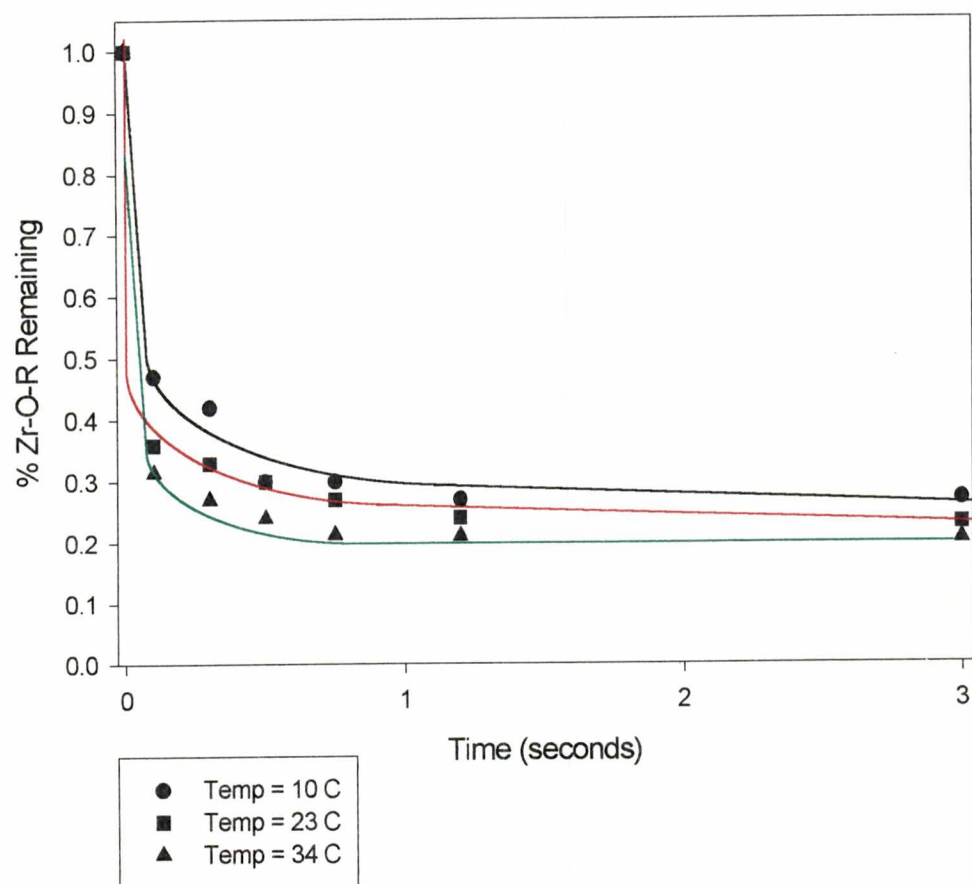


Figure 3-2: Percent of Zr-O-R remaining for A Series

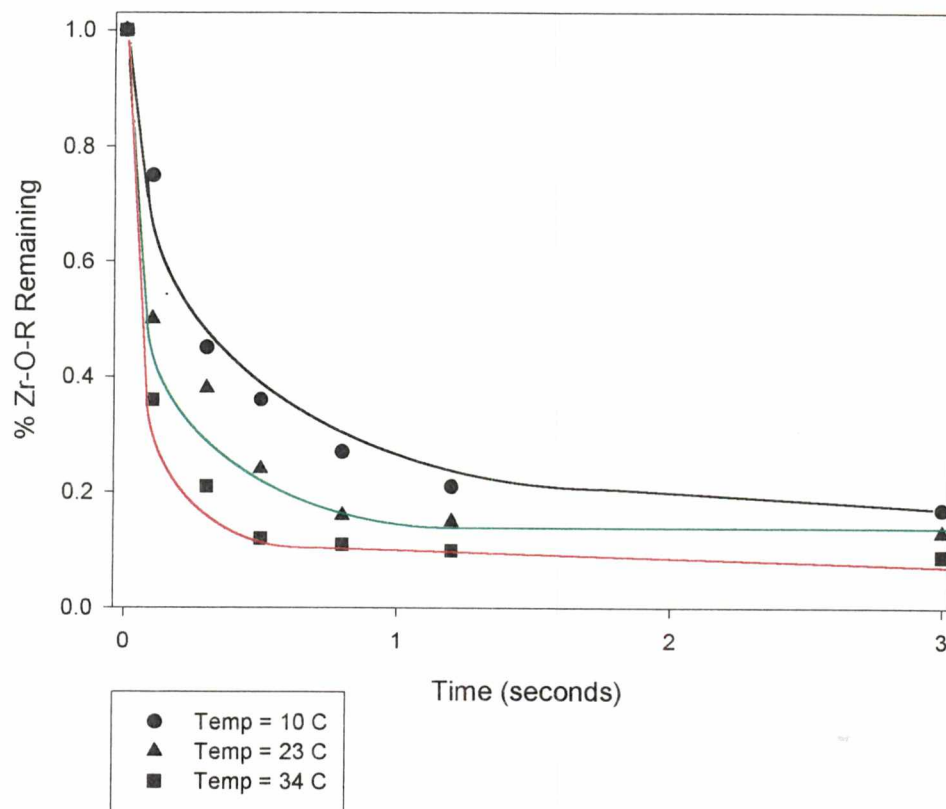


Figure 3-3: Percent of Zr-O-R remaining for B Series

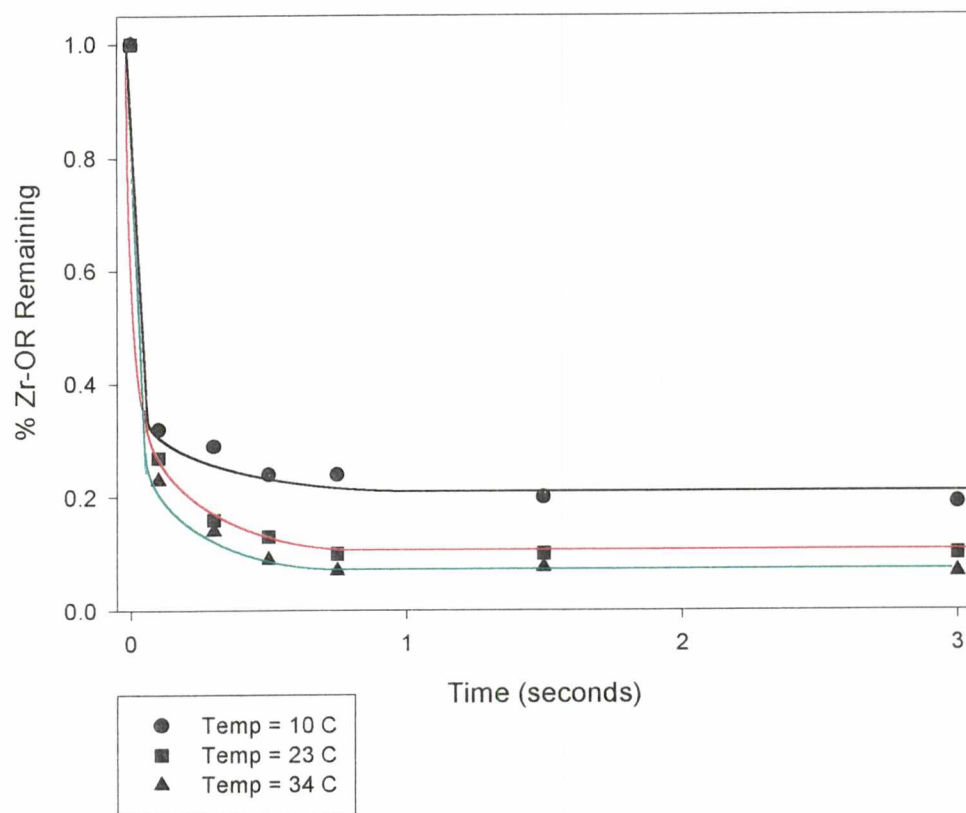


Figure 3-4: Percent of Zr-O-R Remaining for C series

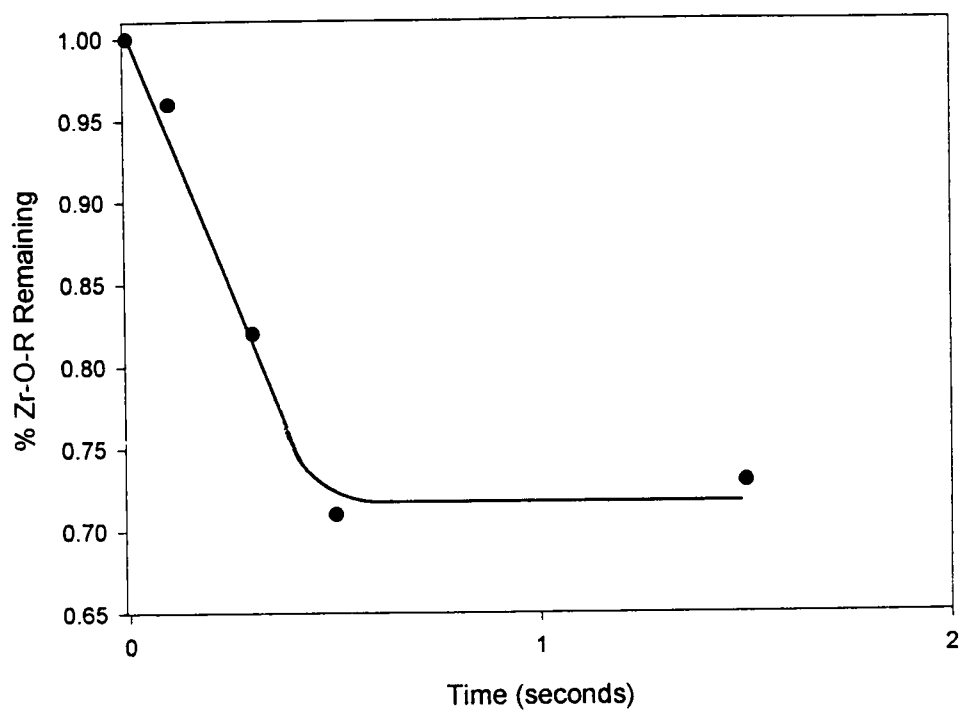


Figure 3-5: Percent of Zr-O-R remaining for D Series at 23 C

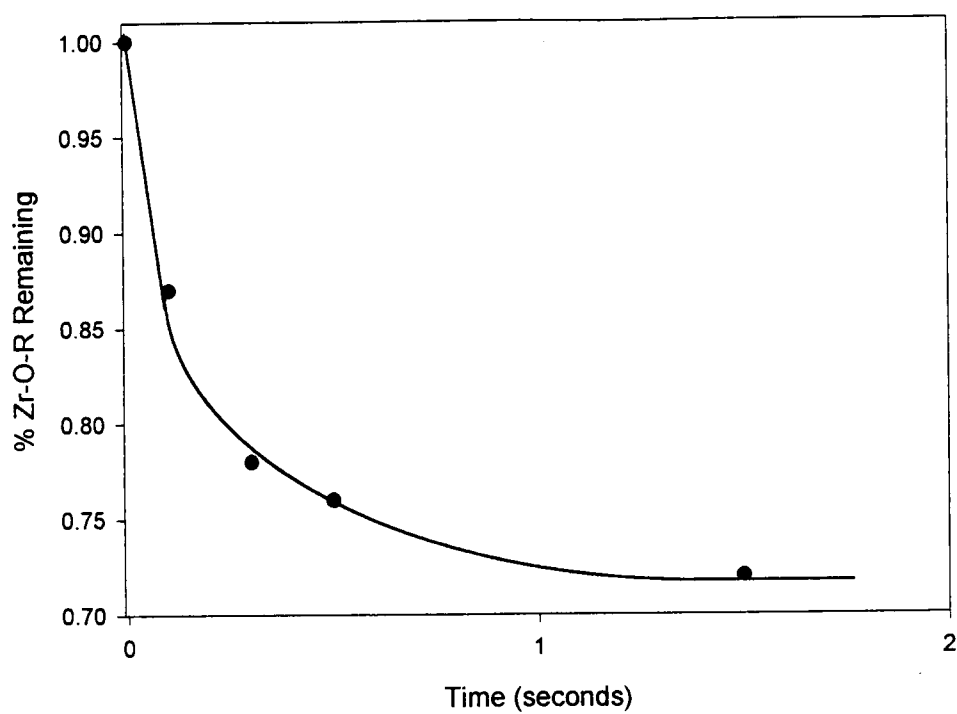


Figure 3-6: Percent of Zr-O-R remaining for E Series at 23 C

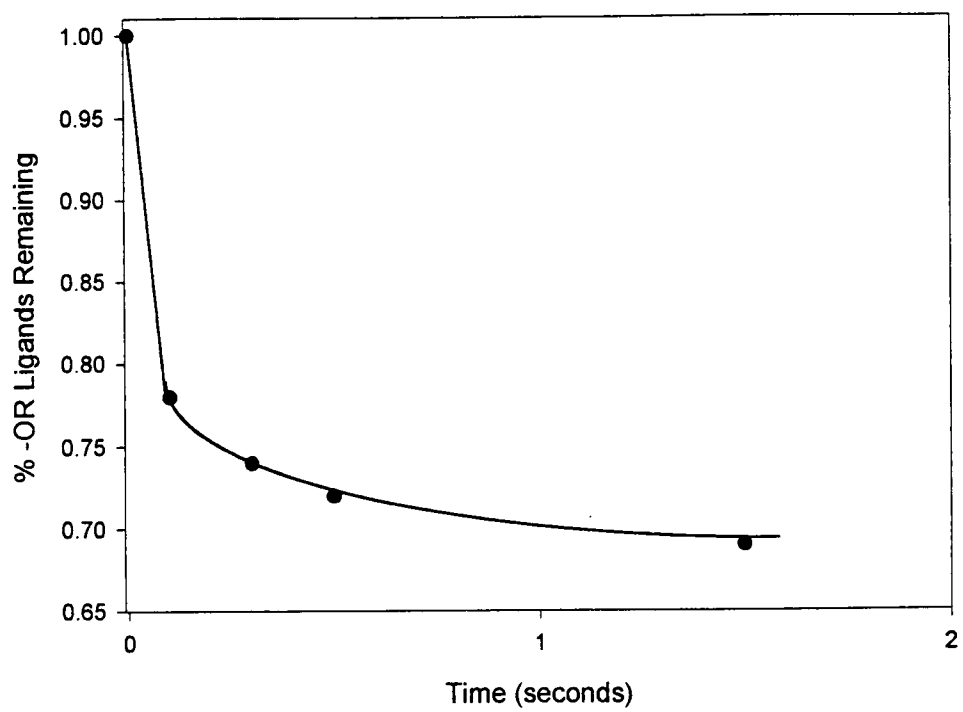


Figure 3-7: Percent of Zr-O-R remaining for F Series at 23 C

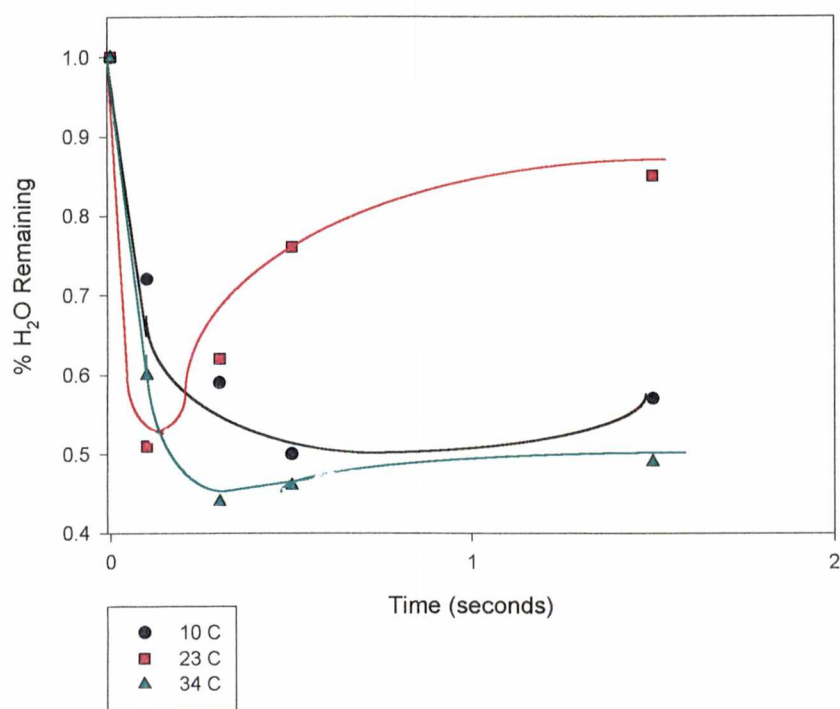


Figure 3-8: Percent of H₂O remaining for A Series

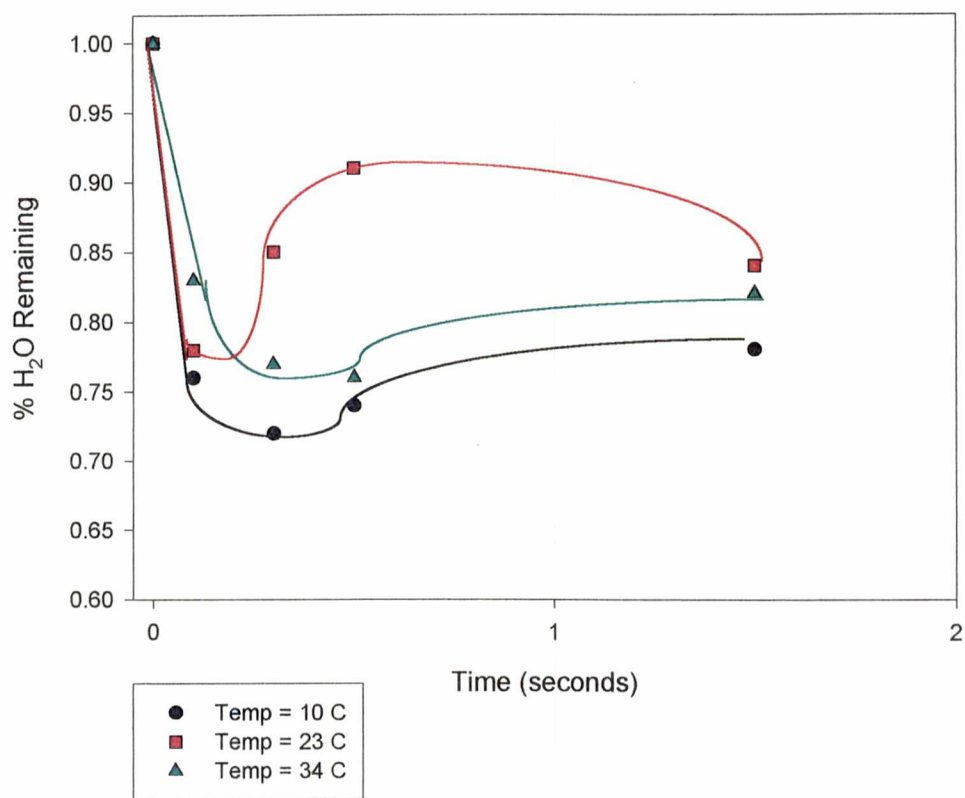


Figure 3-9: Percent of H₂O Remaining for B Series

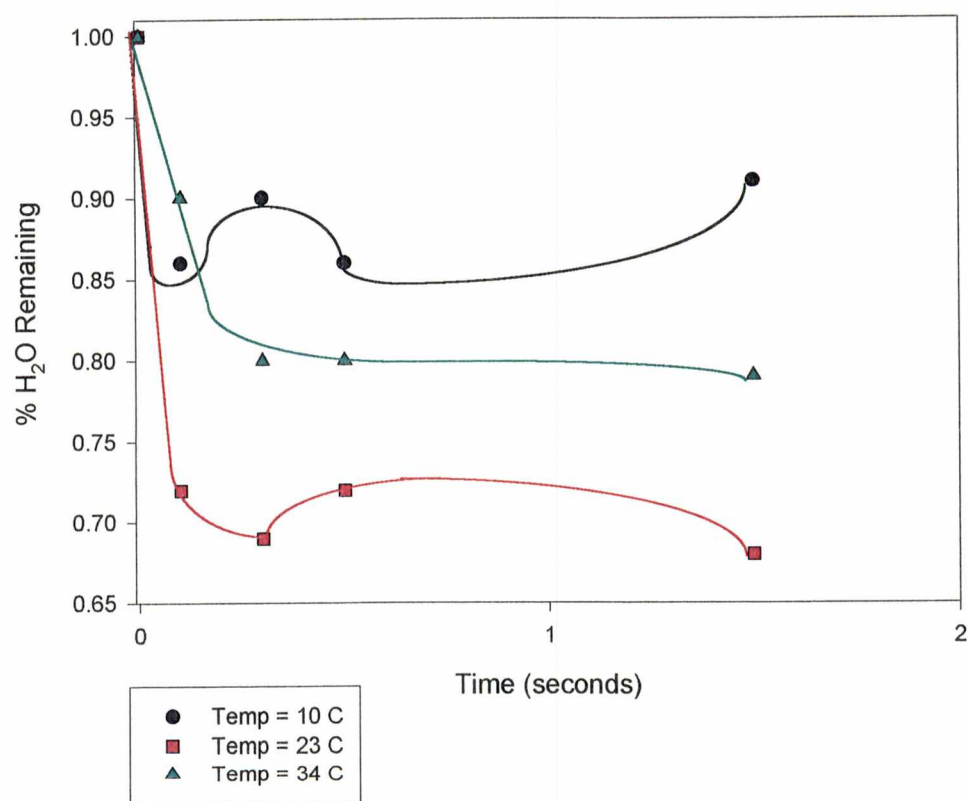


Figure 3-10: Percent of H₂O remaining for C Series

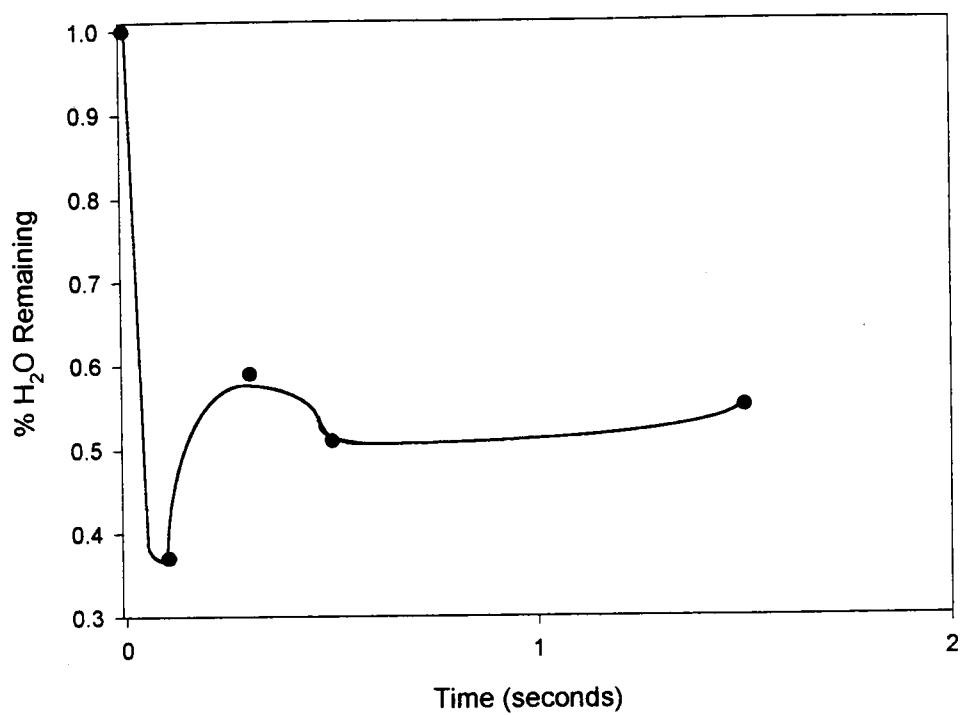


Figure 3-11: Percent H₂O remaining for D Series at 23 C

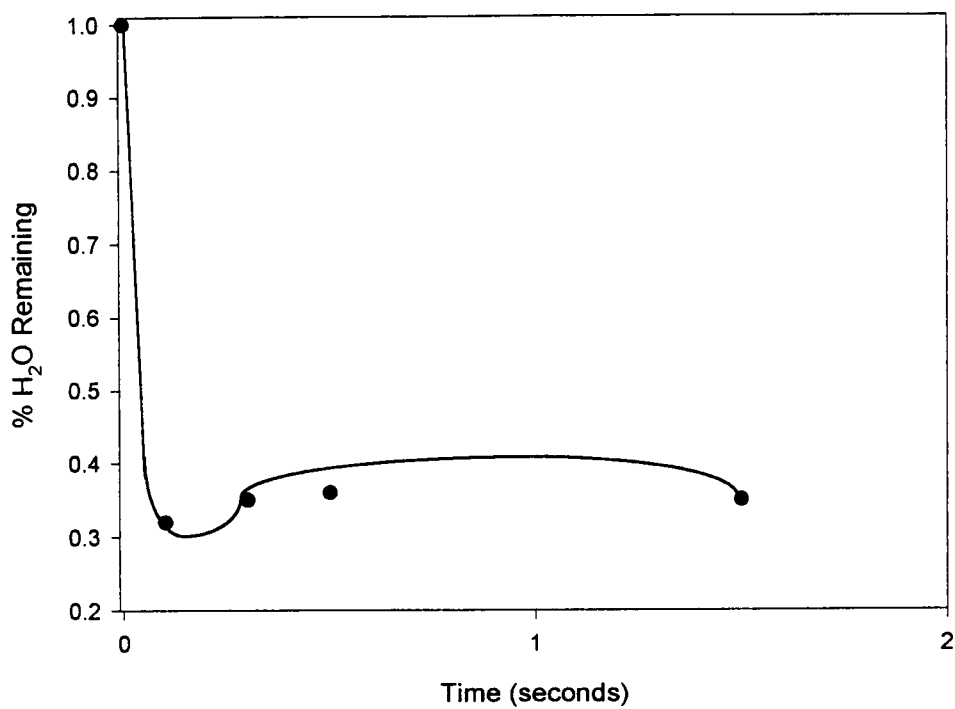


Figure 3-12: Percent of H₂O remaining for E Series at 23 C

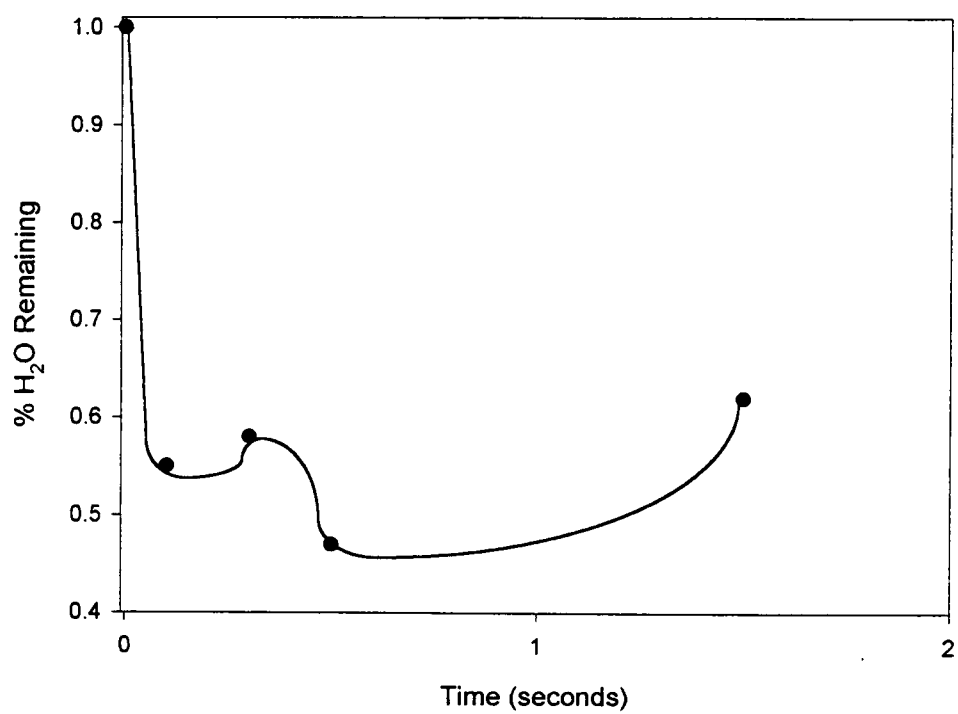


Figure 3-13: Percent of H₂O remaining for F Series at 23 C

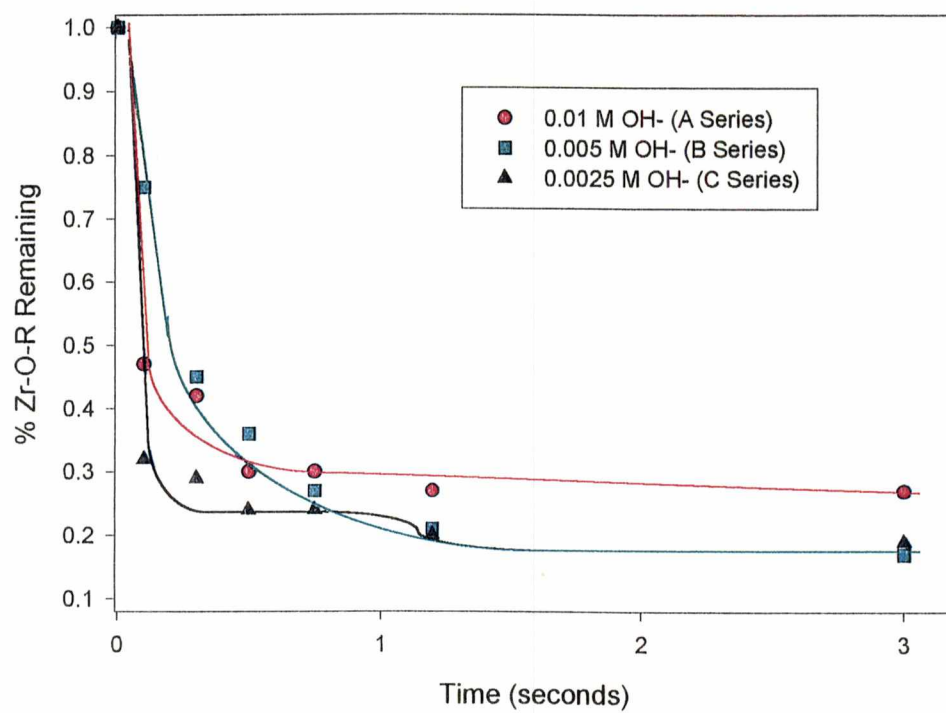


Figure 3-14: Effect of Base upon the hydrolysis of Zr-O-R at 10 C

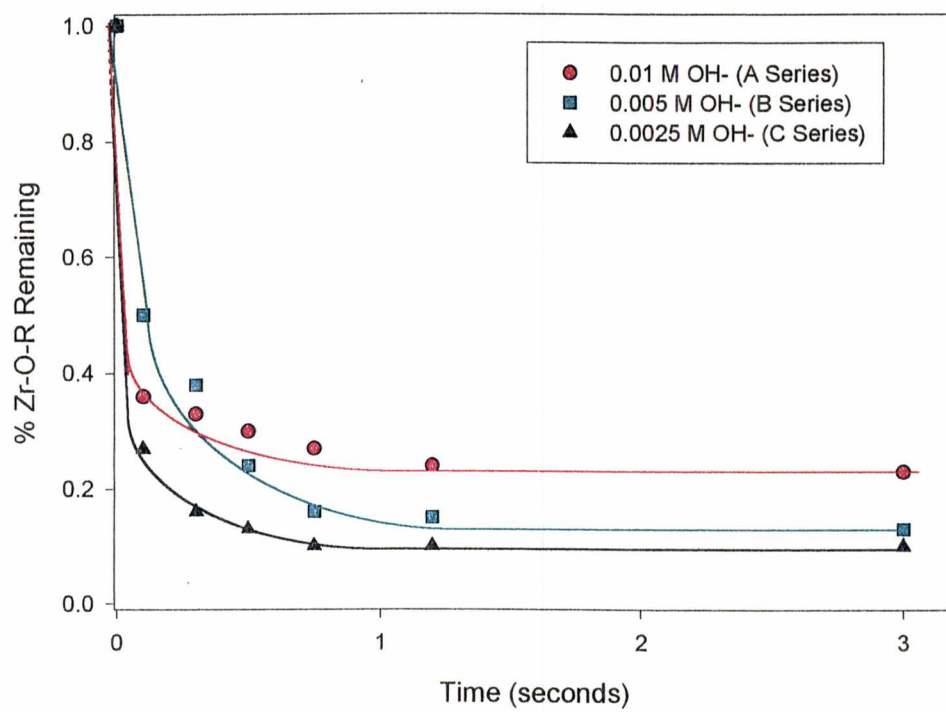


Figure 3-15: Effect of Base upon the hydrolysis of Zr-O-R at 23 C

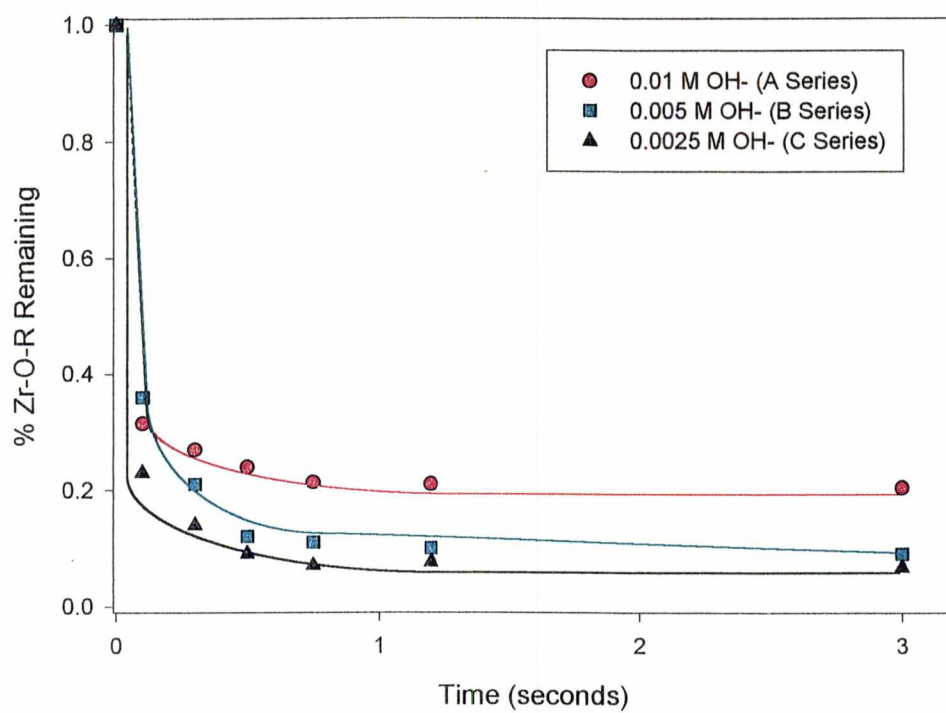


Figure 3-16: Effect of Base upon the hydrolysis of Zr-O-R for at 34 C

Changing the temperature was important in these experiments to qualitatively and quantitatively observe the kinetic phenomena. Figures 3-2 through 3-4 along with Table 3-1 demonstrate how temperature affects the rate and extent of the hydrolysis reactions. From qualitative observation of the data in these figures, as well as from regression analysis (where r^2 was typically around 0.5 to 0.6) it is easily seen that the overall kinetics do not follow a first order exponential decay since the first data point at 100 msec is so sharp with respect to the remaining data points. Figure 3-17 through 3-19 are examples of the difficulty involved in fitting an overall hydrolysis model for the first 3 seconds of reaction. These least squares mathematical fits for the overall hydrolysis scheme were performed using an inverse exponential model. Although this model fits very well mathematically, it is futile to glean much quantitative information from it. For example, at time zero the model goes to infinity; therefore, it was necessary to try $t_{\text{initial}} = 0.000001$ seconds in order for the program to run. Also, the units on the predicted hydrolysis rate constants, K_H , are extremely difficult to resolve. Consequently, it would be nearly impossible to use this in a real-world design such as in the sizing of a reactor needed to yield a certain conversion of reactants. These models are mentioned in this chapter only to illustrate the complexity these reactions. Table 3-2 captures the reaction rate trends that were computed from these models.

In order to quantify the reaction kinetics it, was necessary to change the reaction temperatures. The activation energy was experimentally determined by carrying out the reactions at varying temperatures, namely 10°C, 23°C and 34°C. The equation used to calculate the E_A values was

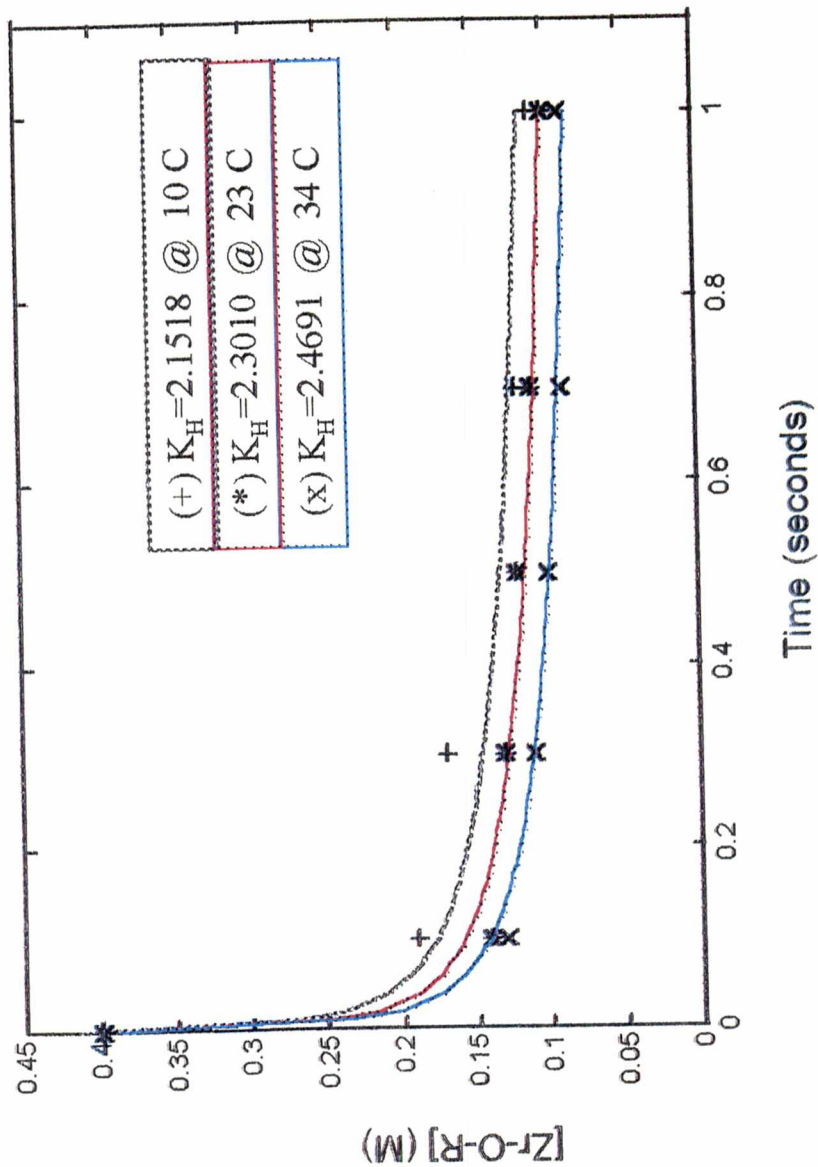


Figure 3-17: 2 Parameter Model Fit for Concentration Data of the Hydrolysis of 0.4 M Zr-O-R, 1.1 M H₂O and 0.01 M OH⁻ at $r_{ZrOR}=1/(K_H t^n)$, where $n \sim 0.2$

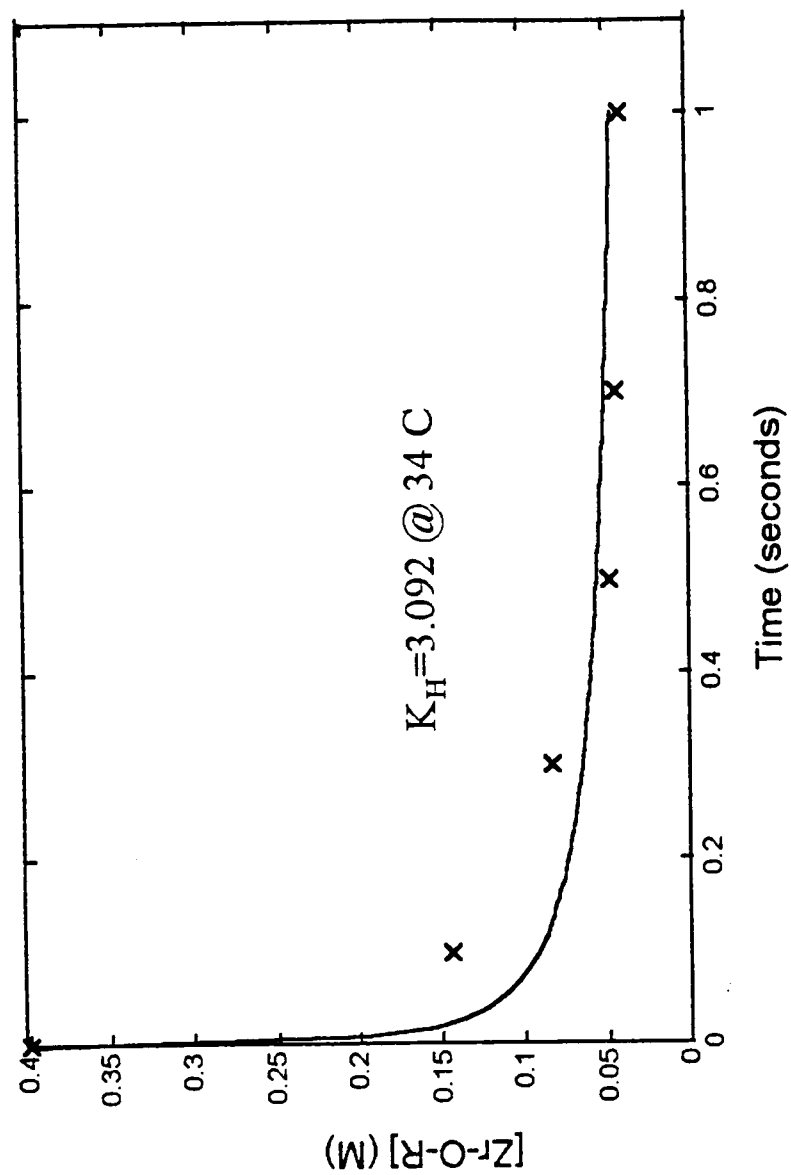


Figure 3-18: 2 Parameter Model Fit for Concentration Data of The Hydrolysis of 0.4 M Zr-O-R, 1.1 M H_2O and 0.005 M OH^- using $-r_{\text{ZrOR}} = 1/(K_H t^{0.335})$

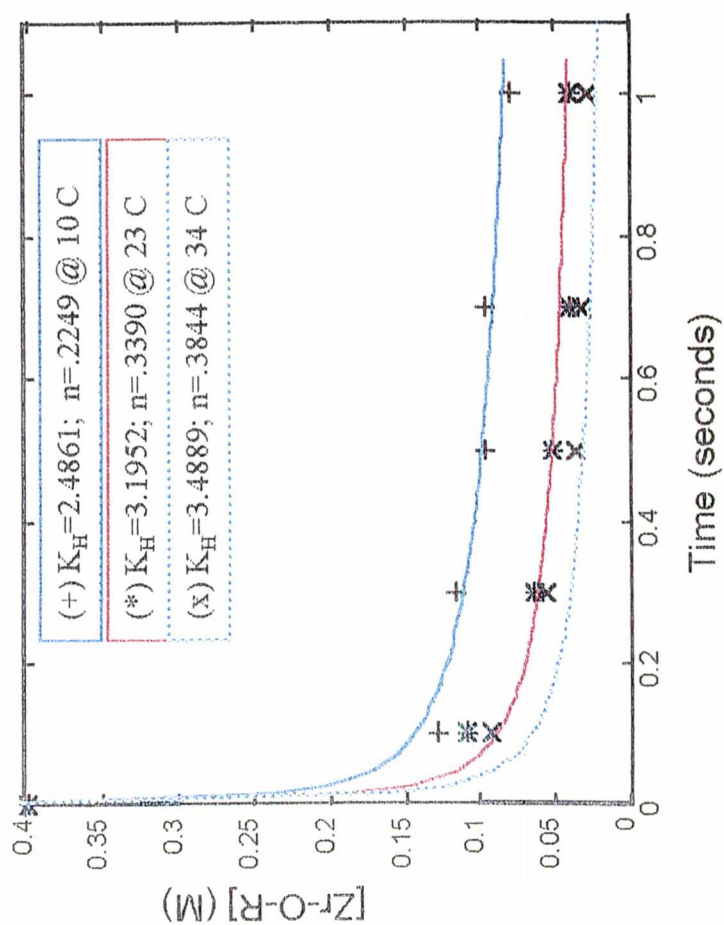


Figure 3-19: 2 Parameter Model Fit for Concentration Data of the Hydrolysis of 0.4 M Zr-O-R, 1.1 M H_2O and 0.0025 M OH^- using $-r_{\text{ZrOR}} = 1/(K_H t^n)$, where n is order of time

Table 3-1: The effect of temperature upon $[\text{Zr-O-R}]$ where $[\text{Zr-O-R}]_0 = 0.4 \text{ M}$

Data Set	Temp (C)	$[\text{Zr-O-R}] \text{ (M)}$ at 100 msecs	$[\text{Zr-O-R}] \text{ (M)}$ at 300 msecs	$[\text{Zr-O-R}] \text{ (M)}$ at 1 sec	$[\text{Zr-O-R}] \text{ (M)}$ at 3 secs
A	10	0.188	0.168	0.12	0.108
	23	0.144	0.132	0.1	0.092
	34	0.126	0.108	0.084	0.082
B	10	0.3	0.18	0.092	0.068
	23	0.2	0.152	0.06	0.052
	34	0.144	0.084	0.044	0.036
C	10	0.128	0.116	0.088	0.076
	23	0.108	0.064	0.04	0.04
	34	0.092	0.056	0.028	0.023

Table 3-2: Rate expressions using inverse exponential decay model

Data Set	Temp (C)	K _H (arbitrary)	Order (n)
A	10	2.158	0.200
	23	2.301	0.200
	34	2.469	0.200
B	10	2.132	0.202
	23	2.545	0.260
	34	3.092	0.335
C	10	2.486	0.225
	23	3.195	0.339
	34	3.489	0.384

$$\ln K_H = \ln A - \frac{E}{R} \left(\frac{1}{T} \right) \quad (3.1)$$

where K_H is the hydrolysis rate constant computed from a first order fit on the first two data points, A is a constant, R is the universal gas constant (8.314 J/mol·K), and T is the absolute temperature in Kelvin units. If one plots $(\ln K_H)$ versus $(1/T)$ the result is a straight line whose slope is proportional to the activation energy (Fogler, 1992).

We have already seen from the above figures that these reactions are too complex to fit with a first order decay for the entire hydrolysis region. However, a reasonable approximation can be made using a first order decay for the first data points, since this is where the majority of the hydrolysis is completed (see Table 3-1). This approximation can be supported from the literature wherein Barringer proposed that 75% of the hydrolysis is completed within 1 second and the remaining occurs at much longer times. The “transition region” from 0 to 100 msec is where the majority of the hydrolysis occurs. The overall chemistry can be observed as a scheme where there are several hydrolysis and, as we shall shortly see, condensation steps. Consequently, it is necessary to apply a first order model to the first two data points, since this is where the hydrolysis proceeds to the point that approximately 3 of the 4 -OR groups are replaced. First order linear regression plots were used to determine these initial slopes so that K_H could be estimated. These plots are found in figures 3-20 through 3-22. The hydrolysis reaction rate was modeled as

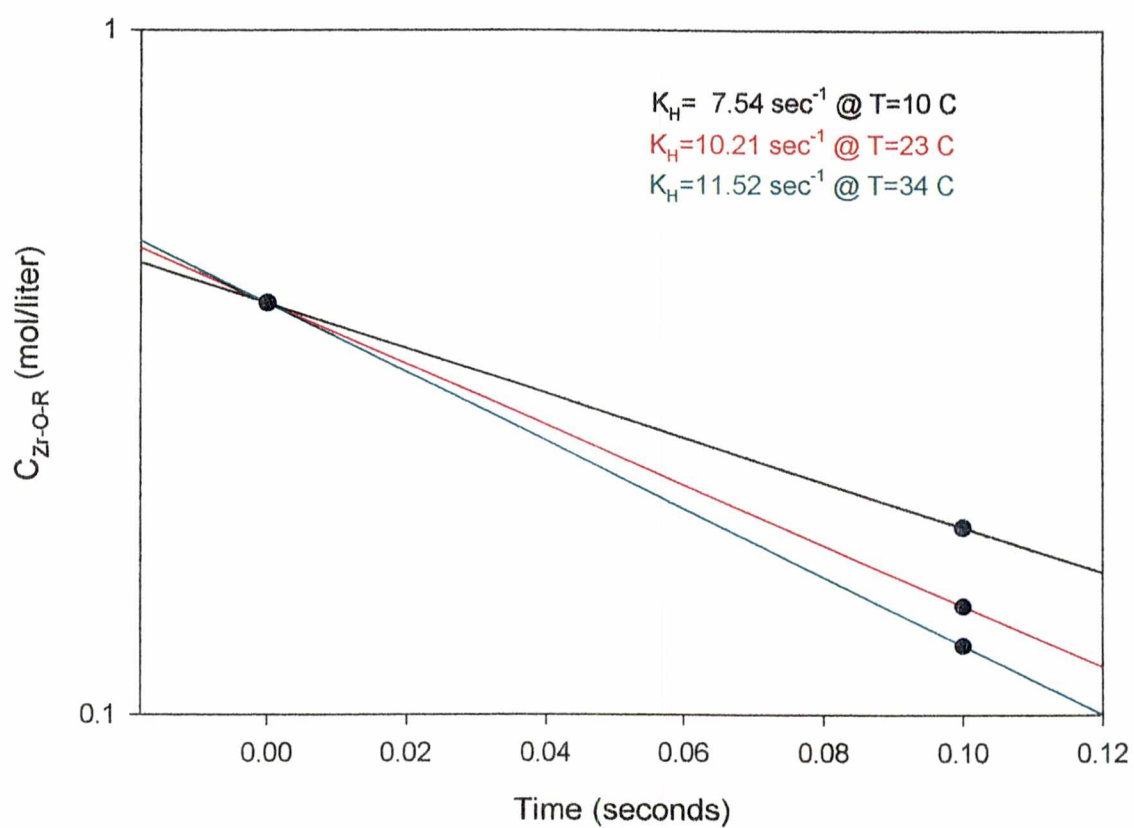


Figure 3-20: First order initial slope analysis of hydrolysis data for A Series

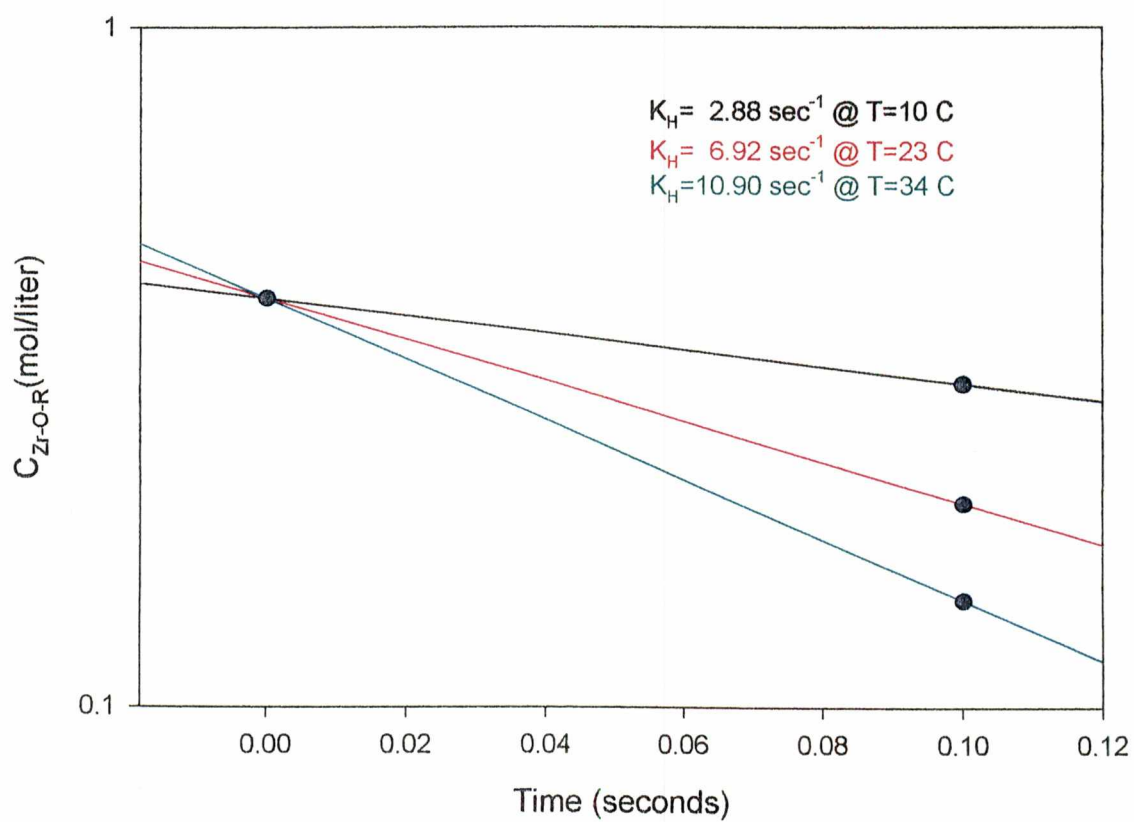


Figure 3-21: First order initial slope analysis of hydrolysis data for B Series

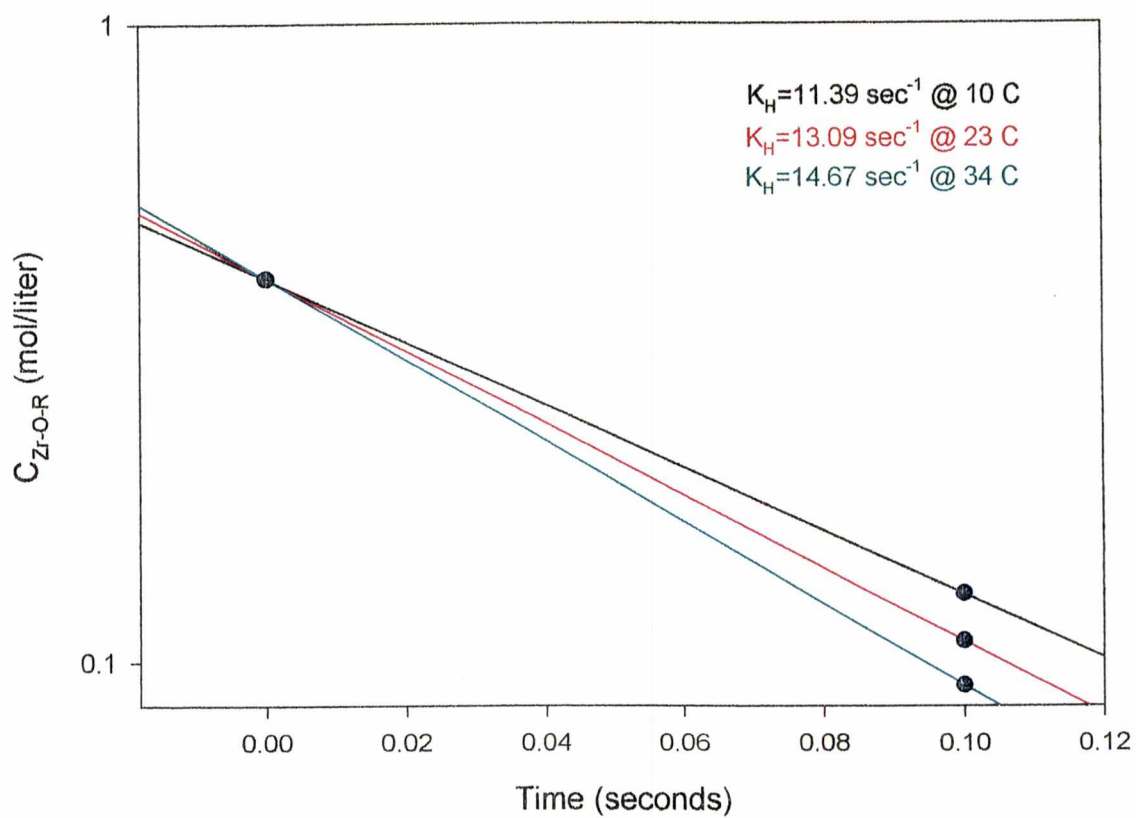


Figure 3-22: First order initial slope analysis of hydrolysis data for C series

$$-r_{ZrOR} \approx K_H [Zr-O-R] \quad (3.2)$$

where units for the rate are given in $\text{mol} \cdot \text{sec}^{-1}$. The analysis method used for the calculation of the initial rates was a graphical technique wherein C_{ZrOR} (mol/l) was plotted on the ordinate of a log scale vs time (seconds) on the abscissa (Fogler, 1992). From the slope of these plots, the first order hydrolysis rate constants, K_H , were calculated according to the following:

$$\ln \frac{C_{ZrOR}}{C_{ZrOR_0}} = -K_H t \quad (3.3)$$

which, upon rearranging and converting to a common log scale, gives,

$$\log\left(\frac{C_{ZrOR}}{C_{ZrOR_0}}\right) = -K_H t/2.3 \quad (3.4)$$

or,

$$K_H = -2.3(\text{slope}) \quad (3.5)$$

where,

$$\text{slope} = \frac{1}{t} \log\left(\frac{C_{ZrOR}}{C_{ZrOR_0}}\right) \quad (3.6).$$

For all calculations, $[\text{ZrOR}]_0$ was 0.4 M.

From Figures 3-23 through 3-25 we can see how the activation energies were computed using equation (3.1). Table 3-3 summarizes both the values of K_H and E_A that were calculated from the experimental FTIR data for the 0 to 100 millisecond time regime.

As predicted from classical chemical reaction kinetics, the trend in these figures is that an increase in temperature drives the hydrolysis rate faster. That is, hydrolysis occurs within this region with a rate law that is first order in substrate. As proposed from Barringer, around 3 of 4 -OR groups are replaced immediately, whereas the remaining are hydroxolated at some later time (Barringer, 1985). Depending upon the amount of initial reactants the hydrolysis may or may not go to completion.

It was initially anticipated that with decreasing base concentration, both Zr-O-R and H_2O conversion would increase. It was also expected that this trend would also follow for increase in temperature. However, when one looks at both Table 3-1 and Figure 3-3, it is seen that the trend for hydrolysis conversion does not necessarily follow the order of decreasing $[\text{OH}^-]$. The expected trends for temperature change hold within the data sets (in other words the data agrees with classical chemical kinetics in terms of temperature), as does the degree of hydrolysis with decreasing inhibitor concentration; however, these trends do not apply outside the data sets. For the data set B, we see that the activation energy barrier is actually greater than it is for data set A, which has more inhibitor present. Furthermore, the calculated K_H values are less than they are for those calculated in the data set A at the same temperature values. From these results, it

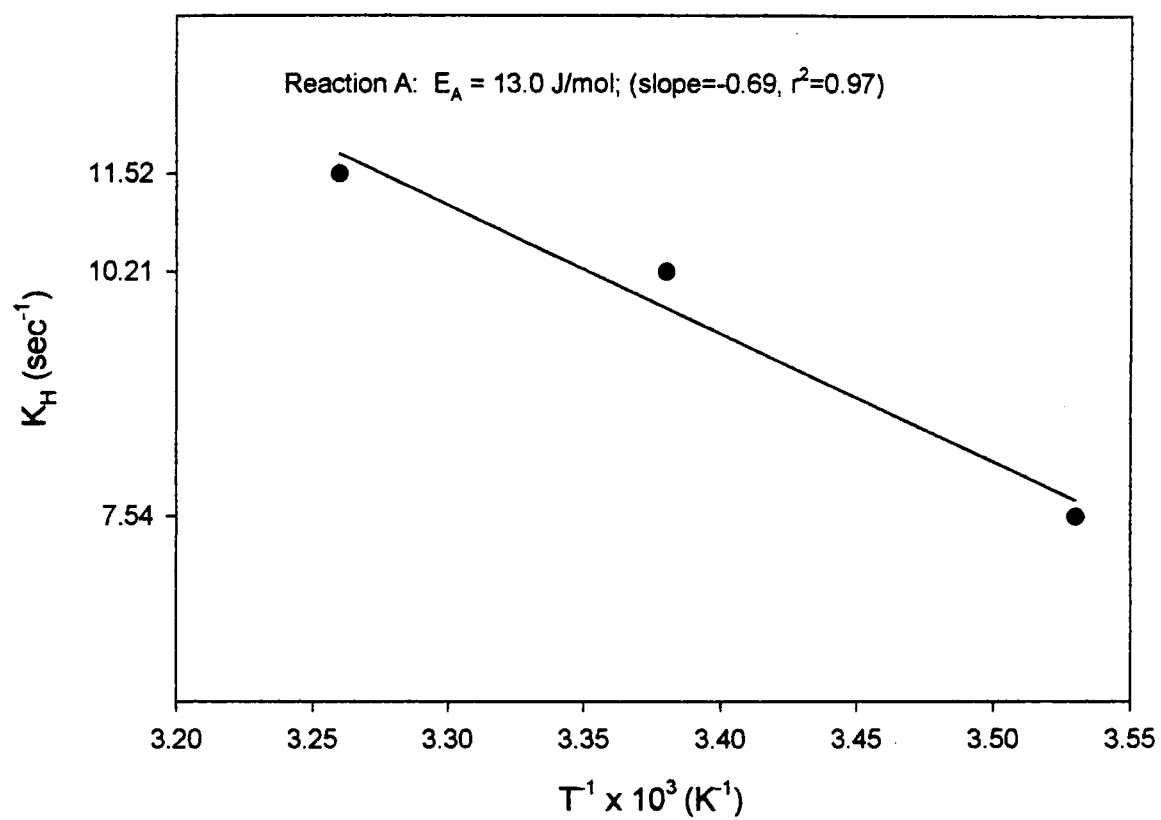


Figure 3-23: Calculation of E_A for A series

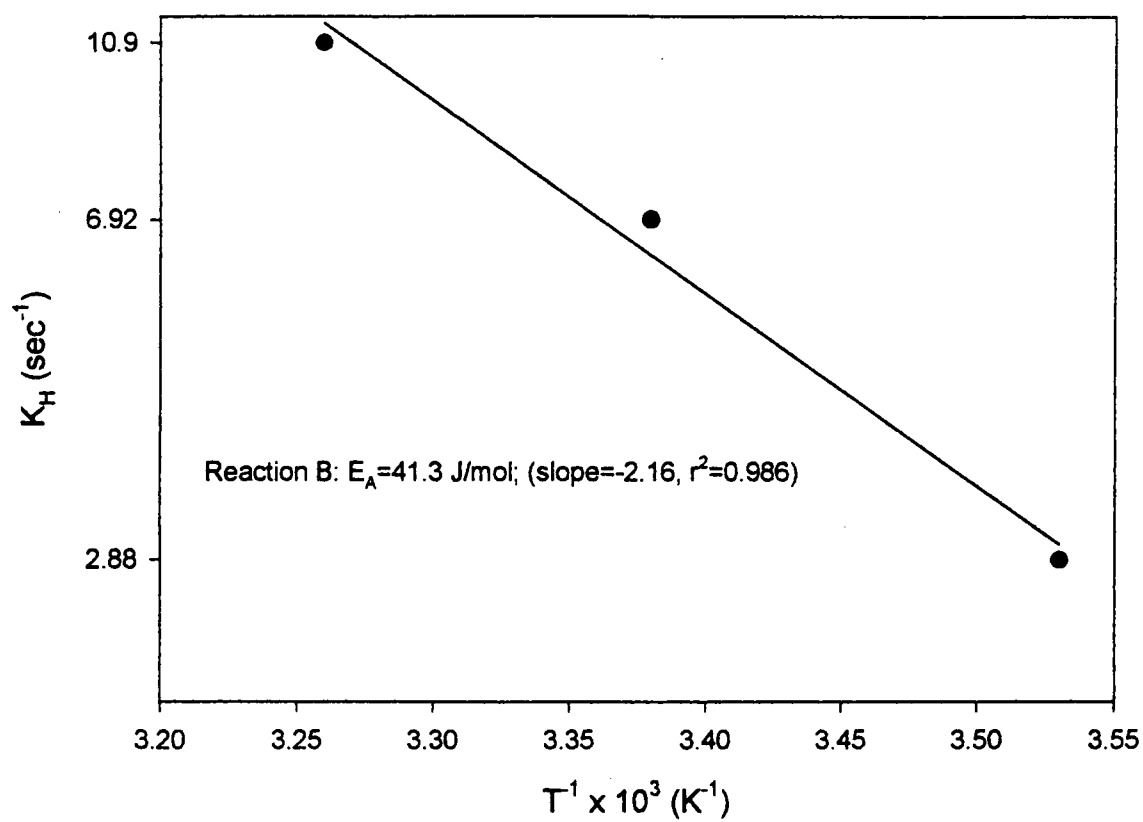


Figure 3-24: Calculation of E_A for B Series

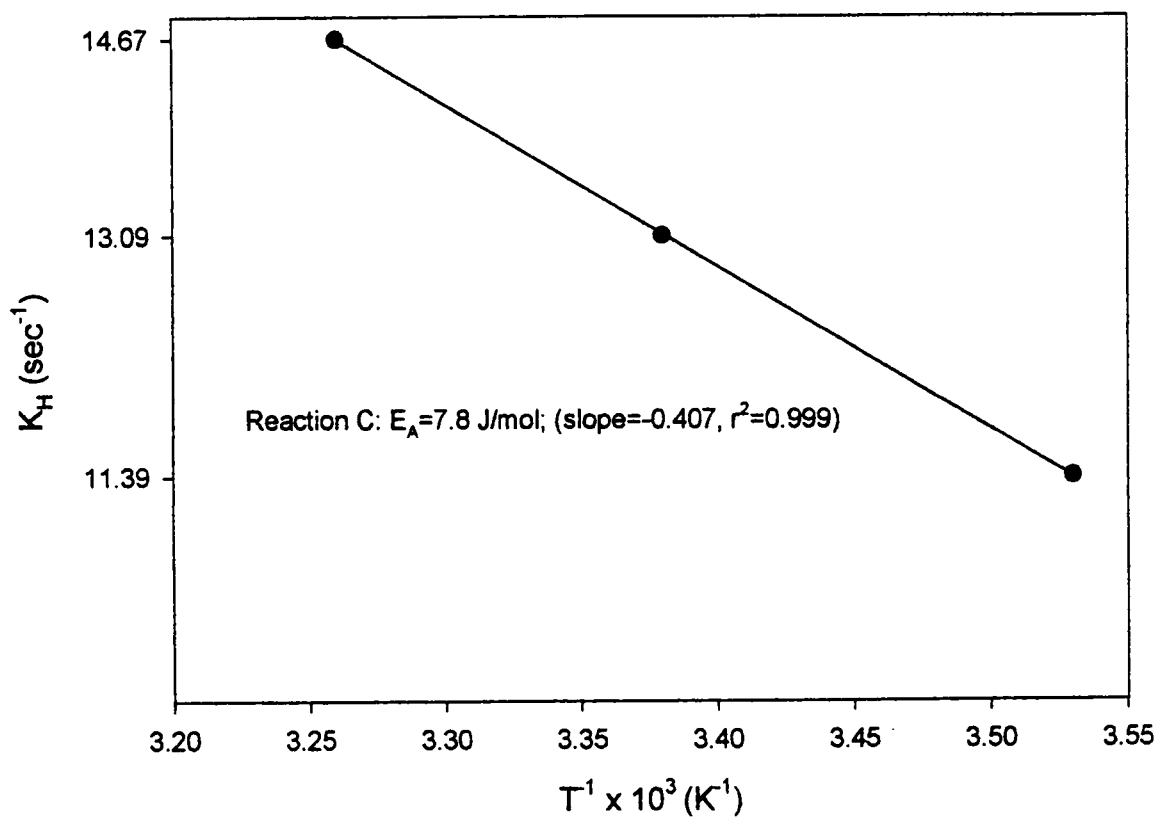


Figure 3-25: Calculation of E_A for C Series

Table 3-3: Summary of experimentally determined hydrolysis rate constants, K_H , and activation energies, E_A , using a first order graphical technique

Data Set	Temp (C)	K_H (sec ⁻¹)	E_A (J/mol)
A	10	7.54	13.00
	23	10.21	
	34	11.52	
B	10	2.88	41.30
	23	6.92	
	34	10.9	
C	10	11.39	7.78
	23	13.09	
	34	14.67	
D	23	0.41	N/A
E	23	1.38	N/A
F	23	2.48	N/A

appears that OH^- competes with H_2O for the d^0 orbitals of the Zr-O-R ligands. Unlike a “true” catalyst such as H^+ , OH^- increases the nucleophilicity of the reaction media, thus making the mechanisms unpredictable in terms of the detailed chemistry involved. To further understand this phenomenon it is essential to observe the water conversion data in Figures 3-8 through 3-13. In these figures we see an initial burst of water loss due to hydrolysis. After this burst several things happen to the $[\text{H}_2\text{O}]$: a) the water loss continues b) there is an increase in water concentration, or c) the water level hits a steady-state value. Although it is not possible to decouple hydrolysis and condensation, it is possible to give predictions for which condensation mechanism describes the data. As already discussed in detail in the INTRODUCTION, condensation proceeds via alcoxolation or oxolation, wherein an alcoxolation mechanism implies that alcohol is produced and an oxolation mechanism results in the production of water. If water fluctuation did not occur in this study, it would not necessarily imply a mechanism wherein hydrolysis is completed before condensation begins. Instead it could be concluded that condensation occurs by alcoxolation alone since water is not produced during this phase. From these figures it is extremely difficult to speak of the detailed chemistry since an apparent trend associated with base concentration does not exist. We do see, however, the appropriate experimental trend for the two extreme cases, A and C. Table 3-4 gives a clearer summary of these results.

From the FTIR experiments we can know the hydrolysis rates, the condensation mechanisms and the resulting products, even though there is a very complex decoupling of $[\text{OH}^-]$, $[\text{H}_2\text{O}]$ and $[\text{Zr}]$ that is not yet fully understood. Combined with the

Table 3-4: Summary of hydrolysis and condensation of zirconium alkoxides:
Reaction data after 0.5 seconds: $[\text{Zr-O-R}]_0 = 0.4 \text{ M}$ and $[\text{H}_2\text{O}]_0 = 1.1 \text{ M}$ for
all samples recorded

$[\text{OH}^-]$ (M)	T (C)	$[\text{H}_2\text{O}]/[\text{H}_2\text{O}]_0$	$[\text{Zr-OR}]/[\text{Zr-OR}]_0$	Apparent Condensation Mechanism
0.01	10	0.5	0.3	Oxolation and Alcoxolation: $[\text{H}_2\text{O}]$ rises steadily but not drastically
	23	0.76	0.3	Oxolation (drastic rise in $[\text{H}_2\text{O}]$ after 100 msecs)
	34	0.46	0.24	Oxolation and Alcoxolation ($[\text{H}_2\text{O}]$ changes steadily)
0.005	10	0.74	0.36	Oxolation
	23	0.91	0.24	Oxolation : (very drastic change in $[\text{H}_2\text{O}]$)
	34	0.76	0.12	Oxolation
0.0025	10	0.86	0.24	Oxolation
	23	0.72	0.13	Alcoxolation ($[\text{H}_2\text{O}]$ does not change after 100 msecs)
	34	0.8	0.09	Alcoxolation

exceptionally fast hydrolysis, the intrinsic competition between water and base for d^0 orbitals as well as the simultaneous condensation mechanisms that occur, these systems are very difficult to quantify. It is apparent that the rate law depends upon $[\text{Zr-O-R}]$, $[\text{H}_2\text{O}]$ and $[\text{OH}^-]$ so that is very difficult to predict an overall quantitative rate expression for these reactions. It appears that both water and base are competing for open sites. Partial charge theory combined with experimental results that give more information into the charge and composition of the reaction media at any given time must be employed to give a more thorough analysis of the chemistry and physics of these reactions.

3.2.2 SAXS Results

Small-angle X-ray scattering experiments were also performed in this study to investigate the condensation mechanisms that occurred. The theoretical background information as well as the motive for performing these experiments have been discussed in Chapters 1 and 2 of this thesis. The primary parameters that were studied during these experiments were growth kinetics and early-stage structural transitions. That is, Guinier analysis was performed to determine both the size and rate of change of the radius of gyration, and Porod analysis was used to determine the fractal dimensions and the relative structural evolutions during the condensation pathways.

Figure 3-26 shows the growth kinetics curve of data taken in the Guinier regime at different times along the reaction coordinate for 0.4 M Zr-O-R , 1.1 M H_2O at varying $[\text{OH}^-]$. From observation of the R_g data, it is obvious that particles are growing during the same time that hydrolysis is occurring. That is, in the first seconds of reaction, wherein most of the hydrolysis has occurred according to our previous discussions, we

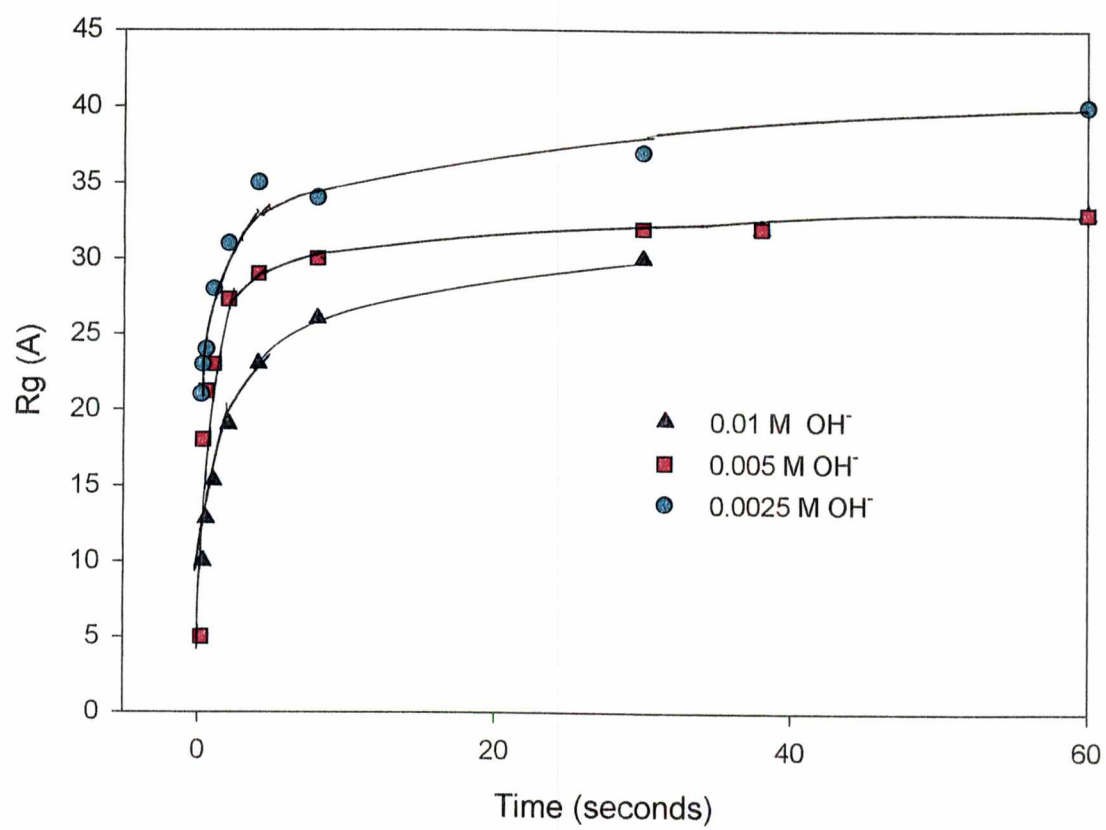


Figure 3-26: Growth Kinetics for 0.4 M Zr-O-R, 1.1 M H_2O at Varying $[OH^-]$

see very rapid particle growth. As hydrolysis data demonstrate a very steep initial slope, condensation growth kinetics also reveal a very steep initial slope wherein primary particles are being formed. Unlike hydrolysis, wherein it is difficult to elucidate the effect that base has upon conversion of Zr-O-R ligands to Zr-OH ligands, the base dependence in the condensation growth curves is more tractable. We see from Figure 3-26 that a decrease in $[\text{OH}^-]$ gives both a faster growth rate, dr_g/dt , and a larger primary particle size. Final product sizes for the primary cluster were measured to be $\sim 32\text{-}40 \text{ \AA}$. (See Figure 3-26). This result further demonstrates that hydrolysis and condensation are not isolated events as proposed by Barringer. These values do not increase from these sizes even up to the point of gelation, although gelation clearly illustrates a polymeric network that is visible to the naked eye. For example, the system that gelled in 10 minutes (A series) had the same R_g value at 9 minutes as it did at 60 seconds. This phenomenon was also true for both B and C series experiments. Gelation was considered to have occurred once a viscous material was visible.

From the analysis of the Porod regions, fractal dimensions were determined. See Figure 3-27 for the early stage structural transition data obtained from Porod analyses. Final values for the D_f are 1.8, 1.9 and 2.1 for $[\text{OH}^-]=0.01 \text{ M}$, 0.005 M and 0.0025 M , respectively. In this case it is apparent that the absolute value of the Porod slope increases with decreasing $[\text{OH}^-]$. Since it is commonly known in the literature that base catalyzed alkoxide gels tend to form more highly branched gels than their acid catalyzed counterparts, this trend is anticipated. That is, the increase in D_f for this series implies that branching is occurring so that the net result goes from a swollen branched polymer,

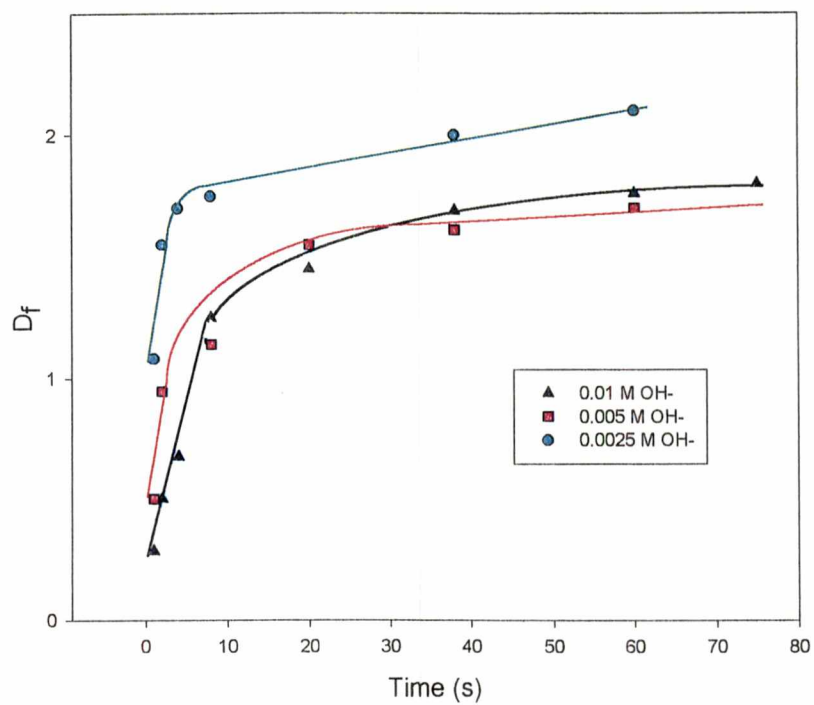


Figure 3-27: Early Stage Structural Transition for 0.4 M Zr-O-R, 1.1 M H₂O at Varying [OH⁻]

$D_f \sim 2$, to a randomly branched polymer, $D_f \sim 2.2$.

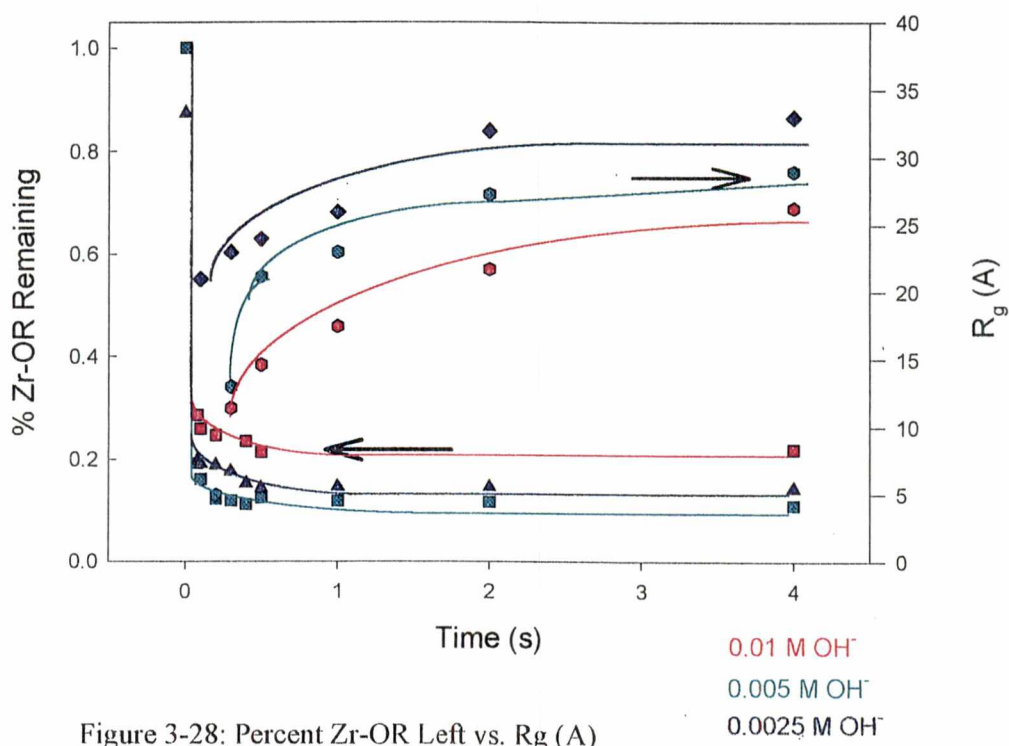
It is possible to utilize these results to predict an aggregation mechanism. For values of $D_f \sim 2.5$, the growth occurs by a diffusion-limited aggregation scheme (Brinker, 1992). Therefore, we can see from the data that these primary particles grow by reaction-limited cluster aggregation (RLA). In RLA, chemistry plays more of a role in aggregation than in a case that is mass-transfer controlled. The fact that the R_g does not increase even up to gelation, although the system is visibly getting larger, adds evidence to the fact that the initial growth occurs by a condensation mechanism that it is governed by RLA phenomena. That is, the gels are constructed with monomeric units or clusters that are of the same size dimensions as the final R_g sizes. Because these eventually form gels that are visible to the naked eye, it is obviously absurd to conclude that the gel network is of these dimensions. Therefore, it is reasonable to conclude that the initial burst of R_g is due to the hydrolysis and condensation reactions. Subsequent growth then occurs by diffusion-limited aggregation processes (DLA) wherein these monomeric or oligomeric clusters collide and stick together to form the resultant gels. DLVO theory, discussed in Chapter 1, and intermolecular forces ultimately determine the outcome of these diffusion processes (Zukoski, 1992).

This is, again, verified by the experimentally determined values of D_f for the primary particles. Literature values of $D_f < 2.1$ indicate that the growth mechanism for primary particles occurs by reaction rather than by diffusion (Brinker, 1990). Then too, it can be seen from the Zr-OR percent conversion plots that a) elimination of -OR groups is not a complete reaction during the initial stages of hydrolysis, and b) that $[H_2O]$ appears

to grow or fluctuate during this same period of time. These results suggest that chemical reactions are occurring while primary particles are being formed. From the plots, we also see that a residual amount of -OR groups is always present. In time, however, the relative concentration of these residual groups eventually decreases with respect to the hydroxylated moieties. It is assumed that these residual amounts are related to the steric hindrance of the particles as they grow. As the alkoxy groups are more completely hydrolyzed, there will be less steric hindrance on the individual polymeric species. A less sterically hindered species has less resistance to traverse and thus grow by diffusion-controlled aggregation (DLA). Therefore, it is apparent from the FTIR and SAXS data that there is a combination of RLA and DLA processes en route to the production of these zirconia oxide gels. Figure 3-28 summarizes these previous discussions as it contains both reaction and growth data obtained from FTIR and SAXS analysis.

3.3 Summary

In this chapter I have presented and discussed the data that was observed from my studies into the hydrolysis and condensation mechanisms of zirconium alkoxides. Using FTIR and SAXS techniques, I have successfully investigated these reactions on a time scale as low as 100 milliseconds. From these experimental results a database was accumulated that provides an array of information about these mechanisms. Among the parameters that were varied for the experiments were temperature, base and water concentrations. Reaction and aggregation growth kinetics were then studied from these



results. The quality of data that exists from these experiments provides both an impetus for further analyses with the rapid-mixing technique as well as a foundation for more thorough kinetic models to be written for these mechanisms.

4. SUMMARY AND RECOMMENDATIONS

The rapid mixing technique was successfully used in this study to investigate the hydrolysis and condensation of zirconium butoxides. There exists an array of promising results from these preliminary experiments. With the aid of the rapid-mixing technique, we were able to collect hydrolysis and condensation rate data as early as 100 msec into the reactions. The instrumental analyses that were combined with this method were FTIR and SAXS.

Our research group at Oak Ridge National Laboratory has investigated both the acid and base catalyzed reactions of zirconium alkoxides. Some experimental data for these reactions catalyzed by acids are now in press for publication (Singhal, 1997). Although our group has collaborated in this effort to elucidate early stage reaction phenomena for both the acid and base cases, the focus of this thesis has been the base catalyzed reactions. It can be noted, therefore, that our research group at Oak Ridge National Laboratory along with our collaborators who share joint authorship in these studies, Michael T. Harris, from the University of Maryland at College Park and Amit Singhal, of Oak Ridge National Laboratory, are the first researchers in the world to experimentally investigate the earliest stage kinetics of zirconium butoxides catalyzed by either base or acid.

In this particular study, experiments were performed to investigate the hydrolysis and condensation of zirconium (IV) butoxides catalyzed by quaternary tetramethyl ammonium hydroxide in ethanol. The results are to be published in the *Journal of*

Materials Chemistry or *Journal of Materials Research*. Chapter 3 of this thesis, entitled ANALYSIS, contains the results that were found in this investigation as well as the discussion of the data. In this chapter, I would like to highlight a few of the major results and demonstrate that the rapid-mixing technique is indeed the method of choice for elucidating early stage kinetic phenomena.

As already discussed in detail, the hydrolysis and condensation of zirconium alkoxides are extremely difficult to resolve. However, we were able to collect quality data that demonstrated thorough agreement with literature predictions as well as reproducibility.

Combining both FTIR data and SAXS data, it was determined that hydrolysis and condensation are overlapping reactions. Nevertheless, the majority of the hydrolysis is completed within 1 second. During this same time, condensation is also occurring. The condensation mechanisms were determined to consist of both alcoxolation and oxolation. That is, during the reaction, the water concentration initially decreased due to hydrolysis and then either fluctuated or reached a steady state value. From this data, it was concluded that the former case involved condensation via an oxolation mechanism, and that the latter case suggested an alcoxolation mechanism.

As predicted from classical chemical engineering reaction kinetics, the increase of temperature drove the hydrolysis reactions faster. By changing the temperature it was possible to compute both a rate law and the activation energies for these reactions. Since the percent change in [Zr-O-R] ligand was much greater in the first 100 milliseconds than for the rest of the reaction, hydrolysis was modeled as a first order

reaction in substrate. Although the reaction did proceed faster for an increase in temperature, the hydrolysis did not proceed faster for greater $[H_2O]/[OH^-]$ although gelation time increased significantly. From this, it was concluded that OH^- plays a major role in competing with water for the empty d^0 orbitals of the Zr-O-R ligands, since the lowest and highest ratios did exhibit this behavior but the middle ratio did not. In this sense, OH^- does not behave as a "true" catalyst. Further experiments must be performed that detail the charge analysis during the reaction in order to fully grasp the detailed chemistry and how the $[OH^-]$ affects the hydrolysis conversion.

There was a more definable trend that occurred with the kinetic growth data as the reaction proceeded through a condensation mechanism. From SAXS analysis it was discovered that with decreasing base concentrations, the primary particles both grew faster and were larger in size. Also, it was determined that with less base the fractal dimensions increased. This increase in D_f for the series implies that branching is occurring, and that these particles are less dense than their acid-catalyzed counterparts. It was concluded that the polymeric clusters are formed from a reaction-limited aggregation (RLA) mechanism as opposed to a diffusion-limited aggregation scheme (DLA). However, once these primary particles are formed, condensation does proceed by diffusion.

The lack of data in the transition area from 0 to 100 msec is one the difficulties of the current setup. Limitations on the minimum volume that is mechanically possible prevent the acquisition of data in this region. This has posed a problem in fitting model parameters to the consumption data, since most of the hydrolysis of the Zr-O-R groups

occurs within 1 second, and the largest change actually occurs in this experimentally flawed "transition region." Since volume is a fixed entity, the reaction times could be improved with a faster pump.

In addition to the volume limitations, there is also a materials limitation with the current set-up. The current setup could be further improved with a more durable flow-through scheme. The glass capillary reactors were so sensitive to flow that bursting was a frequent phenomenon. This problem increased the already present difficulties associated with using rapid-mixing for SAXS experiments. For future experiments, it is suggested that a flow-cell be commercially customized for this method. This would eliminate the bursting as well as provide a more homogeneous material wherein local density gradients are minimized. Also, the cell would be more durable to ultrasonification for cleaning purposes.

Finally, there may be a way to improve the quality of data in the low scattering regimes, wherein particles are just beginning to form. The beryllium windows that were used in the sample insert should be changed to a higher purity quality. Although this is not a concern with 1 meter geometry since the background is not sensitive to larger impurities in the material, this does pose a problem at 5 meter geometry. For example, a higher quality beryllium window gives an empty-beam scattering intensity of $I_s \sim 50$ Hz, whereas the beryllium used for the flow-through setup had an empty-beam scattering of $I_s \sim 150$ Hz. This would allow our group to investigate more thoroughly both structural and growth information when particles are initially forming.

The above mentioned suggestions would most likely enhance this flow-through

technique by making it more tractable and accurate particularly in the earliest stages were most of the detailed chemistry occurs. These, however, were not serious limitations to the method, only ways of improving the quality of an already excellent technique.

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VITA

Jason Tylor Zielke was born in Monmouth, Illinois on March 28, 1972. He was raised in Southern Illinois where he attended elementary and secondary schools. In 1990 he graduated from Herrin High School in Herrin, Illinois. In August of 1990 he entered Southern Illinois University at Carbondale, and graduated in August 1994 with a B.S. in Chemistry and a minor in mathematics. Immediately after finishing undergraduate studies at SIU-C, he began graduate school at the University of Tennessee-Knoxville to earn a Master's degree in Chemical Engineering. From August 1994 to May 1995 he served as a graduate teaching assistant. From June 1995 to July 1997 he served as a graduate research assistant at the Oak Ridge National Laboratory in Oak Ridge, Tennessee. The Master's degree was received in August, 1997.