SOME DIELECTRIC STUDIES OF MOLECULAR AND INTRAMOLECULAR MOTIONS

A THESIS SUBMITTED BY

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IN PARITIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
OF
MASTER OF SCIENCE

TO

LAKEHEAD UNIVERSITY
THUNDER BAY, ONTARIO
1978

ABSTRACT

Dielectric relaxation studies of a series of polar diaryl molecules and of some analogous rigid molecules dispersed in atactic polystyrene and poly(vinyltoluene) have been carried out. Preparation of both polymer matrices and the dielectric measurements using a General Radio 1615-A capacitance bridge and a Hewlett-Packard Q-meter with appropriate temperature-controllable cells have been described. The experimental data as a function of frequency at different temperatures were subjected to analysis by a series of computer programmes written in the APL language. The activation energy barriers for the dielectric relaxation processes were obtained by the application of the Eyring rate equation.

A number of polar rigid molecules has been studied to provide a wide background knowledge of relaxation and activation parameters for comparison with those of flexible molecules of analogous size. Attempts have also been made to correlate the molecular relaxation absorptions by classification of the polar rigid molecules into three categories in terms of their dipole positions. It is apparent from the present study that the inclination of the molecular dipole to the principal axes may be a factor in determining the magnitude of the observed relaxation time and the activation parameters and this is in line with what was previously found by investigations in the liquid state. To this end, studies have been made of some disc-like molecules such as 9-bromoanthracene and 9-bromophenanthrene. Comparison of their Eyring analysis results with the other elongated molecules showed that the molecules exhibited different contributions for rotation about the principal axes.

Near the glass-transition temperature, (Tg), a cooperative process was attributed to the microbrownian motions of a variety of molecules with a large apparent activation energy which is, of course, not to be interpreted as the 'barrier' required to reorient a solute molecule. Tg was also estimated to be about 320K for solutes of 7% by weight in the polystyrene matrix. Similarly, for 2,2'-bipyridine in poly(vinyltoluene), it was about 270K at the same concentration.

Attempts have been made to study the effect of activation parameters for some rigid molecules and biphenyl derivatives in different matrices of polystyrene and poly(vinyltoluene). In the case of 4-substituted biphenyls and other rigid molecules, the influence of the medium on the dielectric absorption was examined. However, this change of medium was not sufficient to separate the molecular and intramolecular processes completely in biphenyls.

An overlapping of absorption processes was observed in substituted biphenyls, one corresponding to the intramolecular ring-ring rotation occurred at the higher temperature side, while the lower temperature absorption was ascribed to the molecular relaxation. The energy barriers for rotation around the central C_1-C_1' bond for biphenyl were found in most cases to be in the range 15 to 35 kJ mol^{-1}.

ACKNOWLEDGEMENT

The work described in this thesis was carried out at Lakehead University, Thunder Bay, Ontario, Canada, in 1976-78, under the direction of Dr. S. Walker. I wish to express my sincere gratitude to my research supervisor for his invaluable suggestions and guidance throughout this work.

I am indebted to my research colleagues, especially to Dr. C. K. McLellan, Dr. S. P. Tay, and Mr. M. Desando for their many helpful discussions. Thanks are also due to Mr. B. K. Morgan for his indispensable technical assistance.

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CHAPTER I

BASIC THEORY

INTRODUCTION

In the study of relaxation processes, the variation of both temperature and frequency can be very valuable. The radio and microwave bridge techniques are useful for studying dielectric relaxation processes in the frequency range 10^2 to 10^{10} Hz.

Dielectric absorption techniques have been widely employed in the various studies of relaxation process. Microwave measurement has proved to be an effective method in observing molecular structures(1) and extensive reviews of experimental dielectric studies are frequently made in liquids and solutions.(2) These studies are preferred in the investigation of molecular relaxation. Moreover, dielectric measurement is also well known for polymers.(3) During recent years, dielectric studies have been made of polar solutes dispersed in polymer matrices.(4,5) Owing to the viscosity and the structure of the polymer matrix, sometimes the molecular process may be slowed down without appreciably affecting the intramolecular process so as to allow analysis of both the processes independently, which may be overlapped in solution. Up to now, this method is considered to be a most promising procedure for determining an intramolecular energy barrier.(6,7) The technique can be used to evaluate energy barriers, and sometimes the result can be compared with that determined by the other relaxation methods.

THEORIES OF STATIC PERMITTIVITY AND DIPOLE MOMENT

The study of the dielectric properties of dipolar materials is concerned mainly with polarization changes, particularly of the orientational type where a dipole alters its orientation. The calculation of the permittivity of an isotropic polar material is in terms of the permanent dipole moment of the molecules (μ) and their distortion polarizability (α), when the applied field is either constant or varying so slowly that all types of polarization can maintain equilibrium with it. Then, the total polarization of a polar molecule in an electric field involves both orientation (P_O) and distortion (induced) polarizations. The orientation polarization is due to orientation of the permanent dipole moment. The distortion polarization is due to the induced moments which are produced by arising from the displacement of the electronic charges and the nuclei in molecules. The former is called electronic polarization (P_E) while the latter is termed atomic polarization (P_A).

Debye(8) found the dipolar polarization and the earliest solution to the static permittivity. To account for the presence of a permanent dipole moment within a molecule, the total molar polarization (P_T) is given by the Clausius-Mossotti-Debye equation.

$$P_T = P_o + P_A + P_E = \frac{(\varepsilon_o - 1)}{(\varepsilon_o + 2)} \times \frac{M}{d} = \frac{4\pi N}{3}(\alpha + \frac{\mu^2}{3kT}) \quad \text{I-1}$$

where $P_o = 4\pi N\mu^2/9kT$ is the contribution to the polarization arising from the partial alignment of the permanent dipoles by the applied field. ε_o is the static permittivity or the static dielectric constant of the material, α is the induced polarizability. N is Avogadro's number, k the Boltzmann constant, μ the electric dipole moment, T the absolute temperature, M the gram molecular weight and d the density of the molecule. This theory has been used successfully for very dilute dipolar gases and also applied to very dilute solutions of dipolar molecules in a non-polar solvent. However, these are somewhat inadequate for dense gases or pure polar liquids.

Onsager(9) gave the first derivation of the static dielectric constant for a condensed phase of dipolar molecules. According to the Onsager theory, the orientation polarization of a simple liquid is given by the expression

$$\frac{(\varepsilon_o - n^2)(2\varepsilon_o + n^2)}{\varepsilon_o(n^2 + 2)^2} \frac{M}{d} = \frac{4\pi N\mu_o{}^2}{9kT} \quad \text{I-2}$$

where n is the refractive index. Initial tests of this equation seem to suggest that it leads to values of μ_o in agreement with those deduced from measurements on vapors. For a polar liquid, n^2 is equal to the dielectric constant, ε_∞, measured at frequencies so high that the dipole orientation contributions have vanished. Thus, the Eqn. (I-2) becomes:

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

The actual dipole moment μ of the molecule is used to substitute for the value of μ_o. ε_∞ may also be termed as the optical dielectric constant and defined as:

$$\frac{n^2 - 1}{n^2 + 2} \frac{M}{d} = P_E + P_A = \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \frac{M}{d} = \frac{4\pi N}{3} \alpha \qquad \text{I-4}$$

Further, the Debye equation is yielded by the difference between Eqn (I-1) and (I-4) as:

$$\left(\frac{\varepsilon_o - 1}{\varepsilon_o + 2} - \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \right) \frac{M}{d} = \frac{4\pi N \mu^2}{9kT} \qquad \text{I-5}$$

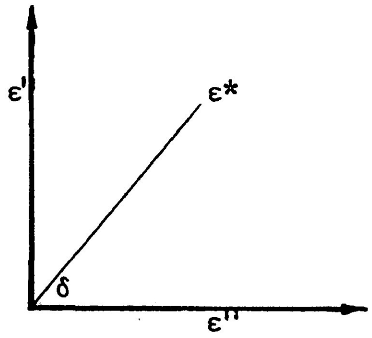
Re-arrangement gives:

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

The Onsager equation differs from that of Debye by the factor $3\varepsilon_o\ (\varepsilon_\infty + 2)/[(2\varepsilon_o + \varepsilon_\infty)(\varepsilon_o + 2)]$. As ε_o approaches ε_∞, this factor approaches 1 and the Onsager equation tends to the Debye.

THEORIES OF DIELECTRIC RELAXATION

The basic theories dealing with dielectric absorption are well established. The dielectric constant or permittivity, ε', is a frequency dependent quantity which is characteristic of the medium between two charges or two electrodes. It may be expressed in terms of its polarizability which is a function of the frequency of the applied electric field. It is also defined as the ratio of the capacitance of a condenser with material between the parallel conducting plates to the capacitance of the same condenser when the material is replaced by a vacuum. For most simple polar molecules, as the frequency of an applied electric field is continuously increased, the reorientation of dipoles will, at some stage, lag behind the field, and the polarization falls off so that it contributes less and less to the total permittivity. Two important effects accompany this lag: Owing to the phase displacement (δ) in the dipole rotations, a dissipation of energy occurs in the medium. It is a feature which gives rise to the term "dielectric loss". At high frequencies when the dipole becomes unable to respond to the field the dielectric constant then is governed by solely atomic and electronic polarizations. When the dipole lags behind the field the behaviour of the dielectric constant can be represented by a phase diagram.(10)



Clearly, the energy dissipation factor or the loss tangent is known as:

$$\tan \delta = \varepsilon''/\varepsilon' \qquad \text{I-7}$$

In the frequency region, where the dissipation occurs, the dielectric constant is a complex quantity (ε^*) given by:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \qquad \text{I-8}$$

where $i = \sqrt{-1}$ is the operator representing rotation through 90^o in the phase diagram, and $i^2 = -1$. ε' is the real part of the dielectric constant (even though it may vary with frequency) and the imaginary part ε'' is known as the dielectric loss factor.

The frequency dependence of the dielectric constant ε' and dielectric loss ε'' in the region of dielectric absorption for a system characterized by a single discrete relaxation time is given by the Debye equation:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1+i\omega\tau} \qquad \text{I-9}$$

where ε_0 and ε_∞ are the low and high frequency limiting values of ε^*, respectively. ω is the angular frequency in rad s^{-1} and τ is the the characteristic relaxation time in seconds. It is defined as the time in which the polarization is reduced to 1/e times of its original value.

On separation into real and imaginary parts, the following equations are obtained:

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1+\omega^2\tau^2} \qquad \text{I-10}$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1+\omega^2\tau^2} \qquad \text{I-11}$$

The simplest version of the absorption function provides a curve symmetrical about ε''_{max} . In the $\log\nu$ plot, the maximum occurs when

$\omega\tau = 2\pi\nu\tau = 1.$

A Cole-Cole plot is given by elimination of $\omega\tau$ from these equations to obtain:

$$(\varepsilon' - \frac{\varepsilon_0 + \varepsilon_\infty}{2})^2 + (\varepsilon'')^2 = (\frac{\varepsilon_0 - \varepsilon_\infty}{2})^2 \qquad \text{I-12}$$

The locus of ε' and ε'' gives a semi-circle of radius $(\varepsilon_0 - \varepsilon_\infty)/2$ with the center lying on the abscissa. Thus, the values of ε_0 and ε_∞ will be yielded from its intersection with the ε' axis.

Many non-spherical molecules show a broader dispersion curve and lower maximum loss than would be expected from the Debye relationships. In such cases, Cole and Cole(11) suggested that the permittivity may follow the empirical equation by considering a mean effective relaxation time τ_0.

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1+(i\omega\tau_0)^{1-\alpha}} \qquad \text{I-13}$$

where α is the distribution parameter measured in units of $\pi/2$ rad. and may vary between 0 and 1. The simple Debye equation is obtained when the α value is equal to zero.

Similarly, Eqn. (I-13) can be separated into real and imaginary parts to yield analogous Cole-Cole plot where the centre of the semi-circle lies below the abscissa:

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_0-\varepsilon_\infty)(1+(\omega\tau_0)^{1-\alpha}\sin(\alpha\pi/2))}{1+2(\omega\tau_0)^{1-\alpha}\sin(\alpha\pi/2)+(\omega\tau_0)^{2(1-\alpha)}} \qquad \text{I-14}$$

$$\varepsilon'' = \frac{(\varepsilon_0-\varepsilon_\infty)(\omega\tau_0)^{1-\alpha}\cos(\alpha\pi/2)}{1+2(\omega\tau_0)^{1-\alpha}\sin(\alpha\pi/2)+(\omega\tau_0)^{2(1-\alpha)}} \qquad \text{I-15}$$

The mean relaxation time τ_0 can be obtained from a plot of log(v/u) versus log ω according to the relation:(2)

$$\frac{v}{u} = (\omega\tau_0)^{1-\alpha} \qquad \text{I-16}$$

where v is the distance between the experimental point and ε_0 in the Cole-Cole plot and u is that between ε_∞ and the same experimental point.

A large variety of functions has been considered for the representation of non-Debye types of absorption. The Fuoss-Kirkwood relation(12), which is an empirical expression used in analyzing experimental data, is frequently used:

$$\varepsilon' = \varepsilon''_{max}\ \text{sech}(\beta \ln(\omega/\omega_{max})) \qquad \text{I-17}$$

The mean relaxation time characterizing the dipole motion giving rise to the absorption is indicated by $\tau_o = 1/\omega_{max} = 1/2\pi\nu_{max}$ where ν_{max} (Hz) is the frequency at which the maximum loss factor, ε''_{max}, is observed. β is an empirical constant known as the distribution parameter, which is a measure of the breadth of the relaxation distribution. It may have values between 0 and 1. The value β=1 corresponds to the Debye equation.

The Fuoss-Kirkwood formulation does not deal with the real part of the complex dielectric permittivity, nor with its limiting values at high and low frequencies, ε_o and ε_∞, respectively. However, the total dispersion for each dielectric absorption process is given by:

$$\Delta\varepsilon' = \varepsilon_o - \varepsilon_\infty = \frac{2\varepsilon''_{max}}{\beta} \qquad \text{I-18}$$

The relation between the two distribution factors of relaxation time, Fuoss-Kirkwood β and the Cole-Cole α, was considered by Poley(13):

$$\beta\sqrt{2} = (1-\alpha)/\cos((1-\alpha)\pi/4) \qquad \text{I-19}$$

The Cole-Davidson function$^{(14)}$ also describes expression of non-Debye types of absorption:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1+i\omega\tau_0)^h} \qquad \text{I-20}$$

where h is again a constant having values batween 0 and 1, with h=1 corresponding to the Debye equation. It may also be deduced to be:

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)(\cos^h(\phi)\ \cos(h\phi)) \qquad \text{I-21}$$

$$\varepsilon'' = (\varepsilon_0 - \varepsilon_\infty)(\cos^h(\phi)\ \sin(h\phi)) \qquad \text{I-22}$$

where ϕ = arc tan ($\omega\tau$). A skewed arc results from the plot of ε'' versus ε' at various frequencies from the Davidson-Cole equation.

This equation seems to be very successful in representing behaviour of substances at low temperatures. It is often employed to interpret the dielectric absorption, particularly for a relaxation mechanism involving cooperative motion of the surroundings as the dipolar molecular relaxation.

The Cole-Cole and Cole-Davidson types of behaviour can be understood as arising from the existence of a continuous spread of relaxation times, each of which alone would give rise to a Debye type of behaviour. However, there are many molecules whose absorption can be characterized by more than one discrete relaxation process, each of which may have contributed independently to the total dispersion. For such systems, the analysis of dielectric data becomes more complicated. Budó(15) considered that the complex dielectric constant of the overall absorption could be represented as the sum of the Debye terms according to the general expression:

$$\varepsilon^* = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)\sum_{k=1}^{n} \frac{C_k}{1+i\omega\tau_k} \qquad \text{I-23}$$

where τ_k is the relaxation time characteristic of the kth mode of relaxation, the factor C_k is representing the individual fraction of kth mode to contribute the total dispersion $\sum_{k=1}^{n} C_k = 1$.

For an example of two relaxation times, such behaviour is described by the following equations:

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)\left(\frac{C_1}{1+\omega^2\tau_1^2} + \frac{C_2}{1+\omega^2\tau_2^2}\right) \qquad \text{I-24}$$

$$\varepsilon'' = (\varepsilon_0 - \varepsilon_\infty)\left(\frac{C_1\omega\tau_1}{1+\omega^2\tau_1^2} + \frac{C_2\omega\tau_2}{1+\omega^2\tau_2^2}\right) \qquad \text{I-25}$$

where C_1 and C_2 are the weight factors of the two contributing absorptions, and $C_1 + C_2 = 1$. It is shown that the shape of the Cole-Cole plot is influenced by the ratios τ_1/τ_2 and C_1/C_2. When both ratios are large enough, the dielectric absorption data may be separated into two **distinct** absorption systems.(16)

It is noted that the Cole-Cole equation, the Fuoss-Kirkwood relation and Cole-Davidson equation are the relationships generally used for the analysis of dielectric data.

Dielectric relaxations are rate processes. Eyring has treated dipole rotation by analogy with a chemical rate process. The mean rate coefficient, k_r, was identified with the reciprocal of the relaxation time τ in which a dipole acquires sufficient energy to pass over the potential barrier from one equilibrium position to the other. Such molecular rate processes usually follow the empirical Arrhenius equation for rate coefficients.

$$k_r = 1/\tau = A \exp(-\Delta H_A/RT) \qquad \text{I-26}$$

where A is a numerical constant and ΔH_A is the Arrhenius activation enthalpy per mole.

For the factor A, absolute rate theory arrives at different values according to the model envisaged for the restricted rotation. The most frequently used value is Eyring's:

$$A = (kT/h) \exp(\Delta S_E/R) \qquad \text{I-27}$$

where ΔS_E is an arbitrary "entropy of activation" which is adjusted to fit the observation. Therefore, the Eyring equation is obtained as:

$$\tau = (h/kT)\ \exp(\Delta H_E/RT)\ \exp(-\Delta S_E/R) \qquad \text{I-28}$$

where h is the Planck's constant, k the Boltzmann constant, R the universal gas constant, and T the absolute temperature.

From this equation, it appears that a graph of $\log(\tau T)$ against $1/T$ should be rectilinear. However, no absolute significance can be attached to the values of ΔS_E obtained in this way. It is widely quoted and used in the dielectric relaxation studies.

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CHAPTER II

APPARATUS AND EXPERIMENTAL PROCEDURE

THE GENERAL RADIO BRIDGE

The model 1615-A capacitance bridge is manufactured by the General Radio Company and is used in conjunction with their model 1310-B sine wave signal generator and a model 1232-A tuneable amplifier/null detector. An oscilloscope is used to facilitate these measurements. The capacitance and conductivity of a sample are measured in the frequency range from 50 to 10^5 Hz.

The frequency scale of the signal generator was calibrated against the power line frequency (60 Hz) by Lissajous figure comparisons with an oscilloscope for several output frequencies.

The capacitor connected to the General Radio bridge contained the polystyrene matrix sample clamped between the electrodes. The electrode assembly is shown in Fig. II-1. It is a three-terminal assembly with an outer diameter of 5.08 cm. The low electrode has a diameter of approximately 3.81 cm. and is surrounded by a guard ring electrode of outer diameter 5.08 cm. This type of electrode assembly reduces considerably any error caused by fringing of the electric field at the edges of the measurement area. It is used in such a way that the capacitance measured is solely that between the high and low electrodes. The

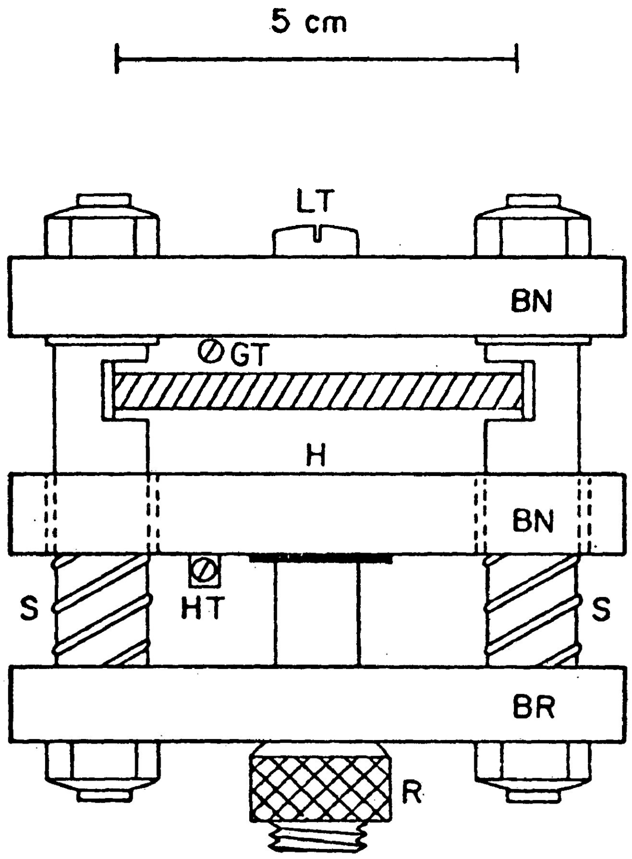

Figure II-1: Three-terminal electrode assembly for dielectric measurements on solid disks.

<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 assembly was mounted in an aluminum chamber which could be sealed off from the atmosphere. Two tubes allowed the chamber to be purged with dry nitrogen gas which was maintained at a slight positive pressure to prevent the entry of atmosphere moisture during low-temperature measurements. The chamber was equipped with a heating coil of nichrome wire wrapped around its exterior. Power to the heater winding was provided by a Beckmann/ RIIC model TEM-1 temperature controller which sensed the chamber temperature via a small thermocouple placed in a well in the chamber wall. Cooling of the chamber was accomplished by placing on its flat top a container of liquid nitrogen. To maintain a stable temperature, an appropriate number of sheets of paper was inserted between the chamber and the liquid nitrogen container so that the heater current was about 2 amps. corresponding to a power of about 8 watts. Measurement of the sample in this cell was carried out only after the sample had reached thermal equilibrium with the chamber case, as judged by stability of the capacitance and conductivity readings within the temperature accuracy of ±0.1K.

The measurement of capacitance (C), conductivity (G) and dissipation factor (D) of a sample disc can be related to the components of the complex permittivity by the following relations(1):

$$\varepsilon' = C/C_o \qquad \text{(II-1)}$$

$$\varepsilon'' = G/\omega C_o \qquad \text{(II-2)}$$

and $$\varepsilon'' = \varepsilon' \, (D \times \nu \times 10^{-3}) \qquad \text{(II-3)}$$

where the real permittivity is defined as the ratio of the capacitance C of the condenser with the dielectric to the capacitance C_o without the sample. G is the conductivity of the system and ω the frequency applied to the system. ω which is equal to $2\pi\nu$ is the angular frequency of the applied field in radians s^{-1}, and D the dissipation factor of the system.

Since it is difficult to obtain C_o through measurement, C_o may be calculated from the relation(2):

$$C_o = \frac{0.2244 A_1}{d_1} \qquad \text{(II-4)}$$

where A_1 is the effective area of the plates in square centimeters, d_1 is the spacing of the plates in centimeters, and C_o is the capacitance in the units of picofarads. Elimination of C_o from these equations gives:

$$\varepsilon' = \frac{C d_1}{0.2244 A_1} \qquad \text{(II-5)}$$

$$\varepsilon'' = \varepsilon' G/\omega C \qquad \text{(II-6)}$$

The effective area of the cell electrode plates A_1 was found by measuring the capacitance of the cell containing a standard quartz disc of diameter 5.08 cm. and thickness 0.1367 cm. supplied by Rutherford Research Products Co. with a dielectric constant of 3.819.

THE Q-METER

Dielectric measurements on the polystyrene disc samples at frequencies in the range 25×10^3 to 15×10^6 Hz were made using a Hewlett-Packard model 4342A Q-meter connected via a model 4342 adapter plate supplied by the aforementioned Rutherford Research Products Co. to a cell designed by Mr. B.K. Morgan of this laboratory. A diagram of this cell is shown in Fig. II-2. Basically, the cell consists of two capacitors sharing a common plate. One capacitor has the sample between the common plate and the case (ground), and the other has an air gap partially filled with a 2.54 cm. diameter quartz disc between the common plate and the high electrode. The thickness of the air gap in the reference capacitor may be adjusted by screwing up or down a threaded shaft on which the quartz disc rests. The whole assembly is clamped together by a spring bellows bearing upon the low (ground) electrode of the sample capacitor. A switch arm mounted on the common central

Key to Figure II-2 on facing page

SB	Spring bellows
L	Low electrode in contact with case
CP	Centre plate
H	High electrode
I	Insulating supports for high electrode (four)
G	Locating guides for centre plate (three)
TC	Thermocouple in well
H	Handle for operation of switch
N	Nitrogen gas inlet (outlet not shown)
S	Switch assembly
BP	Banana plug connectors for low (case) terminal
HC	High electrode connection strip
Q	Quartz spacer
SA	Sample (2" dia. disk) location
E	Electric heater coil

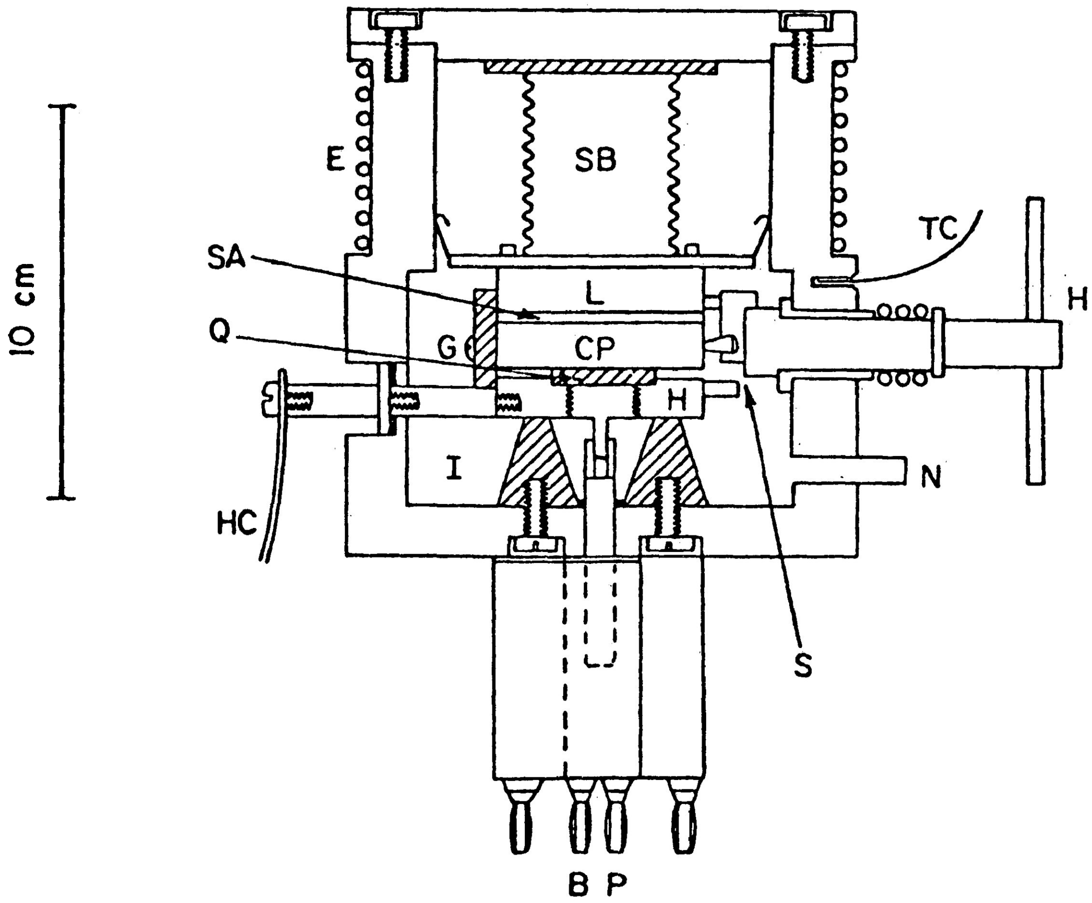

Figure II-2: The Morgan tri-electrode cell for Q-meter.
(key on facing page)

plate allows this plate to be connected either to the high or low side. When it is connected to the low plate of the sample capacitor, the common plate then becomes the low plate for the reference capacitor, and the sample capacitor is removed from the circuit. When the common plate is connected to the high plate of the reference capacitor, this capacitor is removed from the circuit, and the common plate becomes the high plate of the sample capacitor. In this manner the switch allows the Q-meter to examine either the sample capacitor or the reference capacitor.

The cell case was similar to that of the cell used with the General Radio bridge, and temperature control of the cell and sample was accomplished in the same manner.

The experimenter places the sample in the appropriate location and adjusts the spacing of the reference capacitor plates so that the two capacitors have, as nearly as possible, the same capacitance value. This is judged by an ability to achieve resonance of the Q-meter circuits at the same settings of the capacitance controls of the meter for both capacitors. This adjustment is done only once at the beginning of a set of measurements on a sample, since the value of the capacitance is not important, as will be seen later. All that matters is that the two should be the same.

In principle the difference in capacitance between reference and sample capacitors may be related to the dielectric constant of the sample if this parameter is known for at least one frequency. However, attempts to use this information gave no consistent values for the dielectric constant of the sample, and therefore, these data were not used.

The important data were values of dielectric loss factor ε'' as a function of frequency for the present study. If one assumes that the conductivity, G, of the measurement system consists of two additive components, one each for the sample and the measurement system alone, then one obtains Eqn. II-7 after employing Eqn. (II-1) and (II-2) and bearing in mind the definitions of loss tangent and of Q.

$$\begin{aligned}(\tan \delta)_s &= \frac{G_x - G_r}{\omega C} \\ &= \frac{G_x}{\omega C} - \frac{G_r}{\omega C} \\ &= \frac{1}{Q_x} - \frac{1}{Q_r} \\ &= \frac{Q_r - Q_x}{Q_x} \times \frac{1}{Q_r} \\ &= \frac{\Delta Q}{Q_x} \times \frac{\Delta C_r}{2C_r} \qquad \text{(II-7)}\end{aligned}$$

where $(\tan \delta)_s = \tan \delta$ for the sample only. Q_x is the Q value for the capacitor being examined, ΔQ is the difference in Q values for sample and reference, C_r is the capacitance of the reference capacitor, ΔC_r is the width of the peak of Q vs. C for the reference capacitor measured at $Q_r/\sqrt{2}$, and the subscripts x and r refer to the corresponding values when measured for the sample and reference capacitors, respectively.

In the dielectric measurement, the value of C_r is not determined; however, it was adjusted to be equal to the value of the sample capacitor, C_x. Application of Eqn. (II-1) and (II-4) and then Eqn. (I-8) yields:

$$\varepsilon''_s = \frac{(\Delta Q)(\Delta C_r)(d_1)}{(Q_x)(2\times 0.2244 A_1)} \qquad \text{(II-8)}$$

where ε''_s is the dielectric loss factor of the sample, d_1 is the sample thickness in centimeters. A_1 is the effective area of the cell electrodes in one of the capacitors, and the remaining quantities are defined as in Eqn. (II-7).

PURIFICATION OF SAMPLES

The polystyrene used in the preparation of the matrix samples was obtained from Haven Industries, Inc., Philadephia, U.S.A.

(Lot #700-228-20) and had a nominal molecular weight of 230,000 (MW).

The solutes were procured from various manufactures and were purified appropriately prior to use, wherever it was considered necessary.

In general, biphenyls were purified by dissolving them in ethanol, recrystallizing them, and then drying them in a vacuum oven. The melting points were then compared with the literature data.(3)

POLYSTYRENE MATRIX DISC PREPARATION

Solutions of solutes in polystyrene were prepared in the following manner to produce solid disks. The desired weight of solute was placed in a ceramic crucible, and to this was added the required weight of polystyrene pellets. This mixture was then dissolved in trans-1,2-dichloroethylene, a non-polar solvent, and the crucible placed in a drying oven at approximately 375K. As the dichloroethylene solvent evaporated, the crucible was removed periodically from the oven and its contents stirred with a stainless steel spatula to ensure that the remaining solution was uniform. When the mixture had lost enough dichloroethylene to become extremely viscous, the crucible was transferred into a vacuum oven at approximately 360K, and the pressure reduced by a single-stage rotary pump. This caused the plastic mass to expand a great deal into a foam as the remaining dichloroethylene evaporated under the vacuum oven conditions. The sample was placed in the oven for at least one hour for evaporation of the last traces of dichloroethylene. The sample has to be checked until the polystyrene matrix contains less than 1% of solvent by weight.

Pure polystyrene disks were prepared in the same procedures without the solute.

In a few cases where the boiling point of the solute was low (e.g. below about 400K), the procedure was altered. In these cases, no trans-1,2-dichloroethylene was used. Instead, the desired weight of polystryrene was dissolved directly in a large excess of the liquid which was to become the solute, and the evaporation process carried out as before, except that the final evaporation in the vacuum oven was halted when the total sample weight indicated that the matrix contained the desired amount of solute.

The matrix material was placed in a stainless steel die equipped with polished tungsten carbide faces of 5.08cm diameter. A heating sleeve was placed around the die and was heated to a temperature necessary to melt the matrix material. The temperature used depended on the solute concentration, being about 410K for pure polystyrene and about 390K for matrices containing less than 10% by weight solute. Heating was accomplished in 20 to 30 minutes. The sample was then pressed by applying a force of 5 tons to the moving element of the die. Then the heating sleeve was raised out of the way and a fan was used to cool down the die to room temperature in about 30 minutes. The die was disassembled and the moving element pressed out of the die collar. The edges of the sample, a disc of diameter 5.08cm, were lightly smoothed with a sharp knife blade and the sample thickness measured with a micrometer at ten points to yield an average value. The sample weight was recorded, and from this weight and the weights of solute and polystyrene originally used, the molar concentration C of the solute was calculated by the formula.(4, 12, 13)

$$C = \frac{\text{Wt. of solute used}}{\text{M.wt. of solute}} \times \frac{\text{Wt. of disc}}{\text{Wt. of P.S. + solute}} \times \frac{1000}{\text{Vol. of disc}}$$

To reduce mechanical strain, disks were stored for at least one day in a desiccator before measurement. The same procedure was adopted to prepare a polyvinyl toluene matrix except the die temperature were lower than those for a polystyrene matrix.

The polar solute content was usually about 7% by weight. The concentration of the solutes was so low in the matrices that they could mono-molecularly dispersed(5) to eliminate any strong internal electric field. Moreover, such a low concentration would not affect the relaxation process appreciably, for Borisova and Chirkov(6) showed that the energy barrier for relaxation of small molecules in a polystyrene matrix is independent of concentrations less than 5-7 mole percent.

Samples of pure solids were prepared by grinding the solid with a mortar and pestle, placing the powder in the die and pressing it at room temperature with a force of 30 tons.

EXPERIMENTAL RESULTS

The analysis of experimental data as functions of frequency and temperature was carried out by a computer program written in the APL language. The loss factor due to the solute itself, $\Delta\varepsilon''_{\text{solute}} = \varepsilon''_{\text{matrix}} - \varepsilon''_{\text{p.s.}}$, was obtained by subtracting the values for pure polystyrene from those observed for the matrix solution. For each temperature, the data of dielectric loss factor as a function of frequency were analysed by the Fuoss-Kirkwood equation, Eqn. (I-17). By an iteration procedure, the value of ε''_{max} is determined which provides the best straight line fit to the plot of $\cosh^{-1}$ $(\Delta\varepsilon''_{max}/\Delta\varepsilon'')$ against $\ln(\nu)$. The value of the distribution parameter, β, is obtained from the slope of this line, and the frequency of maximum dielectric loss, ν_{max}, from this slope and the intercept of the line on the $\cosh^{-1}$ axis. Moreover, a 95% confidence interval was chosen as a good representation of experimental error for both the Fuoss-Kirkwood distribution parameter, β, and $\log(\nu_{max})$.

The Fuoss-Kirkwood equation does not deal with the real part of the complex dielectric permittivity, nor with its limiting values at low and high frequencies, ε_o and ε_∞, respectively. However, the total dispersion for each dielectric absorption process is given by Eqn.(I-18).

The Cole-Cole distribution equation is also commonly used to describe the frequency dependence of dielectric permittivity in a system involving a distribution of relaxation times as mentioned in Chapter I.

The Cole-Cole distribution parameter α, may be obtained from the Fuoss-Kirkwood distribution parameter β, by Eqn. (I-19).

Therefore, in order to obtain ε_∞, the Fuoss-Kirkwood formulation was supplemented with the Cole-Cole equations. Several estimates of ε_∞ were obtained from the Cole-Cole equation through the given experimental values of ε' at various frequencies. The average ε_∞ was calculated, along with a value for ε'_γ at the frequency of maximum loss. A computer program performed this work and calculated the average of these estimates.

The value of the effective dipole moment involved in the dielectric relaxation process may now be calculated from either the Debye equation (I-6) or the Onsager equation (I-2).

$$\mu^2 = \frac{27000\ kT\ (\varepsilon_0 - \varepsilon_\infty)}{4\pi NC\ (\varepsilon' + 2)^2} \qquad \text{(II-9)}$$

$$\mu^2 = \frac{9000\ kT\ (2\varepsilon_0 + \varepsilon_\infty)(\varepsilon_0 - \varepsilon_\infty)}{4\pi NC\ \varepsilon_0 (\varepsilon_\infty + 2)^2} \qquad \text{(II-10)}$$

where: $(\varepsilon_o - \varepsilon_\infty) = 2\varepsilon''_{max}/\beta$ (Eqn. (I-18)).

ε' is the value of ε' at ν_{max}, that is, $(\varepsilon_\infty + \varepsilon_o)/2$.

ε_o is the static dielectric constant derived from ε_∞ and Eqn. (I-18).

N is Avogadro's number, 6.023×10^{23} molecules mol^{-1}

C is the solute concentration in moles per liter

k is the Boltzmann constant 1.38054×10^{-16} erg K^{-1}.

and T is the temperature in K.

These two equations yield μ in units of e.s.u.-cm. It is more common to express this parameter in Debye units, where $1D = 1 \times 10^{-18}$ e.s.u.-cm.

The Fuoss-Kirkwood analysis and calculations of ε_∞ and μ were carried out at each temperature. (Values of ε' from Q-meter data were unreliable, so ε_∞ and μ could not be calculated). Further processing of the results of these analyses from the several temperatures employed for a particular sample was then carried out. To begin, attempts were made to estimate the values of dipole moment at temperatures above those of measurement. The simplest procedure is that employed by Davies and Swain(5) which assumes that the dipole moment is a linear function of temperature. This appeared to give reasonable results in their work although there is little theoretical basis for such a procedure. However, it is well established that in many cases the variation of ε_o and ε_∞ with temperature may be described by an equation of the form log $(\varepsilon) = aT + b$(7). Extrapolated values of ε_o and ε_∞ derived in this manner have been used in conjunction with Eqn. (II-9) to estimate dipole moments at higher temperatures, which agree in most cases with those from the Davies-Swain technique. The Davies and Swain procedure would seem best suited to cases where only a short temperature extrapolation is necessary.

In the present study, dipole reorientation was considered as a rate process(8) and the energy barrier opposing the dielectric relaxation process was obtained by use of the Eyring rate equation (I-28), a procedure commonly adapted in dielectric works.(4, 9, 10) A linear form is obtained from Eqn. (I-28).

$$\ln(T\tau) = \frac{\Delta H_E}{RT} - (\frac{\Delta S_E}{R} - \ln(h/k)) \qquad \text{(II-11)}$$

Plots of log (τT) versus $(1/T)$ yield good straight lines and values of the enthalpy of activation, ΔH_E, and the entropy of activation, ΔS_E, were obtained from the slope and intercept, respectively, of such graphs by a computer program based on Eqn. (II-11). In order to obtain a more accurate value of ΔS_E, it is preferable to measure the dielectric loss of the matrices through a wide temperature and frequency range with both the General Radio bridge and Q-meter.

Standard statistical techniques(10) have been provided in the fitting and analyses of the data for linear functions, viz, the relation between log ν_{max} and β values from the Fuoss-Kirkwood analyses, as well as the enthalpy and entropy of activation from the Eyring analysis. Any experimental point which deviated from the calculated line by more than its allowed confidence interval, i.e. 95% confidence interval, was deleted from a repeat run of the EYRING Program.

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CHAPTER III

MOLECULAR RELAXATION

INTRODUCTION

Generally, dielectric relaxation can be viewed as a temperature dependent phenomenon. In the earlier investigations, dielectric relaxation was carried out upon solutions of polar molecules in solvents with different viscosities.(1,2) Later, more attentions were paid to the viscous mixtures of hydrocarbons-nujol.(3,4) Recently a polystyrene matrix has been employed to achieve a much more viscous medium.(5,6) It was seen that molecular size, shape, viscosity of the media and the dipole direction tend to affect the molecular relaxation time and activation parameters of the solute molecules **in the very dilute solutions.**

To verify the above statement, some findings are employed to help illustrate the relationships.

Pitt and Smyth(1) measured three rigid ketone molecules, namely anthrone, fluoronone and phenanthrenequinone, of fairly similar size and shape in benzene solution, and the corresponding enthalpies of activation (ΔH_E) were found to be 9.0, 8.4, and 11.0 kJmol^{-1} respectively. In studying some aromatic halides, Hassell indicated that a slight change was found in activation energy (ΔH_E) from 5.9 to 9.2 kJmol^{-1} by increasing the size of the molecules from fluoro- to iodo-benzene. Kalmam and Smyth(3) found out that there was generally an increase in the enthalpy of activation when the shape of the molecule was elongated rather than spherical. From their observations, they indicated that for the spherical molecule of 2,2'-dichloropropane, the activation enthalpy was found to be 6.7 $kJmol^{-1}$, whilst for the elongated molecule of 4-bromobiphenyl, it was 37.6 $kJmol^{-1}$.

However, Pitt and Smyth(8) found that there was a different relaxation time between the two large, oblate, ellipsoidal molecules of metal-free heptaphenyl chlorophenyl porphyrazine and ferric octaphenyl porphyrazine chloride in benzene solution which are almost the same size and shape. They suggested that the difference in relaxation time could be attributed to the fact that the dipole moment of chloroporphyrazine lies in the plane of the molecule, while the ferric complex is perpendicular to the molecular plane. A similar effect has been found in 2-iodobiphenyl and 4-iodobiphenyl(4). The effect of the difference in dipole position is very large in the biphenyls. For instance, 4-iodobiphenyl has a relaxation time of 3.3×10^{-9}s, five and a half times that of 2-iodobiphenyl which is 6.0×10^{-10}s.

The Eyring rate expression is often used for evaluating activation parameters. From the available literature data, Higasi(9) provided linear plots of ΔH_E versus ΔS_E for a variety of pure liquids. Davies and Edwards(5) also obtained a similar relation for polar solutes of various sizes and shapes dispersed in polystyrene matrices.

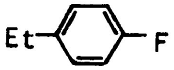
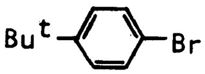
A recent study of the dielectric absorption of polar molecules in a polystyrene matrix has shown the extent of molecular rotational mobility possessed by rigid polar molecules in the amorphous solid phase.(5,18) One of the aims of these studies was to explore the use of media such as polystyrene to reduce the freedom of the whole-molecule reorientation, whilst perhaps not too greatly disturbing the intramolecular motion of polar groups whose independent contribution to the dielectric relaxation and energy factors for the intramolecular motion should become more directly evaluated. Thus, before extensive intramolecular studies of solute molecules in such a matrix are made, it is desirable to have a wider background knowledge of what influences the entropy of activation and to what extent concepts developed for dilute solutions can be applied to the matrix work.

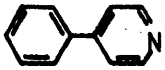
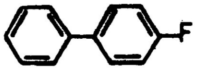
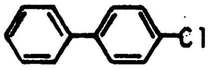
DISCUSSION

In the case of rigid molecules, the frequency of maximum absorption, molecular relaxation parameters and energy factors of dipole orientation in polystyrene are closely related to the shape and size of the molecules. The polar rigid molecules studied in the present work have been classified into three groups in terms of their dipole positions - the dipole component lying either on the long axis or on the short axis or between the principal axes of the molecules.

The Eyring analyses for the variety of rigid molecules and non-rigid molecules have been presented under separate headings in Table III-1 to Table III-3. In general, the relaxation time and free energy (ΔG_E) are meaningful only within a given temperature range of the experimental observation.

The following compounds are included in the first groups, the dipole moments of which lie on the long axis:

NO.	Name	Structure
1	4-Fluoro-ethylbenzene	
2	4-Bromo-tert-butylbenzene	

3	4-Phenyl-pyridine	
4	4-Fluorobiphenyl	
5	4-Chlorobiphenyl	
6	4-Bromobiphenyl	

The Eyring analyses in Table III-1 include halobenzenes, halotoluenes and more elongated biphenyls. It can be seen from the table that the enthalpy of activation (ΔH_E) increases as the size and length of the molecules increase. Here, activation enthalpy is an overall term combining changes in the medium with the solute reorientation process. According to Davies et al.(15) such behaviour could be understood qualitatively if the activation energy was needed primarily to displace the adjacent solvent media so that the more energy was required for ΔH_E, the larger the local disorder would be, ΔS_E. Smyth et al.(3) described the difference between the entropy of activation for the spherical shaped molecules and the elongated ones as due to an increase in the disturbance of the surrounding molecules upon rotation of the elongated molecules.

As the halogen substituents are in the sequence from fluoro- to iodo- atoms in polystyrene, the enthalpy of activation changes from ∿9 to 15 kJmol^{-1} in halobenzenes; from 13 to 42 kJmol^{-1}(10) in halotoluenes and from 52 to 89 kJmol^{-1} in halobiphenyls. When viewed from the structures of both substituted benzenes and 4-substituted biphenyls, the activation energy ΔH_E increased apparently as the size of the substituent increased. As the size of 4-fluoro-ethylbenzene was compared with fluorobenzene, fluorotoluene and 4-bromo-ethylbenzene, the length of the molecules increased in the order of fluorobenzene, fluorotoluene, 4-fluoro-ethylbenzene, and 4-bromo-ethylbenzene.

The corresponding activation enthalpy followed by the same sequence, 9, 13, 25 and 38 $kJmol^{-1}$, respectively. Moreover, the relaxation times of correspondence at 200K also increased from 1.2×10^{-9}s, 7.7×10^{-8}s, 3.8×10^{-7}s to 6.9×10^{-4}s. Meanwhile, another important parameter to be noted is the free energy (ΔG_E) which is a function of temperature. For these four molecules, the corresponding sequence was 14.1, 21.0, 23.8 and 36.2 $kJmol^{-1}$ at 200K for the free energy of activation. Consequently, the absorption process found in 4-fluoro-ethylbenzene can be regarded as having the same reorientation mechanism as the other rigid molecules,

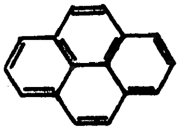
When the length and volume of a molecule increase, such as from ethyl to tert-butyl and from a fluorine to a bromine atom, the activation parameter and molecular relaxation time would be expected to be much higher. In the case of 4-bromo-tert-butylbenzene, it was found to have an activation enthalpy of 54 $kJmol^{-1}$ which was apparently larger than that of 38 $kJmol^{-1}$ in 4-bromo-ethylbenzene and 33 $kJmol^{-1}$ in 4-bromotoluene. Fig. III-1 shows the dielectric absorption curve for 4-bromo-tert-butylbenzene, and Fig. III-2 gives a typical Eyring plot of log (τT) versus $1/T$ from which ΔH_E and ΔS_E are evaluated. Likewise, 4-bromo-tert-butylbenzene also had the largest relaxation time amongst the three molecules at 200K. The corresponding relaxation time was increased in the sequence of 1.7×10^{-5}s, 6.9×10^{-4}s and 6.8×10^{-2}s respectively, for 4-bromotoluene, 4-bromo-ethylbenzene and 4-bromo-tert-butylbenzene. All of these features bore out the characters of the molecular relaxation process for 4-bromo-tert-butylbenzene.

Furthermore, a similar sequence was found in 4-biphenyl derivatives. For 4-phenylpyridine, 4-fluoro-, 4-chloro-, 4-nitro- and 4-bromobiphenyls, the sequence of ΔH_E value is 38, 52, 80, 86 and 89 $kJmol^{-1}$ which may be explained by the molecule with a larger halogen atom encountering a greater resistance from the surrounding polystyrene segments than the one with a smaller atom. It seemed likely that there would be a linear dependence for a given series of molecules when the shape is very similar, and the inclination of the molecular dipole to the principal axes is the same. A plot of ΔH_E against ΔS_E obtained from the present study and literature data of polystyrene is shown in Fig.III-3. It appeared that a linear equation was found mathematically in these molecules:

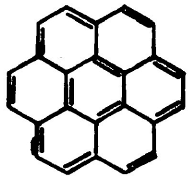
$$\Delta S_E(JK^{-1}mol^{-1}) = -65.8 + 2.07\ \Delta H_E(kJmol^{-1}) \qquad (III-1)$$

It was considered by Cooke$^{(7)}$ that the barrier which led a rigid molecule to reorient in solution might be attributed to the resistance produced by the neighbouring molecules of its environment. In order to reorient, the dipolar molecule displaced the molecules surrounding it and worked against the attractive forces of the liquid in passing from an equilibrium position of orientation to the activated state. The activation state was regarded as a condition which involved a volume expansion within the liquid due to the displacement of neighbours by the orienting molecule. In the study of a number of rigid polar molecules in solutions of n-hexane, benzene, carbon tetrachloride and p-xylene, Cooke found that the activation volume, i.e. the volume swept out in going from the initial to the activation state, and the activation energy were dependent on the size of the "cavity or hole" which was determined by the geometry of the molecule.

It is desirable to know how the swept volumes influence the energy barriers. But first of all, it is important to examine how a molecule reorients in the dielectric absorption studies. The principle of a molecule rotating through the center of mass would seem to explain certain dielectric phenomena. Mountain(11) suggested that it would appear necessary to consider both the volume and the center of mass of a molecule when a qualitative comparison of molecular relaxation times was made. Fyfe et al.(12,13) have investigated two symmetric molecules, pyrene and coronene, in the solid state by nmr studies.



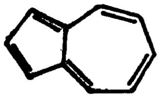
Pyrene



Coronene

Broad-line nuclear magnetic resonance and spin-lattice relaxation time measurement on solid coronene indicated the presence of a molecular reorientation process at 160K. The activation energy for the process has been determined around 25 kJ mol^{-1}, and the nature of the motion deduced as being reorientated in the plane of the molecule. For crystalline pyrene, the measurements revealed a transition over the temperature range 225-285K which was attributed to the reorientation of pyrene molecules about the axis perpendicular to the molecular plane. The activation energy for the molecular motion is around 57 $kJmol^{-1}$. In the example of coronene, which is a disk-like molecule, it is apparent that the swept-out volume for both a barrel-like motion and an end-to-end tumbling process would be much larger than that of the in-plane rotation. Owing to its symmetry, coronene approximately rotated in its own space around the Z-axis which is perpendicular to the plane of the molecule. This seemed quite reasonable for such a big molecule which had a relatively low activation barrier of 25 $kJmol^{-1}$ to rotation.

However, the symmetry of a molecule may be destroyed with substituted groups and the rotation point shifted as the mass center alters. In the investigation of how the swept volumes influenced the energy barrier on asymmetric molecules, Mazid(16) indicated that for solutes in a polystyrene matrix, the activation energy increased with the mean rotational volume and that the dipole rotated most probably around the center of mass. In the study of azulene,



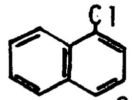
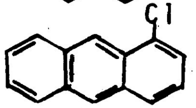
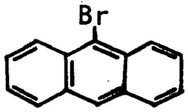
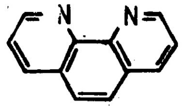
Azulene

Fyfe and Kupferschmidt(14) also found that the rotation of the molecule passes through the center of gravity of the molecule.

From this view, the swept volumes are calculated for dipole reorientations through the mass center by the use of either the dimensions from Courtauld molecular models or from scale drawings constructed from known bond lengths and van der Waals radii.(15) The volumes were assumed to be composed of two half-cylinders and their rotation was arbitrarily considered through 180° about the two axes perpendicular to the molecular dipole. The rotational volumes about the X, Y, and Z axes are designated V_x, V_y, and V_z respectively. The mean volumes are obtained by the arithmetic mean. e.g. $V_{mean} = (V_y + V_z)/2$. It has been found that within the limits of error, there is a linear relationship between the mean swept volume around the center of mass and the activation energies of mono-substituted benzenes(16). An analogous correlation also exists for 4-substituted biphenyls. Biphenyl derivatives are considered to be non-coplanar. At different dihedral angles, for each molecule, the volumes around each particular axis differ while the deviation among their mean volumes is small. A list of the swept out volumes and the relaxation times of 4-substituted biphenyls with various dihedral angles is given in Table III-4. It is notable that the relaxation time is likewise increased as the size of substituent increases. For example, the reorientation time of 4-bromobiphenyl at 300K, 4.1×10^{-4}s is much longer than that of 4-fluorobiphenyl, 3.5×10^{-6}s.

Crossley(19) suggested that sometimes the mean relaxation time is more related to the length of the molecule than to its volume when different directions of the dipole rotations were considered. From the analyses that follow, it can be seen that agreement was found with this concept.

The molecules belonging to the second group have their dipole perpendicular to the long axis of the molecule. They are:

No.	Name	Structure
7.	1-chloronaphthalene	
8.	1-chloroanthracene	
9.	9-bromoanthracene	
10.	1,10-phenanthroline	

The Eyring analyses collected in Table III-2 are 1-halonaphthalenes and haloanthracenes. It appeared that the changes of activation parameters were smaller than those in the first group when there was an increase in the molecular size. Nevertheless, an analogous linear relationship between activation enthalpy (ΔH_E) and entropy (ΔS_E) was found and is shown in Fig. III-4. Grubb and Smyth(17) reported the relaxation times for 1-chloronaphthalene and 1-bromonaphthalene in dilute solution of nujol and considered the relations between solvent viscosity and relaxation time, namely that "the liquid structure of nujol contains holes which make possible solute molecule rotation with much greater ease than would be expected from the resistance to flow evidenced by the high viscosity". In a polystyrene matrix, Tay and Walker(18) found only a small increase in activation enthalpy of the 1-halonaphthalenes when there is a definite increase in molecular size and volume as shown in Table III-2. They assumed that the slight changes in ΔH_E values from 18 $kJmol^{-1}$ to 22 $kJmol^{-1}$ for corresponding molecules from 1-chloro- and 1-iodonaphthalene are due to the hole inside the polystyrene medium which is adequate for the solute molecule to sweep out a cylindrical barrel-like volume. They suggested that for halo-substituted naphthalene molecules, the axes, about which molecular rotation is possible, pass through the mass center of the molecule as well. Rotational volumes and relaxation times about some 1-halonapthalenes and anthracenes are listed on Table III-5. The increase in the relaxation time with increasing molecular size is more apparent than that of activation energy. At 200K, the corresponding relaxation times for 1-chloro-, 1-bromo- and 1-iodonaphthalenes are 5.2×10^{-9}, 1.4×10^{-8} and 2.1×10^{-7}s, respectively.

Another two molecules involved with the same inclination of the main dipole to the main principal axis are 9-bromoanthracene and 1-chloroanthracene where the former is larger in size. With respect to their size, it might be expected that the activation energy would be larger for the former. However, the activation energy and entropy for 9-bromoanthracene are 35 $kJmol^{-1}$ and 20 $JK^{-1}mol^{-1}$, while those for 1-chloroanthracene are 55 $kJmol^{-1}$ and 42 $JK^{-1}mol^{-1}$respectively. A remarkable freedom of reorientation is observed for the spherical-like molecule, camphor, with quite a small activation energy 4 $kJmol^{-1}$ by Davies et.al.$^{(5)}$ Similarly, coronene, which was mentioned previously, is a symmetric disc-like molecule. It required 25 $kJmol^{-1}$ activation energy for such a big molecule to reorient in the plane of the molecule in the solid state. In the cases of camphor and coronene, the more symmetric the molecule shape is, the less the energy barrier may be. It is interesting to note that the center of mass in 9-bromoanthracene is found much closer to the center of the whole molecule than that in 1-chloroanthracene. Table III-5 shows that the swept out volumes for these two molecules are similar in both barrel and in-plane motions. Since rotation occurs through the center of mass, it is likely the preferred motion for 9-bromoanthracene is as a disc-like molecule in its own space, while 1-chloroanthracene may be treated as composed of two half-cylinders which rotate through 180°, in their in-plane motion as shown in Fig. III-5.

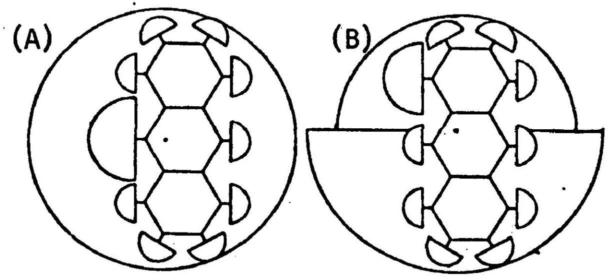


FIG. III-5: The Volumes Swept Out in In-plane Motion for (A) 9-Bromoanthracene & (B) 1-Chloroanthracene

The absorption process of 9-bromoanthracene may be attributed to the reorientation in the plane of the molecule which would have the minimum energy requirement for molecular rotation, while the volume for the tumbling motion of 1-chloroanthracene would be larger. Therefore, it would seem feasible that the activation energy and entropy would be lower in 9-bromoanthracene than in 1-chloroanthracene due to the disturbance of surrounding molecules. Moreover, a similar result was found for the relaxation time. The value of τ_{200K} of 9-bromoanthracene was 3.7 X 10^{-5}s as compared to the value of 4.7 X 10^{-1}s of 1-chloroanthracene which was strikingly longer than the former one.

In the investigation of dibenzothiophene and dibenzothiophene sulfone, Desando(20) found that in the same temperature range, 200-230K, the enthalpies of activation were very similar and were 39 kJmol^{-1} amd 40 kJmol^{-1} respectively, which was comparable to the value of 9-bromoanthracene. When the size, shape and dipole location of the molecules are considered, these are significantly different from 4-phenylpyridine and 4-fluorobiphenyl. Despite the small volumes of 4-phenyl pyridine and 4-fluorobiphenyl, larger energy barriers are found for their elongated shape and main dipole position. As mentioned in the first group, the corresponding values of ΔH_E are 38 $kJmol^{-1}$ and 52 $kJmol^{-1}$ respectively. This led to the view that the activation parameters and the relaxation time are much dependent on the inclination of the molecular dipole. In the study of dibenzothiophene and dibenzothiophene sulfone, one may assume that owing to the small size of the oxygen atom, the swept-out volumes of both molecules may not indicate much difference. It is also notable that with the other parameters such as the entropy of activation, the free energy of activation and relaxation times for them are very similar. The corresponding values are $\sim$22 $JK^{-1}mol^{-1}$ for ΔS_E, $\sim$34 $kJmol^{-1}$ for ΔG_{200K} and $\sim 2.5 \times 10^{-4}s$ for τ_{200K} respectively.

1,10-phenanthroline was chosen as another molecule to be investigated in the group. In the temperature range, 212-243K, one set of absorption peaks was found for 1,10-phenanthroline with the activation enthalpy of 49 $kJmol^{-1}$ and entropy of 53 $JK^{-1}mol^{-1}$ which were quite reliable for such a molecule. At 200K, the values obtained from the activation free energy and relaxation time were found to be 38.7 $kJmol^{-1}$ and $3 \times 10^{-3}s$ as expected.

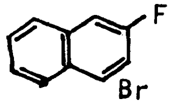
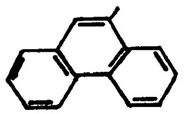
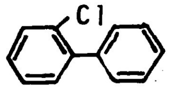
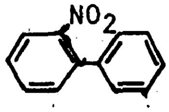
The linear relationship between ΔH_E and ΔS_E obtained for the second group molecules is:

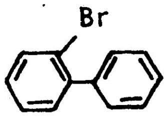
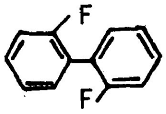
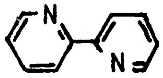
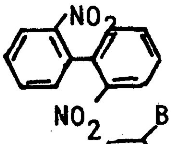
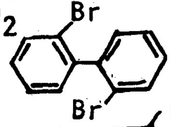
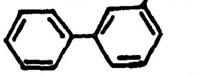
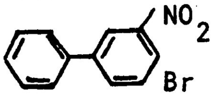
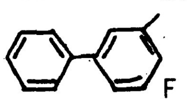
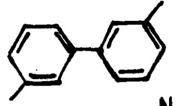
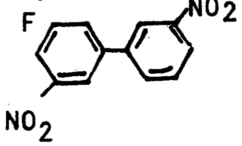
$$\Delta S_E(\mathrm{J\,K^{-1}mol^{-1}}) = -34.2 + 1.51\ \Delta H_E(\mathrm{kJmol^{-1}}) \qquad \text{(III-2)}$$

The characteristic feature for this group of molecules is that when a molecule rotates as a disc or a sphere from one equilibrium position of orientation to another, it involves a change of position which is comparatively smaller than in the first group mentioned before.

It seems worthwhile to employ a more extensive study on the relationship of the inclination of the dipole to the principal axes with the relaxation and activation parameters.

In the third group, the molecules have the dipole lying between the principal axes in the plane of the molecule. They are:

No.	Name	Structure
11	2-Fluoronaphthalene	
12	9-Bromophenanthrene	
13	2-Chlorobiphenyl	
14	2-Nitrobiphenyl	

No.	Name	Structure
15	2-Bromobiphenyl	
16	2,2'-Difluorobiphenyl	
17	2,2'-Bipyridine	
18	2,2'-Dinitrobiphenyl	
19	2,2'-Dibromobiphenyl	
20	3-Chlorobiphenyl	
21	3-Nitrobiphenyl	
22	3-Bromobiphenyl	
23	3,3'-Difluorobiphenyl	
24	3,3'-Dinitrobiphenyl	

In the cases of rigid molecules belonging to this group, the molecule itself would possibly rotate about all three principal axes. However, for non-rigid molecules, it is expected that two orthogonal dipole components may relax independently, such that the dipole component along the bond which is parallel to the molecule requires the whole molecule to turn over, while the perpendicular one will relax at a rate given by intramolecular rotation. Then, it is highly desirable to identify the enthalpies of activation obtained from a molecule which exhibits both molecular and intramolecular absorptions in a matrix. Since in the polystyrene matrices, the dipole of the solute molecule is part of a non-rigid molecular structure, Davies and Edwards(15) found that strikingly different mechanisms can contribute to the dipole relaxation. One of the aims of this study was to explore the use of such media to reduce the freedom of the whole-molecule reorientation, that is lengthen the molecular relaxation time, whilst providing sufficient free volumes for the intramolecular motion. Before extensive intramolecular studies of solute molecules are made, it is desirable to have a wider background knowledge of the molecular process for rigid and non-rigid molecules in this group.

The Eyring analysis data for this group are collected in Table III-3. 2-Halonaphthalenes, with only the molecular process involved, are chosen for the investigation. Tay and Walker(18) pointed out that the effect of decreasing the angle of inclination (θ) of the resultant molecular dipole to the longest axis (i.e. X-axis) leads to an increase in the ΔH_E value. This was observed for 1-bromo-(θ:90°) with ΔH_E:17.6 $kJmol^{-1}$, 2-bromo- (θ:30°) with ΔH_E:34.7 kJmol^{-1} and 2,3-dibromonaphthalene (θ:0°) with ΔH_E:38.5 kJmol^{-1}. It is noteworthy here that the activation energy changes with the inclination of dipole location. Since 2-halonaphthalenes are more elongated than 1-halonaphthalenes, the rotation energy for 2-halonaphthalenes may be expected to be nearer in magnitude to that of the molecules having their dipole on the long axis. A significant increase in the enthalpy, ΔH_E, in the sequence from 2-fluoro (ΔH_E:21.4 kJmol^{-1}) to 2-iodonaphthalene (ΔH_E:40.6 kJmol^{-1}) is obtained. A similar relation between the swept out volume and relaxation time is also shown in Table III-6.

As comparable with 2-halonaphthalenes, 9-bromophenanthrene, a disc-like molecule, is given further attention here. A quite small volume of activation enthalpy 31.0 kJmol^{-1} was reported by McLellan$^{(21)}$ for 9-bromophenanthrene. It is apparent that the rotational volume for this molecule through the center of mass is much smaller for in-plane motion than around the other principal axes. It seemed that 9-bromophenanthrene had a major contribution to its relaxation by rotation about the Z-axis which is perpendicular to the plane of the molecule, such that, with a low energy barrier and zero entropy of activation, it may rotate almost as freely as 9-bromoanthracene. Meanwhile, its short relaxation time τ_{200K} of 3.3 X 10^{-5}s is also in the same order as that for 9-bromoanthracene.

According to the data of rigid molecules, some substituted biphenyls were chosen for further observations. In these non-rigid biphenyl derivatives, an overlapping process was found in each of these compounds. When the Eyring graph is plotted, two intersecting lines are required to fit the experimental data. Some typical Eyring plots of log τT against $1/T$ are shown in Fig. III-6 to III-9 for 3 -bromobiphenyl, 2,2'-difluorobiphenyl, 2,2'-dibromobiphenyl and 2-nitrobiphenyl. The data provided in Table III-3 for the Eyring parameters in ortho- and meta- substituted biphenyls indicated that remarkable features of molecular relaxation were revealed in the high temperature regions. Furthermore, when biphenyls are combined with rigid molecules, a linear correlation still existed between ΔH_E and ΔS_E and the relationship plot is shown in Fig. III-10.

The increase in the enthalpy of activation from 49 kJmol^{-1} for 2-chlorobiphenyl to 57 kJmol^{-1} for 2-bromobiphenyl appears to be in accord with the increasing size of the molecules. This is also the case from 44 kJmol^{-1} for 3-chlorobiphenyl to 67 kJmol^{-1} for 3-bromobiphenyl. The variation of activation enthalpies among those more spherically shaped 2-substituted biphenyls, 8 kJ mol^{-1}, is less than for 3-substituted biphenyls, 23 $kJmol^{-1}$. Further, the relaxation times for 3-substituted biphenyls are approximately 10 - 10^2 times longer than those for 2-substituted biphenyls. For example, 2-chlorobiphenyl and 3-chlorobiphenyl have τ_{300K} values of 8.1×10^{-8} and 1.1×10^{-6}s respectively in the absorption temperature 210-280K. Therefore, it may reasonably be said that the larger activation energy barriers and the longer relaxation time for 3-substituted biphenyls may be attributed to the larger volumes swept out by rotating the molecules.

The study was extended to disubstituted biphenyls. In the case of 2,2'-dibromobiphenyl, the activation enthalpies obtained for the high and low temperature absorption regions were 43 $kJmol^{-1}$ and 22 $kJmol^{-1}$ respectively. In the low temperature region, the value of 22 kJ mol^{-1} was relatively small even in comparison with a small rigid molecule, such as 35 $kJmol^{-1}$ of 2-bromonaphthalene. It seemed too small for the whole molecule to rotate with such a low energy. On the other hand, the high temperature absorption process was more reasonable to be considered as the molecular process for 2,2'-dibromobiphenyl. Similar results have been obtained for the other 2,2'-disubstituted and 3,3'-disubstituted biphenyls in their high temperature processes. The difference of activation energy between 2,2'-difluoro- to 2,2'-dibromobiphenyl was only 5 kJmol^{-1} which showed an insignificant effect upon the molecular size. This is possibly because the shape of this series of molecules is symmetric and somewhat spherical, and hence the swept out volume does not differ appreciably. Likewise, owing to the small fluorine atoms, there is only a slight difference between the volume of 2,2'-difluorobiphenyl and 3,3'-difluorobiphenyl. Hence, a similar value of activation energy ∿36 kJmol^{-1} was yielded for both molecules. As a large substituted nitro group was displaced, the length of the molecule would increase; therefore, 3,3'-dinitrobiphenyl was expected to employ a higher energy 56 kJmol^{-1} in the high temperature absorption region.

For all these biphenyl derivatives, free energy of activation and relaxation time values seem somewhat anomalous for a molecular process. In general, the variations among 2-substituted, 2,2'-disubstituted and 3,3'-disubstituted biphenyls are smaller than that of 3-substituted biphenyls. The relaxation times at 300K for those molecules are in the range 10^{-7} to 10^{-8}s while for 3-substituted biphenyls in the order of 10^{-6}s. The maximum difference of ΔG_{300K} is around 12.5 $kJmol^{-1}$ between the smallest 2,2'-difluorobiphenyl and the large molecule, 3-nitrobiphenyl. It seems that the apparent lack of consistency in the free energies and the relaxation times may be best attributed to the overlapping effects between a molecular and intramolecular process.

A dependence on the ΔH_E and the dihedral angle (ϕ) was reported for the molecular process by investigation of 9-fluorenone and benzophenone in o-terphenyl solution(22) and a series of other compounds in polystyrene.(20) In general, the ΔH_E value increases as the dihedral angle increases. For example, in a comparison of the size of 9-fluorenone and benzophenone, the former is larger and planar, and the activation energy obtained was 19.3 $kJmol^{-1}$ which was much smaller than that of the latter 35.8 $kJmol^{-1}$, a non-planar molecule. In the study of biphenyl derivatives, the dihedral angle is defined as the angle between the planes of the two inter-rings of biphenyls and it is assumed to be zero at the cis-state. The magnitude of the dihedral angle has been estimated from the electron-diffraction,(23) H^1 and ^{19}F nmr chemical shifts(24,25) and the photoelectron spectroscopy methods.(26) Both electronic and steric effects are mentioned by Maier and Turner. Table III-8 lists the inter-plane angle of biphenyl derivatives. For these biphenyls, when the steric hindrance is ignored, it is assumed that the twisting angle between the two rings approaches the value of biphenyl itself, i.e. :$45^\circ \pm 10^\circ$. If there was no steric effect, the most stable configuration could be a coplanar configuration. However, a fairly large deviation from coplanarity will not reduce greatly the stability of the molecule or destroy all of the inter-ring resonance energy. Fig. III-11(27) shows that there is considerable resonance energy of biphenyl even though the twist may be quite large. At even as large a twist angle as 45°, there is still 50% resonance energy. Therefore with some inner-plane angles, it is reasonable to believe that the coplanar arrangement should lead to a stable state.

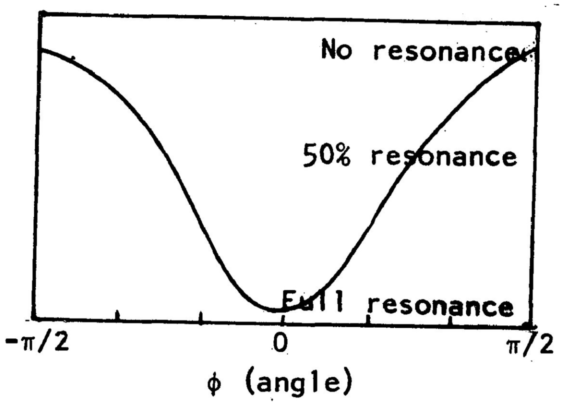


Fig. III-11: The excess resonance energy of biphenyl over two benzene rings as a function of the angle of twist between the phenyl groups.

The dihedral angle of 2-fluorobiphenyl is 49° and that of 2-bromobiphenyl is 74°. The activation energy of 57 $kJmol^{-1}$ for the molecular process of the latter would be expected to be larger than that for the former, 32 $kJmol^{-1}$. However, it is less than the energy barrier of 69 $kJmol^{-1}$ for 4-phenylpyridine, which is smaller in size and involved in somewhat cooperative motion. It seemed that the high temperature process found in 2-bromobiphenyl may be attributed chiefly to the molecular process. 2-Chlorobiphenyl has a size between 2-fluoro- and 2-bromobiphenyls and the dihedral angle, 66°, with the ΔH_E of 50 $kJmol^{-1}$ which is feasible for the molecular relaxation. In the 2,2'-disubstituted biphenyls, the dihedral angle of bromo-, 75°, is bigger than that of fluoro-, 60°, and the activation enthalpy for the molecular process would appear to increase in the same order. It is noted that in the low temperature absorption, ΔH_E increases in the order of bromo- (22 $kJmol^{-1}$), nitro- (28 $kJmol^{-1}$) then fluoro- (30 $kJmol^{-1}$), contrary to the expectation from the dihedral angle point of view. However, the expected sequence of energy is obtained in the high temperature process with fluoro- (ΔH_E: 38 $kJmol^{-1}$), nitro- (ΔH_E: 38 $kJmol^{-1}$) and bromo- (ΔH_E: 43 $kJmol^{-1}$). The slight variation of activation energy may be due to two kinds of possibilities. One may be attributed to the fact that they possess similar shapes. The other explanation is that the internal reorientation process may contribute to overlap with the molecular process and result in misleading ΔH_E values.

In the biphenyl derivatives, particularly for 2-substituted and 2,2'-disubstituted biphenyls, the change of the inter-plane angle depends on the size of substituents. Owing to the steric hindrance effect, the larger the size of the substituted group the greater the dihedral angle. Therefore, it would seem that for the molecular process, the increase in the size of the ortho-substituent of the molecule would increase the angle at which the two rings are inclined to each other, and thus should lead to an increase in the activation energy.

Another effect is the conjugative effect. This effect is rather important in interpreting the intramolecular ring-ring rotation by means of the bond character between the two phenyl rings. Monosubstituted biphenyls always have higher dipole moments than the corresponding naphthalenes for which the position of substituent is the same, but have smaller dipole moments than monosubstituted benzenes. This is inferred from configuration and conjugation effect for biphenyl derivatives due to their non-coplanarity. A dipole along one bond or grouping

has a polarizing effect upon the remainder of the molecule. Everard and Sutton(28) have discussed in detail the interactions between a substituted group and the aryl radical to which it is linked. Here, the radical is defined simply as a species having one or more unpaired electrons. The interaction between the two rings comprises:
(a) the inductive effect (I effect), arising through polarization of the radical by the electric field of the substituent, and
(b) the mesomeric effect (M effect), arising from the tendency towards the formation of a π-bond between the substituent and the carbon atom to which it is linked, and causing modifications in the character of the other bonds present in the radical.

Smith et al.(29) suggested that owing to the greater length of the conjugated system, it would be expected that the M effect in ring-substituted derivations of biphenyls would be greater than that in the corresponding derivatives of benzene. However, it is only when a conjugated hydrocarbon radical is ortho- or para- to the substituent in the primary benzene ring that the M effect of the substituent can extend through the whole of the hydrocarbon skeleton. When the substituent is on the meta- position, no such extension of the conjugation can occur, and indeed, the M effects of the substituted group and of the hydrocarbon radical will tend to act in opposition to one another. In accordance with this view, the dipole moments of 3-substituted biphenyls are actually slightly higher than those of the corresponding benzene derivatives, but are much closer to the latter than the moments of the 2- and 4-substituted compounds. This relation is seen to be obvious in Table III-7.

TABLE III-7

Comparison of Observed Dipole Moments(29) of Nitrosubstituted Compounds

Compound	Nitro-benzene	2-Nitro-biphenyl	3-Nitro-biphenyl	4-Nitro-biphenyl
μ(D)	4.01	3.70	4.12	4.36

The polarizability of the benzene nucleus in the biphenyl compounds is greater in the plane of the ring than that along the axes orthogonal to it. The induced moment in the second ring varies with the inter-plane angle. (30,32)

$$\mu_I = \{\sqrt{3}\mu_{Phx} + (\mu_y - \sqrt{3}\mu_x) \cos^2 \frac{\phi}{2}\} \cos \frac{\phi}{2}$$

where μ_{Phx} is the moment of the corresponding mono-derivative of benzene . μ_x and μ_y are the induced moments produced at the center of each ring. ϕ is the angle between the plane of the rings.

An induced moment in the second ring partially opposes the primary moment. The effect is smaller for the coplanar than for the orthogonal arrangement of the rings that leads to a small dipole moment for 2-substituted biphenyls. In 4-nitrobiphenyl, both -I and -M effects, which are directly away from the rings, operate in the same way and tend to increase the moment. The results of these two effects is increased significantly by the introduction of the second ring, therefore confirming that these effects are transmitted through the center bond linking the two aromatic rings. However, in 4-halobiphenyls, the -I effect operates in the reverse way to the +M effect, so that the former tends to increase the dipole moment while the latter tends to decrease it. The effective dipole moments obtained from the Debye equation for biphenyl derivatives are shown in Table III-8 as compared with the literature data.(29) For 4-halobiphenyls, effective **dipole** moments obtained are slightly smaller than those in the literature data. Some of the substituted biphenyls are difficult to assess since their high frequency absorption occurs on the Q-meter which does not lead to accurate values of the dipole moment.

A useful parameter is the distribution parameter for relaxation time, β. A wider distribution range was usually found for the molecular process. But, if there were overlapping processes, the value of β may be misleading. For all the β values obtained in biphenyls, it appeared that the molecular process in 4-substituted biphenyl has lower β values ($\sim$0.2) than the other overlapping processes, where the average β value is higher than 0.2. The β values are listed in the appendix.

The linear equation of ΔH_E and ΔS_E among the third group molecules is:

$$\Delta S_E(\mathrm{JK^{-1}mol^{-1}}) = -65 + 2.3\ \Delta H_E(\mathrm{kJmol^{-1}}) \qquad \text{(III-3)}$$

The equation for these groups of molecules is not so reliable as that for the first and second groups owing to the error caused by overlapping effects of biphenyl derivatives.

Conclusion

The low value of about 0.2 for the distribution parameter, β, of all the molecules studied here is similar to that observed by Davies et al.(5) and Tay et al.(18) for a molecular relaxation process. It is apparent from the solutes considered above that the inclination of the molecular dipole to the principal axes may be a factor in determining the magnitude of the observed relaxation time and the activation parameters. This agreed well with the observation by Cooke and Walker(31) for large ellipsoidal molecules and one large disk-like molecule in dilute solution.

In the comparison of the three equations III-1 to III-3 for molecular relaxation in polystyrene, the sequence of slope in the ΔS_E and ΔH_E equation is found to be 2.3 (III) > 2.07 (I) > 1.51 (II). As the dipole lies on the axis perpendicular to the long axis of the molecule, a small energy barrier is usually needed for the molecule to reorient in either barrel or in-plane rotation which would disturb only a small part of the surrounding molecules. However, if the dipole inclines between the principal axes, it would seem possible that the molecule reorientating around all three axes would employ a larger activation energy and a larger entropy than the other situations. In view of this, it is also reasonable to have the slope value for the equation (III-3) closer to the first one (III-1). In general, the main factor for a linear function is determined by the slope rather than by the intercept, consequently, the ΔS_E will be decided predominantly by ΔH_E and its slope. From what has been mentioned above, it can be noted undoubtedly how important is the dipole inclination to the molecular relaxation process.

In many cases, it is feasible to identify the relaxation time of a molecule as a whole by its dependence on the nature of the surrounding medium. For example, Dicarlo and Smyth(4) indicated that only one absorption process was observed for 2-bromobiphenyl in nujol with the activation enthalpy being 25 $kJmol^{-1}$. By changing the media from nujol to polystyrene, an overlapping process was found for the same molecule, namely, low and high temperature processes. The corresponding values of activation enthalpy were 31 and 57 $kJmol^{-1}$ respectively. This obviously suggests the capability of detecting intramolecular rotation in polystyrene. This will be discussed further in Chapter VI.

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TABLE III-1 DIELECTRIC RELAXATION AND EYRING ACTIVATION PARAMETERS FOR HALOBENZENES, HALOTOLUENES, 4-HALO-ALKYLBENZENES AND 4-SUBSTITUTED BIPHENYLS IN POLYSTYRENE MATRICES

Molecule	T(K)	τ(s)			ΔG_E(kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
		150K	200K	300K	150K	200K	300K		
Fluorobenzene*	94 - 118	9.1×10^{-9}	1.2×10^{-9}	1.4×10^{-10}	--	14.1	16.8	9	--
Chlorobenzene*	89 - 125	4.3×10^{-7}	5.7×10^{-8}	6.8×10^{-9}	--	20.5	26.5	9	-59
Bromobenzene*	101 - 130	1.1×10^{-6}	6.5×10^{-8}	3.5×10^{-9}	--	20.8	24.9	13	-41
Iodobenzene*	129 - 163	1.9×10^{-5}	5.7×10^{-7}	1.6×10^{-8}	--	24.4	28.6	16	-43
Fluorotoluene*	101 - 145	7.0×10	7.0×10^{-8}	3.7×10^{-9}	--	21.0	--	13	-41
Chlorotoluene*	163 - 196	1.6×10^{-3}	5.8×10^{-6}	1.9×10^{-8}	--	28.2	29.2	26	-9
Bromotoluene*	176 - 214	1.8×10^{-2}	1.7×10^{-5}	1.4×10^{-8}	--	30.1	28.4	33	16
Iodotoluene*	199 - 241	1.7×10^{0}	3.1×10^{-4}	5.1×10^{-8}	--	34.9	31.6	42	33
4-Bromo-ethylbenzene*	206 - 254	1.9×10^{0}	6.9×10^{-4}	2.2×10^{-7}	--	36.2	35.3	38	9

* : Data provided through the courtesy of H.A.Khwaja(10)

TABLE III-1 continued.....

Molecule	T(K)	τ(s) 150K	τ(s) 200K	τ(s) 300K	ΔG_E (kJ mol^{-1}) 150K	ΔG_E (kJ mol^{-1}) 200K	ΔG_E (kJ mol^{-1}) 300K	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
4-Fluoro-ethylbenzene	139 - 184	7.0×10^{-5}	3.8×10^{-7}	1.9×10^{-9}	23.9	23.8	23.4	25 ± 2	4 ± 14
4-Bromo-tert-butylbenzene	244 - 286	4.7×10^{3}	6.8×10^{-2}	8.9×10^{-7}	43.7	43.9	38.7	54 ± 5	51 ± 17
4-Phenylpyridine	214 - 266	8.8×10^{0}	3.5×10^{-3}	1.3×10^{-6}	38.5	38.9	39.6	38 ± 4	-7 ± 15
4-Fluorobiphenyl	254 - 298	7.7×10^{3}	1.8×10^{-1}	3.5×10^{-6}	47.0	45.4	42.2	52 ± 2	33 ± 7
4-Chlorobiphenyl	295 - 325	9.8×10^{9}	8.6×10^{2}	7.4×10^{-5}	64.6	62.4	49.8	80 ± 5	100 ± 16
4-Nitrobiphenyl	290 - 315	--	1.5×10^{4}	4.6×10^{-4}	--	64.4	53.8	86 ± 9	106 ± 29
4-Bromobiphenyl	307 - 342	1.5×10^{12}	2.7×10^{4}	4.1×10^{-4}	70.9	65.3	54.0	88 ± 4	112 ± 13

TABLE III-2 DIELECTRIC RELAXATION AND EYRING ACTIVATION PARAMETERS FOR HALONAPHTHALENE, HALOTHRACENE AND RIGID AROMATIC COMPOUNDS IN POLYSTYRENE MATRICES

Molecule	T(K)	τ(s)			ΔG_E(kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
		150K	200K	300K	150K	200K	300K		
1-Chloronaphthalene	103 - 138	4.2×10^{-7}	9.4×10^{-9}	1.9×10^{-10}	17.6	17.6	17.6	18 ± 1	-1 ± 10
1-Bromonaphthalene*	108 - 137	9.0×10^{-7}	3.0×10^{-8}	6.0×10^{-10}	19	19	21	16 ± 1	-14 ± 5
1-Iodonaphthalene*	129 - 225	3.0×10^{-5}	2.0×10^{-7}	2.0×10^{-9}	23	23	23	22 ± 2	-2 ± 12
1-Chloroanthracene	252 - 296	4.2×10^{4}	4.7×10^{-1}	4.7×10^{-6}	49.1	47.1	42.9	55 ± 5	42 ± 19
9-Bromoanthracene**	174 - 217	--	3.7×10^{-5}	2.1×10^{-8}	--	31.4	29.4	35 ± 1	20 ± 3
1,10-phenanthroline	212 - 243	7.9×10^{1}	3.0×10^{-3}	1.0×10^{-7}	41.3	38.7	33.4	49 ± 2	53 ± 7
Dibenzothiophene***	201 - 231	6.0×10^{-1}	2.0×10^{-4}	5.9×10^{-8}	39.2	34.1	31.9	39 ± 3	22 ± 15
Dibenzothiophene sulfone***	204 - 231	1.1×10^{0}	3.0×10^{-4}	7.0×10^{-8}	36.0	34.8	32.4	40 ± 3	24 ± 12

* : Data provided through the courtesy of S.P.Tay.(18) ** : C.K.McLellan.(21) *** : M.Desando.(20)

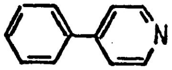
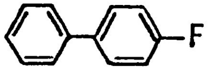
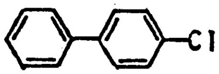
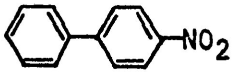
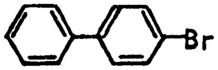
TABLE III-3 DIELECTRIC RELAXATION AND EYRING ACTIVATION PARAMETERS FOR 2-HALONAPHTHALENES, 9-BROMOPHENANTHRENE AND SOME SUBSTITUTED BIPHENYLS IN POLYSTYRENE MATRICES

Molecule	T(K)	τ(s) 150K	200K	300K	ΔG_E(kJ mol^{-1}) 150K	200K	300K	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
2-Fluoro-naphthalene	138 - 173	9.5×10^{-5}	9.7×10^{-7}	8.8×10^{-9}	24.3	25.3	27.2	21 ± 1	-19 ± 5
2-Chloro-naphthalene*	198 - 243	3.0×10^{-1}	1.6×10^{-4}	1.0×10^{-7}	34	34	34	35 ± 2	4 ± 11
2-Bromo-naphthalene*	198 - 243	3.0×10^{0}	5.0×10^{-4}	6.0×10^{-8}	37	36	32	43 ± 1	35 ± 5
2-Iodi-naphthalene*	238 - 294	6.0×10^{3}	1.0×10^{-1}	2.0×10^{-6}	47	45	41	52 ± 5	38 ± 21
9-Bromo-phenanthrene**	170 - 210	--	3.3×10^{-5}	--	--	31.1	--	31 ± 2	0 ± 8
2-Chlorobiphenyl	213 - 260	5.5×10^{1}	2.2×10^{-3}	8.1×10^{-8}	40.9	38.2	32.8	49 ± 4	54 ± 15
2-Nitrobiphenyl	233 - 272	2.7×10^{2}	9.2×10^{-3}	2.8×10^{-7}	42.9	40.5	35.8	50 ± 5	47 ± 18
2-Bromobiphenyl	248 - 313	4.6×10^{3}	3.6×10^{-2}	2.5×10^{-7}	46.4	42.8	35.6	57 ± 4	72 ± 14

TABLE III-3 continued.....

Molecule	T(K)	τ(s) 150K	τ(s) 200K	τ(s) 300K	ΔG_E(kJ mol^{-1}) 150K	ΔG_E(kJ mol^{-1}) 200K	ΔG_E(kJ mol^{-1}) 300K	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1}mol^{-1})
2,2'-Difluoro-biphenyl	230 - 274	1.7×10^{-1}	7.2×10^{-5}	2.6×10^{-8}	33.7	32.4	29.9	38 ± 3	25 ± 14
2,2'-Dinitro-biphenyl	212 - 247	8.8×10^{-1}	3.4×10^{-4}	1.2×10^{-7}	35.0	35.0	33.7	38 ± 2	14 ± 9
2,2'-Dibromo-biphenyl	215 - 293	2.5×10^{0}	3.7×10^{-4}	4.8×10^{-8}	37.0	35.2	31.5	43 ± 3	37 ± 13
3-Chlorobiphenyl	225 - 280	9.1×10^{1}	1.1×10^{-2}	1.1×10^{-6}	41.5	40.8	39.3	44 ± 4	15 ± 14
3-Nitrobiphenyl	256 - 301	7.7×10^{4}	5.9×10^{-1}	4.0×10^{-6}	49.9	47.5	42.5	57 ± 1	49 ± 4
3-Bromobiphenyl	261 - 323	1.6×10^{6}	1.7×10^{0}	1.6×10^{-6}	53.7	49.2	40.3	67 ± 4	90 ± 12
3,3'-Difluoro-biphenyl	175 - 265	2.7×10^{-2}	1.5×10^{-5}	7.2×10^{-9}	31.4	29.8	26.7	36 ± 1	31 ± 3
3,3'-Dinitro-biphenyl	259 - 311	7.2×10^{2}	7.8×10^{-3}	7.5×10^{-8}	44.1	40.2	32.6	56 ± 8	77 ± 27

TABLE III-4 THE SWEPT OUT VOLUMES (A^3 per molecule) AND THE MEAN RELAXATION TIMES OF SOME RIGID BIPHENYL DERIVATIVES WITH VARIOUS DIHEDRAL ANGLES (ϕ)

Molecular Structure	$\phi(0^{\circ})$			$\phi(90^{\circ})$			ϕ*			(s)
	V_Y	V_Z	V_{mean}	V_Y	V_Z	V_{mean}	V_Y	V_Z	V_{mean}	τ_{300K}
	618	335	477	472	481	477	524	$(\sim 45^{\circ})$ 387	456	1.3×10^{-6}
	690	375	532	523	540	532	577	(46°) 440	509	3.5×10^{-6}
	794	441	618	605	641	623	624	(53°) 553	589	6.7×10^{-5}
	783	425	604	567	641	604	650	$(\sim 45^{\circ})$ 503	577	4.6×10^{-4}
	861	503	682	640	765	703	657	(55°) 662	659	4.2×10^{-4}

* Data obtained from ref.(25).

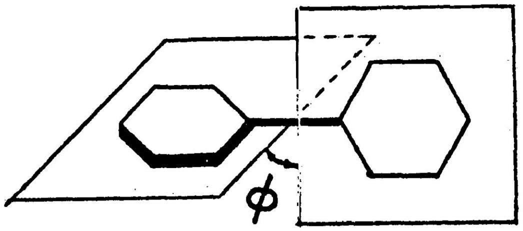


TABLE III-5 THE SWEPT OUT VOLUMES ($Å^3$ per molecule) AND THE MEAN RELAXATION TIMES OF SOME 1-HALONAPHTHALENES AND ANTHRACENES

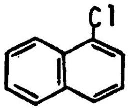
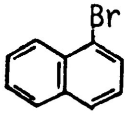
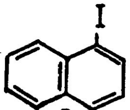
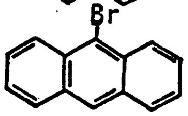
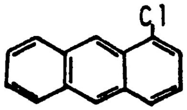
Molecular Structure	V_X	V_Y	V_Z	(s) τ_{200K}
	415	--	232	9.4×10^{-9}
	465	--	282	3.0×10^{-8}
	515	--	332	2.0×10^{-7}
	661	--	419	3.7×10^{-5}
	608	--	413	4.7×10^{-1}

TABLE III-6 THE SWEPT OUT VOLUMES (Å^3 per molecule) AND THE MEAN RELAXATION TIMES OF 2-HALONAPHTHALENES AND 9-BROMOPHENANTHRENE

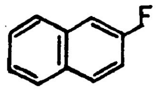
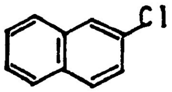
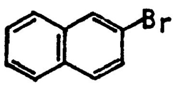
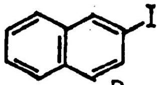
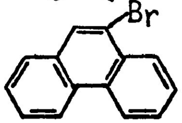
Molecular Structure	V_X	V_Y	V_Z	(s) τ_{200K}
	349	481	266	9.7×10^{-7}
	382	548	315	1.6×10^{-4}
	398	598	365	5.0×10^{-4}
	448	664	398	1.0×10^{-2}
	796	758	406	3.3×10^{-5}

TABLE III-8 COMPARISON OF THE EFFECTIVE DIPOLE MOMENTS OBTAINED WITH THE LITERATURE DATA FOR SOME NON-PLANAR BIPHENYL DERIVATIVES IN POLYSTYRENE MATRICES

Compound	ϕ*	μ(D) (lit.)	μ(D) (obs.)
4-Fluorobiphenyl	46°	1.49	1.05
4-Chlorobiphenyl	53°	1.66	1.39
4-Nitrobiphenyl	-	4.36	3.18
4-Bromobiphenyl	55°	1.66	1.28
3-Chlorobiphenyl	-	1.65	1.36
3-Nitrobiphenyl		4.12	2.61
3-Bromobiphenyl	-	1.64	1.47
2-Chlorobiphenyl	66°	1.42	1.14
2-Nitrobiphenyl	-	3.70	1.98
2-Bromobiphenyl	74°	1.50	1.29
4-Phenylpyridine	-	2.65	2.25

* The dihedral angle (ϕ) is assumed to be zero at the cis-state.

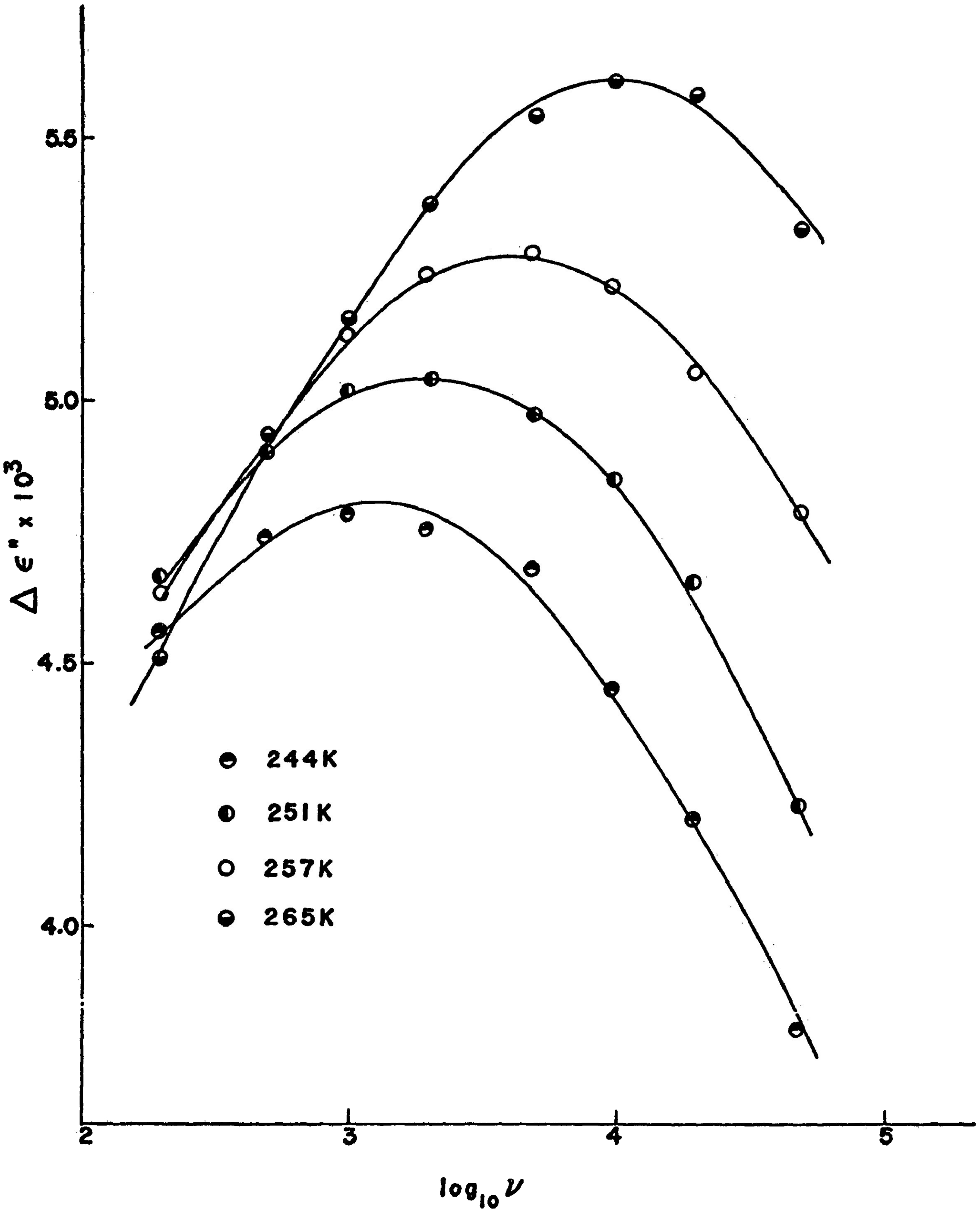


FIG.III-1: Dielectric Loss Factor $\Delta\varepsilon'' = \varepsilon''_{(matrix)} - \varepsilon''_{(polystyrene)}$ vs. logν for 0.35M 4-Bromo-tert-butylbenzene in a Polystyrene Matrix.

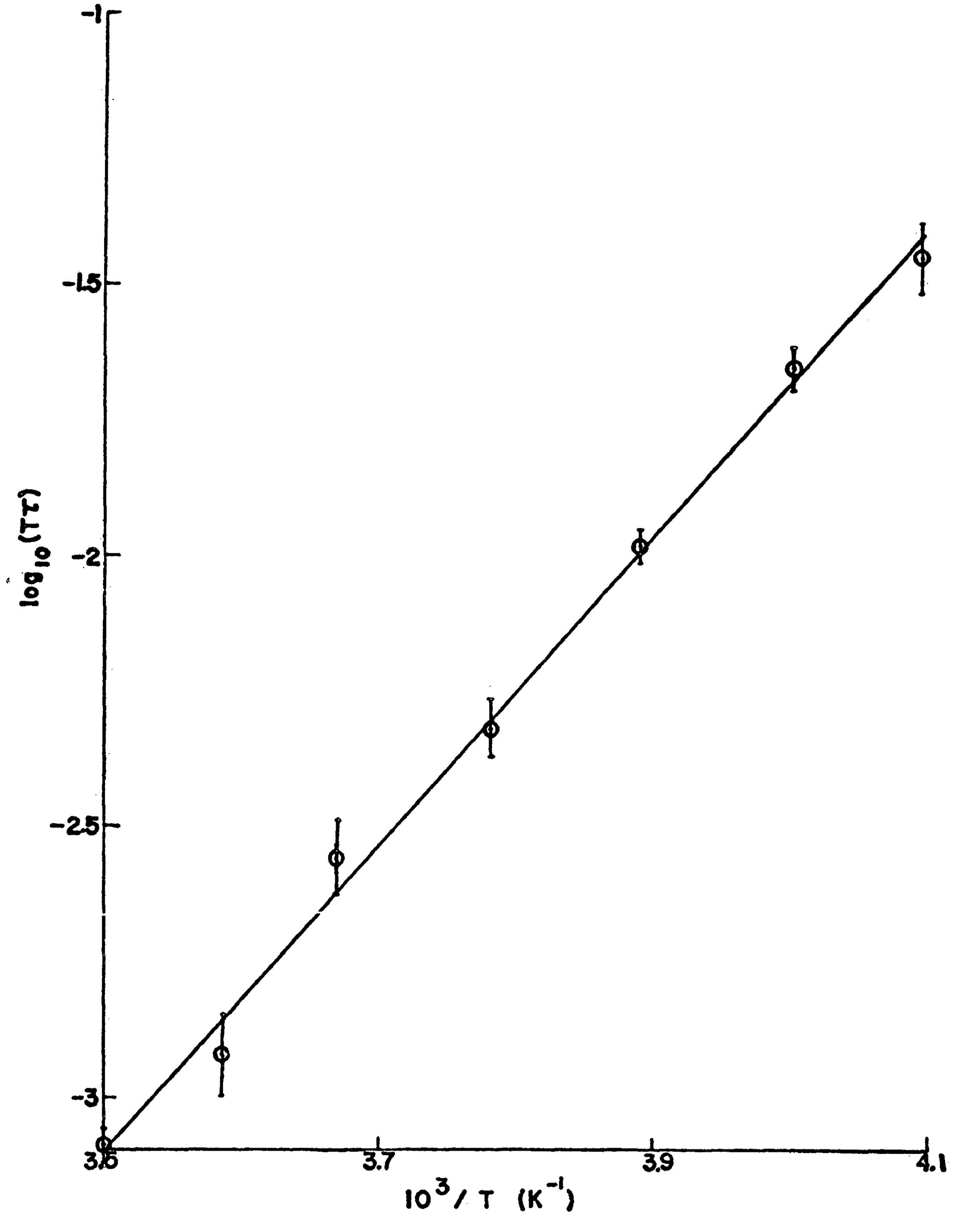


FIG. III-2: Eyring Plot of log(τT) vs. 1/T for 0.35M 4-Bromo-tert-butylbenzene in a Polystyrene Matrix. The Vertical Bars Represent 95% Confidence Intervals on log(τT) Values.

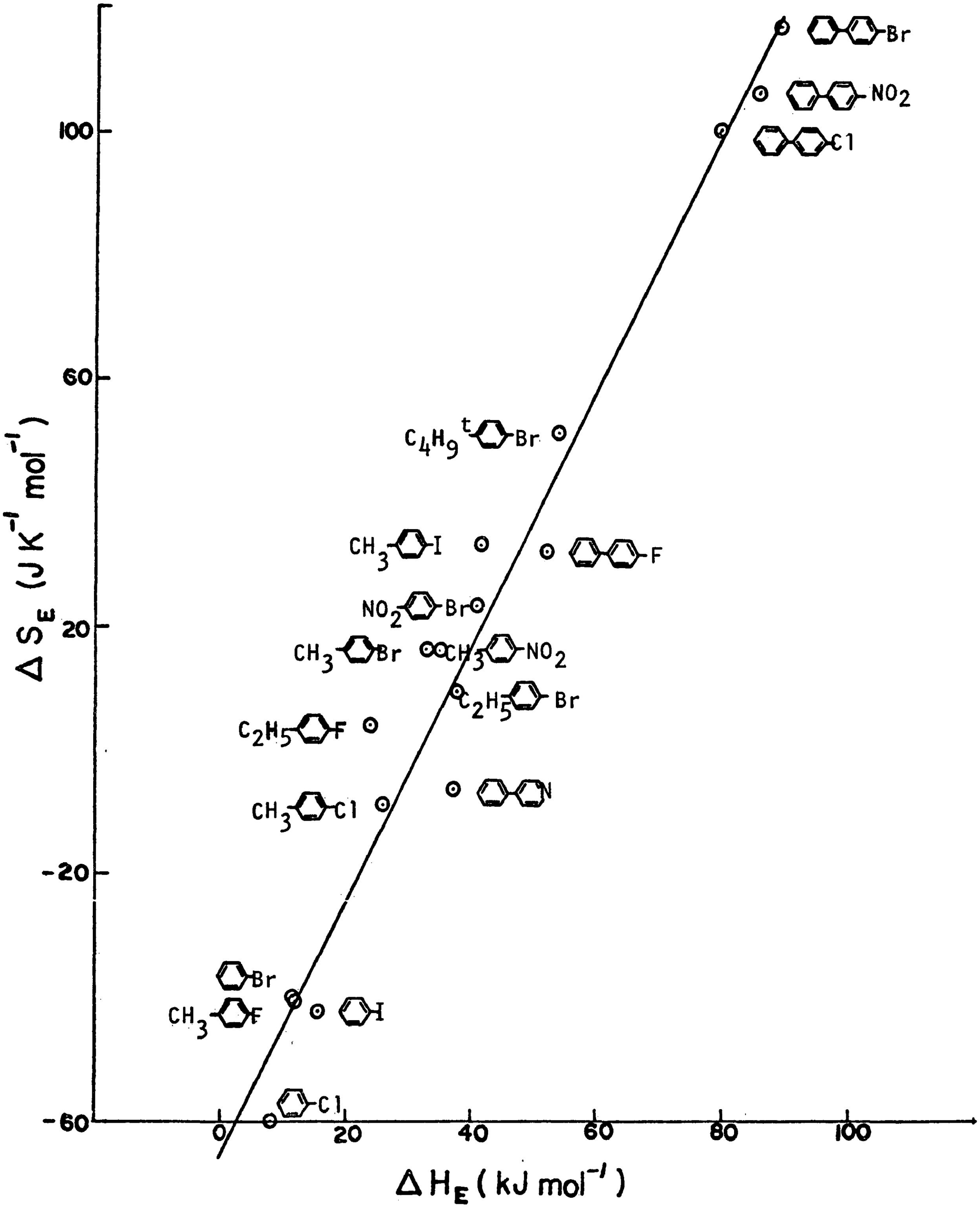


FIG. III-3: Plot of ΔH_E vs. ΔS_E for Some Rigid Molecules with Dipole Lying on the Long Axis of the Molecules.

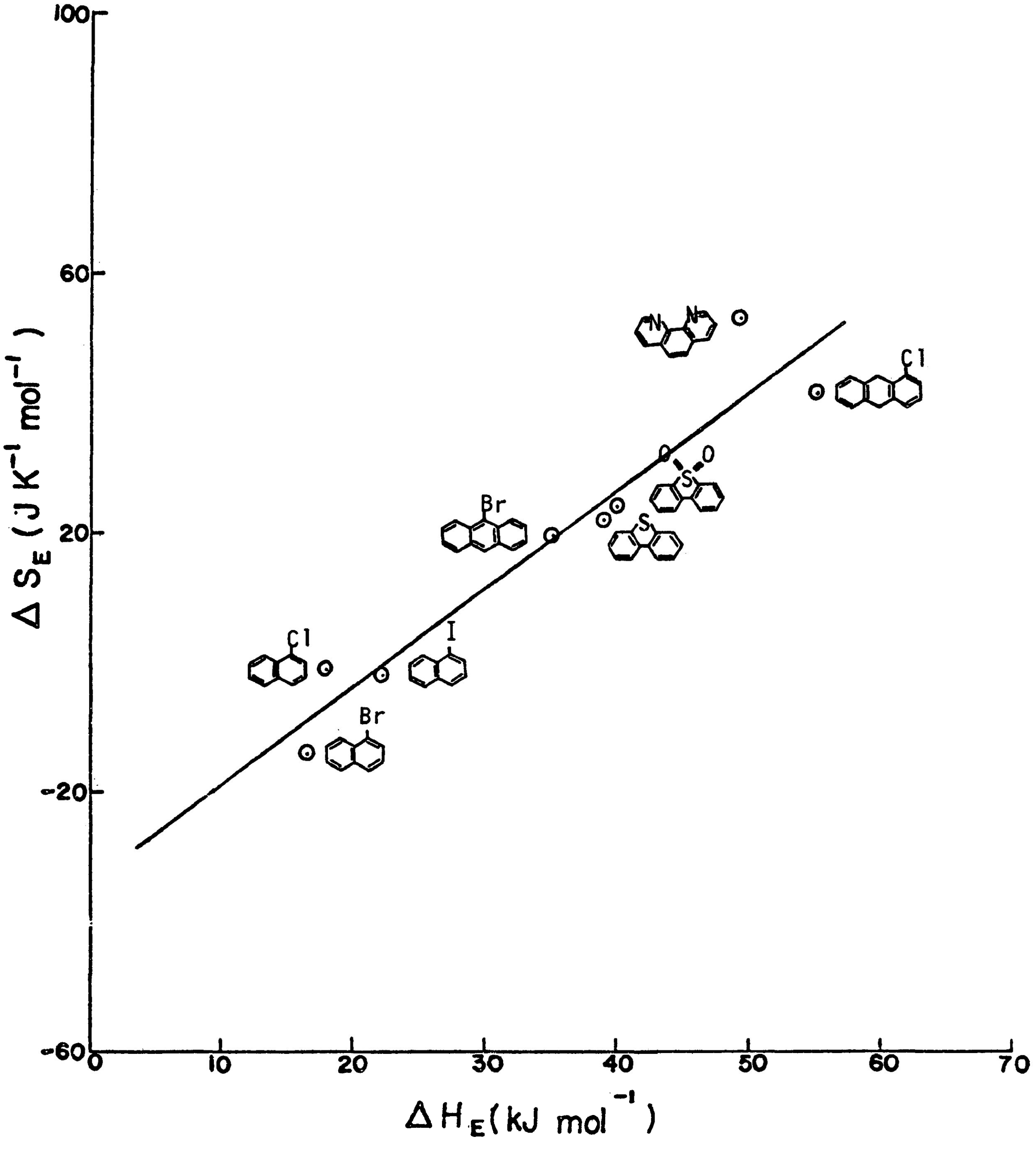


FIG. III-4: Plot of ΔH_E vs. ΔS_E of Some Rigid Molecules with Dipole Along or Parallel to the Short Axis of the Molecules.

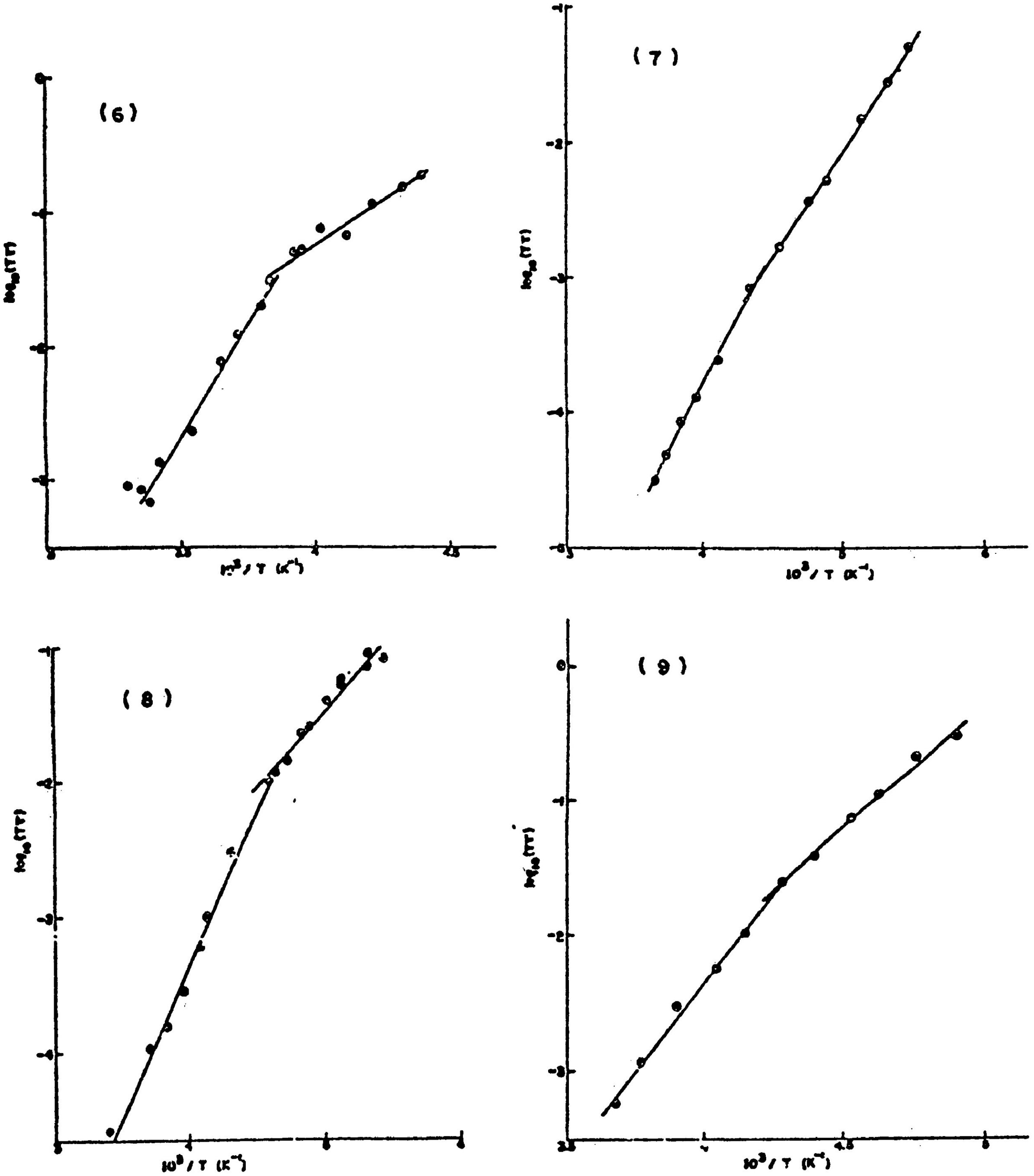


FIG. III-6 to III-9: Eyring Plots of log(τT) vs. 1/T for 0.32M 3-Bromobiphenyl$^{(6)}$, 0.28M 2,2'-Difluorobiphenyl$^{(7)}$, 0.25M 2,2'-Dibromobiphenyl$^{(8)}$, and 0.37M 2-Nitrobiphenyl$^{(9)}$ in a Polystyrene Matrix.

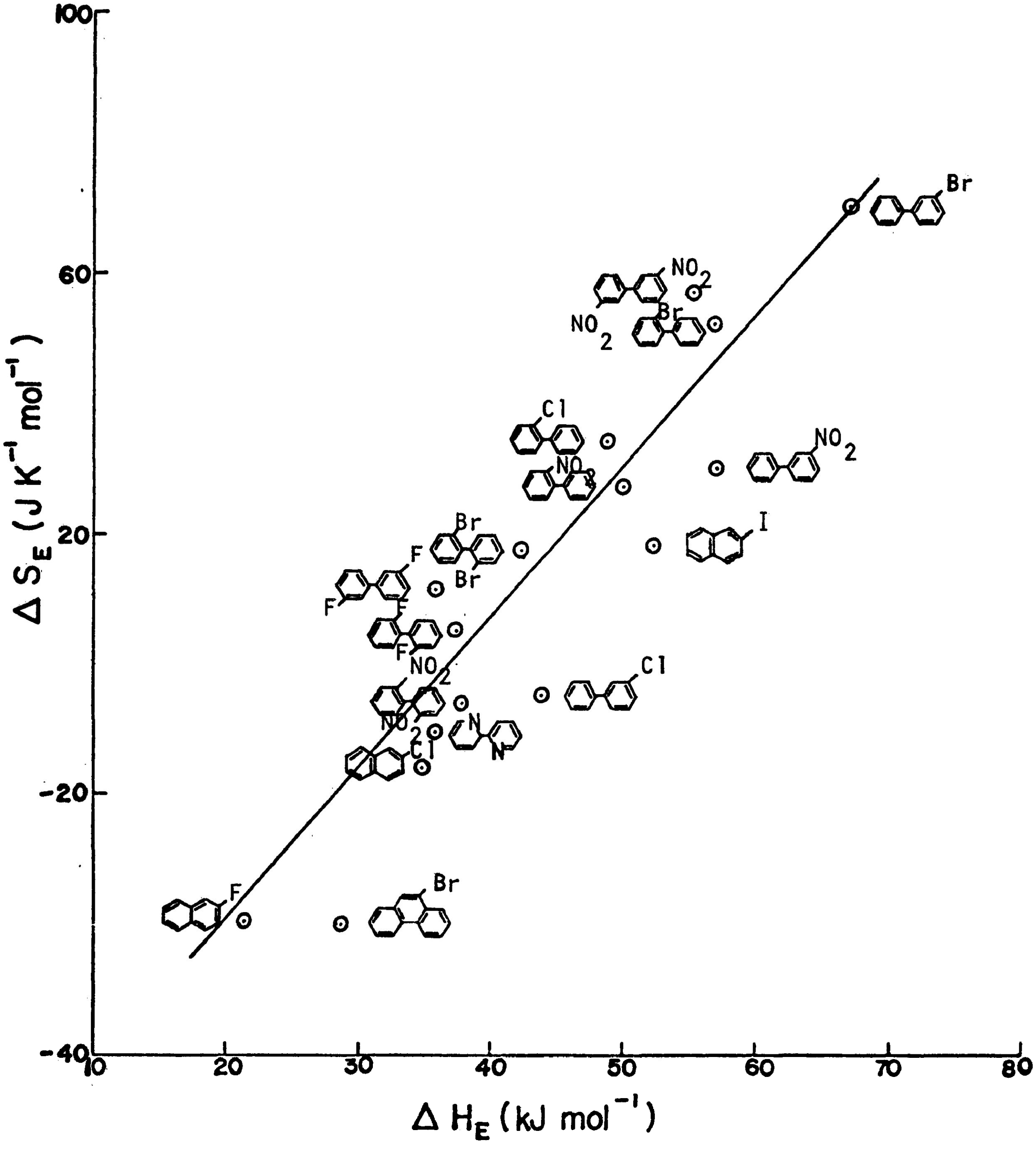


FIG. III-10: Plot of ΔH_E vs. ΔS_E for Some Molecules with the Dipole Lying Between the Principal Axes in the Plane of the Molecules.

CHAPTER IV

COOPERATIVE PROCESS IN POLYMER MATRICES

COOPERATIVE PROCESS IN POLYMER MATRICES

INTRODUCTION

It is now apparent that both amorphous solid polymers(1,2) and supercooled non-associated molecule liquids(3-6) may exhibit quite similar dielectric relaxation behaviour. Davies and Edwards(7) have studied also the low frequency dielectric relaxation of dilute solutions of anthrone and cholest-4-en-3-one in a polystyrene matrix. These studies have shown that a portion of the mean square solute dipole moment $<\mu^2>$ may be relaxed by a low frequency (co-operation) relaxation of the solute molecules, which is characterized by a large apparent activation energy and asymmetric loss curves which are far broader than a single relaxation time process. Such processes are termed co-operative.

Hains and Williams(8) studied DBP (di-n-butyl phthalate) in polystyrene and reported that at low DBP concentrations those DBP molecules which were bound in the immediate vicinity of the polymer chain, might move only in co-operation with the motions of the polymer chains as the cooperative Brownian motions. Anthrone and nitrobenzene in o-terphenyl were investigated in the supercooled liquid state,(9) and the broad asymmetric loss curves were found far removed from a single relaxation time behaviour. Baker et al.(10) reported that in studying the dipole loss of polystyrene and its derivatives, the loss peaks for all those materials exhibited an asymmetric and broad curve.

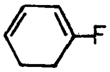
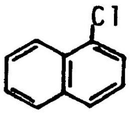
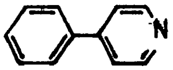
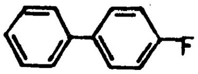
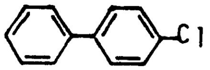
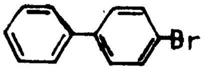
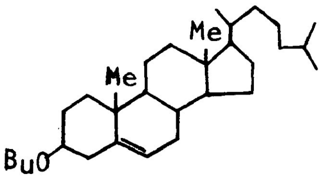
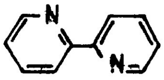
A large apparent activation energy is another feature of the cooperative process. Shears and Williams(6) found that the activation energy was around 260 kJ mol^{-1} in dielectric studies of dipolar solutes in supercooled decalin. Broens and Muller(11) indicated that α-relaxation peak of polystyrene was in the temperature range 393-418K over the frequency range 10^2-10^5 Hz, and an apparent activation energy of 330 kJ mol^{-1} was evaluated. Here, the cooperative motion to be discussed in this chapter may be similar to the α-process in polymer studies.(1,2) The present work presents a more explicit and wider investigation of dielectric relaxation at low frequency, i.e. high temperature, in both polystyrene and polyvinyl toluene matrices.

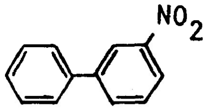
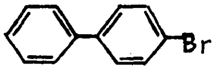
DISCUSSION

The cooperative relaxation process was attributed to the microbrownian motions of the dipolar molecules, and the remarkable features were (1) the low frequency (i.e. high temperature) at which this process occurred; (2) its rapid variation with temperature;

(3) the breadth and asymmetric nature of the loss curves; and
(4) a large apparent activation energy.

The molecules investigated in the present work are:

No.	Name	Structure	Matrix
1	Fluorobenzene		p.s.
2	1-Chloronaphthalene		p.s.
3	4-Phenyl pyridine		p.s.
4	4-Fluorobiphenyl		p.s.
5	4-Chlorobiphenyl		p.s.
6	4-Bromobiphenyl		p.s.
7	Cholesteryl butyl ether		p.s.
8	2,2'-Bipyridine		p.v.t.

No.	Name	Structure	Matrix
9	3-Nitrobiphenyl		p.v.t.
10	4-Bromobiphenyl		p.v.t.

The dielectric permittivity and loss of fluorobenzene, 1-chloronaphthalene, 4-chlorobiphenyl, 4-bromobiphenyl, and cholesteryl butyl ether at low concentrations in polystyrene have been measured from 10^2 to 10^5 Hz at several temperatures between 350-380K. At such high temperatures, the distribution of relaxation times of those solutes in polystyrene matrices has been attributed to hindered motions which were different from their molecular processes. The dielectric behaviour of these molecules has shown features which appeared to be common to all despite differences in the molecular size and dipole position. Therefore, the following explanation involves the general features of relaxation rather than that of specific molecules.

In the study of polymers, Ishida$^{(1)}$ pointed out that at a temperature that is well above the glass transition temperatures (Tg), the shape of the α-absorption curve did not change. However, below Tg the loss factor (Δε'') versus logν curve was quite broad as shown in the molecular process, which would become sharper when temperature was increased. The α-absorption curve in the amorphous polymer was given by:$^{(12)}$

$$(\varepsilon^*-\varepsilon_\infty)_\alpha/(\varepsilon_o-\varepsilon_\infty)_\alpha = \{(1 + i\omega\tau_o x)(1 + i\omega\tau_o x^{-1})\}^{-\frac{1}{2}} \tag{IV-1}$$

at considerably higher temperatures than the glass transition temperature. In Eqn. (IV-1), τ_o is the mean relaxation time, ω is the angular frequency, and x is the characteristic constant in the polymer which is given by:

$$x = \{(4A + B + C + 4D)/(B + C + 4D)\} \tag{IV-2}$$

Here, A is the restoring force constant related to the intrachain interactions between the nearest neighbours along the main chain in the rotational microbrownian motions. B is an interchain restoring-force constant due to interaction between the nearest neighbour chains. C is an interchain restoring-force constant arising from middle-range and long-range dipole-dipole interaction. D is the entropy elastic-force constant. As x tended to unity, Eqn. IV-1 tended to the Debye curve:

$$(\varepsilon^*-\varepsilon_\infty)/(\varepsilon_o-\varepsilon_\infty) = 1/(1 + i\omega\tau_o) \tag{I-9}$$

where τ_o becomes the single relaxation time τ_1. The deviation of

Eqn. IV-1 from the Debye curve was due to the fact that the dipoles were combined with one another by the main chain in the amorphous solid state since x tended to unity as A and D approached zero. For polyethylene isophthalate and polyvinyl acetate, Ishida reported that the asymmetry of the observed curves agreed fairly well with the asymmetry of the theoretical absorption curve, and he concluded that the asymmetric shapes were attributed to the characteristic nature of amorphous polymers.

Analogous loss curves were obtained from fluorobenzene, 1-chloronaphthalene, and cholesteryl butyl ether which is in accord with Ishidu's report. Fig. IV-1 shows the dielectric loss factor ε'' against $\log\nu$ for fluorobenzene in polystyrene. At the same temperature range, a secondary absorption process was also apparent for 4-chlorobiphenyl and 4-bromobiphenyl. However, it was not completely separated from the molecular process as were the small molecules, fluorobenzene and 1-chloronaphthalene, where the normal molecular absorption occurred in the temperature regions 94-118K and 103-138K respectively. A loss plot of 4-bromobiphenyl is shown in Fig. IV-2. The interesting features of these results were the high temperature of relaxation process and its rapid variation with temperature where both were quite different from the molecular process mentioned in Chapter III. Fig. IV-3 shows the normalized loss curve for the data of Fig. IV-1 for fluorobenzene. The excellence of the superposition showed that the shape of the loss process was essentially independent of temperature in the studied range.(6) It bore a quantitative similarity to the curves obtained by Williams and Hains(4) for dilute solutions of anthrone, camphor and phthalic anhydride in o-terphenyl and by Shears and Williams(6) for various concentrations of fluorenone in o-terphenyl.

Johari and Goldstein(5) measured the dielectric micro-brownian (α) process with the activation energy in the range, 230 to 293 kJ mol^{-1}, in a large number of supercooled small molecular systems. They emphasized the similarity between the behaviour of these systems and that of amorphous polymers. An apparent activation energy near 260 kJ mol^{-1} was found for some small molecules in the supercooled, o-terphenyl, liquid state.(4) The activation energy for the cooperative process of di-n-butyl phthalate dispersed in polystyrene(8) remained approximately constant around 300 kJ mol^{-1} which is close to that commonly found for the glass-transition (α) process in amorphous polymers and for polystyrene in particular.(2)

Data from Eyring analyses are given in Table IV-1, and the activation energy around 230 kJ mol^{-1} may be accounted for by a cooperative reorientation process between solute and polystyrene molecules. For example, activation energies of fluorobenzene found in both molecular relaxation and the high temperature process were ∿9 kJ mol^{-1} and 257 kJ mol^{-1} respectively which were significantly different. In the similar temperature range 350-370K, anthrone and cholest-4-en-3-one were studied in polystyrene. Davies and Edwards(7) reported that a large activation energy around 230 kJ mol^{-1} was obtained for both molecules and suggested that considerable work was done by the reorientating molecule in displacing the adjacent polymer chain of the rubber-like polystyrene.

All of the characteristic features observed, such as the high temperature at which the process occurred, asymmetric loss curves which varied rapidly with temperature changes and the apparently large activation energy, ...etc. strongly indicated that a cooperative process was observed in fluorobenzene, 1-chloronaphthalene, 4-chlorobiphenyl, 4-bromobiphenyl, and cholesteryl butyl ether.

Moreover, a linear relationship existed in the Eyring analysis plot of $\log\tau T$ against $1/T$. A typical example of fluorobenzene is shown in Fig. IV-4. In terms of Eyring transition state theory, as extended by Kauzmann(13), Smyth et al.(3) indicated that various values ranging from 105 kJ mol^{-1} to 293 kJ mol^{-1} with decreasing temperature for rigid molecules in supercooled decalin, i.e. the Arrhenius plots of the relaxation time, were non-linear.

In view of the distribution of relaxation times, Davies et al.(7) pointed out that since the β values increase as the temperature increases, when the value of β is extrapolated beyond very high temperatures (well above Tg), its value will finally approach 1 as a certain temperature is reached, i.e. normal liquid solution behaviour is then anticipated. The attainment of that state will also be accompanied by a marked fall in the activation energy corresponding to the change in the character of the polystyrene medium. In the present work, the β values of fluorobenzene increased from 0.35 to 0.60 as the temperature increased from 351 to 367K. Similar consequences of high β values corresponding with high temperatures were observed in the other four molecules, namely, 1-chloronaphthalene, 4-chlorobiphenyl, 4-bromobiphenyl, and cholesteryl butyl ether. The corresponding values obtained were in the range 0.26-0.57, 0.22-0.56, 0.23-0.68, and 0.34-0.37 respectively.

It is notable that the portion of $<\mu^2>$ which was not relaxed by local motions would be relaxed by the microbrownian motions of the environment, making a contribution to the cooperative process. The cooperative mechanism involves the motion of a reasonably large portion of the solution which is involved in the orientation of the polar molecule. Williams(8) explained that the mechanism of molecular and cooperative processes would be that, at low concentrations, certain molecules are 'free' to reorientate, uninfluenced by the polymer matrix, leading to the molecular process, while others are 'bound' in the immediate vicinity of polymer chains. These bound molecules may move only in cooperation with the motions of the polymer chain, leading to the cooperative process which corresponds then to the α relaxation of the plasticized polymer.

Davies and Edwards$^{(7)}$ suggested that the dipole component (μ_{coop}) responsible for the cooperative absorption which decreased markedly as the temperature increased was derived from ε''_{max} and β. If the dipole (μ_m) obtained from the molecular process were extrapolated linearly beyond higher temperature range, an estimate of μ(total) could be made. This was found to be given by the value of $(\mu_m^2 + \mu_{coop}^2)^{\frac{1}{2}}$. Shears and Williams$^{(6)}$ studied fluorenone at four concentrations, 5, 8, 15, and 22.5% (W/W) in o-terphenyl over a range of temperature and frequency (1 - 10^5 Hz) and reported that the total mean square dipole moment $<\mu^2>$ is relaxed by a consideration of a low and high frequency process. In the temperature range 359-377K the effective dipole moment of the co-operative relaxation process (μ_{coop}) for 1-chloronaphthalene increased. For the molecular process in 1-chlorohaphthalene, the dipole moment (μ_m) was found to increase from 0.61 to 0.79D at the temperatures between 103 and 138K. Accordingly, a value of μ(total) near 2.0D was evaluated by extrapolation of μ_m and μ_{coop} at a temperature of 363K. It is in reasonable agreement with the literature value 1.60D.(14) Likewise, similar decreased dipoles were found in the cooperative process for 4-chlorobiphenyl and 4-bromobiphenyl as well. The data are shown in the Fuoss-Kirkwood analyses in the appendix.

In the case of phenyl pyridine and 4-fluorobiphenyl in polystyrene, in addition to the molecular absorption in the region 214-266K and 254-298K respectively, another absorption process was revealed at higher temperatures 297-326K in the frequency range 10^4-10^7 Hz. The activation enthalpy of 69 kJ mol^{-1} obtained in the high temperature process for 4-phenyl pyridine was considerably larger than that of 38 kJ mol^{-1} for the molecular process. The corresponding values for 4-fluorobiphenyl were 102 kJ mol^{-1} and 52 kJ mol^{-1} respectively. The resulting values were lower than that of 230 kJ mol^{-1} for a particular cooperation motion but higher than those observed for a molecular relaxation and may be explained by the observation of Schmieder and Wolf(15) who observed the α-peak of atactic amorphous polystyrene and suggested that a small shoulder to the α-peak is in the 323K region.

Another point to be noted was that the low β values around 0.2 for both molecules implied a wide range of relaxation times. Hence, the molecular process associated with the cooperative motion may be overlapped in this investigation region. In other words, the solute reorientation which is in cooperation with a matrix may be considered and it may be due to the fact that the available local 'free volume' increased with rising temperature. An Eyring analysis plot of 4-phenylpyridine is given in Fig. IV-5.

In order to gain more extensive information on cooperative motion, 2,2'-bipyridine was studied in polyvinyltoluene. A plot of loss factor ε'' versus logν is shown in Fig. IV-6 in the range of frequencies 10^4-10^7 Hz and at temperatures between 358-382K. The absorption process corresponds well with features such as rapid variation with temperature, and the asymmetric nature of the curves as was the case with fluorobenzene. Fig. IV-7 shows the plot of the normalized dielectric loss factor $(\varepsilon''/\varepsilon''_{max})$ against $\log(\nu/\nu_{max})$ for different temperatures. The curve of this molecule is consistent with that of fluorobenzene in polystyrene, being asymmetric on the high frequency side. High β values were expected for such a process and were, indeed, observed as being 0.33-0.47. Furthermore, the fairly large activation energy of 141 kJ mol^{-1} was estimated. It was evident that this absorption process was mainly determined by the solvent molecules of polystyrene due to the cooperative nature of reorientation, which is unrelated to the molecular size, shape, and dipole inclination of the solute. The value of activation energy, 141 kJ mol^{-1}, in polyvinyl toluene was considerably smaller than that of 230 kJ mol^{-1} in polystyrene whereas it was comparable with that of 130 kJ mol^{-1} for rubber.(13) It may be due to the different structures and properties of the polymers. In the medium of polyvinyl toluene, 3-nitrobiphenyl, and 4-bromobiphenyl were of particular interest in view of the other results obtained in these studies. Owing to their low β values and large Eyring parameters, an overlapping of the molecular relaxation with cooperative reorientation may be employed in both molecules. For 3-nitro biphenyl, the data were analyzed at each temperature in terms of a single absorption of the Fuoss-Kirkwood type. Different processes in the limits of lower and higher temperatures were separated into two straight lines from the Eyring analysis. Certainly the low temperature process with an activation energy of 76 kJ mol^{-1} was ascribed to the molecular process. The activation energy yielded in the high temperatures was 132 kJ mol^{-1} which was much larger than that of 76 kJ mol^{-1} for the molecular process; however, when it is compared with the value of 141 kJ mol^{-1} of the cooperative relaxation in 2,2'-bipyridine, the difference was relatively small. The low β value (0.13 - 0.16) at the high temperature range strongly suggested that the cooperative reorientation and the molecular relaxation processes overlapped.

In poly(vinyltoluene), an absorption process was found for 4-bromobiphenyl at temperatures between 307-336K, with quite a large activation enthalpy around 143 kJ mol^{-1} and the entropy of activation of 283 J K^{-1} mol^{-1}. It was most probable that there was some contribution of cooperative motion for such high temperatures owing to the apparently large values of Eyring parameters. Furthermore, the β value between the range 0.18 - 0.20 was inconsistent with the concept that the molecular relaxation process may be overlapped with the cooperative process.

In the dielectric study of dilute solutions of small molecules in o-terphenyl in the supercooled liquid state, Williams and Hains(4) emphasized that the apparent activation energy near 260 kJ mol^{-1} should not be interpreted as the 'barrier' required to reorient a solute molecule, i.e. the dielectric process is significantly feasible for cooperative motion. Similarly, from the present study of several solute molecules in polystyrene at low concentration, the magnitude of activation energy obtained for the cooperative motion is around 230 kJ mol^{-1} and the activation entropy is about 450 J K^{-1} mol^{-1}. Such is also the case for poly(vinyltoluene) with

ΔH_E ∿140 kJ mol^{-1} and ΔS_E ∿250 J K^{-1} mol^{-1} respectively. It is in good agreement with the cooperative nature of the process. Levi(16) took values of ΔH_E and ΔS_E from various sources and found that there is a linear relation between them, and that the larger the ΔH_E, the more positive the ΔS_E becomes. Likewise, the data showed that there is a close dependence of ΔH_E and ΔS_E upon molecular structure of polymers. The present data together with Levi's bore out the linear ΔH_E - ΔS_E relation for polymers as shown in Fig. IV-8. A linear regression analysis yields an equation of:

$$\Delta S_E \ (\mathrm{J\ K^{-1}\ mol^{-1}}) = -67.5 + 2.49 \ \Delta H_E \ (\mathrm{kJ\ mol^{-1}}) \qquad (\mathrm{IV}\text{-}3)$$

In the examination of molecular motion and the glass-transition of dilute solutions in polystyrene and poly(vinylchloride), Ishida et al.(17-19) found that the dielectric transition temperature could be regarded as the temperature at which the dielectric relaxation time is about 100 s, which is in accord with the correlation time for micro-brownian motion of the α-process. On the basis of this procedure, the glass-transition temperature (Tg) was estimated to be about 320K for fluorobenzene, 1-chloronaphthalene, 1-chlorobiphenyl, 1-bromobiphenyl, and cholesteryl butyl ether at the low concentration of 7% by weight in the polymer matrix. It is determined by two ways, either from the plot of temperature dependence of the dielectric loss factor or from the linear relation between log τ and 1/T. Corresponding plots for fluorobenzene are shown in Figure IV-9 and IV-10. In a similar manner, Tg for 2,2'-bipyridine in poly(vinyltoluene) was ∿270K at the same concentration. This is different from the case of the molecular relaxation processes discussed in Chapter III. For a molecular process, it always has a short relaxation time which cannot approach the order of 10^2 s at the observed temperatures. The value of Tg ∿330K is examined by Adachi et al.(17) for the solute of 7% by weight in polystyrene. In other words, the experimental result at 320K in the present situation agreed well with theirs. The molecular relaxation of a solute in polymer media can be distinguished from the cooperative motion of the solute with the polymer. The cooperative process has similar characteristics to the α-process in polymers. For the cooperative motion, the change of Tg depends mainly upon the concentration of the dipolar solute,(18) more than on the molecular size, shape, or dipole components.

CONCLUSION

Altogether, the asymmetric loss curve, the high β values, the decrement of dipole moment, the glass-transition temperature determination and the large apparent activation energy were in favour of cooperative motion for fluorobenzene, 1-chloronaphthalene, 4-chlorobiphenyl, 4-bromobiphenyl, and cholesteryl butyl ether at the temperatures bewteen 350 - 380K in the polystyrene and 2,2'-bipyridine (358-382K) in the poly(vinyltoluene) matrices. Meanwhile, some contribution of the cooperative process involved in 4-phenyl pyridine, 4-fluorobiphenyl, 3-nitrobiphenyl, and 4-bromobiphenyl in either of the matrices was also likely. It is strikingly notable that the dielectric study of the cooperative process of molecules at low concentration of a dipolar solute in a polymer matrix agrees well with the results of molecular motion in the supercooled liquid state and also the behaviour of solid polymer.

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TABLE IV-1 DIELECTRIC RELAXATION AND EYRING ACTIVATION PARAMETERS FOR VARIOUS SIZES OF MOLECULES IN BOTH POLYSTYRENE AND POLY(VINYLTOLUENE) MATRICES

Molecule	T(K)	τ(s) 200K	τ(s) 300K	τ(s) 350K	ΔG_E(kJ mol^{-1}) 200K	ΔG_E(kJ mol^{-1}) 300K	ΔG_E(kJ mol^{-1}) 350K	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
(in polystyrene)									
Fluorobenzene	94 - 118	1.2×10^{-9}	1.4×10^{-10}	--	14.1	16.8	--	9	--
	351 - 367	--	2.1×10^{3}	7.3×10^{-4}	--	92.6	65.2	257 ± 30	548 ± 82
1-Chloro-naphthalene	103 - 138	9.4×10^{-9}	1.9×10^{-10}	--	17.6	17.6	--	18 ± 1	-1 ± 10
	359 - 377	--	9.7×10^{3}	3.8×10^{-3}	--	95.4	69.9	255 ± 53	529 ± 145
4-Phenyl-pyridine	214 - 266	3.5×10^{-3}	1.3×10^{-6}	--	38.9	33.6	--	38 ± 4	-7 ± 15
	297 - 326	--	6.1×10^{-7}	1.0×10^{-8}	--	37.8	32.6	69 ± 5	104 ± 17
4-Fluoro-biphenyl	254 - 298	1.8×10^{-1}	3.5×10^{-6}	--	45.4	42.2	--	52 ± 2	33 ± 7
	298 - 325	--	2.5×10^{-6}	6.2×10^{-7}	--	41.3	31.2	102 ± 17	203 ± 54
4-Chloro-biphenyl	295 - 325	8.6×10^{2}	7.4×10^{-5}	--	62.4	49.8	--	80 ± 5	100 ± 16
	364 - 375	--	1.5×10^{3}	7.3×10^{-3}	--	91.7	71.9	211 ± 48	397 ± 131
4-Bromo-biphenyl	307 - 342	2.7×10^{4}	4.1×10^{-4}	--	65.3	54.0	--	88 ± 4	112 ± 13
	368 - 379	--	1.5×10^{4}	2.2×10^{-2}	--	97.5	75.0	233 ± 37	450 ± 99
Cholesteryl butylether	368 - 380	--	--	1.5×10^{-1}	--	--	80.7	226 ± 30	414 ± 81
(in polyvinyltoluene)									
2,2'-Bipyridine	203 - 228	2.0×10^{-3}	1.7×10^{-6}	--	38.0	40.4	--	33 ± 6	-24 ± 28
	358 - 382	--	1.1×10^{-1}	3.0×10^{-5}	--	68.0	55.9	141 ± 10	242 ± 27
3-Nitrobiphenyl	266 - 297	6.5×10^{1}	1.0×10^{-5}	--	55.3	44.8	--	76 ± 7	104 ± 26
	288 - 310	--	5.0×10^{-6}	2.2×10^{-9}	--	43.1	35.6	132 ± 11	297 ± 38
4-Bromobiphenyl	307 - 336	--	1.8×10^{-3}	4.4×10^{-7}	--	57.8	43.6	143 ± 7	283 ± 22

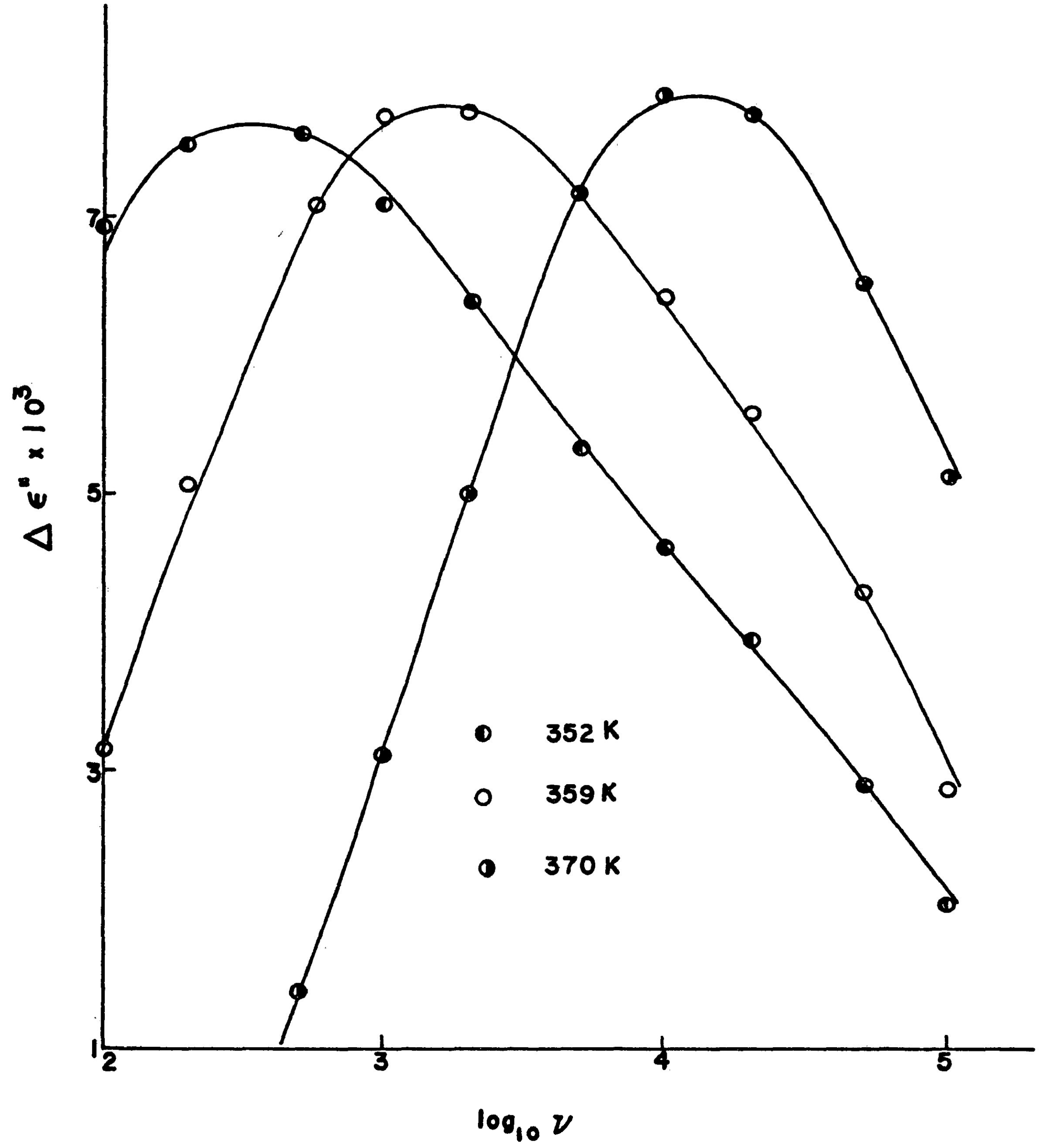


FIG. IV-1: Dielectric Loss Factor $\Delta\varepsilon''$ vs. $\log\nu$ for Fluorobenzene in a Polystyrene Matrix at Temperatures as Indicated.

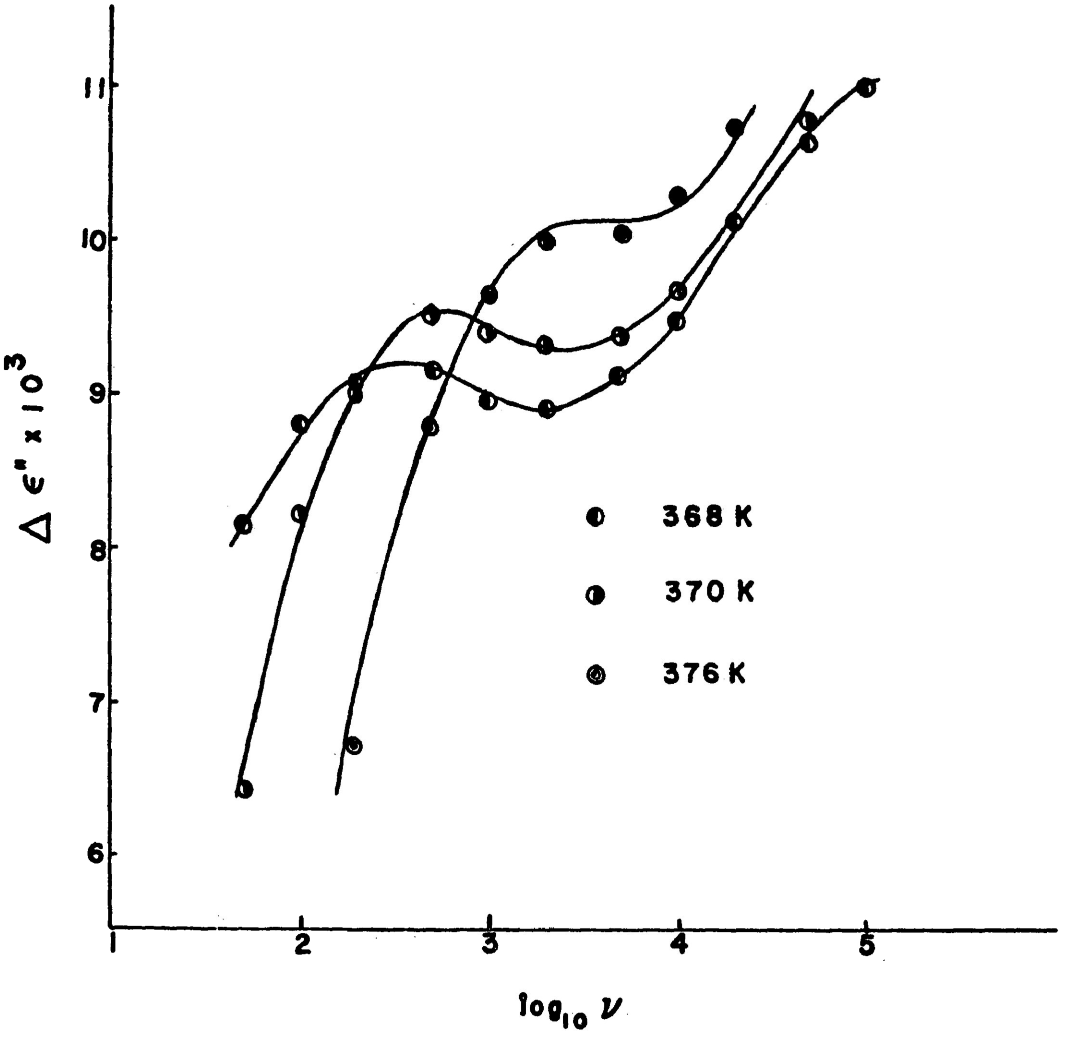


FIG. IV-2: Dielectric Loss Factor $\Delta\varepsilon''$ vs. $\log\nu$ for 0.33M 4-Bromobiphenyl in a Polystyrene Matrix at Temperatures as Indicated.

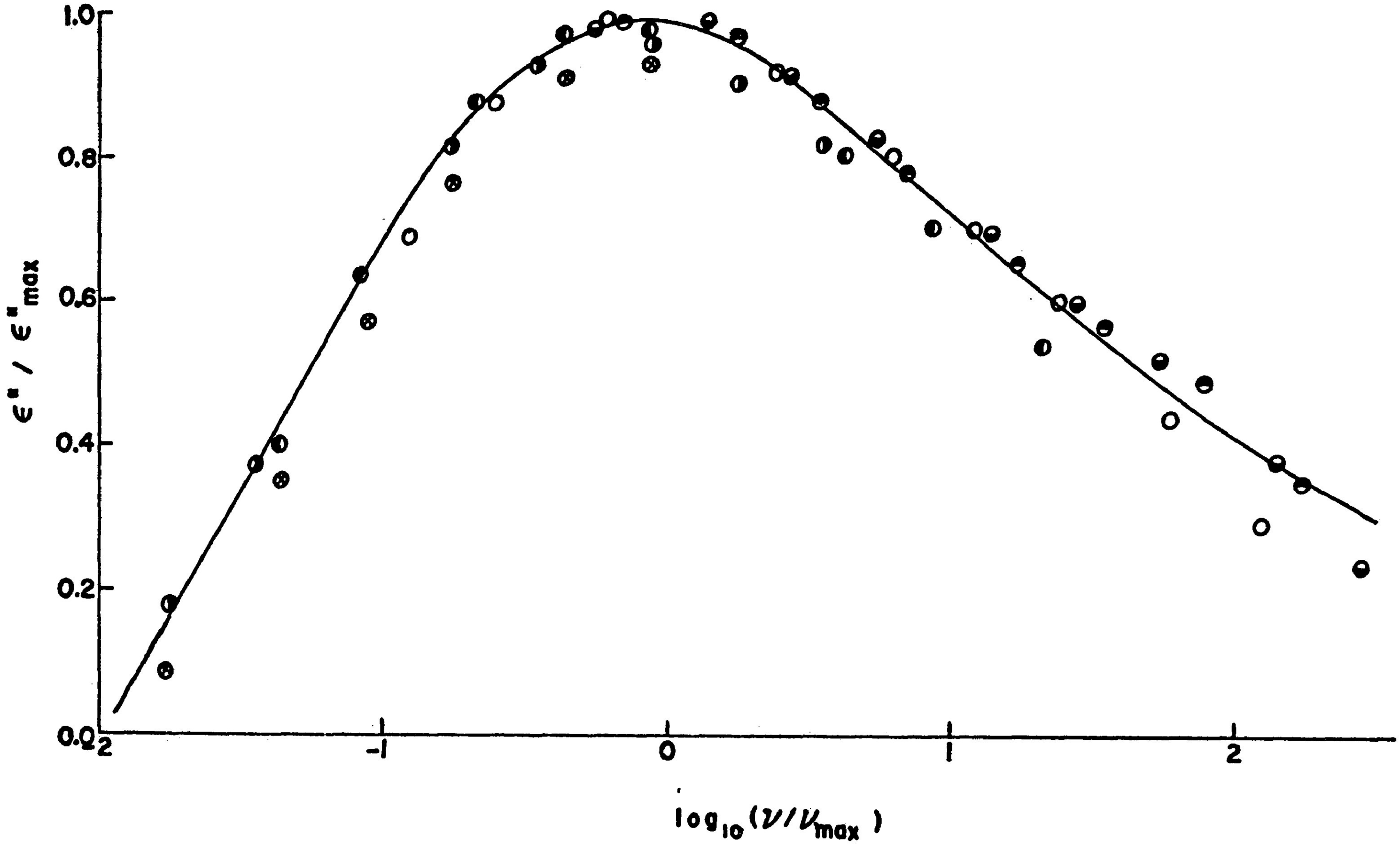


FIG. IV-3: Plot of ($\varepsilon'' / \varepsilon''_{max}$) vs. log(ν / ν_{max}) for Fluorobenzene in Polystyrene at ◓, 351K; ◒, 352K; ○, 356K; ◐, 359K; ◑, 363K; and ⊗, 367K.

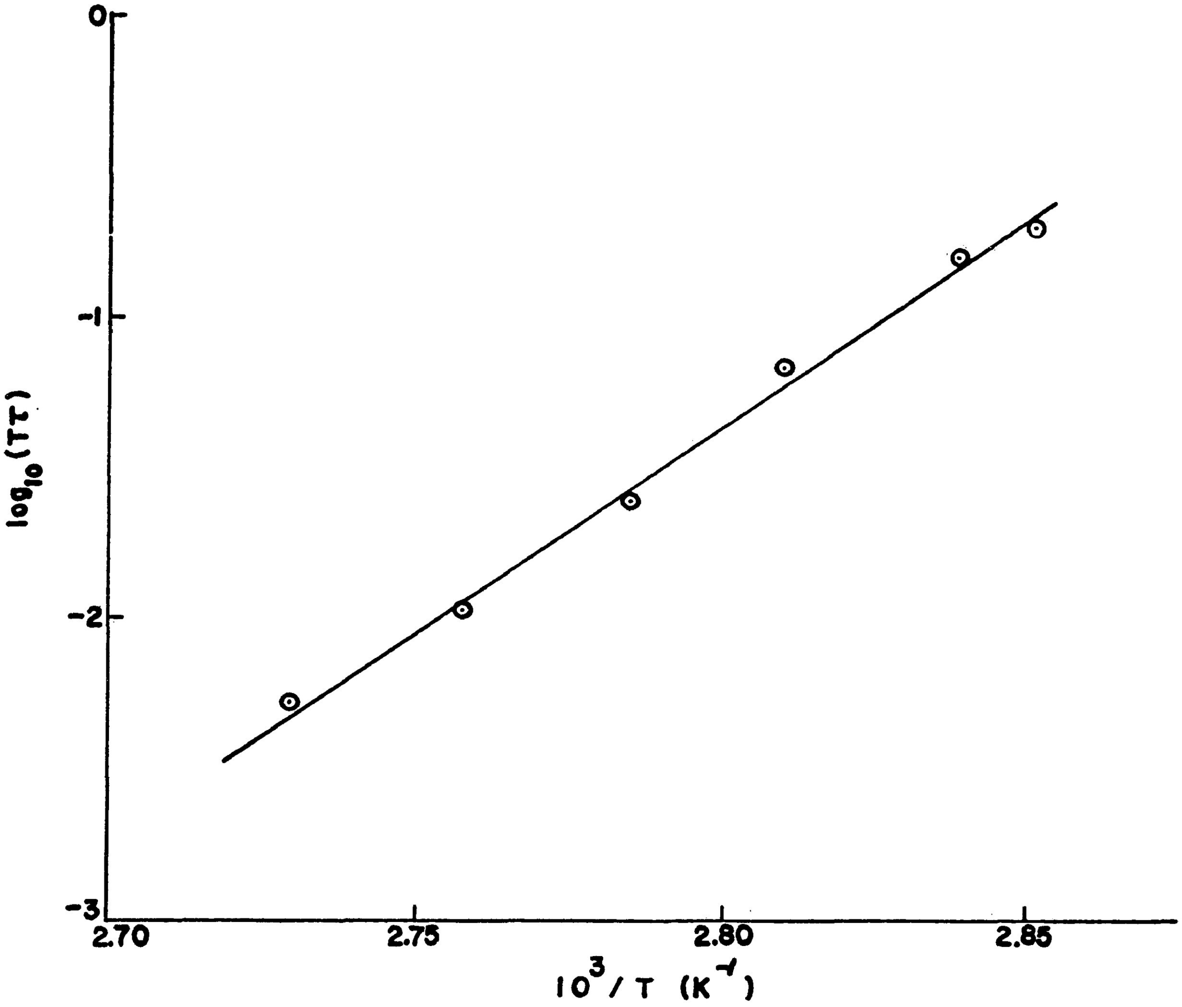


FIG. IV-4: Eyring Plot of log(τT) vs. 1/T for Fluorobenzene in a Polystyrene Matrix Around T_g.

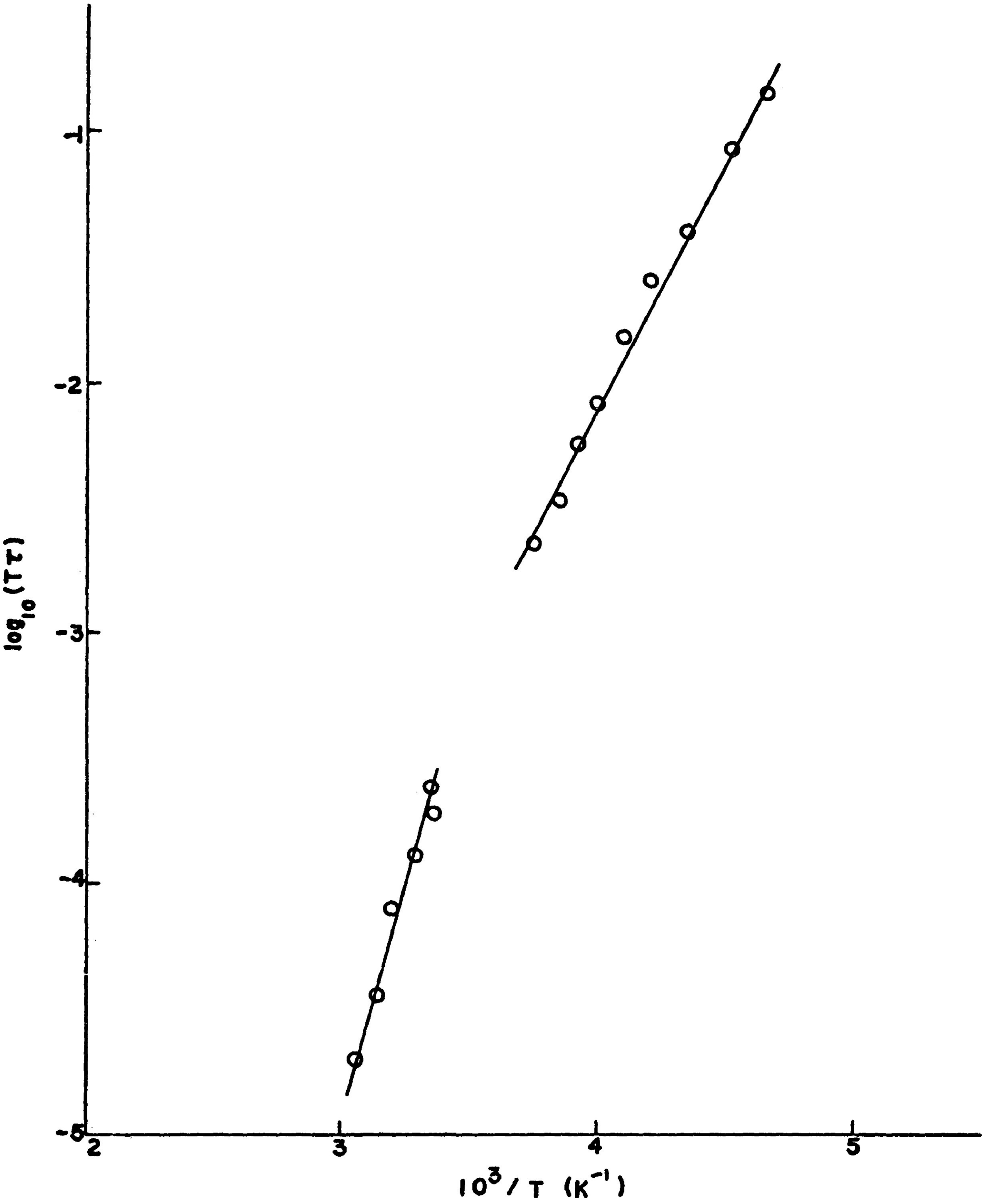


FIG. IV-5: Eyring Plot of $\log(\tau T)$ vs. $1/T$ for 0.46M 4-Phenyl pyridine in a Polystyrene Matrix.

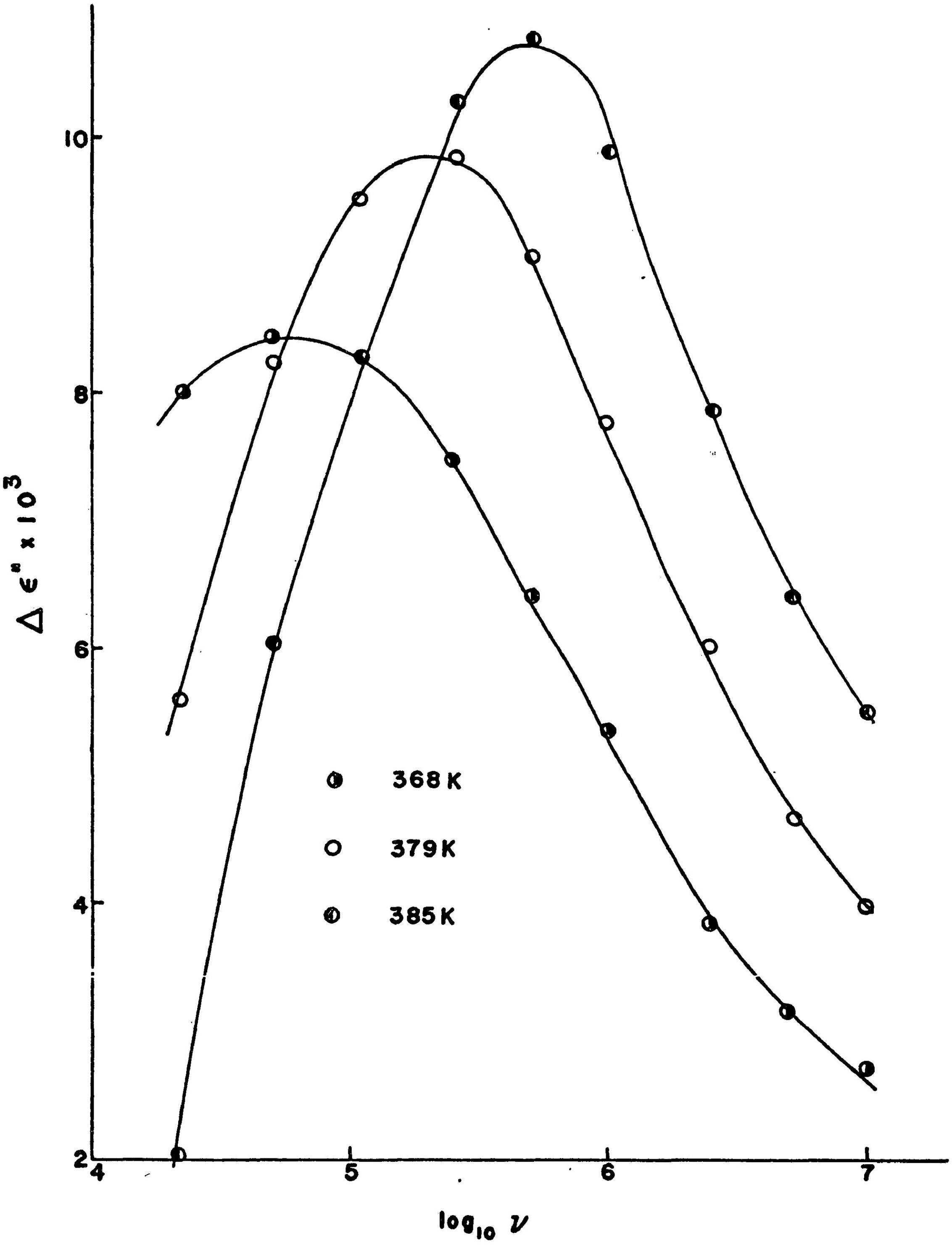


FIG. IV-6: Dielectric Loss Factor $\Delta\varepsilon''$ vs. $\log\nu$ for 0.46M 2,2'-bipyridine in a Poly(vinyltoluene) Matrix at Temperatures as Indicated.

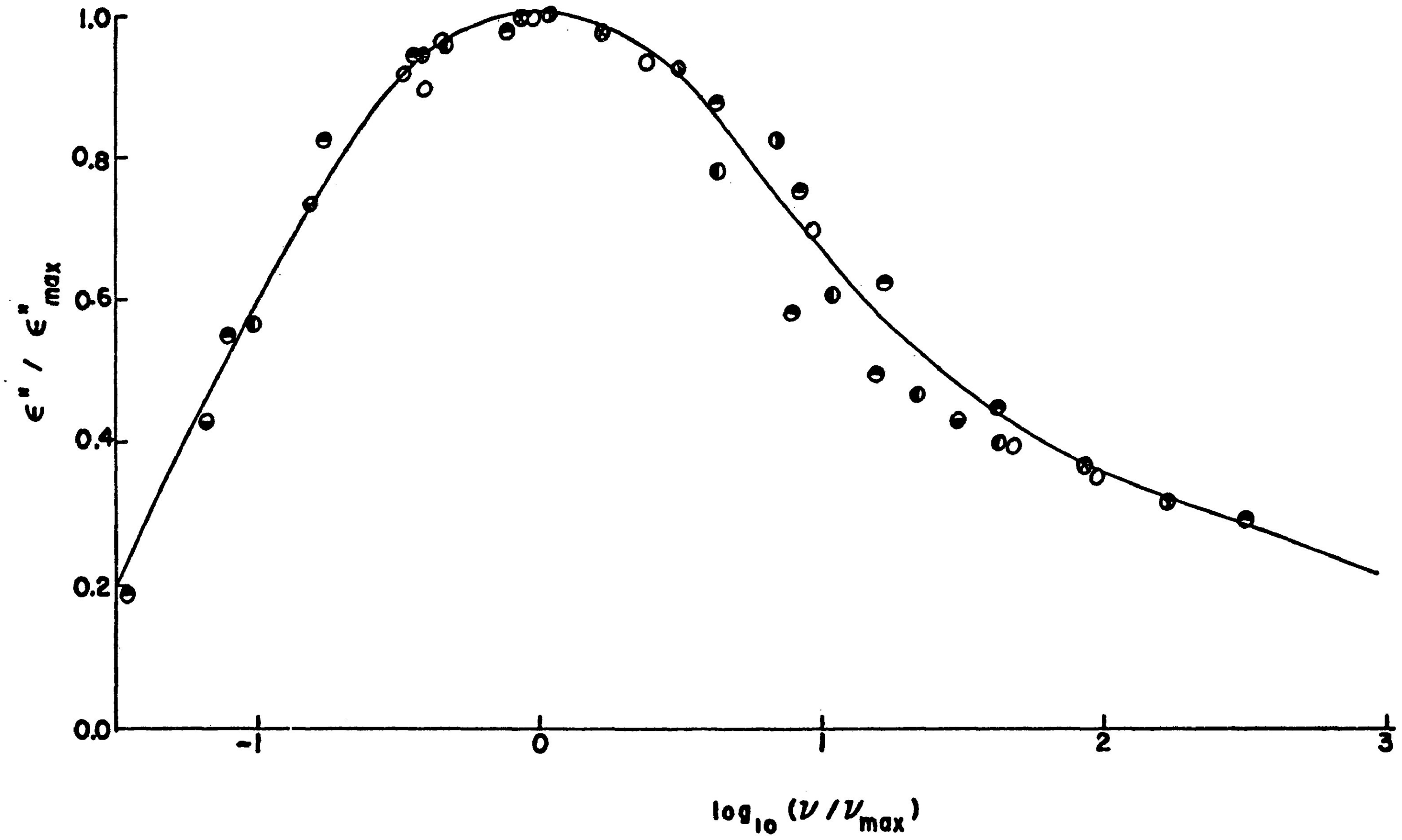


FIG. IV-7: Plot of ($\varepsilon'' / \varepsilon''_{max}$) vs. log(ν / ν_{max}) for 0.46M 2,2'-Bipyridine in Poly(vinyltoluene) at ◑, 358K; ⊗, 368K; ○, 373K; ◐, 379K; ◒, 382K; and ◓, 385K.

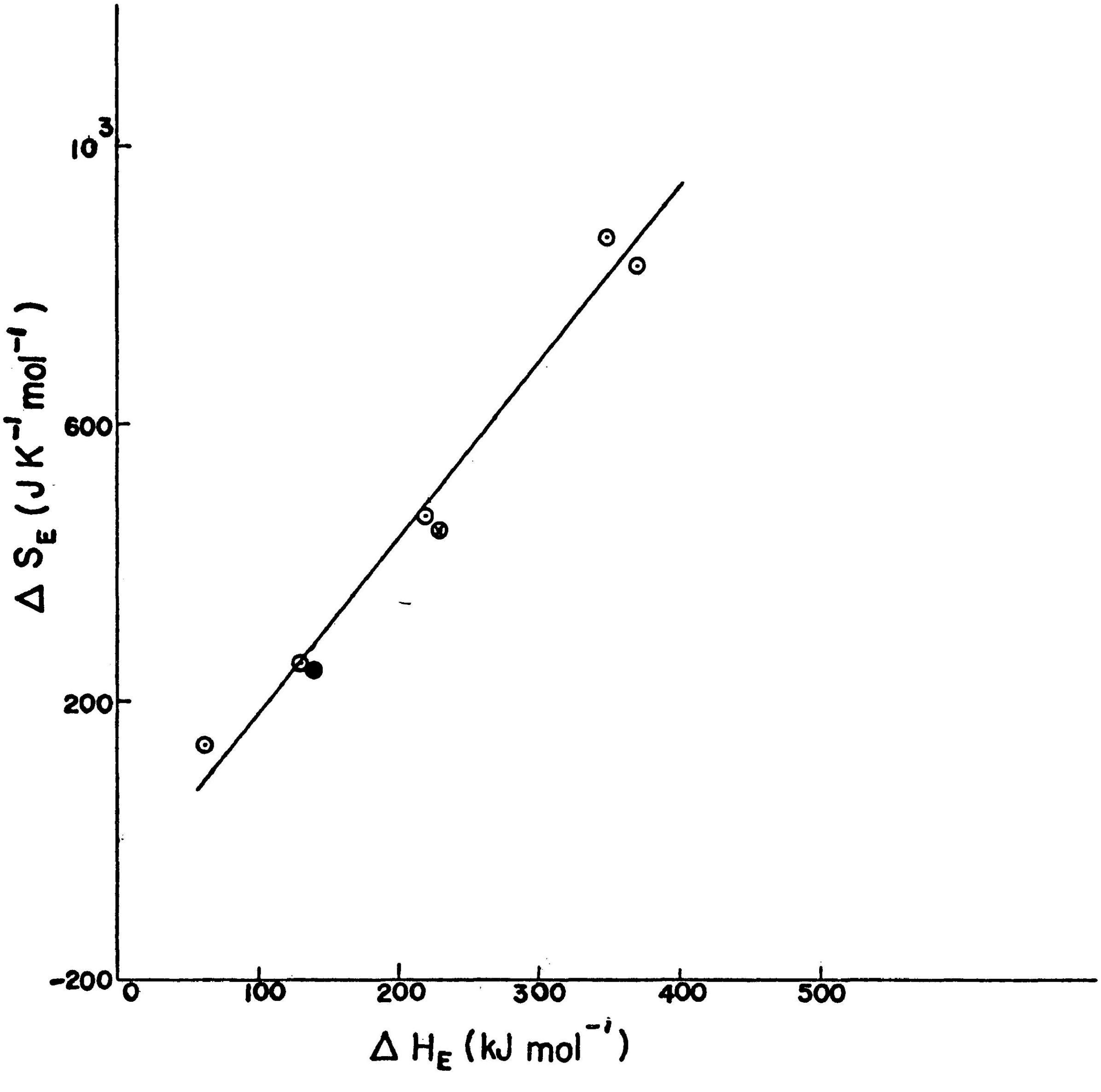


FIG. IV-8: Plot of Eyring Parameters ΔH_E vs. ΔS_E Showing Polystyrene Data ⊗, Poly(vinyltoluene) Data ●, and Levi's Data ⊙.(16)

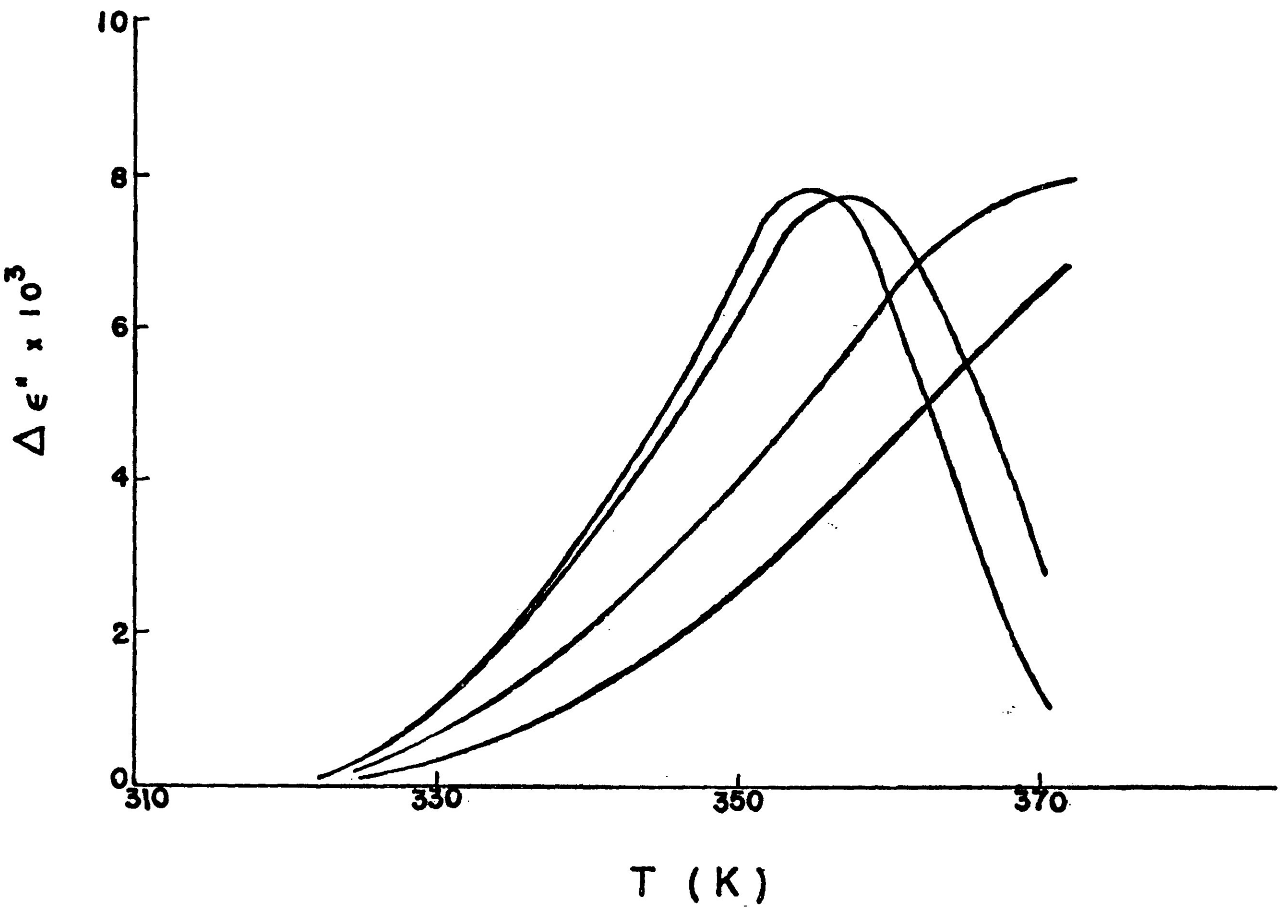


FIG. IV-9: Temperature Dependence of $\Delta\varepsilon''$ for Fluorobenzene in Polystyrene.

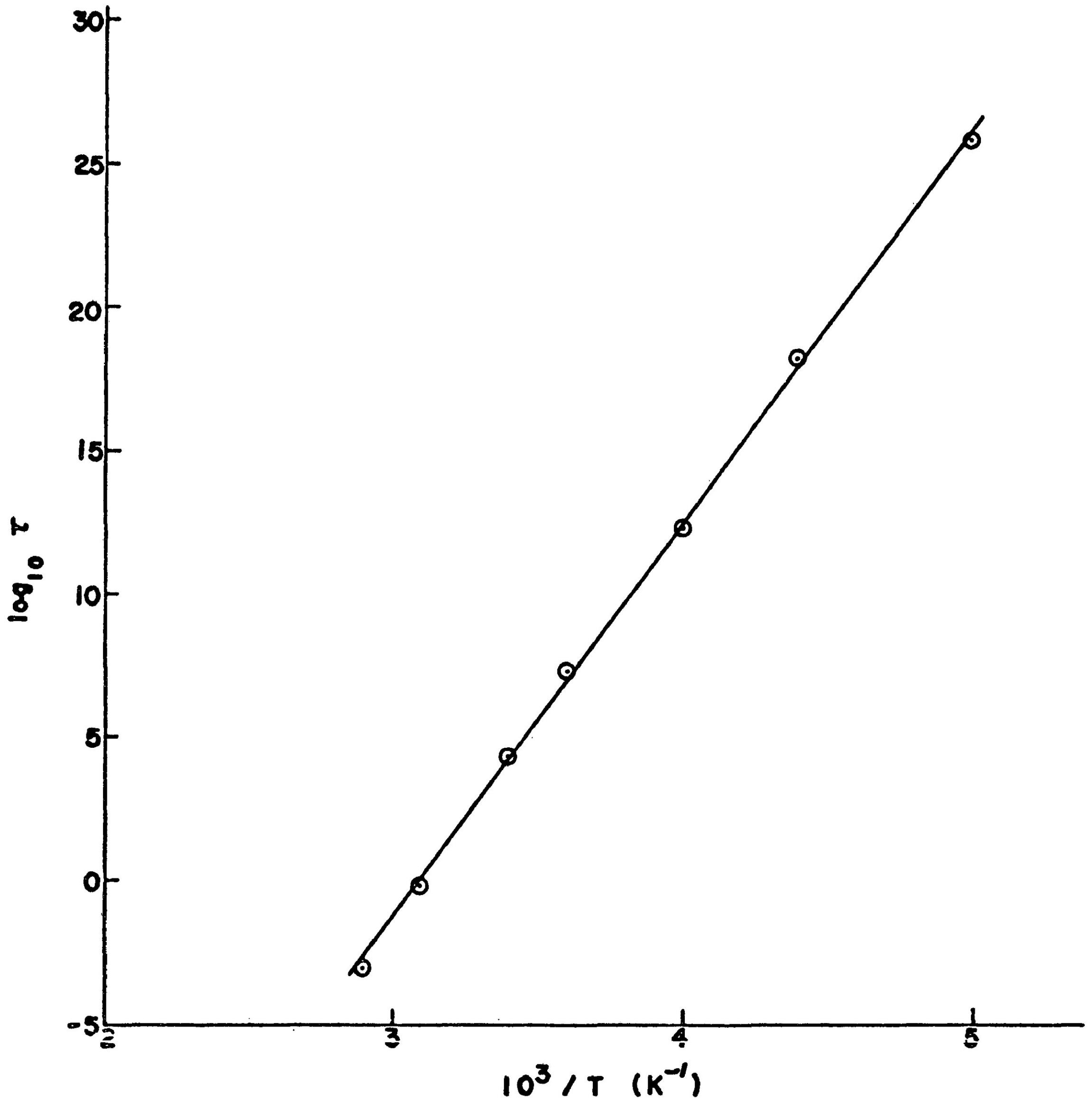


FIG. IV-10: Plot of logτ vs. 1/T for Fluorobenzene in a Polystyrene Matrix.

CHAPTER V

THE INFLUENCE OF POLYMER MEDIA ON DIELECTRIC RELAXATION

INTRODUCTION

Dielectric measurements have been carried out in the past upon solutions of polar molecules in solvents of different viscosities in order to investigate the relation between dielectric relaxation time, viscosity and angle of inclination of the molecular dipole to the principal axes within a molecule.

For a rigid molecule, Debye and Fischer have frequently employed dielectric studies relating the molecular relaxation time to the viscosity and molecular dimensions. In the investigation of 1-chloronaphthalene and 1-bromonaphthalene in dilute solutions in decalin and nujol, Grubb and Smyth(1) reported that around 293K, the relaxation times of 1-chloronaphthalene were 21 ps in decalin and 62 ps in nujol, while for 1-bromonaphthalene the corresponding values were 26 ps and 85 ps respectively. They found that the ΔG_E values also increased with increasing viscosity and molecular size, as has been observed in a number of other liquids.(2,3) As an extension of such work, Tay(4) chose to increase the viscosity of the surrounding medium considerably and examined the 1-halonaphthalenes in a polystyrene matrix. A longer relaxation time of 190 ps was found for 1-chloronaphthalene and 600 ps for 1-bromonaphthalene at 300K. A similar result was shown in the Eyring parameters.

In the non-rigid molecules, instead of the single relaxation time of a molecular process, at least a partial reorientation of the dipole may occur at a rate determined by that of an intramolecular configuration change. By studying the dielectric relaxations in a medium which preferentially increases the relaxation time of the molecular process, while making little change in the relaxation time of intramolecular rotation, Lakshmi et al.(15) have examined the influence of the medium on aldehyde groups rotation and on molecular relaxation. The polymers used were atactic and isotactic polystyrene, polyethylene and polypropylene. They found that the study of the dielectric absorption of the aldehyde group in these polymer matrices appeared to be more apparent than similar studies in dilute liquid-phase solutions.

One technique used to reduce the rate of rotation of a molecule, in some cases even to suppress it, is to dissolve the solute in a solid polymer matrix and to examine it at low temperature. Even if molecular rotation were not totally eliminated, it would be considerably slowed down. Dielectric measurements of Frank et al.(16), Davies et al.(7,8), and Crossley et al.(14) have indicated that dipolar molecules dispersed in a polystyrene matrix behaved somewhat as if in a medium of very high viscosity. The frequency at which the maximum value of the dielectric loss factor occurred was then considerably lower than that in the case of a liquid solution. Further, this effect of viscosity on the relaxation time may be expected to be more pronounced for molecular rotation, which involves the motion of a species of large volume, rather than for the motion of much smaller groups within the molecule.

It is the purpose of this chapter to discuss the activation parameters for some rigid molecules and biphenyl derivatives in different matrices of polystyrene and poly(vinyltoluene). And finally to assess the influence of the medium on the different processes.

EXPERIMENTAL:

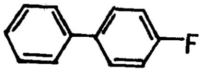
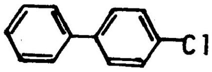
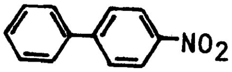
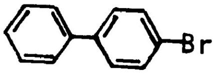
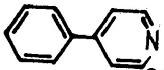
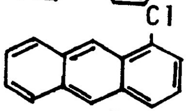
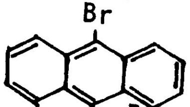
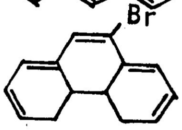
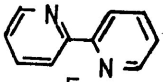
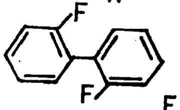
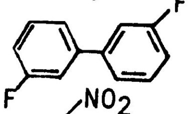
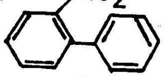
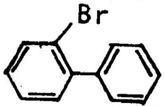
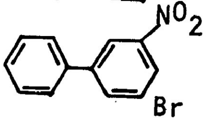
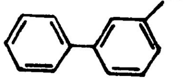
The dielectric measurements have been made on a General Radio 1615A capacitance bridge in the frequency range 50 to 10^5 Hz. The measuring cell was a three-terminal, circular, parallel plate capacitor mounted in a temperature-controlled chamber purged with dry nitrogen gas. The cell may be operated from liquid nitrogen temperature to about 400K. Additional measurements were made by using a Hewlett-Packard 4342A Q-meter with a temperature-controlled two-terminal cell in the range 2.5×10^4 to 1.5×10^7 Hz. The apparatus and measurement techniques have been described in Chapter II.

The polystyrene matrices were prepared as described in Chapter II. The same procedure was adopted to make the samples in poly(vinyltoluene) except that the preheated temperature for poly(vinyltoluene) was ten degrees lower than that for polystyrene. The poly(vinyltoluene) purchased commercially was polymerized by mixed isomers.

DISCUSSION

The Fuoss-Kirkwood analyses results are listed in the appendix and the Eyring activation parameters in Table V-1. Typical plots of ε'' versus $\log\nu$ for 4-nitrobiphenyl and 2-nitrobiphenyl are shown in Fig. V-1 and V-2. The corresponding plots of $\log\tau T$ against $1/T$ are shown in Fig. V-3 and V-4 respectively.

The following compounds were discussed in the study:

No.	Name	Structure
1	4-Fluorobiphenyl	
2	4-Chlorobiphenyl	
3	4-Nitrobiphenyl	
4	4-Bromobiphenyl	
5	4-Phenylpyridine	
6	1-Chloroanthracene	
7	9-Bromoanthracene	
8	9-Bromophenanthrene	
9	2,2-Bipyridine	
10	2,2'-Difluorobiphenyl	
11	3,3'-Difluorobiphenyl	
12	2-Nitrobiphenyl	
13	2-Bromobiphenyl	
14	3-Nitrobiphenyl	
15	3-Bromobiphenyl	

The activation enthalpy of rigid biphenyls, i.e. 4-substituted biphenyls, in polystyrene was increased in the order of substituents from fluorine, chlorine, nitro group to bromine atoms. The corresponding values of activation energy were 52, 80, 86 and 89 kJ mol^{-1} respectively. Similarly, the analogous sequence was found in poly(vinyltoluene) matrices to be: F- (ΔH_E: 74 kJ mol^{-1}), Cl- (ΔH_E: 91 kJ mol^{-1}), NO_2- (ΔH_E: 117 kJ mol^{-1}) and Br- (ΔH_E: 143 kJ mol^{-1}). The correspondence of activation entropy from the above fluoro- to bromobiphenyls in poly(vinyltoluene) was found to be 105, 136, 195 and 283 J K^{-1} mol^{-1} respectively which were larger than those values in polystyrene, that is 33, 100, 106 and 117 J K^{-1} mol^{-1} respectively. This bore out quite well what Davies et al.(7) mentioned; if the activation energy is largely needed to displace adjacent solvent molecules or groups, the larger the energy (ΔH_E) required and the larger the local disorder as reflected in the ΔS_E value.

At 300K, the corresponding values of relaxation time in these two media for 4-fluoro-, 4-chloro-, 4-nitro and 4-bromobiphenyls were 3.5×10^{-6}, 6.7×10^{-5}, 4.6×10^{-4} and 4.2×10^{-4}s in polystyrene and 4.4×10^{-6}, 7.4×10^{-5}, 2.1×10^{-3} and 1.8×10^{-3}s in poly(vinyltoluene) respectively. Thus, it appeared that the relaxation times changed when the medium and molecular size altered.

The first relation to be examined between viscosity η and the molecular relaxation time has been expressed by Debye's equation(9).

$$\tau = \frac{4\pi\eta a^3}{kT} \qquad \text{(V-1)}$$

where a is the radius of a spherical molecule moving in a continuous viscous fluid having a coefficient of viscosity η, k is the Boltzmann constant and T, the absolute temperature. Fischer(10) developed an equation, which permitted the molecule to be either spherical or ellipsoidal in shape, from the Perrin theory.(11) The equation was similar in form to that of Debye except that it involved a molecular structure factor (fz) and it was in the form:

$$\tau = \frac{4\pi f_z \eta abc}{kT} \qquad \text{(V-2)}$$

a, b, c are the lengths of the semi-axes of the molecular ellipsoid, z = a, b, c, and f_z is a factor which gives the ratio of the relaxation time about an ellipsoid axis to that of a sphere of equal volume and f_z describes the dependence of τ on the direction of the molecular dipole with respect to the principal axes of inertia. In the case of liquids, these equations were derived in consideration of the effect of the medium on the relaxation behaviour of the rotational motion of a dipolar molecule.

It was found from experimental data that the molecular relaxation time was approximately proportional to the volume of the rotating species and the viscosity of the medium. Atactic polystyrene is an amorphous polymer with no rigidly-defined or specific crystalline lattice structure. The arrangement of the phenyl ring on the chain is random, and there is a very high waste of space and free volume which is defined as the volume of the cage minus the volume of the solute molecule. Doolittle(12) applied an empirical equation to represent high accuracy viscosities of ordinary liquids of low molecular weight and the relation was shown as:

$$\eta \propto \frac{1}{V_f} \qquad \text{(V-3)}$$

where V_f was the free volume.

From the relation of Eqns. (V-1) and (V-2), the molecular relaxation time (τ) is proportional to the viscosity (η). The Arrhenius relation expresses that the relaxation time is the reciprocal of a mean rate coefficient which is a function of the Arrhenius activities energy. Finally, the relationship between the free volume and the energy barrier is given by:

$$V_f \propto \exp(-A/R_T) \qquad \text{(V-4)}$$

Where A is the Arrhenius activation enthalpy which is equivalent to the surface free energy which is employed to create a void of volume V_f to deal with the reorientation of the solute.

Normal atactic polystyrene is an amorphous polymer with no rigidly-defined or specific crystalline lattice structure. The arrangement of the phenyl ring on the chain is random, and there is a very high waste of space and free volume. In poly(vinyltoluene), the structure is analogous to that of polystyrene except for the extra-methyl group in either the ortho-, meta-, or para-position of the phenyl ring on the chain. Here, poly(vinyltoluene) is polymerized by mixed isomers, i.e. 2-methyl, 3-methyl and 4-methyl styrenes. Owing to its slightly complicated phenyl-branches, the "cavity" within side-branches could be slightly smaller, leading to a decrease in free volume. A larger activation energy (ΔH_E) was usually found for molecular relaxation processes in poly(vinyltoluene) as compared with polystyrene (see later).

An expected variation of activation enthalpy and entropy for the molecular relaxation was observed in both polystyrene and poly(vinyltoluene) matrices. In polystyrene, 4-phenylpyridine showed dielectric absorption in the temperatures between 214-266K, with an activation energy of 38 $kJmol^{-1}$ and activation entropy of -7 $JK^{-1}mol^{-1}$. The corresponding values of 52 $kJmol^{-1}$ and 40 $JK^{-1}mol^{-1}$, which were larger than those values in polystyrene, were found in poly(vinyltoluene) in about the same temperature range. Similar results were also observed in the study of elongated 4-substituted biphenyls which have been discussed before. It seemed that the small free volume in poly(vinyltoluene) needs a higher activation energy in order to reorientate the molecules.

Three rigid, disc-like molecules studied here are 1-chloroanthracene, 9-bromoanthracene and 9-bromophenanthrene. The dielectric absorption in these compounds was due to the entire molecular relaxation in both polymer matrices. The values of the activation energy in polystyrene mentioned in Chapter III were 55 $kJmol^{-1}$ for 1-chloroanthracene, 35 $kJmol^{-1}$ for 9-bromoanthracene and 31 kJmol^{-1} for 9-bromophenanthrene. In poly(vinyltoluene), the corresponding values of ΔH_E increased to 72, 47 and 46 kJmol^{-1} respectively. Smyth(13) has emphasized that a disc-like molecule would reorient with much lower medium resistance by rotation about an axis perpendicular to its plane. The in-plane motion for these disc-like molecules has been interpreted in detail in Chapter III. Therefore, it is expected that the activation energy for these molecules would be considerably smaller than those for elongated 4-substituted biphenyls in poly(vinyltoluene). The low value of $\sim$0.2 of the distribution parameter β for relaxation time for those rigid molecules found in poly(vinyltoluene) is close to that observed in polystyrene (8,15) for a molecular relaxation process.

Knowledge of the behaviour of the rigid dipoles of various sizes and shapes in the media was a prerequisite for dielectric studies. With rigid solutes, the molecular dipole may be considered to be a probe inserted into the non-polar polymers where its behaviour reflects the conditions within these media.

2,2'-Bipyridine and a set of non-rigid biphenyls were investigated in poly(vinyltoluene). As in the case of the substituted biphenyls mentioned in polystyrene matrices, an overlapping process was also found in the poly(vinyltoluene)medium for all non-rigid biphenyl derivatives. According to the results of rigid molecules, it seemed that larger Eyring parameters and longer relaxation times would be expected in poly(vinyltoluene) rather than in polystyrene for a molecular process. The correspondence was found in the high temperature region for these biphenyl derivatives. In the case of 2,2'-difluorobiphenyl, the activation energy of 38 kJmol^{-1} in polystyrene was raised to 47 kJ mol^{-1} in poly(vinyltoluene). Similarly, the activation energy of 36 kJmol^{-1} increased to 46 kJmol^{-1} in the corresponding media for 3,3'-difluorobiphenyl. However, in the low temperature range 180-230K, the activation enthalpies for 2,2'-difluorobiphenyl in polystyrene and poly(vinyltoluene) were very similar, being 30 kJmol^{-1} and 36 kJmol^{-1} respectively; these values were near that of 34 kJmol^{-1} for 3,3'-difluorobiphenyl in poly(vinyltoluene). Moreover, the free energy of activation for these two biphenyls, $\sim$30 kJmol^{-1} at 300K, was found not changed in the different matrices for the low temperature process. This effect was not employed in the high temperature. The values of ΔG_{300K} were $\sim$30 kJmol^{-1} for 2,2'-difluorobiphenyl and $\sim$26 kJmol^{-1} for 3,3'-difluorobiphenyl in both polystyrene and poly(vinyltoluene). It seemed that the difference of activation free energy between molecules was exhibited more apparently in the high temperature process. Just as in the case of the activation enthalpy, the values of the entropy of activation are larger in poly(vinyltoluene) than in polystyrene within the same temperature range. The ΔS_E value of 25 J K^{-1} mol^{-1} increases to 55 $JK^{-1}mol^{-1}$ for 2,2'-difluorobiphenyl and that of 31 $JK^{-1}mol^{-1}$ to 65 $JK^{-1}mol^{-1}$ for 3,3'-difluorobiphenyl when the matrix is changed from polystyrene to poly(vinyltoluene). It is likely that the high temperature process obtained in the disubstituted biphenyls is more comparable to the molecular process for the rigid molecules in the different media.

In order to gain more informations about the influence of the medium, 2-nitro-, 2-bromo-, 3-nitro- and 3-bromobiphenyls were also studied in poly(vinyltoluene), then compared with those data in polystyrene. 3-nitrobiphenyl showed dielectric absorption in the temperature region, 256-301K, with an activation enthalpy of 57 $kJmol^{-1}$, an activation entropy of 49 $JK^{-1}mol^{-1}$ and an activation free energy of 42.5 $KJmol^{-1}$ at 300K, together with a relaxation time of 4.0 X 10^{-6}s at 300K in polystyrene. In poly(vinyltoluene), the corresponding values for 3-nitrobiphenyl were 76 $kJmol^{-1}$. 104 $JK^{-1}mol^{-1}$, 44.8 $kJmol^{-1}$, and 1.0 X 10^{-5}s respectively around the same temperatures. When compared with the analogous rigid molecules these parameters indicate that the molecular process was observed in, 3-nitrobiphenyl. Meanwhile, 2-bromobiphenyl, with a bigger halogen-atom at the ortho-position to replace the nitro-group of 3-nitrobiphenyl at the meta-position, gave a similar activation energy value of 57 $kJmol^{-1}$ and an entropy value of 72 $JK^{-1}mol^{-1}$ for the high temperature process in polystyrene, The corresponding values increased to 80 $kJmol^{-1}$ and 123 $JK^{-1}mol^{-1}$ respectively in poly(vinyltoluene) which are close to the values 76 $kJmol^{-1}$ and 104 $JK^{-1}mol^{-1}$ for 3-nitrobiphenyl. It would be expected that 2-nitrobiphenyl would have a smaller activation energy than 2-bromobiphenyl. In fact, 2-nitrobiphenyl yielded the value of 67 $kJmol^{-1}$ in poly(vinyltoluene) which as expected is larger than the value of 50 $kJmol^{-1}$ in polystyrene at the same temperatures, 233-277K. However, this remarkable feature was not apparent for 3-bromobiphenyl. Its size is larger than 3-nitrobiphenyl whilst the ΔH_E value of the former is only 72 $kJmol^{-1}$ which is less than that of 76 $kJmol^{-1}$ for the latter. This seems rather unusual. An overlap of intramolecular and molecular processes could account for this behaviour.

Another point to note is that the relaxation time for the solute to reorient in poly(vinyltoluene) is always longer than that in polystyrene. For example, 3-nitrobiphenyl has a relaxation time, τ_{300K}, of 4.0×10^{-6}s in polystyrene which lengthens to 1.0×10^{-5}s in poly(vinyltoluene). However, there is an exception in 3-bromobiphenyl. At 300K, the relaxation time of 3-bromobiphenyl in poly(vinyltoluene) is 4.8 X 10^{-7}s. It is shorter than that of 1.6 X 10^{-6}s in a polystyrene matrix around the temperature range between 26.-312K and leads to the conclusion that the overlapping process was exhibited for 3-bromobiphenyl, as discussed before.

From all the data obtained, the activation energy, ΔH_E, and relaxation time, τ, values in poly(vinyltoluene) are always higher than the corresponding values for those in polystyrene. The medium has played a considerable part in causing the difference in these parameters. A molecular process may be expected to indicate considerable variation in relaxation time and Eyring activation parameters by a change in local environment. However, an intramolecular process, such as the inter-rings rotation in biphenyls, may be expected to be somewhat reasonably independent of such a modification. The larger activation enthalpy, entropy and longer relaxation time obtained for non-rigid substituted biphenyls in poly(vinyltoluene) may be interpreted by the greater difficulty for such molecules to reorient in such a medium. In other words, it appeared that poly(vinyltoluene) was a more suitable matrix for the detection of the intramolecular rotation of biphenyls. However, owing to its high loss factor (ε'' is at least about twice or three times the value in polystyrene), the accuracy of the measurement of dielectric absorption could be decreased, particularly for the low dipole component solute molecules.

For the low temperature process found in poly(vinyltoluene), there is almost no variation of the activation energy among all substituted biphenyls. The ΔH_E values which were observed in the range 32-37 kJ mol^{-1} did not change with molecular size and the dihedral angle between the planes of the two rings. This is completely different from the remarkable features of a molecular process. Thus, the low temperature process is treated as an intramolecular one and will be discussed in more detail in Chapter VI for non-rigid substituted biphenyls.

The Eyring plot of log(τT) versus 1/T for 2-nitrobiphenyl in poly(vinyltoluene) is shown in Fig. V-4. The resultant plot fitted two intersecting straight lines. Crossley et al.(14) found two intersecting lines in the Eyring plot for a study of 2-acetylnaphthalene in polystyrene. They suggested that one could be ascribed to a molecular relaxation process and the other to group relaxation, where the overall absorption was dominated by different processes in the limits of lower and higher temperatures. The tail of the intramolecular peaks overlapped and extended into the absorption peaks due to the molecular rotation which was not apparent in the dielectric loss plots, but was shown in the Eyring plots. Therefore, it seems that the difference in viscosity and structure between polystyrene and poly(vinyltoluene) is still not sufficient enough to separate the molecular and intramolecular processes.

2,2'-Bipyridine was chosen for comparison with the substituted biphenyls. On comparison of 2,2'-difluorobiphenyl with 2,2'-bipyridine, which are very similar in size and main dipole positions, they would be expected to exhibit similar molecular relaxation times. Owing to the steric effect, a large dihedral angle (60°) was found in 2,2'-difluorobiphenyl and an even larger one in 2,2'-bipyridine which exhibits almost a trans-configuration and makes the molecule near coplanar.(15) One absorption process has been found for 2,2'-bipyridine in the medium of poly(vinyltoluene). If the process obtained belongs to the molecular relaxation, the Eyring parameters and relaxation time would be larger and longer as is apparent in these parameters for the rigid molecules. In fact, no experimentally significant difference in ΔH_E was obtained between the two polymer media. When the β value was considered, it was found to be in the range of 0.31 - 0.54 in polystyrene and 0.26 - 0.49 in poly(vinyltoluene) and is much larger for 2,2'-bipyridine than for the other biphenyl derivatives. In the same medium of poly(vinyltoluene), the values of activation of enthalpy and entropy for the two molecules, 2,2'-bipyridine and 2,2'-difluorobiphenyl, were comparable in the temperature range 187-232K. The corresponding values are 33kJ mol^{-1} and -24 J K^{-1} mol^{-1}, 36 kJ mol^{-1} and 10 J K^{-1} mol^{-1}, respectively. For 2,2'-difluorobiphenyl, this low temperature process was not considered to be a molecular process since the Eyring parameter increments of the molecule from polystyrene to poly(vinyltoluene) matrices were found for the high temperature process from 248-283K. The evidence seems to favour the occurrence of intramolecular rotation for 2,2'-bipyridine. However, a change was yielded in the free energy of activation between the two media. In polystyrene, the value of ΔG_{200K} was observed to be 33.9 kJ mol^{-1} for 2,2'-bipyridine which agreed well with that of 31.6 kJ mol^{-1} and 32.4 kJ mol^{-1} in 2,2'-difluorobiphenyl for both the low and high temperature processes. In poly(vinyltoluene), the value of the former was increased to 38 kJ mol^{-1} as compared to that of 36 kJ mol^{-1} for2,2'-difluorobiphenyl in the high temperature region which was considered to be a molecular process.

Another striking point is that owing to the small dipole moment around 0.61D, the loss factor of 2,2'-bipyridine in both media is always too low to be measured accurately, and this leads to appreciable error in the related parameters. It is difficult to decide whether it is an intramolecular or an overlap of the molecular and intramolecular process.

Evidence is not conclusive at the present time as to the type of relaxation mechanism responsible for the observed data. However, it would seem that the contribution from the molecular process would be very small.

CONCLUSION

Altogether, the experimental data indicated that the difference of the activation parameters and relaxation times was due to the influence of the medium on the dielectric absorption. Nevertheless, the structure of both polystyrene and poly(vinyltoluene) is not much different, and was not sufficient to separate the two processes completely in biphenyls. At least, from the Eyring graph of $\log\tau T$ vs. $1/T$, the overall absorption governed by the intramolecular process and the molecular process in the limits of low and high temperatures respectively was indicated. The intramolecular ring-ring rotation of biphenyl derivatives will be described in the next chapter.

Furthermore, some interesting work could be suggested for the future. If a non-polar polymer medium having a high glass transition temperature, low dielectric loss factor, and the chain structure sufficiently different from polystyrene and poly(vinyltoluene) were chosen, it should be feasible to separate the absorptions of the intramolecular and molecular processes.

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TABLE V-1 DIELECTRIC RELAXATION AND EYRING ACTIVATION PARAMETERS FOR SOME RIGID MOLECULES AND BIPHENYL DERIVATIVES IN POLY(VINYLTOLUENE)MATRICES

Molecule	T(K)	τ(s) 150K	τ(s) 200K	τ(s) 300K	ΔG_E(kJ mol^{-1}) 150K	ΔG_E(kJ mol^{-1}) 200K	ΔG_E(kJ mol^{-1}) 300K	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
4-Fluorobiphenyl	263 - 301	7.4×10^{7}	1.9×10^{1}	4.4×10^{-6}	58.5	53.2	42.7	74 ± 5	105 ± 16
4-Chlorobiphenyl	282 - 312	9.0×10^{11}	8.6×10^{3}	7.4×10^{-5}	70.2	63.4	49.8	91 ± 12	136 ± 39
4-Nitrobiphenyl	309 - 330	7.8×10^{17}	4.3×10^{7}	2.1×10^{-3}	87.3	77.5	58.1	117 ± 10	195 ± 33
4-Bromobiphenyl	307 - 336	2.5×10^{22}	7.2×10^{9}	1.8×10^{-3}	100.2	86.1	57.8	143 ± 7	283 ± 22
4-Phenylpyridine	236 - 277	4.8×10^{3}	9.8×10^{-2}	1.8×10^{-6}	46.5	44.5	40.5	52 ± 5	40 ± 19
1-Chloro-anthracene	255 - 298	6.5×10^{7}	2.8×10^{1}	1.0×10^{-5}	58.3	53.8	44.9	72 ± 9	90 ± 34
9-Bromo-anthracene	198 - 240	1.2×10^{1}	7.5×10^{-4}	4.3×10^{-8}	38.9	36.4	31.2	47 ± 2	52 ± 8
9-Bromo-phenanthrene	206 - 259	7.4×10^{0}	5.2×10^{-4}	3.2×10^{-8}	38.4	35.7	30.5	46 ± 5	53 ± 23

TABLE V-1 continued.....

Molecule	T(K)	τ(s) 150K	τ(s) 200K	τ(s) 300K	ΔG_E(kJ mol^{-1}) 150K	ΔG_E(kJ mol^{-1}) 200K	ΔG_E(kJ mol^{-1}) 300K	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
2,2'-Bipyridine	203 - 228	2.1×10^{0}	2.0×10^{-3}	1.7×10^{-6}	36.8	38.0	40.4	33 ± 6	-24 ± 28
2,2'-Difluoro-biphenyl	248 - 283	9.5×10^{0}	5.9×10^{-4}	3.2×10^{-8}	38.7	36.0	30.5	47 ± 3	55 ± 12
3,3'-Difluoro-biphenyl	233 - 263	1.1×10^{0}	8.8×10^{-5}	6.1×10^{-9}	36.1	32.8	26.3	46 ± 7	65 ± 27
2-Nitrobiphenyl	236 - 277	2.2×10^{5}	2.6×10^{-1}	2.7×10^{-7}	51.2	46.2	35.7	67 ± 5	103 ± 21
2-Bromobiphenyl	276 - 301	9.0×10^{8}	7.3×10^{1}	6.5×10^{-6}	61.6	55.5	43.4	80 ± 12	123 ± 43
3-Nitrobiphenyl	266 - 297	3.7×10^{8}	6.5×10^{1}	1.0×10^{-5}	60.5	55.3	44.8	76 ± 7	104 ± 26
3-Bromobiphenyl	283 - 312	3.4×10^{6}	1.4×10^{0}	4.8×10^{-7}	54.6	48.8	37.2	72 ± 17	116 ± 57

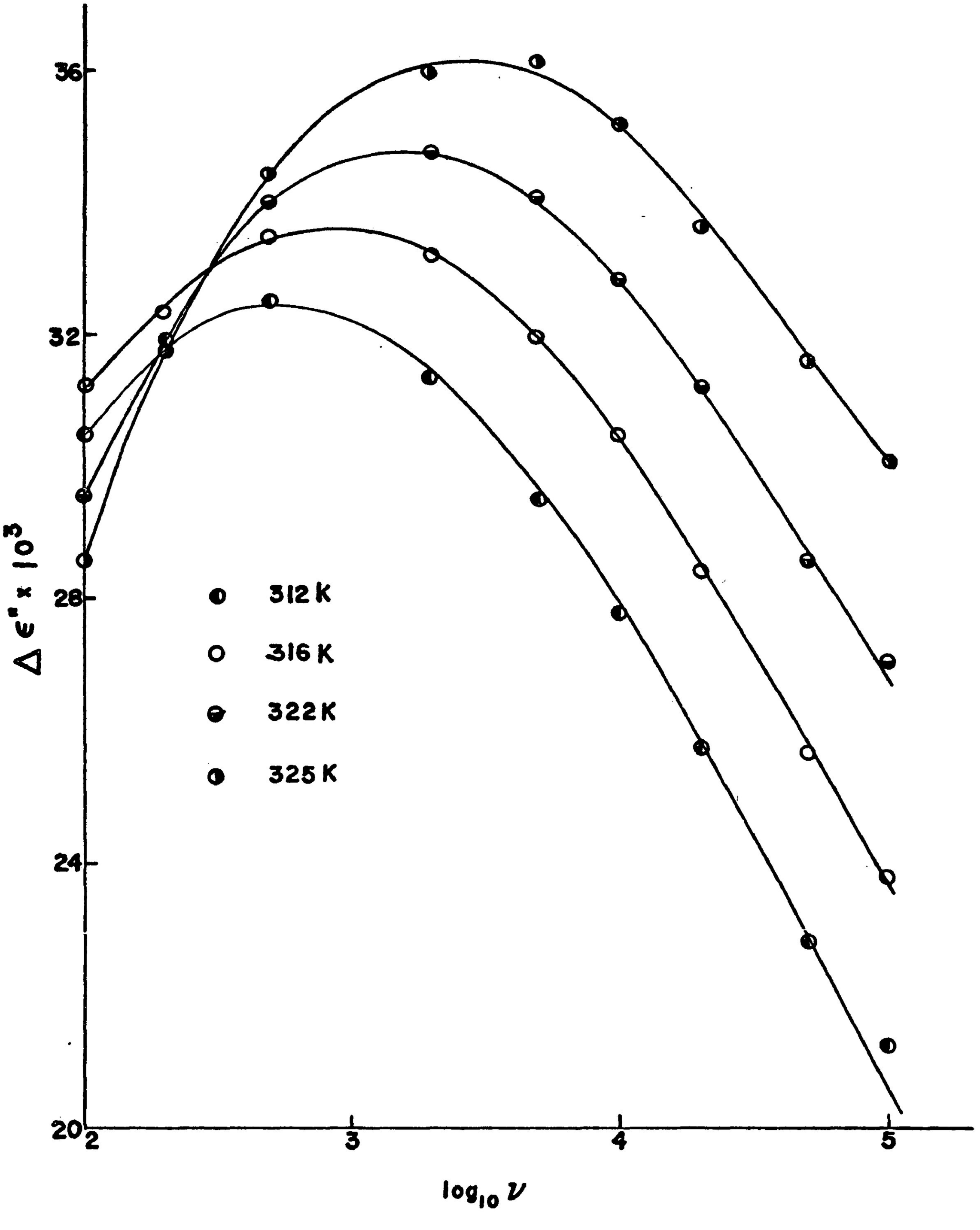


FIG. V-1: Dielectric Loss Factor $\Delta\varepsilon'' = \varepsilon''_{(matrix)} - \varepsilon''_{(poly(vinyltoluene))}$ vs. logν for 0.20M 4-Nitrobiphenyl in a Poly(vinyltoluene) Matrix.

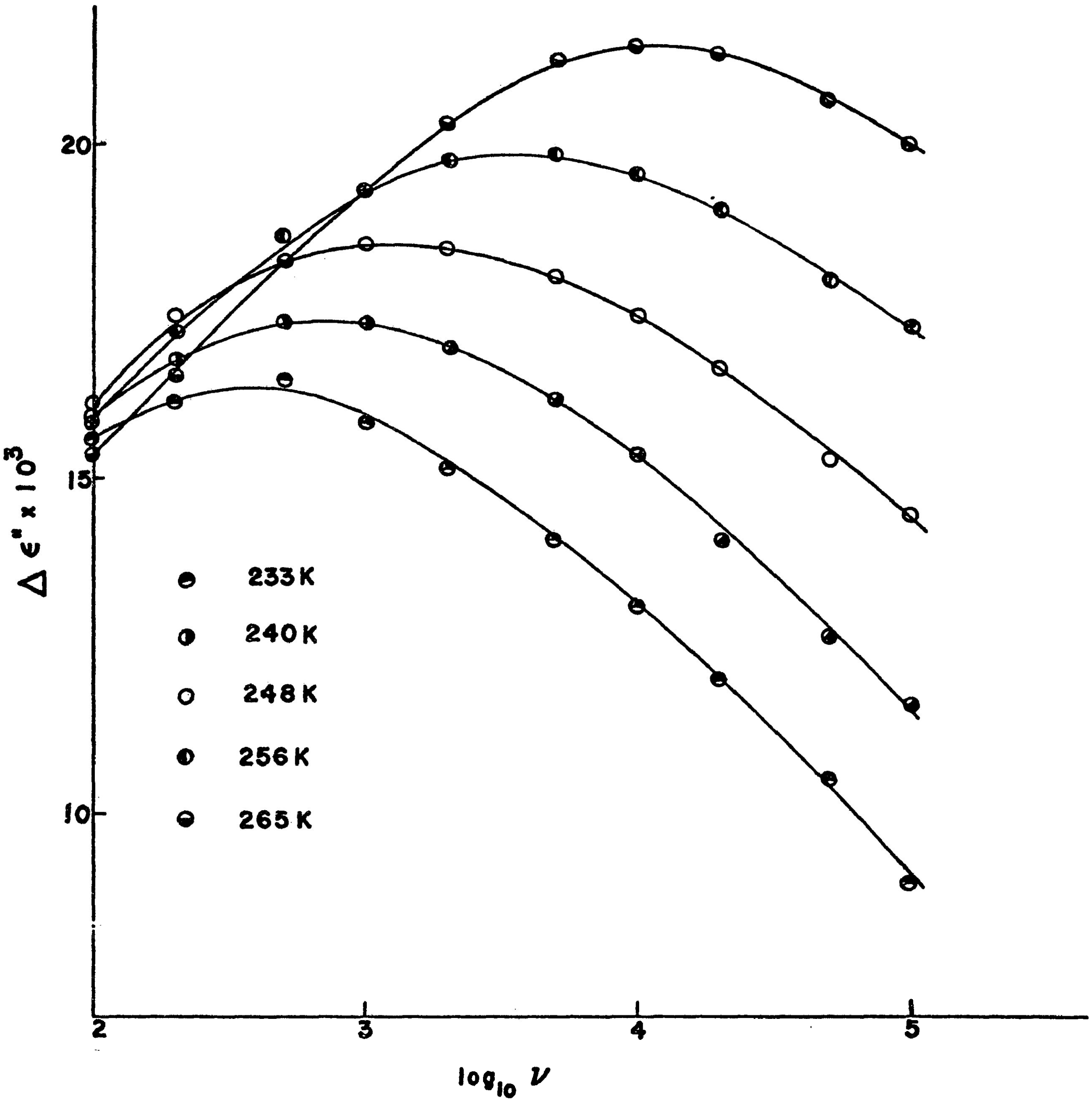


FIG. V-2: Dielectric Loss Factor Δε'' vs. logν for 0.32M 2-Nitrobiphenyl in a Poly(vinyltoluene) Matrix.

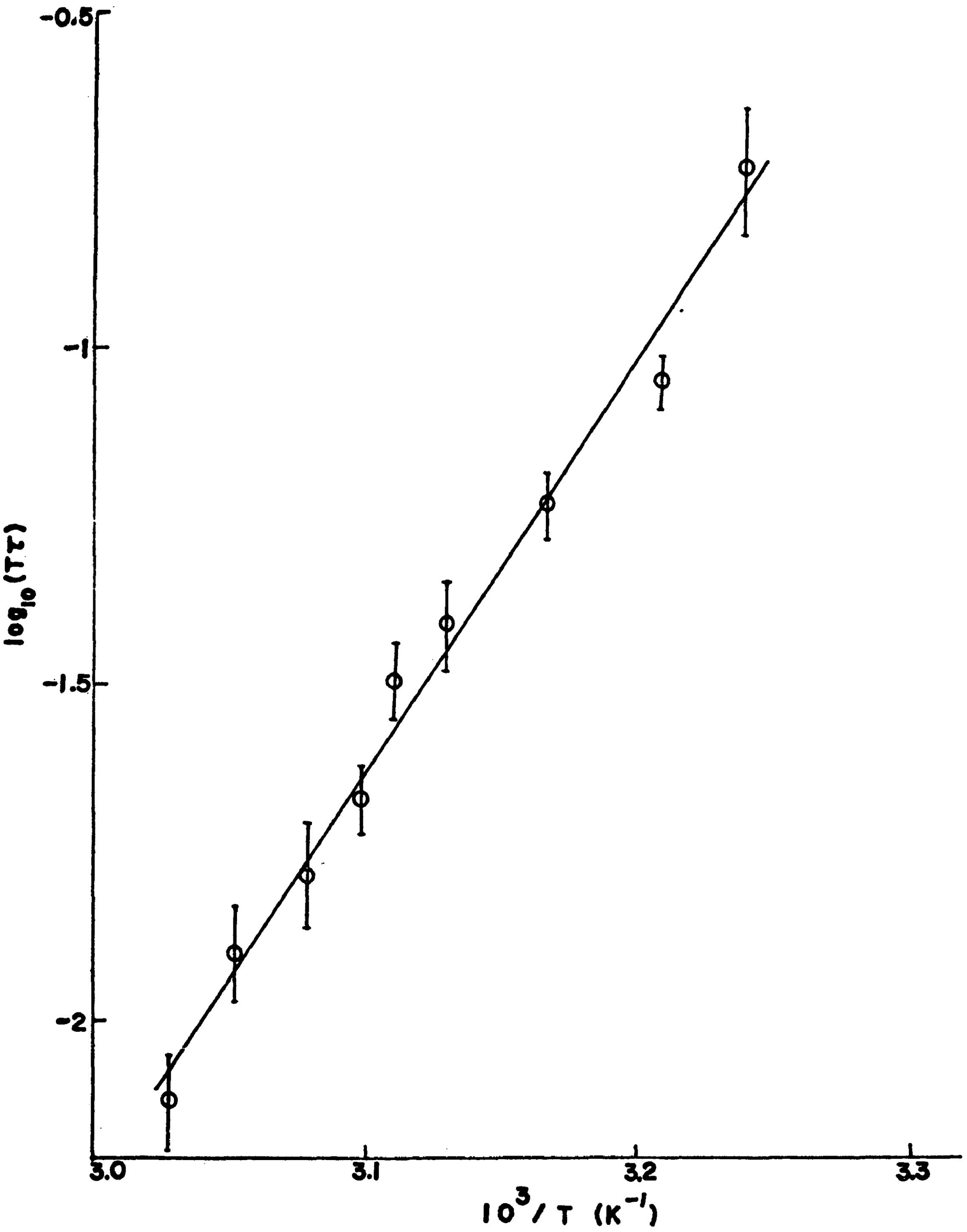


FIG. V-3: Eyring Plot of log(τT) vs. 1/T for 0.20M 4-Nitrobiphenyl in a Poly(vinyltoluene) Matrix. The Vertical Bars Represent 95% Confidence Intervals on log(τT) Values.

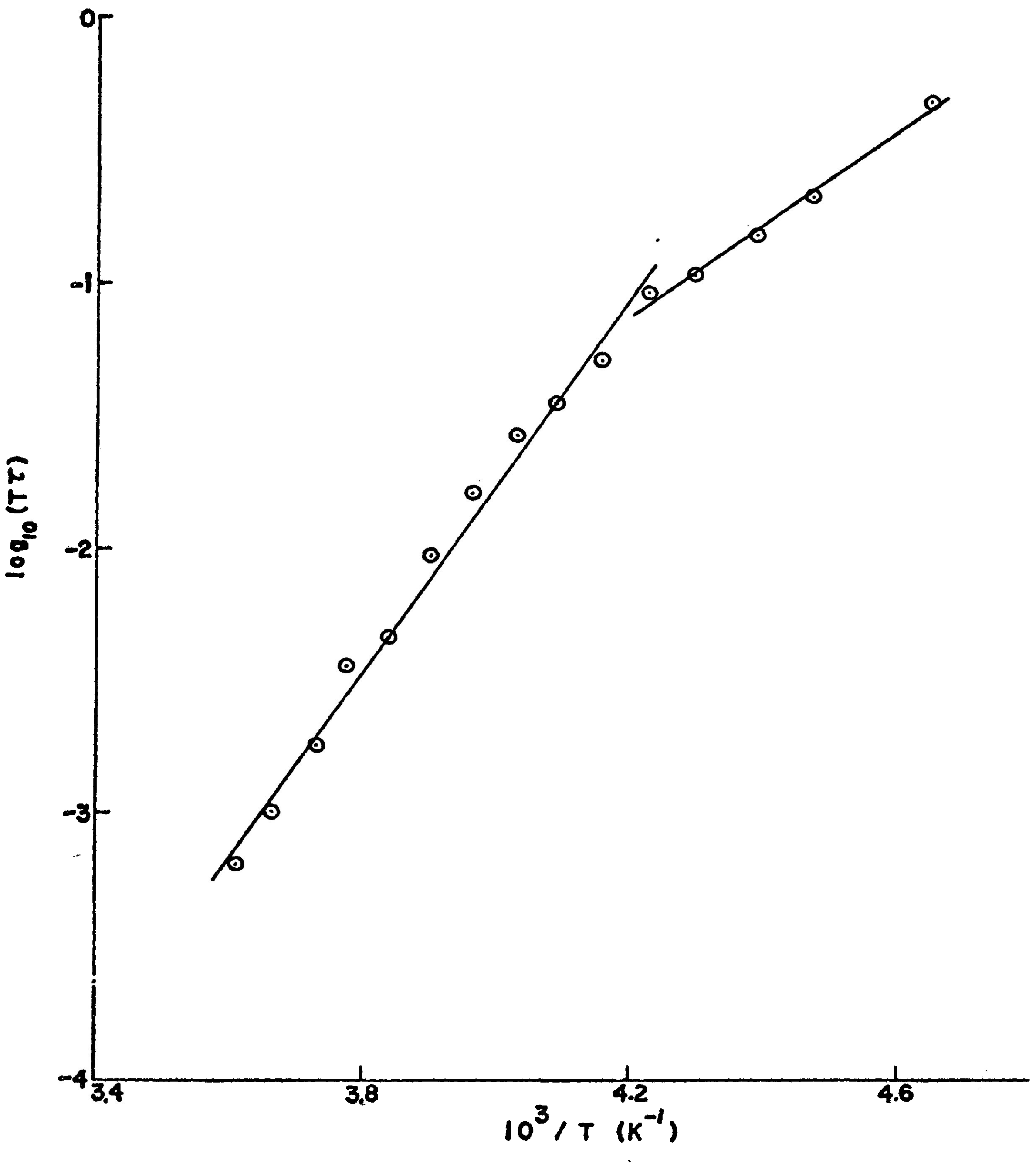


FIG. V-4: Eyring Plot of log(τT) vs. 1/T for 0.32M 2-Nitrobiphenyl in a Poly(vinyltoluene) Matrix.

CHAPTER VI

INTRAMOLECULAR MOTION OF BIPHENYLS

INTRAMOLECULAR MOTION OF BIPHENYLS

INTRODUCTION

The conformation of biphenyls has been intensively investigated theoretically and experimentally throughout the last forty years. It has been clearly ascertained that biphenyl is planar in the solid state by means of X-ray diffraction(1) whereas the two phenyl rings are twisted by 42°(2), and the potential barrier against rotation about the $C_{ar}—C_{ar}$ bond is 8.4 to 16.7 $kJmol^{-1}$ in the vapor phase by electron diffraction methods. It has been suggested by Bastiansen *et al.* that non-bonded interaction between hydrogen atoms is the cause of the non-planarity of biphenyl. Moreover, the repulsive part of this interaction, usually called steric hindrance, is generally recognized as an important factor for the determination of molecular conformation. Pauling(3) also suggested that steric interaction between the ortho-hydrogens should result in biphenyl being non-planar. The restricted rotation of barriers around the central carbon-carbon (C_1-C_1') single bonds between sp^2-type hybridized carbon atoms is determined predominately by the substituent effects and the steric hindrance effects. From the racemization approach an Arrhenius activation energy of 63.1 $kJmol^{-1}$ is reported for optically activated 2,2'-dimethylbiphenyl(4) to racemize at temperatures between 243 - 273K. The value obtained for the racemization of 2,2'-dibromo-4,4-dicarboxyl biphenyl is 75.2 $kJmol^{-1}$.(5)

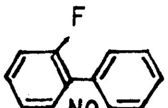
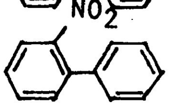
In regard to the conformation of the phenyl group in the ortho-alkylated biphenyls, Suzuki(6) proposed a correlation between the rotation angle of the two planar phenyl groups and the ultraviolet absorption spectra. Furthermore, Mislow *et al.*(7) and Hasegawa(8) also reported a similar correlation from n.m.r. studies.

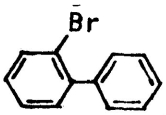
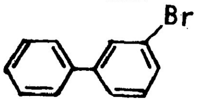
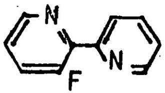
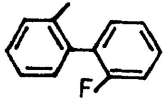
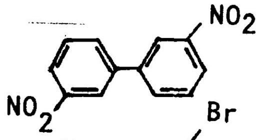
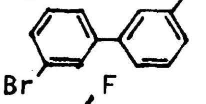
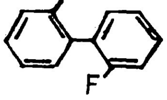
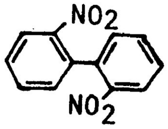
N.m.r. techniques have been used to investigate conformational changes in various types of molecules. The energy barriers which can be evaluated by n.m.r. are usually lower than 80 kJ mol^{-1}. The spin-lattice relaxation time studies in n.m.r. probed the information about internal motion in biphenyl derivatives.(9,10) In the study of biphenyl radical ions, Fong and Sullivan(11) showed that the conformation of, and barriers to rotation in, radical ions of biphenyl derivatives are greatly different from those of the neutral compounds. They predicted that both the biphenyl anion and cation radicals should have shorter $C_1 - C_1'$ bonds, more planar structure, and larger barriers to rotation through 90° than the neutral biphenyl molecule. A calculated value for rotation about the $C_1 - C_1'$ bond of 66.0 kJ mol^{-1} was found in the 4,4-dihydroxybiphenyl cation radical (12) and attributed to the increase of the bond order of the $C_1 - C_1'$ bond.

In the present work, the dielectric measurement of biphenyls in polystyrene and poly(vinyl toluene) was used to examine the factors that determine the internal relaxation about the C_1-C_1' bond. The substituted effects were studied in terms of the electromegativity of the substituents while the effects of the steric hindrance were investigated on the basis of the position and size of the substituents.

DISCUSSION

In a molecule such as biphenyl the resonance energy depends upon the double-bond character between the two phenyl rings. Fairly large deviations from coplanarity occur in biphenyl itself. It is interesting to have more information about the energy barrier for the inter-rings rotation of biphenyls through the dielectric study, owing to the partial double-bond character between the two phenyl rings still existing in spite of the hindered effects caused by the substituents. Accordingly, the following biphenyl derivatives were chosen for this study.

No.	Name	Structure	Matrices
1	2-Fluorobiphenyl		p.s.
2.	2-Nitrobiphenyl		p.s. & p.v.t.

No.	Name	Structure	Matrices
3	2-Bromobiphenyl		p.s. & p.v.t.
4	3-Bromobiphenyl		p.s. & p.v.t.
5	2,2'-Bipyridine		p.s. & p.v.t.
6	2,2'-Difluorobiphenyl		p.s. & p.v.t.
7	3,3,'-Dinitrobiphenyl		p.s.
8	3,3'-Dibromobiphenyl		p.s.
9	2,2'-Difluorobiphenyl		p.v.t.
10	2,2'-Dinitrobiphenyl		p.s.

The Eyring analysis results for all these molecules are presented in Table VI-1. It was found from the experimental data that the dielectric absorption of these biphenyls was complicated owing to an overlapping of group and molecular processes. The two absorption peaks are so close to each other that the Fuoss-Kirkwood analysis analyzes them as one process. The overlapping effect of the substituted biphenyls was revealed from the Eyring plot, where there are two intersecting lines fitted in the adjacent temperature region. 3,3'-Dinitrobiphenyl is an example, The corresponding plots of Fig. VI-1 and Fig. VI-2 exhibit the dielectric loss curve and Eyring plot of $\log\tau T$ against $1/T$. Crossley *et al.*(13) have reported dielectric relaxation in 2-acetylnaphthalene and found two such overlapping processes. The lower temperature (202 - 232K) data yielded ΔH_E of 34 kJ mol^{-1} and ΔS_E of -24 J K^{-1} mol^{-1}, while those at higher temperatures (242 - 277K) showed ΔH_E of 87 kJ mol^{-1} and ΔS_E of 179 J K^{-1} mol^{-1}. They indicated that these results suggested that the overall absorption is composed of the different processes in the limits of lower and higher temperature regions.

The low temperature absorption of 3,3'-dinitrobiphenyl in polystyrene gave activation enthalpy and entropy of 25 kJ mol^{-1} and -44 J K^{-1} mol^{-1} respectively. The results, compared with those for the smaller rigid molecule 4-phenylpyridine in the same medium, with ΔH_E of 38 kJ mol^{-1} and ΔS_E of -7 J K^{-1} mol^{-1}, suggested that the values of 3,3'-dinitrobiphenyl were too low to demonstrate a molecular reorientation. On the other hand, the activation enthalpy of 56 kJ mol^{-1} was obtained at the high temperature range which is relatively large in comparison with that of rigid 4-phenylpyridine. In consideration of the relaxation time, the value of 3.5×10^{-3} s at 200K for 4-phenylpyridine was larger than that of 1.8×10^{-4} s for 3,3'-dinitrobiphenyl in the low temperature process, whilst shorter than 7.8×10^{-3} s at its high temperature range. As mentioned in Chapter IV, a cooperative motion only occurred around the glass transition temperature which can be determined when the mean relaxation time is of the order of 100 s. It was found that Tg of polystyrene matrix at such dilute solutions studied here is higher than room temperature. Thus, neither of the processes for 3,3'-dinitrobiphenyl could be the cooperative one. In other words, it was more reasonable to allot the high temperature data of 3,3'-dinitrobiphenyl to the molecular relaxation and the low one to an intramolecular motion. At best though, the ΔH_E values are only limiting values owing to the overlap of the two processes.

Several molecules with 2,2'-disubstituents have also been investigated in polystyrene matrices. 2,2'-Difluorobiphenyl showed dielectric absorption at the low temperature range 183-230K, with a ΔH_E of 30 kJ mol^{-1}, a ΔS_E of -6 J K^{-1} mol^{-1}, and ΔG_{200K} of 33.4 kJ mol^{-1} respectively, which agreed well with the theoretical data $\sim$33.4 kJ mol^{-1} of Farbrot and Skancke(14). They estimated the equilibrium conformations and the barriers for the internal rotation in a series of ortho-substituted fluorobiphenyls from a theoretical study. The gross-features of the method were considered by the variation of the π-electron energy (E_π), the core energy (E^{core}), and the van der Waals interaction between non-bonded atoms (E_{nb}), as functions of the angle of rotation around the central $C_1 - C_1'$ bond. The total π-electron energy is given by:

$$E_\pi = \sum_i (\varepsilon_i + < \psi_i \mid H^{core} \mid \psi_i >) \qquad (VI-1)$$

where ε_i are the eigenvalues of the self-consistent Fock operator, and $< \psi_i \mid H^{core} \mid \psi_i >$ are matrix elements in the molecular orbital representation. The sum of E_π and the core-repulsion energy is:

$$E = E_\pi + E^{core} \qquad (VI-2)$$

As both E_π and E^{core} vary by changing conformations of the molecules, E given by Eqn. (VI-2) will be a function $E(\phi)$ of the angle of rotation around the bond $C_1 - C_1'$. The conjugation energy is obtained from the relation:

$$E_{conj} (\phi) = E (\phi) - E (90^o) \qquad (VI-3)$$

The van der Waals interaction energy E_{nb} between two atoms or groups is expressed as a function of the interatomic distance r_p. The well-known formula due to Hill$^{(15)}$ is given as:

$$E_{nb} = -2.25\ \varepsilon(r^*/r)^6 + 8.28 \times 10^5\ \varepsilon \exp(-r/0.0736\ r^*) \quad (VI-4)$$

where r* and ε are the interaction parameters. r* represents the sum of van der Waals radii of interatoms or intergroups while ε is a parameter specific to them. The numerical values of these parameters and of the appropriate van der Waals radii were taken from a compilation by Eliel *et al.*(16) The variation of the total energies against the different angle of rotation for 2,2'-difluorobiphenyl in Fig. VI-3 indicated that two energy minima were found, one at around 45° from the planar cis-form, and the other at about 150°. The energy difference between these conformers and the one corresponding to $\phi = 90^{\circ}$ was found to be around 30.9 kJ mol^{-1}. It is remarkable to see that the experimental data of activation energy, 30 kJ mol^{-1}, is of the same order as the theoretical value of Farbrot and Skancke as the activation entropy approached zero. The relaxation of rotation around the C_1-C_1' bond through a limited angle may be interpreted as due to the steric hindrance offered by the fluorine atoms. In a biphenyl

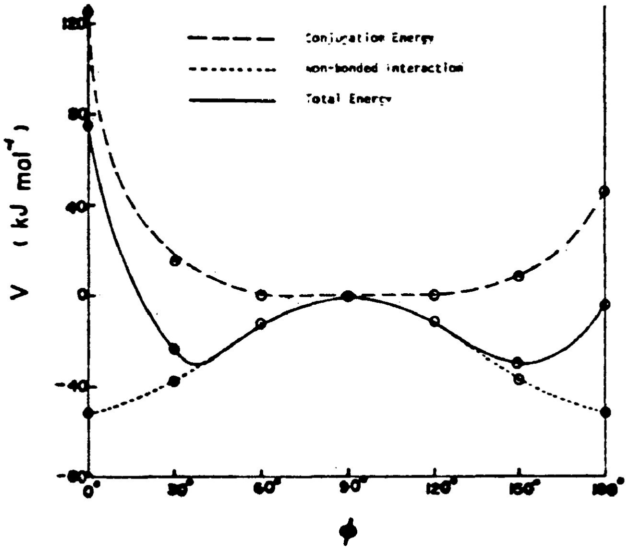
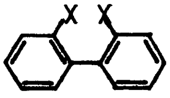
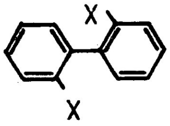


FIG. VI-3: The Potential Energy for the Inter-rings Rotation of 2,2'-Difluorobiphenyl.

containing one ortho-substituent in each ring, there are two possible limiting conformations with the closest approach to coplanarity in the cis-conformation (A) and the trans-conformation (B). Both the electron diffraction data(17) and the dipole moment studies(18) indicated that in this group of compounds, the values obtained for the equilibrium inter-planar angle (ϕ) correspond nearer to cis-conformations.



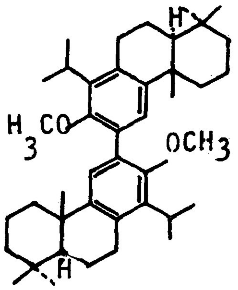
(A)



(B)

As a result, 2,2'-difluorobiphenyl was found to be a non-planar cis-formation where the angle of rotation was around 60°.(17)

From the dielectric results reported here on increasing the size and volume of the substituents from 2,2'-difluoro-, 2,2'-dinitro-, to 2,2'-dibromobiphenyls, the activation enthalpy and entropy were found relatively changed from 30 kJ mol^{-1} and -6 $\text{J K}^{-1}\text{ mol}^{-1}$; 28 kJ mol^{-1} and -39 $\text{J K}^{-1}\text{ mol}^{-1}$; to 22 kJ mol^{-1} and -58 $\text{J K}^{-1}\text{ mol}^{-1}$, respectively. The same effect in a series of 2,2'-disubstituted biphenyls has been studied by u.v. absorption sepectroscopy; Beaven and Hall(19) reported that even a single substituent in one of the ortho-positions of biphenyl resulted in a detectable blue shift and reduction in intensity of the conjugation band. In the case of 2,2'-dihalobiphenyls, the blue shift and intensity reduction are progressively larger from F- to Br-; in 2,2'-di-iodobiphenyl, the spectrum does not show a conjugation band. A value of inter-planar angle (ϕ:75°) was found in 2,2'-dibromobiphenyl by Bastiansen.(17) It is notable that the significantly lower barrier to the inter-ring rotation as obtained here for 2,2'-dibromobiphenyl is to be attributed to the decrease of conjugation along the C_1 - C_1' bond for the large dihedral angle (ϕ). In the n.m.r. study of podototarin derivatives,(21) Colebrook and Jahnke determined the activation energy of podototarin dimethyl ether

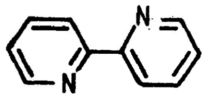


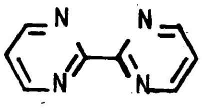
Podototarin Dimethyl Ether

around 25.1 kJ mol^{-1} and the entropy of activation around -31 J K^{-1} mol^{-1}. It is likely that the rotation around the C_1 - C_1' bond could be through a small angle owing to the steric hindrance and the conjugated effects offered by the substituents.

In view of the work on 2,2'-disubstituted biphenyls, where the molecule is far from planar, it is of interest to study 2,2'-

bipyridine, where the ortho substituents have been replaced by the more polarizable nitrogen lone-pairs. In order to know the behaviour of 2,2'-bipyridine, it is feasible to compare it with a simple model molecule pyridine. Relaxation times for pyridine in carbon tetrachloride solution have been reported between 5.0×10^{-12} s and 7.8×10^{-12} s at 298K. If the bipyridine molecules were rigid, the Debye relaxation time would be longer than that of pyridine; however, a relaxation time, τ_{300K}, of 2×10^{-12} s was observed in carbon tetrachloride. Rather the short relaxation time for 2,2'-bipyridine indicated a rapid intramolecular rotation, and a preference for the trans-configuration may be expected owing to its small dipole moment about 0.61D. Coulson(20) proposed that there are two effects appearing in 2,2'-dipyrimidine and 2,2'-bipyridine, which are not found in the biphenyl situation. These are (1) forces due to the formal charges on the N atoms leading to a tendency to rotate from planarity; and (2) interactions of a dipole-dipole type, arising from the lone-pair electrons on the N-atoms, which would appear to increase the force


2,2'-Bipyridine


2,2'-Dipyrimidine

of deformation. From electron diffraction measurement on the vapor state, Bastiansen(22) found a mean interplanar angle of 20° from the trans-configuration and reported that the spectrum indicated the inter-ring rotation through large angles. N.m.r. measurements of the chemical shift between the 3,3'- and 5,5' protons have been interpreted to support the trans-configuration for 2,2'-bipyridine in dilute solution.(23) X-ray evidence showed a trans-configuration for solid 2,2'-bipyridine(24) as well. Thus, the high conjugation of the C_1 - C_1' bond would give the bond appreciable double bond character and restrict the freedom of rotation about this bond. From the present dielectric absorption of 2,2'-bipyridine in polystyrene, an activation energy of 36 kJ mol^{-1} was obtained with a relaxation time of 1.7 x 10^{-4} s at 200K. Furthermore, the high β value, in the range 0.31 - 0.54, indicated a relatively narrow distributions of relaxation times and is close to those observed by Davies and Swain(25) for the intramolecular ring inversion of cyclohexyl derivatives. They commented that "the increase in β would be expected for an intramolecular dipole motion as this would be appreciably less dependent upon the cooperative movement of the adjacent polystyrene units than is the whole molecular rotation". It is also noted that the dipole values slightly decreased from 0.24D to 0.20D as the temperature increased from 193 to 230K. These features indicate that for the molecule 2,2'-bipyridine the process observed is not solely molecular relaxation.

In a comparison of 2,2'-dibromobiphenyl with 2,2'-bipyridine, the former is much larger in size and in twisting angle. It is not feasible for 2,2'-dibromobiphenyl with a smaller energy barrier of 22 kJ mol^{-1} to be ascribed to a molecular relaxation. Hence, the inter-ring rotation may be found for 2,2'-dibromobiphenyl at the low temperature range 187 - 217K. Meanwhile, it is reasonable for 2,2'-bipyridine to employ a higher energy barrier owing to the restricted reorientation for the high conjugated $C_1 - C_1'$ bond.

So far as can be seen, the increasing ortho-substitution is known to result in increasing rotation around the central "single" bond. Therefore, work of monosubstituted biphenyls would also be very worthwhile. Only one absorption process has been detected for 2-fluorobiphenyl in the polystyrene medium at the temperatures between 193-230K. It offered the value of 32 kJ mol^{-1} for the activation enthalpy and that around zero for the entropy of activation. Farbrot *et al.*(14) have demonstrated 2-fluorobiphenyl in their theoretical study and noted that it has an energy minimum at around 30° rotation from the planar. The rotation angle is somewhat smaller than that observed by Bastiansen(2), namely 49 ±5°. The predicted value of the barrier for the internal rotation in this molecule is around 33.4 kJ mol^{-1}. The potential energy curve, plotted in Fig. VI-4, showed a probable relaxation of the rotation around the $C_1 - C_1'$ bond through

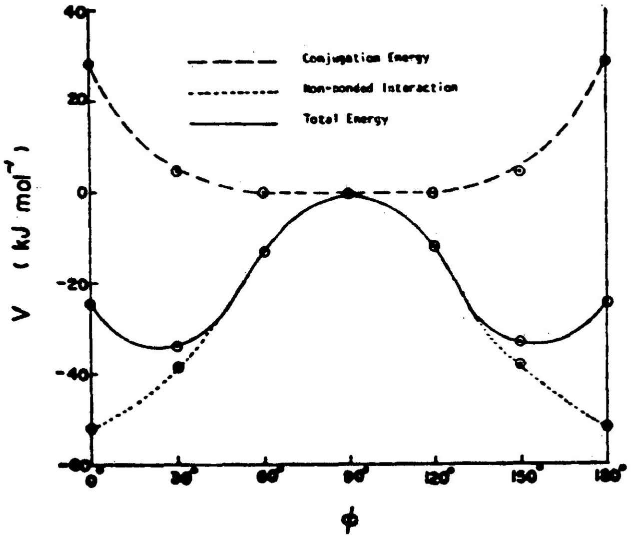


FIG. VI-4: The Potential Energy for the Inter-rings Rotation of 2-Fluorobiphenyl.

30° to 150°. Owing to the entropy of activation approaching zero, the present value of activation energy is in qualitative agreement, and internal rotation may be ascribed for 2-fluorobiphenyl. However, according to the molecular size and dipole direction, the molecular process has a similar energy barrier in the temperature range of observation. This is borne out by the low β values in the range 0.18 - 0.20 which suggest that some contribution to the molecular relaxation may be involved with the intramolecular ring-ring rotation for 2-fluorobiphenyl.

Another two ortho-substituted biphenyls, namely, 2-nitrobiphenyl and 2-bromobiphenyl were chosen in the same matrix polystyrene. Owing to the steric hindrance of the ortho-substituent, the reduction of conjugation between the two phenyl rings can be considered. Therefore, analogous energy barriers for 2-bromo- and 2-nitrobiphenyl to rotate in a certainly limited angle may be expected as in the case for 2-fluorobiphenyl. Experimentally, in the temperature range 204-233K, the corresponding values of ΔH_E and ΔS_E for both molecules were 36 kJ mol^{-1} and -12 J K^{-1} mol^{-1}, 31 kJ mol^{-1} and -35 J K^{-1} mol^{-1}, respectively. They are in the same order as those of 2-fluorobiphenyl.

In the present work the only meta substituted biphenyl with an overlap process observed in polystyrene is 3-bromobiphenyl. A quite small activation enthalpy of 25 kJ mol^{-1} and an activation entropy of -74 J K^{-1} mol^{-1} were obtained in the temperature range 228 - 261K. These values are much too small to be attributed to a molecular relaxation process, since, for example, the rigid molecule 2-bromonaphthalene$^{(27)}$ which is smaller in size, has the corresponding values of 34.7 kJ mol^{-1} and 0.4 J K^{-1} mol^{-1}. Thus, the absorption process observed here must relate to an intramolecular one.

Apart from the activation enthalpy discussed, there are several remarkable features to show the correlation with the behaviour of intramolecular motion.

It is interesting to note that, independent of the size and volume of the molecules, an apparent free energy of activation at 200K ∿33 ±3 kJ mol^{-1} was obtained in the polystyrene matrices study of these molecules. The value is quite different from those of rigid molecules which always exhibit increasing ΔG_E with increasing size of the molecules for a molecular process in a given temperature range. It seems strongly evident that the absorption examined at low temperatures between 180 - 240K in polystyrene was mainly attributed to the inter-ring rotation for all substituted biphenyls.

In view of medium studied in Chapter V, the variation of activation parameters was found to be apparent for the molecular process. Meanwhile, since the free volume of poly(vinyltoluene) would be rather small, its probability of separating different processes is expected to be better than that of polystyrene. 2,2'-Difluorobiphenyl in poly(vinyltoluene) gave an activation enthalpy of 36 kJ mol^{-1} and an activation free energy of 33 kJ mol^{-1} at 200K. They are comparably close to the data observed in polystyrene around the same temperatures. The intramolecular rotation of 3,3'-difluorobiphenyl which is not readily apparent in polystyrene is revealed in poly(vinyltoluene), though it still involved an overlap of the molecular and intramolecular processes. The activation energy for the inter-ring rotation in poly(vinyltoluene) for 3,3'-difluorobiphenyl was found to be 34 kJ mol^{-1}, with an activation entropy of 15 J K^{-1} mol^{-1} and free energy ΔG_{200K} of 31.1 kJ mol^{-1}, respectively. Similar results are observed for the low temperature absorptions of 2-nitrobiphenyl and 2-bromobiphenyl, i.e., there is no relative change in ΔH_E with the different media. The corresponding values of ΔH_E in poly(vinyltoluene) are 34 kJ mol^{-1} and 32 kJ mol^{-1} which agreed well with the ΔH_E of 36 kJ mol^{-1} for 2-nitrobiphenyl and 31 kJ mol^{-1} for 2-bromobiphenyl in poly(vinyltoluene). These absorptions are neither influenced by the matrices nor relevant to the substituted groups. 3-Bromobiphenyl in poly(vinyltoluene) employed an activation enthalpy of 37 kJ mol^{-1} and an activation entropy of -17 J K^{-1} mol^{-1} which are higher than those in polystyrene. In this case the difference of the activation energy for 3-bromobiphenyl in both media may be due to the error of activation energy in poly(vinyltoluene) through the overlap of the absorption of the two processes. However, the size and shape of the molecules for the intramolecular rotation are much less dependent on the medium. As a consequence in the study of activation energy in both polystyrene and poly(vinyl toluene), the activation energy from either the low or high temperature part of the absorption is in appreciable error. In the ^{13}C n.m.r. study, Levy *et al.*(27) measured ^{13}C spin-lattice relaxation times (T_1's) of the compound 3-aminobiphenyl in various solvent systems and found that both molecular tumbling and internal motion have to be considered. There would appear to be little doubt that the low temperature values are related to the inter-rings rotation while the high ones mentioned in Chapter IV and V are related to molecular relaxation.

On consideration of the free energy of activation, 3-bromobiphenyl had an activation free energy of 41.9 kJ mol^{-1} in poly(vinyl toluene) and 47.1 kJ mol^{-1} in polystyrene. These values are in good agreement with ΔG_{311K} of 40.5 kJ mol^{-1}, which was estimated from the n.m.r. study of the effective rotational correlation time (τ_{eff}).(28) Similarly, an approximately constant value of ΔG_{200K} 38 ±2 kJ mol^{-1} was obtained for mono-substituted biphenyls in both media, as in the case of disubstituted biphenyls with values of 33 ±3 kJ mol^{-1}. This showed the feature for the C_1-C_1' bond rotation examined in the present study.

The relaxation distribution parameter β is another point to note. In general, low β values imply a wide range of relaxation times which suggest a molecular process. The β values for rigid biphenyls are in the range 0.16 - 0.20.These are lower than those over 0.2 in the other biphenyl derivatives. It also shows those β values observed for biphenyls in the low temperature region are higher than those for rigid molecules. For instance, β is 0.25 - 0.28 for 2,2'-difluorobiphenyl, 0.23 - 0.27 for 2-bromobiphenyl in polystyrene, and 0.24 - 0.26 for 3-bromobiphenyl in poly(vinyl toluene). Particularly, the β value for 2,2'-bipyridine is relatively high at a similar temperature range, being 0.31 - 0.54 in polystyrene. Thus, the β values, in general, favour the presence of an intramolecular process in these systems.

Levi(29) explained the negative entropy changes found in certain dielectric relaxation processes. Negative values of ΔS_E should always be expected to be accompanied by low values of ΔH_E. It can be inferred that if a given polar molecule, is dispersed in a solvent and rotates in an electric field, it causes little lattice disorganization and will show a negative entropy. If no appreciable energy is required for lattice disorganization, such as is the case for intramolecular rotation, which causes less surrounding disturbance, the negative entropy term would be concerned. In the present data, negative or quite small entropies of activation were found for the low temperature process for these biphenyl derivatives. This is in good agreement with the behaviour for inter-ring rotation.

With regard to the dihedral angle, the activation energy does not increase with the increase of the dihedral angle as mentioned in the molecular process. On the contrary, the bigger the twisting angle, and the less the resonance energy to be overcome, the smaller ΔH_E should be expected. The dihedral angle for 2-fluorobiphenyl (49°) is smaller than that for 2-bromobiphenyl (74°). Thus, it would be expected that the 2-bromobiphenyl might have the lower ΔH_E for the intramolecular process. The ΔH_E value of 31 kJ mol^{-1} for the low temperature absorption in 2-bromobiphenyl is similar to that in 2-fluorobiphenyl, (32 kJ mol^{-1}). It is possibly due to the overlap effect in polystyrene. On the other hand, the influence of the dihedral angle was more apparent in di-substituted biphenyls, especially for 2,2'-disubstituted biphenyls in their low temperature processes. The dihedral angle of bromo- ($\phi:75^{\circ}$) is more twisted than that of the nitro-group ($\phi:60^{\circ}$)(30) and fluoro- ($\phi:60^{\circ}$). The activation energy obtained was increased in the order of bromo- (22 kJ mol^{-1}), nitro-group (28 kJ mol^{-1}), then fluoro- (30 kJ mol^{-1}) in polystyrene. This is the expected sequence for an intramolecular process since the larger twisting angle is less than the conjugation between C-C_1 bond and a smaller activation energy is needed to overcome the rotation barrier. The ΔH_E values for 2,2'-dinitro- and 2,2'-difluorobiphenyl are virtually the same as ~~is~~ the twist angle ($\phi:60^{\circ}$). Thus, although the sizes and polarity of these groups differ the fact that the intramolecular rotational angle is similar appears to lead to a similar intramolecualr rotational barrier.

Altogether, it would seem that the low temperature process in substituted biphenyls involves rotation around the central C_1-C_1' bond.

CONCLUSION

This study showed that the dielectric data indicated a contribution from the intramolecular C_1-C_1' bond in the different substituted biphenyls for cases where the dipole does not lie along the long axis. The steric and conjugative effects of internal rotation in a biphenyl compound have gradually become more understood.(9,26) The experimental results show that the low value of ΔH_E is found in the range 15 to 35 kJ mol^{-1} for those substituted biphenyls. This ΔH_E value is somewhat larger than some literature values,(10,31) but is in good agreement with the other approaches.(9,21) In conclusion, the dielectric study of the intramolecular motion of biphenyls bore out that intramolecular motion occurs and gives at least a rough estimate of the magnitude of the energy barrier for the process.

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TABLE VI-1 DIELECTRIC RELAXATION AND EYRING ACTIVATION PARAMETERS FOR SOME BIPHENYL DERIVATIVES IN BOTH POLYSTYRENE AND POLY(VINYLTOLUENE) MATRICES

Molecule	T(K)	τ(s)			ΔG_E(kJ mol^{-1})			ΔH_E	ΔS_E
		150K	200K	300K	150K	200K	300K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
(In polystyrene) 2-Fluorobiphenyl	183 - 239	4.3×10^{-2}	5.3×10^{-5}	5.9×10^{-8}	32	32	32	32 ± 3	0 ± 14
2-Nitrobiphenyl	204 - 233	5.1×10^{0}	2.8×10^{-3}	1.3×10^{-6}	37.9	38.5	39.7	36 ± 4	-12 ± 19
	233 - 272	2.7×10^{2}	9.2×10^{-3}	2.8×10^{-7}	42.9	40.5	35.8	50 ± 5	47 ± 18
2-Bromobiphenyl	204 - 228	1.5×10^{0}	2.2×10^{-3}	2.9×10^{-6}	36.4	38.2	41.7	31 ± 4	-35 ± 19
	248 - 313	4.6×10^{3}	3.6×10^{-2}	2.5×10^{-7}	46.4	42.8	35.6	57 ± 4	72 ± 14
3-Bromobiphenyl	228 - 261	1.1×10^{0}	5.6×10^{-3}	2.6×10^{-5}	36.0	39.7	47.1	25 ± 5	-74 ± 22
	261 - 323	1.6×10^{6}	1.7×10^{0}	1.6×10^{-6}	53.7	49.2	40.3	67 ± 4	90 ± 12
2,2'-Bipyridine	193 - 230	2.9×10^{-1}	1.7×10^{-4}	8.7×10^{-8}	34.3	33.9	32.9	36 ± 2	9 ± 11
2,2'-Difluorobiphenyl	183 - 230	2.5×10^{-2}	4.2×10^{-5}	6.3×10^{-8}	31.3	31.6	32.2	30 ± 1	-6 ± 5
	230 - 274	1.7×10^{-1}	7.2×10^{-5}	2.6×10^{-8}	33.7	32.4	29.9	38 ± 3	25 ± 14
2,2'-Dinitrobiphenyl	185 - 206	1.4×10^{-1}	4.1×10^{-4}	1.1×10^{-6}	33.4	35.4	39.3	28 ± 2	-39 ± 11
	212 - 247	8.8×10^{-1}	3.4×10^{-4}	1.2×10^{-7}	35.7	35.0	33.7	38 ± 2	14 ± 9
2,2'-Dibromobiphenyl	187 - 217	1.8×10^{-2}	1.6×10^{-4}	1.3×10^{-6}	30.9	33.8	39.6	22 ± 3	-58 ± 16
	215 - 293	2.5×10^{0}	3.7×10^{-4}	4.8×10^{-8}	37.0	35.2	31.5	43 ± 3	37 ± 13
3,3'-Dinitrobiphenyl	193 - 259	3.6×10^{-2}	1.8×10^{-4}	7.7×10^{-7}	31.7	33.9	38.0	25 ± 3	-44 ± 13
	259 - 311	7.2×10^{2}	7.8×10^{-3}	7.5×10^{-8}	44.1	40.2	32.6	56 ± 8	77 ± 27

TABLE VI-1 continued.....

Molecule	T(K)	τ(s)			ΔG_E(kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
		150K	200K	300K	150K	200K	300K		
(in poly(vinyltoluene))									
2-Nitrobiphenyl	215 - 236	9.9×10^{0}	9.1×10^{-3}	7.4×10^{-6}	38.7	40.5	44.0	34 ± 4	-35 ± 19
	236 - 277	2.2×10^{5}	2.6×10^{-1}	2.7×10^{-7}	51.2	46.2	35.7	67 ± 5	103 ± 21
2-Bromobiphenyl	236 - 276	1.7×10^{1}	2.3×10^{-2}	2.7×10^{-5}	39.4	42.0	47.2	32 ± 4	-52 ± 16
	276 - 301	9.0×10^{8}	7.3×10^{1}	6.5×10^{-6}	61.6	55.5	43.4	80 ± 12	123 ± 43
3-Bromobiphenyl	229 - 244	1.6×10^{1}	7.6×10^{-3}	3.2×10^{-6}	39.4	40.2	41.9	37 ± 10	-17 ± 42
	283 - 312	3.4×10^{6}	1.4×10^{0}	4.8×10^{-7}	54.6	48.8	37.2	72 ± 17	116 ± 57
2,2'-Bipyridine	203 - 228	2.1×10^{0}	2.0×10^{-3}	1.7×10^{-6}	36.8	38.0	40.4	33 ± 6	-24 ± 28
2,2'-Difluoro-biphenyl	187 - 232	2.1×10^{-1}	1.3×10^{-4}	7.1×10^{-8}	33.9	33.4	32.4	36 ± 1	10 ± 6
	248 - 283	9.5×10^{0}	5.9×10^{-4}	3.2×10^{-8}	38.7	36.0	30.5	47 ± 3	55 ± 12
3,3'-Difluoro-biphenyl	180 - 233	3.2×10^{1}	3.2×10^{-5}	2.3×10^{-8}	39.6	31.1	30.0	34 ± 2	15 ± 11
	233 - 263	1.1×10^{0}	8.8×10^{-5}	6.1×10^{-9}	36.1	32.8	26.3	46 ± 7	65 ± 27

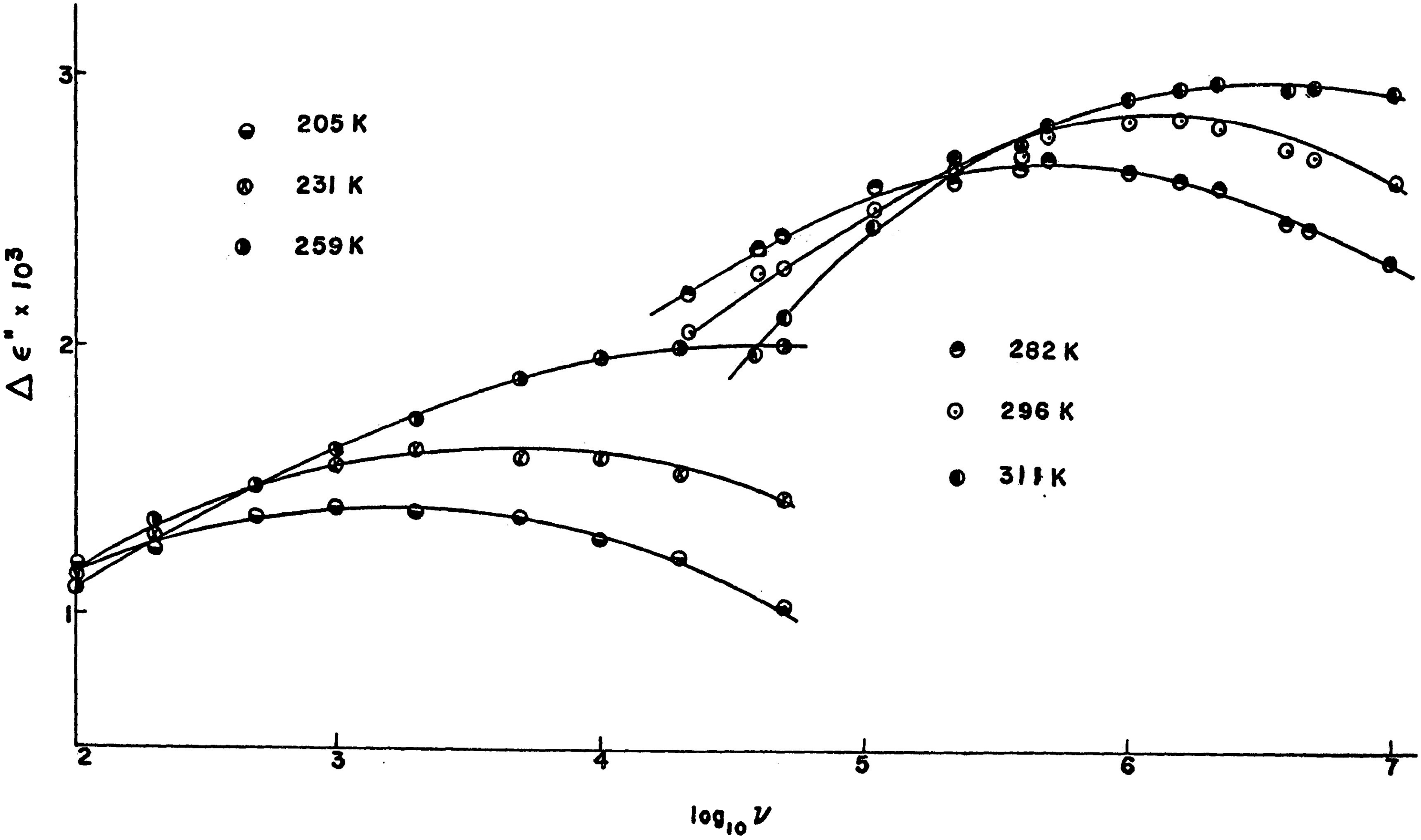

FIG. VI-1: Dielectric Loss Factor Δε" vs. logν for 0.31M 3,3'-Dinitrobiphenyl in a Polystyrene Matrix.

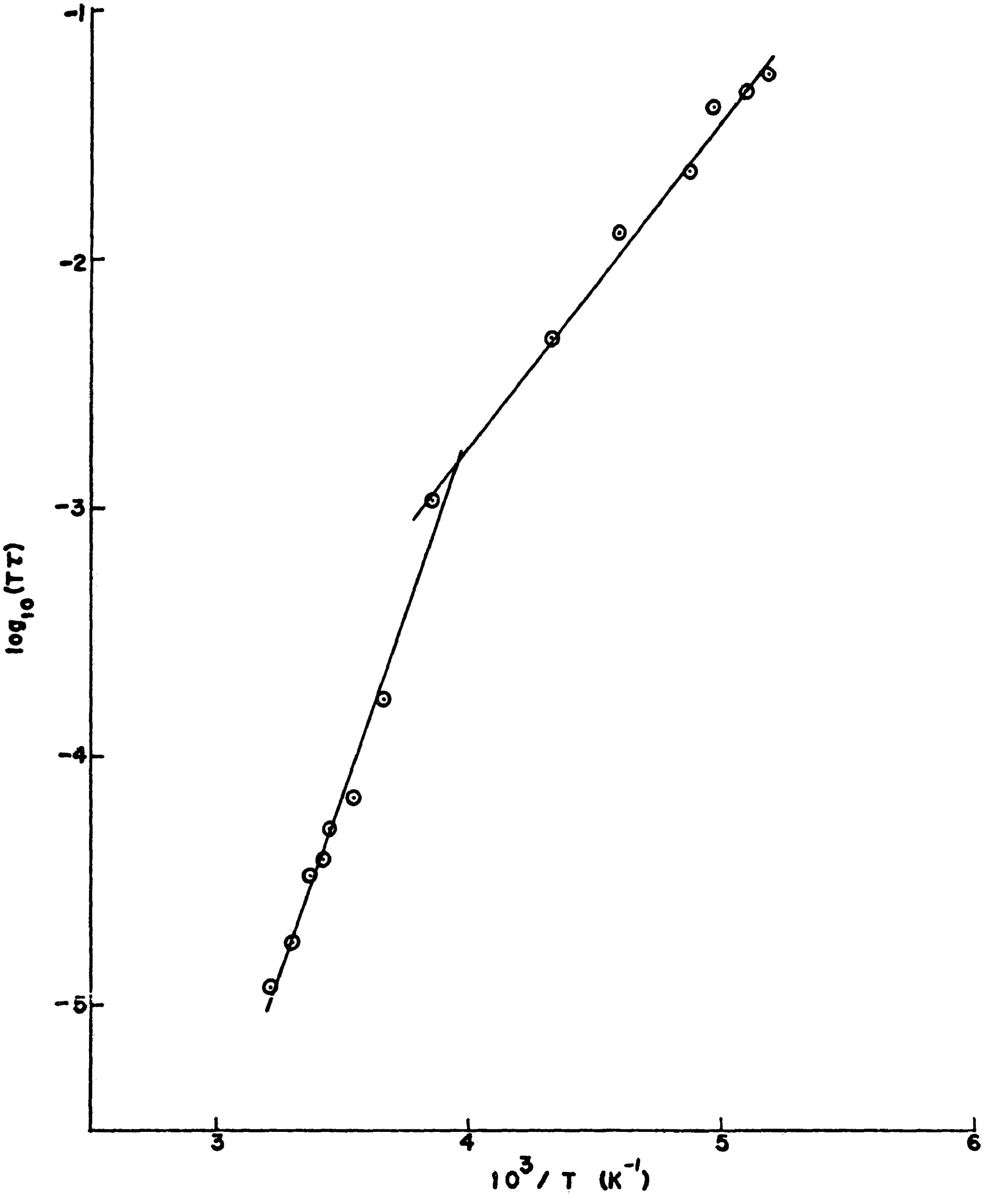

FIG. VI-2: Eyring Plot of log(τT) vs. 1/T for 0.31M 3,3'-Dinitrobiphenyl in a Polystyrene Matrix.

VII

APPENDIX

TABLE 1 - FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS (μ) FOR SOME RIGID MOLECULES IN POLYSTYRENE

T(K)	$10^6\tau(s)$	$10^3\varepsilon''_{max}$	$\log\nu_{max}$	β	ε_∞	μ(D)
0. M Fluorobenzene						
350.6	572.5	7.38	2.44	0.35		
352.2	443.9	7.65	2.55	0.35		
355.9	193.8	7.92	2.91	0.38		
359.1	68.5	7.94	3.37	0.44		
362.6	28.4	7.86	3.75	0.51		
366.5	14.3	8.22	4.05	0.60		
0.23M 4-Fluoro-ethylbenzene						
139.0	306.6	3.80	3.72	0.16	2.64	0.81
147.0	119.9	4.11	3.12	0.15	2.64	0.88
154.1	37.7	4.30	3.63	0.15	2.64	0.94
156.6	28.0	4.42	3.76	0.14	2.65	0.99
164.5	12.9	4.80	4.09	0.14	2.65	1.06
169.8	7.6	4.97	4.32	0.14	2.65	1.07
174.4	4.0	5.15	4.60	0.15	2.65	1.09
184.4	1.1	5.65	5.16	0.16	2.65	1.14
0.35M 4-Bromo-tert-butylbenzene						
244.3	138.4	4.81	3.06	0.19	2.69	0.89
250.6	85.0	5.03	3.27	0.18	2.70	0.94
257.2	39.8	5.27	3.60	0.18	2.70	0.98
264.5	17.6	5.60	3.96	0.19	2.70	1.01
272.7	9.9	5.89	4.20	0.19	2.70	1.02
279.0	4.2	6.24	4.57	0.19	2.70	1.08
285.6	2.8	6.52	4.75	0.20	2.71	1.08
0.54M 2-Fluoronaphthalene						
137.7	471.3	8.58	2.53	0.17	2.52	0.78
143.6	273.9	9.02	2.76	0.16	2.52	0.76
149.9	94.6	9.43	3.23	0.16	2.53	0.88
153.2	66.6	9.63	3.38	0.14	2.52	0.94
155.3	49.4	9.87	3.51	0.14	2.52	0.96
156.8	46.0	9.93	3.64	0.14	2.52	0.97
167.3	14.3	10.93	4.05	0.16	2.54	0.98
172.6	8.5	11.28	4.27	0.17	2.54	0.99

TABLE 1 continued.....

T(K)	$10^6\tau(s)$	$10^3\varepsilon''_{max}$	$\log\nu_{max}$	β	ε_∞	$\mu(D)$
		0.53M 1-Chloronaphthalene				
102.7	374.3	6.93	2.63	0.18	2.40	0.61
109.3	121.0	7.49	3.12	0.16	2.40	0.70
112.8	51.0	7.90	3.49	0.18	2.41	0.68
119.2	19.2	8.56	3.92	0.20	2.42	0.70
122.5	10.0	9.03	4.20	0.19	2.42	0.73
128.1	5.9	9.48	4.43	0.22	2.43	0.72
137.5	1.6	10.39	5.01	0.21	2.44	0.79
359.3	468.4	10.16	2.53	0.26	2.79	1.06
363.7	125.9	10.41	3.10	0.31	2.73	1.00
367.6	44.0	10.70	3.56	0.38	2.79	0.91
370.6	23.4	11.03	3.83	0.45	2.79	0.86
372.9	14.1	11.32	4.05	0.50	2.79	0.83
376.5	10.0	11.54	4.20	0.57	2.79	0.78
		0.45M 1,10-Phenanthroline				
211.8	570.3	13.97	2.45	0.20	2.56	1.22
215.2	344.4	14.54	2.66	0.22	2.56	1.21
218.3	233.5	14.79	2.83	0.23	2.57	1.20
233.2	119.3	15.25	3.13	0.24	2.58	1.20
228.2	63.5	15.64	3.40	0.26	2.59	1.19
233.8	37.0	16.15	3.63	0.27	2.60	1.20
238.2	22.9	16.59	3.84	0.28	2.61	1.20
243.2	12.7	17.12	4.10	0.27	2.61	1.24
		0.53M 1-Chloroanthracene				
252.3	293.8	6.09	2.73	0.18	2.34	0.90
258.2	204.8	6.36	2.89	0.19	2.35	0.95
262.8	136.8	6.50	3.07	0.17	2.35	0.99
267.7	67.0	6.70	3.27	0.17	2.36	1.01
272.9	56.8	7.00	3.45	0.19	2.37	0.99
277.4	33.0	7.17	3.68	0.18	2.38	1.04
281.7	19.9	7.43	3.90	0.18	2.38	1.06
287.6	11.2	7.75	4.15	0.18	2.39	1.09
295.6	6.3	8.05	4.40	0.18	2.39	1.11

TABLE 1 continued.....

T(K)	$10^6\tau(s)$	$10^3\varepsilon''_{max}$	$\log\nu_{max}$	β	ε_∞	$\mu(D)$
		0.23M Cholesteryl butylether				
367.5	3870	14.05	1.61	0.34		
369.9	2004	15.13	1.90	0.36		
372.5	1390	16.44	2.06	0.36		
374.6	866	17.29	2.26	0.37		
379.9	318	17.43	2.70	0.37		

TABLE 2 - FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS (μ) FOR RIGID BIPHENYL DERIVATIVES IN POLYSTYRENE

T(K)	$10^6\tau(s)$	$10^3\epsilon''_{max}$	$\log\nu_{max}$	β	ϵ_∞	μ(D)
		0.46M 4-Phenylpyridine				
213.6	654.4	18.88	2.39	0.24	2.60	1.29
220.9	369.5	19.76	2.63	0.23	2.61	1.37
229.4	173.3	20.65	2.96	0.22	2.61	1.45
237.1	108.2	21.62	3.17	0.21	2.62	1.54
243.2	63.3	22.25	3.40	0.20	2.62	1.64
250.6	33.1	22.98	3.68	0.18	2.61	1.76
254.3	22.7	23.34	3.85	0.18	2.61	1.76
259.0	13.0	23.84	4.09	0.18	2.61	1.81
265.8	8.5	24.72	4.27	0.19	2.62	1.81
297.3	0.8	25.85	5.32	0.22		
304.4	0.4	26.29	5.58	0.22		
311.9	0.3	26.77	5.79	0.22		
318.7	0.1	27.91	6.15	0.22		
326.0	0.1	29.05	6.41	0.23		
		0.44M 4-Fluorobiphenyl				
253.9	172.6	5.87	2.96	0.17	2.58	0.96
261.2	90.5	6.00	3.25	0.17	2.59	1.00
267.9	51.4	6.22	3.49	0.18	2.58	0.98
274.1	27.2	6.23	3.77	0.17	2.58	1.04
282.6	13.6	6.45	4.07	0.19	2.59	1.02
291.1	6.5	6.55	4.39	0.19	2.58	1.04
298.1	4.1	6.65	4.59	0.20	2.58	1.04
304.8	1.0	5.52	5.21	0.19		
309.9	0.8	5.56	5.31	0.18		
315.0	0.3	5.68	5.69	0.20		
319.2	0.2	5.59	5.83	0.18		
324.5	0.1	5.70	6.22	0.17		

TABLE 2 continued.....

T(K)	$10^6\tau(s)$	$10^3\varepsilon''_{max}$	$\log\nu_{max}$	β	ε_∞	$\mu(D)$
		0.40M 4-Chlorobiphenyl				
295.0	120.3	9.95	3.12	0.18	2.65	1.36
301.4	61.9	10.15	3.41	0.18	2.65	1.38
306.9	31.0	10.40	3.71	0.17	2.65	1.43
311.4	17.9	10.62	3.95	0.17	2.65	1.47
315.9	11.9	10.87	4.13	0.18	2.65	1.46
320.3	9.0	11.00	4.24	0.19	2.66	1.44
324.7	5.7	11.47	4.44	0.20	2.66	1.42
364.1	430.6	10.68	2.57	0.23		
366.6	263.1	10.72	2.78	0.33		
369.7	127.9	11.04	3.10	0.39		
372.0	109.8	11.18	3.16	0.48		
375.2	50.3	11.55	3.50	0.56		
		0.33M 4-Bromobiphenyl				
306.9	183.8	8.72	2.94	0.19	2.92	1.32
312.1	105.2	8.88	3.18	0.19	2.93	1.33
316.0	66.0	9.06	3.38	0.19	2.93	1.36
318.9	44.0	9.25	3.56	0.20	2.94	1.33
324.8	26.5	9.62	3.78	0.19	2.95	1.40
342.3	4.8	9.61	4.53	0.23		
367.7	423.5	9.17	2.58	0.23		
369.9	290.7	10.34	2.74	0.35		
370.4	272.0	9.54	2.77	0.36		
373.5	130.4	10.57	3.09	0.42		
376.4	62.5	10.80	3.41	0.53		
379.3	46.0	11.40	3.54	0.68		

TABLE 3 - FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS (μ) FOR SOME SUBSTITUTED BIPHENYLS AND 2,2'-BIPYRIDINE IN POLYSTYRENE

T(K)	$10^6\tau$(s)	$10^3\varepsilon''_{max}$	$\log\nu_{max}$	β	ε_∞	μ(D)
		0.47M 2-Fluorobiphenyl				
183.2	407.0	6.51	2.59	0.17	2.51	0.86
192.1	124.4	6.82	3.11	0.18	2.52	0.87
201.9	38.5	7.15	3.62	0.18	2.53	0.90
207.6	20.0	7.38	3.90	0.18	2.53	0.92
224.9	5.4	7.80	4.47	0.18	2.55	0.98
233.5	3.2	8.07	4.70	0.20	2.56	0.98
238.5	2.2	8.11	4.85	0.20	2.57	0.98
		0.43M 2-Chlorobiphenyl				
212.9	282.7	6.82	2.75	0.21	2.76	0.84
221.5	122.4	7.12	3.11	0.20	2.76	0.88
228.1	61.5	7.27	3.41	0.19	2.76	0.93
235.4	25.0	7.50	3.80	0.20	2.76	0.94
242.7	11.3	7.66	4.15	0.19	2.75	0.98
249.4	5.0	7.90	4.50	0.20	2.75	0.99
254.9	2.9	8.11	4.75	0.22	2.75	0.98
259.5	1.8	8.34	4.94	0.22	2.74	0.99
		0.51M 3-Chlorobiphenyl				
225.3	435.2	7.93	2.56	0.18	2.63	0.95
234.5	177.2	8.57	2.95	0.18	2.63	0.98
241.0	117.4	8.95	3.13	0.18	2.63	1.04
248.6	63.2	9.33	3.40	0.17	2.64	1.10
257.3	25.9	9.72	3.79	0.18	2.64	1.12
261.9	13.4	9.93	4.07	0.19	2.64	1.10
267.3	9.9	10.21	4.20	0.19	2.64	1.13
273.0	7.0	10.51	4.35	0.19	2.64	1.15
279.8	4.1	10.73	4.59	0.18	2.64	1.21

TABLE 3 continued.....

T(K)	$10^6\tau(s)$	$10^3\varepsilon''_{max}$	$\log\nu_{max}$	β	ε_∞	$\mu(D)$
0.36M 3-Nitrobiphenyl						
255.7	244.9	30.05	2.81	0.20	2.65	2.14
261.2	140.9	30.98	3.05	0.20	2.65	2.19
269.3	62.5	32.68	3.41	0.20	2.65	2.29
274.9	37.2	34.10	3.63	0.20	2.65	2.37
280.4	22.0	35.43	3.86	0.21	2.66	2.39
286.1	12.6	36.62	4.10	0.20	2.65	2.48
293.9	6.7	38.28	4.37	0.20	2.66	2.54
300.6	3.7	40.62	4.63	0.21	2.67	2.60
0.37M 2-Nitrobiphenyl						
204.4	1523.8	16.04	2.02	0.22	2.56	1.35
210.4	1022.7	16.97	2.19	0.21	2.57	1.44
216.1	516.5	17.81	2.49	0.22	2.58	1.45
220.8	332.3	19.30	2.68	0.21	2.63	1.54
227.4	168.8	20.09	2.97	0.21	2.63	1.61
233.4	105.5	20.90	3.18	0.21	2.64	1.66
241.2	43.3	21.81	3.56	0.21	2.64	1.70
247.5	23.1	22.52	3.84	0.22	2.64	1.74
256.2	11.8	23.76	4.13	0.24	2.66	1.71
265.1	4.3	25.21	4.56	0.24	2.66	1.79
272.3	2.1	26.58	4.87	0.25	2.66	1.85
0.57M 2,2'-Bipyridine						
193.3	395.1	1.23	2.61	0.31	2.75	0.24
194.3	309.1	1.26	2.71	0.33	2.75	0.24
205.6	89.7	1.26	3.25	0.32	2.75	0.25
210.5	52.6	1.25	3.48	0.36	2.75	0.23
215.5	29.6	1.20	3.73	0.36	2.75	0.23
219.5	24.3	1.30	3.82	0.54	2.75	0.20
229.5	9.7	1.17	4.22	0.48	2.75	0.21

TABLE 3 continued.....

T(K)	$10^6\tau(s)$	$10^3\varepsilon''_{max}$	$\log\nu_{max}$	β	ε_∞	$\mu(D)$
0.40M 2-Bromobiphenyl						
204.0	1565.2	5.92	2.01	0.27	2.64	0.71
209.8	883.0	6.20	2.26	0.27	2.65	0.73
216.1	464.6	6.46	2.54	0.27	2.65	0.76
222.0	311.7	6.75	2.71	0.26	2.66	0.80
228.4	198.2	6.92	2.91	0.24	2.66	0.85
248.3	31.3	7.39	3.71	0.22	2.67	0.96
255.2	15.7	7.59	4.01	0.21	2.67	1.02
264.2	7.3	7.82	4.34	0.21	2.67	1.04
273.5	3.4	8.03	4.67	0.22	2.68	1.04
280.9	1.0	6.35	5.18	0.22		
288.0	0.7	6.45	5.37	0.24		
300.2	0.3	6.59	5.79	0.24		
305.3	0.2	6.58	5.95	0.22		
312.6	0.1	6.86	6.29	0.25		
0.32M 3-Bromobiphenyl						
227.5	803.8	4.14	2.30	0.24	2.45	0.79
231.2	644.4	4.31	2.39	0.23	2.46	0.82
237.4	468.9	4.58	2.53	0.23	2.47	0.85
242.7	270.9	4.86	2.77	0.22	2.48	0.90
248.6	294.2	5.48	2.73	0.19	2.49	1.03
252.7	201.1	5.28	2.90	0.20	2.49	1.00
254.6	198.1	5.73	2.91	0.17	2.49	1.12
260.6	115.2	5.93	3.14	0.16	2.50	1.19
262.5	75.0	5.55	3.33	0.16	2.51	1.15
268.9	45.4	6.22	3.55	0.18	2.51	1.17
273.7	28.1	6.41	3.75	0.17	2.51	1.22
282.5	8.7	6.72	4.27	0.16	2.51	1.32
287.7	3.0	5.15	4.73	0.23		
295.5	2.3	5.05	4.74	0.22		
301.0	1.2	5.30	5.13	0.20		
313.0	0.5	5.27	5.50	0.20		
323.2	0.2	5.60	5.82	0.24		

TABLE 3 continued.....

T(K)	$10^6\tau(s)$	$10^3\varepsilon''_{max}$	$\log\nu_{max}$	β	ε_∞	$\mu(D)$
0.28M 2,2'-Difluorobiphenyl						
182.6	269.7	9.30	2.77	0.25	2.63	1.04
187.9	143.7	9.49	3.04	0.25	2.63	1.06
194.6	74.5	9.71	3.33	0.25	2.63	1.10
204.6	25.1	10.08	3.80	0.25	2.63	1.15
210.0	17.1	10.25	3.97	0.26	2.64	1.15
218.9	7.6	10.79	4.32	0.27	2.64	1.18
230.0	3.5	10.91	4.65	0.28	2.65	1.20
242.7	1.0	10.62	5.21	0.28		
252.7	0.5	10.90	5.51	0.29		
259.8	0.3	10.89	5.69	0.27		
268.3	0.2	11.31	5.95	0.29		
273.8	0.1	11.72	6.13	0.32		
0.31M 2,2'-Dinitrobiphenyl						
185.4	1569.4	6.82	2.01	0.20	2.64	0.97
190.6	1049.8	7.25	2.18	0.20	2.65	1.01
193.4	757.4	7.28	2.32	0.20	2.65	1.01
196.4	562.7	7.63	2.45	0.20	2.66	1.05
201.4	360.0	7.97	2.65	0.20	2.66	1.07
206.4	239.8	8.29	2.82	0.20	2.66	1.12
211.9	90.9	10.00	3.24	0.20	2.70	1.20
219.8	40.3	10.63	3.60	0.21	2.70	1.25
226.3	21.0	11.35	3.88	0.21	2.70	1.30
234.0	9.8	12.39	4.21	0.22	2.70	1.36
240.9	6.2	13.04	4.41	0.21	2.70	1.46
246.9	3.8	13.88	4.63	0.21	2.71	1.51

TABLE 3 continued.....

T(K)	$10^6\tau$(s)	$10^3\varepsilon''_{max}$	$\log\nu_{max}$	β	ε_∞	μ(D)
		0.25M 2,2'-Dibromobiphenyl				
187.4	457.6	3.20	2.54	0.23	2.81	0.67
187.8	370.6	2.70	2.63	0.26	2.65	0.60
194.4	289.5	2.74	2.74	0.25	2.66	0.63
194.6	271.1	3.31	2.77	0.22	2.81	0.72
199.0	200.0	2.81	2.90	0.22	2.66	0.68
203.9	126.0	3.86	3.10	0.24	2.81	0.85
206.4	112.9	2.94	3.14	0.23	2.66	0.70
210.9	68.2	3.02	3.37	0.23	2.66	0.71
215.4	53.7	5.03	3.47	0.23	2.80	0.87
216.9	46.6	3.17	3.53	0.23	2.66	0.74
231.2	12.5	3.43	4.10	0.22	2.66	0.82
241.8	4.1	3.77	4.59	0.20	2.67	0.91
245.0	2.4	3.57	4.81	0.25		
252.1	1.1	3.88	5.16	0.27		
260.4	0.6	4.00	5.42	0.26		
269.2	0.4	4.11	5.60	0.24		
293.1	0.2	4.80	6.26	0.24		
		0.42M 3,3'-Difluorobiphenyl				
174.5	415.2	9.40	2.58	0.17	2.58	1.04
191.8	40.9	10.21	3.59	0.17	2.58	1.11
199.7	14.0	10.57	4.06	0.17	2.58	1.16
207.5	6.5	11.01	4.39	0.19	2.58	1.15
222.7	1.5	10.26	5.02	0.21		
233.1	0.6	9.62	5.46	0.21		
235.3	0.5	11.92	5.52	0.24		
239.1	0.3	10.25	5.71	0.23		
241.9	0.3	12.18	5.76	0.22		
247.8	0.2	11.41	5.95	0.19		
250.7	0.1	13.10	6.05	0.25		
256.4	0.1	11.28	6.16	0.21		
261.0	0.1	11.35	6.30	0.23		
264.9	0.1	11.56	6.49	0.23		

TABLE 3 continued.....

T(K)	$10^6\tau(s)$	$10^3\varepsilon''_{max}$	$\log\nu_{max}$	β	ε_∞	$\mu(D)$
		0.31M 3,3'-Dinitrobiphenyl				
192.9	279.3	1.68	2.76	0.22	2.38	0.40
195.8	234.1	1.39	2.83	0.22	2.41	0.41
201.0	204.7	1.73	2.89	0.18	2.58	0.48
204.9	106.4	1.39	3.17	0.21	2.38	0.49
217.2	57.2	1.60	3.44	0.16	2.44	0.61
230.6	20.3	1.57	3.89	0.18	2.41	0.58
259.0	3.8	2.03	4.62	0.20	2.53	0.64
272.9	0.4	2.62	5.41	0.21		
282.0	0.2	2.69	5.83	0.20		
292.3	0.1	2.79	6.09	0.18		
296.0	0.1	2.87	6.14	0.21		
303.0	0.1	2.86	6.43	0.20		
310.8	0.0	2.98	6.63	0.19		

TABLE 4 - FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS (μ) FOR DISC-LIKED MOLECULES IN POLYVINYLTOLUENE

T(K)	$10^6\tau$(s)	$10^3\epsilon''_{max}$	$\log\nu_{max}$	β	ϵ_∞	μ(D)
		0.38M 1-Chloroanthracene				
254.7	1432.5	5.81	2.05	0.22	2.44	0.90
265.1	663.8	6.21	2.38	0.20	2.44	0.98
274.7	189.5	6.59	2.92	0.14	2.43	1.15
279.3	115.0	6.87	3.14	0.14	2.44	1.16
283.8	61.3	7.11	3.41	0.15	2.44	1.19
288.9	34.3	7.22	3.67	0.15	2.44	1.26
295.0	14.0	7.49	4.06	0.14	2.41	1.35
297.6	11.1	7.91	4.15	0.12	2.44	1.39
		0.36M 9-Bromoanthracene				
197.9	956.4	1.25	2.21	0.21	2.08	0.44
203.8	467.3	1.33	2.53	0.21	2.08	0.46
216.7	170.4	1.56	3.28	0.19	2.11	0.54
221.7	49.3	1.77	3.58	0.23	2.12	0.51
233.6	11.1	1.98	4.16	0.21	2.15	0.60
240.4	10.7	2.21	4.44	0.23	2.17	0.60
		0.38M 9-Bromophenanthrene				
206.3	230.9	2.28	2.84	0.13	2.34	0.83
213.6	67.1	2.51	3.38	0.16	2.37	0.90
218.8	56.8	2.79	3.45	0.17	2.39	0.94
226.0	27.5	3.03	3.76	0.16	2.41	0.92
230.8	10.9	3.22	4.16	0.12	2.41	0.91
238.4	3.6	2.54	4.65	0.24		
248.0	2.1	2.77	4.88	0.23		
259.2	0.8	3.11	5.32	0.21		

TABLE 5 - FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS (μ) FOR RIGID BIPHENYL DERIVATIVES IN POLYVINYLTOLUENE

T(K)	$10^6\tau$(s)	$10^3\varepsilon''_{max}$	$\log\nu_{max}$	β	ε_∞	μ(D)
		0.37M 4-Phenylpyridine				
235.9	546.7	22.86	2.46	0.16	2.61	1.79
241.5	376.9	22.60	2.63	0.19	2.61	1.85
247.7	220.8	23.41	2.86	0.18	2.61	1.95
254.5	103.7	24.12	3.19	0.18	2.61	2.01
260.5	52.0	24.78	3.49	0.18	2.60	2.07
266.1	29.1	25.60	3.74	0.18	2.60	2.16
271.6	17.4	26.56	3.96	0.16	2.60	2.18
276.8	10.2	27.45	4.19	0.10	2.60	2.22
		0.41M 4-Fluorobiphenyl				
262.6	306.5	10.22	2.72	0.19	2.49	1.26
269.3	151.8	10.49	3.02	0.17	2.52	1.37
275.4	77.5	11.04	3.31	0.16	2.54	1.45
280.4	36.2	11.56	3.64	0.17	2.55	1.46
284.3	27.1	11.93	3.77	0.17	2.56	1.50
289.2	14.0	12.02	4.06	0.17	2.57	1.49
295.9	6.2	12.39	4.41	0.17	2.56	1.56
300.8	3.8	12.67	4.61	0.19	2.57	1.50
		0.45M 4-Chlorobiphenyl				
282.9	635.2	12.14	2.40	0.19	2.47	1.40
290.0	278.5	12.97	2.76	0.18	2.50	1.48
296.8	137.7	10.33	3.06	0.18	2.26	1.40
301.2	56.9	10.81	3.45	0.19	2.30	1.41
307.1	29.7	12.00	3.73	0.21	2.33	1.43
312.0	17.1	12.68	3.98	0.21	2.40	1.46
		0.23M 4-Bromobiphenyl				
306.8	523.3	7.20	2.48	0.18	2.66	1.55
311.9	176.3	8.74	2.96	0.20	2.66	1.62
317.3	82.9	9.17	3.28	0.19	2.66	1.71
321.0	38.4	8.92	3.62	0.19	2.66	1.69
325.0	20.3	9.40	3.89	0.19	2.66	1.76
329.7	9.5	9.59	4.22	0.20	2.66	1.75
332.3	7.2	10.13	4.35	0.20	2.66	1.77
335.6	3.4	10.74	4.67	0.19	2.64	1.91

TABLE 5 continued.....

T(K)	$10^6\tau$(s)	$10^3\varepsilon''_{max}$	$\log\nu_{max}$	β	ε_∞	μ(D)
		0.20M 4-Nitrobiphenyl				
308.5	601.2	31.85	2.42	0.18	2.63	3.43
311.6	292.0	32.54	2.74	0.20	2.64	3.35
315.8	188.2	33.61	2.93	0.19	2.63	3.51
319.4	123.5	34.20	3.11	0.18	2.62	3.63
321.5	97.1	34.85	3.21	0.19	2.64	3.55
322.9	67.5	35.06	3.37	0.19	2.61	3.59
325.0	51.3	36.24	3.49	0.19	2.63	3.62
327.7	38.9	37.62	3.61	0.19	2.64	3.73
330.3	23.4	38.43	3.83	0.18	2.64	3.87

TABLE 6 - FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS (μ) FOR SOME SUBSTITUTED BIPHENYLS AND 2,2'-BIPYRIDINE IN POLYVINYLTOLUENE

T(K)	$10^6\tau$(s)	$10^3\varepsilon''_{max}$	$\log\nu_{max}$	β	ε_∞	μ(D)
0.32M 2-Nitrobiphenyl						
214.9	2212.9	13.87	1.86	0.22	2.55	1.41
223.4	936.8	16.14	2.23	0.24	2.56	1.48
227.7	659.6	15.85	2.38	0.21	2.56	1.57
232.8	449.6	16.87	2.55	0.20	2.56	1.66
233.3	431.8	16.29	2.57	0.20	2.55	1.83
236.3	381.2	16.67	2.62	0.19	2.55	1.93
240.5	209.3	17.34	2.88	0.20	2.56	1.93
244.5	139.6	17.99	3.06	0.20	2.55	2.00
248.2	105.9	18.42	3.18	0.18	2.55	2.14
252.3	61.7	19.08	3.41	0.19	2.55	2.14
256.2	36.0	19.78	3.65	0.18	2.55	2.23
260.3	17.8	20.35	3.95	0.19	2.55	2.22
264.8	13.5	21.42	4.07	0.19	2.54	2.34
268.1	6.7	21.92	4.38	0.17	2.53	2.49
272.7	3.6	21.72	4.64	0.19	2.54	2.35
276.9	2.3	24.05	4.84	0.17	2.52	2.65
0.21M 2-Bromobiphenyl						
235.5	1062.8	2.99	2.18	0.24	2.48	0.82
246.9	474.7	3.43	2.53	0.25	2.49	0.88
252.8	380.0	3.51	2.62	0.21	2.49	0.96
258.6	231.2	3.61	2.84	0.19	2.50	1.06
263.8	185.2	3.93	2.93	0.20	2.50	1.09
269.8	104.9	3.86	3.18	0.16	2.50	1.21
275.5	94.6	4.15	3.23	0.15	2.50	1.31
283.1	41.7	4.52	3.58	0.15	2.50	1.38
293.2	11.6	4.47	4.14	0.14	2.46	1.46
296.0	7.0	5.05	4.35	0.14	2.51	1.55
301.2	4.9	4.87	4.51	0.16	2.49	1.45

TABLE 6 continued.....

T(K)	$10^6\tau(s)$	$10^3\varepsilon''_{max}$	$\log\nu_{max}$	β	ε_∞	$\mu(D)$
0.29M 3-Nitrobiphenyl						
266.4	484.6	37.73	2.52	0.18	3.06	2.62
270.3	277.0	37.05	2.76	0.18	2.94	2.66
273.4	222.5	38.12	2.86	0.17	2.93	2.82
276.2	178.9	39.34	2.95	0.17	2.93	2.87
280.6	112.0	40.48	3.15	0.16	2.93	3.00
283.9	61.2	41.52	3.41	0.15	2.90	3.16
287.6	42.6	43.06	3.57	0.16	2.90	3.15
293.1	19.8	44.22	3.91	0.16	2.87	3.24
293.4	18.9	45.32	3.93	0.16	2.88	3.30
294.9	12.2	46.62	4.12	0.14	2.84	3.61
300.3	4.7	49.30	4.53	0.15	2.84	3.61
300.4	5.8	47.62	4.44	0.14	2.82	3.62
303.4	2.7	48.94	4.78	0.13	2.77	3.84
306.1	1.5	51.31	5.02	0.14	2.76	3.89
309.9	0.9	55.11	5.27	0.14	2.76	3.99
0.27M 3,3'-Difluorobiphenyl						
179.8	360.3	7.14	2.65	0.15	2.55	1.21
184.4	175.1	6.88	3.00	0.17	2.43	1.16
191.1	101.7	7.15	3.20	0.15	2.43	1.30
192.9	83.2	7.76	3.28	0.14	2.55	1.34
196.5	35.7	7.40	3.65	0.13	2.43	1.41
199.9	37.8	8.01	3.63	0.14	2.55	1.43
202.3	24.7	7.63	3.81	0.15	2.45	1.31
207.2	14.2	8.02	4.05	0.16	2.45	1.31
208.6	15.1	8.55	4.02	0.17	2.56	1.33
222.7	3.2	7.79	4.70	0.17		
233.0	1.6	8.40	5.00	0.19		
237.0	0.9	8.63	5.25	0.24		
242.9	0.7	8.94	5.39	0.19		
247.5	0.3	9.15	5.71	0.22		
252.6	0.2	9.39	5.83	0.20		
257.4	0.2	9.41	5.97	0.20		
262.6	0.1	9.81	6.27	0.19		

TABLE 6 continued.....

T(K)	$10^6\tau$(s)	$10^3\varepsilon''_{max}$	$\log\nu_{max}$	β	ε_∞	μ(D)
0.73M 2,2'-Bipyridine						
202.5	1388.4	1.07	2.06	0.51	2.47	0.17
208.1	923.0	0.93	2.33	0.46	2.48	0.17
212.3	762.7	0.98	2.37	0.42	2.49	0.19
217.7	383.6	0.97	2.62	0.38	2.50	0.19
222.6	233.3	0.97	2.83	0.37	2.51	0.20
224.7	198.3	0.96	2.91	0.32	2.51	0.21
227.7	144.4	0.91	3.04	0.26	2.55	0.22
0.46M 2,2'-Bipyridine						
357.8	10.0	7.38	4.20	0.33		
368.3	2.7	8.41	4.77	0.37		
373.1	1.5	9.11	5.02	0.39		
378.6	0.7	9.80	5.35	0.44		
381.7	0.5	10.26	5.51	0.47		
0.19M 2,2'-Difluorobiphenyl						
187.3	534.4	7.25	2.47	0.22	2.61	1.24
192.9	285.8	7.52	2.75	0.22	2.62	1.27
197.3	194.4	7.76	2.91	0.22	2.62	1.30
197.8	166.1	7.81	2.98	0.21	2.62	1.33
207.5	60.4	8.20	3.42	0.21	2.64	1.40
211.6	42.3	8.36	3.58	0.21	2.64	1.43
216.9	22.2	8.58	3.86	0.20	2.65	1.48
221.7	13.7	8.82	4.06	0.21	2.66	1.49
227.5	8.8	9.32	4.26	0.23	2.67	1.48
232.0	5.6	9.37	4.46	0.24	2.67	1.46
248.0	2.2	9.29	4.87	0.25		
255.0	1.0	9.33	5.22	0.26		
261.6	0.6	9.68	5.44	0.28		
269.1	0.3	9.68	5.73	0.27		
276.9	0.2	9.87	5.97	0.27		
282.8	0.1	10.12	6.16	0.27		

TABLE 6 continued.....

T(K)	$10^6\tau(s)$	$10^3\varepsilon''_{max}$	$\log\nu_{max}$	β	ε_∞	$\mu(D)$
		0.24M 3-Bromobiphenyl in poly(vinyltoluene)				
229.1	388.6	3.91	2.61	0.26	2.56	0.81
234.2	282.7	4.09	2.75	0.25	2.57	0.85
237.7	180.8	4.16	2.95	0.25	2.58	0.87
241.1	136.7	3.89	3.07	0.25	2.40	0.88
244.2	118.9	3.93	3.13	0.24	2.40	0.92
252.5	39.1	4.08	3.61	0.21	2.41	1.01
258.6	11.2	4.33	4.14	0.19	2.42	1.09
263.1	10.4	4.43	4.18	0.19	2.42	1.12
268.5	5.3	4.42	4.48	0.20	2.43	1.16
274.0	3.2	4.20	4.70	0.27		
282.8	2.6	4.34	4.78	0.22		
294.8	0.9	4.51	5.25	0.24		
302.1	0.5	4.74	5.53	0.22		
307.4	0.2	4.75	5.83	0.20		
312.4	0.1	4.70	6.10	0.17		