This is to certify that the

thesis entitled

TIME-RESOLVED RAMAN STPECTROSCOPIC STUDIES
OF TITANIUM ALKOXIDE HYDROLYSIS
USING UV EXCITATION

presented by

Mark J. Payne

has been accepted towards fulfillment
of the requirements for

M. S. degree in Chemical Engineering

Major professor

Date August 18, 1986

Time-Resolved Raman Spectroscopic Studies of Titanium Alkoxide Hydrolysis Using UV Excitation

By

Mark J. Payne

A Thesis

Submitted to
Michigan State University
in partial fulfilment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemical Engineering

1986

ABSTRACT

Time-Resolved Raman Spectroscopic Studies of Titanium Alkoxide Hydrolysis Using UV Excitation

By

Mark J. Payne

In order to evaluate the efficacy of using Raman spectroscopy to study the hydrolysis of titanium alkoxides, a preliminary study was done wherein Raman spectra were recorded for various titanium alkoxides (ethoxide, isopropoxide, isobutoxide) as a function of concentration and laser excitation wavelength. It was found that fluorescence which appeared in the Raman spectra when visible excitation was used (514.5 nm) did not appear when uv excitation (363.8 nm) was used. Also, the titanium alkoxides exhibited a preresonance enhancement as the excitation wavelength approached the uv.

Hydrolysis kinetics measurements were carried out using a time-resolved Raman spectroscopy system with uv excitation. The initial rate of hydrolysis was measured as a function of alkoxide concentration, water to alkoxide ratio, and alkoxy ligand group length. Hydrolysis rates were found to increase with increasing alkoxide concentration and water to alkoxide ratio and with

decreasing group length. Curvefitting of the resulting spectrum indicates the presence of a band at 1011 cm^{-1} whose intensity increases during the hydrolysis reaction, suggesting the existence of a polymeric species postulated in earlier publications.

This work is dedicated to the memory of my father and my brother Jim. I miss them both very much.

ACKNOWLEDGEMENTS

I would like to thank Sandia National Laboratories for the support for this project through contract #21-2885 and Professor Kris A. Berglund for his guidance and advice. I would also like to thank the members of the Shared Laser Facility, and in particular, Professor G. E. Leroi, Professor G. T. Babcock and their graduate students for their help.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

This work is presented as two papers. The first, "Raman Spectroscopic Studies of Titanium Alkoxides Using UV Excitation" was peer reviewed and will appear in the published proceedings of the Materials Research Society 1986 Spring Meeting. The second, "Time-Resolved Raman Spectroscopic Studies of Titanium Alkoxide Hydrolysis" will be submitted for publication to the Journal of the Americal Ceramics Society and appears in their standard form. The first paper outlines the advantages of using uv excitation for studying the Raman spectra of titanium alkoxides. The second work outlines the results of kinetics measurements of the hydrolysis reaction of three titanium alkoxides: ethoxide, isopropoxide, and isobutoxide.

These papers constitute a preliminary study on the use of time-resolved Raman spectroscopy in the study of metal alkoxide hydrolysis and raise questions which may be answered in subsequent studies. A summary of results, recommendations for future work, and an appendix containing a more complete presentation of the data obtained than could be presented in the papers appear after the second paper.

RAMAN SPECTROSCOPIC STUDIES OF TITANIUM ALKOXIDES USING UV EXCITATION

Mark J. Payne and Kris A. Berglund, Departments of Agricultural and Chemical Engineering, Michigan State University, East Lansing, MI 48824.

ABSTRACT

The use of Raman spectroscopy can be greatly hindered by the presence of fluorescing impurities. Even at low concentrations, fluorescence can completely obscure the Raman signal. In the current study, Raman spectra were recorded for various titanium alkoxides (ethoxide, isopropoxide, isobutoxide) as a function of concentration and laser excitation wavelength. It has been shown that fluorescence can be avoided by using uv-excitation (363.8 nm). In addition, titanium alkoxides exhibit a preresonance Raman enhancement as the excitation wavelength appreaches the UV. This result is confirmed by a uv-visible absorption spectrum of the isopropoxide.

INTRODUCTION

Interest in metal alkoxides has increased in areas such as sol-gel processing[1] and more specifically, hydrolytic synthesis of ceramic powders.[2] Very little information has been published concerning Raman spectra of these compounds.

The Raman effect is a very weak photophysical event. It can be overwhelmed by fluorescence of the molecule being studied or of impurities, even at very low concentrations. When fluorescence obscures Raman spectra, two steps occur. The first step involves absorption of radiation as the molecule is promoted to an electronically excited state. The second step involves the release of radiation of slightly lower energy, since some energy is lost due to thermal degradation. When Raman spectra are taken, one scans for radiation of slightly lower energy than the incident radiation. Thus, fluorescence and Raman effects can coincide, and fluorescence, being the stronger effect, will dominate.

Although the Raman effect occurs at any excitation wavelength, there can be advantages in using one excitation wavelength over another. A correct choice of the laser line would take into account the following considerations. first, light scattering is related to wavelength. The intensity of the scattered light is inversely proportional to wavelength raised to the fourth power. Thus, by using excitation of a lower wavelength, Raman scattering of the same intensity can be obtained at a much lower laser power. Secondly, if the excitation wavelength corresponds to an absorbance band for the molecule being studied, resonance enhancement will occur, and the intensity of certain peaks in the Raman spectrum will be greatly increased. Finally, fuorescence may be avoided by a correct choice of excitation wavelength. When the excitation wavelength is changed, the fluorescing molecule is no longer supplied with the energy needed for the electronic transition, and the wavelengths being scanned for the Raman spectrum will move from

those in which the fluorescing molecule releases radiation.

In the current work, the effect of changing concentration and excitation wavelength were examined. This is a preliminary study in a research program to evaluate the efficacy of using time-resolved Raman spectroscopy to study of the kinetics of hydrolysis reactions of three titanium alkoxides (ethoxide, isopropoxide, and isobutoxide).

MATERIALS AND METHODS

Titanium tetraisopropoxide (TiPT) was obtained from both DuPont and Aldrich Chemical Company, Inc. Titanium tetraisobutoxide (TiBT) and tetraethoxide (TET) were obtained from Morton/Thiokol, Inc. Reagent grade isopropanol (iPrOH) was used for the isopropoxide and isobutoxide solutions. Completely dry ethanol was obtained by adding titanium isopropoxide to 200 proof ethanol and stirring overnight. After distillation, ethoxide could be added to the ethanol with no precipitation occuring.

The Raman system used in the current study was a SPEX 1877 Triplemate with an EG&G Princeton Applied Research OMA II detection system equipped with a Coherent Innova 90-5 Ar^+ laser. Typical laser powers were 100-150 mW at 363.8 nm and 200 mW at 488 nm and 514.5 nm. A Perkin-Elmer Lambda 3A UV/Vis Spectrophotometer was used for the absorbance spectrum.

RESULTS

Figures 1 and 2 show the Raman spectrum of 25% TiPT (from Aldrich) in isopropanol using 488 nm and 363.8 nm excitation. The sloping baseline in Figure 1 indicates the presence of fluorescence. The spectrum using 514.5 nm excitation was totally obscured by fluorescence, and no Raman peaks were visible. As can be seen in Figure 2, the fluorescence has been avoided by using 363.8nm excitation. Thus, quality Raman spectra were not

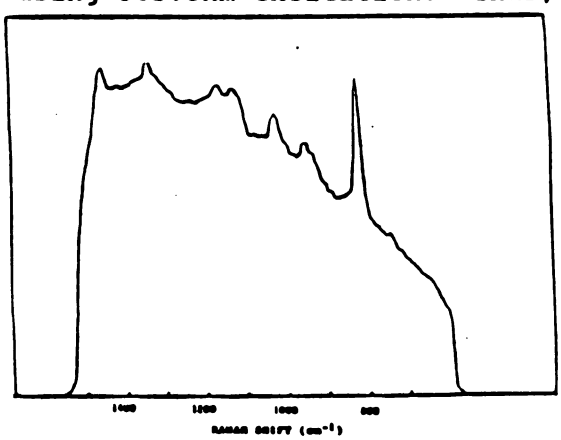


Figure 1. Raman spectrum of 25% TiPT in iPrOH, using 363.8 nm excitation.

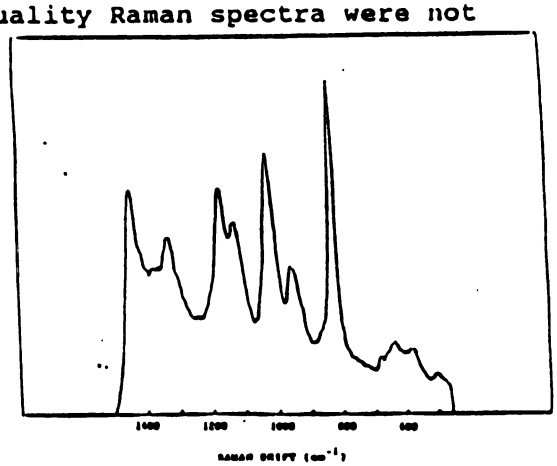


Figure 2. Raman spectrum of 25% TiPT in iPrOH using 488 nm excitation.

attainable using visible excitation due to fluorescence, while changing the excitation wavelength to the uv resulted in good spectra.

The fluoresence observed is not inherent to the alkoxides. As the samples aged, the fluorescence became more pronounced. It is unclear what causes the fluorescence. Possibilities include an absorbed impurity and polymerization of the alkoxides. It was noticed that the alkoxides develop a yellow color as they age, which can be removed via vacuum distillation.[2] However, this failed to reduce the fluorescence in the Raman spectra when visible excitation was used.

Another advantage in using uv excitation for the alkoxides is that a preresonance condition is obtained. Figures 3 and 4 show an increase in intensity of the 1025 cm^{-1} and 1180 cm^{-1} peaks when 363.8 nm excitation is used. Both figures show a range of concentrations of TiPT (from DuPont) in isopropanol.

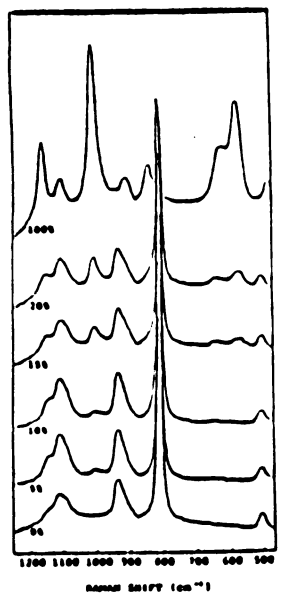


Figure 3. Raman spectra of varying concentrations of TiPT in iPrOH using 514.5 nm excitation.

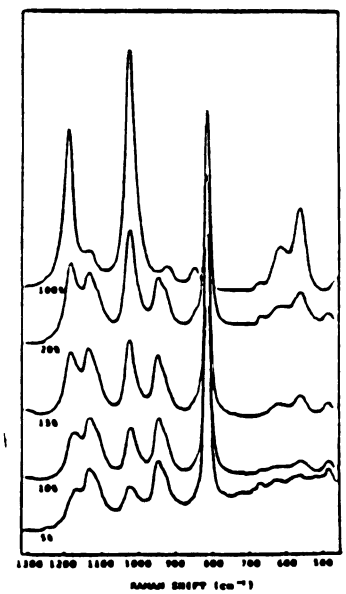


Figure 4. Raman spectra of varying concentrations of TiPT in iPrOH using 363.8 nm excitation.

These spectra were taken before the alkoxides had a chance to age and develop the fluorescence seen in Figure 1. The absence of flouresence in the newer samples at 514.5 nm excitation is striking.

The uv absorbtion spectrum of TiPT was taken to verify the

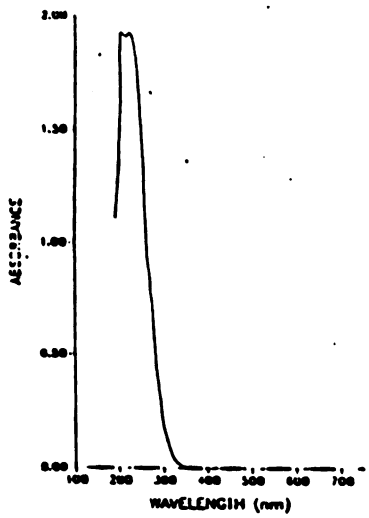


Figure 5. Absorption spectrum of .275 mM TiPT in iPrOH in a 1 cm path length cell with an iPrOH reference.

preresonance condition. As expected, Figure 5 shows a strong absorption in the uv. An isopropanol reference was used against 2.75×10^{-4} molar TiPT (from Aldrich) in isopropanol, using a 1 cm path length cell. The molar absorbtivity was calculated to be about 7000 M^{-1} $cm.^{-1}$ It would be expected that if TiPT solutions were excited with laser lines further into the uv that the intensity of the 1025 cm^{-1} and 1180 cm^{-1} peaks would increase further.

Using uv excitation for TiBT in isopropanol has similar advantages. 363.8 nm excitation results in a reduction in fluorescence and preresonance of the 1023 cm^{-1} and 1176 cm^{-1} peaks, as can be seen in Figures 6 and 7.

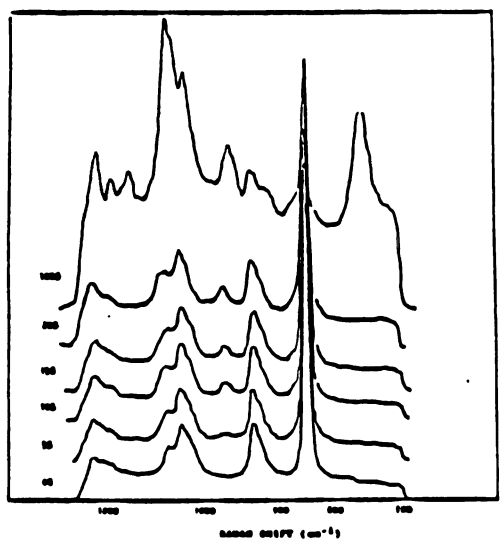


Figure 6. Raman spectra of varying concentrations of TiBT in iPrOH using 514.5 nm excitation.

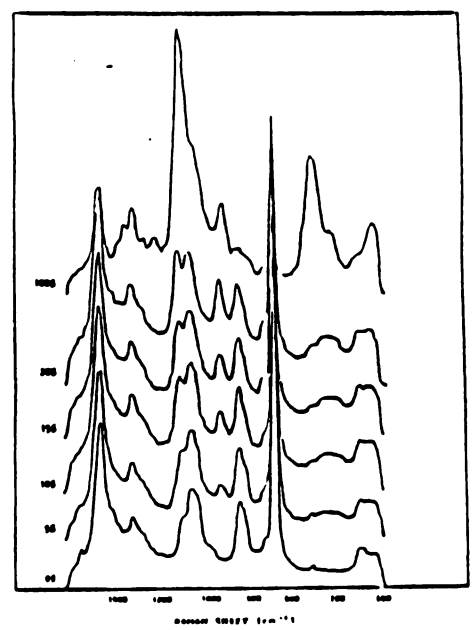


Figure 7. Raman spectra of varying concentrations of TiBT in iPrOH using 363.8 nm excitation.

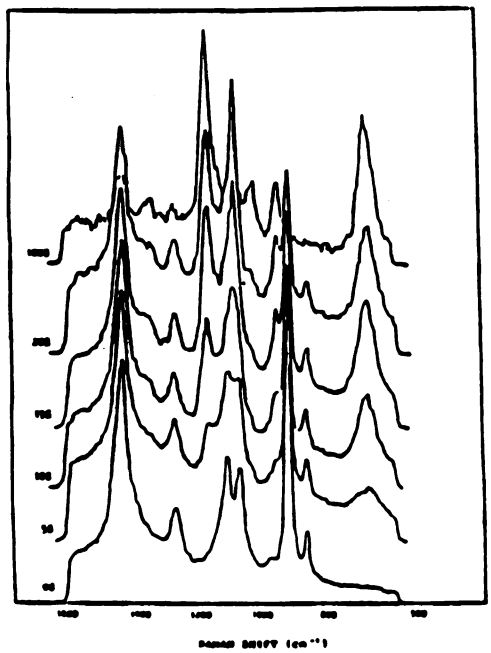


Figure 8. Raman spectra of varying concentrations of TET in ethanol using 363.8 nm excitation.

Figure 8 is a concentration study of TET in ethanol at 363.8 nm excitation. The TET spectrum at 514.5 nm excitation was completely obscured.

CONCLUSION

Using uv excitation in the study of titanium alkoxides has been found to have advantages. First, lower laser power was necessary due to the reciprocal dependance of Raman scattering on wavelength. Second, fluorescence which appears in the spectra of older samples when visible excitation is used does not appear in the uv-excited spectra. Third, the preresonance condition intensifies some of the peaks in the spectra. These effects combine to make the uv a good choice of excitation wavelength for studying titanium alkoxides.

ACKNOWLEDGEMENT

This work was supported by Sandia National Laboratories through contract #21-2885.

REFERENCES

1. D.W. Johnson, Jr., Am. Cer. Soc. Bull. 64(12) 1597-1602 (1985)
2. K.A. Berglund, D.R. Tallant, R.G. Dosch, Second International Conference on Ultrastructure Processing of Ceramics, Glasses, and Composites. Palm Coast, Fla. February 25 to March 1, 1985.

Time-Resolved Raman Spectroscopic Studies of Titanium Alkoxide Hydrolysis

Mark J. Payne[+] and Kris A. Berglund

Departments of Agricultural and Chemical Engineering, Michigan State University, East Lansing, Michigan 48824.

Time-resolved Raman spectroscopy was used to study the initial rate of hydrolysis of titanium alkoxides. Parameters studied include alkoxide concentration, water to alkoxide ratio, and alkoxy ligand group length. Initial hydrolysis rates were found to increase with increasing alkoxide concentrations, increasing water to alkoxide ratio, and decreasing group length. The presence of a band in the Raman spectrum at 1011 cm^{-1} which increases during the early stages of the hydrolysis reaction may indicate existence of a polymeric species postulated in earlier publications.

I. INTRODUCTION

The use of sol-gel processing in the synthesis of ceramic powders is currently of great interest. The reproducibility of particle size distributions, high product purity, and high density after sintering of precipitation products contribute to the potential

[+]Now with AGA Gas, 3300 Lakeside Avenue, Cleveland OH 44114

widespread use of the sol-gel technique.[1-4] In order to scale-up the production of ceramic powders, information must be obtained on the kinetics of the hydrolysis reaction. This study uses titanium alkoxides as a model system, illustrating a method for studying the kinetics of metal alkoxide hydrolysis. The simplest expression for the reaction to produce hydrous oxides (using titanium as an example) is as follows:[5]

$$Ti(OR)_4 + 4\ H_2O \text{ ----> } Ti(OH)_4 + 4\ ROH$$

Subsequently, ceramic powders are produced by calcination and sintering, which is described by the following reaction:

$$Ti(OH)_4 \text{ ----> } TiO_2 + 2\ H_2O$$

A particularly powerful application of the sol-gel technique is production of mixed oxides such as $BaTiO_3$ by simultanious hydrolysis of $Ti(OR)_4$ and $Ba(OR')_2$. In this case, the relative rates of hydrolysis of the titanium and barium alkoxides may have a large impact on the homogeneity of the powder formed. Knowledge of the hydrolysis rates for the individual metal alkoxides will allow the study of the effect of relative reaction rates on product homogeneity.

Titanium alkoxide hydrolysis has been studied previously by Bradley, et. al.[6] who found that some titanium alkoxides (such as ethoxide and isopropoxide) tend to polymerize, resulting in octrahedrally 6-coordinated titanium. It is assumed that these structures are not

stable compounds and that they are short-lived.

It is also suggested that titanium alkoxides can achieve octrahedral 6-coordination through solvation of two alcohol molecules around the titanium atom. Ebulliometric studies[6] suggest this structure for titanium isobutoxide.

Bradley, et. al.[6] found that titanium tetraethoxide (TET) forms a stable trimer in ethanol solutions, although at lower concentrations, lower complexity (dimers) and a higher degree of solvation was reported. Russo and Nelson[7] confirmed that TET exists in a trimer form. Polymers can also result from partial hydrolysis of the alkoxides. Bradley et. al.[6] found evidence of Ti-O-Ti grouping in solutions of water and alkoxide in alcohol.

A possible partial hydrolysis product of TET or titanium tetraisopropoxide (TiPT) is $Ti_3O_4(OR)_4$. These trimers are thought to polymerize, forming chain of "infinite" length.

Hartel and Berglund[8] studied the rate of particle formation and growth during the hydrolysis of TiPT. Photon correlation spectroscopy was used to monitor the mean size of the precipitate and the number of particles present. At alkoxide concentrations of 1.5 % and lower, where the alkoxides tend to have a lower complexity and a higher degree of solvation, there seems to be a lower limit below which precipitation does not occcur. They also reported that precipitation seemed to occur more slowly for TiPT

after vacuum distillation. If it is assumed that the newly distilled product has a higher proportion of the volatile monomeric form ($Ti(OR)_4$), one might assume that the polymerization aids the hydrolysis reaction. Polymerization may not be a direct result of partial hydrolysis. The reduction in steric hindrance due to removal of one or more ligands may allow polymerization to occur.

It has also been observed that the ease of hydrolysis depends on alkoxy group length, with shorter groups hydrolyzing more easily than longer[9]. This effect has been correlated with the water-repellent nature of the alcohol corresponding to the alkoxide: alkoxides whose corresponding alcohols are more water repellent will less readily hydrolyze.

The possibility of the reverse reaction has been postulated for titanium secbutoxide:

$$TiOH + ROH \leftrightarrows TiOR + H_2O$$

This reaction would become more favored as the ratio Ti:OR reaches unity[6]. In general, this reaction is not considered important to powder formation.

The speed of the hydrolysis reaction is very fast. Ingebrethsen and Matijevic[10] found that a substantial amount of TET aerosol droplets in water vaper hydrolyzed within 50 msec. The liquid phase reaction, the object of the current study, would be expected to proceed more

slowly.

The current study differs from previous work in that Raman spectroscopy is used to probe the hydrolysis reaction mixture on a molecular scale, analyzing the number and nature of chemical bonds present in the sample. Raman spectroscopy has been shown to be a useful method for studying this system in earlier publications.[11,12] Berglund, et. al.[12] monitored the height of a Raman band due to titanium tetraisopropoxide as a function of time in a time-resolved experiment. This study will expand on this work, measuring the intensity of the same band as a function of alkoxide and water concentrations, and as a function of alkoxy ligand group length.

Raman spectroscopy is a vibrational spectroscopy, which measures the change in energy of a photon as it inelastically collides with a molecule. The Raman effect occurs for incident light of any wavelength, although visible and uv excitation are generally used. As the incident light approaches an electronic absorbance band for the molecule, the bands in the Raman spectrum associated with the bond contributing the exited electron will be greatly enhanced and can overwhelm non-resonating bands in the spectrum. In an earlier study,[11] the authors found that titanium tetraisopropoxide (TiPT) absorbs strongly in the ultraviolet, causing causing a preresonance effect as the excitation wavelength approaches the uv.

Lasers provide an intense, monochromatic light source which is needed for taking Raman spectra, and the fine spatial resolution allows for fine time resolution in the laboratory. The Raman effect is a very fast photophysical event, taking 10^{-10} to 10^{-14} seconds to occur, enabling the study of transient species. Information on the extent of a reaction can be obtained by monitoring the intensity of a band in the Raman spectrum that corresponds to either a reactant or a product. The possible existence of reaction intermediates can be ascertained by the appearence of new bands in the spectra.

The vibrational spectra of titanium alkoxides have been documented. Zeitler and Brown[13] gave the following assignments for infrared absorption: asymmetric stretch of CH_3 at 2907 cm^{-1}, symmetric stretch of CH_3 at 2817 cm^{-1}, asymmetric deformation of C-H at 1470^{-1}, resonance split of C-H at 1391 and 1344^{-1}, symmetric deformation of C-H at 1377^{-1}, $(CH_3)_2CH$ skeletal at 1170^{-1}, C-O stretch and v_3 skeletal at 1131^{-1}, and v_4 skeletal at 851 cm^{-1}. Bradley, et. al.[14] attributed the band at 1005 cm^{-1} to the C-O strech. Assignments for bands in Raman spectra can be inferred from assignments for bands in infrared spectra. Infrared assignments of Bradley, et. al. suggest the following Raman band assignments[14]: large, concerted vibrations are probably responsible for the Raman bands at 159 and 329 $cm,^{-1}$ bands at 564 and 612 cm^{-1} are due to the

Ti-O symmetric stretch, and the (C-O)Ti stretch band appears at 1025 cm.$^{-1}$

Figure 1 is a concentration study of titanium tetraisopropoxide (TiPT) in isopropanol (iPrOH) using 363 nm excitation. The peaks at 820, 956 and 1132 cm^{-1} are due to the isopropanol[15]. In the spaces between these peaks the baseline remains flat, leaving "windows" for viewing Raman peaks of other species in solution. The symmetric Ti-O stretch can be seen at 564 and 612 cm^{-1}, and the (C-O)Ti stretch can be seen between the 956 and 1132 cm^{-1} bands of the iPrOH bands. The position of this peak was measured to be 1032 cm.$^{-1}$

The band at 1032 cm^{-1} has been attributed to the carbon-oxygen stretch when the oxygen is bonded to the titanium atom.[14] It can be seen in Figure 1 that the intensity of this band increases with increasing alkoxide concentration. As the hydrolysis reaction progresses, the bond between the oxygen and the titanium atom is broken, and the carbon-oxygen stretch band no longer appears at this position. Thus, as the isopropoxy ligands are broken off the titanium atom, the peak at 1032 cm^{-1} will decrease in intensity. The intensity of this peak measured during the hydrolysis reaction can be related to the number of ligands still bonded to titanium atoms.

II. METHODS AND MATERIALS

Titanium tetraisopropoxide (TiPT), titanium tetraisobutoxide (TiBT), and titanium tetraethoxide (TET) were obtained from Aldrich Chemical Company, Inc. Reagent grade iPrOH was used for all alkoxide and water solutions. Isobutanol was not used in the isobutoxide system due to the low solubility of water in isobutanol. Isopropanol was used for the ethoxide system for continuity.

It has been found that alkoxide solutions in alcohol can undergo alcohol interchange[9]. Alkoxide solutions were prepared just prior to running the experiments in order to avoid interchange. All spectra were taken within 15 minutes of mixing the solutions. In the absence of kinetic data on this reaction it is not certain whether some exchange had occurred before running the experiments.

The Raman spectrometer system used was a SPEX 1877 Triplemate with an EG&G Princeton Applied Research OMA II detection system. A Coherent Innova 90-5 Ar^+ laser supplied sample illumination with typical laser power in the range of 100-150 mW. The 363.8 nm line was used, as the authors have determined uv excitation to be well-suited for this system[11]. The advantages of this excitation wavelength over those in the visible region include a greater Raman signal due to the fourth order reciprocal dependence of Raman scattering on incident wavelength, exploitation of preresonance enhancement, and avoidance of fluorescence. Fluorescence can be a problem in taking

Raman spectra when the molecule being studied or an impurity absorbs light at the wavelength of the incident light and emits radiadion at the wavelengths being scanned for the Raman effect. Fluorescence, being a much stronger event, can overwhelm the Raman spectrum. Although fluorescence was observed when visible excitation was used, this effect was greatly reduced by using uv excitation.

The alkoxide and water solutions in iPrOH were contacted in a four-jet mixing chamber.[16] The alkoxide and water solutions were loaded into syringes and delivered with a Sage Model 355 Syringe Pump. The laser beam was focused on the mixing cell, which was alligned so that 90-degree scattered radiation could be collected by the Triplemate. The cell had a precision bored quartz reaction chamber with an inside diameter of 1 mm. Fluid velocity in the cell was 38.4 cm/sec.

The mixing in the flow cell was tested at the flow rate used. An HCl solution with a pH near 0 was mixed with an NaOH solution with a pH near 14 using phenolphthalein as an indicator. At flow rates lower than those used in this study, the indicator was visible to the eye, suggesting incomplete mixing of the streams. At the flow rate used there was no color visible at the mixing point or further downstream, suggesting immediate, complete mixing of the streams.

For all experiments, the laser was focused at a point

3.5 cm downstream from the mixing point, giving a residence time of 91 msec. It is assumed that the presence of the laser does not affect the rate of hydrolysis.

Three concentrations of TiPT were used, with values (before mixing) of 6, 8.5, and 10% by weight in iPrOH. Three water to alkoxide ratios were used for each of the TiPT concentrations, with H_2O:TiPT ratios (R) of 2:1, 4:1, and 6:1. One concentration of TiBT and TET was used: 8.5% (before mixing) in iPrOH, also with R values of 2, 4, and 6.

The position of the carbon-oxygen stretch band (1032 cm^{-1} for TiPT) was shifted for the TiBT and TET solutions, as would be expected. However, to avoid confusion, this band will always be referred to as being at 1032 cm^{-1}.

For each concentration, a spectrum was taken as the alkoxide solution was mixed with a pure iPrOH stream to determine the intensity of the alkoxide peak at 1032 cm^{-1} without reaction. Spectra were then taken as the alkoxide solution was mixed with water solutions with R values of 2, 4, and 6, and the decrease in intensity of the 1032 cm^{-1} band due to hydrolysis of the alkoxy ligands was observed. The intensity of this peak during hydrolysis indicates the number of ligands that have been hydrolyzed.

III. RESULTS

Figure 2 is an example of the spectra obtained. It is

the the 8.5% TiPT (initially) mixed with a corresponding H_2O/iPrOH solution with R = 4. The iPrOH bands at 820, 956, and 1132 cm^{-1} can be clearly seen, while the carbon-oxygen stretch peak due to the alkoxide can be seen at 1032 $cm.^{-1}$ The intensity of the baseline is due to noise. A linear baseline was fit to each of the spectra, with the regions between the 956 and 820 cm^{-1} bands and the 1032 and 1132 cm^{-1} bands taken to be the actual baseline. Figure 3 is a portion of the spectrum shown in Figure 2 after the background subraction.

Both the 1032 and 956 cm^{-1} bands in Figure 3 appear to be somewhat asymmetric. All Raman bands due to a single species are symmetric in shape, so asymmetry indicates the presence of two or more overlapping bands. Figure 4 is the result of a computer fit of two Gaussian shaped bands to the baseline corrected spectrum. The poorness of the fit can be clearly seen. Figure 5 is the result of a fit of the data to 3 Gaussian bands: two near 956 cm^{-1} and one near 1032 $cm.^{-1}$ The 956 cm^{-1} seems to be fit well, but the 1032 cm^{-1} band does not, suggesting the presence of another band overlapping the 1032 cm^{-1} band. Figure 6 is the result of fitting the data to four bands. It can be seen that the generated plot is a much closer approximation to the data than those in Figures 4 and 5. Figures 7 and 8 are examples of fitted spectra of TET and TiBT, respectively. Four bands were used to fit both the TET and

TiBT spectra since assymetries similar to those found for TiPT were also found for these spectra.

Of the four bands observed in the spectrum, bands at 945 and 956 cm^{-1} did not change in intensity for different alkoxide and water concentrations and are assumed to be due solely to the iPrOH. An increase in the intensity of bands due to iPrOH would be expected, since it is a product of the hydrolysis reaction, but the actual molar concentration of the alkoxide is very low, and the change in concentration of the iPrOH is very small. The bands at 1032 and 1011 cm^{-1} did change in intensity for different alkoxide concentrations and R values and are assumed to be due to the alkoxide.

Table 1 lists the results from all experiments. Although the data exhibits some scatter, a trend of decreasing intensity of the 1032 cm^{-1} band with increasing R is present for all TiPT and TET experiments. This peak showed no decrease in intensity for the TiBT experiments. The TET peak showed a much greater decrease in intensity than the TiPT. This coincides with the expected result that longer alkoxy group length will correspond with a slower rate of hydrolysis. Changes in laser power and allignment of the mixing cell can cause changes in intensities of all peaks in the Raman spectra equally. As a test, intensities reported in Table 1 were divided by the intensity of the 820 cm^{-1} band of the iPrOH. Relative

changes observed were 1% and less, suggesting negligible drift in laser power and detector response. Figure 9 illustrates the linearity of the plot of the intensity of the 1032 cm^{-1} band vs initial concentration of TiPT.

Figures 10 through 15 are plots of normalized intensities of the 1032 and 1011 cm^{-1} bands (respectively) vs R for the TiPT concentrations studied, Figures 16 and 17 are plots of the normalized intensities of the 1032 and 1011 cm^{-1} bands (respectively) for TET, and Figure 18 is a plot of normalized intensity of the 1011 cm^{-1} band for TiBT. Normalized intensity of the 1032 cm^{-1} band was not plotted for the TiBT since this peak did not show a decrease. Intensities were normalized by dividing the given peak intensity by the intensity of the same peak in the base case (R = 0) spectrum. As expected, the 1032 cm^{-1} band decreased with increasing R for TiPT and TET. The decrease in intensity for TET is greater than that for TiPT, indicating a faster rate of hydrolysis, and the result that the 1032 cm^{-1} band in the TiBT spectra did not decrease in intensity suggests none of the ligands had been hydrolyzed within 91 msec.

In all cases, the 1011 cm^{-1} band increased in intensity when R > 0. It can be seen that the 1011 cm^{-1} peak has a maximum intensity with R = 2 for the 6% TiPT case, a maximum intensity when R = 4 for the 8.5% case, and the intensity of this band remains relatively constant over

R for the 10% TiPT case. It may be that the 1011 cm^{-1} band reaches a maximum value at a lower value of R for the 10% case, continuing the trend from the 6% to the 8.5%. The 8.5% case was repeated and the results are presented in Figures 11 and 14 along with the original 8.5% experiment. Results were consistent for the 1032 cm^{-1} band, but the 1011 cm^{-1} exhibited a high degree of scatter.

The polymerized partial hydrolysis products that have been postulated in the literature should increase in concentration as the alkoxides hydrolyze. By the behavior of the peak at 1011 cm^{-1} one might assume that this band is in some way associated with polymerized alkoxides. As the hydrolysis reaction progresses, one might assume that these structures initially increase in concentration. Then, as more ligands are hydrolyzed, these structures may break down, showing a decrease in concentration.

As shown by Figures 13 and 14, TET showed an increase in normalized intensity of the peak at 1011 cm^{-1} when $R > 0$ that was much smaller than that for the 8.5% TiPT, and the normalized intensity of the corresponding band in the TiBT spectra when $R > 0$ showed an increase that was much greater than for the 8.5% TiPT. This could be explained by the findings of Bradley, et. al.,[6] who found that TET is highly polymerized before hydrolysis, and TiBT exists in a solvated monomer form. If these species must polymerize before they hydrolyze, then TET, already being highly

polymerized, would show a lower relative increase in concentration of polymerized species during hydrolysis. Conversely, TiBT would show a larger relative increase in the concentration of polymerized species during hydrolysis.

A power law expression was used as an empirical model to illustrate the relative effects of changes in concentrations of the reactants. A least squares fit was calculated for the nine TiPT experiments in order to find values for the constants in the expression:

$$- dI/dt = 2.4 \times 10^{-4} \ (TiPT)^{1.5} \ (H_2O)^{1.0}$$

where

$$- dI/dt = \frac{\text{change in intensity of 1032 } cm^{-1} \text{ peak}}{\text{change in time (= 91 msec)}}$$

Measured initial rates are plotted against R along with curves generated from the calculated initial rate equation for 6, 8.5, and 10% TiPT in Figures 19 through 21. All data did not fit the calculated rate equally well; however, this technique does illustrate correct trends. Using more data points and achievement of better signal to noise ratio would result in less scatter. The initial rate -dI/dt is not a classic rate in that it does not describe a rate of disappearence of the alkoxide molecule, but rather, it describes a rate of hydrolysis of alkoxy ligands. Since one water molecule is consumed for each ligand hydrolyzed, one might correlate this rate to the consumption of water.

But since the number of alkoxide ligands is the quantity being measured, it may be more correct to speak in these terms.

None of the relative intensities dropped below .75 in the TiPT experiments. This result, along with the first-order dependence on the water concentration may indicate that the reaction being observed is probably the hydrolysis of the first alkoxy ligand.

Hartel and Berglund[8] presented their results for the nucleation and growth rates of the precipitate formed in the hydrolysis of TiPT in a similar form. The values obtained for the exponents on the alkoxide and water concentrations in their nucleation and growth rate expressions were much higher than those obtained in this study. It seems the precipitation rate (measured by Hartel and Berglund) is more dependent on TiPT and water concentrations than the initial rate of hydrolysis of the alkoxy ligands. Ratios of Hartel and Berglund's exponents on alkoxide and water concentrations for nucleation and growth rate were 1.6 and 1.7, respectively, which are close to the value obtained in this study, 1.5. These results show that the hydrolysis rate of the alkoxides have a higher dependence on alkoxide concentration than on water concentration.

III. DISCUSSION

It has been found that the Raman band associated with the carbon-oxygen symmetric stretch in the alkoxide (1032 cm^{-1}) decreases with increasing alkoxide concentration and with increasing water:alkoxide ratio as the alkoxide is hydrolyzing. Hydrolysis was less complete at the residence time observed (91 msec) for longer alkoxy group lengths. No decrease in intensity of the band studied during the hydrolysis of titanium tetraisobutoxide was observed. This trend is not surprizing considering the increased steric hindrance involved in hydrolysis of alkoxides with longer group lengths.

Examination of the baseline corrected spectra showed an asymetry in the 1032 cm^{-1} band in both the reacting and unreacting solutions. Results of curvefitting indicate a band located at 1011 cm^{-1} is responsible for the observed asymmetry. This band was seen to increase in intensity in the presence of water, and at the residence time studied, reached maxima at different water ratios for differing alkoxide concentrations. The presence of polymerized unreacted alkoxides and partial hydrodrolysis products has been discussed in previous work, and this band may be associated with these species.

The intensity of the 1032 cm^{-1} band did not decrease below 75% of the unreacted intensity. This result, along with the calculated first-order dependence of the rate on water concentration, suggests that hydrolysis of the first

ligand was being observed.

The initial rate of hydrolysis of the alkoxy ligands as studied herein showed a lower dependence on alkoxide and water concentrations than was obtained when particle formation and growth was studied in previous work[8]. The ratio of the exponents on alkoxide and water concentrations obtained in this study (1.5) is similiar to that found in the earlier study. These results indicate that the rate of hydrolysis is more dependent on alkoxide concentration than water concentration when both the initial rate and the overall rate (particle formation) are observed.

IV. ACKNOWLEDGEMENTS

Support was provided by Sandia National Laboratories through contract #21-2885. The work was performed in the Shared Laser Laboratory at Michigan State University.

REFERENCES

1. K.S.Masdiyasni, Cer.Int.8(2) 42-56 (1982).
2. L.L.Hench and D.R.Ulrich, Ultrastructure Processing of Ceramics, Glasses, and Composites John Wiley & Sons, New York, 1984.
3. D.R.Uhlmann, B.J.J.Zelinski, and G.E.Wnek, Mat. Res. Soc. Symp. Proc. Vol. 32, 1984.
4. B.Fegley,Jr. and E.A.Barringer, Mat. Res. Soc. Symp. Proc. Vol. 32, 1984.
5. B.E.Yoldas, J. Mat. Science, 12 1977.
6. D.C.Bradley, R.Gaze, and W.Wardlaw, J. Chem. Soc.
7. W.R.Russo and W.H.Nelson, J. Am. Chem. Soc. 92 1521, 1970.
8. R.W.Hartel and K.A.Berglund, Mat. Res. Soc. Symp. Proc., Spring, 1986.
9. F.A.Cotton, Progress in Inorganic Chemistry, Interscience Publishers, Inc., New York, 1960.
10. B.J.Ingebrethsen and E.Matijevic, J. Coll. Int. Sci. 100, 1984
11. M.J.Payne and K.A.Berglund, Mat. Res. Soc. Symp. Proc.,

Spring, 1986.
12. K.A.Berglund, D.R.Tallant, and R.G.Dosch, Second International Conference on Untrastructure Processing of Ceramics, Glasses, and Composites. Palm Coast, Fla. February 2 to March 1, 1985.
13. V.A.Zeitler and C.A.Brown, J. Phys. Chem. 61, 1174-7 1957.
14. D.C.Bradley, R.C.Mehrotra, D.P.Gaur,Metal Alkoxides, Academic Press, New York, 1978.
15. J.H.S. Green, Trans. Far. Soc. 59, 1559-63 1963.
16. E.F.Caldin, Fast Reactions in Solution, Blackwell Scientific, Oxford, 1964.

Table 1 Intensities of 1032 and 1011 cm^{-1} Bands in Raman Spectra of Hydrolyzing Alkoxides 91 msec After Mixing

Alkoxide	Initial Wt. %	R	Intensity$_1$ 1032 cm^{-1}	Intensity$_1$ 1011 cm^{-1}
TiPT	6.0	0	165	45
TiPT	6.0	2	155	60
TiPT	6.0	4	155	80
TiPT	6.0	6	150	60
TiPT	8.5	0	275	60
TiPT	8.5	2	270	155
TiPT	8.5	4	270	130
TiPT	8.5	6	235	115
TiPT	8.5	0	345	125
TiPT	8.5	2	340	160
TiPT	8.5	4	350	140
TiPT	8.5	6	300	120
TiPT	10.0	0	380	120
TiPT	10.0	2	355	180
TiPT	10.0	4	290	210
TiPT	10.0	6	310	195
TET	8.5	0	230	100
TET	8.5	2	175	120
TET	8.5	4	180	150
TET	8.5	6	160	90
TiBT	8.5	0	170	20
TiBT	8.5	2	180	55
TiBT	8.5	4	170	55
TiBT	8.5	6	170	83

Figure 1

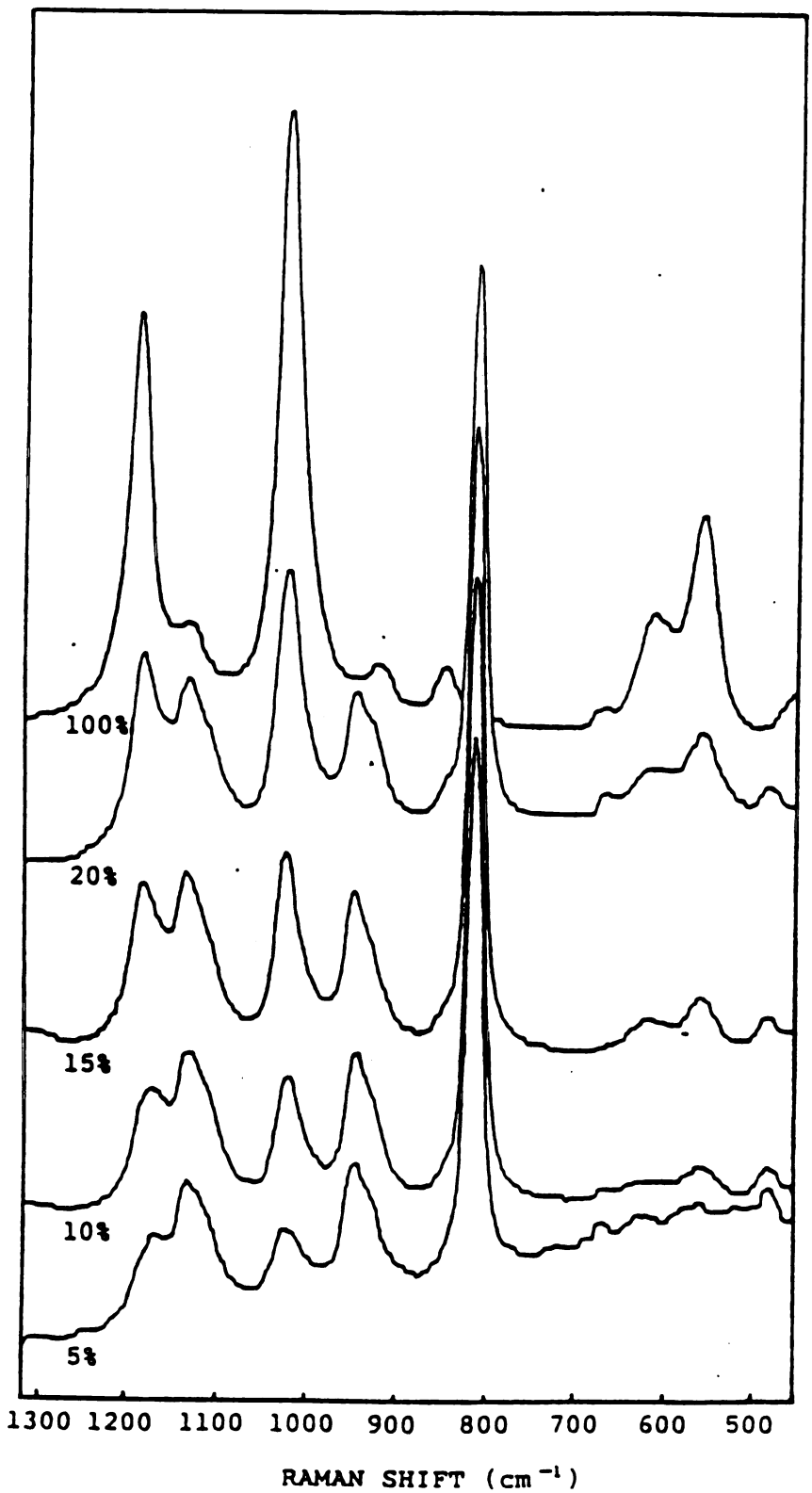

100%
20%
15%
10%
5%
1300 1200 1100 1000 900 800 700 600 500
RAMAN SHIFT (cm⁻¹)

Figure 2

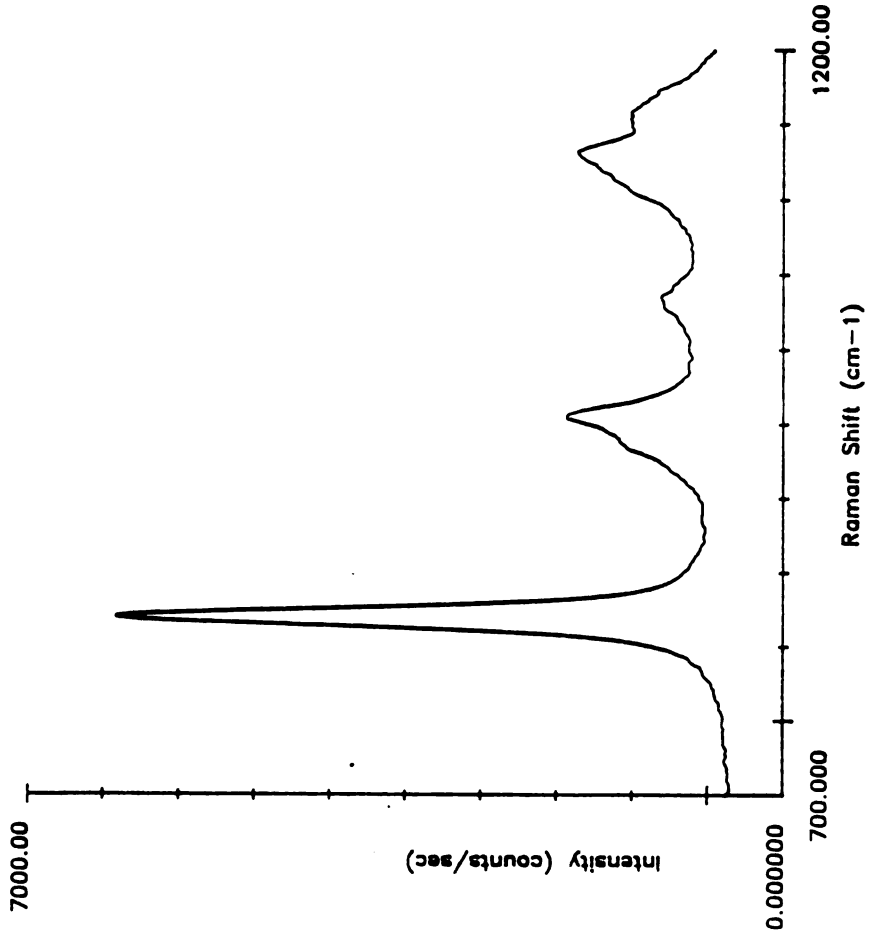

7000.00
0.0000000
Intensity (counts/sec)
700.000
1200.00
Raman Shift (cm-1)

Figure 3

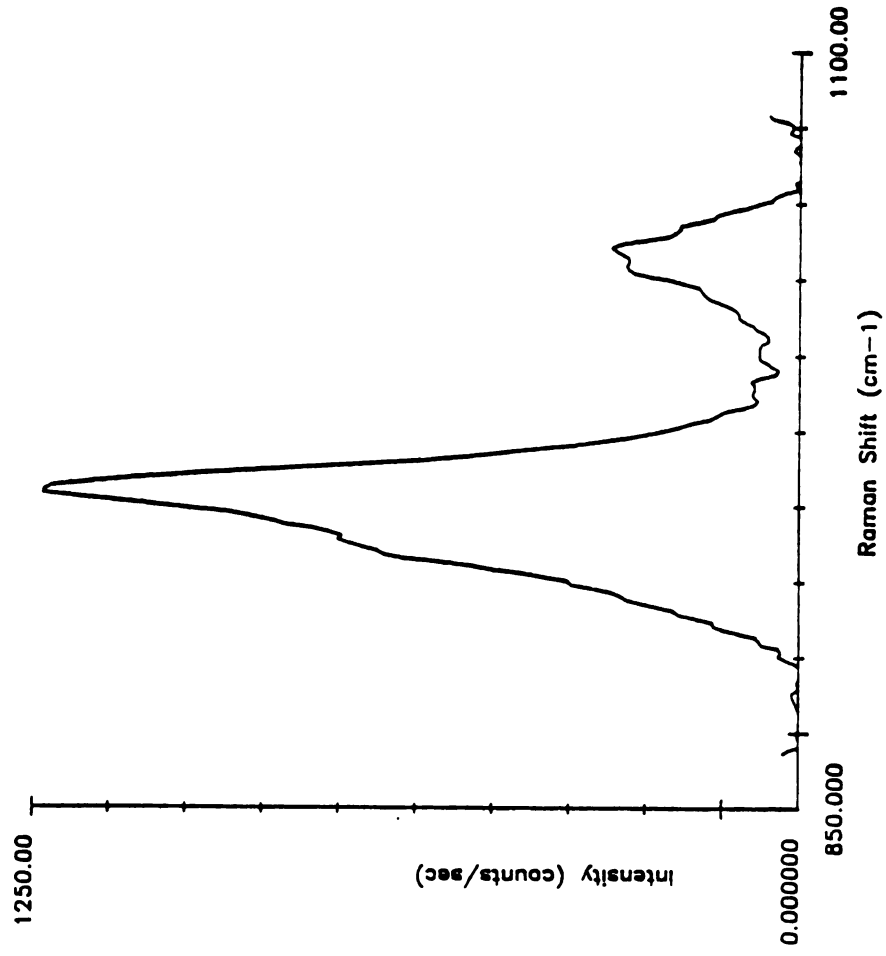

1250.00
0.000000
Intensity (counts/sec)
850.000
1100.00
Raman Shift (cm-1)

Figure 4

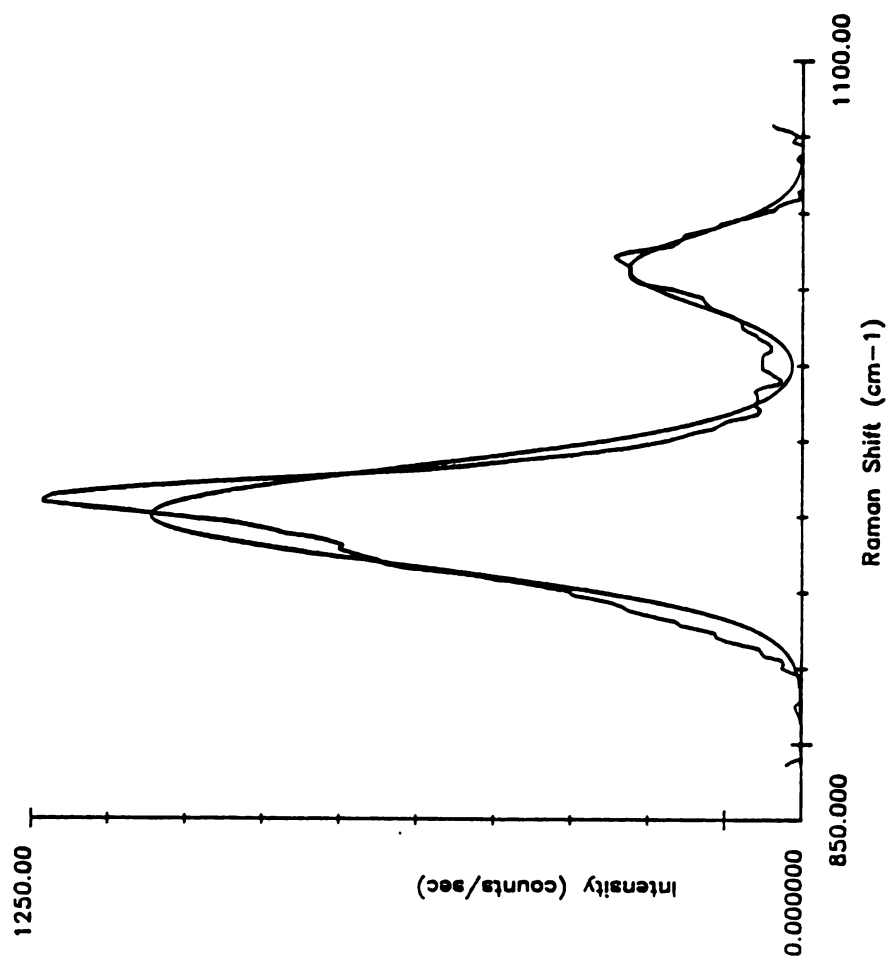

1250.00
0.000000
Intensity (counts/sec)
850.000
1100.00
Raman Shift (cm-1)

Figure 5

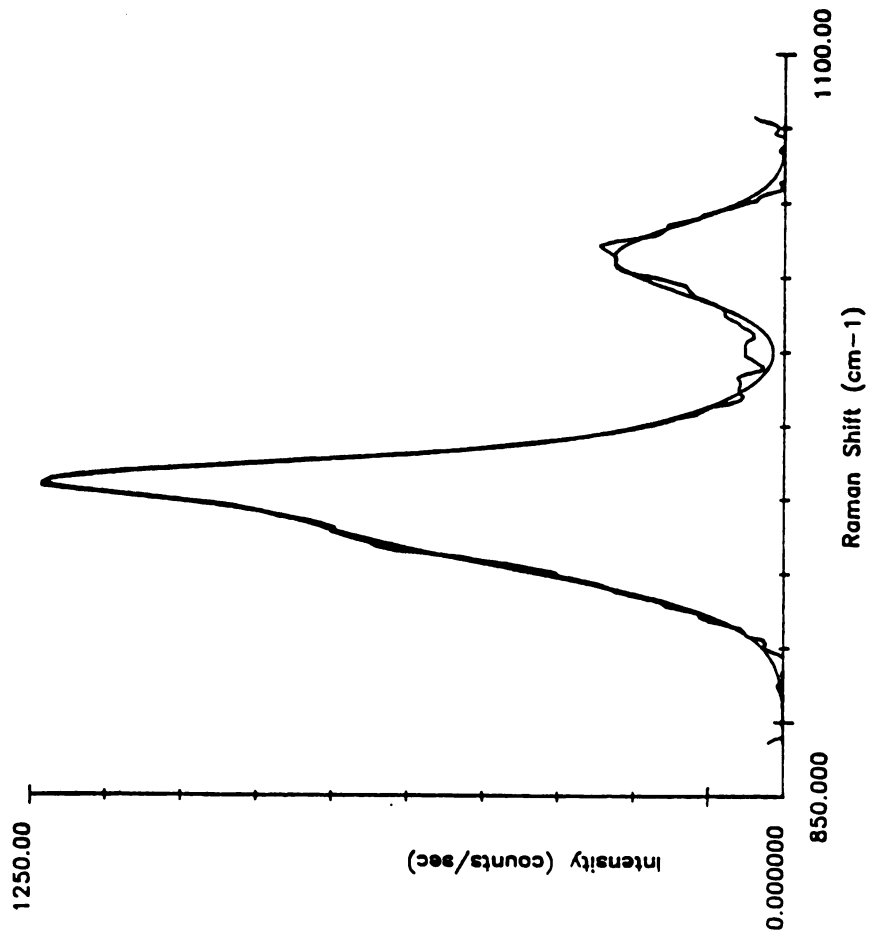

1250.00
0.000000
Intensity (counts/sec)
850.000
1100.00
Raman Shift (cm-1)

Figure 6

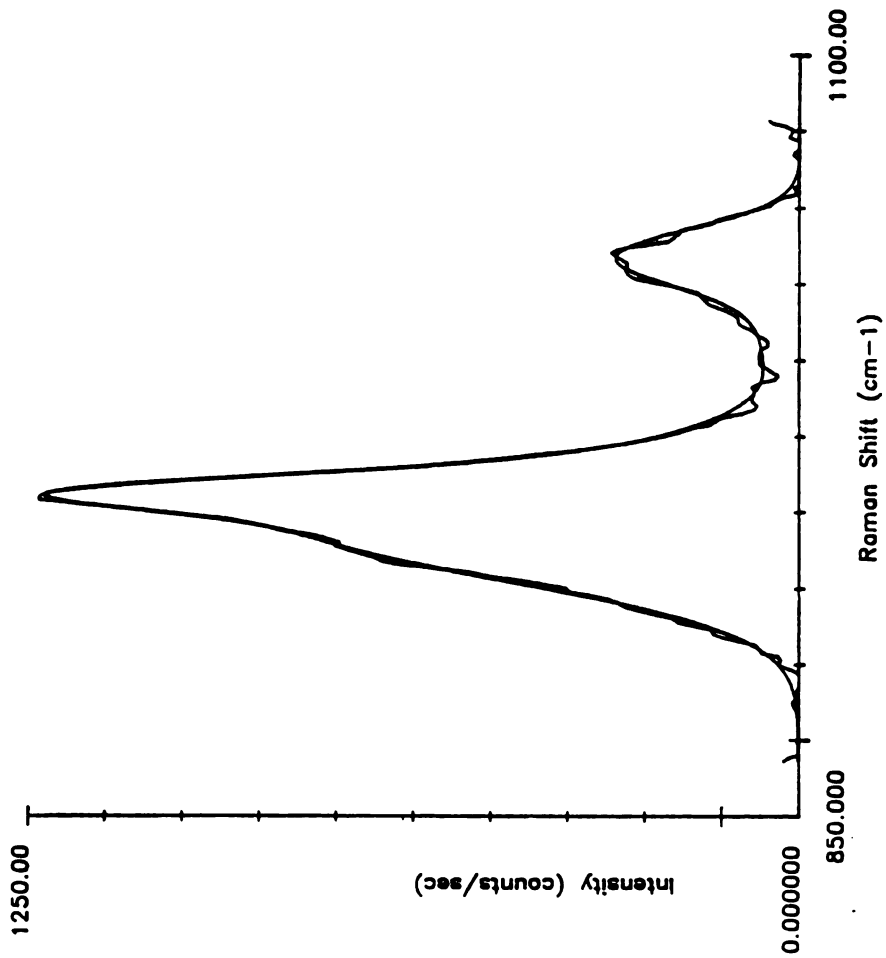

1250.00
0.000000
Intensity (counts/sec)
850.000
1100.00
Raman Shift (cm-1)

Figure 7

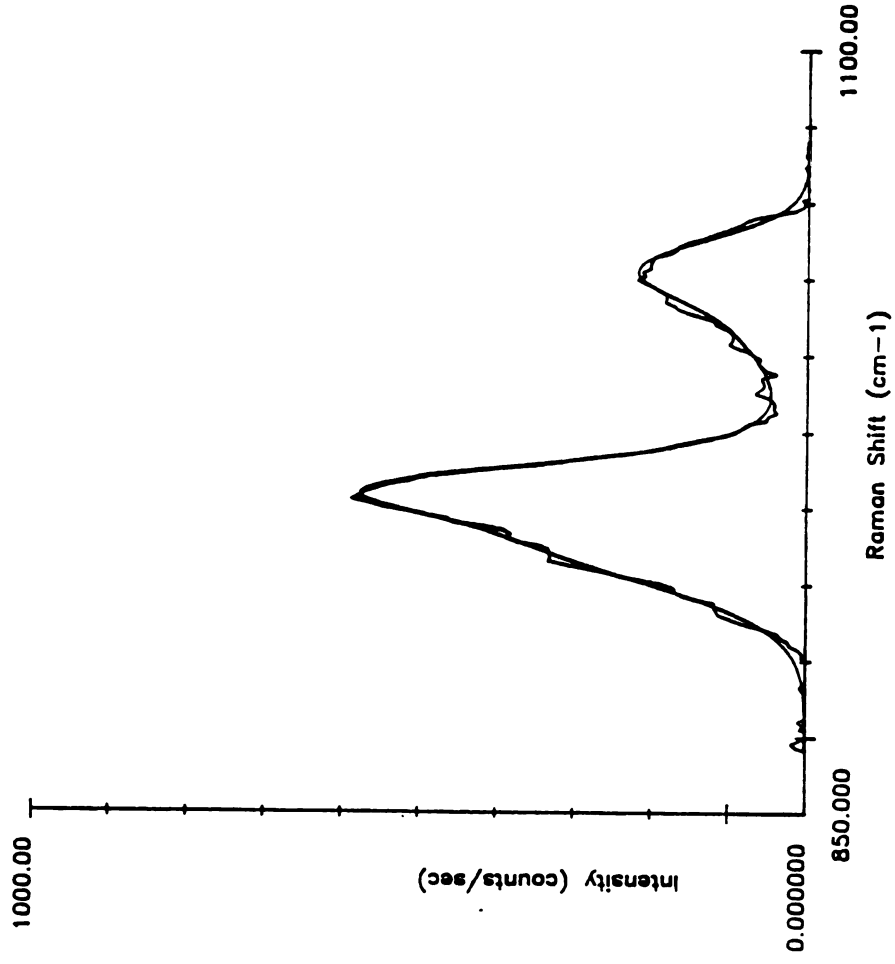
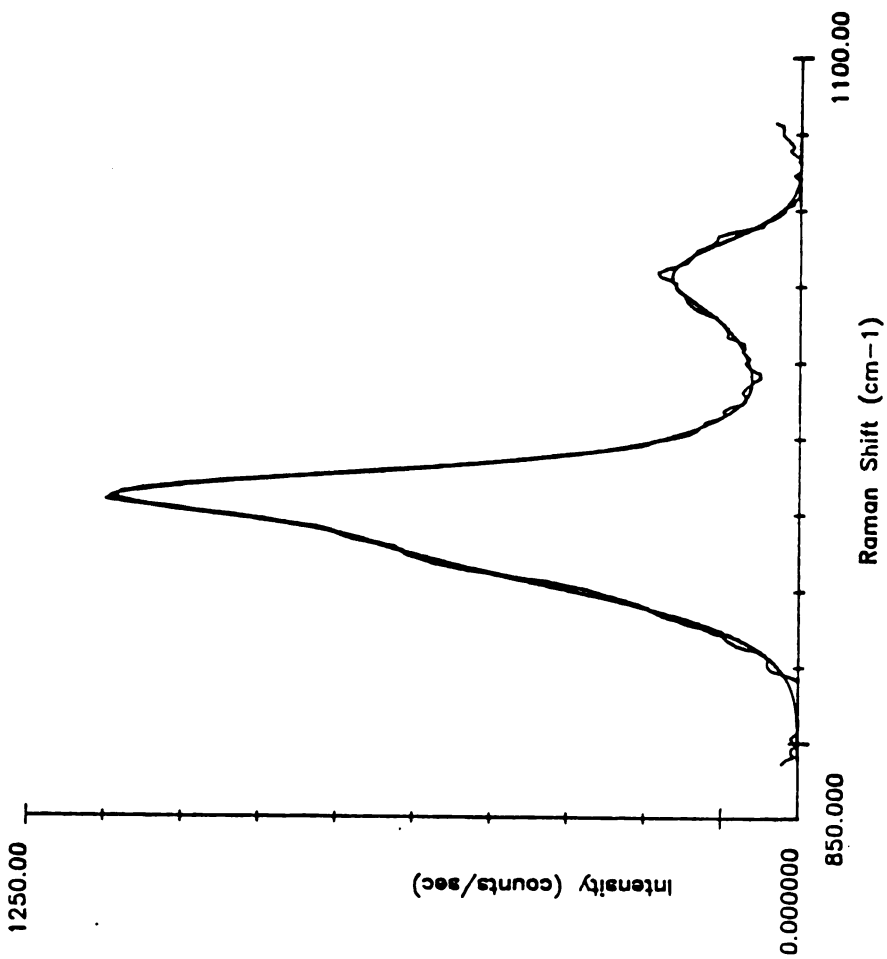

1000.00
0.000000
Intensity (counts/sec)
850.000
1100.00
Raman Shift (cm-1)

Figure 8


1250.00
0.000000
Intensity (counts/sec)
850.000
1100.00
Raman Shift (cm-1)

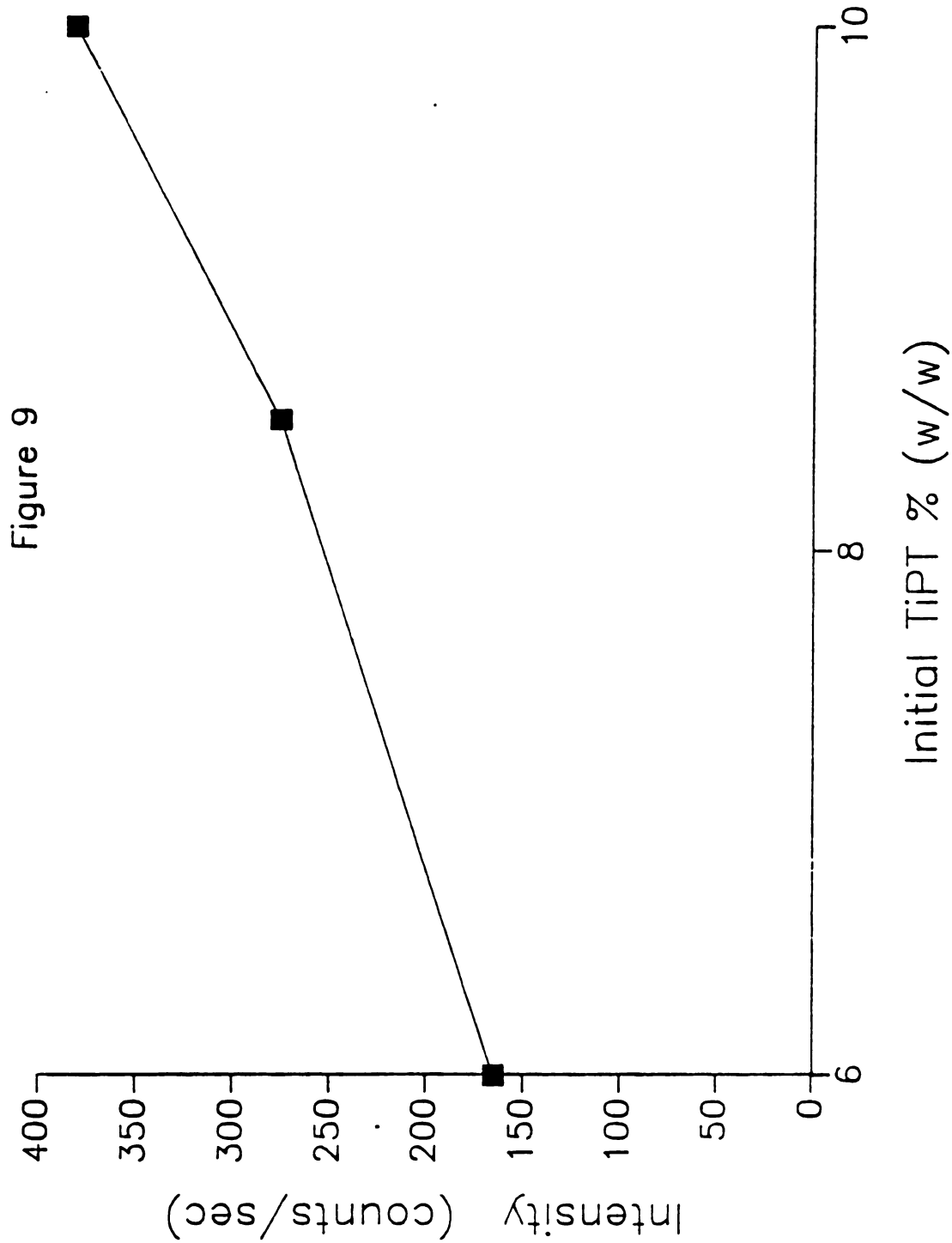

Intensity (counts/sec)
400
350
300
250
200
150
100
50
0
6
8
10
Initial TiPT % (w/w)

Figure 9

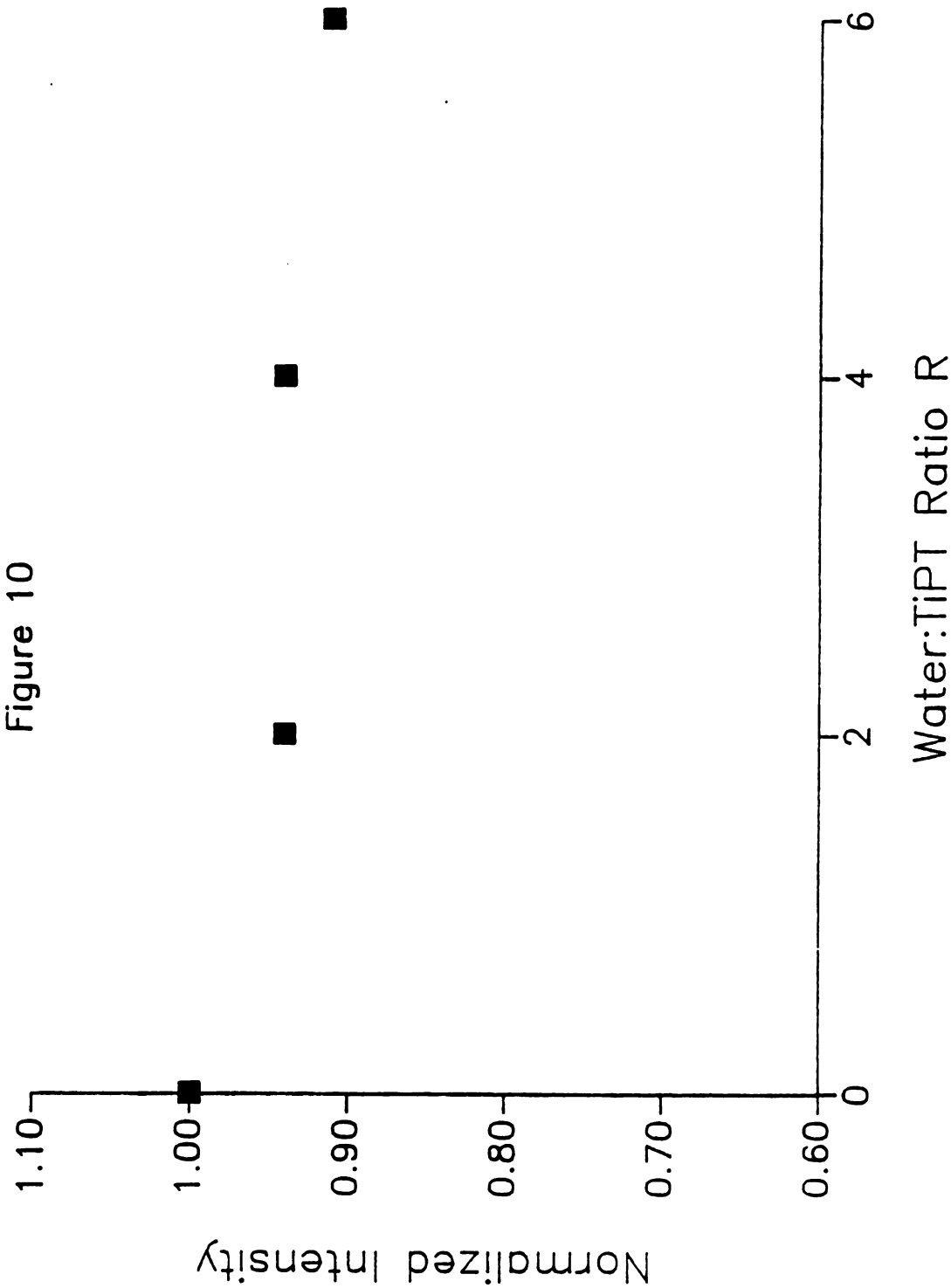

Normalized Intensity
1.10
1.00
0.90
0.80
0.70
0.60
0
2
4
6
Water:TiPT Ratio R

Figure 10

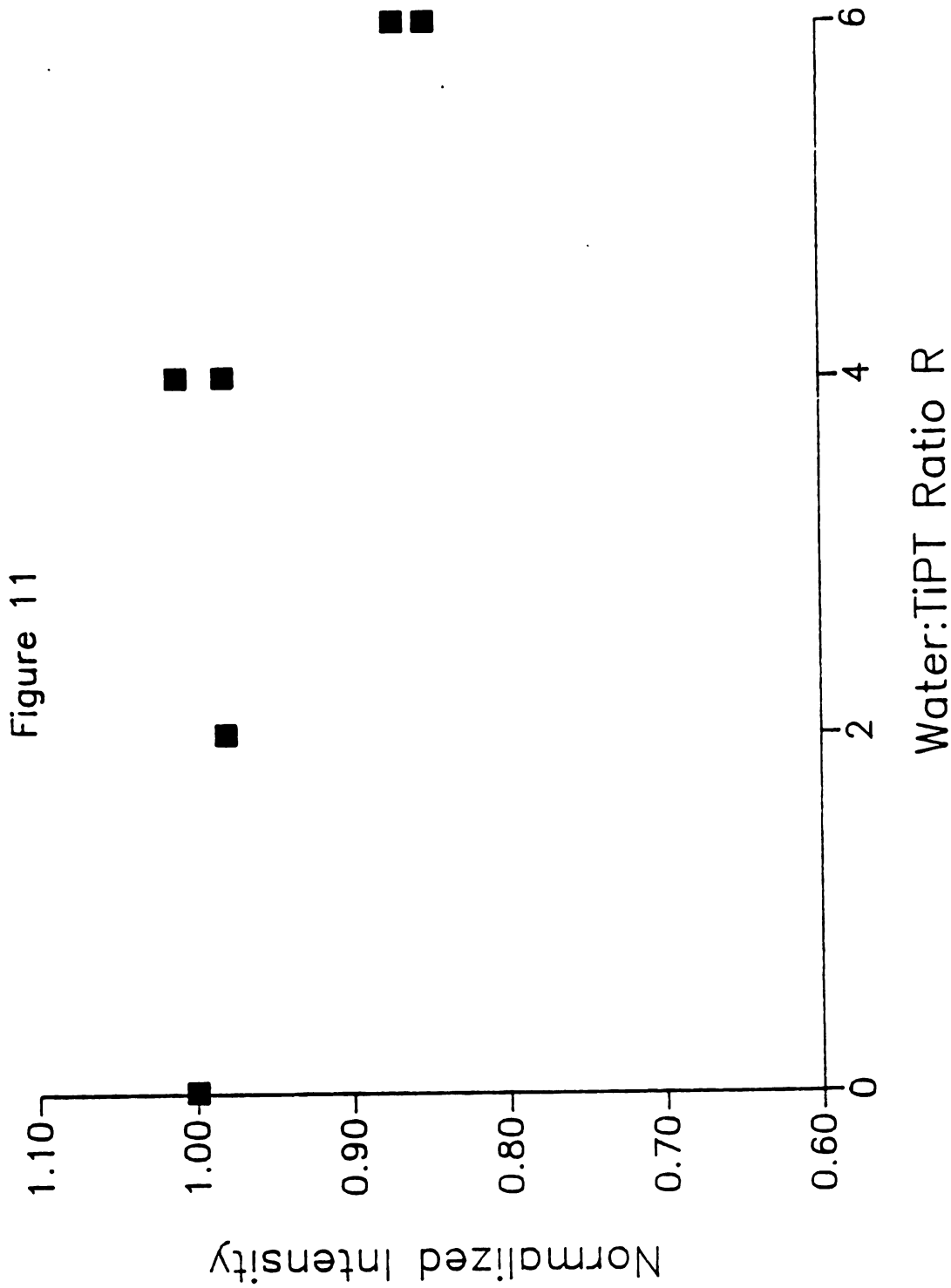

Normalized Intensity
1.10
1.00
0.90
0.80
0.70
0.60
0
2
4
6
Water:TiPT Ratio R

Figure 11

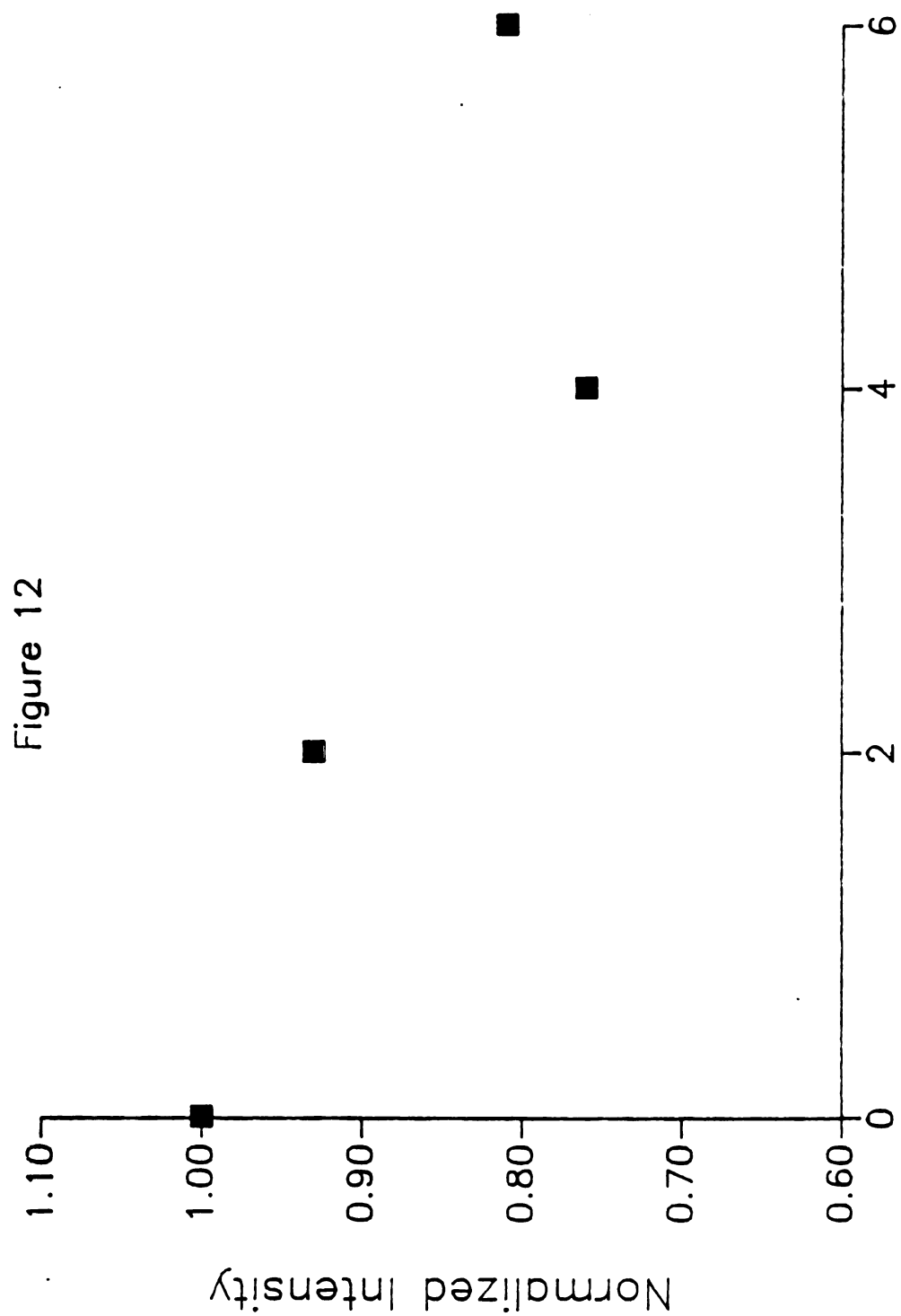

Normalized Intensity
1.10
1.00
0.90
0.80
0.70
0.60
0
2
4
6
Water:TiPT Ratio R

Figure 12

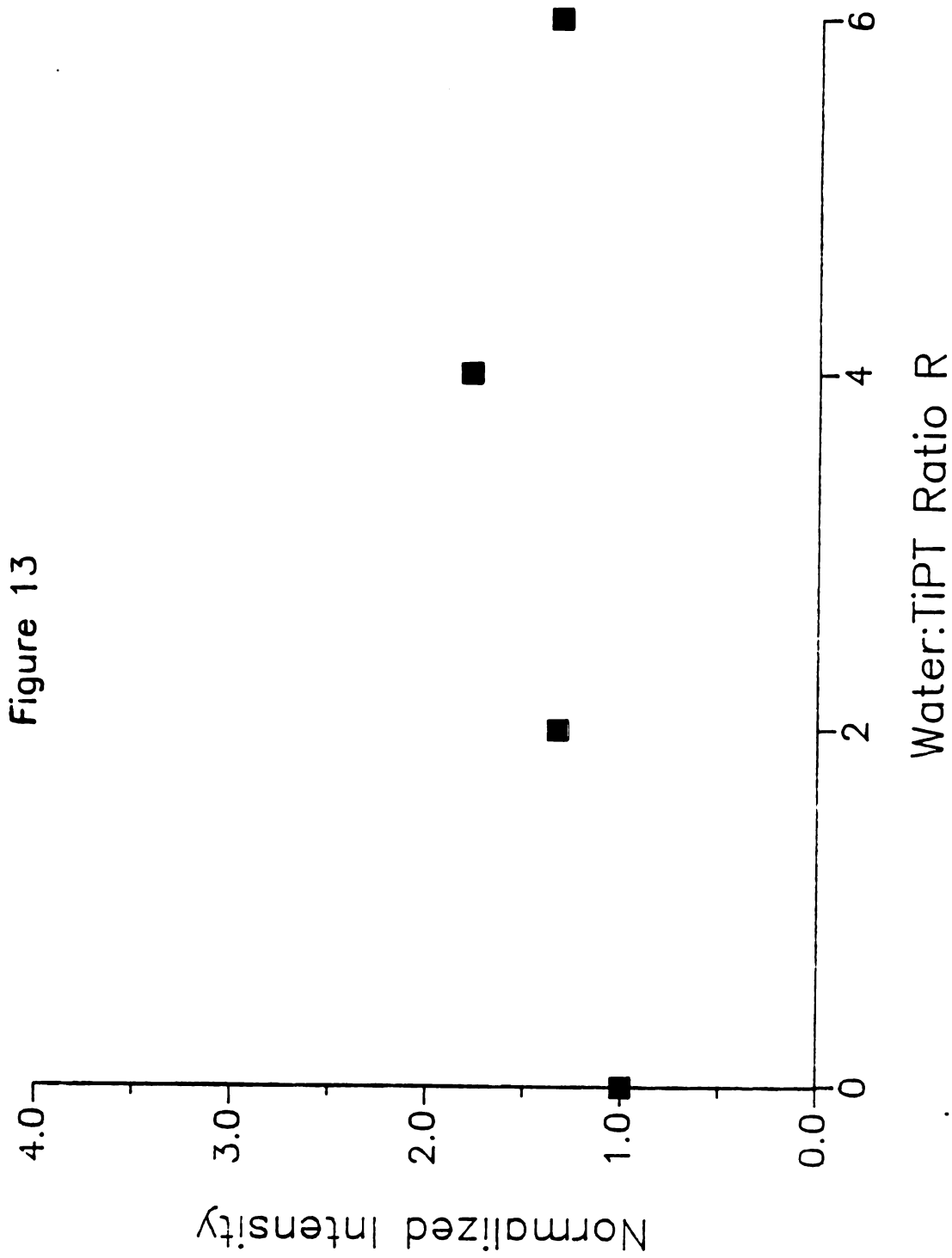


Figure 13

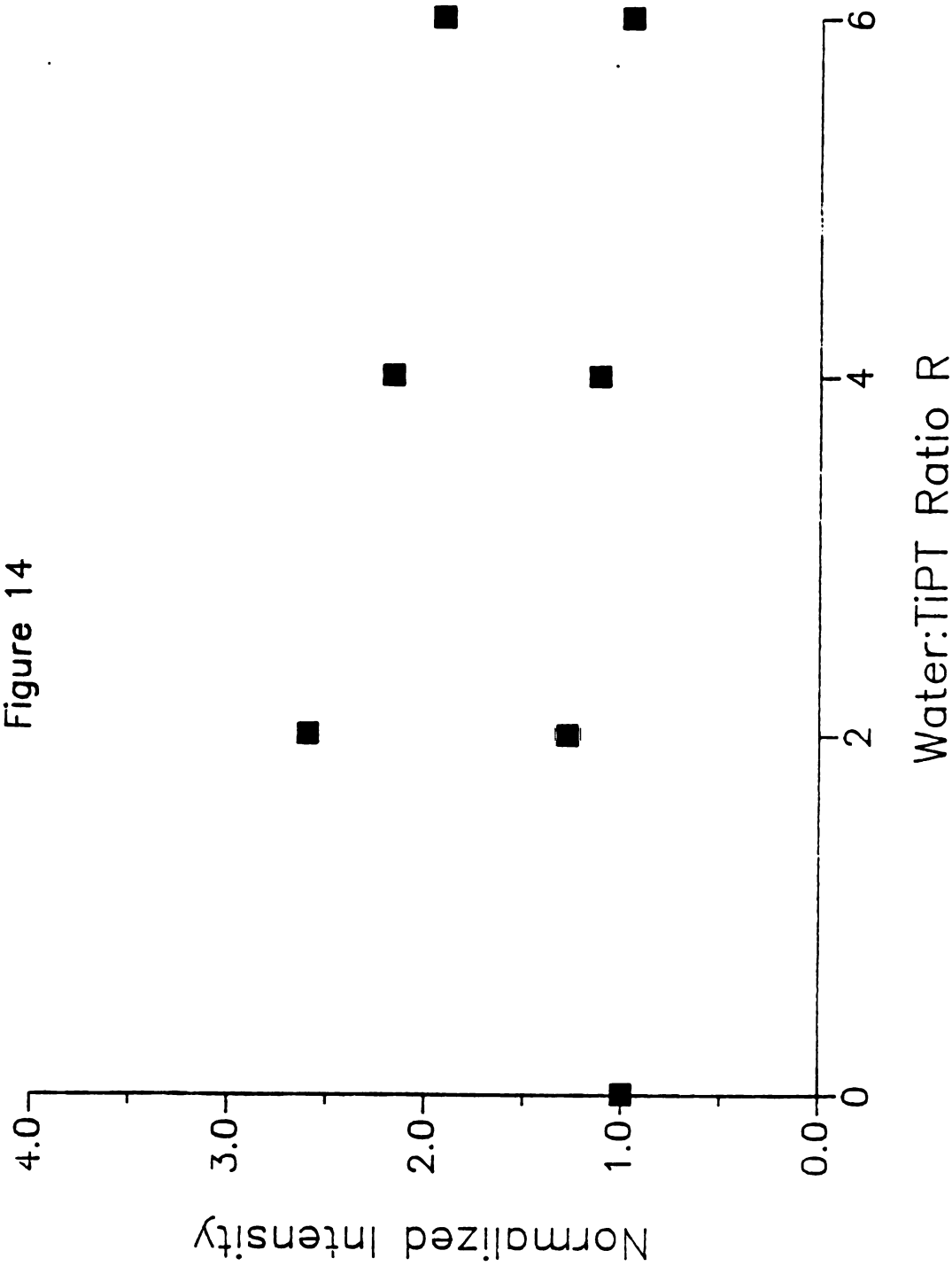


Figure 14

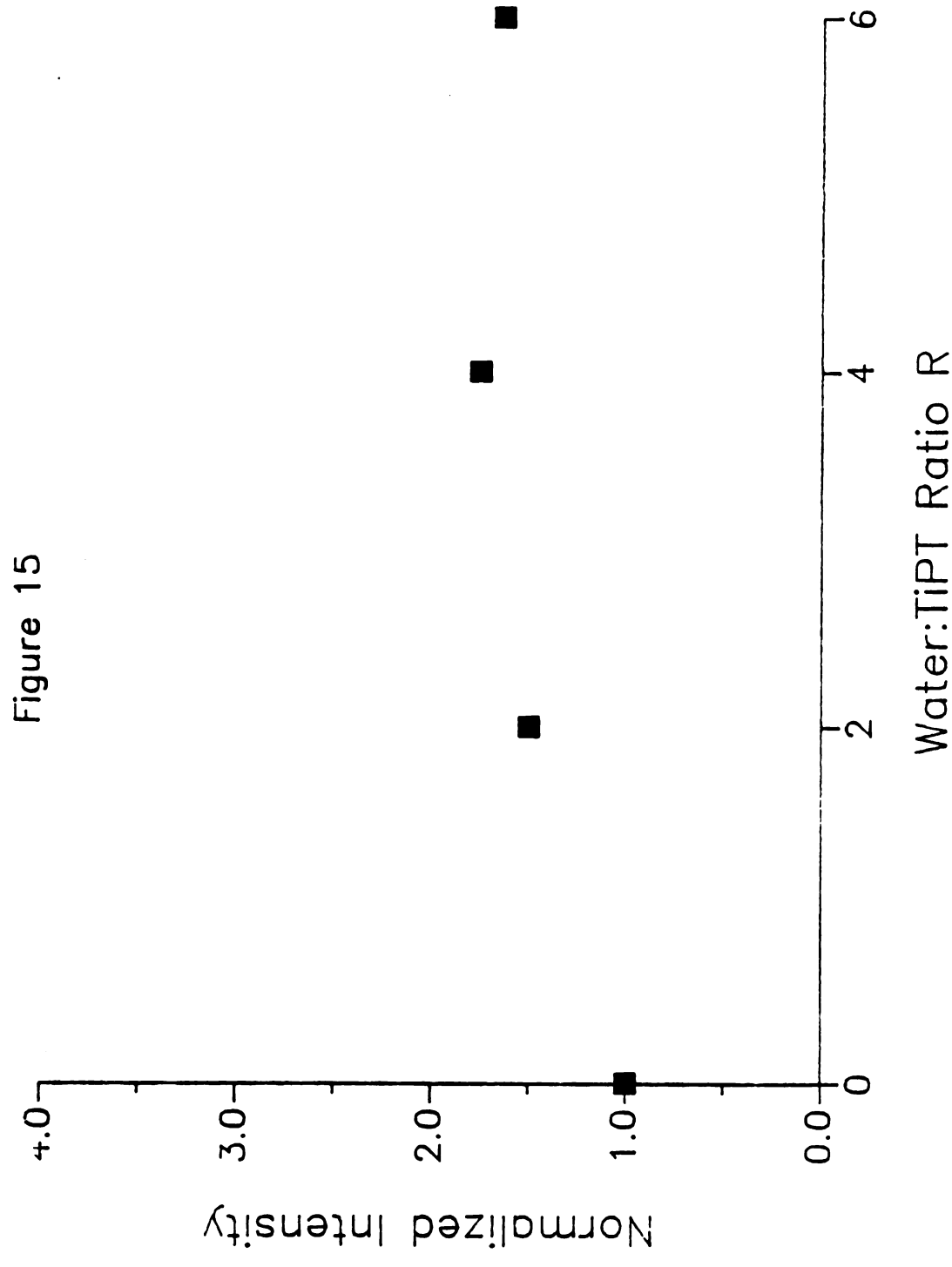


Figure 15

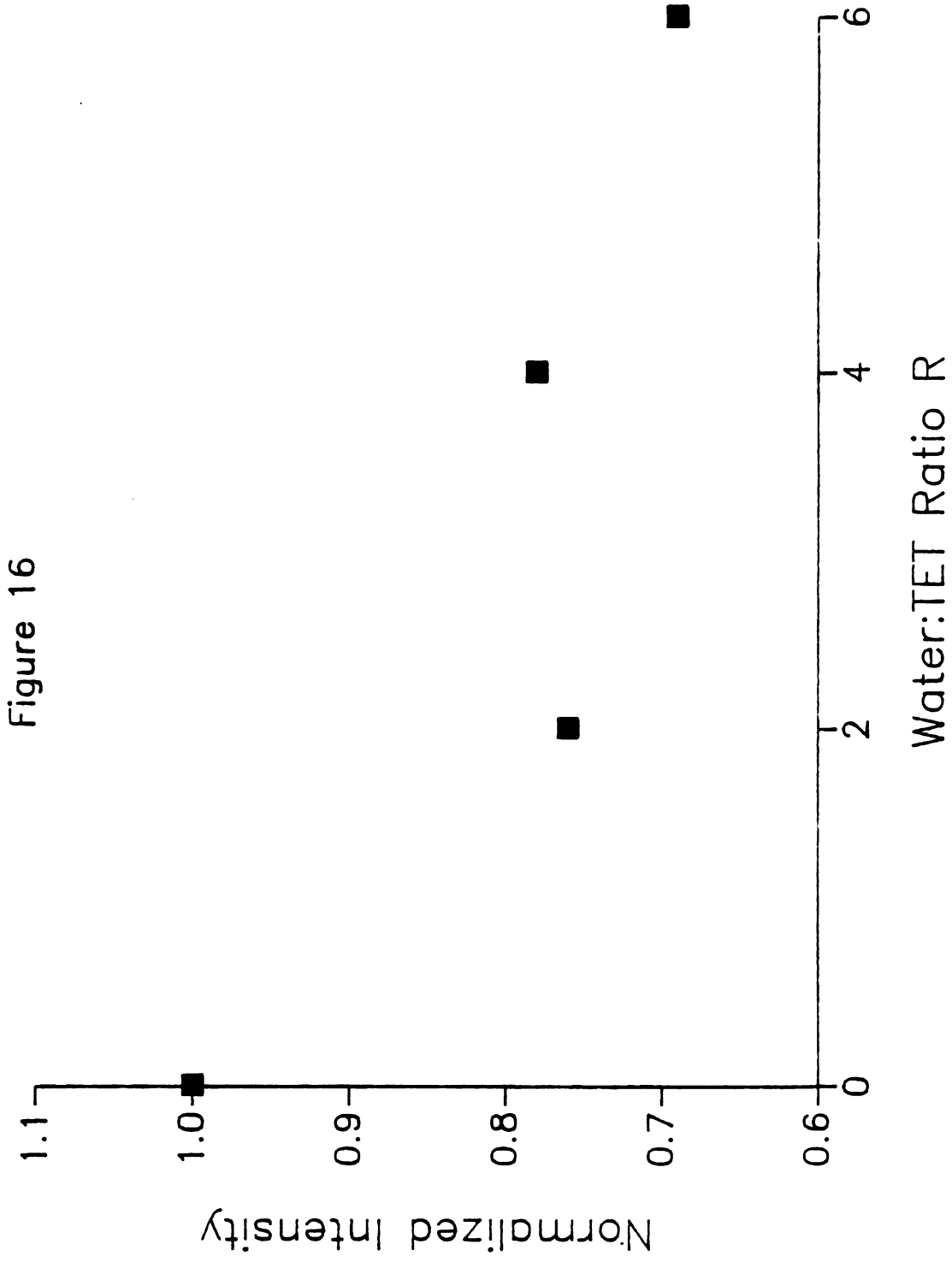


Figure 16

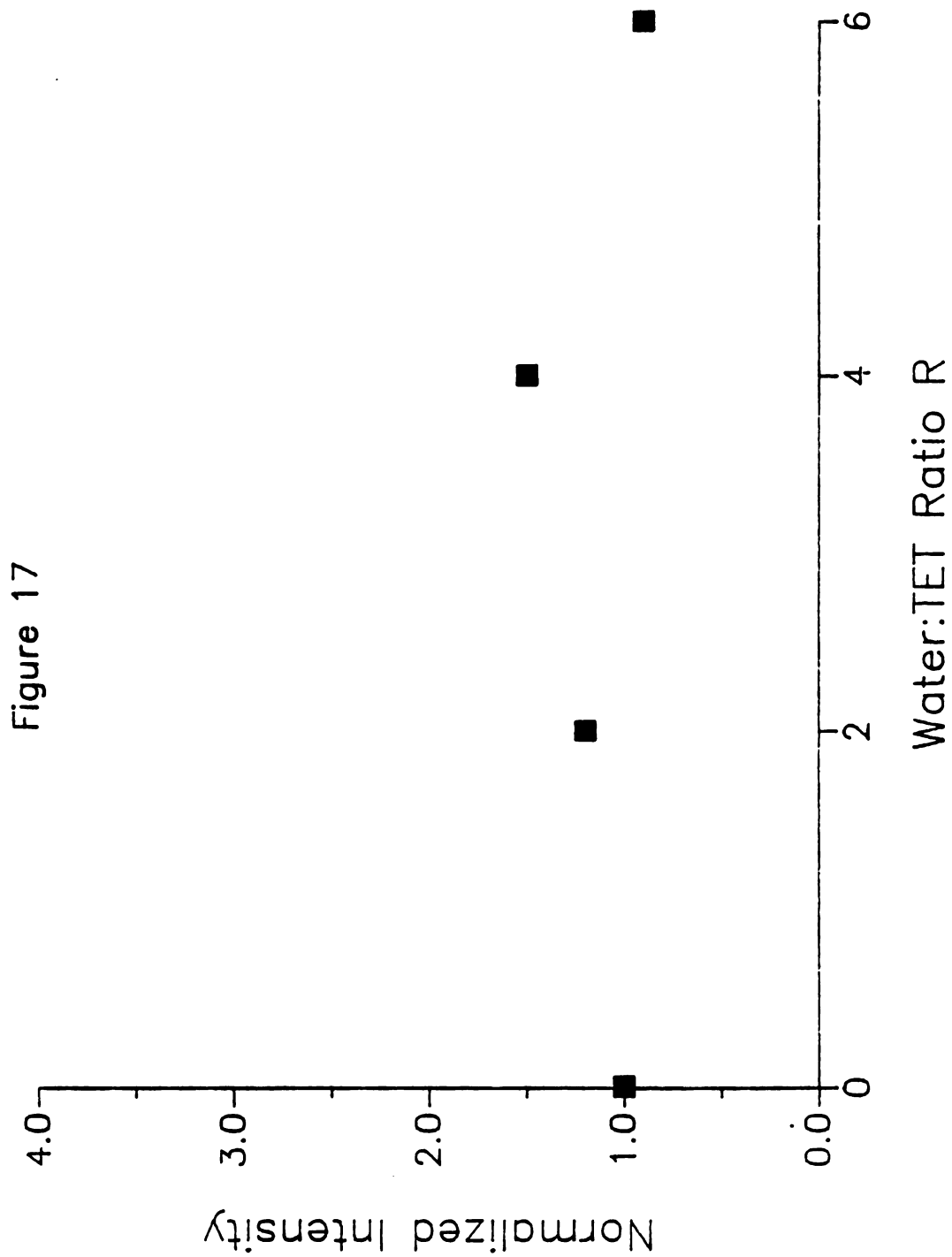


Figure 17

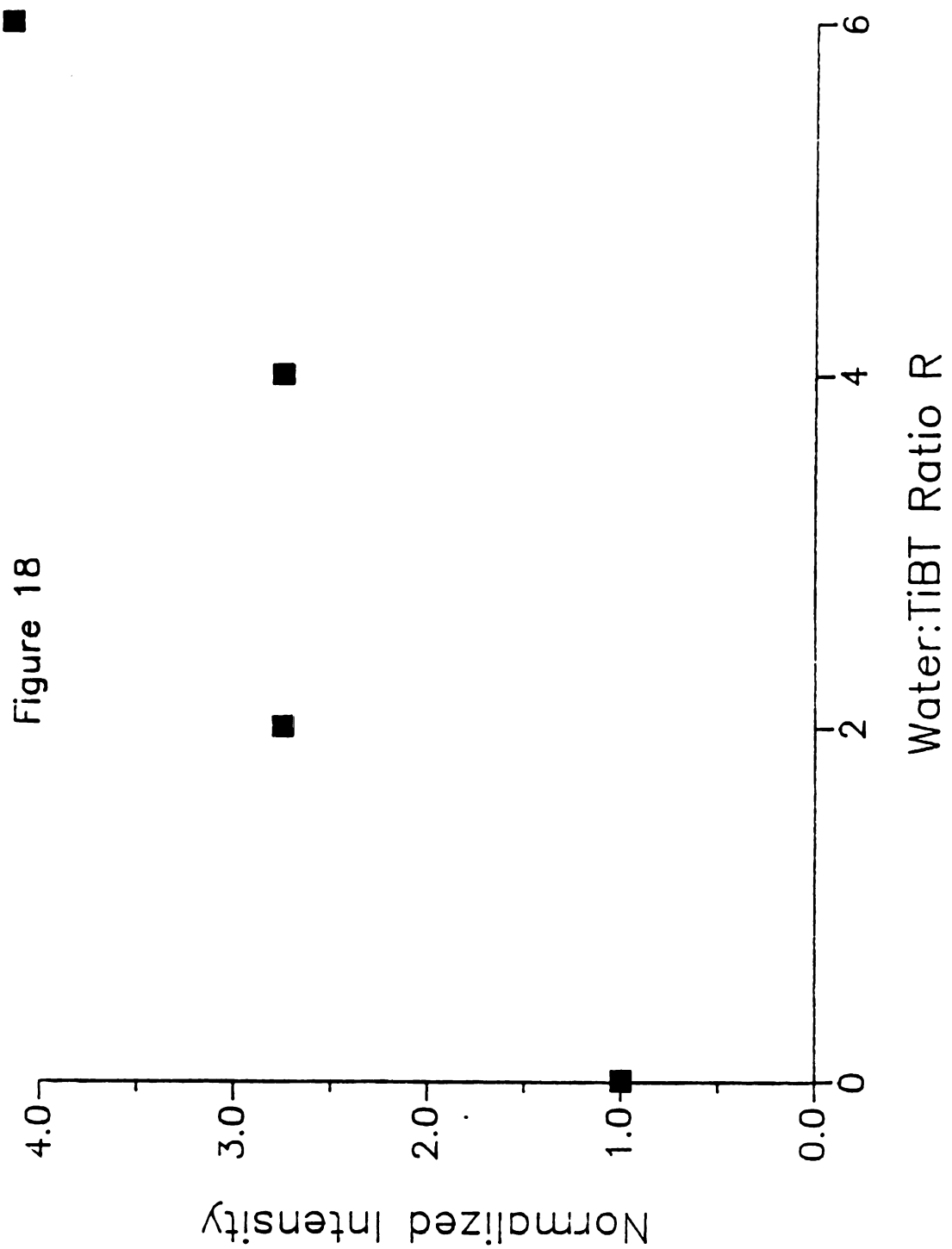
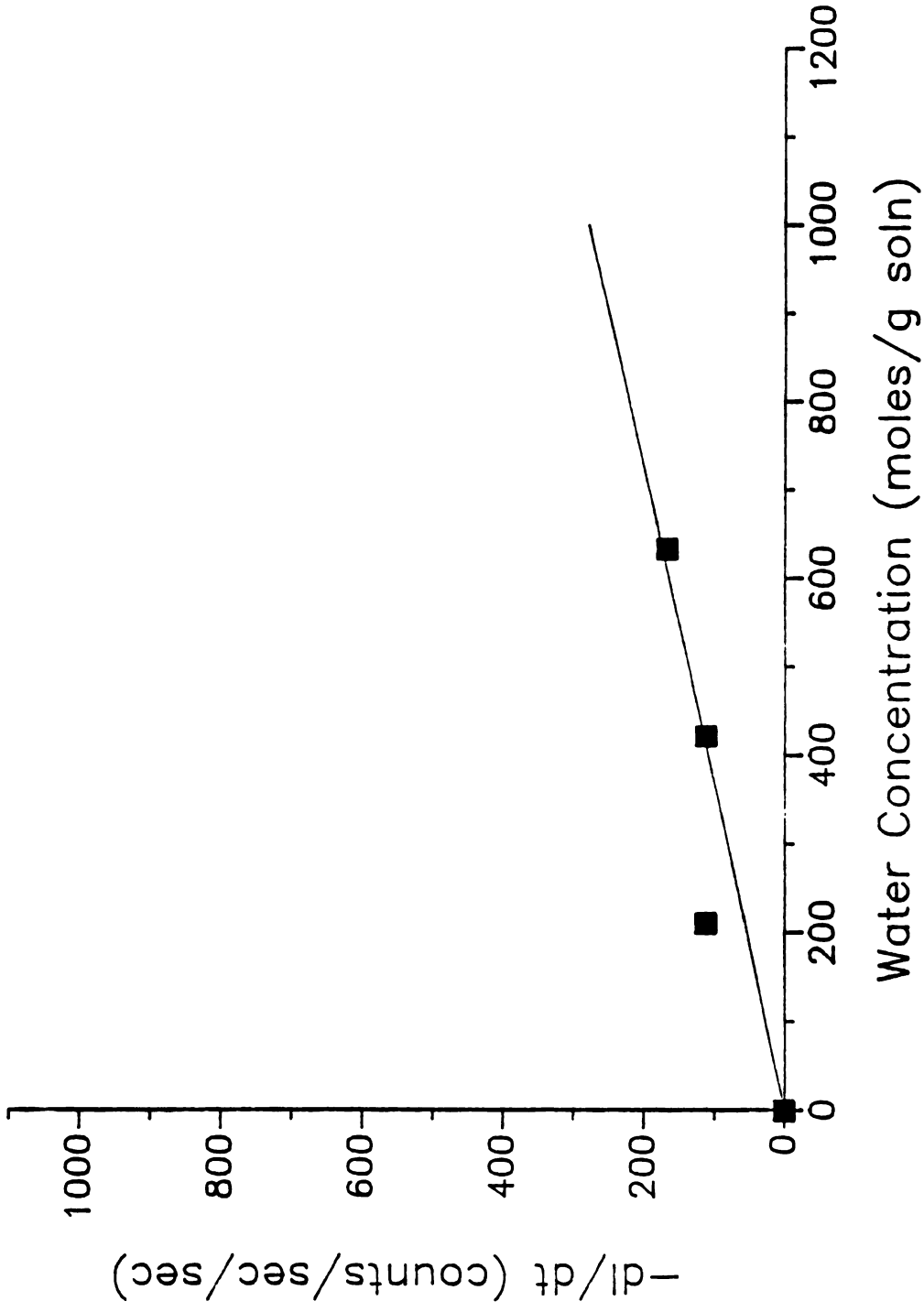


Figure 18

Figure 19


-dI/dt (counts/sec/sec)
1000
800
600
400
200
0
0
200
400
600
800
1000
1200
Water Concentration (moles/g soln)

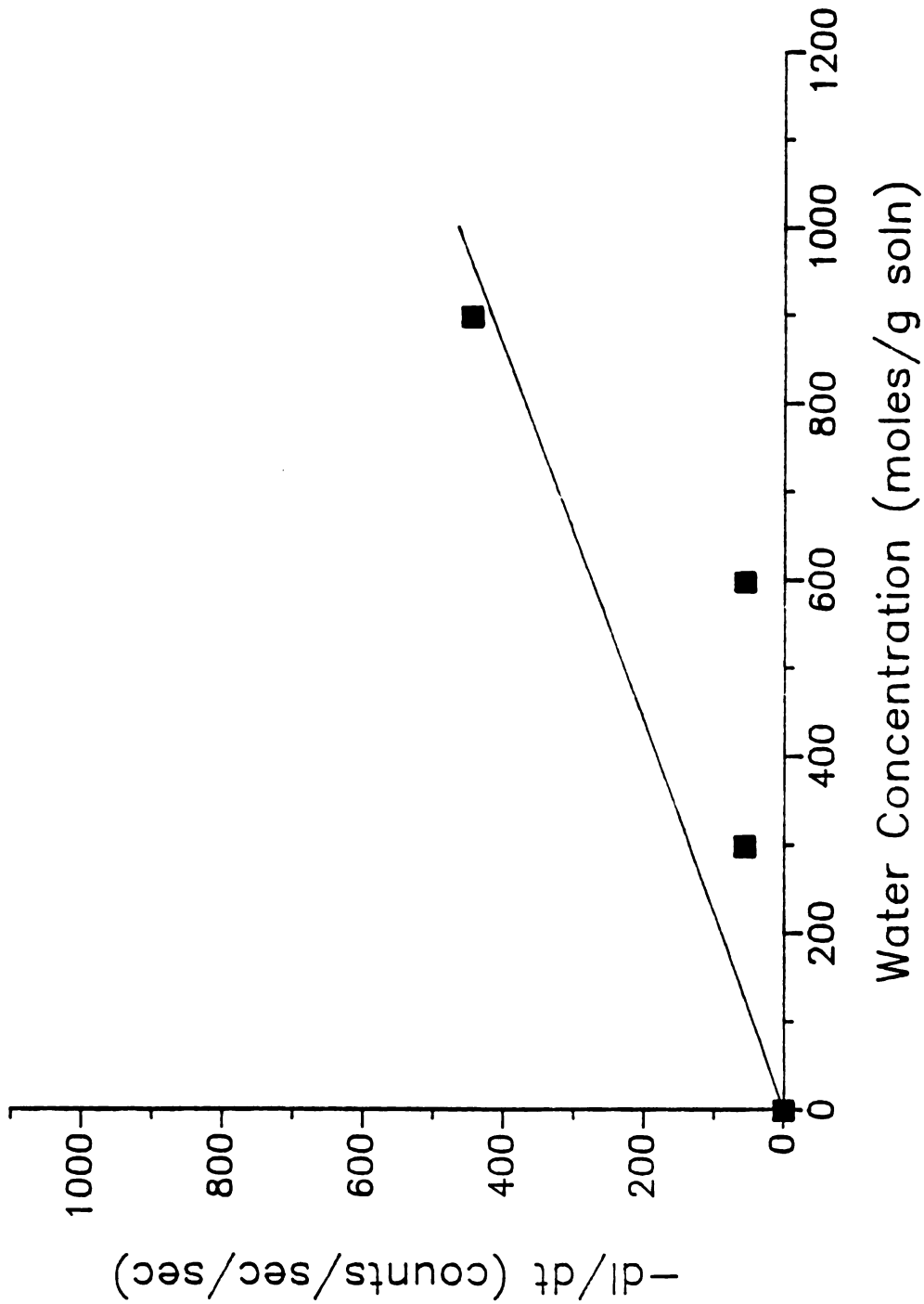

-dI/dt (counts/sec/sec)
1000
800
600
400
200
0
0
200
400
600
800
1000
1200
Water Concentration (moles/g soln)

Figure 20

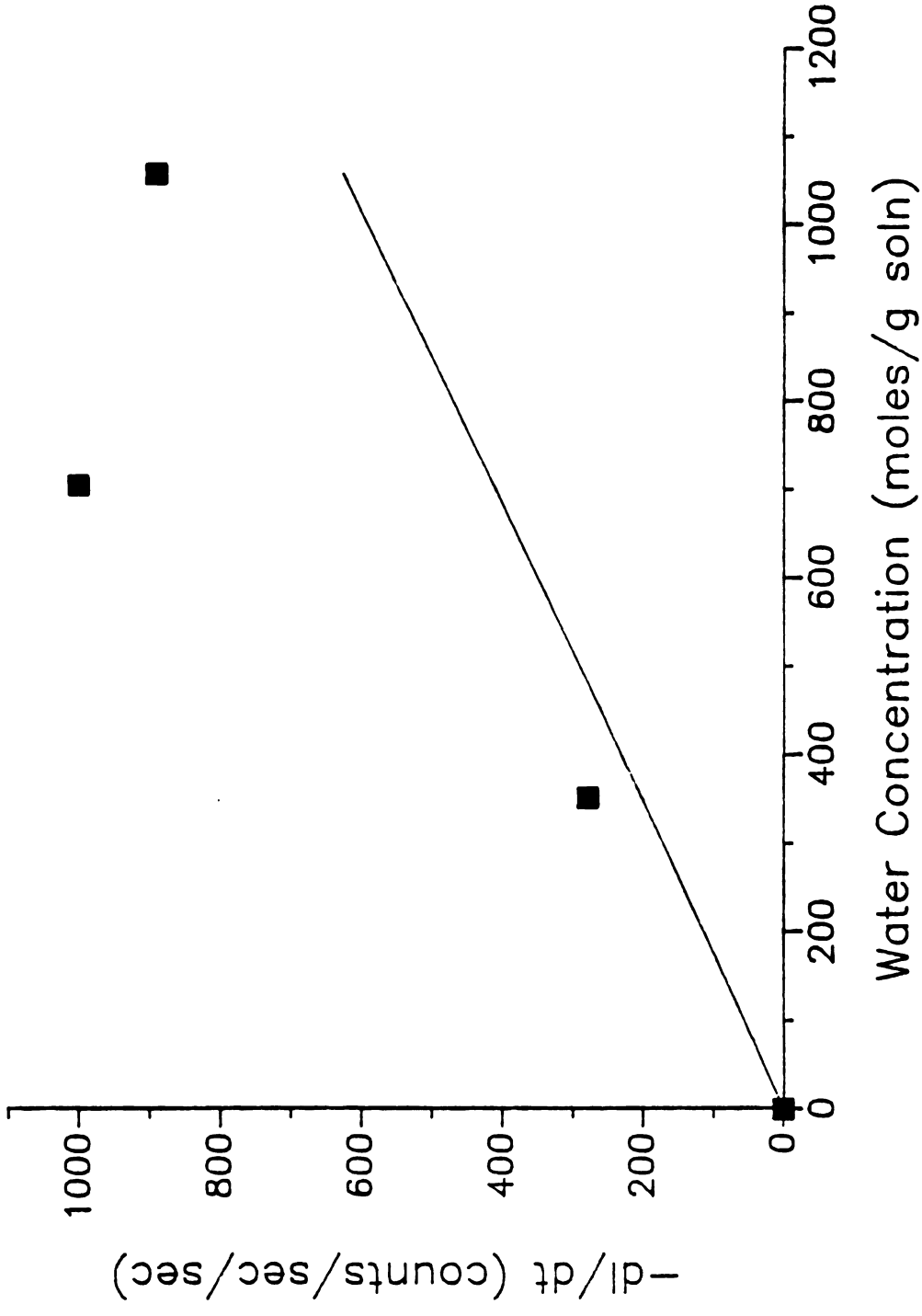

-dI/dt (counts/sec/sec)
1000
800
600
400
200
0
0
200
400
600
800
1000
1200
Water Concentration (moles/g soln)

Figure 21

CONCLUSIONS

The first paper of this presentation, "Raman Spectroscopic Studies of Titanium Alkoxides Using UV Excitation," showed:

1. Fluorescence can be a problem with taking Raman Spectra of titanium alkoxides and that this can be avoided by using uv excitation.
2. A resonance effect is obtained when the excitation wavelength approaches the uv.
3. UV excitation is a good choice of excitation wavelength for the study of titanium alkoxides.

The second paper showed:

4. Raman band associated with the carbon-oxygen symmetric stretch in the alkoxide (1032 cm^{-1}) decreases with increasing alkoxide concentration and with increasing water:alkoxide ratio as the alkoxide is hydrolyzing.
5. Hydrolysis was less complete at the residence time observed (91 msec) for longer alkoxy group lengths.
6. No decrease in intensity of the band studied during the hydrolysis of titanium tetraisobutoxide was observed.
7. An asymmetry exists in the 1032 cm^{-1} band in both the reacting and unreacting solutions.
8. Results of curvefitting indicate a band located at 1011

cm^{-1} is responsible for the observed asymmetry.

9. The 1011 cm^{-1} band increases in intensity in the presence of water, and at the residence time studied, reached maxima at different water ratios for differing alkoxide concentrations.

10. The presence of polymerized unreacted alkoxides and partial hydrodrolysis products has been discussed in previous work, and this band may be associated with these species.

11. The intensity of the 1032 cm^{-1} peak did not decrease below 75% of the unreacted intensity. This result, along with the calculated first-order dependence of the rate on water concentration, suggests that hydrolysis of the first ligand was being observed.

12. The initial rate of hydrolysis of the alkoxy ligands as studied herein showed a lower dependence on alkoxide and water concentrations than was obtained when particle formation and growth was studied in previous work. (See reference 20 in the second paper).

13. The ratio of the exponents on alkoxide and water concentrations obtained in this study (1.5) is similiar to that found in an earlier study. These results indicate that the rate of hydrolysis is more dependent on alkoxide concentration than water concentration when both the initial rate and the overall rate (particle formation) are observed.

RECOMMENDATIONS FOR FUTURE STUDIES

1. Raman spectra of freshly distilled alkoxides should be taken to determine the dependence of the 1011 cm^{-1} peak on the degree of polymerization.
2. Studying the 612 cm^{-1} band of the hydrolyzing alkoxides would result in the determination of the percentage of alkoxide atoms which retain the tetrahedral symmetry which exists in completely unhydrolyzed molecules. By observing this band at different residence times, the time which it takes to hydrolyze the first ligand could be determined.
3. A principal coordinate analysis should be done on the proposed structures of the polymers to determine where peaks due to these species would appear in the Raman spectra.
4. Polarization studies could be done to see if better resolution between the 1032 and 1011 cm^{-1} peaks can be obtained.
5. If lower wavelength excitation could be attained, the preresonance of the 1032 cm^{-1} peak could be exploited more fully, resulting in a better signal to noise ratio.
6. Improvements in the rate expressions could be obtained by using both faster and slightly slower velocities in the mixing cell (being careful to test for adequate mixing).

7. Longer residence times could be obtained at the same velocity if a mixing cell with a longer reaction chamber is constructed.

8. Testing of hydrolysis rates using other concentrations of TET and TiBT would enable the calculation of exponents on alkoxide concentrations in the rate expressions for these reactions.

APPENDIX

LIST OF FIGURES

Figure A16. Raman Spectrum of 10% TiPT in iPrOH 91 msec after mixing with iPrOH solution of R = 6

Figure A17. Raman Spectrum of 8.5% TET in iPrOH 91 msec after mixing with iPrOH solution of R = 0

Figure A18. Raman Spectrum of 8.5% TET in iPrOH 91 msec after mixing with iPrOH solution of R = 2

Figure A19. Raman Spectrum of 8.5% TET in iPrOH 91 msec after mixing with iPrOH solution of R = 4

Figure A20. Raman Spectrum of 8.5% TiBT in iPrOH 91 msec after mixing with iPrOH solution of R = 6

Figure A21. Raman Spectrum of 8.5% TiBT in iPrOH 91 msec after mixing with iPrOH solution of R = 0

Figure A22. Raman Spectrum of 8.5% TiBT in iPrOH 91 msec after mixing with iPrOH solution of R = 2

Figure A23. Raman Spectrum of 8.5% TiBT in iPrOH 91 msec after mixing with iPrOH solution of R = 4

Figure A24. Raman Spectrum of 8.5% TiBT in iPrOH 91 msec after mixing with iPrOH solution of R = 6

Figure A1

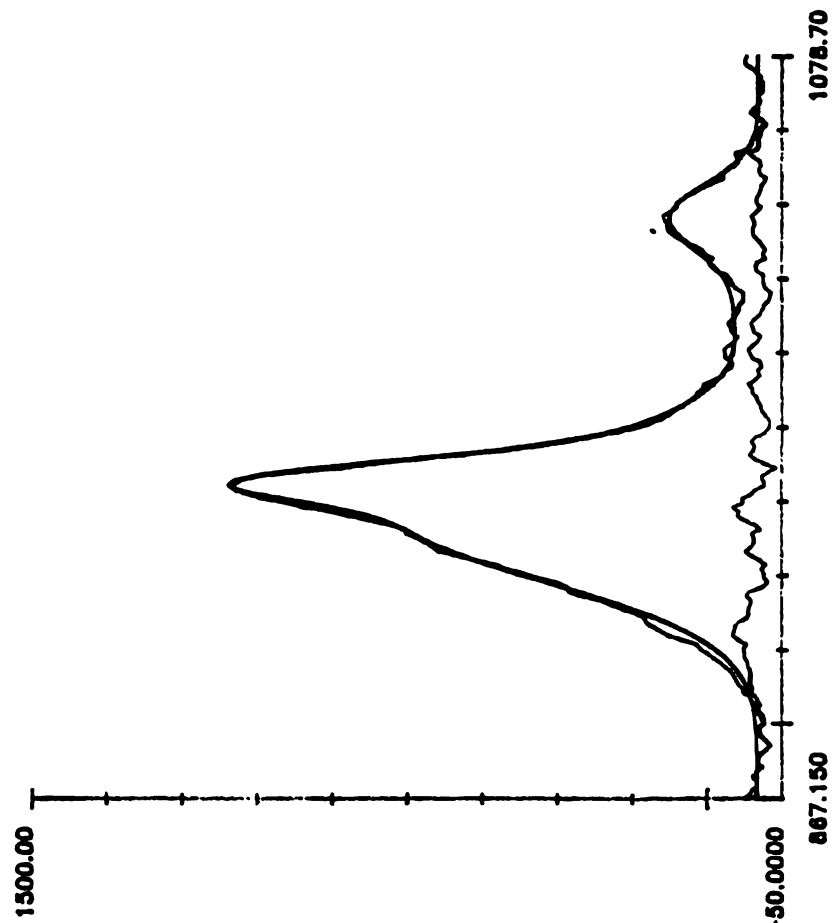
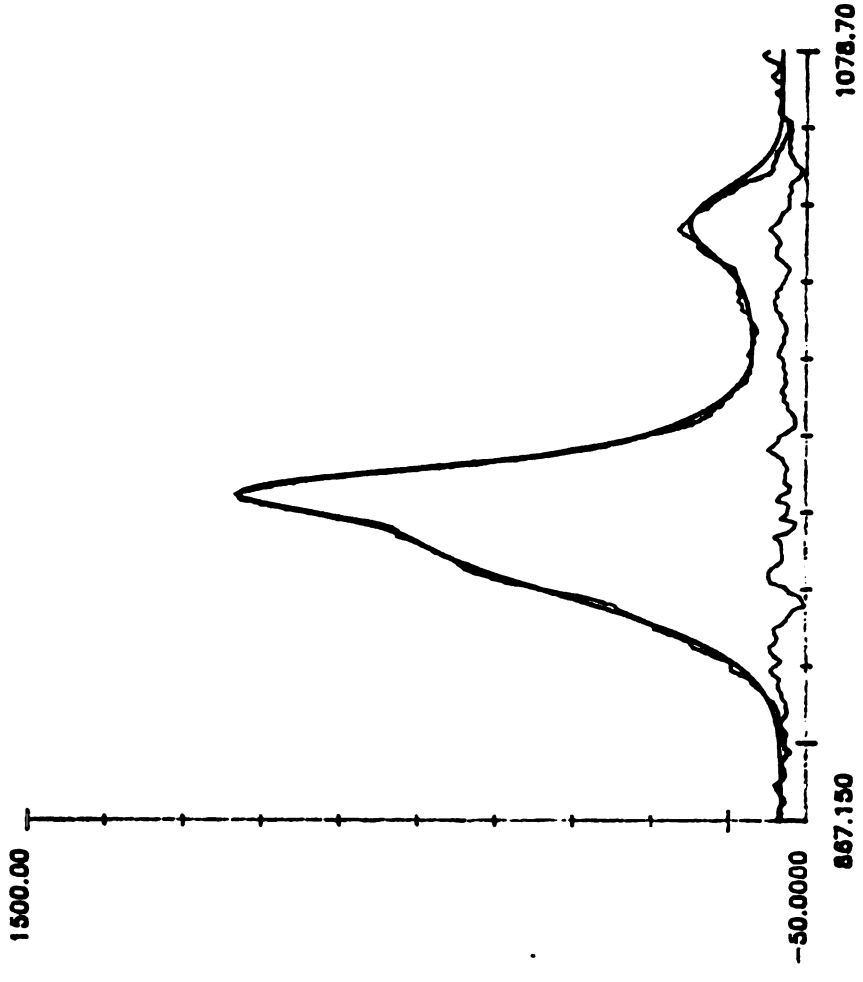


Figure A2



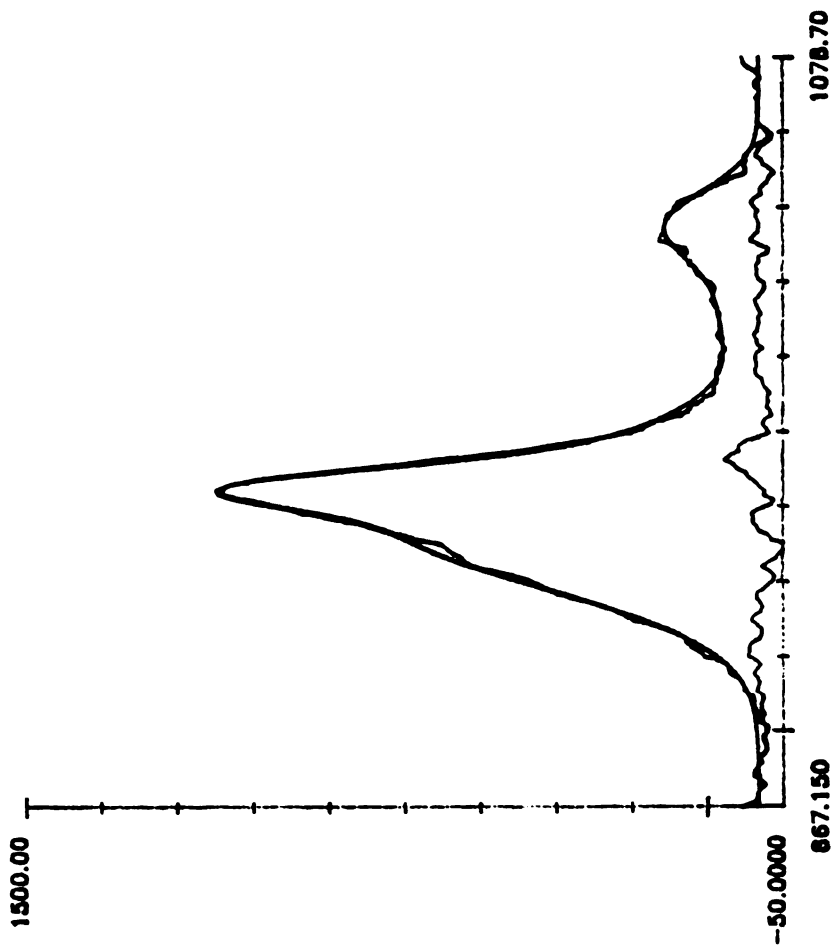
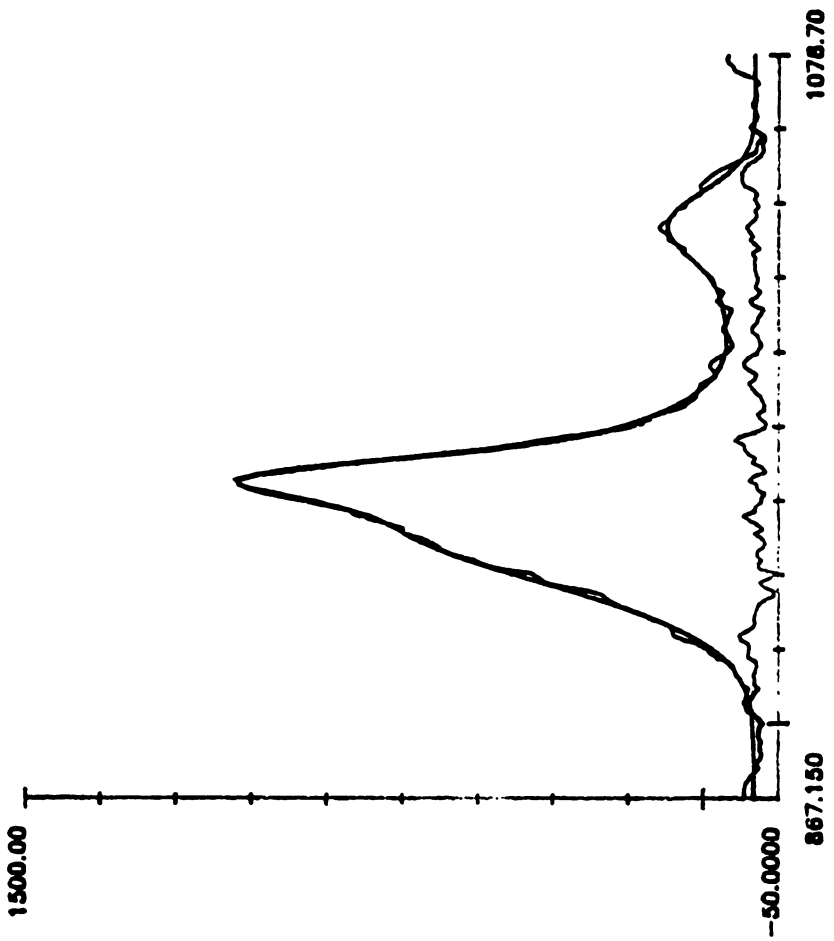


Figure A3

Figure A4



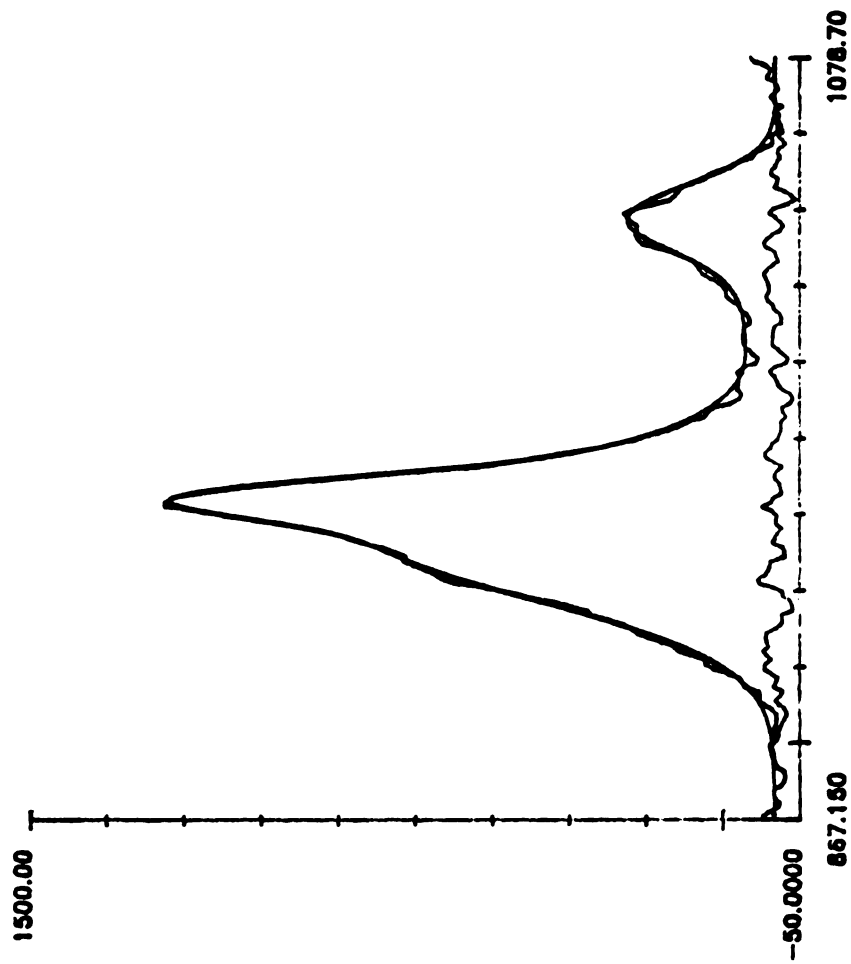


Figure A5

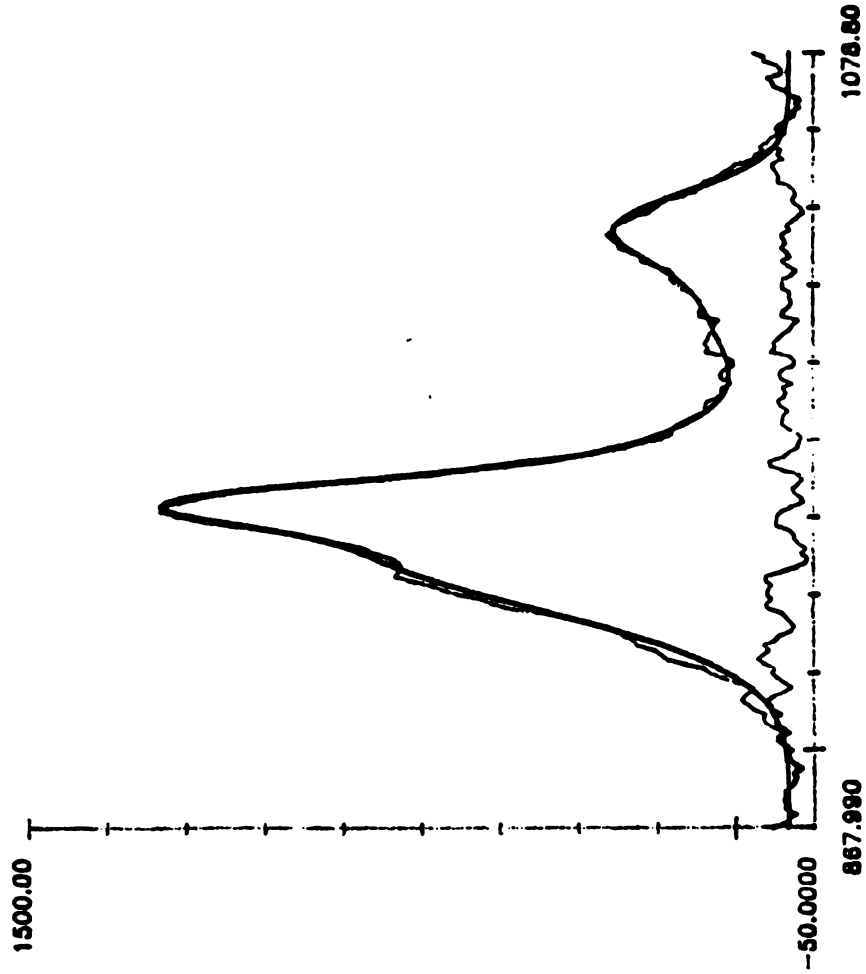


Figure A6

Figure A7

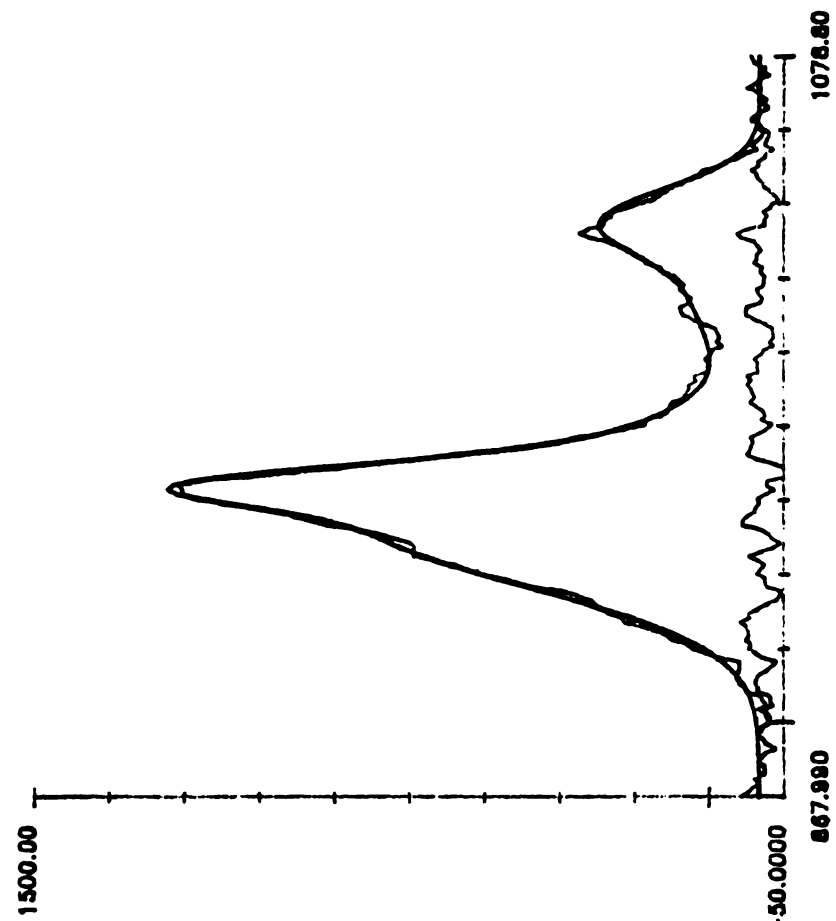
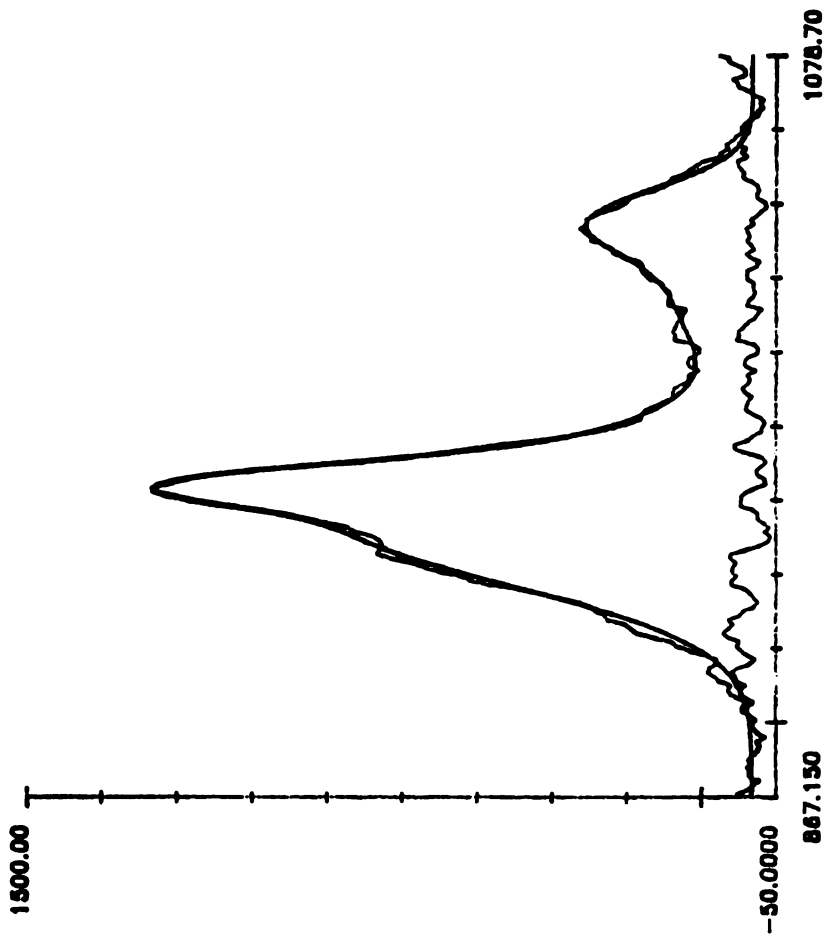


Figure A8



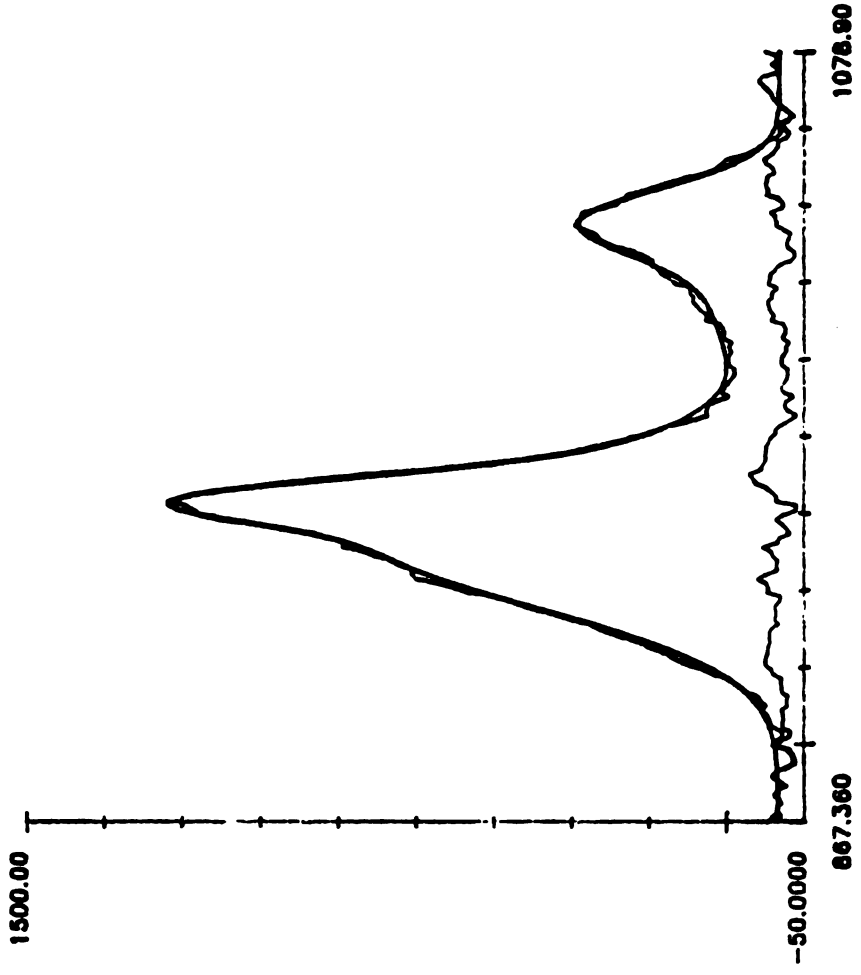


Figure A9

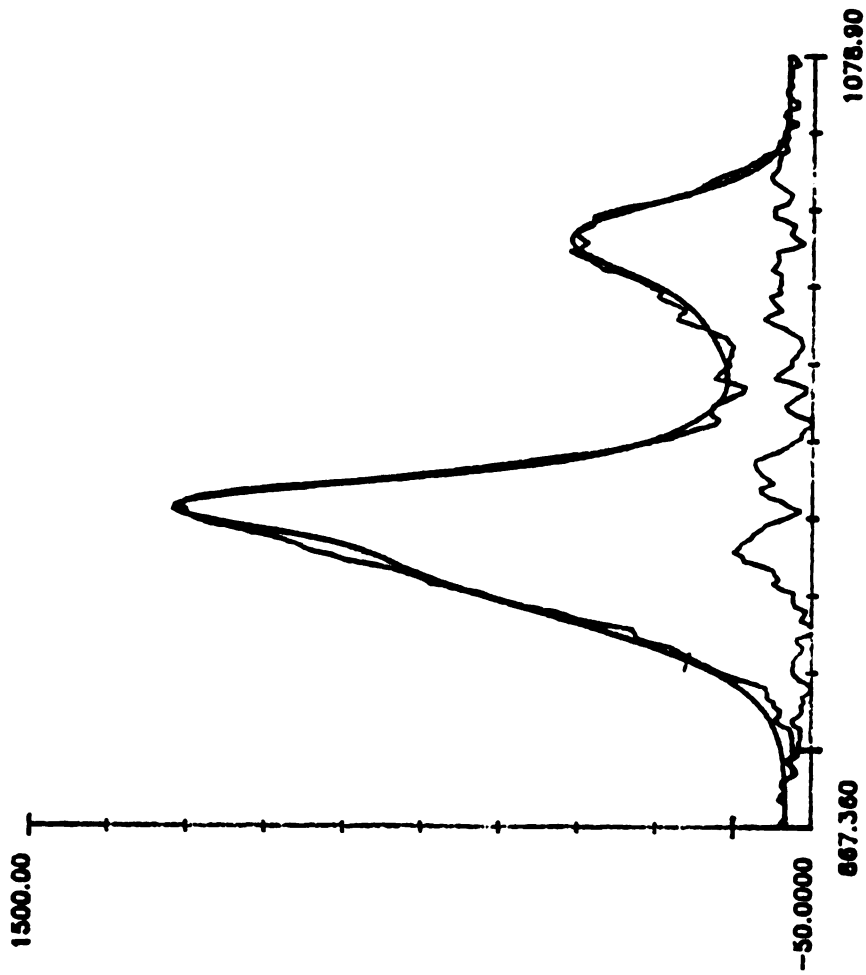


Figure A10

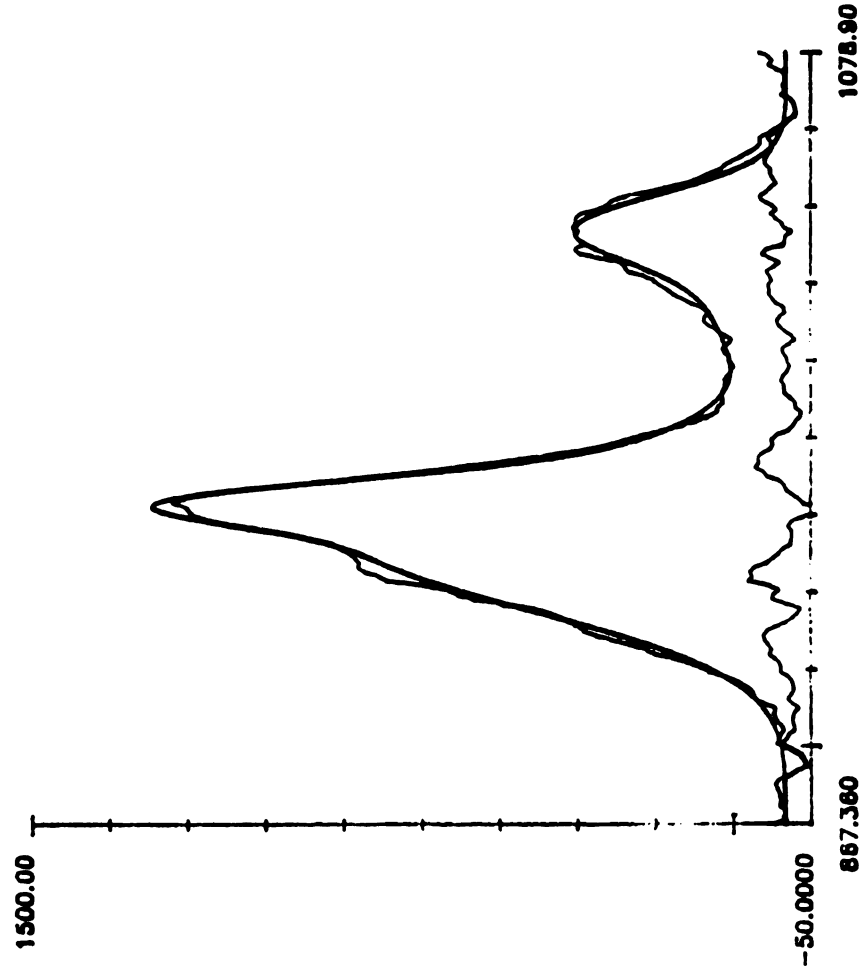


Figure A11

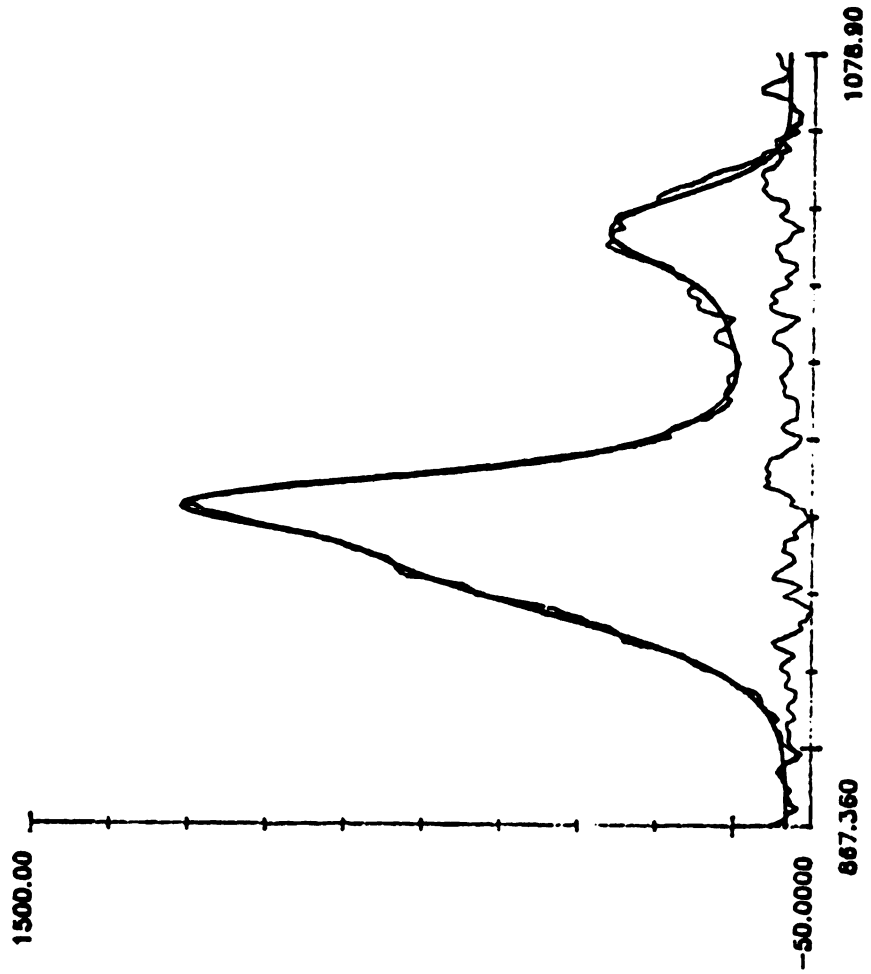
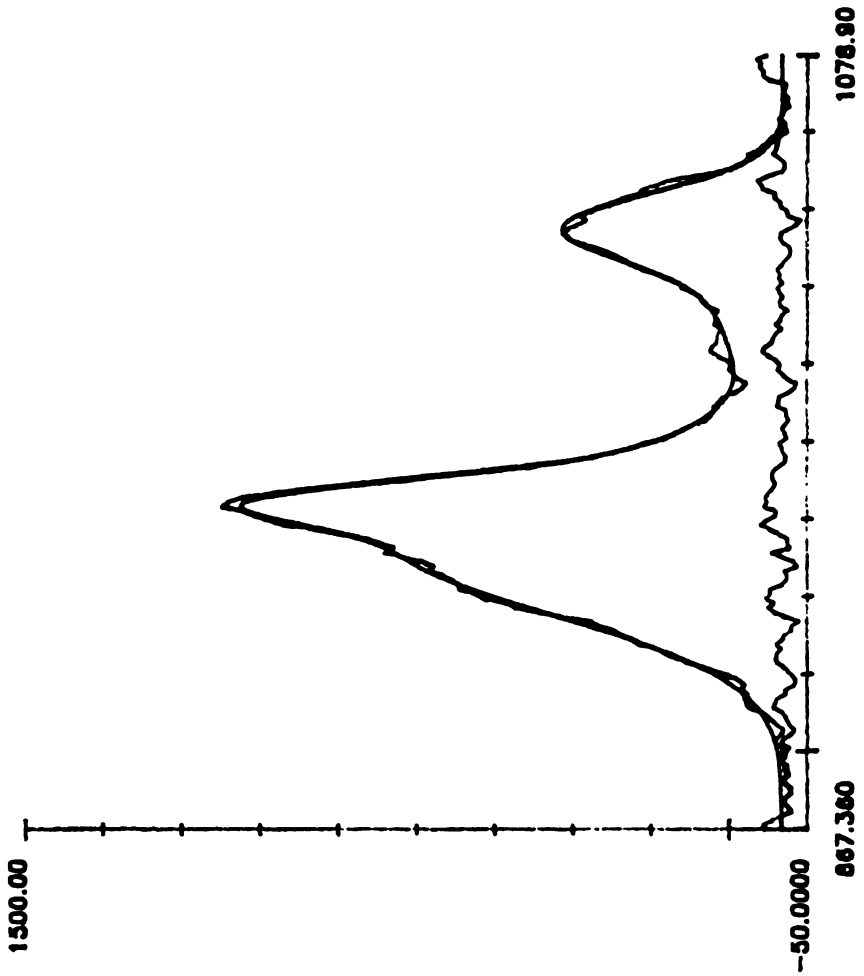


Figure A12

Figure A13



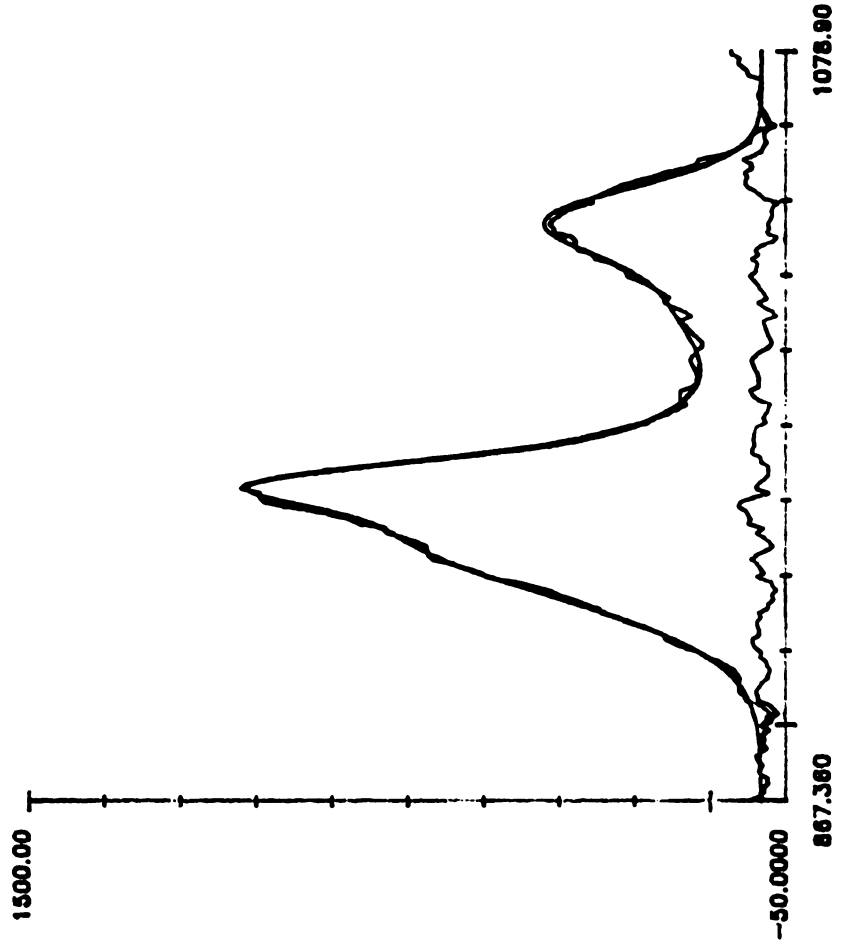


Figure A14

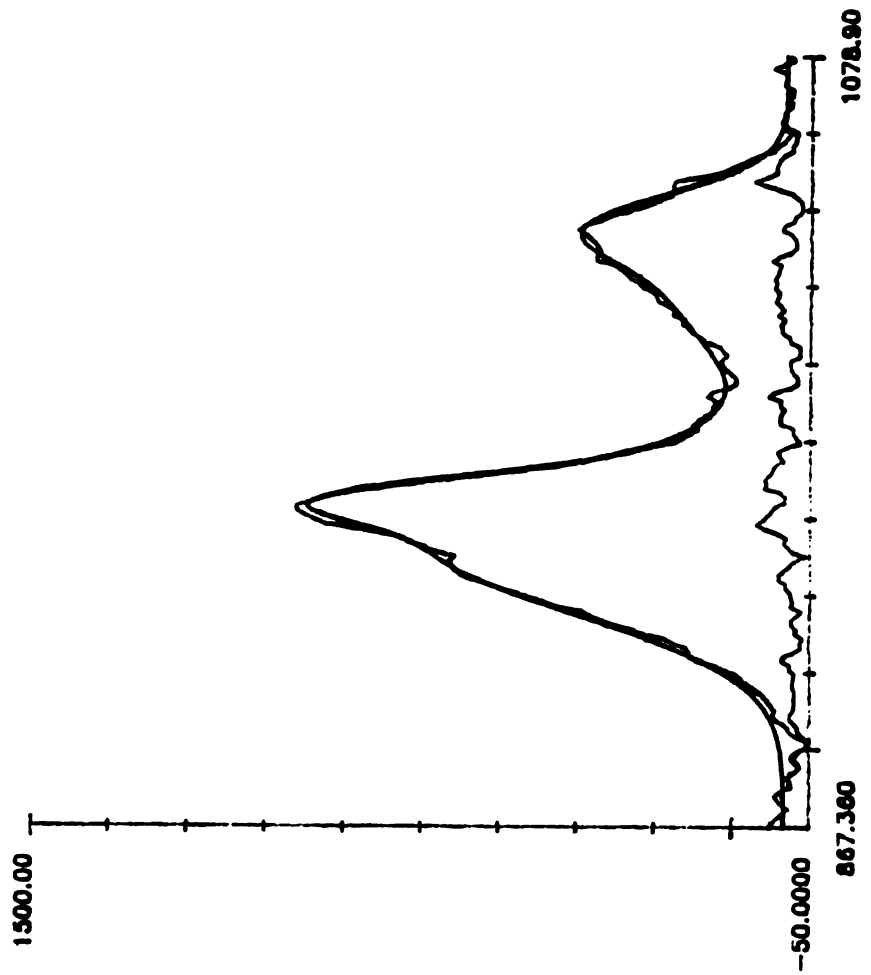


Figure A15

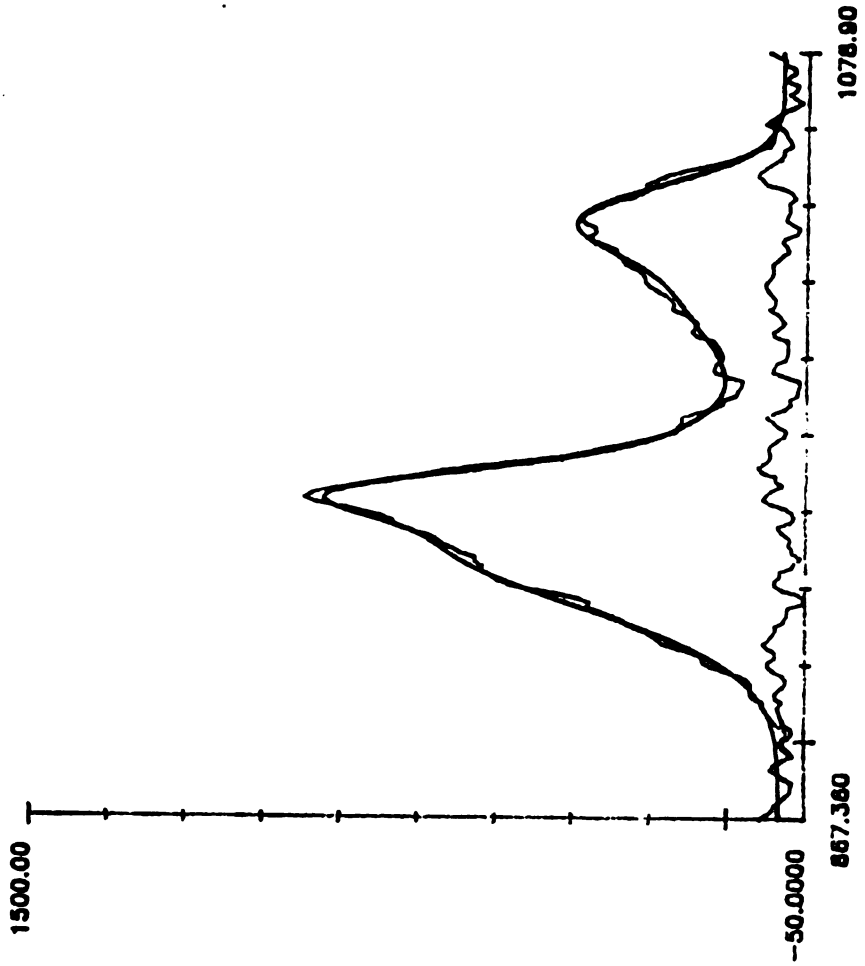


Figure A16

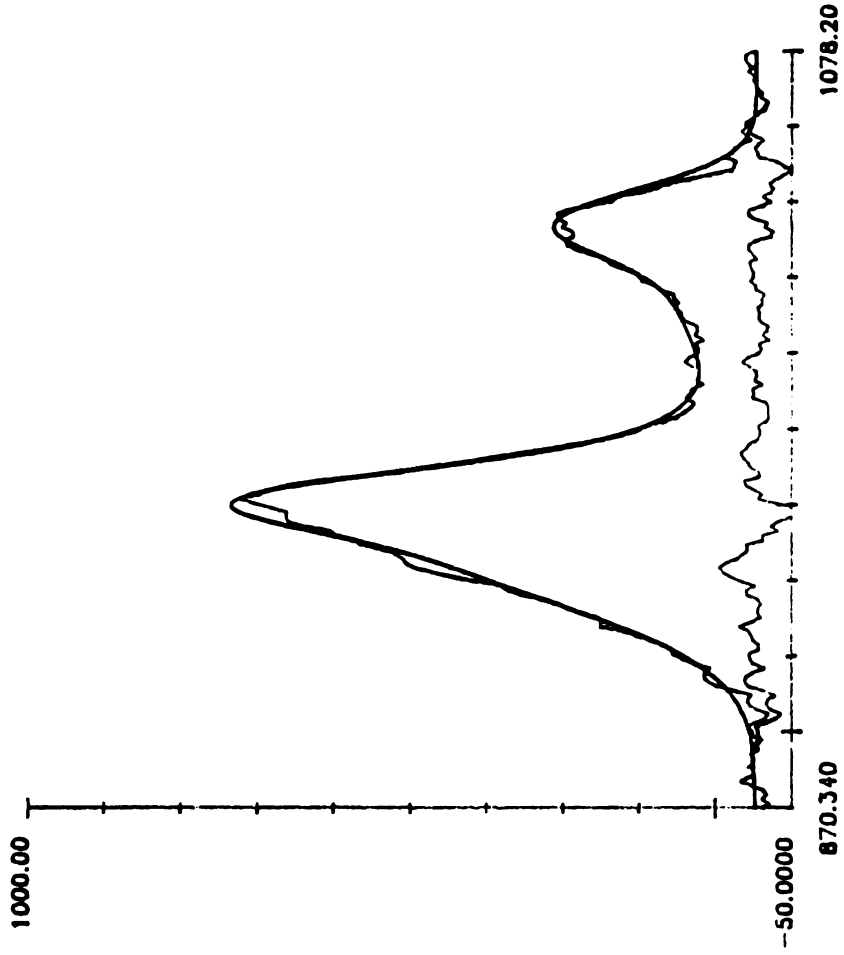
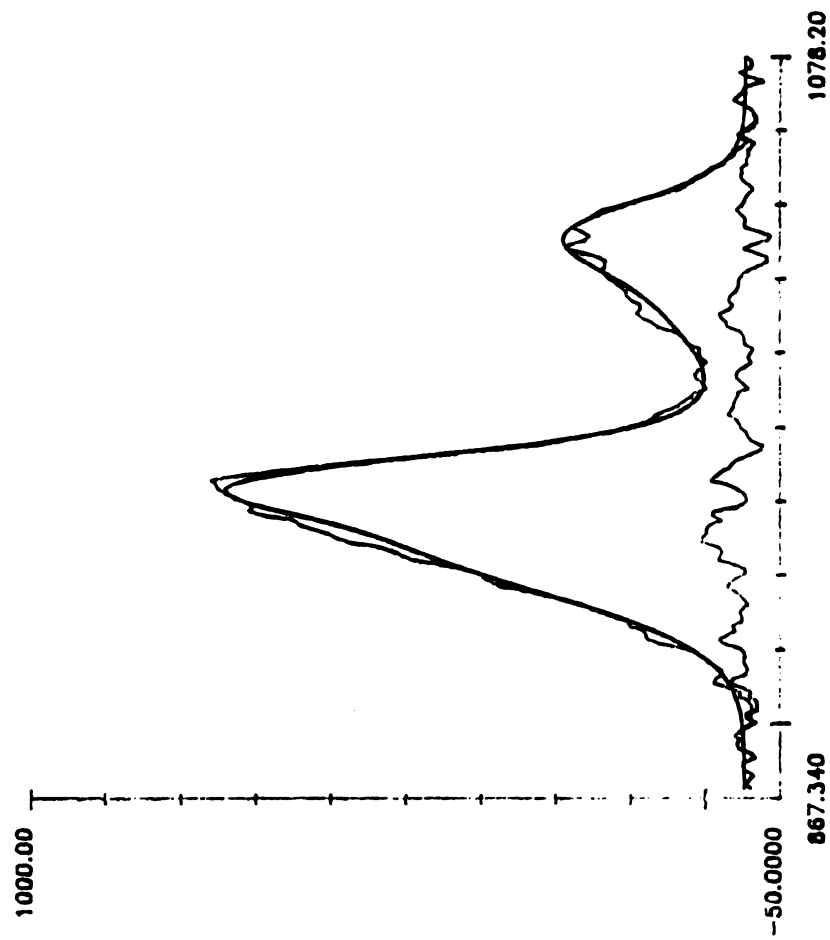


Figure A17

Figure A18



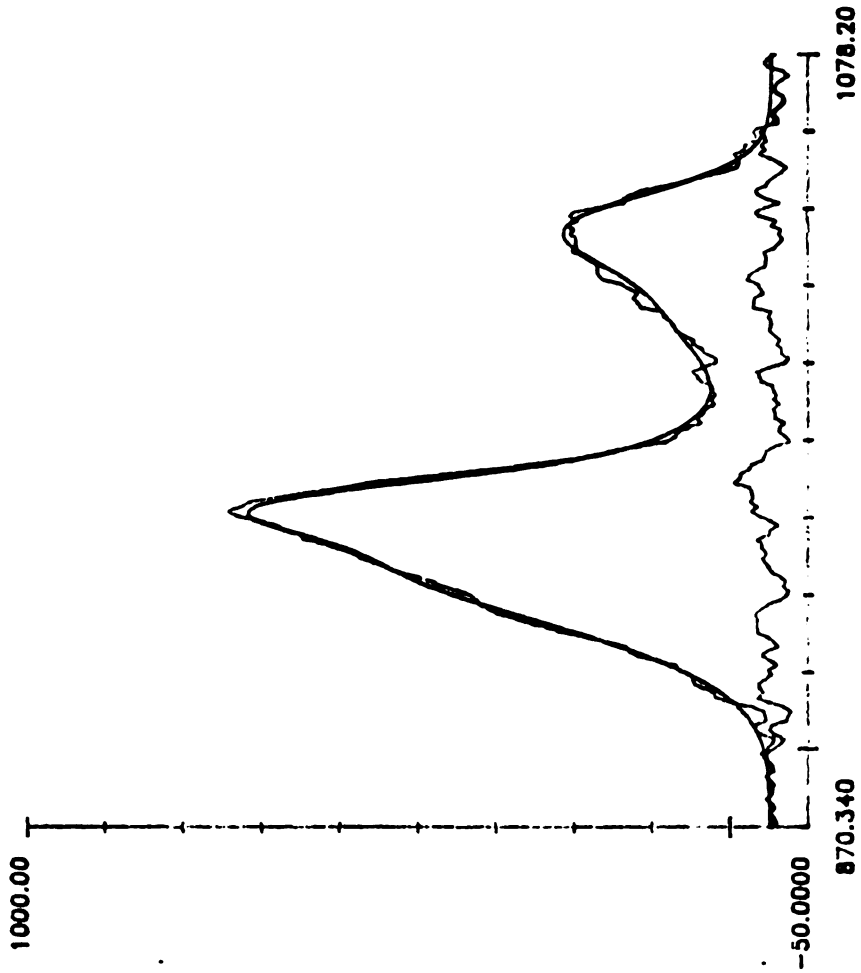
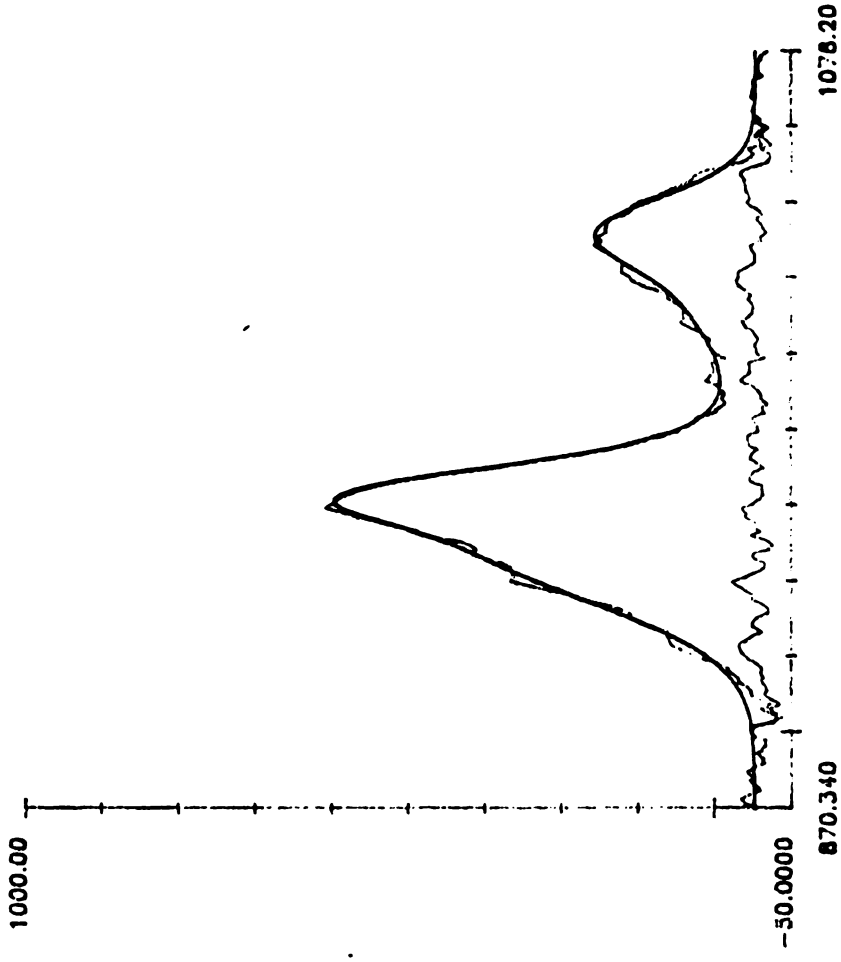


Figure A19

Figure A20



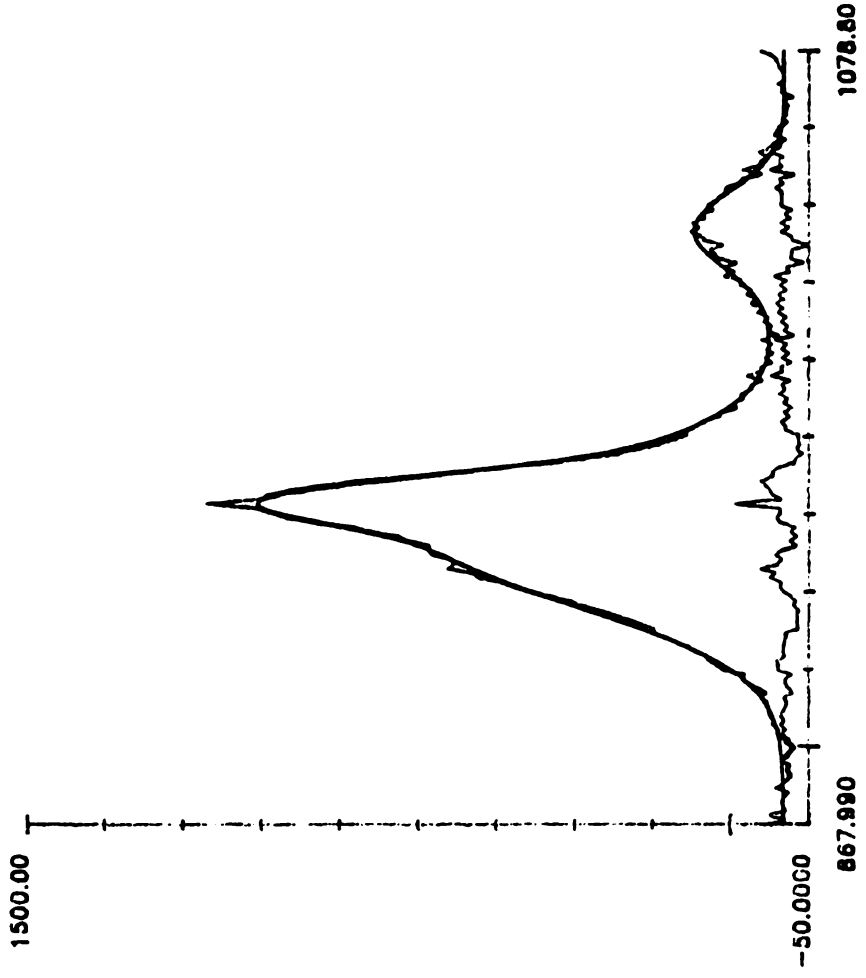


Figure A21

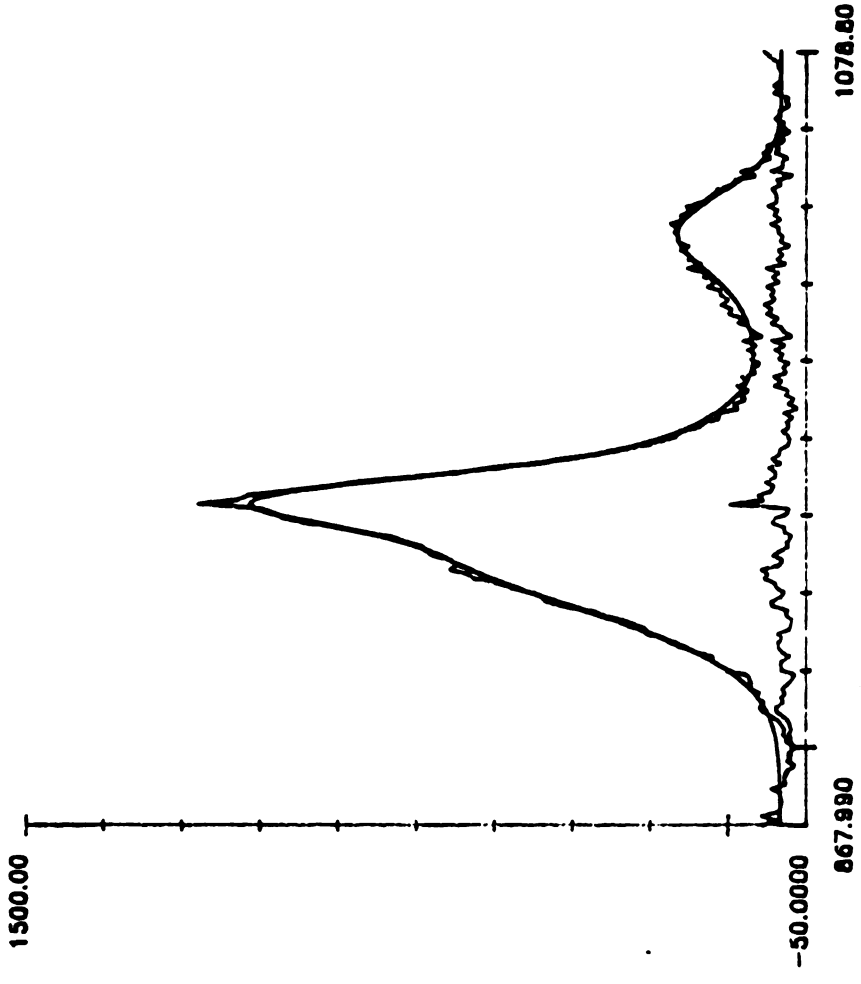


Figure A22

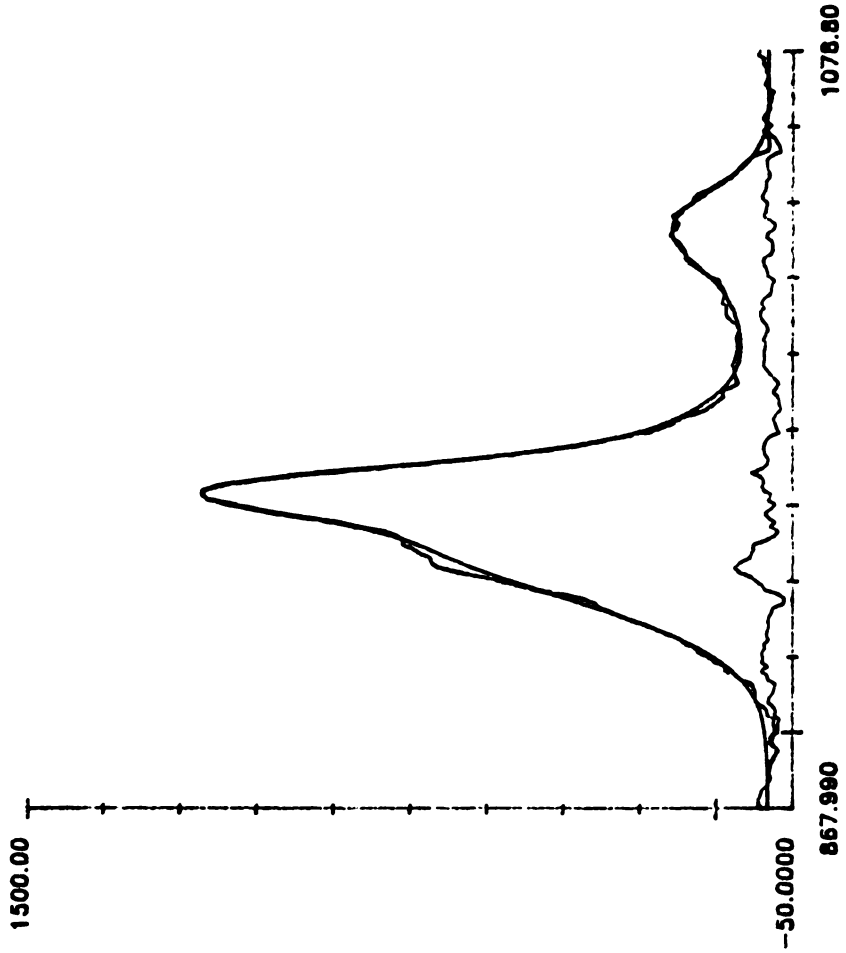


Figure A23

Figure A24