MOLECULAR AND INTRAMOLECULAR RELAXATION PROCESSES
OF
SMALL MOLECULES

A Thesis Submitted By
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ABSTRACT

The dielectric relaxation method was used to determine the activation parameters of some ethane derivatives and simple amides. A General Radio 1615-A capacitance bridge was utilized to obtain the energy barriers of the relaxation processes associated with the polar solute of a compound dissolved in the atactic polystyrene maxtrix. The experimental data obtained from the measurement of the bridge was fed into the computer by means of a series of APL language programmes and the results of the analysis came as an output.

This thesis investigates mainly the molecular and intramolecular relaxation processes of some simple amides and some simple ethane derivatives. Since these compounds are small in size, the energy barrier of the corresponding relaxation processes were compared. The molecular relaxation process of ethane derivatives was used as a reference for the investigation of the molecular relaxation process of simple amides of similar size. Similarly, the relaxation parameters of intramolecular process of the simple amides was compared with those of the simple ethane derivatives.

CONTENTS

CHAPTER I

GENERAL INTRODUCTION

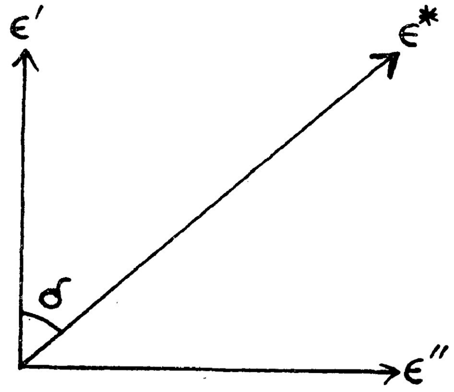
BASIC THEORY

When one investigates the properties of certain capacitors, it leads to the concept of dielectric constant which is better described by the term dielectric permittivity. When alternating current is switched on, the capacitor will have alternating positive charges and negative charges, and these changes depend on the frequency of the alternating current. Dielectric constant can be defined as the ratio of the field strength in vacuum to that in the material for the same amount of charges in the capacitor. It can also be defined as the ratio of the capacitance of a condenser with material between the parallel conducting plates to the capacitance of the same condenser in vacuum. Certain phenomenon can be observed by increasing the frequency of the applied voltage. At first the dielectric material inside the condenser is experiencing a static field and as the frequency increases up to the microwave region, the orientation of dipoles in the field begins to lag behind the oscillations of the applied voltage. This phase difference between the applied voltage and reorientation of the dipoles causes a dissipation of energy as Joule heating, and this is measured by the dielectric loss (ε'') defined below:

$$\varepsilon'' = \varepsilon' \tan\delta \qquad (1)$$

where ε' is the real part of the complex term of the dielectric constant and $\tan\delta$ is the loss tangent or the energy dissipation factor. Equation (2) represents the complex quantity of the dielectric constant in this frequency region.

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \quad \text{where } j = (-1)^{\frac{1}{2}} \tag{2}$$



The above diagram simply illustrates the relationship between ε' and ε'' in the complex quantity of dielectric constant.

The static dielectric constant ε_0 of the material does not vary as much when the frequency of the applied voltage between the condenser plates is very low. There is no lag behind between the applied voltage and the orientation of the polar molecules in a range of low frequencies and this corresponds to no loss of energy in the system, and hence the electric energy is transmitted without loss.

The total polarization of a polar molecule can be described by the Clausius-Mossotti-Debye theories$^{(1)}$ as follow:

$$P_{total} = P_A + P_0 + P_E = \frac{4\pi N}{3}\left(\alpha_E + \alpha_A + \frac{\mu^2}{3KT}\right)$$

$$= \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2}\left(\frac{M}{d}\right) \qquad (3)$$

where

μ ------ electric dipole moment

K ------ Boltzmann constant

α ------ polarizability

N ------ Avogadro's number

T ------ absolute temperature

M ------ gram molecular weight

d ------ density of material

ε_0 ----- static dielectric constant

There are generally three different processes which contribute to the polarization which is described by the above Clausius-Mosotti-Debye equation.

(i) Electronic polarization, P_E, (or deformation of electron cloud) which means the electron density is drawn away from the nuclei.

(ii) Atomic polarization, P_A, (or displacement of ions) due to changes in the mean position of the (δ+) atoms and the (δ-) atoms or due to the change of the relative angles of polar links.

(iii) Orientation polarization, P_0, (or reorientation of electric dipoles) of a permanent dipole moment of a polar molecule. In order to achieve minimum energy, the dipole moment tends to align itself along the field.

Although the above three processes are described by the Clausius-Mossotti-theories, the equation of these theories applying to polar liquids due to the fact that Lorentz field used as a measure of the local field in a dipolar dielectric is not valid.

On the assumption that there exists a cavity which is a sphere in a homogeneous medium, Onsager$^{(2)}$ pushed forward an equation which considers a polarizable rigid point dipole of moment $\vec{m}$ at the centre of a spherical cavity of molecular dimension in a continuous medium of static permittivity ε_o.

$$\frac{(\varepsilon_o - \varepsilon_\infty)(2\varepsilon_o + \varepsilon_\infty)}{\varepsilon_o\ (\varepsilon_\infty + 2)^2}\ \frac{M}{d} = \frac{4\pi N\mu^2}{9KT} \qquad (4)$$

where ε_∞ is the dielectric constant at very high frequency. The above equation only applies to materials which have no strong local forces. The orientation polarization vanishes at high frequency since it cannot follow the change in the electric field. Hence equation (3) becomes:

$$\frac{(\varepsilon_\infty - 1)\ M}{(\varepsilon_\infty + 2)\ d} = \frac{4\pi N(\alpha_E + \alpha_A)}{3} \qquad (5)$$

From (3) and (5), Debye equation follows:

$$\frac{3(\varepsilon_o - \varepsilon_\infty)\ M}{(\varepsilon_o + 2)(\varepsilon_\infty + 2)\ \ d} = \frac{4\pi N\mu^2}{9KT} \qquad (6)$$

From (4) and (6), we can obtain a relationship of dipole moment between the Onsager and the Debye equation as follows:

$$\frac{\mu^2(\text{Onsager})}{\mu^2(\text{Debye})} = \frac{2(\varepsilon_o + \varepsilon_\infty)(\varepsilon_o + 2)}{3\varepsilon_o(\varepsilon_\infty + 2)} = i \qquad (7)$$

For gases at low pressure, ε_o and ε_∞ are practically identical and thus the Onsager equation is reduced to the Debye equation.

Since the molecular polarization can be described by the three mentioned polarization processes, the orientation polarization process will be completely undetectable if the frequency is increased too much. At this high frequency e.g. in the microwave region, it will no longer be able to follow the reversal of the field. This time lag in attaining of equilibrium of molecular orientation leads to a decrease in the orientation polarizability. When the frequency is increased further, the contributions to the polarization of the polar molecule are simply atomic and electronic polarization. When the frequency is still higher than this, the atomic nuclei cannot follow the field and the contribution of polarization is solely electronic polarization.

The orientation polarization process requires 10^{-11} to 10^{-12}s, depending on the frictional resistance of the medium. If the viscosity of the medium is increased (e.g. using polystyrene as a matrix), the solute molecule in the medium cannot respond as fast as the change in electric field in the medium, and the time required for this will be longer. Atomic polarization requires a time of 10^{-12} to 10^{-14}s which corresponds to the infrared region while electronic polarization requires a time of 10^{-15}s which corresponds to the ultraviolet region.

Another parameter which describes the relaxation time is the relaxation time, τ, of a particular dielectric relaxation process, which is defined as the time needed for the exponential decay to 1/e of the orginal value of the polarization.

$$P(t) = P_0 \exp(-t/\tau) \qquad (8)$$

where P_0 ----- specific polarization in a static field

$P(t)$ --- specific polarization at time t in an electromagnetic field

The Debye equation relates ε' and ε'' with the relaxation time (t) which is assumed to be discrete in the region of dielectric absorption.

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{1 + j\omega\tau} \qquad (9)$$

where ω is the angular frequency. The above equation can be resolved into a real part and an imaginary part. The real part has:

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{1 + \omega^2\tau^2} \qquad (10)$$

and the imaginary part has:

$$\varepsilon'' = \frac{(\varepsilon_o - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \qquad (11)$$

From the above two equations, one can arrive at:

$$\left\{\varepsilon' - \frac{\varepsilon_o + \varepsilon_\infty}{2}\right\}^2 + (\varepsilon'')^2 = \left\{\frac{\varepsilon_o - \varepsilon_\infty}{2}\right\}^2 \qquad (12)$$

This is an equation of a circle and can be represented in an Argand diagram as a semi-circle of radius $(\varepsilon_o - \varepsilon_\infty)/2$ with the centre lying on the abscissa. This is called the Cole-Cole plot.$^{(3)}$ This plot will have the form described above when there is only one discrete relaxation time. This Cole and Cole plot should also consider the case of a symmetrical distribution about the mean relaxation time and thus a new parameter (α) is introduced:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{1 + (j\omega\tau_o)^{1-\alpha}} \qquad (13)$$

where α ----- distrubution parameter (values between 0 to 1).

When $\alpha = 0$, one can obtain the Debye equation. From equation (13), one can separate into real and imaginary parts:

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_o-\varepsilon_\infty)\{1+(\omega\tau_o)^{1-\alpha}\sin(\alpha\pi/2)\}}{1 + 2(\omega\tau_o)^{1-\alpha}\sin(\alpha\pi/2)+(\omega\tau_o)^{2(1-\alpha)}} \qquad (14)$$

$$\varepsilon'' = \frac{(\varepsilon_o-\varepsilon_\infty)(\omega\tau_o)^{1-\alpha}\cos(\alpha\pi/2)}{1 + 2(\omega\tau_o)^{1-\alpha}\sin(\alpha\pi/2)+(\omega\tau_o)^{2(1-\alpha)}} \qquad (15)$$

In the case where there is no discrete relaxation time, the centre of the semi-circle of the Cole-Cole plot lies below the abscissa. This type of relaxation process is called the non-Debye type of absorption.

Fuoss and Kirkwood[4] pushed forward a generalized acceptable form of equation (11) which deals with polar solutes or polar end groups of polymers in a continuous range of relaxation time.

$$\varepsilon'' = \varepsilon''_{max} \operatorname{sech}(\beta \ln(\omega/\omega_{max})) \qquad (16)$$

where β is a significant empirical parameter whose inverse relates to the width of the absorption relative to the Debye process (β=1).

$$\tau = 1/\omega_{max} = 1/2\pi\nu_{max}$$

where ν_{max} is the frequency at which the maximum loss factor, ε''_{max} is observed.

From the Fuoss and Kirkwood analysis, ν_{max} can be found from the equation below:

$$\cosh^{-1} \frac{(\varepsilon''_{max})}{\varepsilon''} = 2.303\beta\ (\log\nu_{max} - \log f) \qquad (17)$$

Poley[5] developed an equation which relates β from Fuoss-Kirkwood equation and from Cole-Cole equation.

$$\beta(2)^{\frac{1}{2}} = (1-\alpha)/\cos((1-\alpha)\pi/4) \qquad (18)$$

Molecules which contain a rotable group can have both intramolecular and molecular relaxation processes. The dielectric absorption process can be characterised by two discrete relaxation times which correspond to molecular and intramolecular rotations. Budó[6] suggested the complex dielectric constant could be represented by the superimposition of overlapping Debye equations for multiple discrete relaxation processes.

The following equation describes the two relaxation time processes as

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_0+\varepsilon_\infty)\left\{\frac{C_1}{1+\omega^2\tau^2_1} + \frac{C_2}{1+\omega^2\tau^2_2}\right\} \qquad (19)$$

$$\varepsilon'' = (\varepsilon_0 - \varepsilon_\infty)\left\{\frac{C_1\omega\tau_1}{1+\omega^2\tau^2_1} + \frac{C_2\omega\tau_2}{1+\omega^2\tau^2_2}\right\} \qquad (20)$$

$$C_1 + C_2 = 1 \qquad (21)$$

where C_1 and C_2 correspond to the weighting factors of the two absorptions of the dielectric relaxation process. Actually the Cole-Cole plot will appear to be almost symmetrical with a small C_1/C_2 ratio. Systems with significant τ_1/τ_2 and C_1/C_2 ratios may have the dielectric absorption separated into two distinct absorption regions.

Since dielectric relaxations are rate processes, the relaxation time is the reciprocal of a mean rate coefficient. This kind of process can be described by the Arrhenius equation.

$$k = \frac{1}{\tau} = A \exp\,(-\Delta H_A/RT)$$

where ΔH_A ----- Arrhenius activation enthalpy per mole. Eyring equation is the more common used form.

$$\tau = \frac{h}{k_B T} \quad \exp\left(\frac{-\Delta S_E}{R} + \frac{\Delta H_E}{RT}\right)$$

where

ΔS_E --- activation entropy

h --- Planck's constant

k_B -- Boltzmann's constant

R --- universal gas constant

T --- absolute temperature

By using Fuoss-Kirkwood analysis and Eyring equation, the ΔH_E value and the ΔS_E value for the relaxation process concerned can be determined. The method of analysing experimental results for the determination of the ΔH_E and the ΔS_E value is shown in Chapter II.

Besides the dynamic approach, one can utilize vibrational spectroscopy which is an indirect method to determine the energy barrier of internal rotation. In Chapter III the V_3 energy barrier of internal rotation from literature based on vibrational spectroscopy, is used as a reference. The V_3 energy barrier term is expressed in the potential energy function of a Fourier series which is shown below:

$$V(\alpha) = \frac{V_1}{2}(1-\cos\alpha) + \frac{V_2}{2}(1-\cos 2\alpha) + \frac{V_3}{2}(1-\cos 3\alpha) + \ldots.$$

For a molecule with a three-fold axis of symmetry, the V_1 and V_2 terms are very insignificant relative to the V_3 term in the above region. Hence, the energy barrier of internal rotation of ethane derivatives described in Chapter III can be adequately represented by the V_3 value.

Grindley, Katritzky and Topsom[7] suggested that the results of the direct and indirect techniques cannot be compared directly since ΔH_E is a complex function of the coefficients V_1, V_2 and V_3 of a Fourier series of cosine terms obtained from vibrational spectroscopy. The results obtained by the two different techniques may be very different from each other especially if the ΔS_E value is not close to zero. Hence the V_3 values quoted in Chapter III are mainly used as a tool to show the trend of internal energy barriers of a number of related compounds.

Since Chapter III has mentioned the energy barrier of internal rotation of two compounds determined by the dielectric method in polystyrene matrix, it should be stressed that the energy barriers obtained for the two compounds correspond to the switch from the isomer with the higher energy to that of the lower as suggested by Tay, Walker and Wyn-Jones[8] for molecules with asymmetrical barriers.

AIM AND OUTLINE

The aim of this thesis is to investigate some relaxation processes related to small molecules. Ethane derivatives and simple amides have been chosen to show relaxation processes such as molecular process and intramolecular relaxation process by dielectirc relaxation method in polystyrene matrix. A General Radio 1615A capacitance bridge has been used to obtain the relaxation parameters of a polar solute which has been dissolved in atactic polystyrene. The polystyrene matrix serves as a medium to retard the rate of molecular relaxation process, and hence the separation of molecular relaxation process and intramolecular relaxation process may be possible. The energy barriers of relaxation processes can be determined by means of relaxation times and subsequent Eyring activation parameters. Some of the energy barriers obtained for certain compounds have been compared with those obtained from literature which involves other techniques such as vibrational spectroscopy, ultrasonic and n.m.r. techniques.

Chapter II describes the experimental procedures of the dielectric method used and also the method of analysis of the experimental data.

Chapter III describes some relaxation processes of simple ethane derivatives and the energy barriers of the relaxation processes involved are being evaluated.

Chapter IV studies some relaxation processes of simple amides and the energy barriers of the relaxation processes involved are being evaluated.

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CHAPTER II

EXPERIMENTAL PROCEDURE
of
DIELECTRIC MEASUREMENTS

EXPERIMENTAL PROCEDURE

The dielectric material which is to be placed between two condenser plates was prepared by dissolving the compound to be studied into the polystyrene matrix. The solute and the matrix together formed a disk which the dielectric absorption can be detected by the General Radio bridge.

At first the solute was placed into the crucible and then polystyrene pellets were added into the crucible. Trans-1,2-dichloroethylene was then poured into the crucible so that the solute could be dissolved. The weight of solute and polystyrene was determined by means of an electronic beam balance beforehand. The crucible which contained the three components was put into an oven at about 100(C). Since the boiling point of trans-1,2-dichloroethylene is 47.7(C), it can be evaporated very fast inside the oven. The crucible inside the oven was checked frequently and a stainless steel spatula was used to stir the solution so that it could be homogeneous. As the mixture kept on evaporating, the contents finally became a thick mass, and when it was dried enough, it was taken out and put into a vacuum oven so that the contents of the crucible could be further dried. The vacuum oven was always under reduced pressure with a temperature at about 85(C). The mass inside the crucible was caused to be expanded under reduced pressure to form a foamy mass, thereby the solvent (which was tran-1,2-dichloroethylene) would be greatly reduced. It was desired that the last trace of dichloroethylene should be evaporated away. Sometimes it was very hard to attain this condition. The weight of the crucible and contents were checked frequently to see if there was any dichloroethylene left behind. The content of dichloroethylene should not exceed 1% of the total weight of the content inside the crucible. The solute concentration of the content was about 3% by weight.

The content of the crucible was then poured into a stainless steel die with polished tungstun carbide faces of two inches diameter and a heating sleeve was placed around it. The content in the die was then heated up by this heating sleeve until it reached a temperature of 110(C). The matrix material melted inside the die was detected via a thermocouple, and when the desired temperature of the die was reached, it was then pressed by applying 5 ton force to the element of the die. Then the heating sleeve was raised and the whole die was let cool by directing a stream of cool air from a fan towards it for about 30 minutes. The die was then disassembled and the disk inside the die was taken out by applying 2 ton force

on the element of the die. The edge of the disk was then smoothed by scraping it with a sharp knife blade, and the thickness of the disk was measured twelve times.
The average value of the thickness was then calculated. The molar concentration of the solute was calculated by the equation:

$$C = \frac{\text{weight of solute used}}{\text{molecular wt. of solute}} \times \frac{\text{weight of disk}}{\text{wt. of polystyrene + solute used}} \times \frac{1}{\text{vol. of disk}}$$

The disk was put in a desiccator for a day before use so that the mechanical strain can be reduced.

GENERAL RADIO CAPACITANCE BRIDGE FOR DIELECTRIC MEASUREMENTS

General Radio Company manufactured the model 1615-A capacitance bridge which allowed the measurement of the capacitance and conductivity of a sample in a range of 50 to 10^5Hz if the model 1310-B sine wave signal generator and model 1232-A tuneable amplifier were used in connection.

The polystyrene matrix disk was clamped between electrodes and the capacitance was measured by the Genral Radio bridge. The

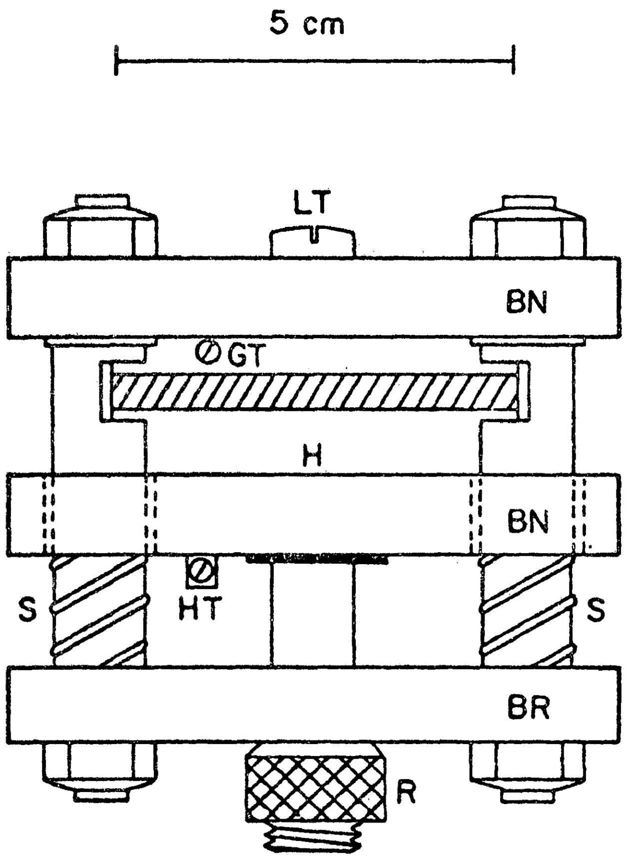

Figure 2.1 : Three-terminal electrode assembly for dielectric measurements on solid disks.

<u>Key</u>:

LT	Low electrode connection terminal
BN	Boron Nitride insulating support plates
GT	Guard ring connection terminal
H	High electrode
HT	High electrode connection terminal
BR	Brass support plate
R	Release nut
S	Steel clamping springs

electrode itself is a three-terminal assembly of outer diameter 2.0" with a low electrode of diameter 1.5" and a guard ring electrode of outer diameter 2.0". Assembly like this reduces any errors caused by fringing of the electric field at the edge of the measurement area. The capacitance measured is solely that between the high and low electrode. Figure 2.1 shows the three-terminal electrode assembly for dielectric measurements on solid disks.

The polystyrene matrix disk was placed between these electrodes and the whole arrangement was being tightened by means of a brass rod screw. This electrode assembly was placed inside an aluminum chamber which was sealed off from the atmosphere for it was air tight. Nitrogen gas was passed through the chamber, so that any trace of moisture, etc. could be removed. This prevented the absorption of moisture by the disk at low temperature. A heating coil of nichrome wire was wrapped around the exterior of the chamber. A container with liquid nitrogen was placed on top of the aluminum chamber to act as the cooling system of the electrode. This cooling system together with the heating system form the device of setting up a thermal equilibrium of the electrodes. A stable temperature must be maintained before any measurement could be taken. The current of the heating system was about 2 amperes while the cooling system was being adjusted by placing paper underneath the nitrogen container. The temperature control was able to detect a temperature difference of +/- 0.1(C).

The General Radio bridge can be used to measure the capacitance(C), conductivity(G), and dissipation factor(D) of the capacitor with the sample between the high and low electrodes. These values were used to measure the dielectric constant and dielectric loss by using the following equations:

$$\varepsilon' = C/C_o \quad (1)$$

$$\varepsilon'' = G/\omega C_o \quad (2)$$

$$\varepsilon'' = \varepsilon'(D x \nu x 10^{-3}) \quad (3)$$

Where D --- Dissipation factor of the system

C --- Capacitance of the system, in units of picofarads

C_o -- Capacitance if sample is replaced by air

G --- Conductivity of the system, in picomhos

$\omega = 2\pi\nu$ = angular frequency of the applied field, in radians/s

C_o can be obtained by measuring the capacitance in the same way except that the sample has to be removed. However, C_o values can be found by using the equation below:

$$C_o = \frac{0.2244A_1}{d_1} \quad (4)$$

where A_1 = effective area of the plates in inch^2

d_1 = spacing of the plates in inches

From equations (1), (2), and (4) we have:

$$\varepsilon' = \frac{Cd_1}{0.2244A_1} \qquad (5)$$

$$\varepsilon'' = \varepsilon' G/\omega C \qquad (6)$$

Equations (3) and (5) were mainly used by the author. In order to obtain accurate dielectric constant values, the value of A_1 was measured periodically to see if the value had changed. This was done by measuring the capacitance of the cell containing a standard quartz disk of diameter 2.0" and the thickness was 0.0538:, which had a dielectric constant of 3.819.

Since the solute was in the polystyrene matrix disk, the readings would be affected by a small amount of contribution of the polystyrene matrix. Hence a pure polystyrene disk was being measured in order to determine the correction factor of the dielectric loss obtained. The dielectric loss contributed by the polystyrene matrix was comparatively small with respect to the dielectric loss of the polar solute.

ANALYSIS OF EXPERIMENTAL DATA

With the data obtained from the General Radio bridge a computerized analysis was carried out. The computer programme was written in the APL language. Fuoss-Kirkwood equation was applied:

$$\cosh^{-1}\left(\frac{\varepsilon''_{max}}{\varepsilon''}\right) = 2.303\beta(\log \nu_{max} - \log\nu)$$

A straight line could be obtained when $\cosh^{-1}\left(\frac{\varepsilon''_{max}}{\varepsilon''}\right)$ was plotted against ln(f). From the slope of this straight line, β can be obtained, and from the slope and intercept, ν_{max} can be obtained. Using standard statistical techniques, the errors in fitting a straight line to a set of graph points can be determined.

The slope and intercept of the calculated straight line was given by the equations below:

$$a = \frac{\sum_{i=1}^{N} (x_i-\overline{x})(y_i-\overline{y})}{\sum_{i=1}^{N} (x_i-\overline{x})^2} \tag{9}$$

$$b = \overline{y} - a\overline{x} \tag{10}$$

where $\overline{x}$ and $\overline{y}$ are the mean values of x and y, respectively.

Statistical variances S_a^2 and S_b^2 of the slope and intercept are given below:

$$S_a^2 = \frac{S_E^2}{\sum_{i=1}^{N} (x_i - \bar{x})^2} \qquad (11)$$

$$S_b^2 = S_E^2 \quad (1/N + \bar{x}^2 / \sum_{i=1}^{N} (x_i - \bar{x}^2))$$

where $S_E^2 = \sum_{i=1}^{N} (y_i(\text{obs}) - y_i(\text{calc}))^2/(N-2)$ (13)

and $y_i(\text{calc}) = ax_i + b$

The confidence intervals for each slope and intercept were given as +/- $t(S_a^2)^{\frac{1}{2}}$ and +/- $t(S_b^2)^{\frac{1}{2}}$ where t is the value obtained from a t-table for the desired degrees of freedom.

The 95% confidence interval was being chosen as the experimental error, i.e. there was a 5% chance that the true value was outside this range.

$$\varepsilon_0 - \varepsilon_\infty = \frac{2\varepsilon''_{max}}{\beta}$$

The above equation was being used in the computer programme of the Fuoss-Kirkwood analysis. From the equation:

$$\beta(2)^{\frac{1}{2}} = (1-\alpha)/\cos((1-\alpha)\pi/4)$$

the relationship between β and α can be found. Thus, the α parameter from the Cole-Cole plot can be found.

Another programme called EINF was used in APL language to find the values of ε_∞ at various temperatures. Equations (14) and (15), with the values of ε' of various frequency at a particular temperature, were fed into the computer: ε_∞ was then automatically calculated with an estimate of error involved.

The dipole moment of the polar solute at a particular temperature can also be calculated through the computer by applying the following Debye and Onsager equations:

$$\mu^2 = \frac{27000\ K_B T(\varepsilon_0 - \varepsilon_\infty)}{4\pi NC(\varepsilon'_m + 2)^2} \qquad (14)$$

$$\mu^2 = \frac{9000\ K_B T\ (2\varepsilon_0 + \varepsilon_\infty)(\varepsilon_0 - \varepsilon_\infty)}{4\pi NC\varepsilon_0\ (\varepsilon_\infty + 2)^2} \qquad (15)$$

where $(\varepsilon_0 - \varepsilon_\infty) = 2\varepsilon''_{max}/\beta$

ε'_m ---- the value of ε' at f_{max} i.e. $(\varepsilon_\infty + \varepsilon_0)/2$

ε_0 ----- the static dielectric constant derived from ε_∞ and equation (2.13).

N ------ the Avogadro's number, $6.02257\times10^{23}\ \frac{\text{molecules}}{\text{mole}}$

C ------ the solute concentration in moles per litre

K_B ----- the Boltzmann constant, 1.39054×10^{-16} erg K^{-1}

T ------ the absolute temperature in K

ε_∞ and μ values were evaluated at a particular temperature for a number of temperatures of the compound studied. In order to obtain the dipole moment at a specific temperature, e.g. 300K, one can utilize Davies and Swain's [2] technique which makes the assumption that the dipole moment is a linear function of temperature, although it does not have a strong theoretical base. However, the calculated result obtained is reasonable. In addition, the variation of ε_0 and ε_∞ with temperature[3] can be interpreted by the equation $\log(\varepsilon) = aT + b$. These extrapolated values of ε_0 and ε_∞ together with equation (14) can be used for the calculation of dipole moments at warmer temperatures. These results usually agree with those of the Davies-Swain technique.

The Eyring rate equation was applied for the calculation of ΔH_E and ΔS_E.

$$\ln(\tau T) = \frac{\Delta H_E}{RT} - \frac{\Delta S_E}{R} - \ln(\frac{h}{K_B}) \qquad (16)$$

A straight line was usually obtained by plotting $\ln(\tau T)$ against $1/T$ if the data obtained were reasonable. ΔH_E can be obtained from the slope and ΔS_E from the intercept. The 95% confidence intervals were chosen to be the standard to see if the points obtained from experimental data fit the straight line. Any experimental data which did not fit this calculated straight line would be deleted by a repeated run of the Eyring programme. ΔH_E value obtained was within 10% error limit usually and it can be accepted as reasonable. ΔS_E values usually had higher values of error. Better values of ΔS_E can be obtained if the data are obtained from a wide range of temperatures.

If the values of the energy barriers obtained are attributed to a molecular relaxation process, these values may probably be different from those of a molecule isolated from others of its own type. The values of energy barriers are thus increased with concentration because the surroundings of a given solute particle will have more solute molecules with more or less the same amount of polymer segment. Since the concentration used in the study of some simple amides and simple ethane derivatives is less than 10%, the effect is not very significant. One can expect still less effect if the energy barrier values obtained are due to intramolecular relaxation process.

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CHAPTER III

DIELECTRIC RELAXATION
of
SOME DERIVATIVES OF ETHANE

3.1 Introduction

Many of the derivatives of ethane have been studied by previous scientists, using a variety of techniques such as n.m.r., i.r., Raman, ultrasonic, etc. There has been quite a lot of controversy about the factors influencing the energy barrier of internal rotations and simple rotation. Some of the values for some compounds obtained by one technique would sometimes differ from other values of the same compounds obtained from other techniques. Even in the simple compound such as ethane itself, the values obtained cover a wide range.[1,2] Table 3.5 shows the variation of energy barrier when hydrogen atoms are displaced by fluorine atom. It would be anticipated that the energy barrier to internal rotation would vary according to the number of fluorine substituents in ethane. However, a consistency for an increase in energy barrier when the ethane was more heavily substituted was not found. From these results alone, it could have established that no regular trend could be related to the amount of substitution. This conclusion was contradicted by the results obtained for the internal rotational energy barrier of chloro-substituted compounds as shown in table 3.6. From these results clearly the energy barrier is dependent on the extent of substitution.

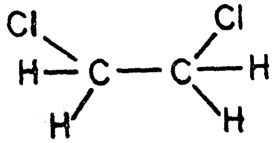
In order to examine more closely the steric hindrance affecting the internal rotational energy barrier, ethane derivatives of different substituents should be compared. Table 3.7 illustrates that the energy barrier of mono-substituted ethane does not increase according to the trend: F < Cl < Br < I. It can be argued that simple steric effect or a combination of steric effect, electrostatic effect and electronegativity cannot successfully explain the irregularity in the trend. As shown in table 3.7 the maximum barrier appears at the chlorine and iodine compound. Ward[3] examined some CF_3 top molecules of the CF_3CH_2X frame, and he found out that the energy barriers of internal rotation has a maximum in CF_3CH_2Br instead of the chloride of the CH_3CH_2X frame of the CH_3 top molecules, where X represents either F, Cl, Br, or I. He suggested that steric effects alone or in combination with polarizability cannot fully account for the behaviour of the trend. However, the CF_3 top molecules with a CF_3CF_2X frame somehow show an increase in energy barrier for the internal rotation of the molecule from F to I as shown in table 3.8. This is possibly due to, at least partially, the size of the substituents with iodine as the largest of the four. The compounds shown in table 3.8 have all their hydrogen atoms replaced by halogens and hence the substituents seem crowded together, thereby the steric factor plays a dominant role. Table 3.9 shows a similar trend for the energy barrier of internal rotations as the size of the substituents increases. CCl_2FCCl_2F shows a dramatic change in energy barrier as two chlorine atoms replace two smaller fluorine atoms as the difference in energy barrier between CCl_2FCCl_2F and CF_2ClCF_2Cl is as large as 18kJ mol^{-1}. This is further evidenced that the energy barrier to internal rotation depends quite significantly upon the size of the substituents especially when all the hydrogen atoms are substituted in ethane.

I.O. Sutherland[4] has pointed out that the rotational energy barrier is increased when the size of the halogen substituent is increased. The results of highly substituted ethane were tabulated and it could be seen that $CFBr_2$-$CHBr_2$ (ΔG_E = 41.8kJ mol^{-1}) had a higher energy barrier than $CFCl_2$-$CHCl_2$ (ΔG_E = 38.0kJ mol^{-1}). In general, the energy barrier of internal rotation is higher if it is highly substituted with large halogen atoms. This n.m.r. technique can only be utilized for highly substituted ethane since the presence of these bulky groups increases the magnitude of the rotational barrier.

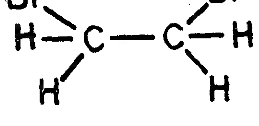
Argument favouring the opposite point of view can be found when the rotational energy barriers of CH_3CH_2F(V_3 = 13.8kJ mol^{-1}) and CH_3CHF_2 (V_3 = 13.4kJ mol^{-1}) are compared. The energy barrier is lowered when one more fluorine atom is substituted into ethane. Hence, it cannot be generalized that the energy barrier of internal rotation of ethane derivatives would be increased, when more of the same substituent groups are substituted for the hydrogen atoms.

In ultrasonic studies, the energy barrier of sym-tetrabromoethane (ΔH = 17.9kJ mol^{-1}) is less than that of 1,1,2-tribromoethane (ΔH = 26.8kJ mol^{-1}).[27] This is another indication for the irregularity of the trend. Therefore more related compounds have to be studied in order to testify which argument is true. Some of the selected compounds were studied by dielectric relaxation method and the list is shown below:

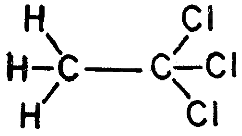
1,2-Dichloroethane



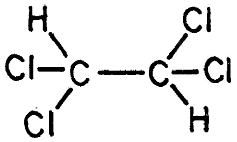
1,2-Dibromoethane



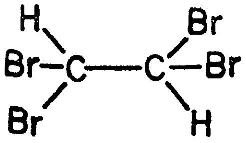
1,1,1-Trichloroethane



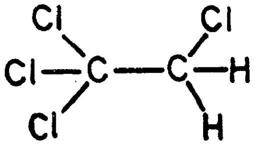
1,1,2,2-Tetrachloroethane



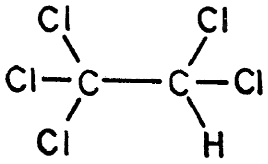
1,1,2,2-tetrabromoethane



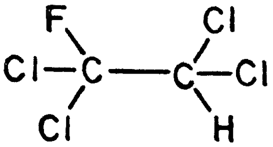
1,1,1,2-Tetrachloroethane



Pentachloroethane



1-Fluoro-1,1,2,2-tetrachloroethane



In the dielectric relaxation studies a compound may be exhibiting a number of processes, namely, molecular relaxation process, intramolecular relaxation process (internal rotation), inversion process (like those in amines) and cooperative processes. Values obtained may not necessarily be assigned to internal rotation; instead many of them have been assigned to molecular process or even cooperative process. Even though the compounds studied are rather simple, the amount of substituents, the size of the substituents and the volume of the substituents may be quite influential to the rotational barriers of the molecular process. In addition, a cooperative process may be quite significant amongst all these relaxation processes studied.

The object in the present study was two fold: (a) to examine any intramolecular processes found in the available temperature and frequency range and to determine their Eyring activation parameters for comparison with available literature data. (b) to study the molecular relaxation processes of these small molecules and determine their Eyring activation parameters. Such data could be of use in the study in chapter 4 of the formamides and acetamides which are molecules of fairly similar size.

3.2 Discussion

Two absorption processes can be found for 1,2-dichloroethane. One family of peaks in our frequency range of 100 to 10^5Hz lies in the temperature range of 93.7-132.8K, and the other process can be found in the range of 267.4-330.9K which is somewhere in the room temperature region. The dielectric relaxation process in the lower temperature range gives a ΔH_E value of 16kJ mol^{-1}. Chlorobenzene[8] has a ΔG_E(100K) value of 14.7kJ mol^{-1} for the molecular process and the ΔG_E(100K) value of 1,2-dichloroethane is 16kJ mol^{-1}. Since these molecules are quite similar in size, and also the temperature range is similar (with chlorobenzene in the range of 81-111K), it is reasonable to assign this lower temperature absorption of 1,2-dichloroethane to a molecular process. The literature value of V_3[9,10] of 1,2-dichloroethane is 23.7kJ mol^{-1} for internal rotation and hence the lower temperature absorption with a lower energy barrier value (ΔH_E = 16kJ mol^{-1}) may suggest again that it is a molecular process. When the points of $\log_{10}\tau T$ vs 1/T were plotted as shown in figure 3.1, they were on a straight line. This suggests that there is no overlap with other processes. It can be supported by examining the plot of ε'' vs $\log_{10}$ frequency and all the curves at various temperatures are highly symmetrical (see figure 10). The relaxation time (τ) at 100K is 1.3×10^{-4}s which is very short and typical to a molecular relaxation process. By examining the relaxation time of similar molecules like chloro- or bromobenzene, they have a value of 2.3×10^{-5}s and 5.5×10^{-4}s respectively. The τ value of 1,2-dichloroethane fits beautifully into this pattern which is typical of the molecular process. The β range found for 1,2-dichloroethane is between 0.296-0.381 which is slightly higher than the usual value of a molecular relaxation process. Since the molecule is not a very large molecule, the volume swept out by this molecule is not very large and thus the energy barrier for this molecular rotation is not great, which is expected. This phenomenon is confirmed by Cooke[11] that the barrier to rotation of a rigid molecule is influenced by the surrounding molecules in the vicinity of the rigid molecule concerned. Hence the larger the molecule, the more resistance will be experienced by the molecule. Since the shape of the molecule is another factor determining the height of the energy barrier, it can be postulated that a similar shape of different molecules would produce similar energy barrier if all the other factors are similar. By comparing the values of ΔH_E in table 3.1, all the molecules have similar energy barrier. This is possibly due to similar size and shape of the compounds.

1,2-Dichloroethane fits in very well within experimental error. Also the apparent dipole moment of this compound for this process has an extrapolated value of 0.489D at 300K. A value such as this is reasonable in a molecular relaxation process although the literature value for the combined dipole moment of all relaxation processes is 1.82D.[9,10] The ΔS_E value in this process is fairly low and hence the ΔG_E value at wide temperature ranges is almost identical to the ΔH_E value (see table 3.1).

An absorption around room temperature was measured and the data were analysed by Fuoss-Kirkwood method and in turn by the Eyring method. Curves of ε'' vs $\log_{10}$ frequency were plotted as shown in figure 3.11. The range of temperature in this absorption was between 267.4-330.9K. The absorption curves of figure 3.11 are unsymmetrical in nature. These unsymmetrical curves may suggest the overlap of two processes. Since it was identified to be a molecular relaxation process around liquid nitrogen temperature as mentioned before, the remaining processes for a simple derivative of ethane can only be assigned as either intramolecular process or cooperative process. A plot of $\log_{10}\tau T$ vs 1/T as shown in figure 3.2 shows one straight line with some points deviating from it at below 300K implying overlapping processes are involved in the temperature range of 267.4-330.9K. The lower temperature range of this plot (i.e. between 267.4-293.2K) may indicate substantial contribution from intramolecular process and the higher temperature range (i.e. between 312.6 and 330.9K) gives a ΔH_E value of 97kJ mol^{-1}.

A cooperative process can be suspected in the higher temperature range. This process involves a portion of the mean square solute dipole moment of a molecule relaxing at a low frequency. The characteristic feature[12] of cooperative process includes (1) absorption at low frequency which means absorption at high temperature; (2) rapid variation of ν_{max} with temperature; (3) broad asymmetric nature of the loss curves; and (4) a large activation energy. For the dielectric relaxation process of 1,2-dichloroethane in the temperature range (312.6-330.9K) which is fairly high, broad asymmetric curves occurred as shown in figure 3.11 and at the same time these curves changed greatly with slight variation of temperature. The energy of activation (ΔH_E = 97kJ mol^{-1}) is too high to be considered as molecular or intramolecular process. The activation energy found by Shears and William[13] was about 260kJ mol^{-1} in dielectric studies of dipolar solutes in supercooled decalin, and the apparent activation energy found by Broens and

Muller[14] for α-relaxation of polystyrene was about 330kJ mol^{-1}. Although the ΔH_E (97kJ mol^{-1}) value of 1,2-dichloroethane is lower than those found by William and Muller as mentioned above, the possibility of assigning the absorption process as cooperative process is still great. Chao[12] examined the cooperative process of ten compounds of which four compounds namely, 4-phenyl-pyridine (ΔH_E = 69kJ mol^{-1}), 4-fluorobiphenyl (ΔH_E = 102kJ mol^{-1}), 3-nitrobiphenyl (ΔH_E = 132kJ mol^{-1}) and 4-bromobiphenyl (ΔH_E = 143kJ mol^{-1}) do not show high energy barriers for the cooperative process. The value of the enthalpy of activation of 1,2-dichloroethane is much lower than 230kJ mol^{-1} for a particular cooperative reorientation process between solute and polystyrene and this may be explained by the fact suggested by Schmieder and Wolf[15] that a small shoulder to the α-peak of atactic amorphous polystyrene was observed. According to Davies _et al_[16], the β value increases with temperature as is the case for 1,2-dichloroethane which exhibits a β range from 0.28 to 0.37 in the temperature range from 312.6 to 330.9. From table 3.3, it can be observed that the ΔG_E value increases with decreasing temperature which is expected since it is harder for the matrix molecule to move with decrease in temperature. Also the relaxation time shown for that compound is in good agreement with other cooperative processes of other compounds.[12] The dipole moment decreases with increase in temperature for cooperative processes as shown in table 3.11. Levi[17] suggested a linear relationship between ΔS_E and ΔH_E can be established for cooperative process and a linear regression analysis gives the equation as shown below:

$$\Delta S_E(\mathrm{J\ K^{-1}\ mol^{-1}}) = -67.5 + 2.49\ \Delta H_E(\mathrm{kJ\ mol^{-1}})$$

The corresponding ΔS_E and ΔH_E values fit reasonably well in the linear relativeship as shown in figure 3.9. Another piece of evidence for the involvement of cooperative process was that the absorption occurred near the glass transition temperature (Tg), since the Tg is lowered by a significant amount when solute was added into the matrix even if the concentration of the solute was small. Thus, Adachi et al[18] have found the value of Tg to be approximately 330K for the solute of 7% by weight in polystyrene. The percentage by weight of 1,2-dichloroethane is similar to that suggested by Adachi and hence the absorption of the cooperative process in the temperature range between 312.6 and 330.9K was expected. Moreover the molecular size, shape and dipole moment components do not significantly affect the glass transition temperature of the matrix and so the temperature range for cooperative process is independent of these factors.

One reason why derivatives of ethane were investigated was to find relationship between the amount of substituents and the energy barrier (ΔH_E) for internal rotation. The groups which act as substituents here were mainly halogen. Consequently the size and electronegativity of the halogen would probably give some suggestion as to how the energy barriers of internal rotation were being influenced. One of the compounds being investigated, which exhibited an absorption for the intramolecular process, was 1,1,2,2-tetrachloroethane. This compound differs from 1,2-dichloroethane in that it has four chlorine atoms with two attaching to each carbon atom. The atomic contribution to the van der Waals volumes of chlorine is 21.4 $Å^3$ while that of hydrogen atom is 5.2 $Å^3$. The difference is relatively great and the effect of this can probably be reflected from the energy barrier of internal rotation. Lide[19] found the V_3 value of internal rotation of simple ethane to be 12.0kJ mol^{-1} while the V_3 value of internal rotation of 1,1,2,2-tetrachloroethane was found to be 49.3kJ mol^{-1}. The bond length of C-H of ethane is about 1.114Å and the bond length of C-Cl of 1,1,2,2-tetrachloroethane is about 1.76[20] Å. If there is any substantial increase or decrease in energy barrier for the tetra-substituted ethane, it will probably be related to the difference in size and bond length and be influenced by other factors such as electronegativity and electrostatic force.

Table 3.10 shows ethane and a series of symmetrically substituted ethane: fluoro-substituted and chloro-substituted. The rotational barrier for both fluoro- and chloro-substituted compound increases with the number of substituted groups. The bond length of C-H in hexafluoroethane is about 1.32Å.[20] Compared to the bond length of C-H in ethane which is 1.114Å. there is not a significant difference. It can be reflected from table 3.10 that an increase of symmetrical substitutions of fluorine does not significantly increase the energy barrier of internal rotation. Nevertheless, a trend can be seen that the energy barrier of internal rotation slightly increases with the number of symmetrical substitution of fluorine. This trend is very pronounced in the case of chloro-substituted compounds. When all the hydrogen atoms are substituted, the energy barrier is greatly increased. The difference in energy barrier between hexachloro-ethane and unsubstituted ethane is about 60kJ mol^{-1}. An increase of more than 10kJ mol^{-1} when ethane is symmetrically substituted by two chlorine atoms. Every subsequent symmetrical substitution of two chlorine atoms increases the energy barrier of internal rotation for more than 20kJ mol^{-1}. The rotational barriers mentioned above were obtained by either microwave i.r. or Raman techniques.

The energy barrier of 1,1,2,2-tetrachloroethane was investigated here by dielectric relaxation methods, and the enthalpy ΔH_E is 28kJ mol^{-1}. It should be remembered that V_3 is not identical to ΔH_E, and hence the value of V_3 from literature cannot be used as a standard for checking the accuracy of the ΔH_E value obtained from dielectric relaxation method. Although the enthalpy of activation of this compound is much smaller than the V_3 value of the literature (see table 3.10), it is still higher than the V_3 value of 1,2-dichloroethane. It is therefore reasonable to postulate that the energy barrier of internal rotation increases with the amount of substitution of halogens in ethane derivatives.

It can be observed in figure 3.3 that the plot of $\log_{10}\tau T$ vs 1/T of 1,1,2.2-tetrachloroethane is a linear relationship. Also, the curves for absorption are highly symmetrical (see figure 3.12). These two facts indicate that there is no overlap from other processes besides the intramolecular process. Tay[21] examined the intramolecular process of dielectric absorption of 1-fluoro-1,1,2,2-tetrachloroethane, and found out the ΔH_E value for this intramolecular process to be 33kJ mol^{-1}.

The temperature range of absorption for the process for both compounds is similar. The ΔG_E(200K) of 1-fluoro-1,1,2,2-tetrachloroethane was found to be 37kJ mol^{-1} while the ΔG_E(200K) of 1,1,2,2-tetrachloroethane was 30kJ mol^{-1}. The difference in the values of ΔG_E(200K) is probably due to the fluorine atom being substituted to the tetrachloroethane. Although the fluorine atom differs only slightly in size with the hydrogen atom, its presence aggravates the crowded situations in 1,1,2,2-tetrachloroethane. The extrapolated dipole moment component at 300K is 0.36D while the extrapolated dipole moment component of 1-fluoro-1,1,2,2-tetrachloroethane at 303.5K is 0.42D.[21] It is not surprising to note that the dipole moment component of both compounds at similar temperatures resemble each other with 1-fluoro-1,1,2,2-tetrachloroethane having a slightly larger value because of the additional electronegative character present in the extra fluorine atom compared with 1,1,2,2-tetrachloroethane. The β range in the temperature range of 168.3 to 214.8K of 1,1,2,2-tetrachloroethane is between 0.34 and 0.54 which is similar to that of 1-fluoro-1,1,2,2-tetrachloroethane in the same temperature range.[21] Also, the ΔS_E values of the two compounds are similar.

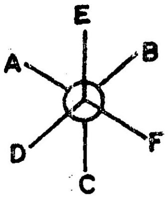
From all of the evidence above, it can be confirmed that the absorption process detected in the temperature range of 168.3 to 214.8K is an intramolecular process. This is also borne out by the high β values.

1,1,2,2-tetrabromoethane differs from 1,1,2,2-tetrachloroethane by the mere fact that bromine atoms replace the chlorine atoms. Table 3.2 has shown that all the parameters of the two compounds are of the same order. Since the dielectric absorption of 1,1,2,2-tetrabromoethane is slightly shifted to a higher temperature range than that of 1,1,2,2-tetrachloroethane, it is not surprising to note that the enthalpy of activation of the former is slightly greater than the latter. The ΔG_E value of the former being 33kJ mol^{-1} is also greater than that of the latter by 3kJ mol^{-1}. The relaxation time at 200K and 300K is of the same order for the two compounds. A larger dipole moment component is observed for the former being 0.43D at 300K. Both compounds have the ΔS_E value almost zero. Furthermore, the β range of the two compounds is very similar. The absorption curves of 1,1,2,2-tetrabromoethane (see figure 3.13) is fairly symmetrical and the plot of $\log_{10}\tau T$ vs 1/T (see figure 3.4) appears as a straight line. Therefore the absorption process detected for 1,1,2,2-tetrabromoethane can be justified to be an intramolecular process when its parameters of Fuoss-Kirkwood analysis and Eyring plots are similar to those of 1,1,2,2-tetrachloroethane and 1-fluoro-1,1,2,2-tetrachloroethane.

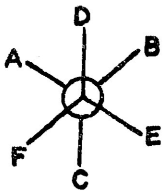
Since the enthalpy of activation of 1,1,2,2-tetrabromoethane is higher than that of 1,1,2,2-tetrachloroethane in the intramolecular process, it can be proposed that the increase in energy barrier of internal rotation is due to, at least partially, the atomic size of bromine which is larger than that of chlorine. The molecular volume of bromine is 27.7 $Å^3$ while that of chlorine is 21.4 $Å^3$. Although the difference between the molecular volume of bromine and chlorine is not great, tetra-substituted ethanes will have an additive difference of a multiple of four. The difference in size between the two compounds will be significantly different from each other, thereby enhancing greater steric hindrance as the $CHBr_2$ groups rotate with respect to one another. Also the difference in electronegativity and polarizability between bromine and chlorine may contribute to a certain extent to the difference in the rotational energy barrier.

It can be seen that the values of ΔG_E at 200K (34kJ mol^{-1}) and ΔH_E (31kJ mol^{-1}) of 1-fluoro-1,1,2,2-tetrachloroethane[21] are somewhat greater than those of 1,1,2,2-tetrachloroethane (ΔG_E at 200K = 30kJ mol^{-1} and ΔH_E = 28kJ mol^{-1}). The difference in the energy barrier reflected by the difference in ΔG_E(200K) and ΔH_E, is clearly due to the presence of fluorine atom in 1-fluoro-1,1,2,2-tetrachloroethane. The increase in electronegativity and the distortion of the symmetrical system of 1,1,2,2-tetrachloroethane when a hydrogen atom is replaced by fluorine, are probably the decisive factors causing the rise in energy barrier of internal rotation of 1-fluoro-1,1,2,2-tetrachloroethane. However, it can be manifested that the size of the substituents and the number of substituent groups are critical in determining the energy barrier. These two factors actually cause a steric hindrance problem thereby increasing the energy barrier of internal rotation when the size and the number of substituent groups are increased. This steric factor which predominates the height of energy barrier is well supported by Sutherland[22] and Binsch[23]. Sutherland investigated the energy barrier of internal rotation by the n.m.r. line-shape technique, and a table of derivatives of ethane[22] were listed. It can be generalized from this table that the energy barrier of internal rotation increases with the size and the number of substituent groups which are, in that case, halogens. The ΔG_E value of 1-fluoro-1,1,2,2-tetrachloroethane agrees very well with that obtained from Tay.[27] When the ΔG_E of 1-fluoro-1,1,2,2-tetrabromoethane is compared with that of 1-fluoro-1,1,2,2-tetrachloroethane, the former is greater than the latter by 4.18kJ mol^{-1}. Other evidence of the importance of size and the number of substituents was reported from Binsch[23]. The two compounds which were studied here by dielectric relaxation method may be a convincing argument in favour of steric hindrance derived from the factors of size and the number of substituent groups.

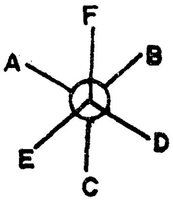
The intramolecular process mentioned above involves a carbon to carbon single bond which rotates freely if the energy barrier is zero. A derivative of ethane can be shown below using Newman projection formula:



(A)

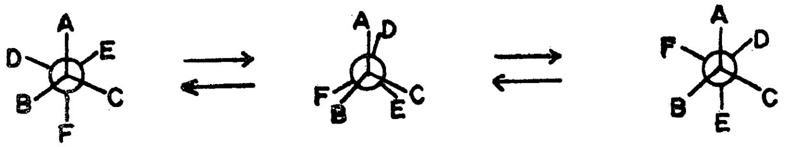


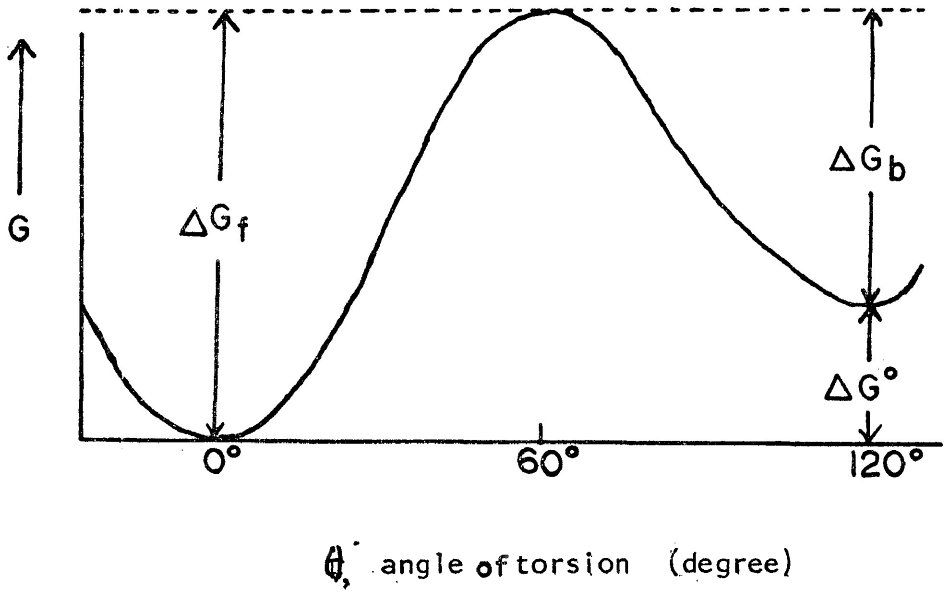
(B)



(C)

Assuming the compound has six different substituents, each substituted methyl group can rotate along the C-C bond with respect to each other. The above figures represent the staggered forms of substituted ethane. If all the substituents are different, one of the above figures may represent the lowest potential energy structure. In order for one substituted methyl group (or unsubstituted methyl group) to rotate from one staggered form to another one, it has to pass through the eclipsed form which can be regarded as transition intermediate.





POTENTIAL ENERGY PROFILE OF SUBSTITUTED ETHANE

The above figure shows the potential energy profile of a molecule going from a staggered to another staggered form where ΔG_f is the change of free energy from the more stable form to the less stable form and ΔG_b is the change of free energy from the less stable form to the more stable form. The difference in free energy for the two staggered form is shown as ΔG^o. Different molecules with different substituent groups give different potential energy profile. The energy profiles of 1,1,2,2-tetrachloroethane, 1,1,2,2-tetrabromoethane and 1-fluoro-1,1,2,2-tetrachloroethane are the same which are shown below:

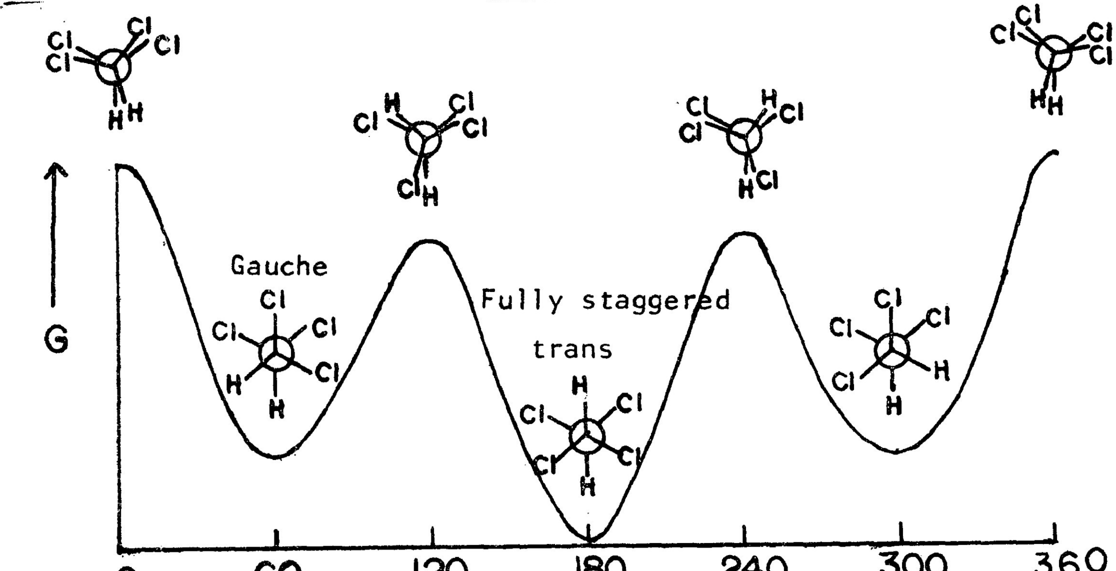


FIGURE (A1) POTENTIAL ENERGY PROFILE OF 1,1,2,2-TETRACHLOROETHANE

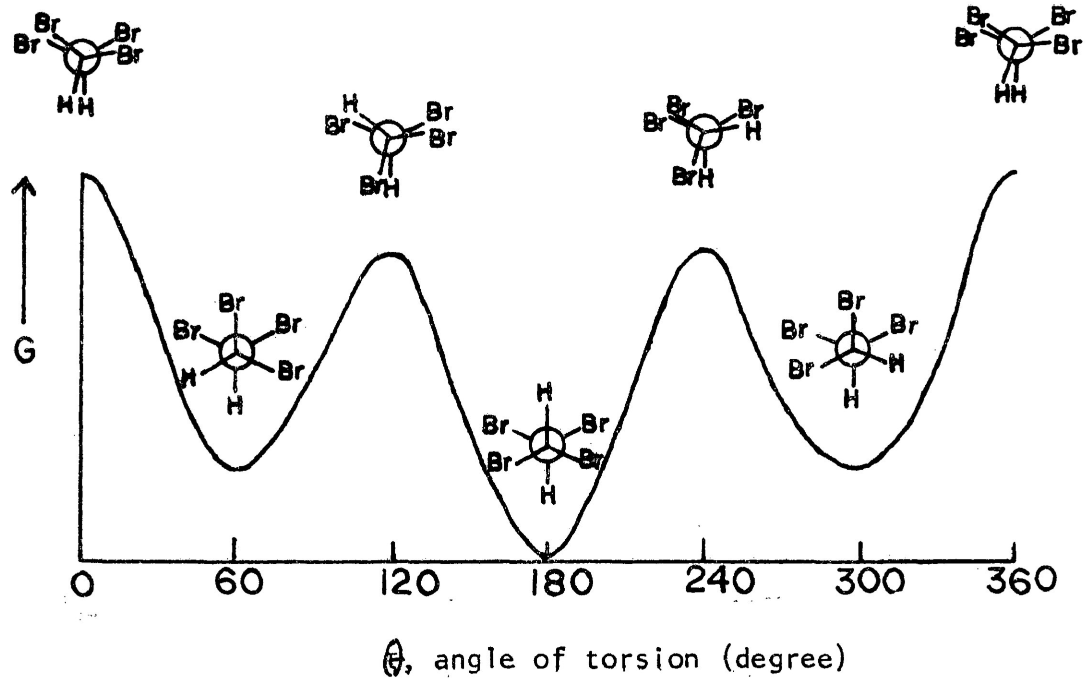


FIGURE (A2) POTENTIAL ENERGY PROFILE OF 1,1,2,2-TETRABROMOETHANE

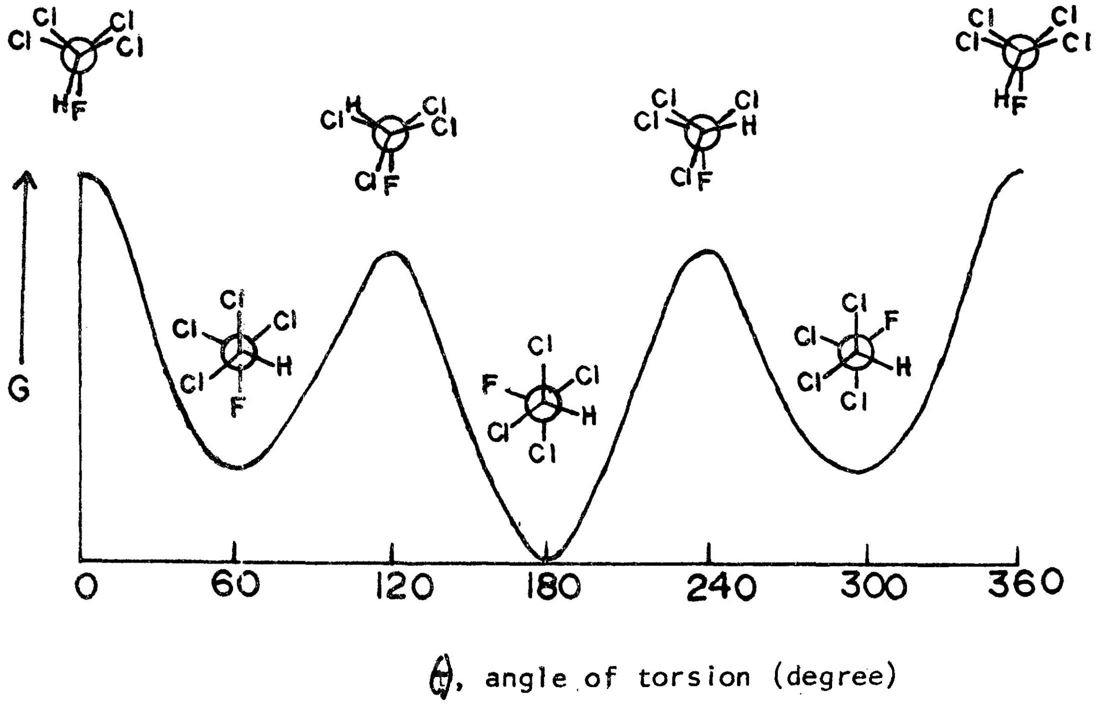


FIGURE (A3) POTENTIAL ENERGY PROFILE OF 1-FLUORO-1,1,2,2-TETRACHLOROETHANE

Tay[21] discussed that for asymmetric barriers such as those shown above, the dielectric technique yields a ΔH_E corresponding to the switch from the isomer with the higher energy to that of the lower. For the three cases mentioned above, it is expected that the energy barrier corresponds to the switch from the gauche form to the fully staggered trans form possessing the minimum potential energy. For 1-fluoro-1,1,2,2-tetra-chloroethane Tay[21] found good correspondence of the ΔH_E value for this transition with those from the ultrasonic and n.m.r. techniques which also employ the Eyring approach.

Many of the compounds which are derivatives of ethane studied here had their absorption around liquid nitrogen temperature. Table 3.1 shows the parameters of various compounds from Eyring analysis. Although the number of substituent groups and the size of them differ in each of the compounds here, the energy barriers of all these derivatives of ethane do not vary too much. Khwaja[24] studied some halobenzenes and some halotoluenes and he found out that there was a slight increase in the enthalpy of activation from fluorobenzene (ΔH_E = 9kJ mol^{-1}) to iodobenzene (ΔH_E = 16kJ mol^{-1}). Actually, fluorobenzene and chlorobenzene have a similar value of enthalpy of activation although they differ in the value of ΔG_E. The situation is not the same when the halotoluenes are examined. The increase in energy barrier of the molecular relaxation process is quite significant from p-fluorotoluene (ΔH_E = 13kJ mol^{-1}) to p-iodotoluene (ΔH_E = 42kJ mol^{-1}). It can be seen that the higher the molecular energy barrier, the higher is the temperature range for molecular absorption to occur. It can be observed that p-iodotoluene has its molecular absorption process occurred well above liquid nitrogen temperature while fluorobenzene, having the lowest energy barrier of all the halobenzenes and halotoluenes, has a lowest temperature range near liquid nitrogen temperature. Chao[12] studied some of the biphenyl derivatives e.g. 3-chlorobiphenyl (ΔH_E = 44kJ mol^{-1}) and 3-bromobiphenyl (ΔH_E = 67kJ mol^{-1}) and the same trend as that of helobenzene was observed. The enthalpy of activation for the biphenyls was observed to be much higher than those of halobenzenes since it is obvious that the size of the molecule predominates the height of the molecular energy barrier. It was also mentioned that the inclination of dipole moment which causes barrel motion or out of plane motion of the molecules, determines the value of energy barrier of the molecular process. When the dipole moment is perpendicular to the principal axis, a small energy barrier of the molecule will be expected due to easier reorientation with respect to either barrel or in-plane rotation.

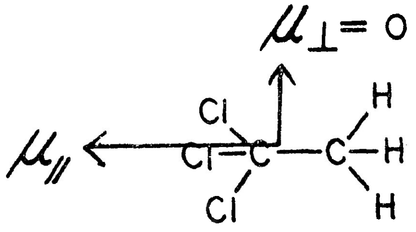
As mentioned before, the intramolecular absorption process of halogenated ethanes occurs in the temperature range of 150K to 250K. This can be shown by 1,1,2,2-tetrachloroethane, 1,1,2,2-tetrabromoethane and 1-fluoro-1,1,2,2-tetrachloroethane. A much lower temperature range absorption process was detected for 1,2-dichloroethane. All the dielectric parameters obtained in this range differ significantly from those of the higher temperature range around room temperature. The enthalpy of activation for the intramolecular relaxation process of the three compounds mentioned is around 30kJ mol^{-1}. The enthalpy of activation obtained for the low temperature range absorption (93.7-132.8K) of 1,2-dichloroethane is only 16±2kJ mol^{-1} which is much lower than those of the former three compounds. Hence it is apparent that the low temperature absorption process of 1,2-dichloroethane does not belong to the intramolecular relaxation process. It seems to be more appropriate to assign this process as the molecular relaxation process. From figure 3.10, the absorption curves around 111.2K are not as symmetrical as those below it. The curves around 100K are very symmetrical indicating that one relaxation process predominates that region, while the curves around 111.2K or above indicate a possibility of overlap with another relaxation process probably intramolecular process. The relaxation time at 100K is found to be 1.3×10^{-4}s which indicates a much faster process than that of intramolecular process of either 1,1,2,2-tetrachloroethane or 1,1,2,2-tetrabromoethane which has a much higher value of τ. The value of ΔG_E at 100K or other temperature of 1,2-dichloroethane is almost identical to the value of ΔH_E which indicates that ΔG_E is independent of temperature. This is due to the fact that ΔS_E is so small that it is almost zero. This dipole moment component has been found to be 0.49D and the β range is between 0.30 to 0.38 which is relatively high. This relatively high β value may be due to a slight overlap between molecular relaxation process and intramolecular process at around 130K. Since the intramolecular process of 1,1,2,2-tetrachloroethane and 1,1,2,2-tetrabromoethane occurs in the range of 150-250K, it is possible for a less substituted molecule like 1,2-dichloroethane to have some absorption for the intramolecular process at around 130K. Therefore a slightly lower value than 16kJ mol^{-1} should be expected to be the true value of molecular relaxation process of 1,2-dichloroethane. However, the points of the plot of $\log_{10}\tau T$ vs 1/T (see figure 3.1) still lie closely along a straight line. If more points had been obtained at higher temperatures than 130K, it should have shown that the points at these higher temperatures would have deviated from the straight line. Unfortunately the general radio bridge covers only the range of frequencies from 10^2 to 10^5Hz.

It is interesting to see how the energy barrier of molecular relaxation process can be affected by a larger substituent group. 1,2,-Dibromoethane mainly differs from 1,2-dichloroethane in the halogen substituent group and electronegativity and polarizability. The molecular volume does not differ too much from chlorine to bromine.[25] The C-Cl bond length only differs slightly with the bond length of C-Br.[20] Hence the overall molecular size of the two molecules is similar. The absorption detected in 1,2-dibromoethane is in the range of 91.6 to 130.7K which is almost identical to that of 1,2-dichloroethane. The relaxation time at 100K where the absorption occurs is very similar for both compounds. 1,2-Dibromoethane has a larger entropy which causes the ΔG_E to change at various temperatures. The change in free energy at 100K is 17kJ mol^{-1} which is just expectedly slightly larger than that of 1,2-dichloroethane. The dipole moment component of 1,2-dibromoethane is found to be 0.76D and the β range is between 0.32 - 0.44, which may suggest an overlap of relaxation processes at around 130K. However, the absorption curves are fairly symmetrical for the entire temperature range as shown in figure 3.14. The Eyring plot shown in figure 3.5 has most of the points lying on a straight line with the exception of two points near liquid nitrogen temperature, where the frequency of maximum absorption cannot be detected very accurately due to the fact that it lies around very low frequency.

1,1,1-Trichloroethane was found to have absorption near liquid nitrogen temperature which is in the range 83.1 - 97.8K. This narrow range of absorption did not yield good results from Eyring analysis. Hence the absorption data were only analysed by Fuoss-Kirkwood method (see table 3.13). The values of ΔG_E were in the range of 10.3 - 12.1kJ mol^{-1} in the temperature range (183.1-97.8K.) which were smaller than the ΔG_E values of 1,2-dichloroethane (16kJ mol^{-1} at 100K) and 1,2-dibromoethane (17kJ mol^{-1} at 100K). Apparently, the energy barrier seems to be lower than the less substituted compound's energy barrier like that of 1,2-dichloroethane. Since the energy barrier is so low, the experimental error will be in the range of ±4kJ mol^{-1}. So it can be said that 1,2-dichloroethane and 1,1,1-trichloroethane have similar magnitude of energy barrier for a molecular relaxation process. The dipole moment component is about 0.2D and the β range is between 0.30

to 0.52. The relaxation time is in the order of 10^{-6}s which is relatively faster than that of 1,2-dichloroethane. These observations differ appreciably from those of 1,2-dibromoethane and 1,2-dichloroethane, because of the fact that there is no substituted halogen at the other carbon. On the whole, the shape of 1,1,1-trichloroethane is relatively more spherical than the others thereby making itself easier to reorientate without disturbing too much of the surrounding molecules. Hence the shape of molecule can be seen to be playing a dominant role in the energy barrier of molecular relaxation process which leads to the lowest free energy of activation at 100K (see table 3.1) of these halogenated ethanes.

Since 1,1,1-trichloroethane is unsymmetrically substituted with three chlorine atoms at one carbon atom and three hydrogen atoms at the other carbon atom, there is no perpendicular dipole moment component and the only dipole moment is along the principal axis as shown in the figure below:



Thus, the intramolecular process along the C-C bond cannot be detected by the dielectric relaxation method. The energy barrier of internal rotation of 1,1,1-trichloroethane has been determined by neutron incoherent inelastic scattering method (or NIIS),[26] and the V_3 value is 25.1±2.5kJ mol^{-1}. The ΔH_2 value of 1,1,2-trichloroethane and 1,1,2-tribromoethane[27] from molecular acoustics method have been found to be 24.3, 26.8kJ mol^{-1} respectively. Clearly, the absorption process detected for 1,1,1-trichloroethane is a molecular process and the activation barrier must be very low for the absorption to be found around liquid nitrogen temperature. The ΔG_E = 11kJ mol^{-1} also supports this argument.

The V_3 value of 1,1,1,2-tetrachloroethane from literature is 36kJ mol^{-1} for the energy barrier of internal rotation.[28] The ΔH_E value obtained in the temperature range of 83.6 to 110K is only 13±2kJ mol^{-1} in the dielectric method. The ΔS_E value is only -6J K^{-1} mol^{-1} which is very close to zero, implying a better possibility for the ΔH_E being identical or close to V_3 for the same type of energy barrier. Since the ΔH_E value obtained is so much smaller than the V_3 value from the literature, it indicates different processes have been compared. The possibility of being identified as an intramolecular process is ruled out, and since the dielectric absorption occurred in a very low temperature like those of other compounds mentioned before, the absorption process is more likely to be a molecular relaxation process. From the graph of $\log_{10}\tau T$ vs 1/T (see figure 3.6), it can be found that the point at the highest temperature in the range deviates itself from the straight line. This deviation is borne out by the absorption curve (see figure 3.15) at the highest temperature in the range. The determination of the frequency for maximum absorption from Fuoss-Kirkwood analysis is not of high degree of accuracy due to the necessity of great extrapolation. Hence, by neglecting this point in the Eyring analysis, a value of ΔH_E of greater accuracy has been obtained. The ΔG_E value at 100K is 14kJ mol^{-1} which is smaller than that of 1,2-dibromoethane. This is probably due to the fact that the bromine atom is larger than the chlorine atom and also the shape of 1,2-dibromoethane is less spherical. As mentioned before, 1,2-dichloroethane has a higher ΔG_E value at 100K due to the fact that it may have some overlap absorption with the intramolecular process. However, the ΔG_E value of 1,1,1-trichloroethane is smaller than that of 1,1,1,2-tetrachloroethane. This is expected since the former compound has one chlorine atom less than that of the latter and also 1,1,1-trichloroethane is more spherical in nature. The additional chlorine atom of the latter surely aggravates the problem of sweeping neighbouring molecules in dielectric absorption. The relaxation time of this compound is similar to those of 1,2-dibromoethane and 1,2-dichloroethane which have similar energy barrier of molecular relaxation process. The dipole moment component of this absorption process is similar to that of 1,2-dibromoethane, and also the β range for this process is between 0.16 to 0.24 which is reasonable for molecular relaxation process.

Pentachloroethane has a slightly higher temperature range than that of 1,1,1,2-tetrachloroethane, and the ΔH_E value (14kJ mol^{-1}) is also slightly greater than that of the latter (13kJ mol^{-1}). Furthermore, it is not suprising to notice the ΔG_E value (16kJ mol^{-1}) at 100K is slightly greater than that of 1,1,1,2-tetrachloroethane (ΔG_E = 14kJ mol^{-1} at 100K) within experimental error. It is quite logical to predict the existing trend that the energy barrier of molecular relaxation process increases with the number of substitution as in the case of intramolecular process. However, the increase in energy barrier of molecular process is not as significant as in the intramolecular process whereby one or two more substituted groups means a jump of about 20kJ mol^{-1}. The plot of $\log_{10}\tau T$ vs 1/T shows a straight line (see figure 3.7) and the absorption curves (see figure 3.16) are quite symmetrical, indicating that only one relaxation process is involved. Also the ΔS_E of this compound is quite small so that V_3 value from i.r. method can be used as valuable comparison. The V_3 value of pentachloroethane from literature[28] is 59kJ mol^{-1} which is much larger than the ΔH_E value of 14kJ mol^{-1} obtained here. Therefore it can be confirmed that the processes involved for the two different values of energy barrier are different. The V_3 value has been identified as the energy barrier of internal rotation, and thus it can be suggested that the dielectric relaxation process in the temperature range (90.2-123.8K) is a molecular relaxation process with dipole moment component and relaxation times at various temperatures similar to those of 1,1,1,2-tetrachloroethane and other compounds exhibiting the molecular process mentioned above.

Tay[21] has determined the energy barrier of internal rotation of 1-fluoro-1,1,1,2-tetrachloroethane by the dielectric method. The activation enthalpy and entropy are 32.8±1.4kJ mol^{-1} and -22±6J K^{-1} mol^{-1} respectively for the gauche→trans process. The activation enthalpy values are in good agreement with those determined by the other dynamic methods, namely the ultrasonic method and the n.m.r. method. Tay also detected another absorption of the dielectric relaxation method at a much lower temperature. It was found to be between 93.7 and 115.4K. The same experiment was also performed here for 1-fluoro-1,1,2,2-tetrachloroethane and the values of all the parameters from Fuoss-Kirkwood and Eyring analysis closely resembled each other. The temperature range in which the absorption occurred here was between 86.4 - 121.8K. The β range was between 0.210 to 0.302 which was not too high to suggest overlap of other processes. The relaxation time at 100K was 4.0×10^{-5}s and the dipole moment component was 0.64D for this process. These two parameters obtained were of the same order as those obtained for pentachloroethane, 1,2-dibromoethane and 1,1,1,2-tetrachloroethane. The ΔG_E at 100K of 1-fluoro-1,1,2,2-tetrachloroethane was found to be 15kJ mol^{-1} which is in between those of 1,1,1,2-tetrachloroethane and pentachloroethane. This was expected since the fluorine atom in 1-fluoro-1,1,2,2-tetrachloroethane occupied a smaller volume than the corresponding chlorine atom of pentachloroethane, but in turn the overall volume of the former was larger than that of 1,1,1,2-tetrachloroethane. Nevertheless these energy barriers differed so little for these molecular relaxation processes. In order to have a significant change in energy barrier for molecular rotation, the size of the compounds or the shape of the compounds must be appreciably different from each other. Tay suggested that this lower temperature absorption process of 1-fluoro-1,1,2,2-tetrachloroethane should be attributed to the molecular process, which agreed with the parameters obtained here by the same technique. Table 3.4 compares the parameters obtained by Tay and those from the author of this thesis for 1-fluoro-1,1,2,2-tetrachloroethane. The activation enthalpy and entropy of Tay and the author resemble each other, which provides good evidence that the dielectric technique is consistent. The absorption curves of 1-fluoro-1,1,2,2-tetrachloroethane can be shown in figure 3.17 and the plots of $\log_{10}\tau T$ vs 1/T of 1-fluoro-1,1,2,2-tetrachloroethane appear as a straight line which indicates substantially no overlap of other processes occurred.

The compounds mentioned above exhibiting a molecular relaxation process all have similar features (see table 3.5), and they are all derivatives of ethane. They showed a molecular relaxation process in similar temperature range near liquid nitrogen temperature with low β values. Only two compounds, namely, 1,2-dichloroethane and 1,2-dibromoethane have slightly higher β values indicating that a slight overlap with intramolecular process is possible. The relaxation time at 100K of all these compounds has its value in the order of 10^{-4} to 10^{-5}s. The dipole moment component of all these compounds is less than one where the literature value of the total dipole moment is between 1 to 2D.[29,30,31] This indicates some portions of the total dipole moment are available for an intramolecular process or cooperative process or a combination of both. The value of ΔS_E of these compounds is very close to zero and hence the variation of temperature does not significantly influence the value of free energy barrier at various temperatures. The values of the enthalpy of activation of all these compounds are very small and resemble each other. Also the values of ΔG_E of these compounds are not significantly different for they have similar size and shape. Khwaja[24] examined the rigid molecules of ortho-substituted benzene and found that the energy barrier of molecular process of these compounds did not differ significantly although various halogens were used to substitute in the ortho position of halobenzenes. This gives the idea that the energy barrier of molecular rotation is not easily changed by merely increasing slightly the volume or size of the molecule. As it is in the case studied here for the derivatives of ethane, increase of the number of halogen substitution or the increase of size and volume of the molecule by means of substituting larger helogen atoms does not alter the molecular relaxation energy barrier very much. A slight increase or decrease of energy barrier for these molecular processess is possible in consideration of the electrostatic factor, electronegativity of various halogen substituents and steric factor. On the whole, the energy barrier of molecular process of halogen derivatives of ethane is quite unaffected by the number of the substituent groups or size of the halogen atoms.

Some of the ethane derivatives investigated here have shown a molecular process All of these compounds exhibiting this process have similar magnitude of the parameters of Fuoss-Kirkwood and Eyring analysis with the exception of some compounds with the molecular process overlapping slightly with other processes such as the intramolecular process. The energy barrier of the molecular rotation of this type of compound i.e. halogen substituted ethane derivatives has approximately the same value. This is especially the case for 1,2-dibromoethane, 1,1,1,2-tetrachloroethane, pentachloroethane and 1-fluoro-1,1,2,2-tetrachloroethane which have very close values of enthalpy of activation. The ΔG_E value of these compounds only differ slightly and hence a noticeable trend of increase of energy barrier due to the increase of the amount of halogen substitution or to the size of the halogen atom cannot be verified because of no significant increase of the overall size of the molecules.

The intramolecular process of 1,1,2,2-tetrachloroethane and 1,1,2,2-tetrabromoethane has been detected by dielectric measurement. The trend of an increase of energy barrier with larger substituent group such as bromine atom instead of chlorine is evident when 1,2-dibromoethane has ΔH_E value 4kJ mol^{-1} greater than that of 1,2-dichloroethane. This trend is also illustrated by table 3.10 when the rotational barrier of 1,1,2,2-tetrachloroethane is greater than that of 1,1,2,2-tetrafluoroethane by more than 30kJ mol^{-1}. Sutherland[22] and Binsch[23] suggested that the steric effect of the larger substituent groups was responsible for the increase in energy barrier of internal rotation.

Cooperative process was also illustrated by 1,2-dichloroethane at a temperature range near the glass transition temperature of polystyrene. This absorption was characterized by much higher energy barrier than intramolecular process or molecular process. The temperature range depends upon the glass transition temperature of the matrix and thus the size and shape and dipole moment of the solute do not affect significantly the energy barrier of this process.

Derivatives of ethane are simple molecules in terms of their structure, yet different relaxation processes, namely intramolecular, molecular, and cooperative process are governed by many factors. These three processes if detected happened to be in different temperature ranges although sometimes there was some degree of overlap of two processes in a particular temperature range. The intramolecular process is governed mainly by the steric factor while the cooperative process is rather unsusceptible to the change in the molecular size and shape of the solute molecules. It would seem likely that the derivatives of ethane are unaffected by the size of the halogen substituent groups for molecular relaxation process. If the overall size and shape of the molecules are altered by replacing much larger substituent groups in ethane, it is quite reasonable to predict a rise in energy barrier of the molecular process.

TABLE 3.1: A Summary of the Relaxation Parameters of the Molecular Process of Some Derivatives of Ethane

Molecule	T(K)	τ(s)	ΔG_E(kJ mol^{-1})			β	μ_{300}	ΔH_E	ΔS_E
	Range	100K	100K	200K	300K	Range	DEBYE	kJ mol^{-1}	J K^{-1} mol^{-1}
1,2-Dichloroethane	93.7 - 132.8	1.3E-4	16	16	16	0.30 - 0.38	0.49	16	
1,2-Dibromoethane	91.6 - 130.7	2.0E-4	17	19	22	0.32 - 0.44	0.76	14	-26
1,1,1,2-Tetrachloroethane	83.6 - 110.0	1.0E-5	14	15	15	0.16 - 0.24	0.83	13	- 6
Pentachloroethane	90.2 - 123.5	1.0E-4	16	18	19	0.19 - 0.29	0.80	14	-16
1-Fluoro-1,1,2,2-tetrachloroethane	86.4 - 121.8	4.0E-5	15	17	19	0.21 - 0.30	0.64	13	-21
1,1,1-Trichloroethane	at 97.8	5.4E-7	11			0.30	0.22		

TABLE 3.2: A Summary of the Relaxation Parameters of the Intramolecular Process of Derivatives of Ethane

Molecule	T(K)	τ(s)	ΔG_E(kJ mol^{-1})			β	μ_{300}	ΔH_E	ΔS_E
	Range	100K	100K	200K	300K	Range	DEBYE	kJ mol^{-1}	J K^{-1} mol^{-1}
1,1,2,2-Tetra-chloroethane	168.3 - 214.8	1.4E-5	29	30	31	0.34 - 0.54	0.36	28±2	-10
1,1,2,2-Tetra-bromoethane	185.7 - 235.4	9.8E-5	33	33	33	0.31 - 0.48	0.43	34±4	4

TABLE 3.3: A Summary of the Relaxation Parameters of the Relaxation Process of 1,2-Dichloroethane in a Higher Temperature Region

1,2-Dichloro-ethane	267.4 - 330.9	2.2E-4 (300K)	82	67	53	0.28 - 0.38	0.23	97±21	147

TABLE 3.4: Comparison of the Relaxation Parameters of the Molecular Process of 1-Fluoro-1,1,2,2-tetrachloroethane by Tay and Author of this work

T(K)	$10^3\varepsilon''_m$	$\log_{10}\nu_m$	β	ε_∞	μ(D)
		Tay's Results			
93.7	1.92	2.83	0.19	2.59	0.32
96.8	2.02	3.01	0.17	2.59	0.36
102.4	2.14	3.65	0.18	2.59	0.37
107.2	2.29	3.91	0.22	2.59	0.35
111.1	2.39	4.15	0.22	2.59	0.36
115.4	2.45	4.30	0.24	2.60	0.36
		Author's Results			
86.4	1.92	2.46	0.23	2.84	0.24
92.3	2.11	2.93	0.22	2.83	0.27
96.2	2.22	3.16	0.21	2.83	0.29
100.8	2.27	3.71	0.21	2.83	0.30
104.7	2.42	4.14	0.21	2.84	0.31
108.2	2.47	4.22	0.22	2.84	0.31
111.5	2.56	4.46	0.23	2.83	0.31
117.7	2.84	4.68	0.29	2.83	0.31
121.8	2.84	4.71	0.30	2.84	0.30

ΔH_E (from Tay) = 13.8kJ mol^{-1}

(from Author) = 13.0kJ mol^{-1}

ΔS_E (from Tay = -19J K^{-1} mol^{-1}

(from Author) = - 21J K^{-1} mol^{-1}

TABLE 3.5 - 3.10: Rotational Energy Barrier of Substituted Ethanes

Compound Formula	Rotational barrier (kJ mol^{-1})	References
Table 3.5		
CH_3CH_3	12.02	19
CH_3CH_2F	13.92	5
CH_3CHF_2	13.42	6,9
CH_3CF_3	13.17	9,32
CH_2FCF_3	15.26	9,33
CHF_2CF_3	15.47	9
CF_3CF_3	16.39	34
Table 3.6		
CH_3CH_3	12.02	19
CH_3CH_2Cl	15.47	35
CH_3CHCl_2	22.15	26
CH_3CCl_3	25.08	26
CH_2ClCCl_3	36.45	28
$CHCl_2CCl_3$	59.36	28
CCl_3CCl_3	73.15	36
Table 3.7		
CH_3CH_2F	13.79	37
CH_3CH_2Cl	14.88	38
CH_3CH_2Br	14.88	39
CH_3CH_2I	13.46	40
Table 3.8		
CF_3CF_3	16.39	34
CF_3CF_2Cl	21.32	41
CF_3CF_2Br	26.75	42
CF_3CF_2I	29.64	42

TABLE 3.5 - 3.10: continued...

Compound Formula	Rotational Barrier (kJ mol^{-1})	References
Table 3.9		
CF_2ClCF_3	21.32	41
CF_2ClCF_2Cl	22.03	41
CCl_2FCCl_2F	40.34	42
Table 3.10		
CH_3CH_3	12.02	19
CH_2FCH_2F	14.76	9,43
CHF_2CHF_2	14.88	9,43
CF_3CF_3	16.39	34
CH_2ClCH_2Cl	23.74	9,10
$CHCl_2CHCl_2$	49.32	9,10
CCl_3CCl_3	73.15	36

TABLES 3.11 - 3.18: Fuoss-Kirkwood Relaxation Parameters of Some Derivatives of Ethane

T(K)	$10^3\varepsilon''$	$\log_{10}\nu_m$	β	ε_∞	μ(D)
		Table 3.11: 1,2-Dichloroethane			
93.7	2.44	2.64	0.38	2.85	0.18
97.6	2.53	2.83	0.38	2.87	0.19
101.0	2.38	3.14	0.35	2.86	0.19
103.2	2.40	3.33	0.31	2.86	0.21
105.4	2.37	3.51	0.36	2.87	0.20
108.2	2.49	3.70	0.34	2.87	0.21
111.2	2.51	3.94	0.33	2.87	0.21
114.4	2.62	4.40	0.30	2.87	0.23
122.9	2.89	4.70	0.37	2.89	0.23
132.8	2.60	5.37	0.35	2.89	0.24
		Results of higher temperature absorption are shown below:			
267.4	1.86	2.59	0.27	2.80	0.31
274.6	1.78	2.81	0.28	2.71	0.31
283.9	1.82	3.09	0.31	2.78	0.31
293.2	1.58	3.21	0.31	2.78	0.29
312.6	1.34	3.55	0.38	2.76	0.25
317.0	1.30	3.76	0.37	2.76	0.25
321.9	1.19	4.04	0.33	2.75	0.26
326.1	1.42	4.31	0.28	2.75	0.28
330.9	1.40	4.42	0.29	2.74	0.27
		Table 3.12: 1,2-Dibromoethane			
91.6	3.42	2.44	0.41	2.89	0.25
95.7	3.78	2.49	0.35	2.89	0.29
100.6	3.93	2.77	0.33	2.89	0.31
104.6	4.03	3.11	0.32	2.89	0.33
109.6	4.26	3.51	0.34	2.89	0.34
113.9	4.44	3.84	0.35	2.89	0.34
117.2	4.59	4.04	0.36	2.89	0.34
122.8	4.86	4.42	0.40	2.90	0.35
130.7	5.05	4.79	0.44	2.91	0.35

TABLES 3.11 - 3.18: Fuoss-kirkwood Relaxation Parameters of Some Derivatives of Ethane

T(K)	$10^3\varepsilon''$	$\log_{10}\nu_m$	β	ε_∞	μ(D)
	Table 3.13 1,1,1-Trichloroethane				
83.1	3.38	4.94	0.33	2.81	0.22
86.8	3.09	4.94	0.34	2.80	0.21
88.8	2.95	4.81	0.39	2.81	0.20
91.7	2.68	4.76	0.43	2.81	0.18
93.5	2.68	4.76	0.52	2.82	0.17
97.8	2.26	5.47	0.30	2.82	0.22
	Table 3.14 1,1,1-Trichloroethane				
168.3	5.21	2.59	0.34	2.71	0.50
174.0	5.28	2.87	0.36	2.71	0.50
182.9	5.30	3.37	0.43	2.72	0.47
186.4	5.24	3.51	0.44	2.72	0.47
191.8	5.24	3.75	0.42	2.72	0.48
195.8	5.24	3.92	0.47	2.73	0.46
205.3	5.19	4.24	0.48	2.73	0.46
214.8	5.11	4.53	0.54	2.74	0.45
	Table 3.15 1,1,2,2-Tetrabromoethane				
185.7	2.58	2.56	0.31	2.69	0.48
191.5	2.66	2.83	0.37	2.70	0.45
195.6	2.64	3.02	0.38	2.70	0.45
201.2	2.63	3.18	0.45	2.70	0.41
206.0	2.63	3.42	0.43	2.71	0.43
215.6	2.60	3.78	0.48	2.72	0.41
225.5	2.51	4.35	0.42	2.72	0.45
235.4	2.62	4.65	0.41	2.73	0.47

Tables 3.11 - 3.18; Fuoss-Kirkwood Relaxation Parameters of Some Derivatives of Ethane

T(K)	$10^3\varepsilon''$	$\log_{10}\nu_m$	β	ε_∞	μ(D)
	Table 3.16 1,1,1,2-Tetrachloroethane				
83.6	6.25	2.74	0.16	2.95	0.52
85.8	6.40	2.89	0.15	2.95	0.55
88.1	6.62	3.16	0.16	2.94	0.55
90.7	6.81	3.47	0.17	2.94	0.56
94.5	7.13	3.80	0.17	2.94	0.57
97.1	7.32	4.03	0.18	2.95	0.57
101.2	7.60	4.43	0.19	2.94	0.59
109.7	8.07	4.72	0.24	2.95	0.55
	Table 3.17 Pentachloroethane				
90.2	3.37	2.45	0.23	2.85	0.35
94.1	3.60	2.64	0.22	2.86	0.37
98.9	3.78	2.95	0.20	2.86	0.40
103.2	3.82	3.45	0.19	2.86	0.43
104.4	3.87	3.57	0.21	2.86	0.42
108.3	4.00	3.82	0.23	2.86	0.41
113.1	4.22	4.21	0.23	2.86	0.43
118.5	4.46	4.49	0.26	2.87	0.43
123.5	4.61	4.65	0.29	2.87	0.42
	Table 3.18 1-Fluoro-1,1,2,2-tetrachloroethane				
86.4	1.92	2.46	0.23	2.84	0.24
92.3	2.11	2.93	0.22	2.83	0.27
96.2	2.23	3.16	0.21	2.83	0.29
100.8	2.27	3.71	0.21	2.83	0.30
104.7	2.42	4.14	0.21	2.84	0.31
108.2	2.47	4.22	0.22	2.84	0.31
111.5	2.56	4.46	0.24	2.83	0.31
117.7	2.84	4.68	0.28	2.83	0.31
121.8	2.84	4.71	0.30	2.84	0.30

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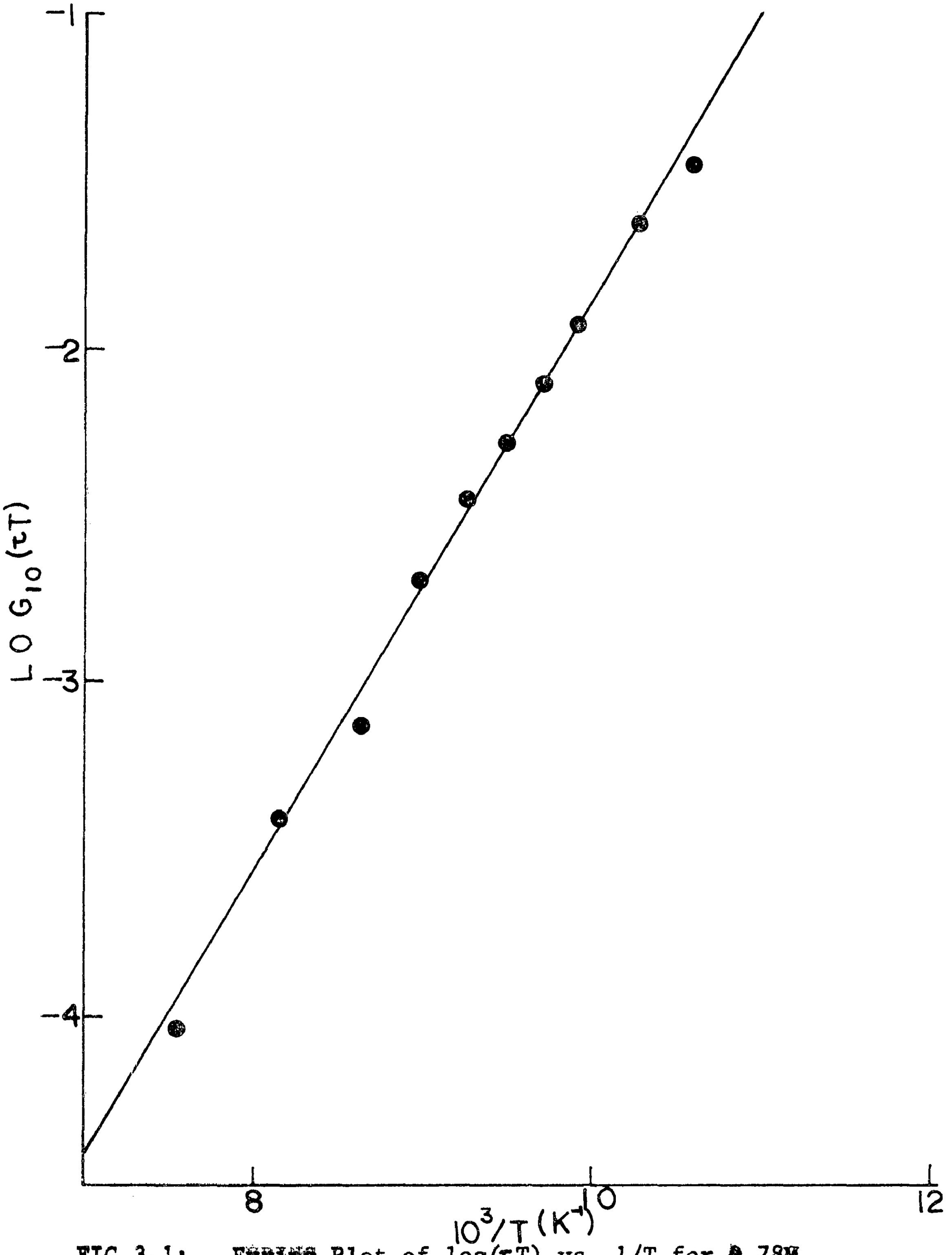


FIG 3.1: Eyring Plot of log(τT) vs. 1/T for 0.78M 1,2-Dichloroethane in a Polystyrene Matrix

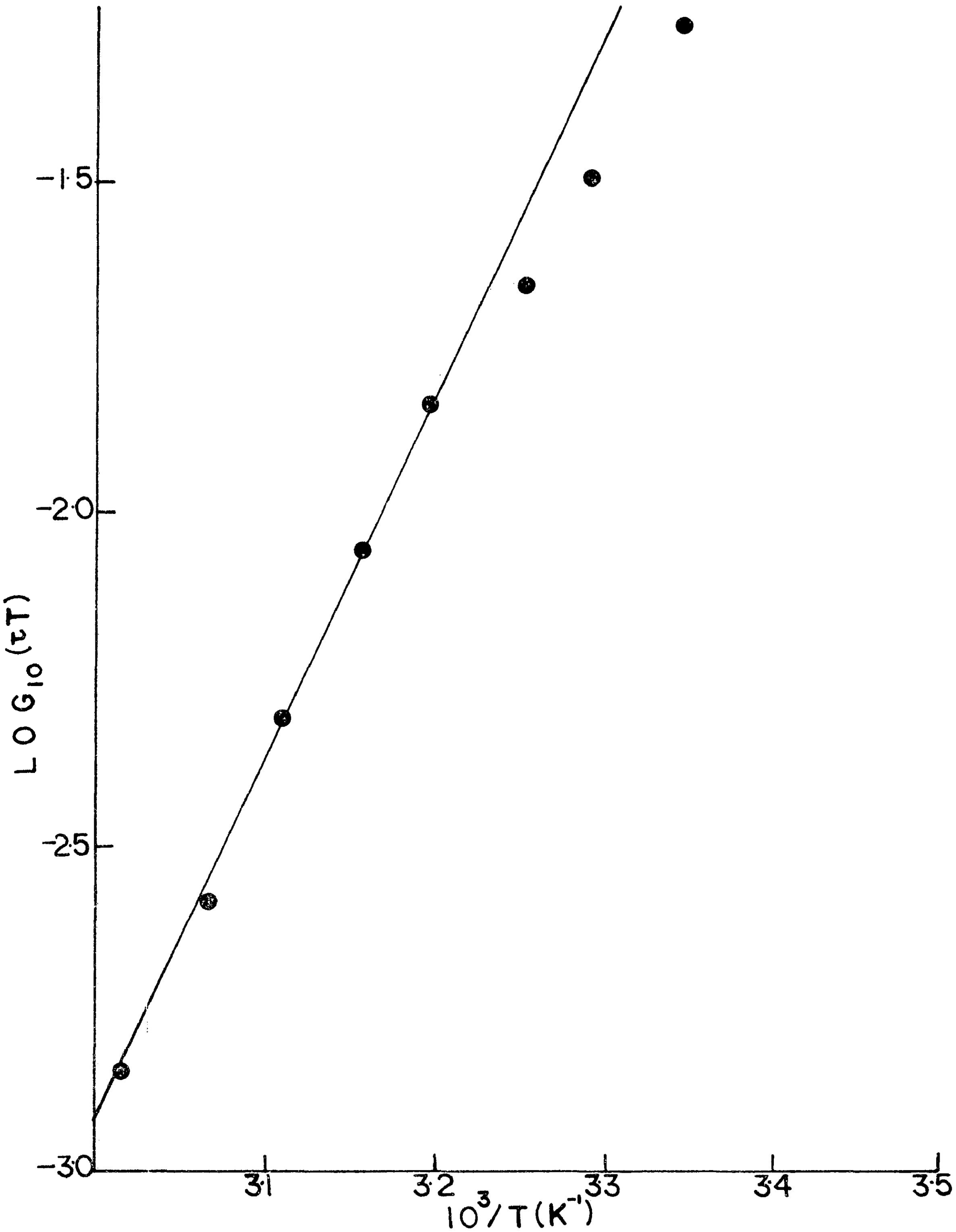


FIG. 3.2: Eyring Plot of log(τT) vs. 1/T (higher temperature region) for 0.78M 1,2-Dichloroethane in a Polystyrene Matrix

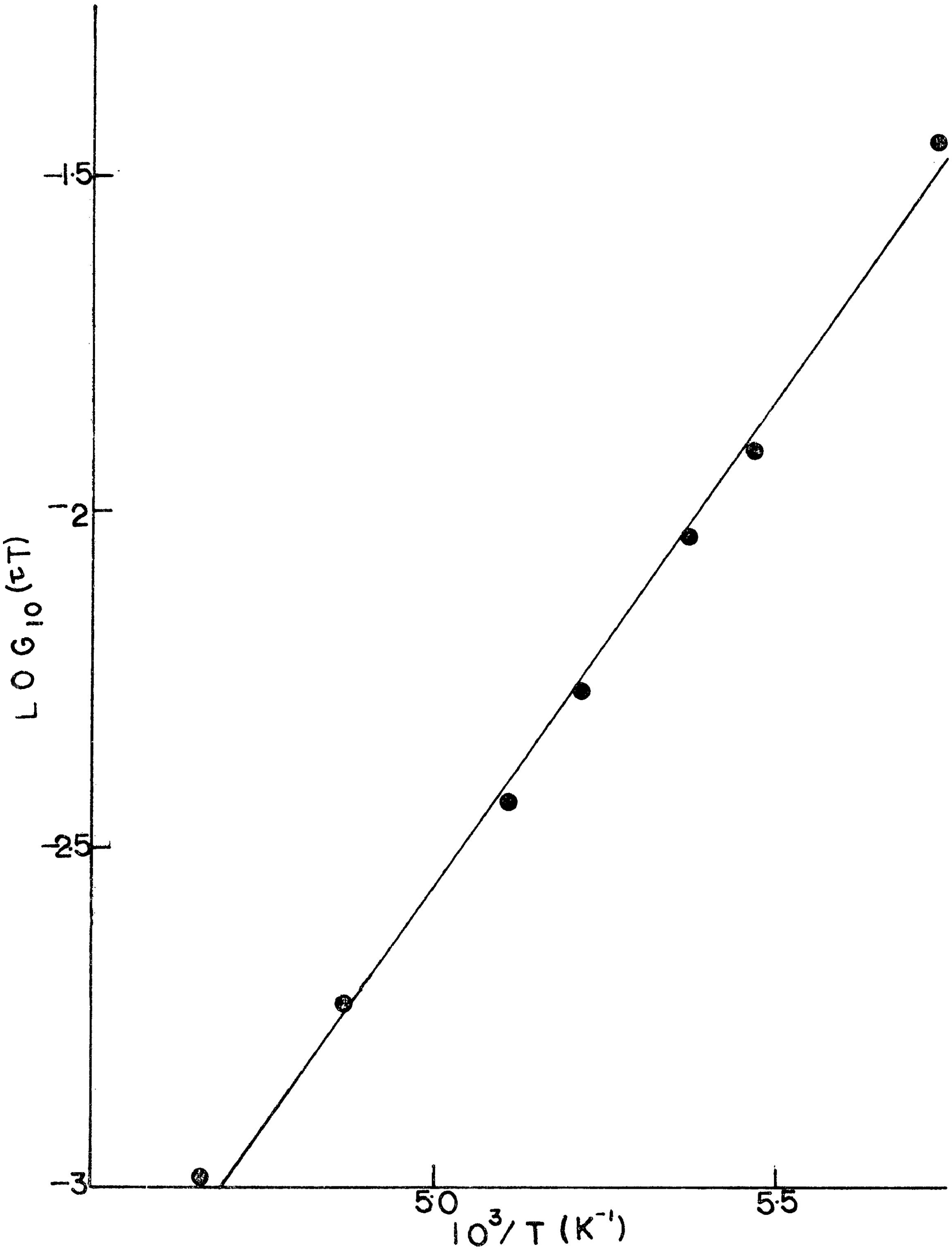


FIG. 3.3: Eyring Plot of log(τT) vs. 1/T for 0.46M 1,1,2,2-Tetrachloroethane in a Polystyrene Matrix

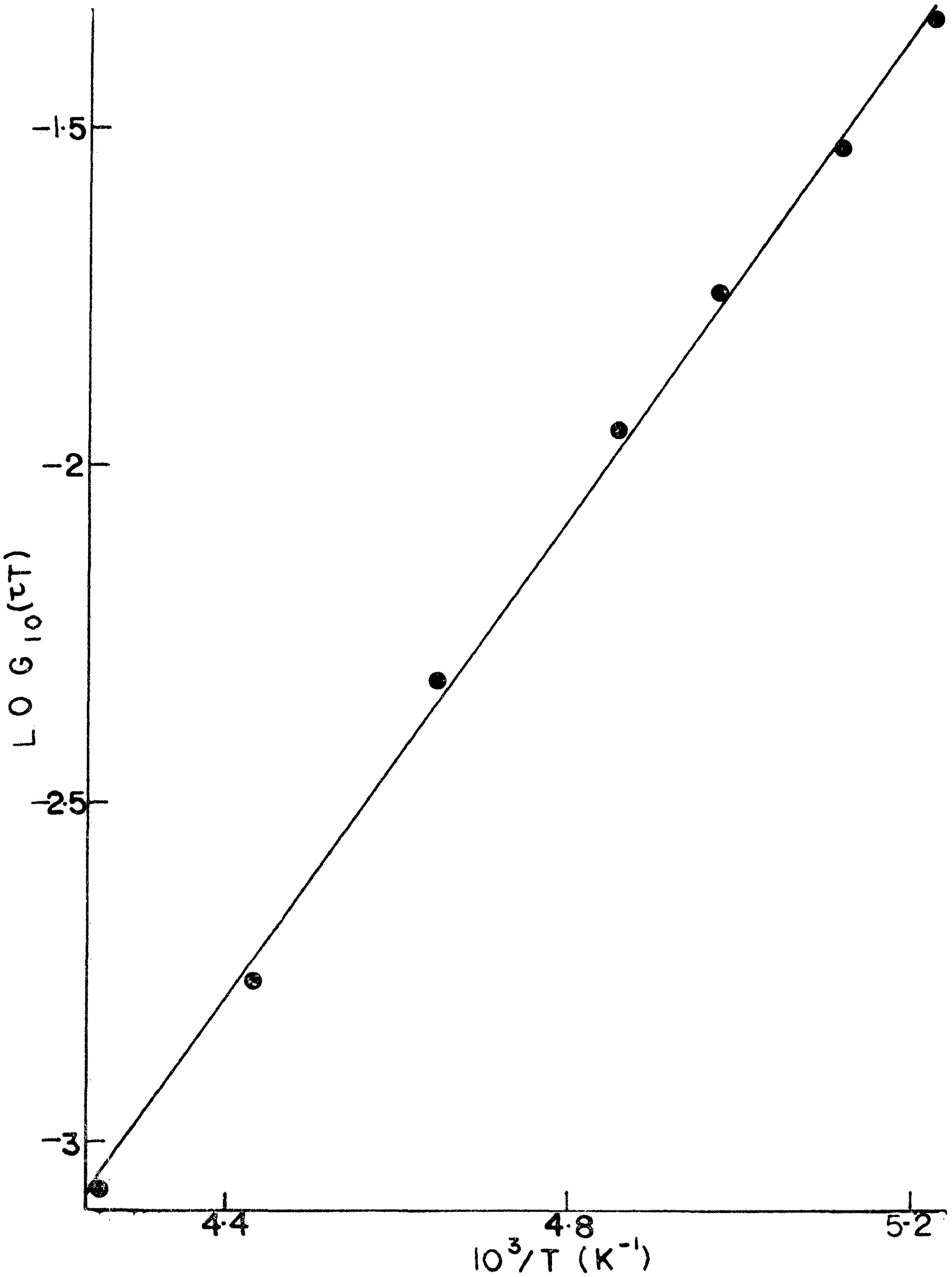


FIG. 3.4: Eyring Plot of log(τT) vs. 1/T for 0.31M 1,1,2,2-Tetrabromoethane in a Polystyrene Matrix

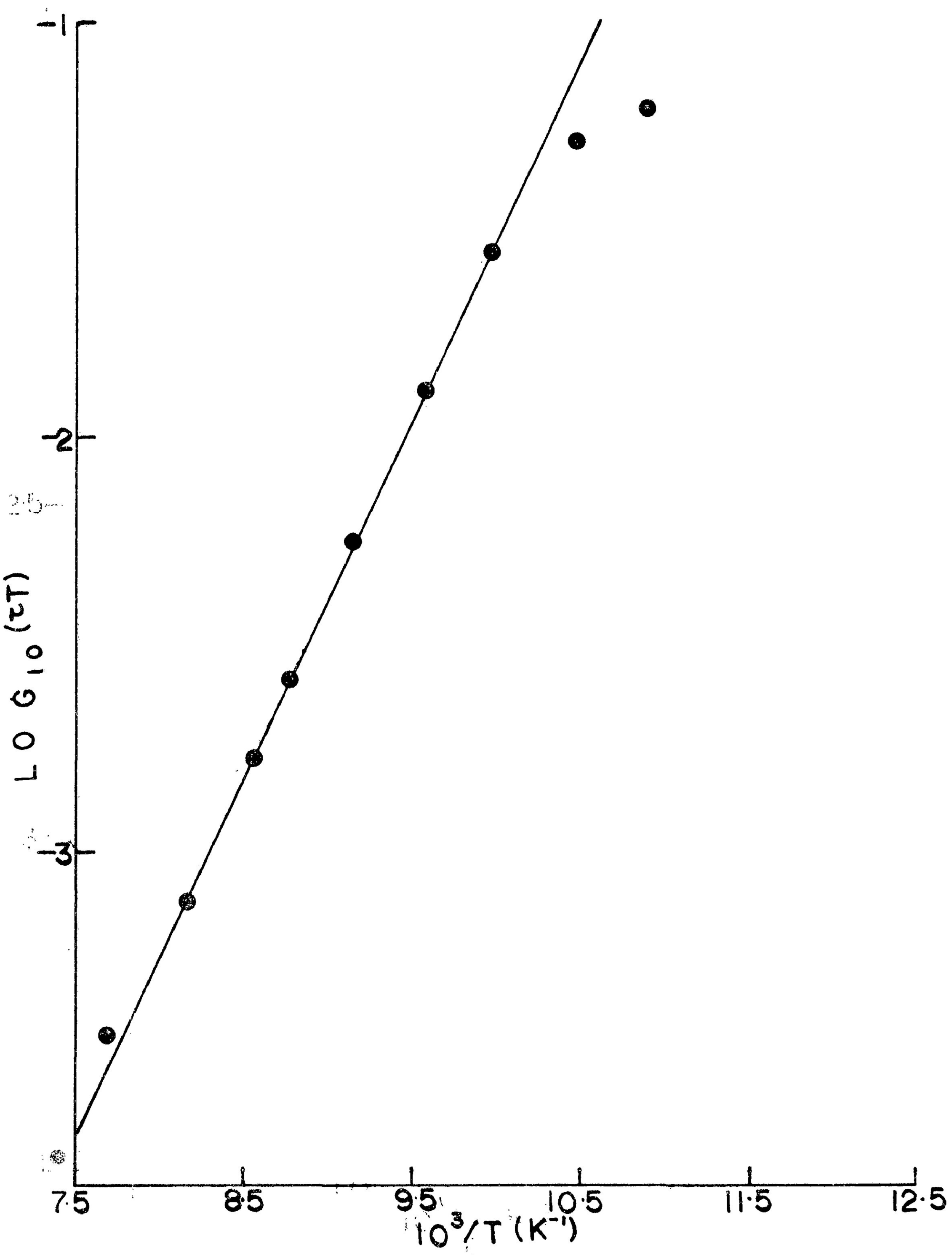


FIG. 3.5: Eyring Plot of log(τT) vs. 1/T for 0.51M 1,2-Dibromoethane in a Polystyrene Matrix

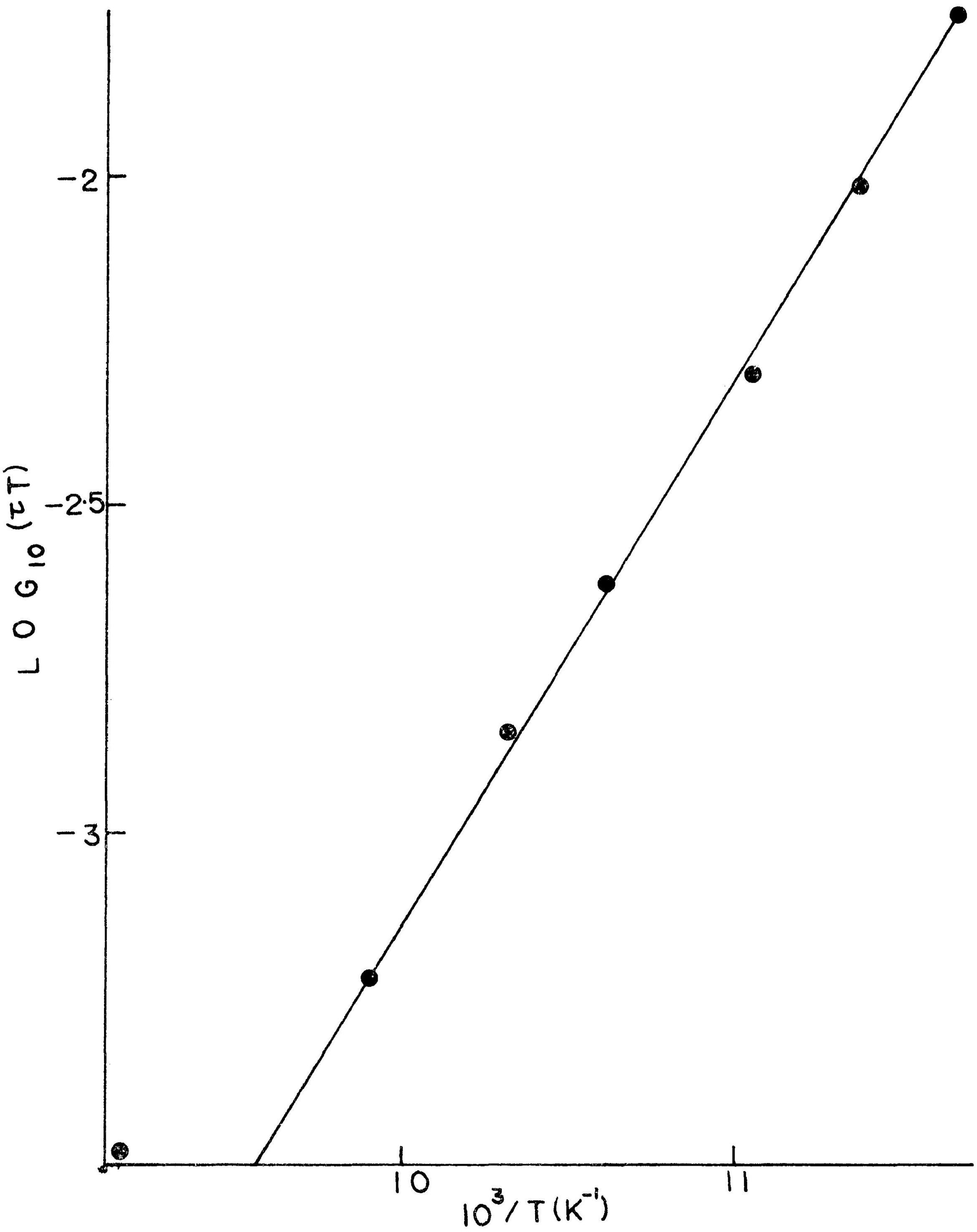


FIG. 3.6: Eyring Plot of log(τT) vs. 1/T for 0.48M 1,1,1,2-Tetrachloroethane in a Polystyrene Matrix

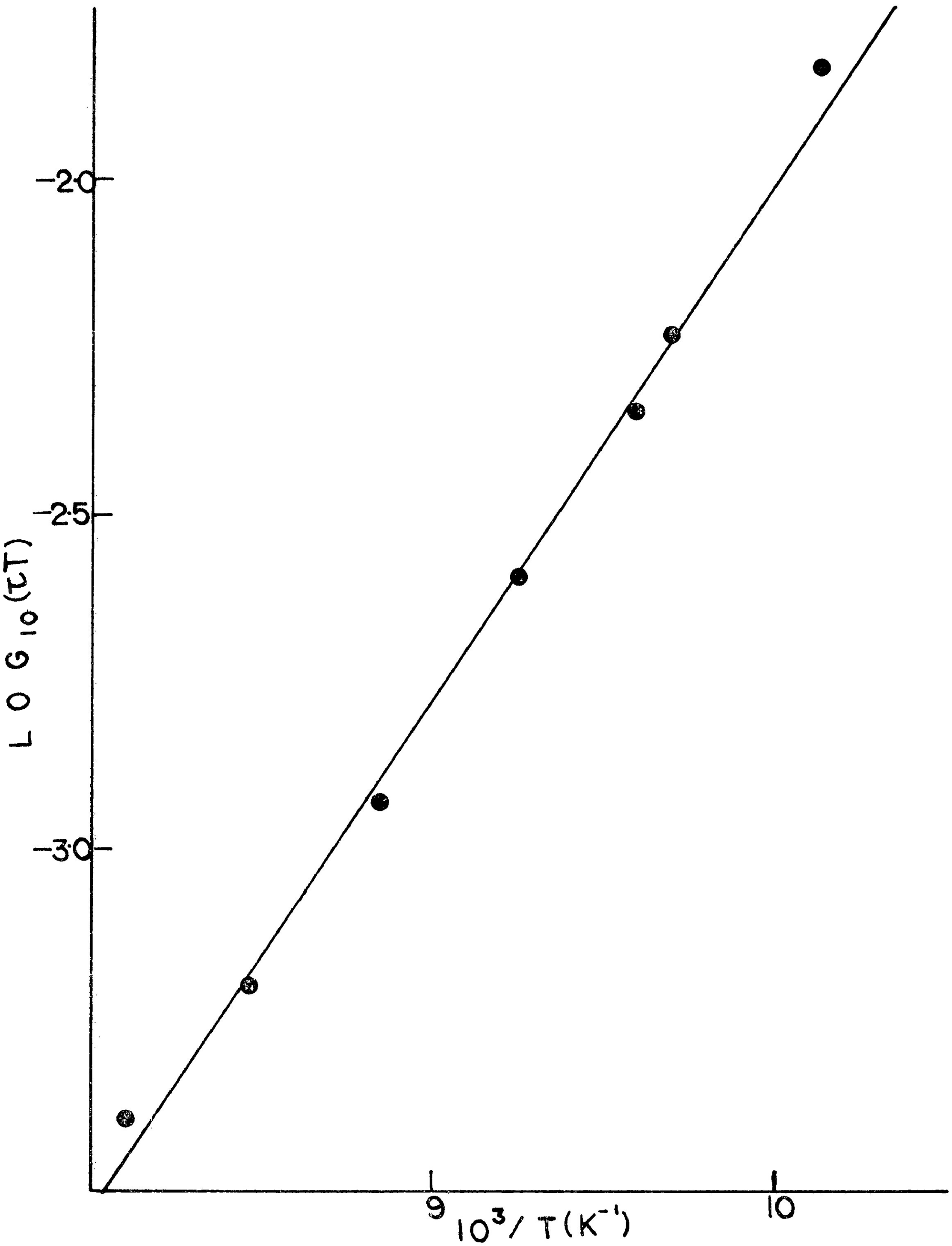


FIG. 3.7: Eyring Plot of log(τT) vs. 1/T for 0.47M Pentachloroethane in a Polystyrene Matrix

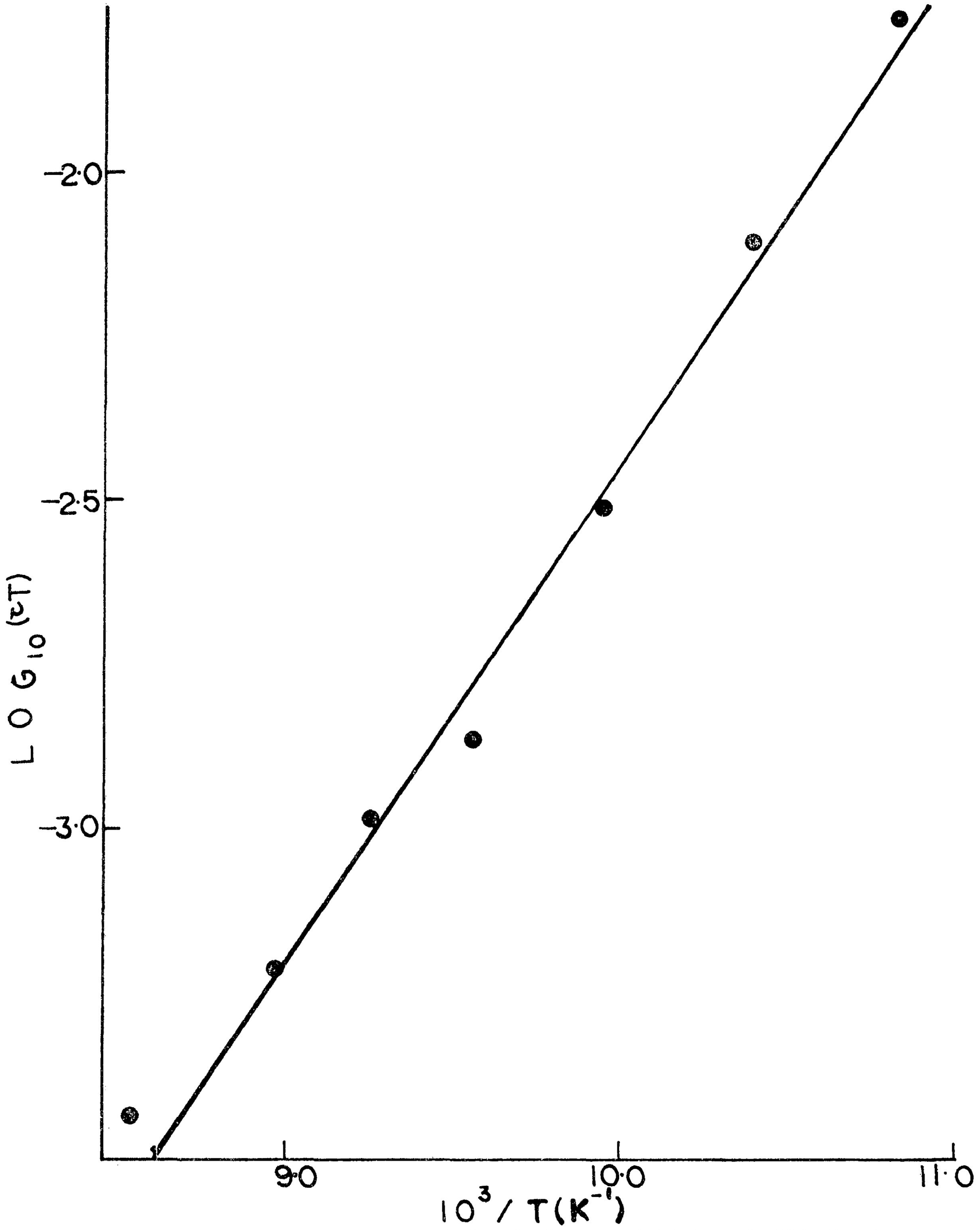


FIG. 3.8: Eyring Plot of log(τT) vs. 1/T for 0.52M 1-Fluoro-1,1,2,2-tetrachloroethane in a Polystyrene Matrix

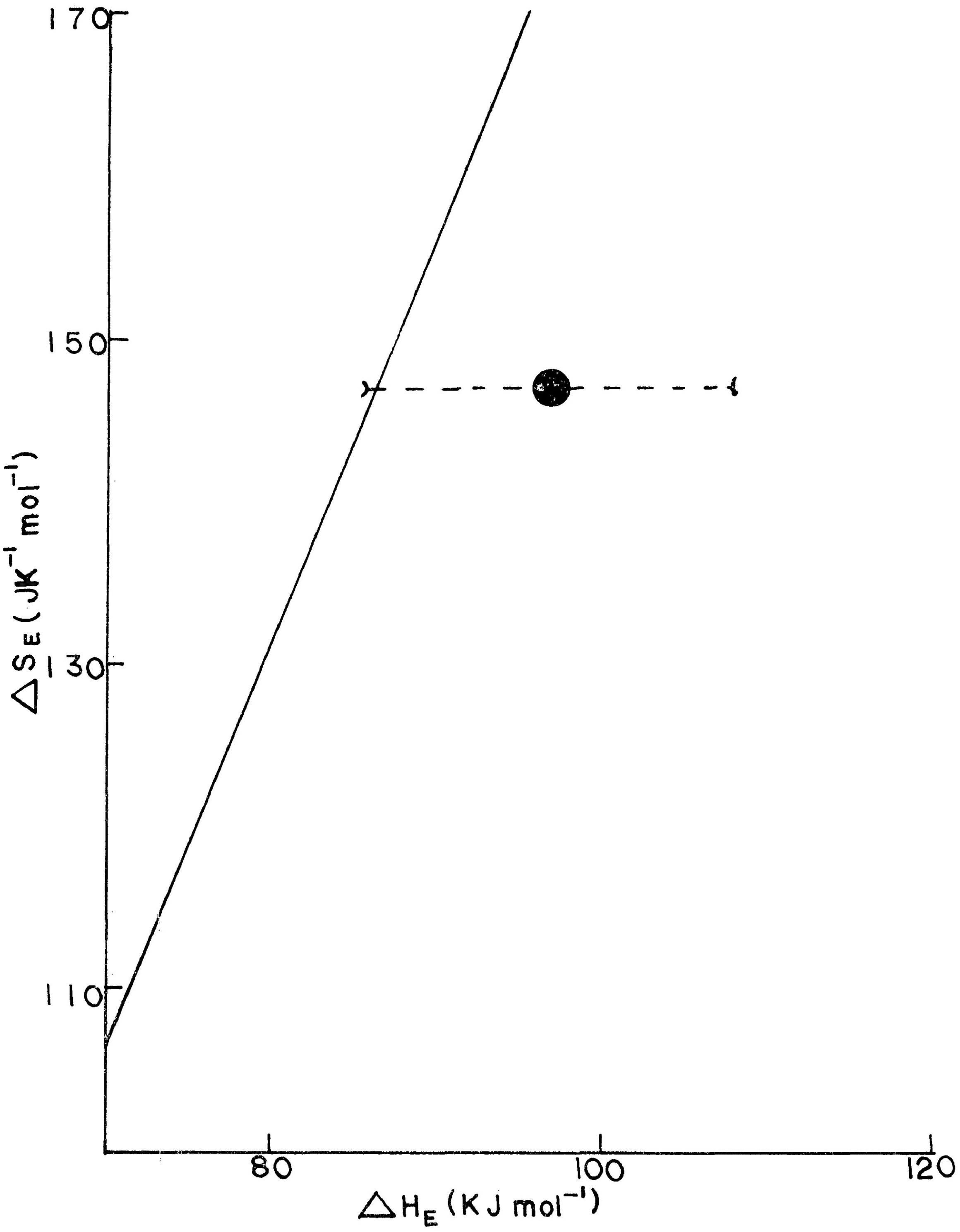


FIG.39: Plot of ΔS_E vs. ΔH_E for the linear relationship $\Delta S_E(JK^{-1}\ mol^{-1}) = -67.5 + 2.49\Delta H_E(kJ\ mol^{-1})$ for the co-operative process which is represented by the solid straight line.
● represents the relationship between ΔS_E and ΔH_E of 1,2-Dichloroethane within experimental error.

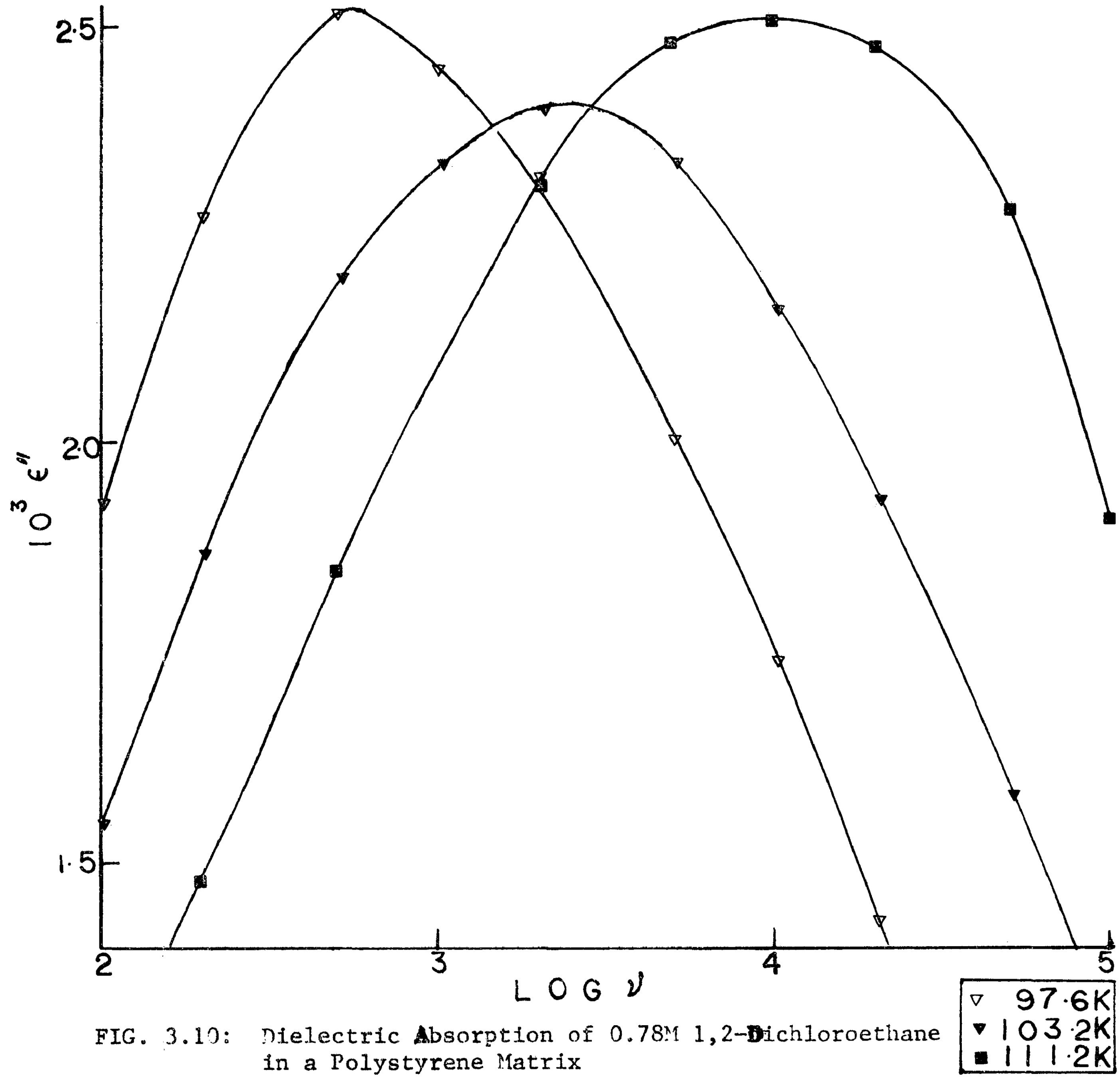


FIG. 3.10: Dielectric Absorption of 0.78M 1,2-Dichloroethane in a Polystyrene Matrix

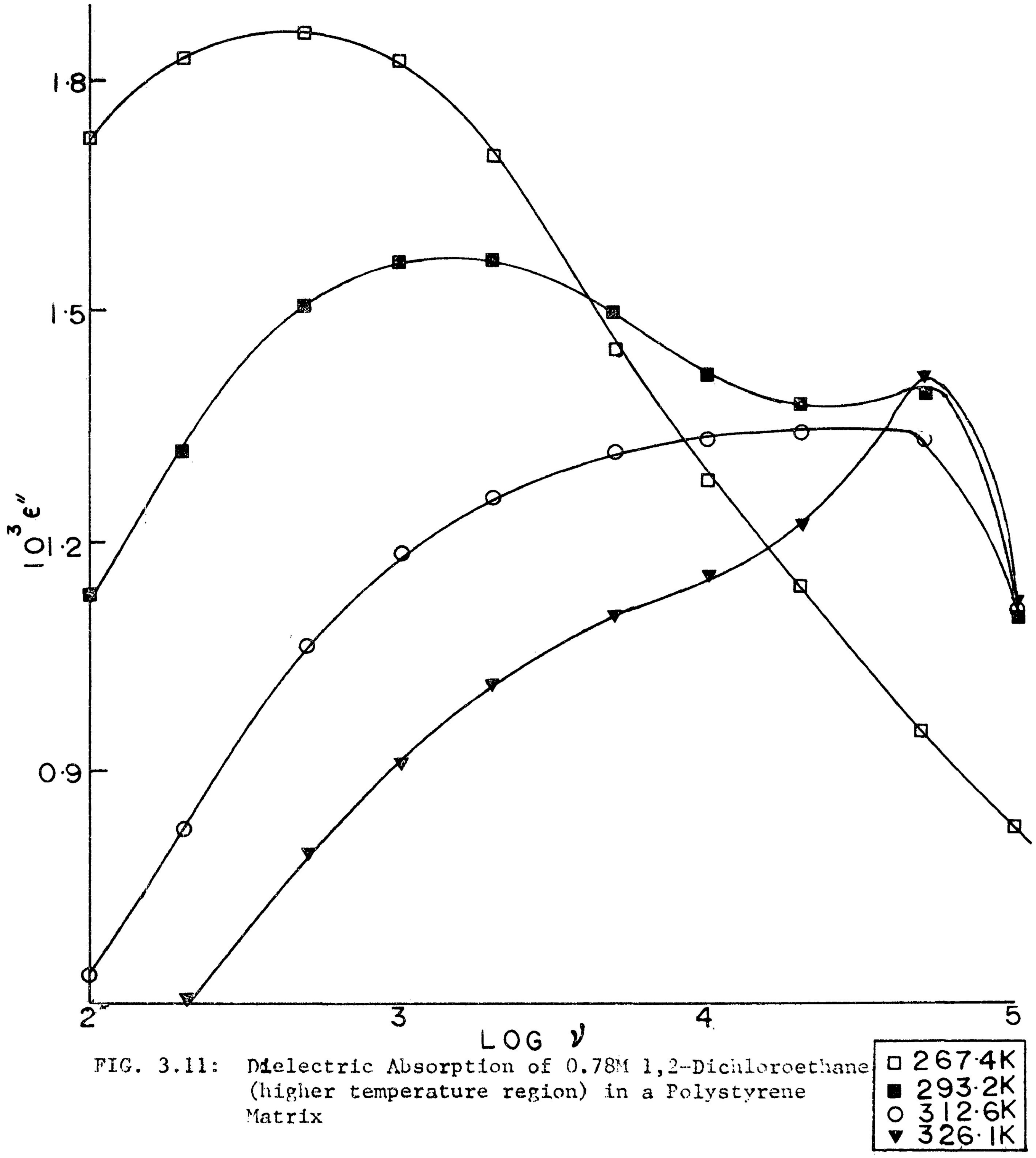


FIG. 3.11: Dielectric Absorption of 0.78M 1,2-Dichloroethane (higher temperature region) in a Polystyrene Matrix

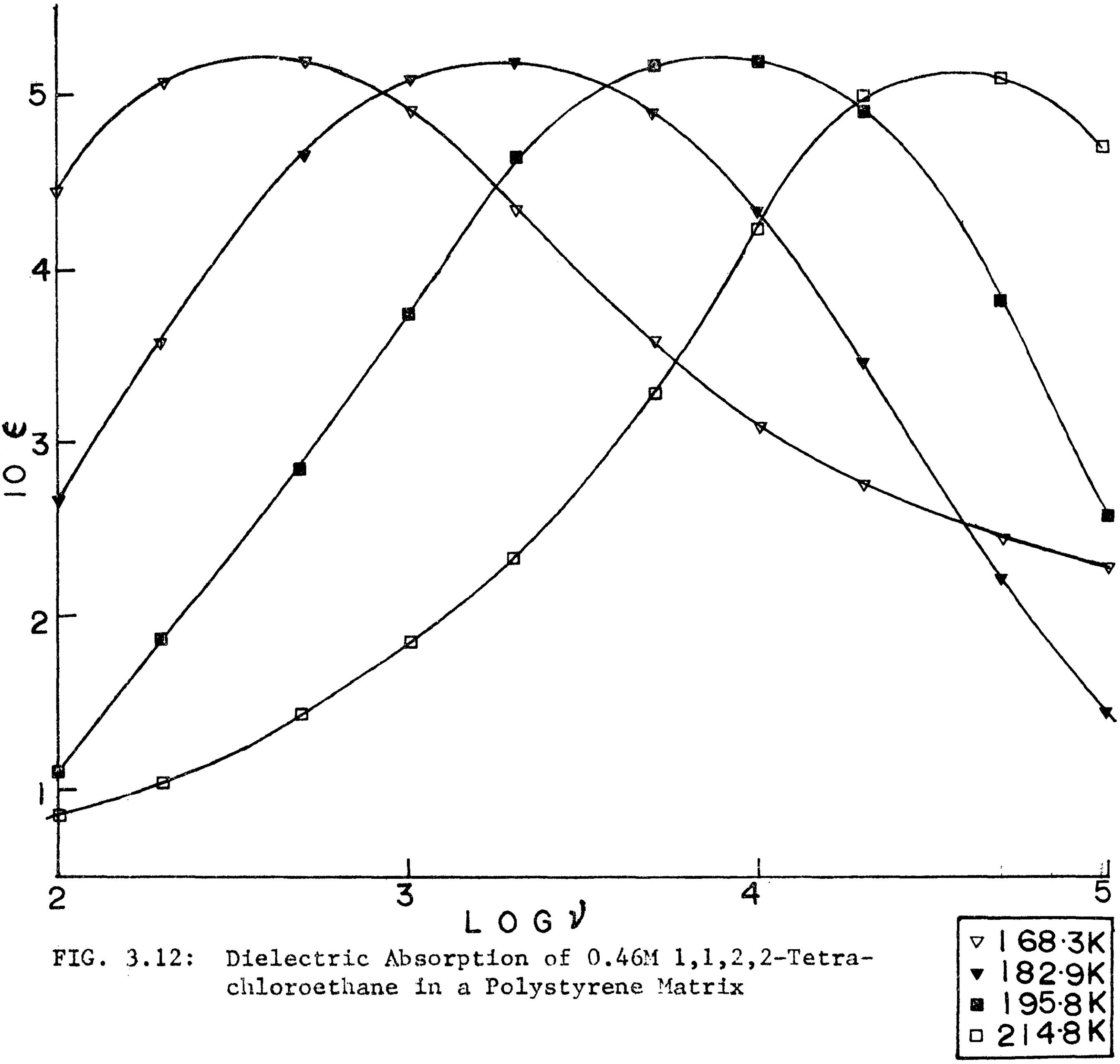


FIG. 3.12: Dielectric Absorption of 0.46M 1,1,2,2-Tetrachloroethane in a Polystyrene Matrix

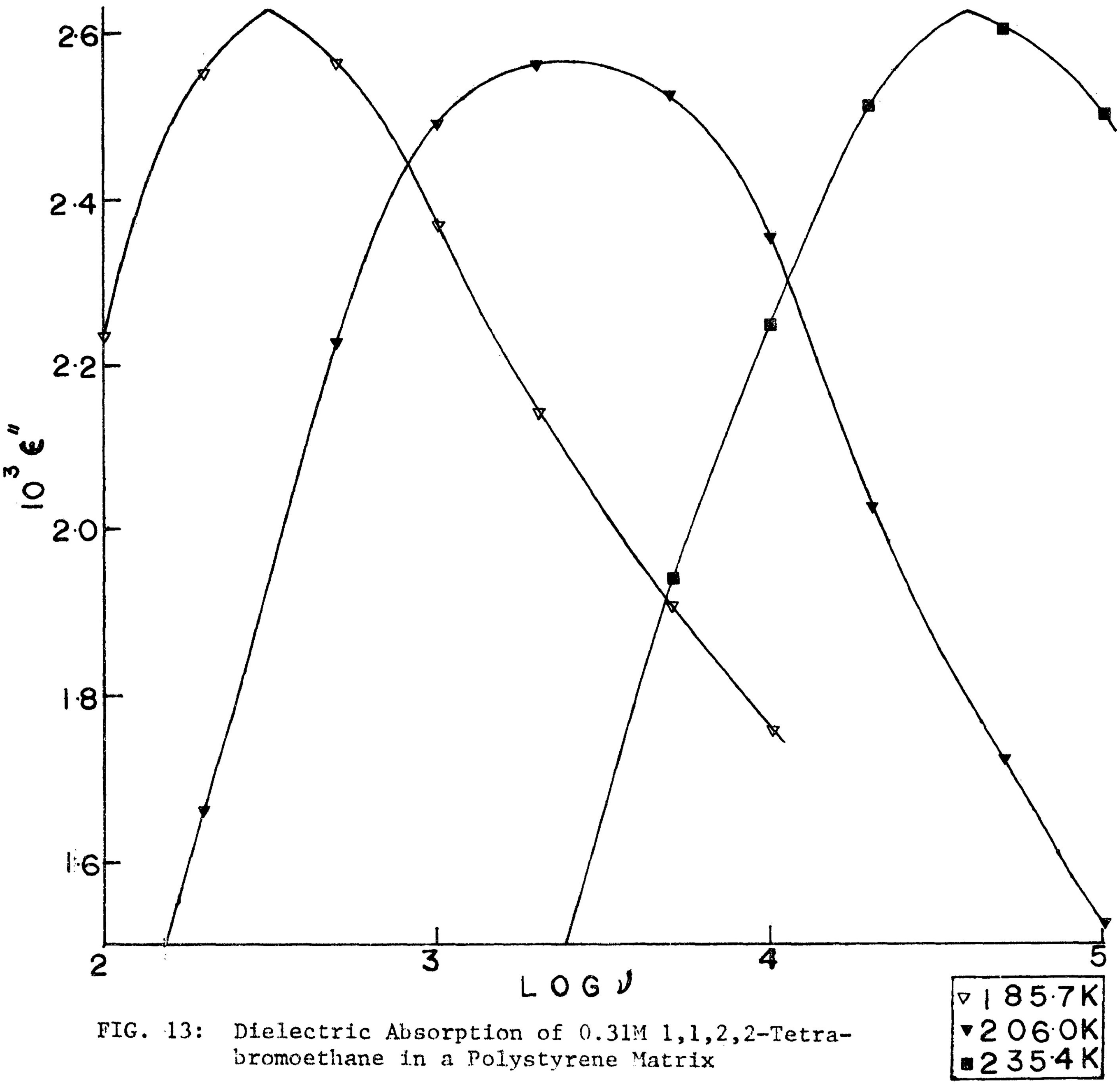


FIG. 13: Dielectric Absorption of 0.31M 1,1,2,2-Tetrabromoethane in a Polystyrene Matrix

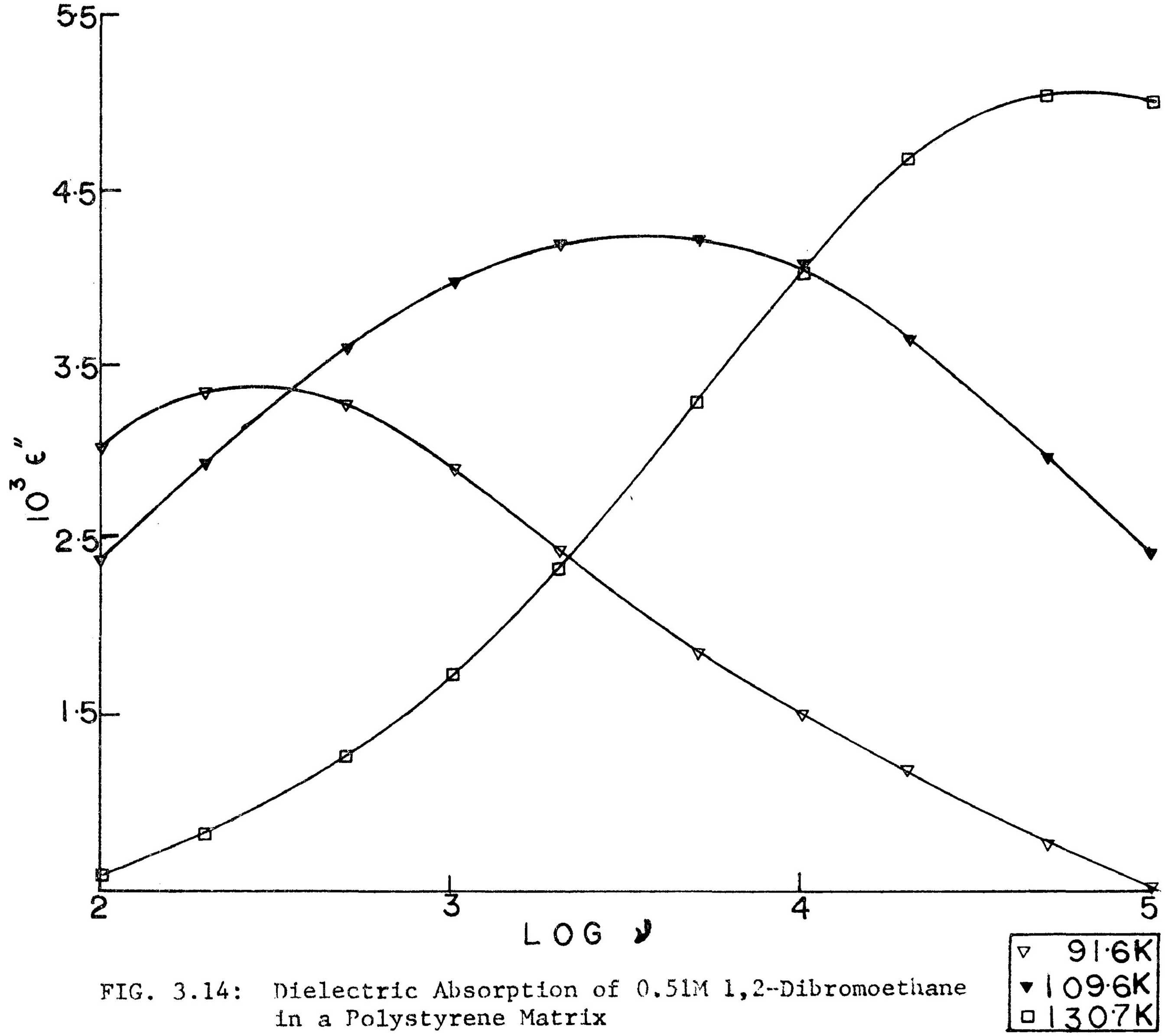


FIG. 3.14: Dielectric Absorption of 0.51M 1,2-Dibromoethane in a Polystyrene Matrix

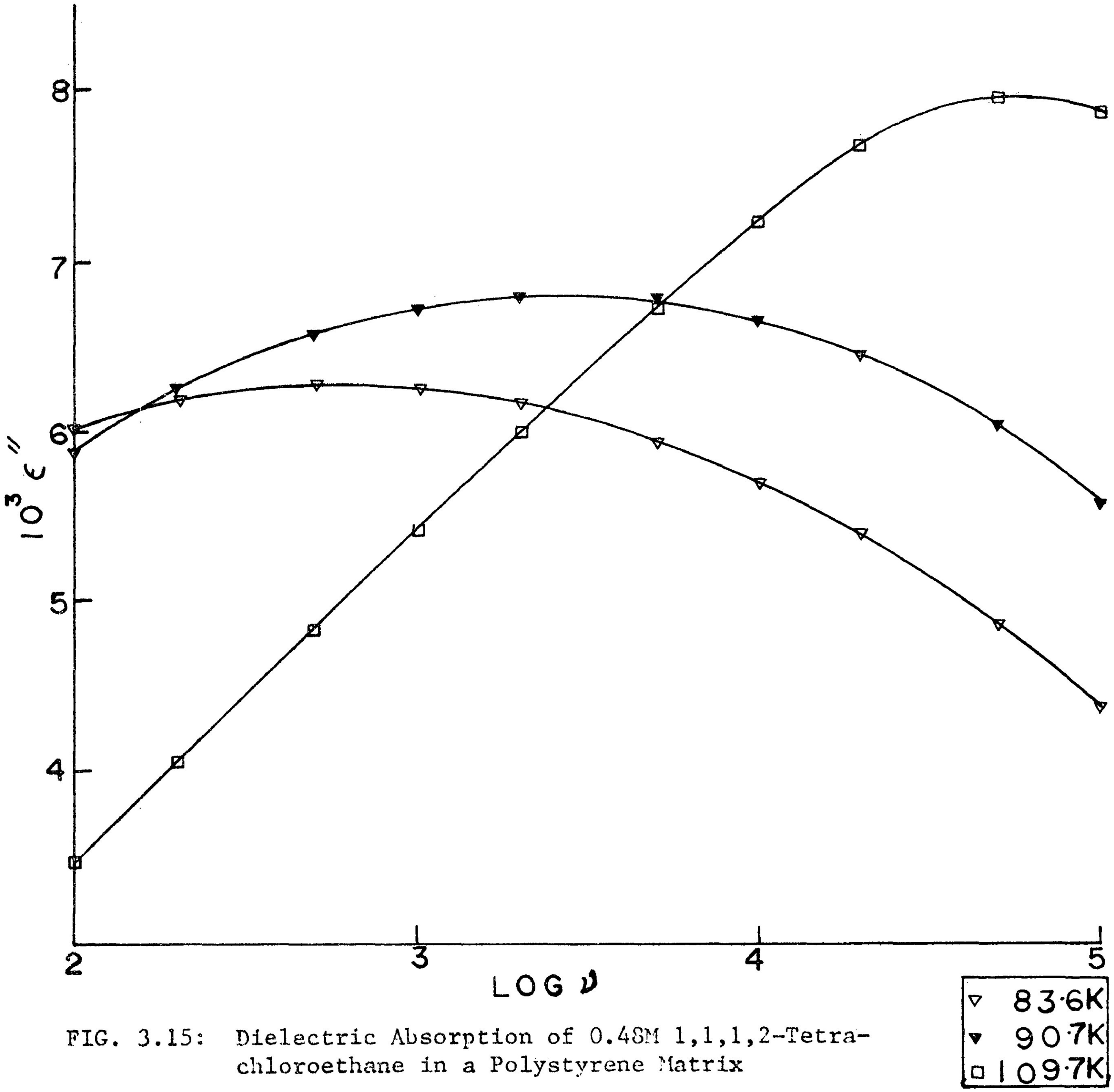


FIG. 3.15: Dielectric Absorption of 0.48M 1,1,1,2-Tetrachloroethane in a Polystyrene Matrix

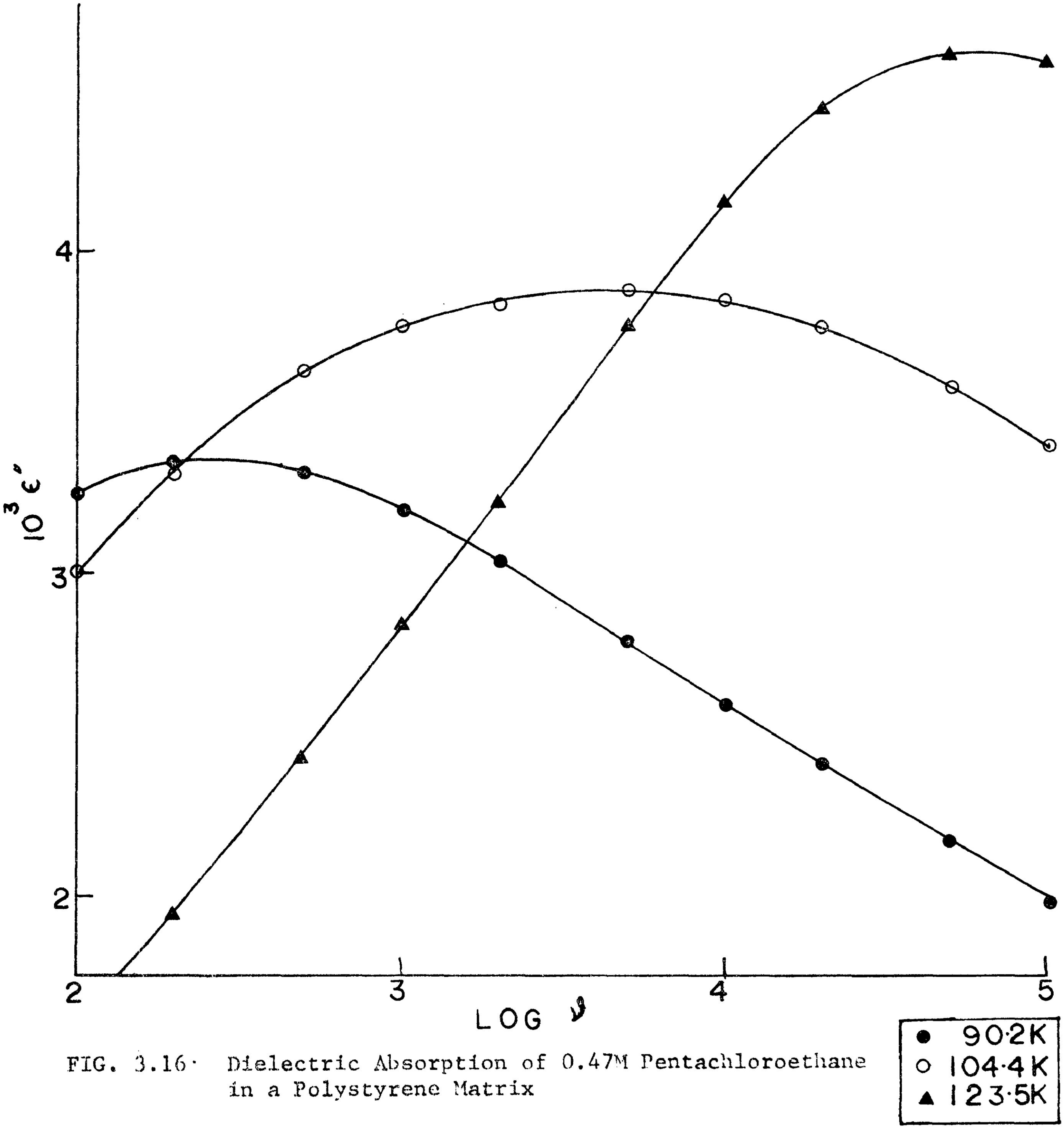


FIG. 3.16· Dielectric Absorption of 0.47M Pentachloroethane in a Polystyrene Matrix

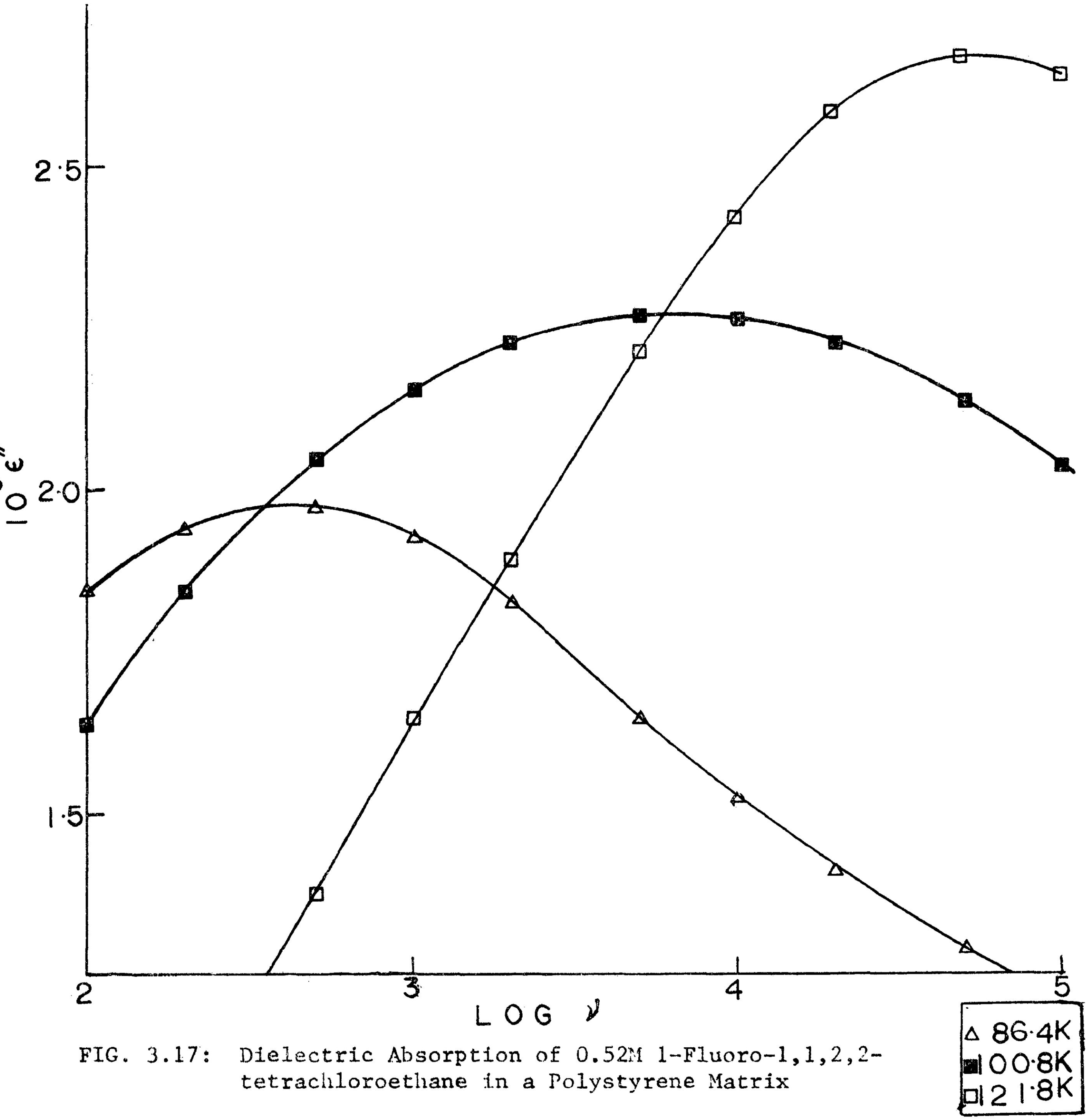


FIG. 3.17: Dielectric Absorption of 0.52M 1-Fluoro-1,1,2,2-tetrachloroethane in a Polystyrene Matrix

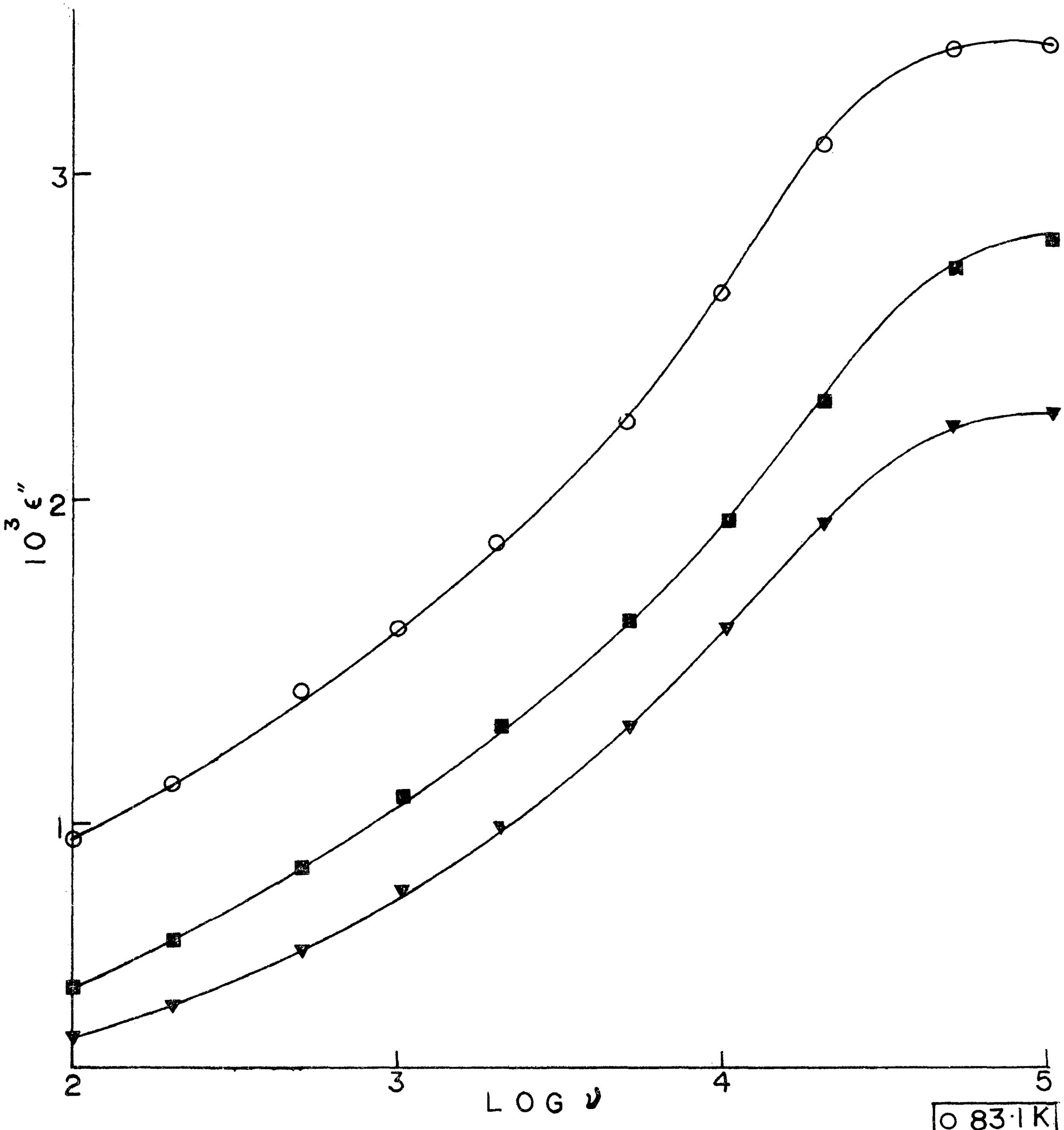


FIG. 3.18: Dielectric Absorption of 0.74M 1,1,1-Trichloroethane in a Polystyrene Matrix

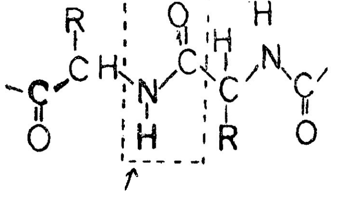
CHAPTER IV

DIELECTRIC RELAXATION STUDIES
of
SOME SIMPLE AMIDES

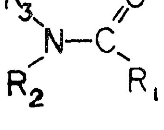
4.1 Introduction

It has been known that internal rotation of a complicated molecule inside a biological system has considerable influence on the chemical properties of that macromolecule which is vital to bio-organisms. As a matter of fact, the internal rotation of the single bonds explains a lot of natural phenomenon of life matter. The macro-molecules of the biological system comprise, in the main, simple molecules which are linked together to form a huge molecule. The three main types of macromolecules are proteins, carbohydrates and nucleic acids. These polymers have their own characteristic shape and structure which can be determined by a combination of various factors including internal rotation of the molecule.

The peptide link is a key for the synthesis of protein molecules which consist of small units of organic molecules joined together through these peptide links. Hence it is reasonable to investigate simple amides, such as alkylamides, which have the type of peptide link structure as shown in the figure below:

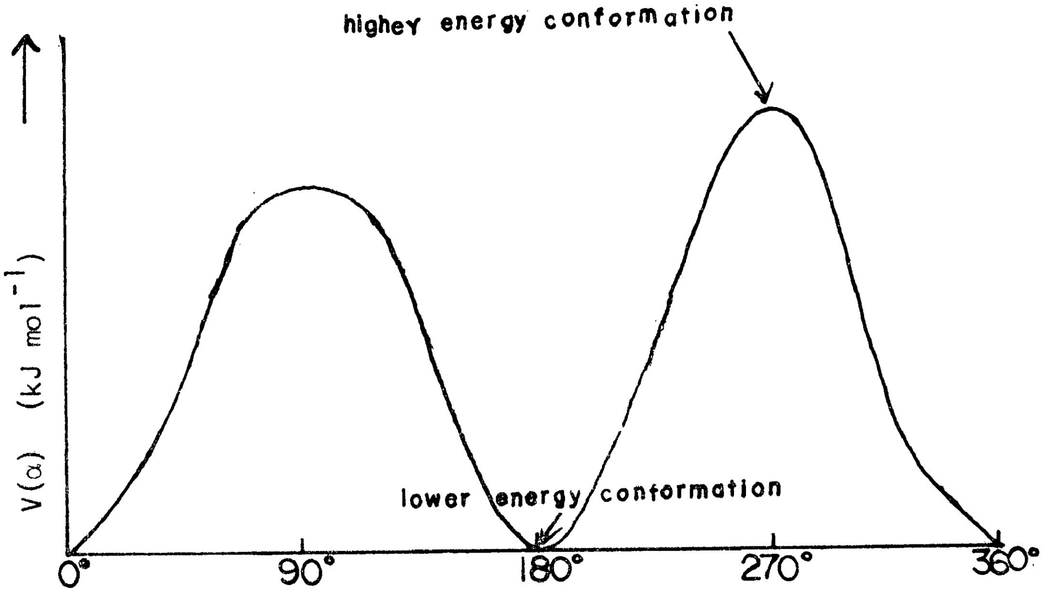


Peptide link



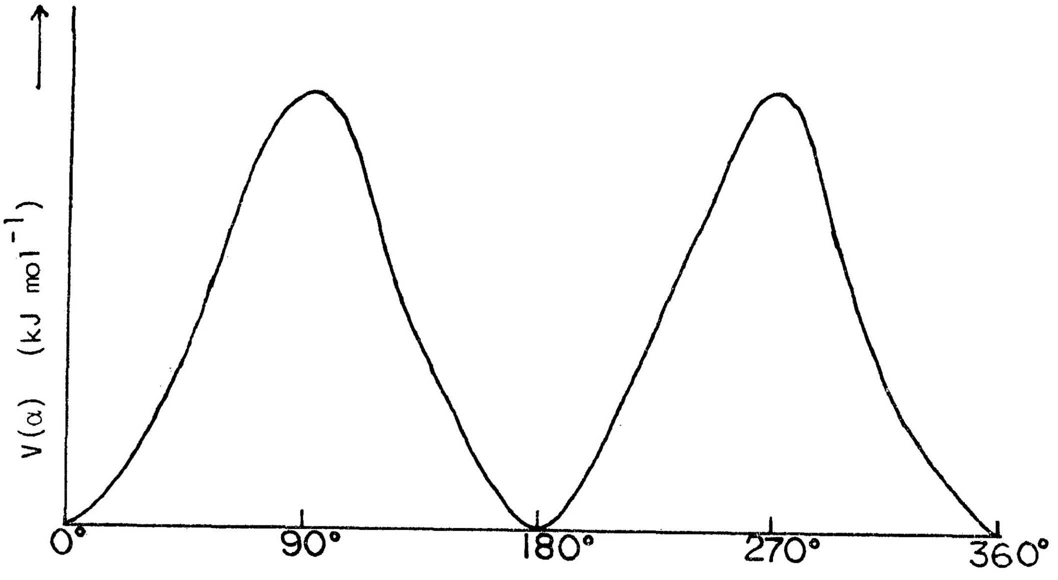
Simple amide

The simplest form of amides is formamide in which all the substituent groups are hydrogen atoms. By the replacement of the hydrogen atoms of formamide with other substituent groups such as methyl group, ethyl group, chlorine atom, etc., other amides are formed. Since these amides contain a C-N bond as shown above, the two groups around the C-N bond can rotate relative to one another to acquire a stable conformation. The potential energy profile of the rotation of the two groups about the bond of simple amides is as shown below:



Torsional Angle α →

POTENTIAL ENERGY PROFILE OF SIMPLE AMIDES (when $R_1 \neq R_2 \neq R_3$)

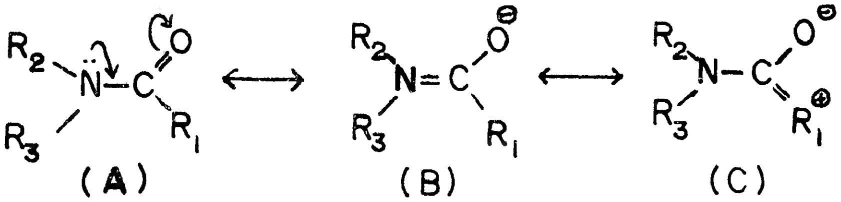


Torsional angle α →

POTENTIAL ENERGY PROFILE OF SIMPLE AMIDES (when $R_2 = R_3 \neq R_1$)

For the protein molecules the N-H bond is trans to the C=O bond so that the hydrogen atom can interact strongly with neighbouring protein molecules. This trans conformation is usually a more stable arrangement for most monosubstituted amides, and the energy barrier of internal rotation about the C-N bond makes the molecule more difficult to attain the cis conformation.

Amides consist of an amino group and a carbonyl group which can rotate with respect to each other around the C-N bond. The nitrogen atom has a lone pair of electrons, and the C-N bond possesses a partial double-bond character. The partial double-bond character of the C-N bond can be caused by the overlap between the filled sp^3 orbitals of nitrogen and the empty p orbital of carbon. Moreover, large substituents attached to the nitrogen atom may result in the flattening of the bondings around the nitrogen atom, thereby lowering the energy barrier and increasing the rate of inversion of the nitrogen atom. The carbon atom of the C-N bond is sp^2 hybridized and the P_z orbital can be utilized for bonding between the oxygen atom of the carbonyl group and itself. Together with the lone pair of electrons of the nitrogen atom and the other attached group, which sometimes possesses electron donating character, resonance structures can be drawn as shown below:

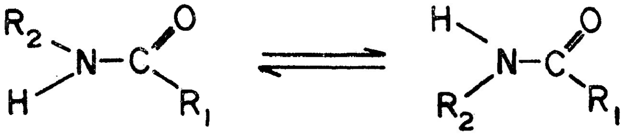


e.g. R_1 = O-M_e R_2 = Alkyl group R_3 = Alkyl group

Structure (B) above is the main contributing factor to the partial double bond character whereas structure (C) reduces this partial double bond character of the C-N bond. Hence an electron-donating substituent group when attached to the carbonyl carbon reduces the energy barrier of the C-N bond of an amide. This postulate was considered by Lustig, Benson and Duy[1] when R_1 of N,N-dimethylamide was a methoxy group which is electron-donating because of the lone pair of electrons of the oxygen atom of the methoxy group. This compound was found to have a ΔG_E value of 62kJ mol^{-1} at 260K, which was much lower than that of N,N-dimethylacetamide (ΔG_E = 79kJ mol^{-1}) found by Mannschreck.[2]

Very likely the energy barrier of the C-N bond of an amide depends on many factors such as steric hindrance, electronic factor. The energy barrier for rotation about the C-N bond may be reduced when large substituents are attached to the nitrogen atom or to the carbonyl carbon on account of the increase in the energy of the lower energy conformation due to steric interaction, thereby lowering the energy difference between this lower energy conformation and the highest energy conformation. However, sometimes the opposite is true owing to the fact that the highest energy conformation is more sterically hindered than the lower energy conformation owing to the bulky substituent groups attached to the nitrogen or the acyl residue.

For N-monosubstituted amides, usually the more stable rotamer is the structure having R_1 and R_2 trans to each other as shown below:



R_1 and R_2 may be alkyl or aryl

This is especially so when this kind of structure occurs in peptide linkage in biological system. The trans rotamer usually has a lower energy content than that of the cis rotamer, and hence there is a difference in the energy contents between the two rotamers. However, this difference is usually fairly small and not detectable because it is probably within the range of experimental error.

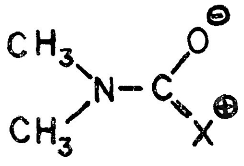
As mentioned before, an amide has a C-N bond with partial double bond character. The increase in the partial double bond character of the C-N bond means an increase in the energy barrier for rotation about this bond. Chapter III has already discussed the various types of energy barriers of ethane derivatives, and these data should give some background for examining the rotational energy barrier of amides later. Since the magnitude of the energy barrier of the co-operative process, molecular process and intramolecular process was found for simple ethane derivatives in the previous chapter, it would be possible to compare the values obtained from simple amides with those of ethane derivatives from various processes. The only difference between the C-C single bond and the C-N single bond is that no inversion barrier can exist in the C-C single bond while it is possible for inversion to occur with the C-N bond in amides.

There are many methods of determining the various kinds of energy barrier of a molecule, such as n.m.r. method, dielectric relaxation method, f.i.r. method, and microwave method. Each of these methods has its own advantages and disadvantages over the other methods. For example, it is difficult to measure the energy barrier of internal rotation of a molecule in the n.m.r. method if it is below 20kJ mol^{-1}.[3] In the dielectric relaxation method, however, energy barriers of a wide range of magnitudes can be detected as long as the absorption falls inside the range of frequencies of the equipment for the available temperature range. For the General Radio bridge, the frequency range is between 50Hz and 10^5Hz. Sometimes the relaxation process of a compound is too fast or too slow to be detected by the bridge used here in this laboratory.

Different methods of measuring energy barrier may not neccessarily give identical results. Quite often, the values by different methods differ quite significantly. Binsch[4] has pointed out that N,N-dimethylformamide alone has a wide range of energy barrier values (29-118kJ mol^{-1} for E_a) from different methods. Also N,N-dimethylcarbamyl chloride has a wide range of energy barrier values with Ea between 31-71kJ mol^{-1}. These two compounds and some other amides were measured in this laboratory by dielectric relaxation method, and the values of the energy barrier obtained may be used to compare with those obtained from other methods. All these simple alkylamides examined have different substituent groups so that a certain trend might be discovered in relation to basic features of molecular structure such as mesomerism and steric effects.

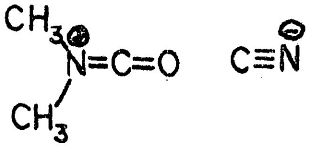
4.2 Discussion

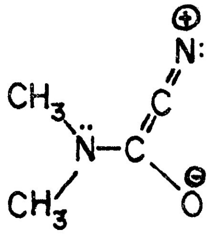
It was already mentioned that amides consist of an amino group and a carbonyl group to which various kinds of substituents can be attached. The amides concerned here are those of alkyl and halogen substituent groups. It has been suggested by many previous workers using various kinds of methods that the energy barrier of the C-N bond is influenced by a combination of factors, namely, steric hindrance, resonance and inductive effect. Kessler[3] seemed to have stressed the importance of resonance effect, although steric effects were also discussed. Sutherland[5] discussed the importance of steric effects especially for those amides with relatively large substituent group attached to the carbonyl carbon. He suggested that the energy barrier decreases when the size of the substituent group of the carbonyl group increases. According to Sutherland, this type of trend indicated the dominating role of steric effect over the electronic effect of the substituent groups. Actually, the bulky substituent group can either increase or decrease the energy barrier of the C-N bond of amide. It has been explained that the amide which contains the bulky substituent group has a higher energy content of the lower energy conformation due to steric hindrance. Thus the difference of energy between the lower energy conformation and the highest energy conformation is reduced by bulky substituent groups, thereby lowering the energy barrier of the compound. Some other amide compounds would probably show an increase of energy barrier with increasing bulky substituent group. This is probably due to the fact that the bulky substituent group destabilizes the highest energy conformation of the compound on account of steric hindrance. Besides the steric factor influencing the energy barrier of the C-N bond of amide, the electronic factor plays a significant role in determining the energy barrier of C-N bond in many circumstances. If an electronegative atom like the halogen atom of the electronegative group attaches to the carbonyl carbon, the rotational energy barrier about the C-N bond of this amide is higher than those having a less electronegative substituent group. The structure shown below illustrates one of the possible contributing resonance structures of a halogen substituted N,N-dimethylamide.

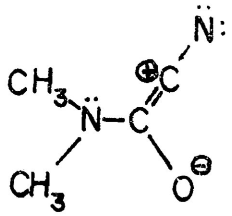


(I)

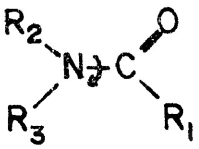
If the molecule has a higher probability of remaining in this resonance form, the compound as shown above will have a less partial double bond character. The electron lone pair of X is delocalized as shown above. Reeves et al[6] has shown that the free energy of activation (ΔG) of internal rotation of the C-N bond increases in the trend X=Br (66kJ mol^{-1}), Cl(70kJ mol^{-1}), F(76kJ mol^{-1}) and H(88kJ mol^{-1}). This trend clearly shows the increase of the rotational barrier of the C-N bond as the electronegativity of the substituent X increases. The double bond between C and X (where X=F, Cl, Br) can be visualized when the halogen atoms are assumed to be sp^2 hybridized with the lone pair of electrons in the p_z orbital. The degree of overlap between this p orbital containing the lone pair and the $2p_z$ orbital of the carbonyl carbon depends on the electronegativity of the halogen orbital. Reeves confirmed this postulation by the comparatively high rotational energy barrier of the C-N bond of N,N-dimethylcarbamyl cyanide in which the cyanide group has high electronegativity which contributes only to a small extent to structure (1) of the various resonance structures. In addition, this compound has a comparatively higher chance of attaining the resonance structure (2) shown below, which enhances the partial double bond character of the C-N bond. Although it can be argued that resonance structure (3) and (4) can contribute to the lowering of the partial double bond character of the C-N bond of N,N-dimethylcyanide, the energy contents associated with these structures are so high that these resonance structures are highly unfavourable.

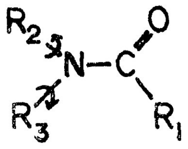

(2)

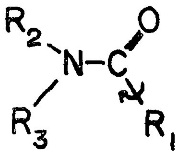

(3)


(4)

Most of the alkylamides studied by previous workers have been shown to be either dominated by steric effects or mesomeric effect for the rotational energy barrier about the C-N bond. The dielectric relaxation method used in this laboratory has been used to show which one of the above mentioned factors is more dominating for the rotational energy barrier about the C-N bond in some simple amides.


(5)

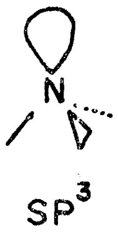

(6)


(7)

The rotational barrier in (5) is for the rotation about the C-N bond which is the main objective of this study. (6) and (7) represent the rotational energy barriers involved for the rotation of the substituent groups attached to the nitrogen atom and the carbonyl carbon respectively. Methyl amine has an energy barrier (V3) of 8.18kJ mol^{-1} (7) for the rotation of the methyl group attached to the nitrogen atom. If the value of the energy barrier detected is approximately of that value, it can probably be assigned as the rotation of a similar group attached to the nitrogen atom in amide. The group rotation shown in (7) should have a higher rotational energy barrier than that of (6) since the substituent group is attached at the carbonyl carbon. An electron donating substituent of R_1 in (7) would cause delocalization of electrons, which would increase the rotational energy barrier of this group. If R_1 is an aromatic ring, there is a better chance of delocalization of electrons through the C-C bond. Acetophenone[8] was found to have an energy barrier (ΔH_E) value of 29.6kJ mol^{-1} for the group rotation of the acetyl group. Thus, the C-R_1 group in (7) may well have a rotational energy barrier of this order of magnitude. Hence, by comparison of the value of the observed energy barrier of a compound with the values of various rotations corresponding to various types of bonds, the assigning of the observed value to a particular type of rotation is usually feasible.

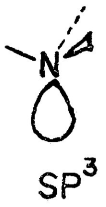
If R_1, R_2 and R_3 are alkyl groups, the rotations of $R_1 \circlearrowright\!\!- C$, $R_2 \circlearrowright\!\!- N$, $R_3 \circlearrowright\!\!- N$ would not be detected because there is a negligible perpendicular dipole moment rotating about the C-N bond or C-C bond.

The absorption exhibited by a particular compound which exhibits both molecular and intramolecular absorptions may appear at different temperatures for a given frequency range. The possible processes which can be observed are, namely, molecular process, intramolecular process, co-operative process and nitrogen inversion process. The main thing we are concerned with here is the intramolecular process which gives information about the rotational energy barrier of the C-N bond in amide. Molecular process depends mainly upon the size and shape of the molecule while intramolecular process is influenced by various factors such as steric hindrance, inductive effect, conjugation and resonance. The kind of substituent around the C-N bond contributes to the various factors mentioned above since individual substituent group possesses its own characteristics which can enhance or lower the energy barrier of the C-N bond in amides. In addition, the size of the substituent group is important in determining the steric factor involved and hence the energy barrier. Co-operative process can be detected only above the glass transition temperature of the matrix which is polystyrene in this case. The characteristic of this type of process is that the energy barrier observed is significantly high compared to all the other processes. There may be another process which can be assigned to the observed absorption in dielectric measurement, and this is the nitrogen inversion process. Ammonia exhibits this type of motion owing to the umbrella effect of the molecule. The molecule is pyramidal in structure and if the molecule inverts very quickly owing to the very low energy barrier, n.m.r. method is unable to detect it sometimes. Ammonia[9,10] has an inversional energy barrier of 25kJ mol^{-1}, while formamide[11] has an inversional energy barrier of 4.44kJ mol^{-1}. The low inversional barrier of formamide is due to the flattening of the pyramidal structure. The bulkiness of the substituent group attached to the nitrogen atom is a factor in determining the inversional energy barrier of the compound. Nitrogen atom has to change from sp^3 to sp^2 hybridization when it goes through the transition planar state, and the energy barrier of the inversion



pyramidal

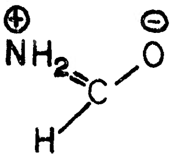
planar



pyramidal

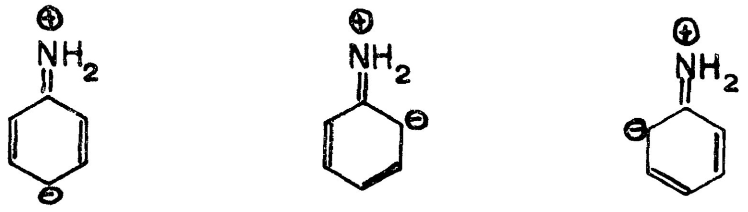
depends on the difference in energy between the pyramidal state and the planar transition state. Besides the steric factor, the electronic effect is another factor influencing the inversional energy barrier. The transition planar state of inversion can be stabilized by electron-attracting substituents such as halogen, oxygen and nitrogen, and hence the energy barrier is lowered. All these factors determine the possibility of the inversional energy barrier of alkylamides.

In recent studies, formamide[12] has been considered as a planar molecule with zero inversion barrier, and the angle between the bisector of the HNH angle and the extension of the C-N bond is also zero. It has been explained by Hirota, Sugisaki et al[14] that the contribution from the resonance structure in (8) causes the whole molecule to be planar.



(8)

Aniline[13] has an inversional energy barrier of 5.4kJ mol^{-1} which is rather low compared to ammonia. This lower barrier is related to the benzene ring attached to the nitrogen atom which tends to flatten the whole molecular structure. Moreover the increase of conjugation through the aromatic ring causes the molecule to become more planar than before. It would seem likely that other amides with fairly large substituent groups tend to planarity as a result of conjugative effect and the repulsion between various substituent groups. Such a low inversion barrier as exhibited by aniline and the highly conjugated amides would not be expected to be detected by our dielectric apparatus in the given temperature and frequency range.



Resonance structures of aniline

The chapter is especially concerned with the enthalpy of activation because this value is independent of the medium. All of the values of ΔH_E obtained are within 10% of experimental error.

The dielectric absorption process of formamide was found in the temperature range 238.7-301.5K. The corresponding enthalpy of activation has a value of 58kJ mol^{-1}. Since formamide is a relatively simple molecule without substituent groups attached to either amino or carbonyl group, the value of energy barrier can only be attributed to rotation about the C-N bond. The value of the enthalpy of activation is much too large to be attributed to nitrogen inversion or molecular relaxation. The enthalpy of activation of an ethane derivative such as dichloroethane, which is larger in size than formamide has a value of 16±2kJ mol^{-1} (see Chapter 3) for the molecular process and is found in the temperature range 93.7 to 132.8K. The possibility of assigning the observed energy barrier to the molecular process can be eliminated. The relaxation time at 300K is 1.8×10^{-6}s which is considered to be too short to be a co-operative process, and also the temperature of the absorption is not at all close to the glass transition temperature which for 7% of solute by weight in polystyrene is ∿330K.[27] Moreover, this observed energy barrier is too low to be considered as a co-operative process. The ΔG_E value at 300K is 40kJ mol^{-1}, which is the lowest value among all the alkylamides studied here, due to a large ΔS_E value (58J K^{-1} mol^{-1}).

There are no electronegative or electron-donating substituents attached to either nitrogen or to the carbonyl carbon for the consideration of electronic effect, and the hydrogen atoms attached do not cause any steric hindrance since the volume occupied by the atom is relatively small. The observed ΔG_E value of formamide can be attributed to rotation about the C-N bond which is characterized by electron delocalization between the amino group and the carbonyl group. As mentioned before, the lone pair of electrons of nitrogen contributes to the partial double-bond character of the C-N bond of formamide, and the resonance structure has been shown in (8) which leads to the planarity of the entire molecule. The absorption curves shown in figure (12) are rather broad and the plot of $\log_{10}\tau T$ vs 1/T in figure (1) has some points deviating from a straight line at the higher temperature region. The ΔS_E(58J K^{-1} mol^{-1}) value of this process is quite large, and hence the value of ΔG_E varies quite significantly at different temperatures. The β value is small which is consistent with the β values of other measured alkylamides. The value of the apparent dipole moment component of this process has been found to be 0.83D at 300K while the literature value of the overall dipole moment[14] of formamide is 3.85D. It was reported by Drakenberg and Forsen[15] that the ΔH_E value of formamide in diethylene glycol dimethyl ether and methyl propyl ketone is 79kJ mol^{-1} and 77kJ mol^{-1} respectively. These values determined by proton magnetic resonance are somewhat higher than the value determined by the dielectric relaxation method, which may, in part, be related to experimental error.

N,N-dimethylformamide differs from formamide in structure by having only two methyl groups attached at the nitrogen atom. Binsch[4] pointed out that the various values of activation energy of N,N-dimethylformamide determined by the n.m.r. technique varied a wide range. The lowest value[4] found was 29.26kJ mol^{-1}, and the highest value[4] 114.53kJ mol^{-1}. This large range of variation was due to different methods being used. Even the n.m.r. method alone, had a variety of energy barrier values. Sutherland[5] criticized some of the n.m.r. methods of evaluation and considered the total line-shape comparison method to be the most preferable. Thus with such a variety of intramolecular energy barriers for N,N-dimethylformamide it seemed worthwhile to obtain a dielectric value for comparison.

N,N-dimethylformamide showed dielectric absorption in the temperature range of (256-335K). This was more or less the same range as in formamide. The ΔG_E value of N,N-dimethylformamide at 300K was found to be 47kJ mol^{-1} which was slightly higher than that obtained from formamide. However, the ΔG_E value depends upon ΔS_E which was found to be 22J K^{-1} mol^{-1}. Since the ΔS_E value depends upon both the solute and the solvent environment, the ΔH_E value for the intramolecular barrier is preferable for comparison.

The plot of ε'' vs log (frequency) as shown in figure (13) appeared to be symmetrical. This suggested that only one process occurred in this temperature range. The plot of $\log_{10}\tau T$ vs $1/T$ (see figure 2) was on a straight line. From this Eyring plot, the ΔH_E value of 54kJ mol^{-1} for this compound was thus lower than that of formamide which was found to be 58kJ mol^{-1}. Although the two methyl groups attaching at the nitrogen atom were supposedly directing electron density towards the nitrogen atom which should result in increasing the partial double bond character of the compound, the ΔH_E value of N,N-dimethylformamide showed a slight decrease in internal rotational energy barrier rather than an increase. This decrease of internal rotational energy barrier could be accounted for by steric hindrance of the lower energy conformation of N,N-dimethylformamide, thereby raising the potential energy of the lower energy conformation. The difference between the lower energy conformation and the highest energy conformation of the compound would be smaller on account of the two methyl groups which made the lower energy conformation more unstable because of the steric factor.

The absorption process in this temperature range of (256-335K) could not be attributed to a molecular process. Molecules of similar size or larger size in substituted ethanes had ΔH_E in the range of (10-20kJ mol^{-1}). In addition, the absorption occurred in a much lower temperature range around 100K. As indicated for formamide any nitrogen inversion would not be detected by our approach.

Since the plot of $\log_{10}\tau T$ vs 1/T was on a straight line and the absorption curves in figure (13) were very symmetrical, it seems likely that there is no overlap with other processes. Further, the absorption could not be attributed to the co-operative process because the temperature range of the absorption was well below 400K. It was indicated by Broens and Muller[16] that the α-relaxation peak of polystyrene was in the temperature range 393-418K. The β value range of N,N-dimethylformamide in dielectric measurement under polystyrene matrix was found to be 0.18-0.29. This relatively low β value range was in contrast to that of the co-operative process. The temperature range (256-335K) of the absorption process found in N,N-dimethylformamide here was well below the glass transition temperature of polystyrene and also the enthalpy of activation was found to be 54kJ mol^{-1}

which was much lower than that of the co-operative processes of other compounds in polystyrene. Hence, it would be reasonable to say that the absorption process found in the temperature range 257 to 335K was an intramolecular process.

The apparent dipole moment component of the intramolecular process of N,N-dimethylformamide was found to be 1.04D which was quite close to the value of that of formamide. The literature value of the total dipole moment was 3.9D at 298K in dioxane.[14] The relaxation time of this intramolecular process was found to be 2.5×10^{-5}s, which was also close to that of fomamide. Rogers and Woodbreg[17] reported a ΔG_E value of 88kJ mol^{-1} of N,N-dimethylformamide at 298K, while it was found to be 47kJ mol^{-1} from dielectric measurement. The different values obtained by the two methods were due to a difference of solvent involved. The former value was obtained through the total line-shape method of the n.m.r. technique.

A comparison of the enthalpy of activation of formamide and N,N-dimethylformamide in table 4.1 showed that N,N-dimethylformamide had a lower energy barrier for internal rotation around the C-N bond. According to electronic effect, the contribution of electron density by the two methyl groups should have slightly increased the energy barrier of N,N-dimethylformamide by enhancing the partial double bond character of the C-N bond. However, the lower energy barrier was observed for N,N-dimethylformamide which indicated that the steric factor may possibly be playing a dominating role. Hence substitution of two methyl groups at the nitrogen atom may cause the energy content of the lower energy conformation to rise more than that of the transition state, making the difference in energy contents smaller than that without substitution.

Acetamide differs from formamide in that the carbonyl group has a methyl group attached. The dielectric absorption was in the temperature range 291.7-335.3K which was slightly higher than that of formamide. The plot of $\log_{10}\tau T$ vs $1/T$ was a straight line (see figure 3). The absorption curves (see figure 14) for various temperatures in this temperature range were fairly symmetrical with the exception that the points at higher frequency deviated slightly from the symmetrical behaviour of the curve. It seemed likely that another process was contributing significantly at the higher frequency side of the absorption. With the help of computer, Eyring analysis could be performed with the points contributing to the unsymmetrical portion of the absorption curves being eliminated. The relaxation time of acetamide was found to be 2.2×10^{-4}s at 300K which was comparatively close to the values of those of formamide and N,N-dimethylformamide. The values of ΔG_E at 300K was found to be 52kJ mol^{-1} which was higher than those of formamide and N,N-dimethylformamide. As before, this could be explained by the fact that formamide had a very high ΔS_E value (58J K^{-1} mol^{-1}) which gave a lower ΔG_E value. However, the ΔH_E value of acetamide (56kJ mol^{-1}) was found to be lower than that of formamide (58kJ mol^{-1}). The medium independent ΔH_E value of acetamide clearly showed that energy barrier was lowered when the hydrogen atom attached to the carbonyl group was replaced by the methyl group. The above comparison of the energy barrier of acetamide and formamide was based on the assumption that the absorption process of formamide and the absorption process of acetamide were both intramolecular relaxation processes.

Since the absorption process of acetamide was found to be in the temperature range 292-335K which was around room temperature, the possibility of assigning this absorption process as a nitrogen inversion process was relatively slim. In the case of aniline, the nitrogen inversion process reported by Tay[18] gave a ΔG_E value of 10kJ mol^{-1} at 300K in dielectric measurement. The temperature range was between 89-131K. The β value was about 0.2. The enthalpy of activation was only 17.3±1kJ mol^{-1}. The above mentioned parameters of acetamide were significantly different from that of aniline (see table 4.2). Hence the absorption process of acetamide in the temperature range 292-335K could not be attributed to the nitrogen inversion process. Indeed, the ΔH_E value was much too large to be attributed to this process.

In chapter 3, the relaxation parameters of the molecular process of some derivatives of ethane were shown in table 3.1. Although these molecules were not exactly the same in size as acetamide, these ethane derivatives had shown that the relaxation parameters were significantly different from those obtained by acetamide in the temperature range 292-335K. The molecular process of the derivatives of ethane was characterized by occurring in a low temperature absorption range which was near to the liquid nitrogen temperature, by the small relaxation time at 300K, by the low ΔG_E value at various temperatures, by the relatively small β value and by the small ΔH_E value which was in the range of 10-20kJ mol^{-1}. Therefore the absorption of acetamide at the temperature range 291.7-335.3K could not be attributed to a molecular relaxation process.

On the other hand, it was also impossible to attribute this absorption process of acetamide to a co-operative process, by reason of the various factors explained below. The absorption curves of acetamide were not broad. The ΔH_E value of acetamide ($56kJ\ mol^{-1}$) was not high enough to be classified as due to the co-operative process. The absorption temperature range was comparatively lower than that characterized by the co-operative process.

Since it was impossible to assign the absorption process of acetamide in the temperature range (292-335K) to be a molecular process, a nitrogen inversion process or a co-operative process, it was reasonable to argue that the absorption process was an intramolecular relaxation process, purely by method of elimination. However, the relaxation parameters of acetamide were similar to those of formamide and N,N-dimethylformamide which had been discussed above. They all had absorptions in the similar temperature range which was around room temperature. The relaxation times of the three compounds at 300K were similar to each other, which were between $10^{-4}s - 10^{-6}s$. Furthermore, the ΔH_E values were quite close to one another. Hence the absorption process of acetamide in the temperature range 292-335K must be attributed to the intramolecular relaxation process.

N-methylacetamide is a compound with an acetyl group as framework. This molecule was investigated by the dielectric method in order to correlate the energy barrier of internal rotation about the C-N bond with a substituent group being attached to the nitrogen atom. N-methylacetamide had a dielectric absorption in the temperature range 391.5-333.5K. The absorption curves in this temperature range appeared to be fairly symmetrical (see figure 15). The plot of $\log_{10}\tau T$ vs 1/T appeared to be a straight line with only very few points in the lower temperature region deviating from the straight line (see figure 4). The temperature range of absorption of N-methylacetamide was found in the same region as acetamide. The relaxation time of N-methylacetamide at 300K was found to be 2.4×10^{-4}s which was very close to the value of acetamide. By examining the relaxation parameters of N-methylacetamide (see table 4.2), all the values were similar to those of acetamide with the exception that the ΔS_E value (52J K^{-1} mol^{-1}) was significantly different. Hence it was reasonable to attribute the relaxation process in this region to be the intramolecular relaxation process as was considered in the case of acetamide.

The ΔH_E value of N-methylacetamide was found to be 68kJ mol^{-1} while the ΔG_E had only a value of 53kJ mol^{-1} because of the high ΔS_E value found in N-methylacetamide. The enthalpy of activation (68kJ mol^{-1}) of N-methylacetamide was significantly higher than that of acetamide (56kJ mol^{-1}). This increase in rotational energy barrier was possibly due to the combination of the steric effect and the electronic effect. The introduction of a methyl group to the nitrogen atom caused the nitrogen atom to have a larger electron density due to the inductive effect of methyl group which pushed electron density toward the nitrogen atom and hence the partial double bond character of the C-N bond was increased due to the availability of electron density from the nitrogen atom which had a lone pair of electrons. The other contributing factor to this relatively large increase in the rotational energy barrier about the C-N bond may be ascribed to the steric effect which raised the energy level of the highest energy conformation by reason of steric hindrance. The attachment of the methyl group to the nitrogen atom made the highest energy conformation more sterically hindered.

The β value of N-methylacetamide was found to be between 0.18 and 0.29 which was almost the same range of N,N-dimethylformamide. The apparent dipole moment component at 300K found from extrapolation was 1.49D, while the literature value of the total dipole moment of the molecule was 3.97D in the solvent of dioxane.[19]

N,N-dimethylacetamide was studied by many scientists by different methods. This compound showed a dielectric absorption process in the temperature range 287-334K. The relaxation time at 300K was found to be 5.2×10^{-4}s which was of the same order as that of N-methylacetamide and acetamide. The β range of N,N-dimethylacetamide (0.201-0.263) was similar to that of N-methylacetamide. The apparent dipole moment component of N,N-dimethylacetamide at 200K for the observed process was extrapolated to be 1.23D while the literature value of the total dipole moment of this compound in benzene at 298K was found to be 3.86D.[20] The ΔG_E (55kJ mol^{-1}) at 300K of N,N-dimethylacetamide was slightly higher than that of N-methylacetamide while the ΔH_E value (66kJ mol^{-1}) of N,N-dimethylacetamide was slightly lower than that of N-methylacetamide. The discrepancy between the trend of the ΔG_E values of the above two compounds was due to the difference between the ΔS_E values which were subjected to relatively larger error. By a comparison of the relaxation parameters of both molecules (see table 4.2), it could be found that all the values were very close to one another. Hence the absorption process of N,N-dimethylacetamide in the temperature range (287-334K) could be attributed to the intramolecular process. The plot of $\log_{10}\tau T$ vs 1/T was found to be approximately a straight line (see figure 4.5). This could be confirmed by the fact that the absorption curves were symmetrical (see figure 4.16).

Since the enthalpy of activation was largely independent of the nature of the medium, this value could be used as a reliable source for comparison of the internal rotational energy barrier of various molecules. N,N-dimethylacetamide differs from N-methylacetamide in structure by having one more methyl group attached to the nitrogen atom. Since two methyl groups contributed greater electron density towards the nitrogen atom than that of only one group from N-methylacetamide, one would expect that the partial double bond character would increase and hence the energy barrier of internal rotation. However, the enthalpy of activation of N,N-dimethylacetamide (66kJ mol^{-1}) was slightly lower than that of N-methylacetamide (68kJ mol^{-1}). Since the difference in energy barrier of internal rotation of the two compounds was less than the experimental error, it would appear that the molecules of N,N-dimethylacetamide was insensitive to the addition of one more methyl group at the nitrogen atom.

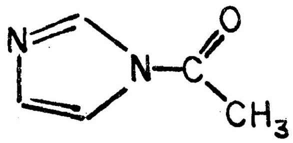
The other molecule with an acetyl framework studied in this laboratory by dielectric measurement was N-ethylacetamide. It has an ethyl group at the nitrogen atom instead of a methyl as in N-methylacetamide. Two distinct regions of dielectric absorption were found for N-ethylacetamide with one region around room temperature and the other in a lower temperature range. The higher temperature range was between 264-327K, while the lower temperature range was between 144-189K.

The enthalpy of activation of the process in the higher temperature region of dielectric absorption was found to be 72kJ mol^{-1}. This value was higher than the value of N-methylacetamide (67kJ mol^{-1}) and N,N-dimethylacetamide (66kJ mol^{-1}). The absorptions were in the same range of N-methylacetamide, N,N-dimethylacetamide and acetamide. The relaxation time of N-ethylacetamide at 300K (4.4×10^{-5}s) was close to the value of tert-butylacetamide (6.1×10^{-5}s) and that of N-methylacetamide (2.4×10^{-4}s). The ΔG_E value at 300K was smaller than that of N-methylacetamide, N,N-dimethylacetamide and acetamide. This was because the ΔS_E value was found to be relatively high (76J K^{-1} mol^{-1}). The range of β values was between 0.25 and 0.33 which suggested the absorption process involved could possibly be an intramolecular one since the usual β value range of molecular process was somewhat lower than this. The apparent dipole moment component of N-ethylacetamide at 300K (1.29D) resembled that of N,N-dimethylacetamide (1.23D) which showed a dielectric absorption in the similar temperature range. The literature value of the total dipole moment of N-ethylacetamide in dioxane was 3.90D.[21] The relaxation parameters of the dielectric absorption at this higher temperature region resembled those of acetamide, N-methylacetamide, N,N-dimethylacetamide and tert-butylacetamide (see table 4.2).

Figure 4.6 showed the plot of $\log_{10}\tau T$ vs 1/T for N-ethylacetamide in the temperature region of 264-327K. The points lay in a straight line with the exception of two points at higher temperature which deviated from the line. These two irregularity points corresponded to the slightly unsymmetrical absorption curves at 312.6K and 3.22K respectively shown in figure 4.17, while the other absorption curves at lower temperatures were fairly symmetrical. The two unsymmetrical curves may suggest an overlap with another process which is possibly the co-operative process. Another absorption process of N-ethylacetamide was found in a much lower temperature region which was possibly due to the molecular process of the molecule. Since formamide has been established to be planar[14], N-ethylacetamide and other small amide molecules discussed here may also be planar. Even if the molecule is slightly out of plane, the energy barrier of nitrogen inversion will be too small to be detected by dielectric measurements.

The lower temperature absorption of dielectric relaxation process was in the range 144-189K. The plot of $\log_{10}\tau T$ vs $1/T$ (figure 4.7) was on a straight line indicating that there was no overlap with other processes. Also the absorption curves in figure 4.18 reinforced this fact because the curves were highly symmetrical. The low β values (0.16-0.23) in the absorption region may indicate the relaxation process was a molecular process.

Mazid[22] found two absorption processes of N-acetylimidazole, with one at a lower temperature range (126-158K) and the other at a higher temperature range (240-297K). The structure of N-acetylimidazole is shown below:



N-ethylacetamide also has the acetyl group and it is similar in length and size to N-acetylimidazole. N-ethylacetamide was found to have both absorption ranges slightly higher than those of N-acetylimidazole. The enthalpies of activation of the higher temperature range of N-ethylacetamide and N-acetylimidazole were

72kJ mol^{-1} and 50kJ mol^{-1} respectively, while the enthalpies of activation of the lower temperature range were 23kJ mol^{-1} and 24kJ mol^{-1} respectively. Mazid ascribed the absorption process in the lower temperature range of N-acetylimidazole to the molecular process and the absorption process of the higher temperature range of the molecule was attributed to the intramolecular process of internal rotation around the C-N bond. It was not surprising to notice that the energy barriers of the molecular processes of both molecules were similar to each other because the size and the structure of both molecules were similar. However, the enthalpy of activation of N-ethylacetamide (72kJ mol^{-1}) of internal rotation was higher than that of N-acetylimidazole (50kJ mol^{-1}). This lower energy barrier of internal rotation of N-acetylimidazole may be due to the fact that the lone pair of electrons of the nitrogen atom attached to the acetyl group furnishes the five-member ring to satisfy the Huckel's rule in order to become aromatic in nature. Hence the partial double bond character of the C-N bond between the acetyl group and the five-membered ring was reduced, thereby the energy barrier of internal rotation of the C-N bond was lowered. From all of the considerations above, it can be concluded that the lower temperature region of dielectric relaxation process of N-ethylacetamide can be assigned to be a molecular process while the higher temperature region of dielectric relaxation process of the molecule can be assigned to be an intramolecular process of internal rotation around the C-N bond.

Compared to the energy barrier of internal rotation of C-N bond in acetamide, N-methylacetamide and N,N-dimethylacetamide, N-ethylacetamide has a higher energy barrier of internal rotation. This observation may be the result of the two factors, namely an electronic effect and a steric effect. Since the ethyl group is a better electron donor than a methyl group, it is thus possible for the partial double bond character of the C-N bond to be increased. The increase in the energy barrier to internal rotation about the C-N bond in N-ethylacetamide over the other mentioned above may also be enhanced by the more bulky ethyl group attached to the nitrogen atom. The overall length of the molecule is longer than acetamide, N-methylacetamide or N,N-dimethylacetamide. The more bulky ethyl group may cause the rise in energy level of the activated state of internal rotation, thereby widening the gap between this state and the lower energy conformation. N,N-dimethylacetamide has two methyl groups attached to the nitrogen atom and hence the nitrogen in N,N-dimethylacetamide should be richer in electron density than that in N-ethylacetamide which contains only one ethyl group. The partial double bond character of the C-N bond in N,N-dimethylacetamide should be greater than that in N-ethylacetamide when electronic effect and inductive effect were considered. Nevertheless, a high energy barrier of internal rotation around the C-N bond for N-ethylacetamide was observed, indicating that the steric factor may be more dominating.

Tert-butylacetamide is another molecule which contains the acetyl group. In structure, it differs from N-ethylacetamide by having a tertiary butyl group instead of an ethyl group attached to the nitrogen atom. Hence it is reasonable to anticipate similar characteristics for at least some of the relaxation parameters. Like N-ethylacetamide, tert-butylacetamide showed two relaxation processes in two different temperature regions, one being around room temperature (279-328K), with the other at a lower temperature region (159-216K).

The lower temperature absorption region of tert-butylacetamide gave an enthalpy of activation of 26kJ mol^{-1} and ΔS_E of -17J K^{-1} mol^{-1} while N-ethylacetamide gave a ΔH_E value of 23 kJ mol^{-1} and a ΔS_E -23J K^{-1} mol^{-1} for the lower temperature absorption region. The ΔG_E values at 200K were found to be 30kJ mol^{-1} and 27kJ mol^{-1} repectively. Both compounds were found to have similar relaxation times at 200K with N-ethylacetamide having a value of $3x10^{-6}$s and tert-butylacetamide a value of

1.34×10^{-5}s. The β values of tert-butylacetamide of this lower temperature absorption region were in the range of (0.16-0.20), and the dipole moment component at 300K was found to have a value of 1.94D. The total dipole moment in dioxane found by Aroney[15] had a value of 3.85D at 298K.

The plot of $\log_{10}\tau T$ vs 1/T of tert-butylacetamide as shown in figure 4.8 lay on a straight line, indicating that there was no overlap with other relaxation processes. As in the case of N-ethylacetamide, the overall absorption of tert-butylacetamide increased with the temperature (see figure 4.19). In matrix work this absorption in the lower temperature region suggests a molecular process which was shown to be the case in cyclohexyl chloride in polystyrene matrix from the dielectric studies by Davies and Swain.[23] The small difference between the enthalpy of activation of N-ethylacetamide and tert-butylacetamide was expected since the tertiary butyl group of the latter was bigger than the ethyl group of the former. However, the length of both molecules was approximately the same. It was also reasonable to expect that the temperature range of absorption of the latter was slightly higher than the former. Consideration of the relaxation parameters of both molecules leads to the conclusion that the dielectric relaxation

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processes of both compounds in the lower absorption region around 170K are similar processes which can be assigned as molecular processes in nature.

The higher temperature absorption was found in the range 279-328K which was approximately in the same range of N-ethylacetamide (264-327K). The ΔH_E value (75kJ mol^{-1}) and the ΔG_E at 300K (49kJ mol^{-1}) were found to be slightly higher than those of N-ethylacetamide. The relaxation time of both compounds happened to be close to each other in that absorption region. The β value range was found to be (0.33-0.41) which was higher than that of the molecular process of both N-ethylacetamide and tert-butylacetamide. Most of the points in the plot of $\log_{10}\tau T$ vs 1/T shown in figure 4.9 were on a straight line with the exception of two points which slightly deviated from it. From figure 4.20 it could be seen that the absorption curves at the centre of the temperature region were fairly symmetrical, while the absorption curves of lower temperatures showed some traces of overlap with another process, probably molecular process, in the higher frequency region of the curves. From the comparison of the molecular relaxation parameters of tert-butylacetamide with those of N-ethylacetamide, it could be concluded that the two processes were similar and hence the absorption process of the former in the higher temperature region around room temperature could be assigned as the intramolecular process of internal rotation about the C-N bond.

Table 4.2 shows a list of small amides containing the acetyl group with acetamide having the lowest energy barrier of internal rotation (ΔH_E = 56kJ mol^{-1}) and tert-butylacetamide the highest energy barrier of internal rotation around the C-N bond (ΔH_E = 73kJ mol^{-1}). The ΔH_E value increases as the amino part of the molecule is substituted with larger group. As it was discussed before, the energy barrier of internal rotation around the C-N bond seemed to be fairly insensitive to the contribution of electron density by the substituent groups to the nitrogen atom. This kind of behaviour can be demonstrated by the comparison of the internal rotational energy barriers of N-methylacetamide (ΔH_E = 68kJ mol^{-1}) and N,N-dimethylacetamide (ΔH_E = 66kJ mol^{-1}). N,N-dimethylacetamide was expected to have a higher internal rotational energy barrier of the C-N bond since two methyl groups could contribute more electron density towards the nitrogen atom, thereby increasing the partial double bond character of the C-N bond. However, this was not observed and the energy barriers for N-methylacetamide and N,N-dimethylacetamide were almost the same within experimental error. It can be noticed that there is a significant jump in internal rotational energy barrier between unsubstituted acetamide and N-methylacetamide. Just by replacing the hydrogen atom by a methyl group, the energy barrier differs by a value of 12kJ mol^{-1}. When the methyl group at the nitrogen atom of N-methylacetamide is replaced by a larger ethyl group, there is an increase of the energy barrier of internal rotation. The same trend can be observed when the ethyl group of N-ethylacetamide is replaced by a tertiary butyl group in tert-butylacetamide. Therefore the steric factor is probably the dominating factor influencing the energy barrier of internal rotation of the C-N bond of small simple amides. The bulky substituent group at the nitrogen atom probably causes the rise of the energy level of the highest energy conformation of internal rotation around the C-N bond, thereby increasing the difference between the energy contents of the lower energy conformation and the highest energy conformation.

Butyramide is a molecule having a propyl group attached at the carbonyl carbon. It is larger in size than both acetamide and formamide. A dielectric relaxation process was found in the temperature range 319-332K. This temperature range was similar to those of formamide and acetamide. The β values of butyramide and acetamide were approximately in the same range. The plot of $\log_{10}\tau T$ vs $1/T$ gave a straight line (see figure 4.10) and the absorption curves were fairly symmetrical (see figure 4.21), indicating that there was no overlap with another process. The relaxation time at 300K was only slightly longer than that of acetamide. The enthalpy of activation and the entropy value were found to be 52kJ mol^{-1} and -27J K^{-1} mol^{-1} respectively. Since acetamide was shown to have an intramolecular process in this temperature region detected by means of dielectric relaxation method in polystyrene matrix, it would be reasonable to assign the absorption process of butyramide under similar conditions, having similar relaxation parameters, to be also an intramolecular absorption process. The dipole moment component of butyramide at 300K was found to be 0.99D for this absorption process while the total dipole moment from literature was 3.85D in dioxane at 298K.[24]

From table 4.3, it can be noticed that the ΔH_E value of butyramide is the lowest amongst the three compounds. All of the three compounds had no substituent groups at the nitrogen atom other than the hydrogen atoms. The decrease in rotational energy barrier about the C-N bond down the list may be favoured by both electronic effect and steric effect. Electronically, the energy barrier of internal rotation would be expected to lower if more electron density is pushed by the substituent group towards the carbonyl carbon, thereby reducing the partial double bond character of the C-N bond. On the other hand, steric hindrance may play a role in increasing the energy content of the lower energy conformation, and hence the difference in energy level between the lower energy conformation and the highest energy conformation is narrowed thereby reducing the energy barrier of internal rotation.

N,N-dimethylcarbamyl chloride differs from N,N-dimethylacetamide and N,N-dimethylformamide by having a chlorine atom substituting at the carbonyl carbon. Unlike chlorine, the methyl group which is attached to the carbonyl carbon in N,N-dimethylacetamide can donate electron density towards the carbonyl carbon.

N,N-dimethylcarbamyl chloride was found to have an absorption process in the region 286-335K, while N,N-dimethylacetamide was found to have an absorption process exactly in the same region (287-334K). The relaxation time of 300K for N,N-dimethylcarbamyl chloride and N,N-dimethylacetamide was found to be 5.7×10^{-4}s and 5.2×10^{-4}s respectively. The β values of the former were found to be in the range of 0.20-0.29, while those values of the latter were found to be in the range of 0.20-0.26 which were very close to each other. The ΔG_E values of both N,N-dimethylcarbamyl chloride and N,N-dimethylacetamide were found to be exactly the same (55kJ mol^{-1}), while the ΔS_E values were found to be 27J K^{-1} mol^{-1} and 37J K^{-1} mol^{-1} respectively. The dipole moment component at 300K of N,N-dimethylcarbamyl chloride and N,N-dimethylacetamide for this absorption region were found to be 1.43D and 1.23D respectively, while the literature values of the total dipole moment were 4.08D[25] and 3.86D[20] respectively. The ΔH_E value of N,N-dimethylcarbamyl chloride was found to be 63kJ mol^{-1} in this dielectric absorption region, while it was found out by Reeves _et al_ that the ΔH_E value was 69kJ mol^{-1} using the complete line-shape-fit method.[26] The ΔH_E value of N,N-dimethylacetamide was found to be 66kJ mol^{-1} in this absorption region. By comparing all the relaxation parameters of N,N-dimethylcarbamyl chloride in this absorption region with those of N,N-dimethylacetamide, the resemblance of all these values of the two compounds suggested that the two absorption processess were similar in nature. Since the relaxation process of N,N-dimethylacetamide was identified as an intramolecular process for the internal rotation about the C-N bond, it would be reasonable to assign the relaxation process of N,N-dimethylcarbamyl chloride in this absorption region to be also an intramolecular process for the internal rotation of the C-N bond. Furthermore, the plot of $\log_{10}\tau T$ vs 1/T gave a straight line (see figure 4.11), and the absorption curves were very symmetrical (see figure 4.22), suggesting that there was no overlap with another process.

Table 4.4 shows the relaxation parameters of the three compounds with the N,N-dimethyl group. Electronically, a higher internal energy barrier for the N,N-dimethylcarbamyl chloride would be expected because of the fact that chlorine atom is electronegative in nature. However, the ΔH_E value of N,N-dimethylcarbamyl chloride (63kJ mol^{-1}) was found to have an energy barrier lower than that of N,N-dimethylacetamide. Since the chlorine atom is approximately the same in size as the methyl group, which is attached to the carbonyl carbon, the steric effect would be expected to be the same. This was observed to be the case for N,N-dimethylcarbamyl chloride and N,N-dimethylacetamide whose ΔH_E values differed only in the range of experimental error. Hence electronic effect in this case had virtually no influence in the internal rotational energy barrier about the C-N bond. This fact could also be confirmed by comparing the ΔG_E value at 300K for both compounds which were exactly identical (55kJ mol^{-1}). However, it can be noticed that there is an increase in internal rotational energy barrier from N,N-dimethylformamide (ΔG_E at 300K = 47kJ mol^{-1}) to N,N-dimethylacetamide or N,N-dimethylcarbamyl chloride. This increase in rotational energy barrier is in good agreement with the steric effect which is caused by the rise in energy content of the highest energy conformation when a larger substituent group is substituted at the carbonyl carbon. Both ΔG_E and ΔH_E show a similar trend for the three compounds with a N,N-dimethyl framework in table 4.4. Hence it can be concluded that the steric factor plays a dominating role in determining the energy barrier of internal rotation about the C-N bond for the simple amide compounds with a N,N-dimethyl group.

All of the simple amides discussed in this chapter showed an intramolecular relaxation process around room temperature. The temperature of absorption varied from 293K in formamide to 335K in acetamide and N,N-dimethylcarbamyl chloride. The relaxation time at 300K varied from 4.0×10^{-3}s in butyramide to 1.8×10^{-6}s in formamide. The β values of this process were usually found to be above 0.2 while the β values in the molecular process of N-ethylacetamide and tert-butylacetamide were found to be smaller. The ΔG_E and ΔH_E values were significantly higher than those obtained in the molecular process. The ΔH_E values in the molecular processes of simple amides such as N-ethylacetamide and tert-butylacetamide were at least 30kJ mol^{-1} lower than those of intramolecular processes of internal rotation of the C-N bond. Since the dimensions of the amide molecules studied here in this chapter were not large, it would be reasonable to expect the

the energy barrier of the molecular process to be in the range of 20-30kJ mol^{-1}. The ΔH_E values of the intramolecular process of the simple amides studied here varied from 52kJ mol^{-1} in butyramide to 75kJ mol^{-1} in tert-butylacetamide. Furthermore, the two processes could be distinguished from each other by distinctly different temperature regions in which the respective relaxation processes occurred. Hence it can be suggested that in general, the molecular process for amide of this size can be detected in the range 140-220K, while the intramolecular process can be detected around room temperature by means of dielectric relaxation method in polystyrene matrix.

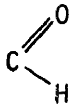
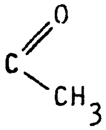
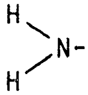
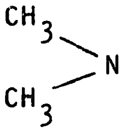
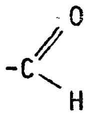
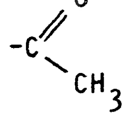
Table 4.1 to table 4.4 showed the simple amides with different groups. Table 4.1 showed two compounds with the  group, table 4.2 showed five compounds with the  group, table 4.3 showed three compounds with  group, and table 4.4 showed three compounds with  group. The purpose of this kind of classification was designed to show the influence of the energy barrier of internal rotation of the C-N bond by various substituent groups at the carbonyl carbon or nitrogen atom. As discussed before, the internal energy barriers of the compounds in table 4.3 fitted both the steric factor explanation and the electronic factor explanation. However, in table 4.1, 4.2 and 4.4, the trend of the variations of the energy barriers of internal rotation around the C-N bond was best explained by the steric factor. Hence it would be reasonable to emphasize the importance of the steric factor involved.

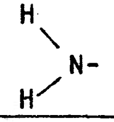
TABLE 4.1: A Summary of the Relaxation Parameters of Some Simple Amides with the  $-\mathrm{C}(=\mathrm{O})\mathrm{H}$ Group

Molecule	T(K)	τ(s)	ΔG_E (kJ mol^{-1})			β	μ_{300}	ΔH_E	ΔS_E
	Range	100K	100K	200K	300K	Range	DEBYE	kJ mol^{-1}	J K^{-1} mol^{-1}
Formamide	238.7 - 301.5	1.8E-6	52	46	40	0.16 - 0.27	0.83	58	58
N,N-Dimethylformamide	256.4 - 334.8	2.5E-5	52	49	47	0.18 - 0.29	1.04	54	22

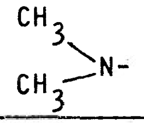
TABLE 4.2: A Summary of the Relaxation Parameters of Some Simple Amides with the $-C(=O)CH_3$ Group



Molecule	T(K)	τ(s)		ΔG_E(kJ mol^{-1})			β	μ_{300}	ΔH_E	ΔS_E
	Range	200K	300K	100K	200K	300K	Range	DEBYE	kJ mol^{-1}	J K^{-1} mol^{-1}
Acetamide	291.7-335.3	2.6E1	2.2E-4	55	54	52	0.34-0.44	0.62	56	13
N-Methyl-acetamide	291.5-333.5	3.2E2	2.4E-4	63	58	53	0.18-0.29	1.49	68	52
N-Ethyl-acetamide	264.2-326.8	1.8E0	4.4E-5	64	56	48	0.25-0.33	1.29	72	76
	144.2-189.2	3.0E-6	2.2E-8	25	27	30	0.16-0.23	1.51	23	-23
Tert-butyl acetamide	278.5-327.7	2.0E2	6.1E-5	65	57	49	0.33-0.41	1.38	75	78
	158.9-215.7	1.3E-5	4.6E-8	28	30	31	0.16-0.20	1.94	26	-17
N,N-Dimethyl-acetamide	286.5-334.3	4.0E2	5.2E-4	61	58	55	0.20-0.26	1.23	66	37

TABLE 4.3: A Summary of the Relaxation Parameters of Some Simple Amides with the  H_2N- Group

Molecule	T(K)	τ(s)	ΔG_E(kJ mol^{-1})			β	μ_{300}	ΔH_E	ΔS_E
	Range	100K	100K	200K	300K	Range	DEBYE	kJ mol^{-1}	J K^{-1} mol^{-1}
Formamide	238.7 - 301.5	1.8E-6	52	46	40	0.16-0.27	0.83	58	58
Acetamide	291.7 - 335.3	2.2E-4	55	54	52	0.34-0.44	0.62	56	13
Butyramide	319.1 - 332.2	4.0E-3	54	57	60	0.37-0.51	0.99	52	-27

TABLE 4.4: A Summary of the Relaxation Parameters of Some Simple Amides with the  $(CH_3)_2N-$ Group

N,N-Dimethyl-formamide	256.4 - 334.8	2.5E-5	52	49	47	0.18-0.29	1.04	54	22
N,N-Dimethyl-acetamide	286.5 - 334.3	5.2E-4	61	58	55	0.20-0.26	1.23	66	37
N,N-Dimethyl-carbamyl chloride	285.6 - 335.1	5.7E-4	60	58	55	0.20-0.29	1.43	63	27

TABLES 4.5 - 4.15: Fuoss-Kirkwood Relaxation Parameters of Some Simple Amides

T(K)	$10^3\varepsilon''$	$\log_{10}\nu_m$	β	ε_∞	μ(D)
TABLE 4.5: Formamide					
238.7	10.32	2.12	0.16	2.73	0.77
248.5	11.57	2.73	0.22	2.74	0.70
259.8	12.20	3.48	0.18	2.72	0.81
273.0	12.91	4.14	0.18	2.71	0.86
281.9	13.22	4.40	0.20	2.72	0.83
296.0	13.33	4.68	0.27	2.70	0.75
301.5	13.62	4.87	0.21	2.71	0.85
TABLE 4.6: N,N-Dimethylformamide					
256.4	18.47	2.08	0.18	2.90	1.17
268.3	18.06	2.62	0.21	2.93	1.10
277.9	17.82	3.02	0.22	2.96	1.08
285.9	17.58	3.40	0.24	2.99	1.02
296.3	16.72	3.72	0.27	2.95	0.97
302.2	16.44	3.87	0.29	2.96	0.94
208.0	16.09	4.06	0.29	2.98	0.94
319.4	15.47	4.40	0.28	2.99	0.94
329.3	15.22	4.61	0.28	3.04	0.95
334.8	15.12	4.81	0.24	3.04	1.03
339.0	16.39	5.73	0.18	3.03	1.25
TABLE 4.7: Acetamide					
291.7	3.46	2.54	0.37	2.66	0.61
294.2	3.36	2.59	0.34	2.63	0.64
298.2	3.49	2.86	0.38	2.67	0.62
302.0	3.35	2.90	0.38	2.64	0.61
304.4	3.50	3.01	0.39	2.67	0.62
307.6	3.36	3.11	0.38	2.64	0.61
309.8	3.46	3.24	0.40	2.67	0.61
314.1	3.27	3.32	0.40	2.65	0.60
316.2	3.44	3.45	0.41	2.67	0.60
320.4	3.19	3.51	0.41	2.65	0.59
324.8	3.19	3.61	0.42	2.65	0.58
329.9	3.16	3.82	0.43	2.66	0.58
335.3	3.04	3.89	0.44	2.66	0.57

TABLES 4.5 - 4.15: Fuoss-Kirkwood Relaxation Parameters of Some Simple Amides...continued

T(K)	$10^3\varepsilon''$	$\log_{10}\nu_m$	β	ε_∞	μ(D)
TABLE 4.8: N-Methylacetamide					
291.5	20.21	2.32	0.18	2.63	1.60
294.7	19.92	2.58	0.20	2.63	1.53
299.0	20.11	2.82	0.22	2.65	1.48
304.0	20.10	3.08	0.24	2.67	1.43
310.7	19.88	3.30	0.25	2.69	1.41
314.8	19.91	3.46	0.26	2.70	1.38
319.6	19.76	3.60	0.27	2.71	1.35
323.7	19.69	3.71	0.28	2.73	1.33
328.9	19.60	3.83	0.29	2.74	1.31
333.5	19.09	4.02	0.28	2.75	1.33
TABLE 4.9: N,N-Dimethylacetamide					
286.5	12.17	1.88	0.20	2.93	1.27
291.6	12.02	2.22	0.22	2.94	1.22
295.7	11.71	2.31	0.21	2.86	1.24
295.9	12.11	2.28	0.21	2.94	1.25
302.6	12.03	2.56	0.22	2.95	1.23
310.4	11.69	2.92	0.24	2.90	1.19
319.8	11.59	3.22	0.25	2.91	1.18
325.3	11.55	3.43	0.26	2.93	1.16
330.6	11.53	3.57	0.26	2.93	1.16
334.3	11.45	3.68	0.26	2.95	1.18
TABLE 4.10: N-Ethylacetamide (higher temperature region)					
264.2	208.0	2.06	0.25	2.90	1.07
273.8	222.2	2.68	0.29	2.97	1.09
283.3	231.1	3.07	0.31	3.06	1.06
292.9	184.3	3.58	0.28	2.97	1.13
303.4	200.3	3.85	0.29	3.04	1.21
312.6	216.3	4.04	0.31	3.18	1.28
322.3	228.2	4.16	0.33	3.35	1.35
326.8	235.2	4.00	0.30	3.41	1.38

TABLES 4.5 - 4.15: Fuoss-Kirkwood Relaxation Parameters of Some Simple Amides...continued

T(K)	$10^3\varepsilon''$	$\log_{10}\nu_m$	β	ε_∞	μ(D)
	TABLE 4.11: N-Ethylacetamide (lower temperature region)				
144.2	9.20	2.31	0.16	2.61	1.00
150.7	9.71	2.66	0.17	2.62	1.01
157.3	10.22	3.00	0.18	2.62	1.03
164.4	10.68	3.36	0.18	2.64	1.05
170.5	11.19	3.70	0.20	2.65	1.10
177.1	12.10	3.80	0.20	2.66	1.20
183.4	12.98	4.19	0.22	2.67	1.12
189.2	13.39	4.37	0.23	2.68	1.13
	TABLE 4.12: Tert-butylacetamide (high temperature region)				
278.5	17.85	2.20	0.39	2.90	1.23
287.7	18.89	2.75	0.36	2.91	1.33
288.9	18.79	2.83	0.36	2.91	1.34
294.5	17.96	3.43	0.33	2.88	1.38
302.9	19.04	3.78	0.32	2.89	1.46
311.0	19.80	4.05	0.34	2.90	1.47
316.9	20.52	4.17	0.36	2.92	1.45
323.3	21.07	4.27	0.39	2.94	1.43
327.7	21.74	4.25	0.41	2.95	1.42
	TABLE 4.13: Tert-butylacetamide (lower temperature region)				
158.9	10.28	2.31	0.17	2.62	1.14
168.2	11.08	2.61	0.16	2.62	1.24
172.2	11.46	2.87	0.17	2.63	1.25
177.2	11.90	3.14	0.16	2.63	1.30
177.8	12.36	3.16	0.17	2.62	1.31
188.3	12.98	3.56	0.17	2.64	1.38
196.4	14.29	3.96	0.20	2.64	1.36
205.8	15.13	4.32	0.20	2.65	1.42
215.7	15.92	4.63	0.20	2.66	1.48

TABLES 4.5 - 4.15: Fuoss-Kirkwood Relaxation Parameters of Some Simple Amides...continued

T(K)	$10^3\varepsilon''$	$\log_{10}\nu_m$	β	ε_∞	μ(D)
	TABLE 4.14: Butyramide				
313.1	3.40	2.11	0.35	2.66	0.83
315.8	3.55	2.15	0.37	2.69	0.82
319.1	3.62	2.16	0.37	2.69	0.84
322.8	3.60	2.37	0.41	2.67	0.80
324.8	3.68	2.32	0.39	2.69	0.83
326.3	3.69	2.34	0.34	2.69	0.89
328.6	3.68	2.43	0.42	2.69	0.80
332.2	3.70	2.51	0.51	2.69	0.74
	TABLE 4.15: N,N-Dimethylcarbamyl chloride				
285.6	12.02	1.85	0.20	2.85	1.49
290.5	12.12	2.40	0.21	2.85	1.46
295.4	12.10	2.24	0.21	2.85	1.46
307.5	11.95	2.73	0.24	2.86	1.41
315.7	11.72	3.01	0.25	2.86	1.37
321.0	11.53	3.19	0.26	2.86	1.35
326.1	11.42	3.37	0.27	2.86	1.32
331.7	11.27	3.53	0.29	2.87	1.28
335.1	11.06	3.63	0.29	2.87	1.28

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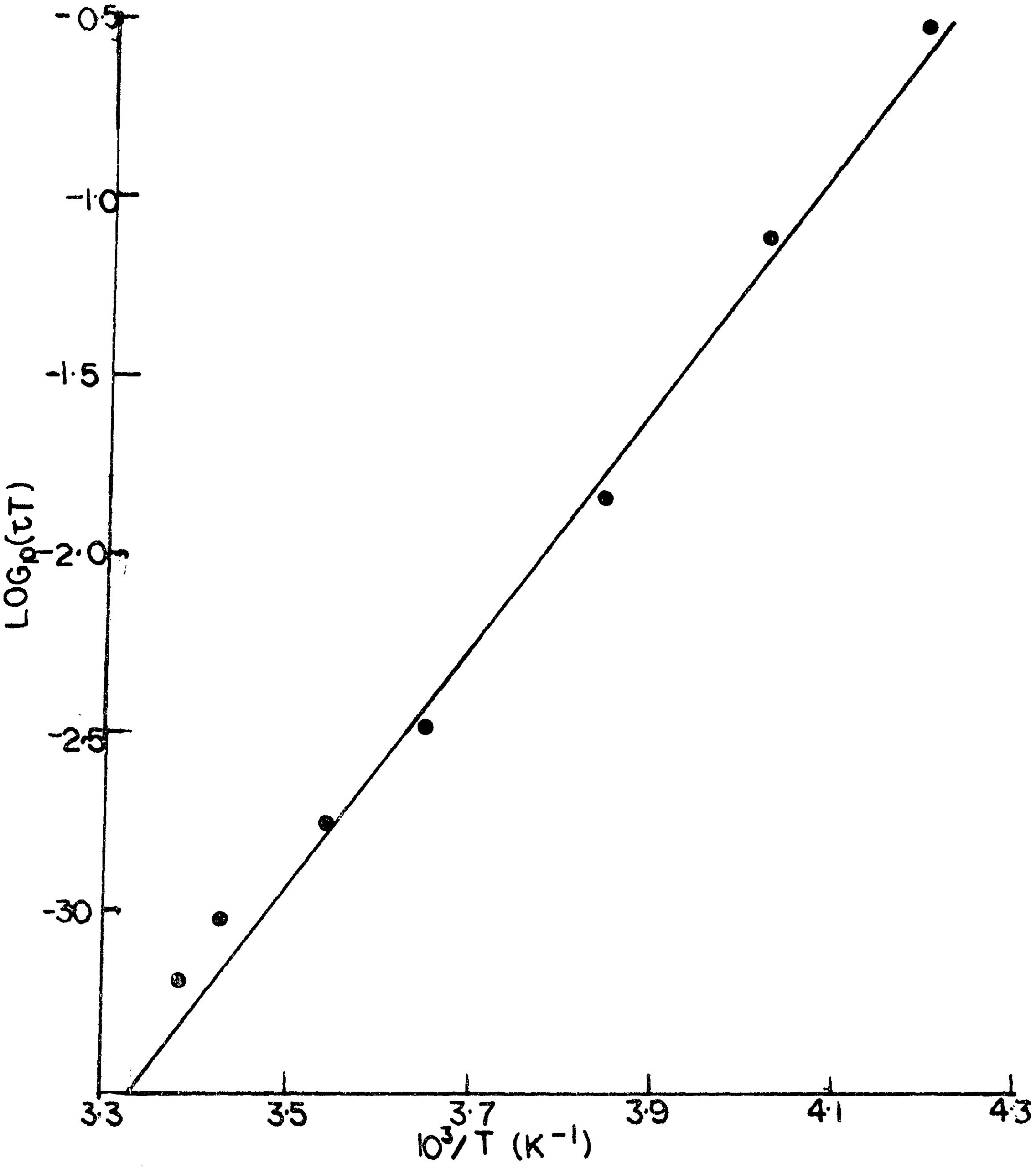

FIG. 4.1: Eyring Plot of log(τT) vs. 1/T for 1.16M Formamide in a Polystyrene Matrix

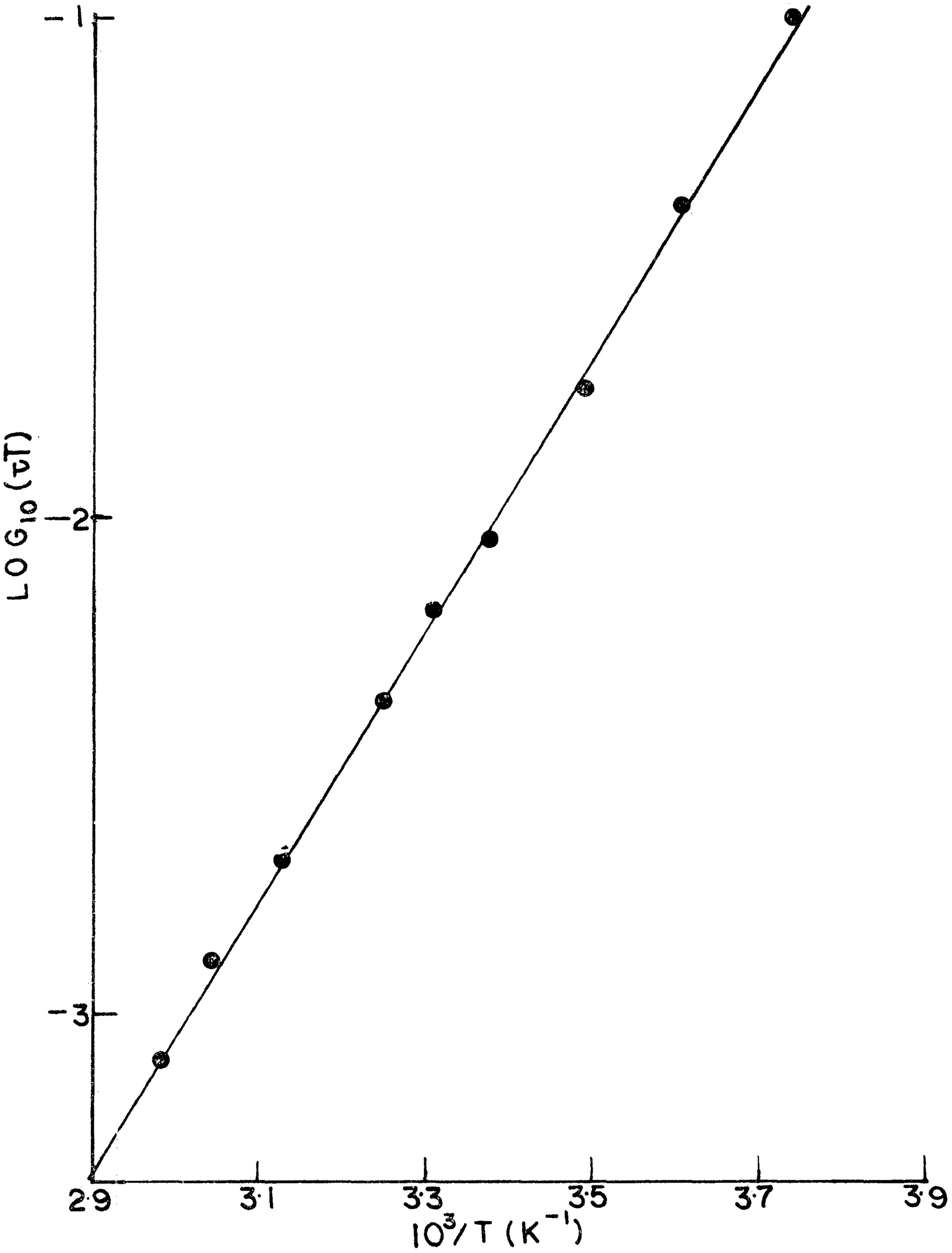

FIG. 4.2: Eyring Plot of log(τT) vs. 1/T for 0.76M N,N-Dimethylformamide in a Polystyrene Matrix

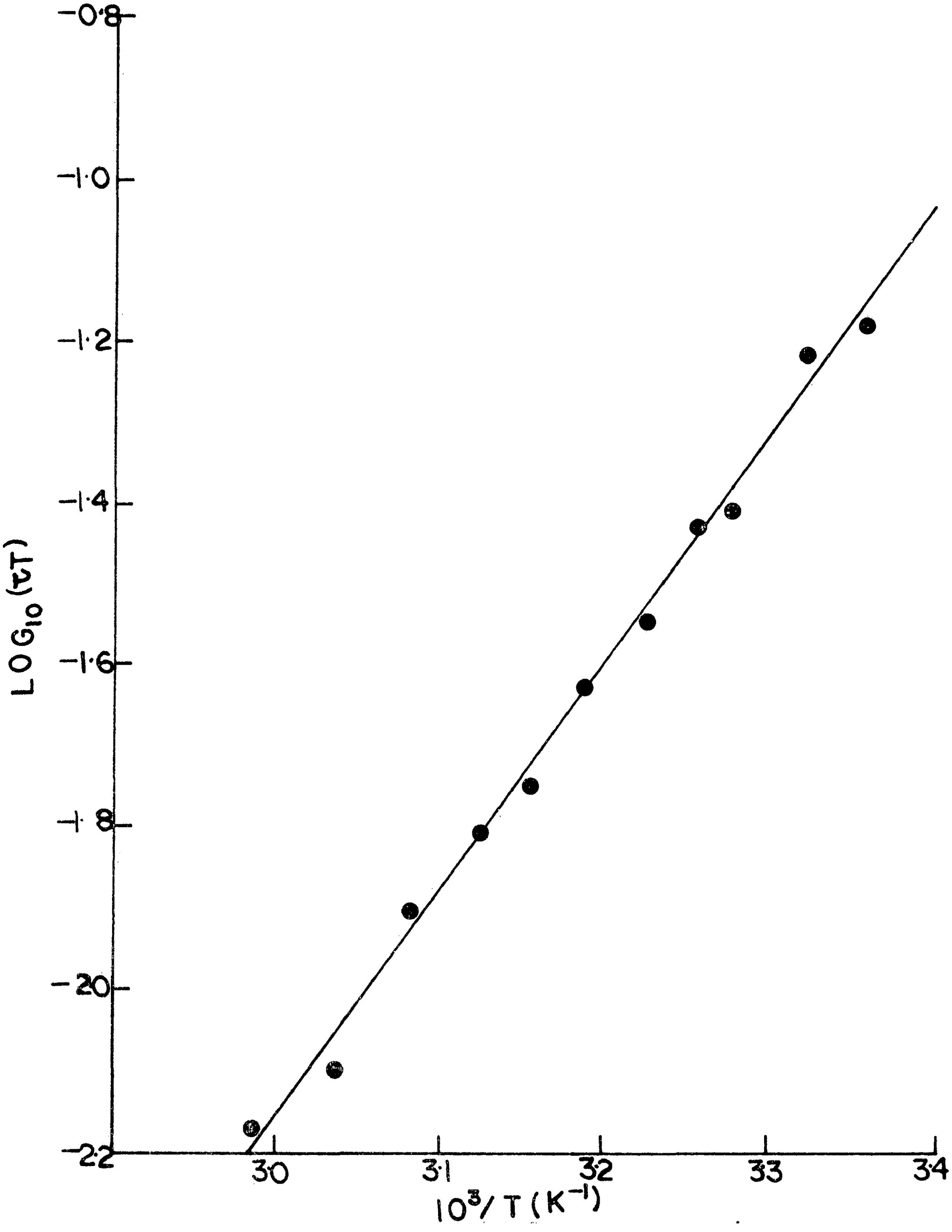

FIG. 4.3: Eyring Plot of log(τT) vs. 1/T for 0.33M Acetamide in a Polystyrene Matrix

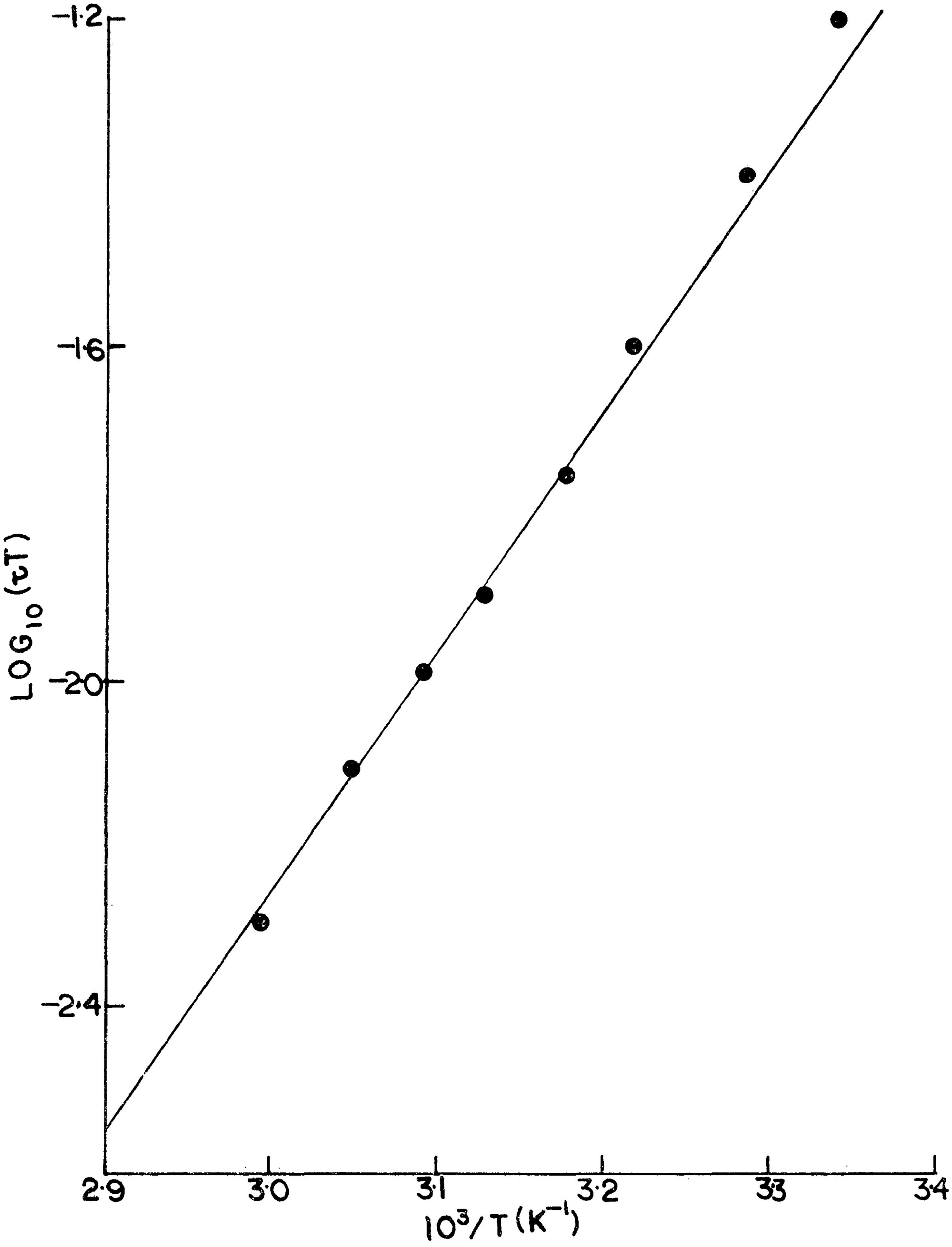

FIG. 4.4: Eyring Plot of log(τT) vs. 1/T for 0.35M N-Methylacetamide in a polystyrene Matrix

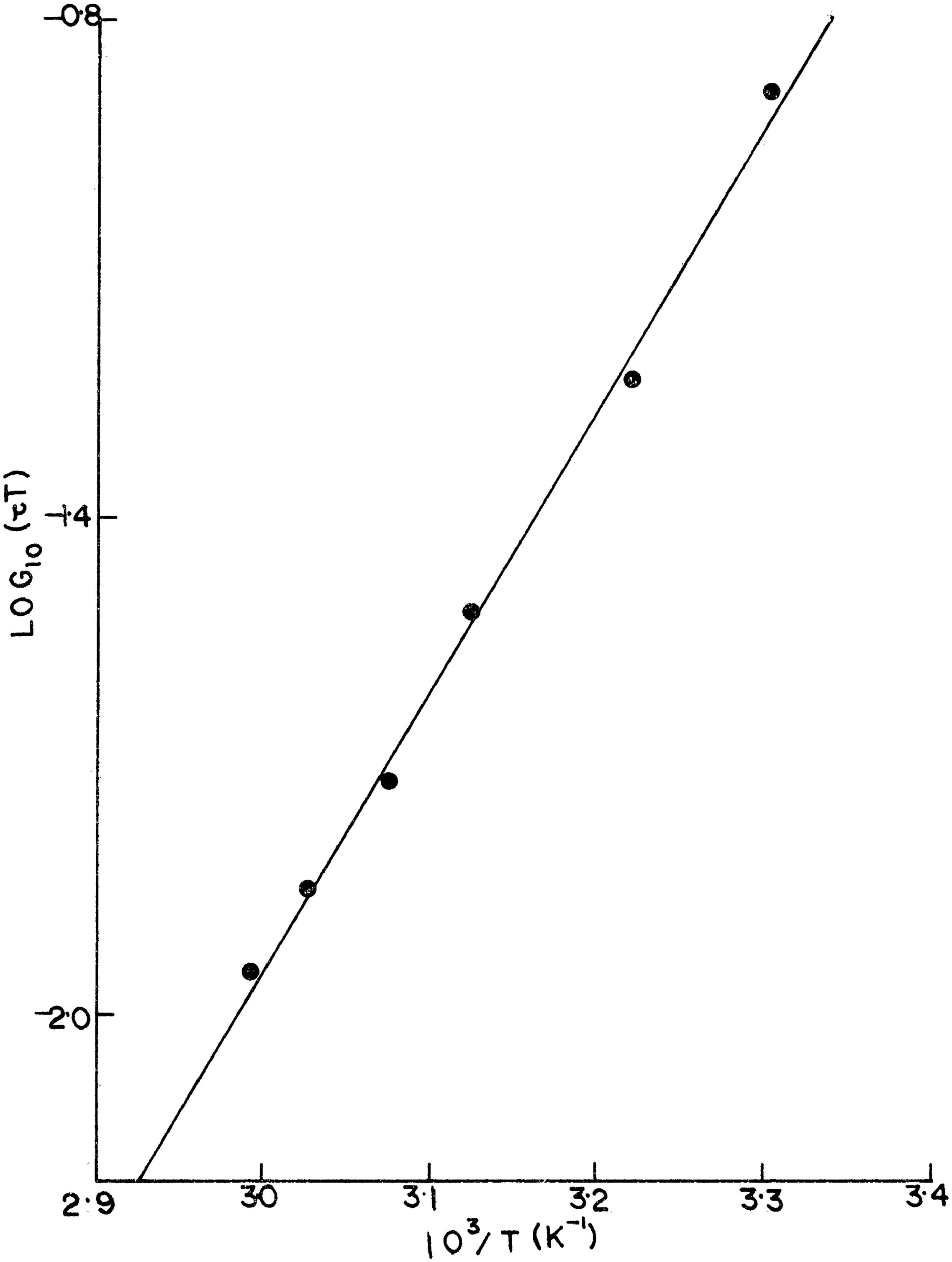

FIG. 4.5: Eyring Plot of log(τT) vs. 1/T for 0.43M N,N-Dimethylacetamide in a Polystyrene Matrix

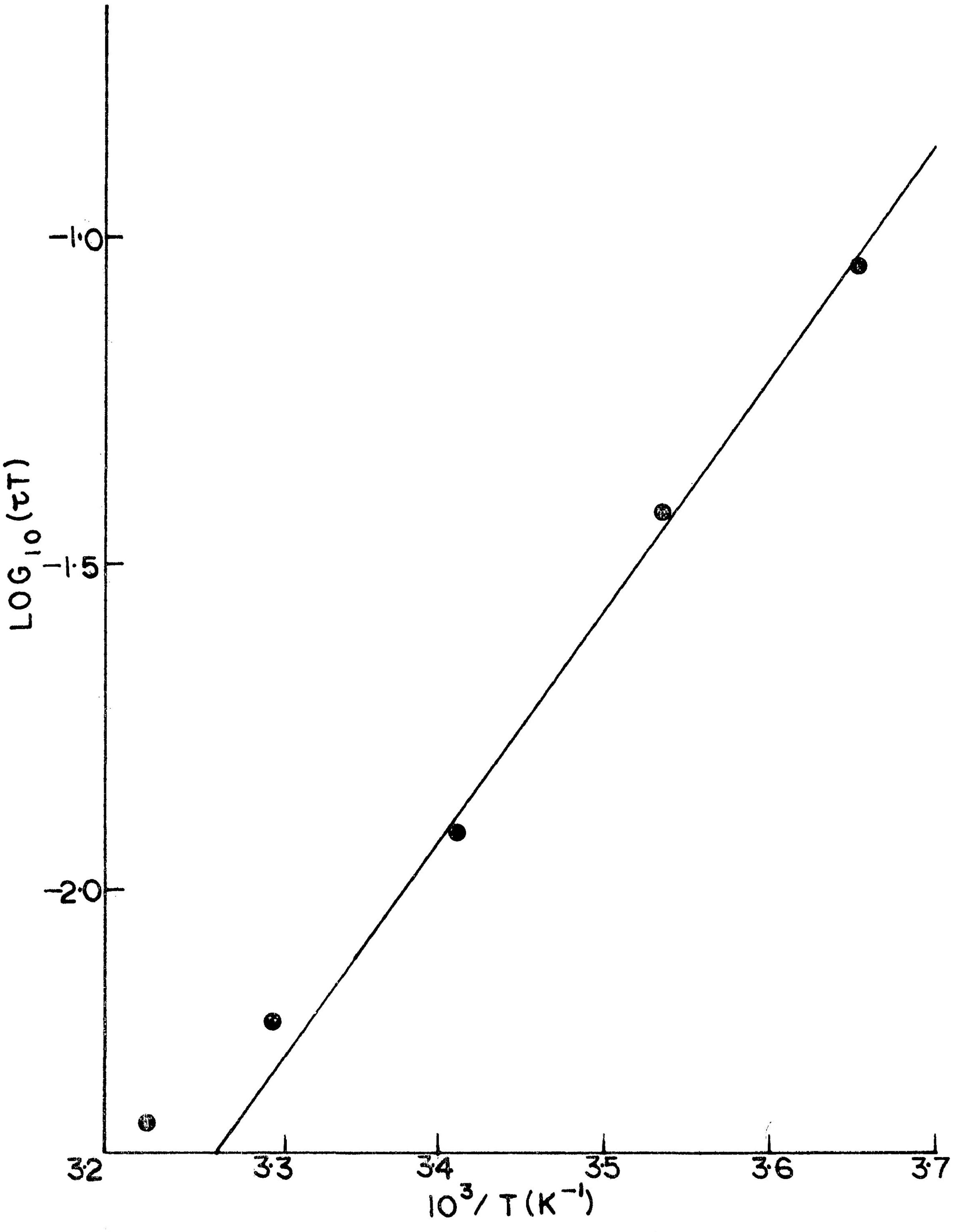

FIG. 4.6: Eyring Plot of log(τT) vs. 1/T for 0.42M N-Ethylacetamide in a Polystyrene Matrix

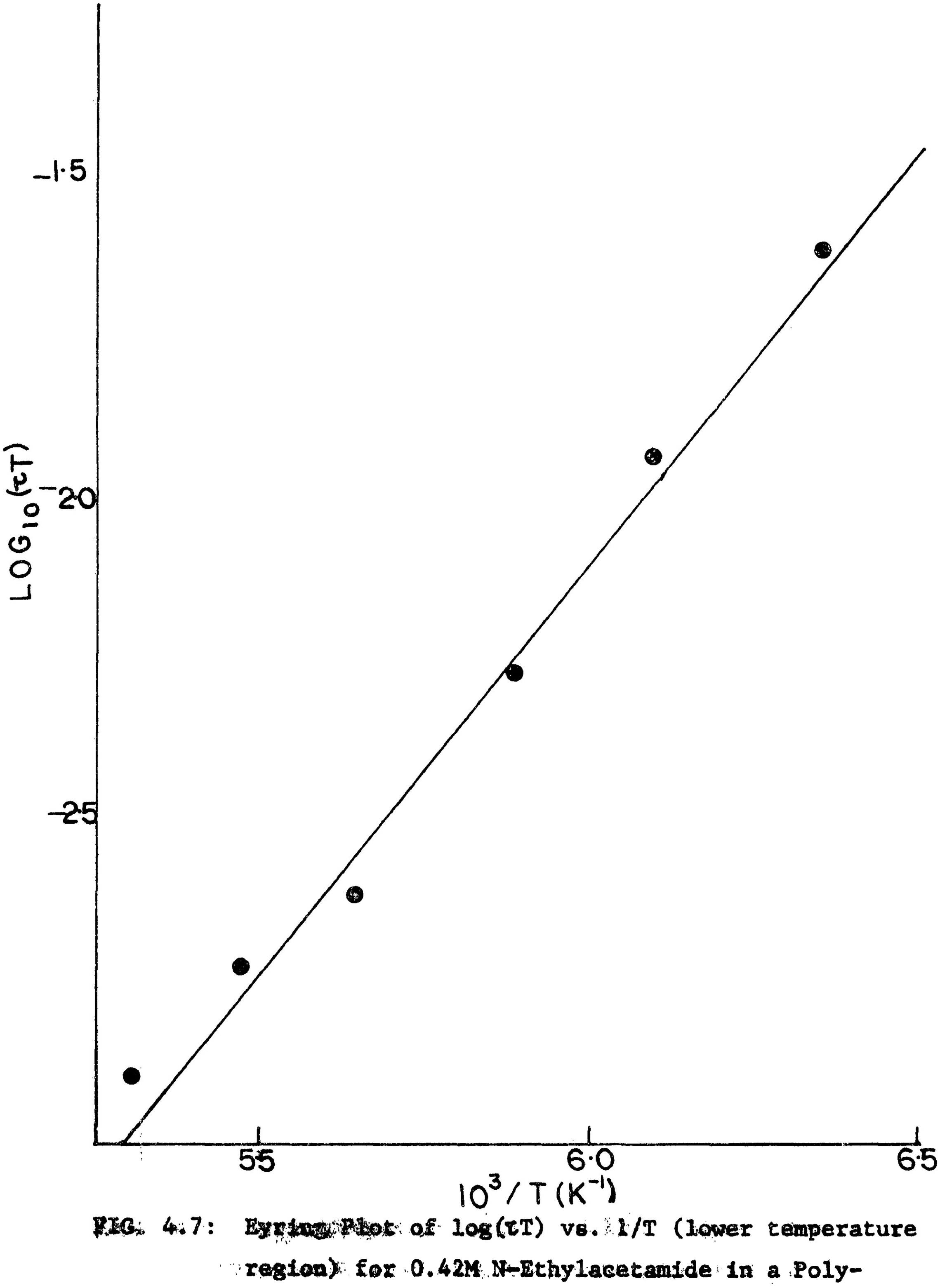

FIG. 4.7: Eyring Plot of log(τT) vs. 1/T (lower temperature region) for 0.42M N-Ethylacetamide in a Polystyrene Matrix

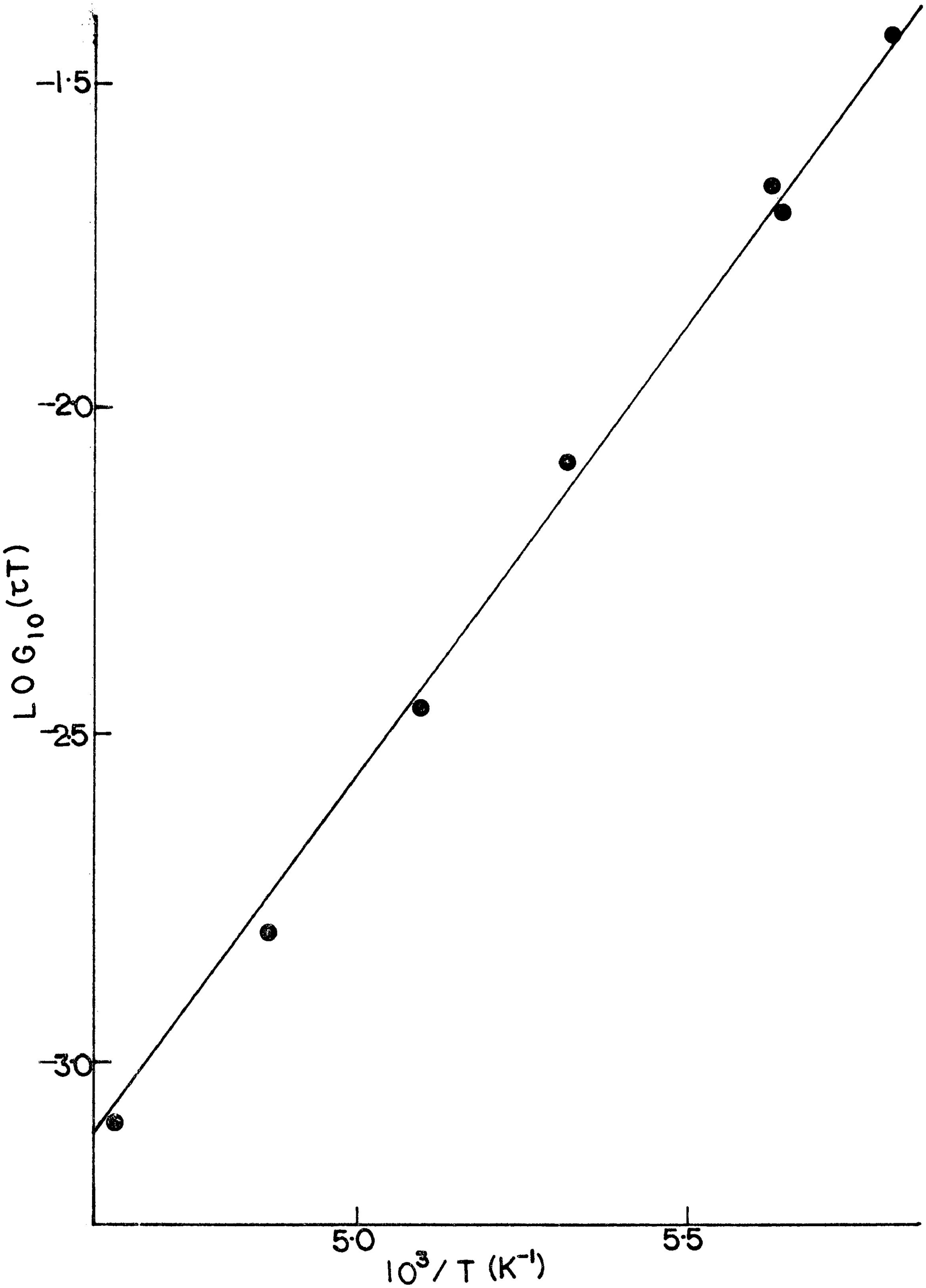

FIG. 4.8: Eyring Plot of log(τT) vs. 1/T (lower temperature region) for 0.50M tert-Butylacetamide in a Polystyrene Matrix

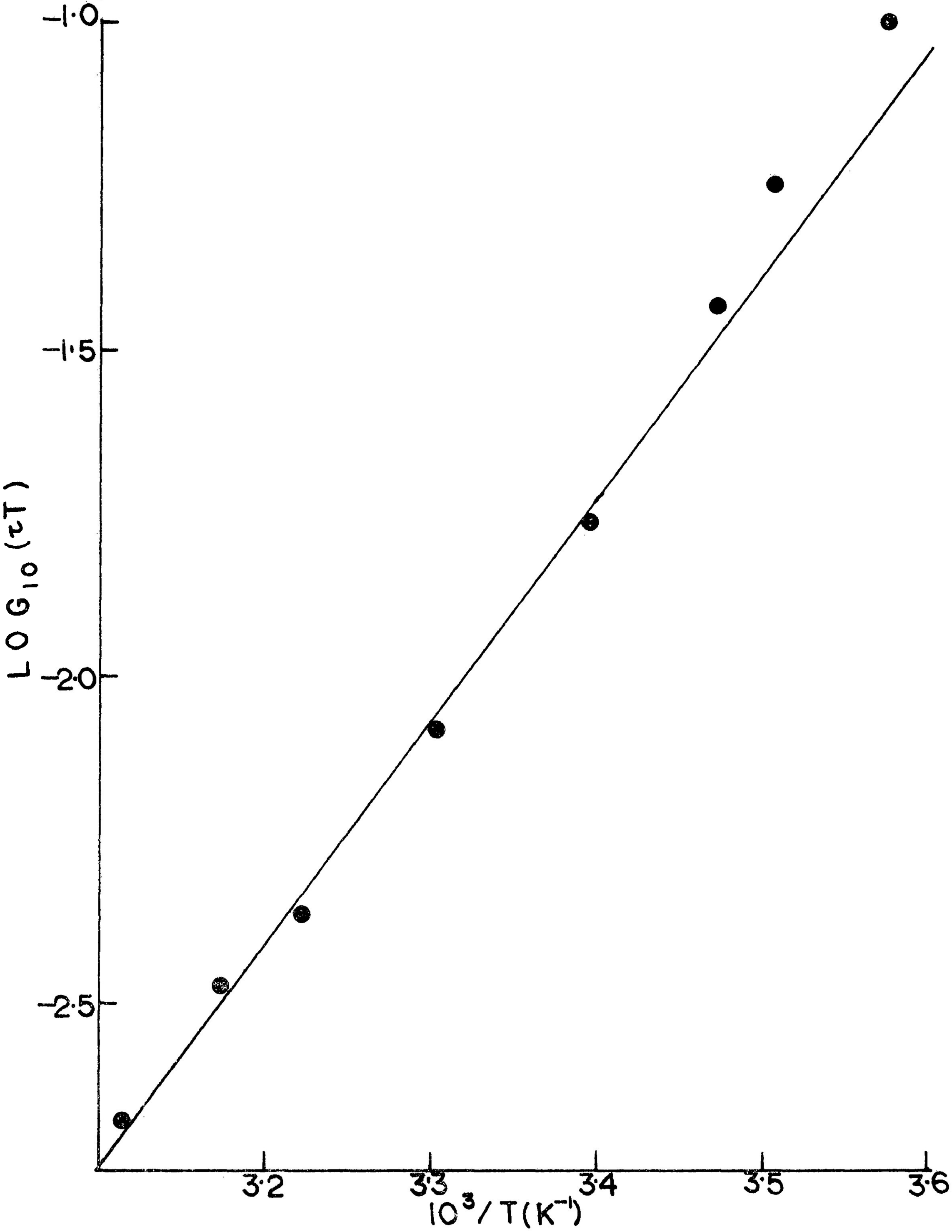

FIG. 4.9: Eyring Plot of log(τT) vs. 1/T for 0.50M tert-Butylacetamide in a Polystyrene Matrix

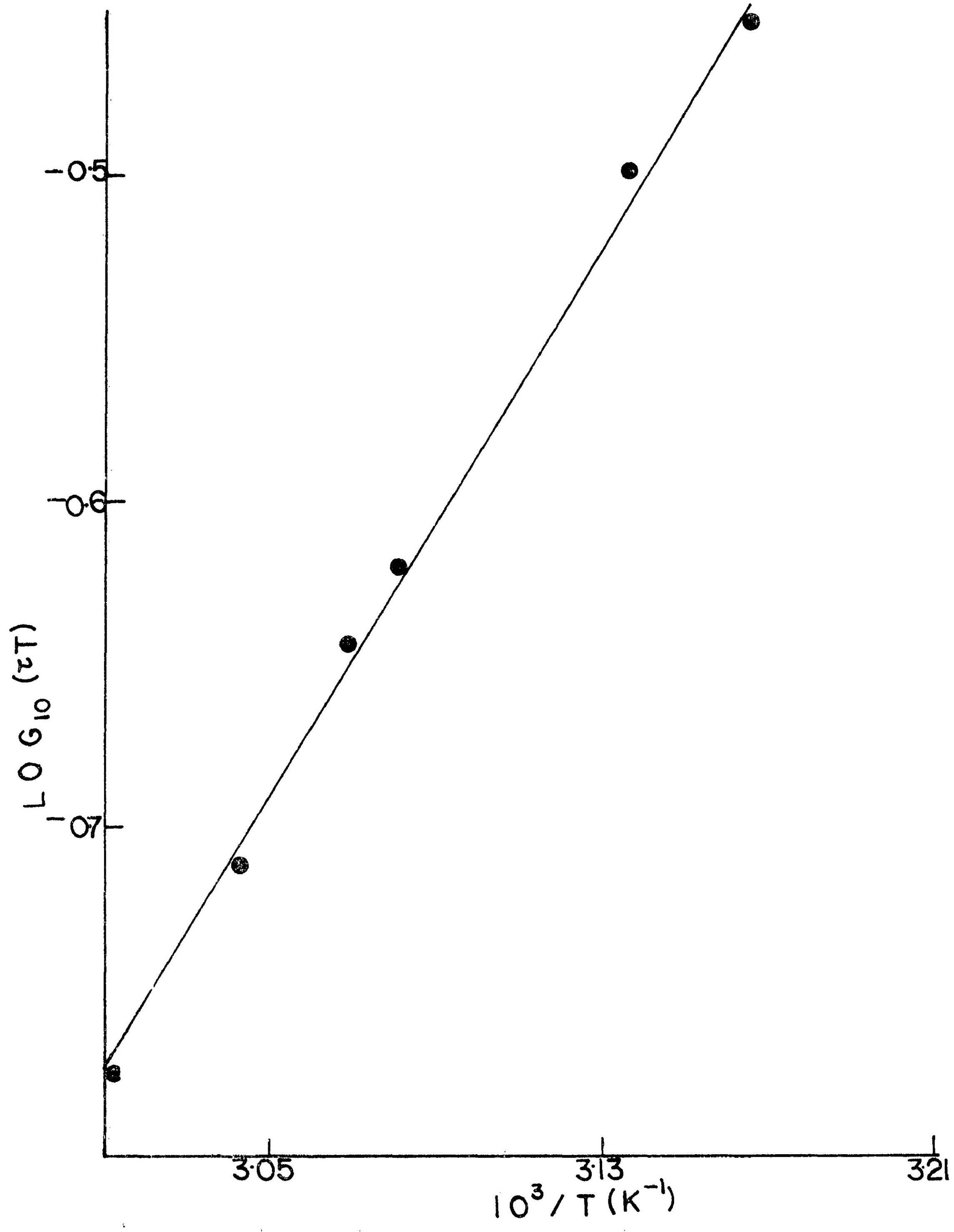

FIG. 4,10: Eyring Plot of log(τT) vs. 1/T for 0.20M Butyramide in a Polystyrene Matrix

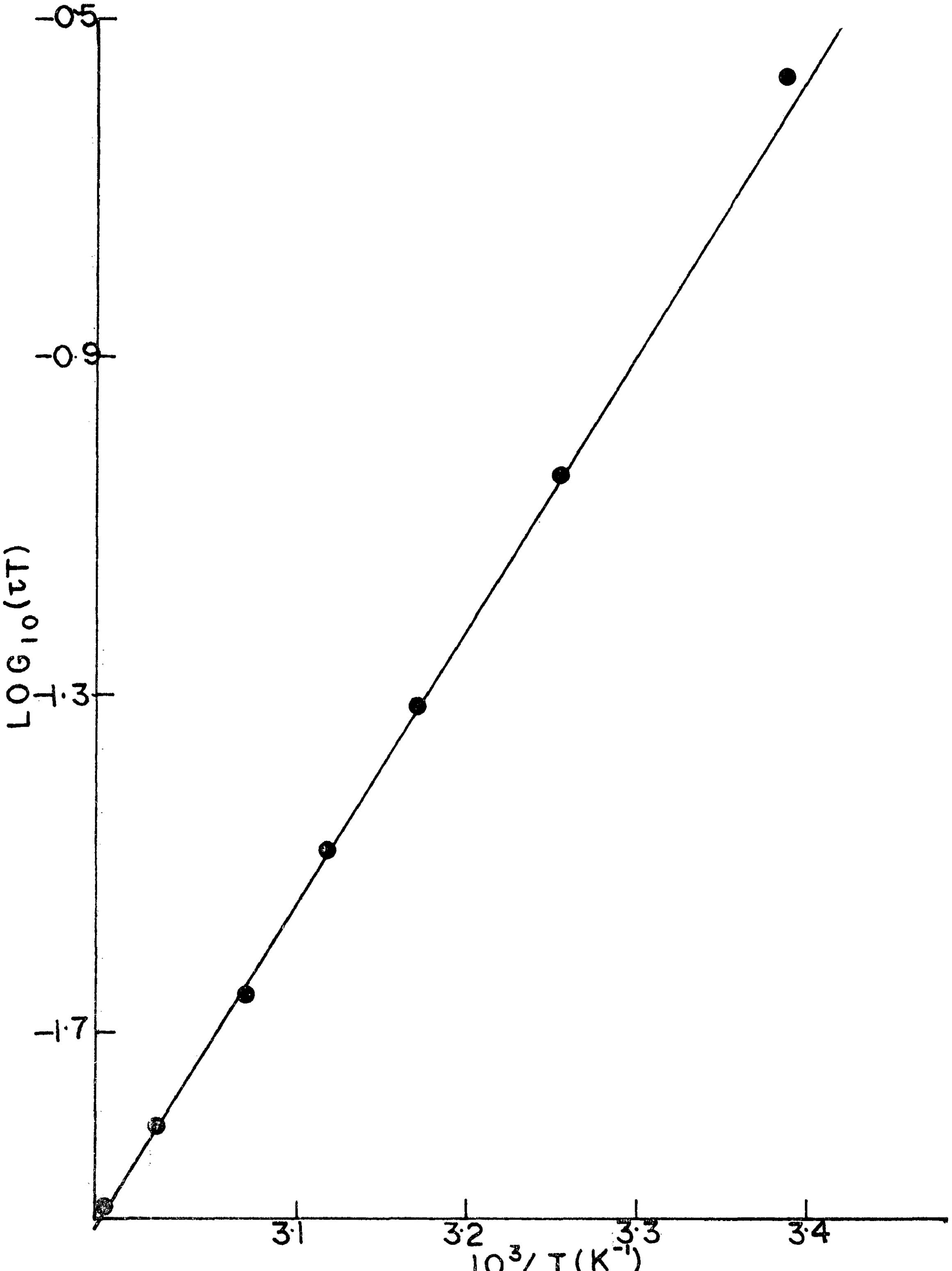

FIG. 4.11: Eyring Plot of log(τT) vs.1/T for 0.32M N,N-Dimethylcarbamyl Chloride in a Polystyrene Matrix

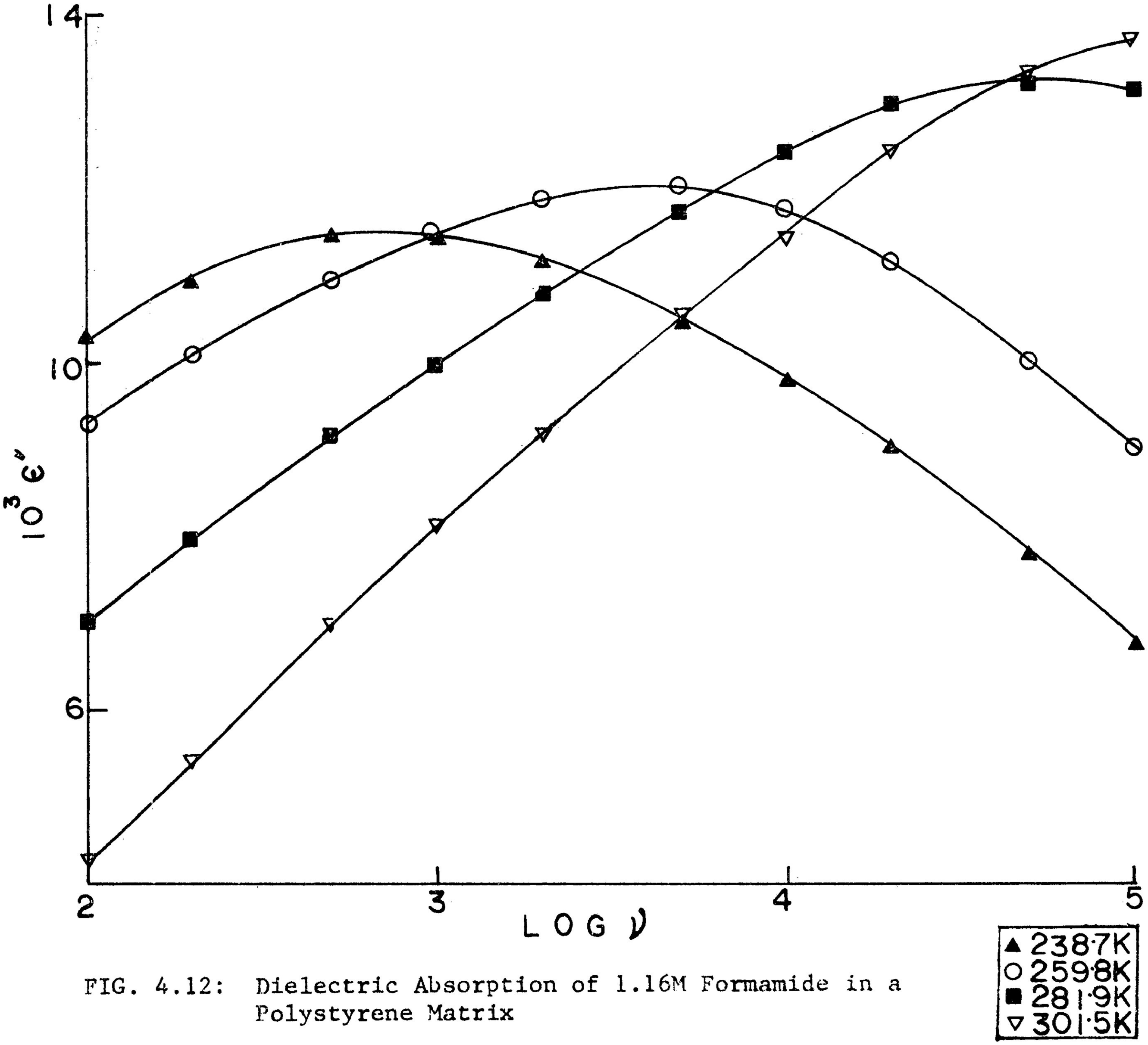

FIG. 4.12: Dielectric Absorption of 1.16M Formamide in a Polystyrene Matrix

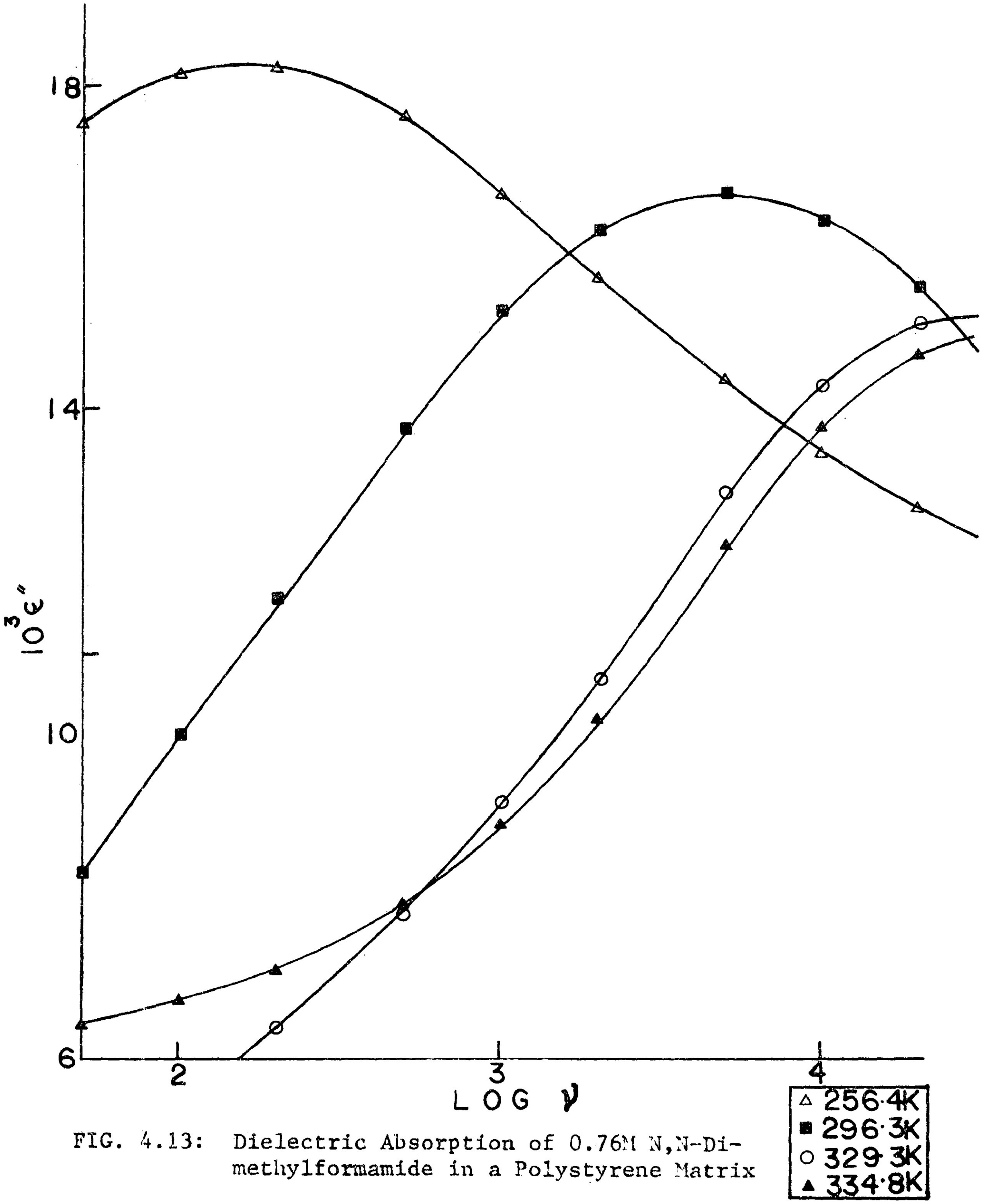

FIG. 4.13: Dielectric Absorption of 0.76M N,N-Dimethylformamide in a Polystyrene Matrix

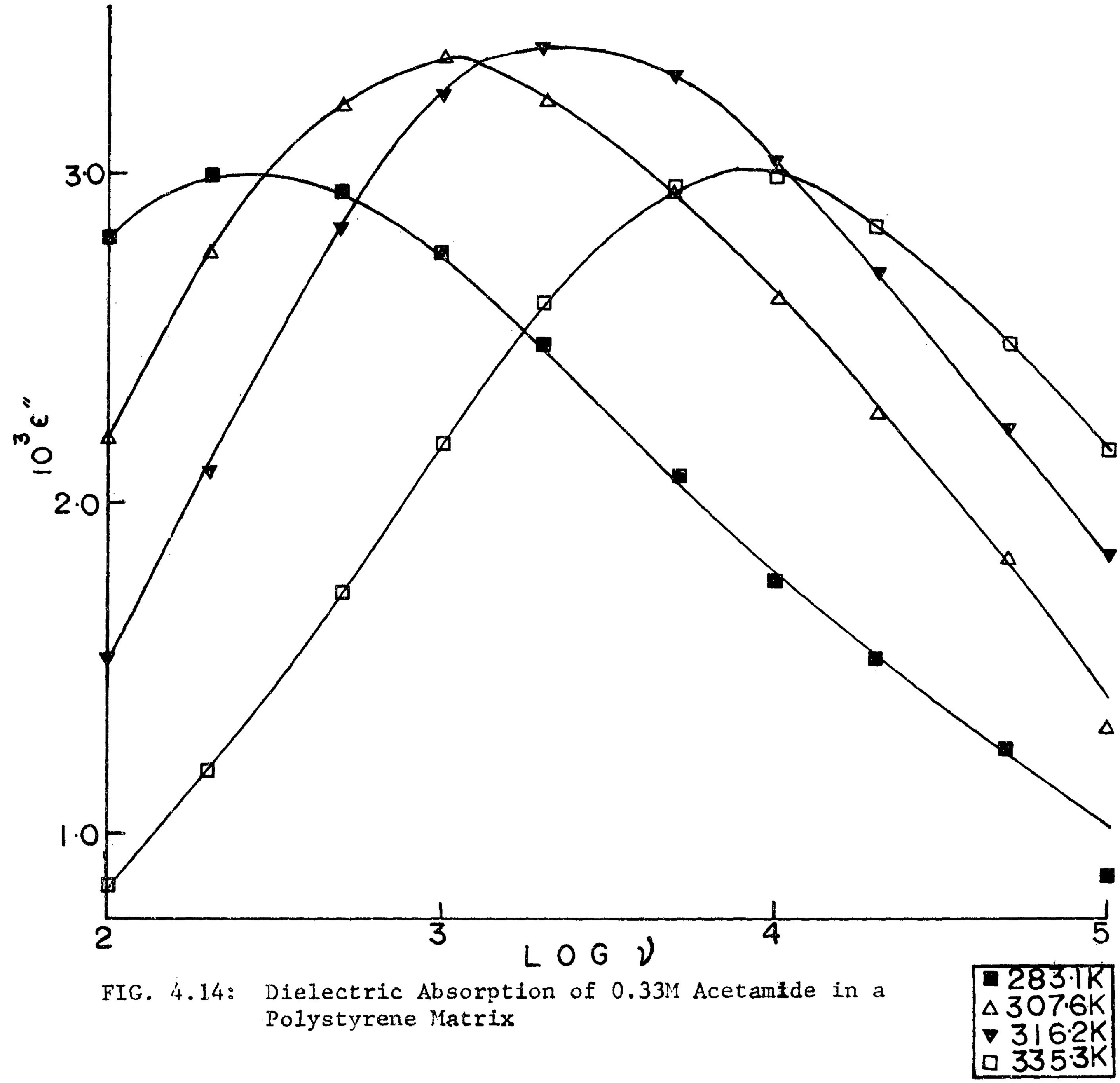

FIG. 4.14: Dielectric Absorption of 0.33M Acetamide in a Polystyrene Matrix

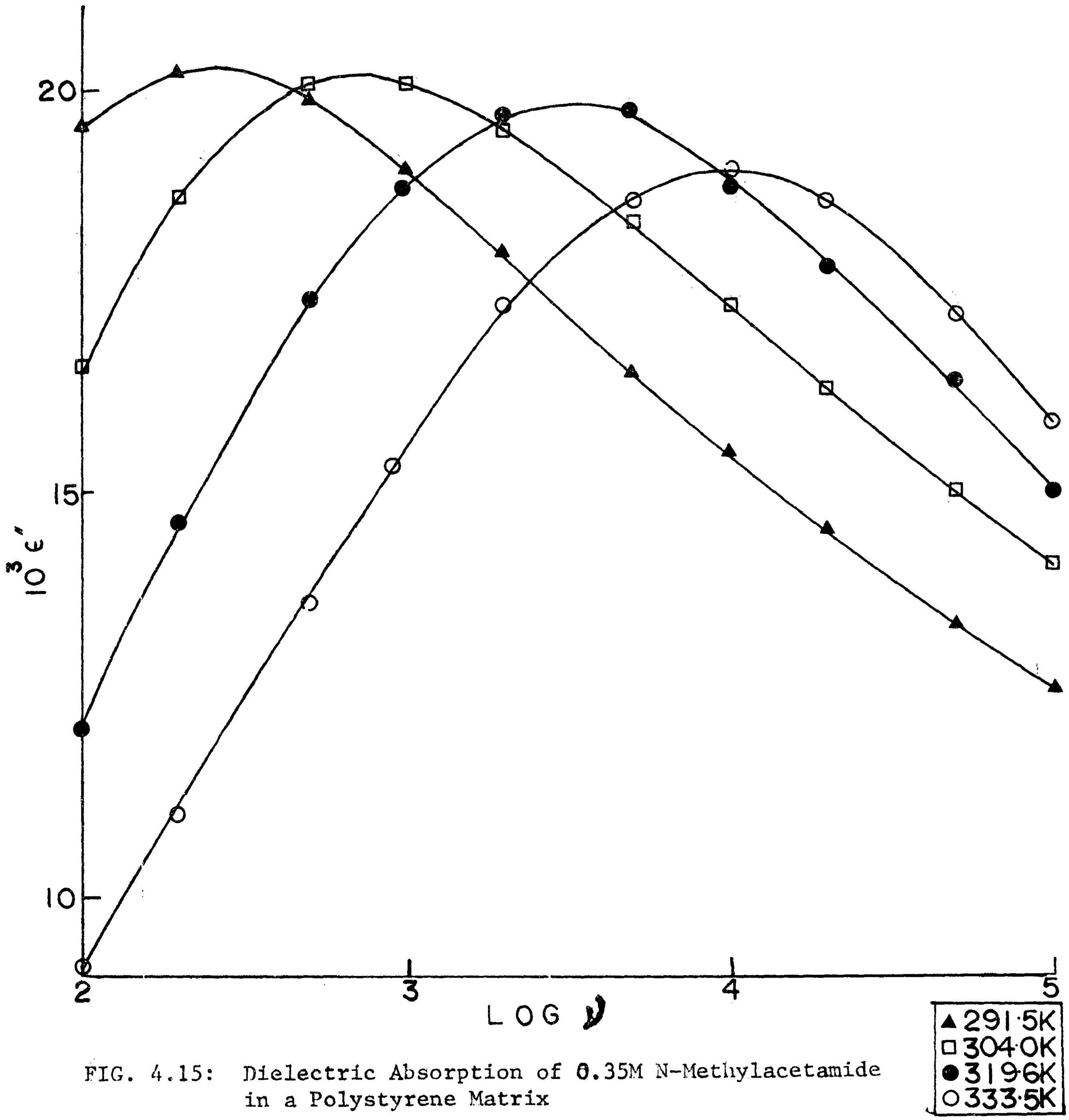

FIG. 4.15: Dielectric Absorption of 0.35M N-Methylacetamide in a Polystyrene Matrix

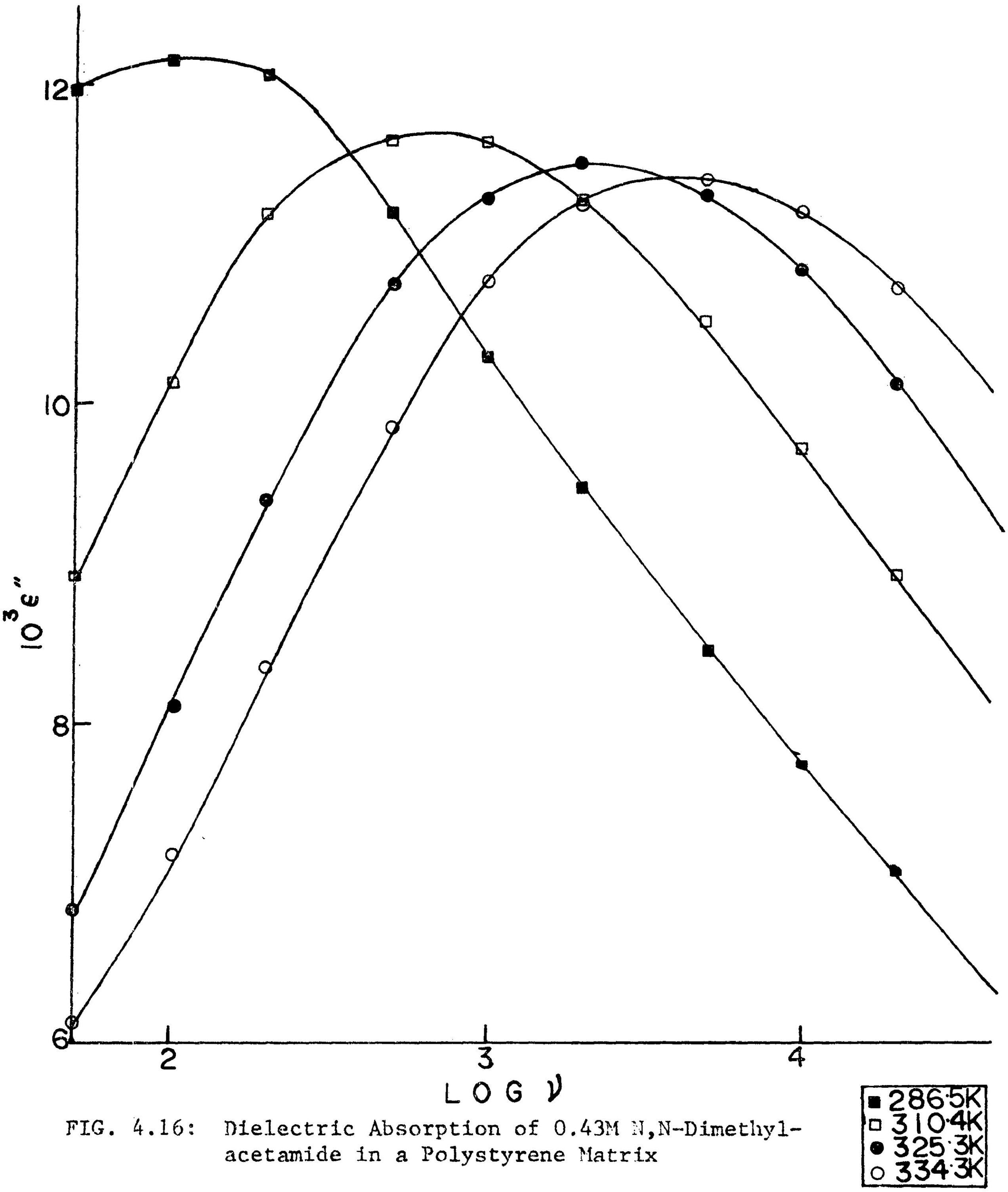

FIG. 4.16: Dielectric Absorption of 0.43M N,N-Dimethylacetamide in a Polystyrene Matrix

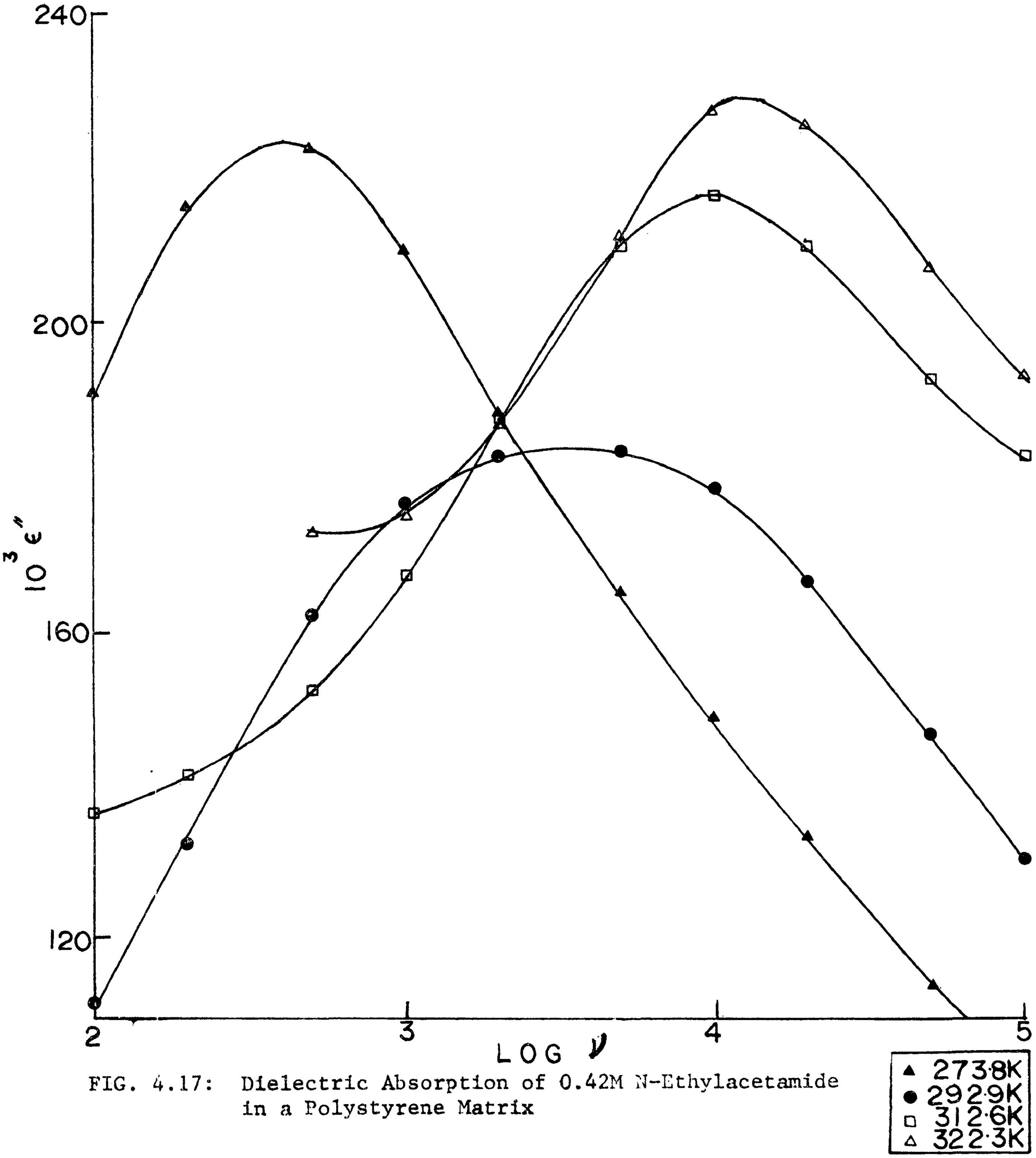

FIG. 4.17: Dielectric Absorption of 0.42M N-Ethylacetamide in a Polystyrene Matrix

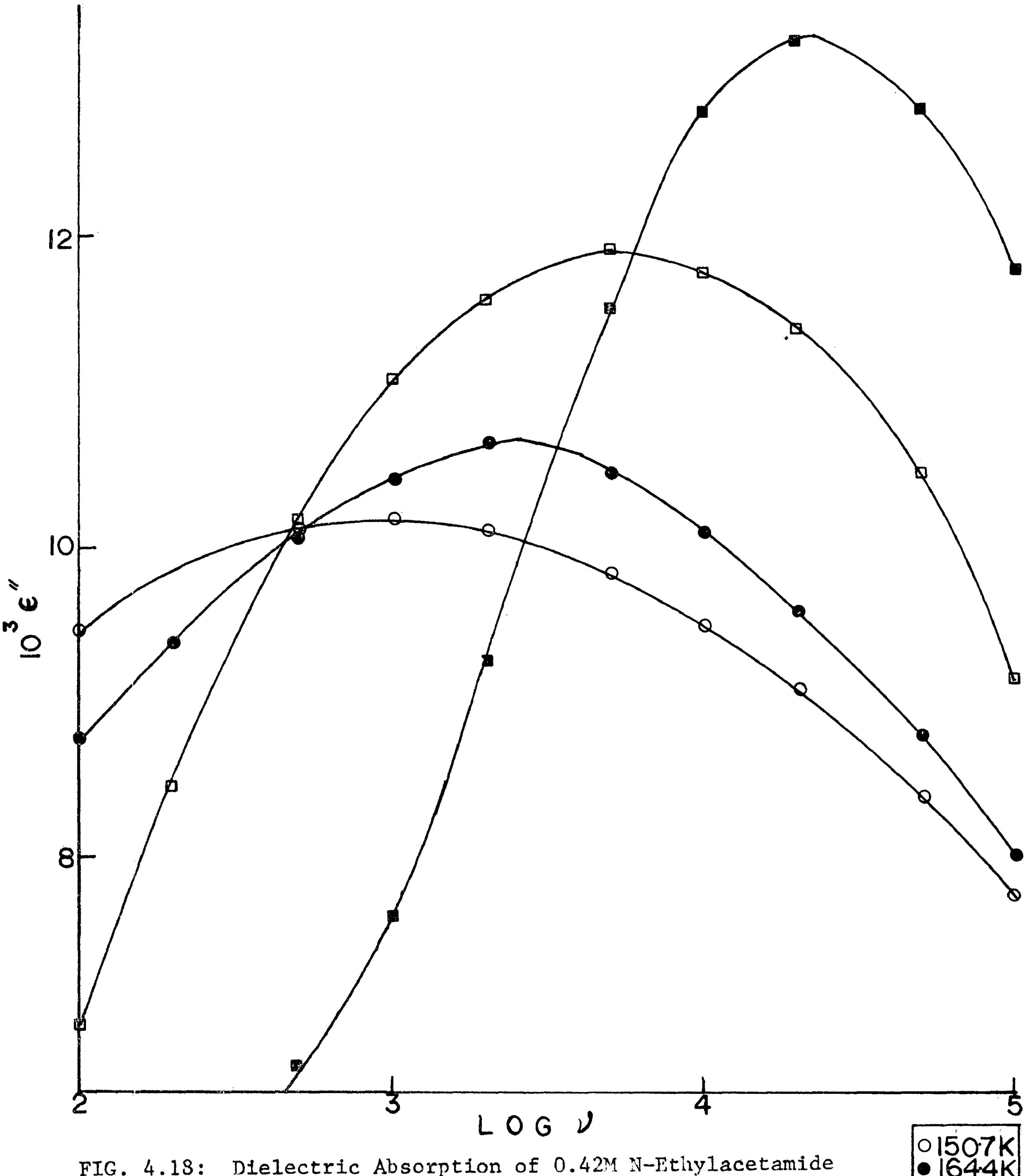

FIG. 4.18: Dielectric Absorption of 0.42M N-Ethylacetamide (lower temperature region) in a Polystyrene Matrix

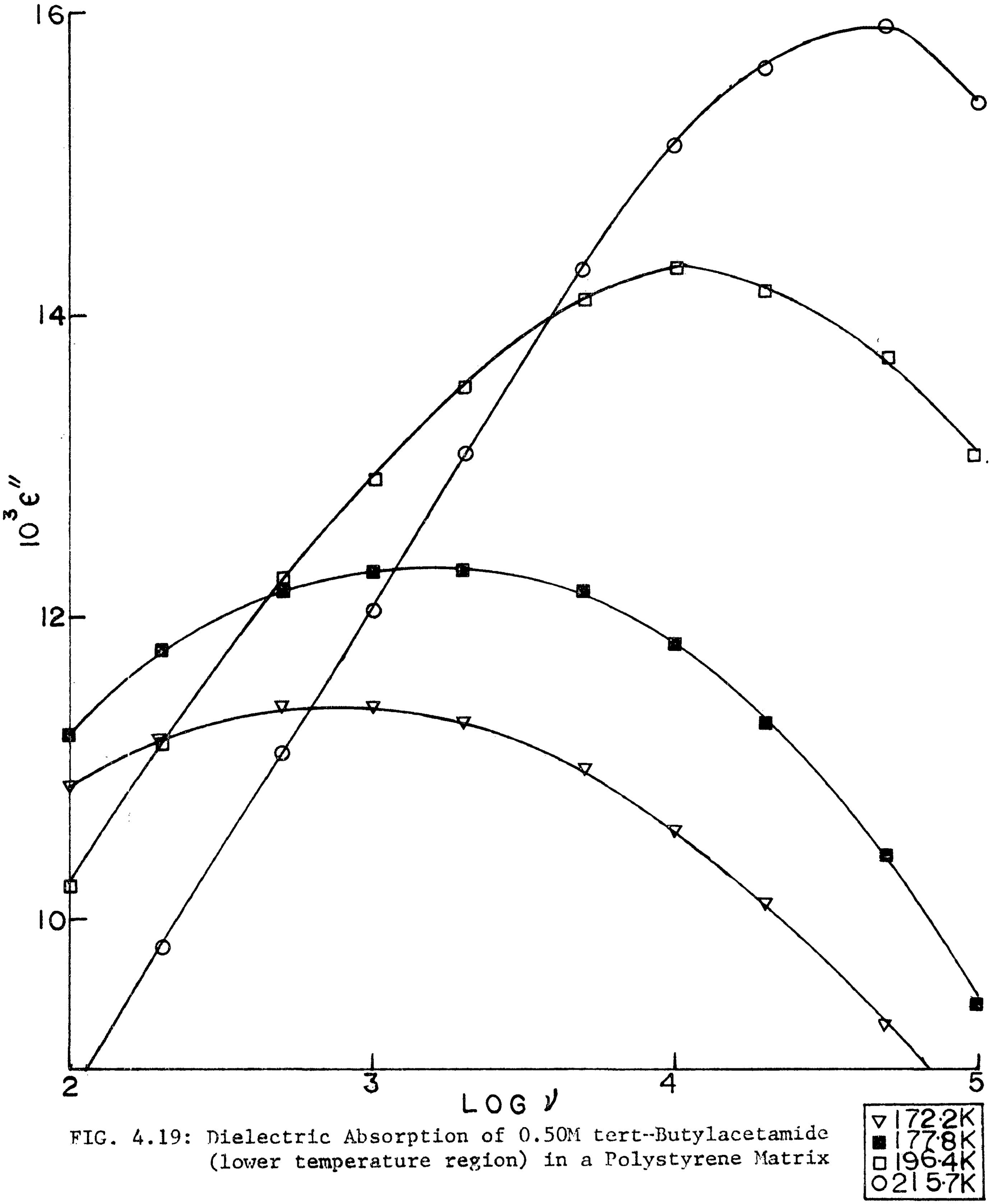

FIG. 4.19: Dielectric Absorption of 0.50M tert-Butylacetamide (lower temperature region) in a Polystyrene Matrix

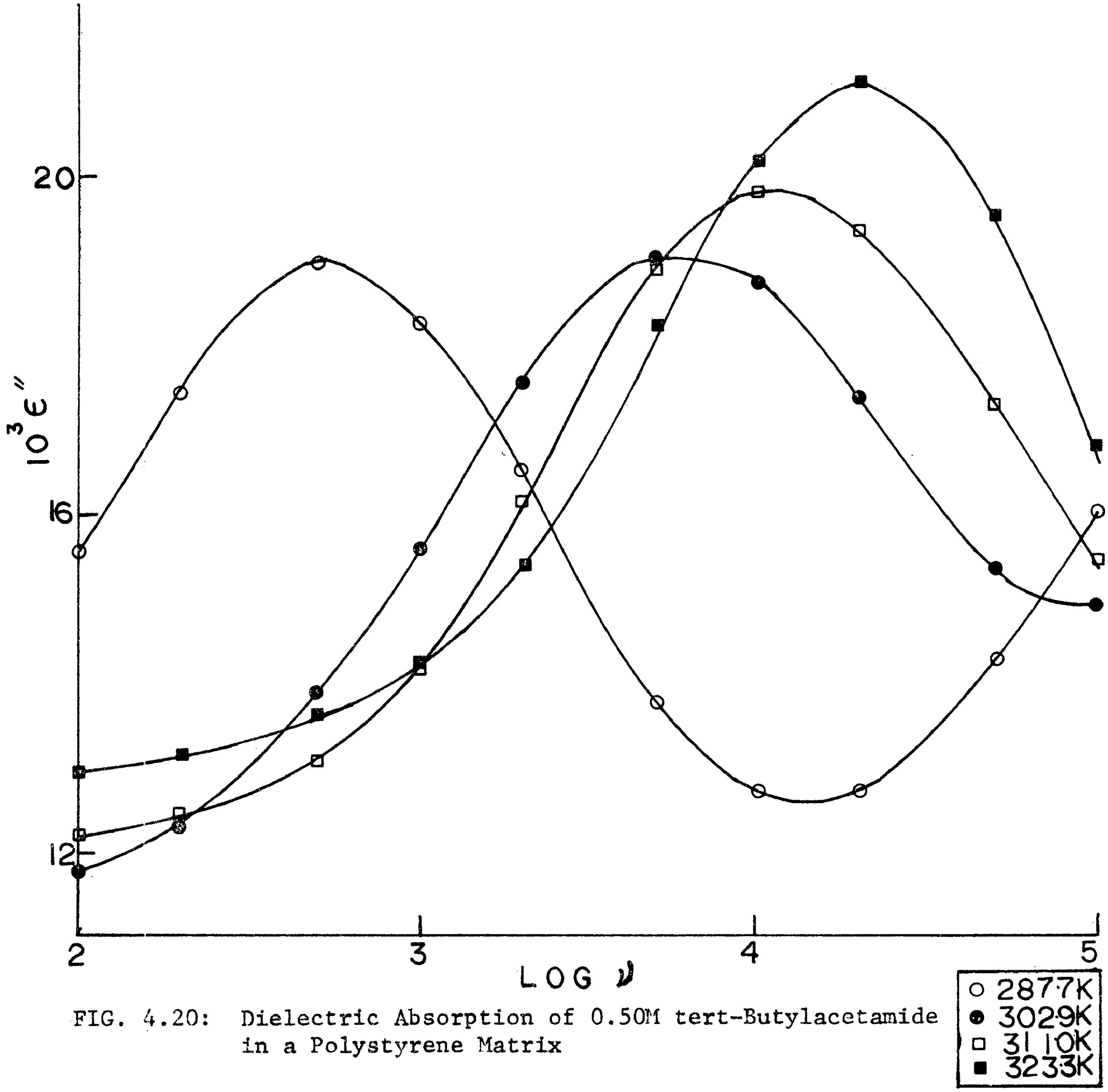

FIG. 4.20: Dielectric Absorption of 0.50M tert-Butylacetamide in a Polystyrene Matrix

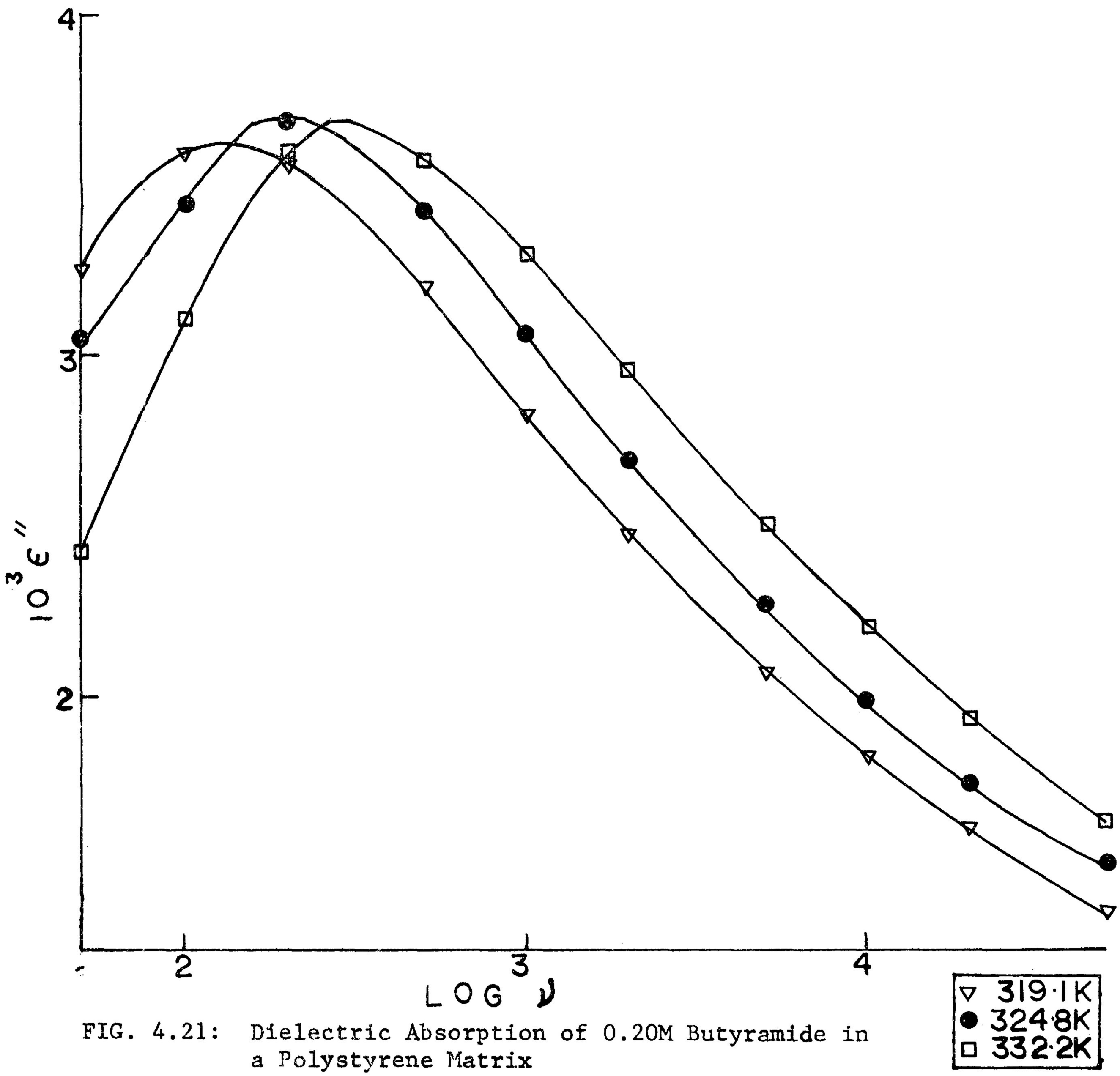

FIG. 4.21: Dielectric Absorption of 0.20M Butyramide in a Polystyrene Matrix

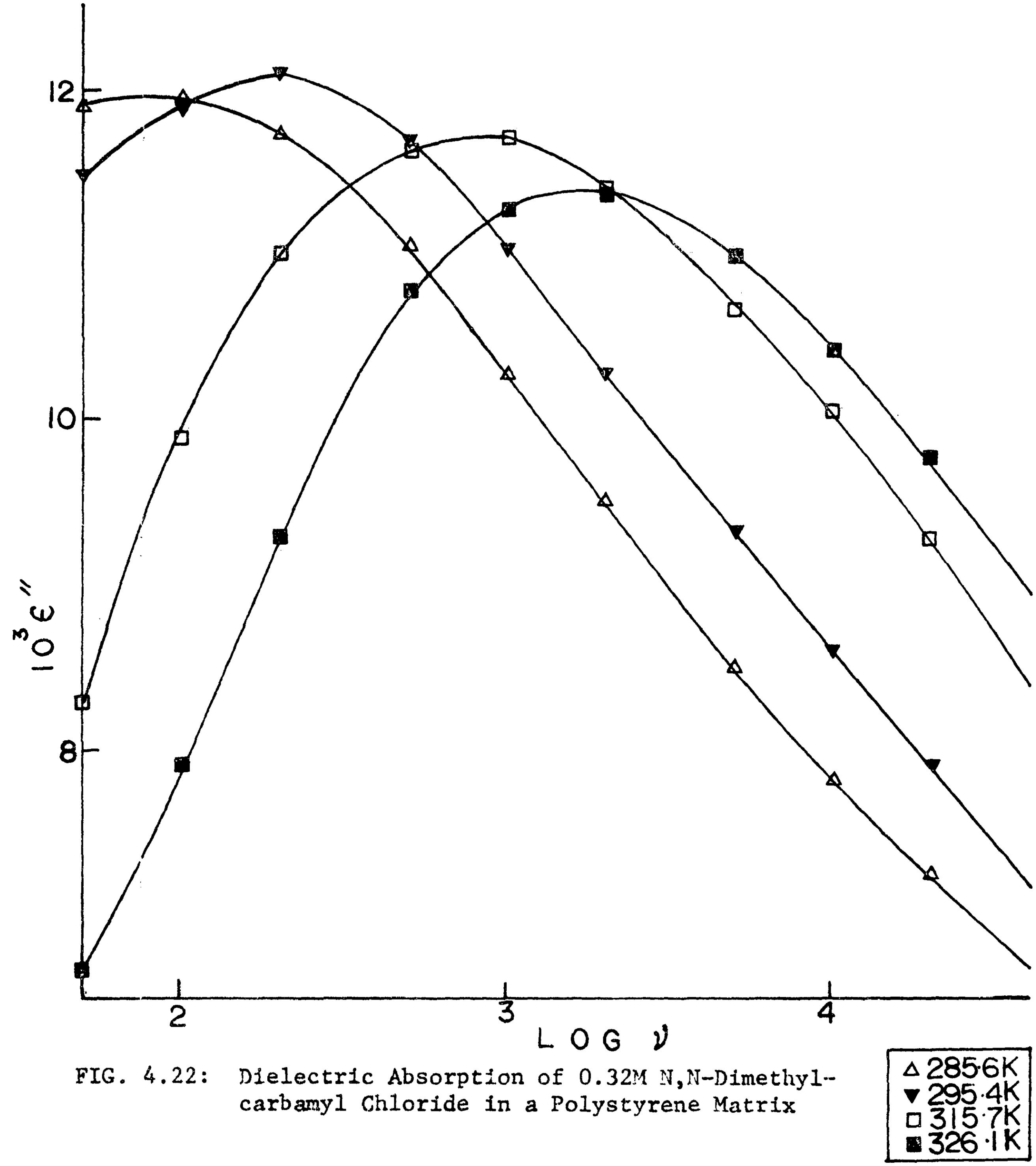

FIG. 4.22: Dielectric Absorption of 0.32M N,N-Dimethylcarbamyl Chloride in a Polystyrene Matrix