SOME DIELECTRIC STUDIES

A THESIS PRESENTED BY

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Summary

Two methods of approach are current in the literature for the interpretation of dielectric relaxation. One is that due to Debye which assumes that the relaxation process has its origin in the retardation of molecular reorientation due to frictional forces acting on the molecule. The other treats dipole rotation as a rate process in which the dipole must acquire a certain amount of energy in order to surmount a barrier separating two equilibrium positions of orientation.

The dielectric relaxation times of some large ketones have been determined at four temperatures using a cell which does not appear to have been used up to this time for measuring the dielectric constant and loss of low loss liquids. The molecules measured were selected because of their size and shape, five were ellipsoidal, and one was disc-like. For the ellipsoidal molecules the position of the dipole within the molecule was varied to investigate its effect on the relaxation time. A number of equations, based on the Debye model, which attempt to account for the size of molecular relaxation time are examined. It is found that only the Fischer equation is satisfactory in predicting the effects of dipole direction within the molecule.

The experimentally measured activation energies for all the large molecules were found to be similar and only a little higher than those observed for smaller molecules. In an attempt to understand these values a model is proposed based on the

energy expended by the molecule during its reorientation process. The approach leads to a method for predicting the effect of solvent on dielectric relaxation time. It is found that the relaxation time depends exponentially on the internal pressure of the medium surrounding the relaxing species, and the activation energy can be accounted for in terms of the product of an activation volume and the internal pressure. From the activation volume an estimate is obtained of the angle through which the dipole rotates. For small molecules it is found that the angle is of the order of 20°, which indicates a fairly large jump accompanying the reorientation. For the larger molecules, however, the angle is much smaller, hence, the behaviour resembles Brownian rotational diffusion.

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APPENDIX

CHAPTER ONE

BASIC THEORY AND EXPERIMENTAL

METHODS

A.Dielectric Polaization and Relaxation (41) (69) (70).

If a dielectric material replaces a vacuum as the medium between
two parallel plates of a charged capacitor it is observed that the
voltage across the plates is reduced. The ratio of the voltage for
the evacuated capacitor to that containing the dielectric is known
as the permitivity, or dielectric constant, of the medium. The
effect of the electric field on the dielectric is equivalent to
charging the surface of the material with a sign opposite to that
of the capacitor plate in which it is in contact , but since the
material contains no net charges this is a result of the dis-
placement of the positive and negative centres of the material by
the field. Thus, positive charges are displaced towards the negative
capacitor plate and vice-versa.

The total charge passing through unit area within the dielectric
parallel to the capacitor plates, is called the polarisation of the
dielectric and is given the symbol P. Three component parts make up
the polarisation and they are defined by the relation:

$$P = P_E + P_A + P_O \qquad 1.1$$

where, P_E is the electronic polarisation and is due to the dis-
placement of the electrons in the atoms of the material, P_A, is the
atomic polarisation and arises from the displacement of the nuclei
of the atoms, P_O, is the orientation polarisation due to the
orientation of permanent molecular dipoles in the field. The
total polarisation of one mole of the material can be written in
terms of its dielectric constant and polarisability in the form:

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{d} \qquad\qquad 1.2$$

$$= \frac{4 \pi N}{3} \left[\alpha + \frac{\mu^2}{3kT} \right] \qquad\qquad 1.3$$

where M is the molecular weight, d is the density, α is the polarisability of the molecule, μ is its permanent dipole moment, k is Boltzmann's constant, and T is the absolute temperature. The term $4\pi N \alpha /3$ is the part of the molecular polarizability due to the atomic and electronic displacements and is thus known as distortion polarisation. The other term $4\pi N \mu^2 / 9 kT$ is the orientation polarization and is observed only in molecules which possess a permanent dipole.

When the dielectric constant is measured at fields of low alternating frequency it has its maximum value which is termed the static dielectric constant, ε_o . As the frequency is increased, however, the dielectric constant is observed to decrease, this phenomenon is known as dispersion of the dielectric constant and has its origin in the response of the molecules of the material to the field. Under the influence of a torque exerted by the field the dipoles rotate towards an equilibrium distribution of orientation against a restraining force. At low frequencies, providing that the molecule is sufficiently small and the retarding force is not great, the dipoles respond instantaneously to the field variation with time, but, as the frequency is increased the motion of the molecules is not sufficiently rapid to maintain equilibrium with the field variation. Hence, there is a time lag in the responce of the molcules with respect to the field and the polarization P_t at any time t , is less than the equilibrium value,

P_o, as described by the equation:

$$P_t = P_o \exp - t / \Upsilon \qquad 1.4.$$

where Υ is the relaxation rate of the dielectric. Since Υ is

defined as the reciprocal rate at which the polarization comes into equilibrium

in responce to a change in the external field to which the material

is subjected it follows from equation 1.4 that Υ is time required

for the polarisation of the medium to decay to 1/e of its

equilibrium value.

B. The Complex Dielectric Constant.

In a perfect capacitor the charging current is $\pi/2$ out
of phase with the alternating potential, however, when the motion
of the molecules of the dielectric suffer relaxation effects the
current acquires a component in phase with the voltage. This gives
rise to dissipation of the energy of the field in the form of joule
heating, and under these conditions the dielectric constant is
represented as a complex number, viz:

$$\varepsilon^* = \varepsilon' - i\varepsilon''$$

where ε' represents the ability of the medium to store the energy
of the field and ε'' is a measure of its ability to dissipate the
field energy. When the field frequency is low ε'' is zero and ε'
approaches ε_0; as the frequency approaches ∞ the dipoles are no
longer able to alter their orientation and the dielectric constant
approaches that of a non-polar material. Under these conditions
ε'' approaches zero and ε' is termed ε_∞, the optical dielectric
constant.

C. Dielectric Dispersion Equations.

Debye (41) showed that when the polarization of a dielectric was characterized by an exponential variation with time, the complex dielectric constant could be related to the relaxation time and the field frequency, ω, by the equation

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau} = \varepsilon' - i\varepsilon'' \qquad (1.5)$$

On separation into real and imaginary parts

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2\tau^2} \qquad (1.6)$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \qquad (1.7)$$

These are known as the Debye dispersion equations and describe the behaviour of the complex dielectric constant as a function of frequency.

Examination of equation (1.7) shows that ε'' approaches zero when $\omega\tau$ is either small or large, while for the value $\omega\tau = 1$ it is a maximum. Hence, by determining the frequency at which ε'' has its maximum the relaxation time can be evaluated. The behaviour of ε' and ε'', as represented by equations (1.6) and (1.7) is illustrated in fig. 1.1.

Elimination of $\omega\tau$ from equations (1.6) and (1.7) gives the relationship between ε' and ε'':

Fig 1.1 TOTAL POLARISATION VS. LOG FREQUENCY
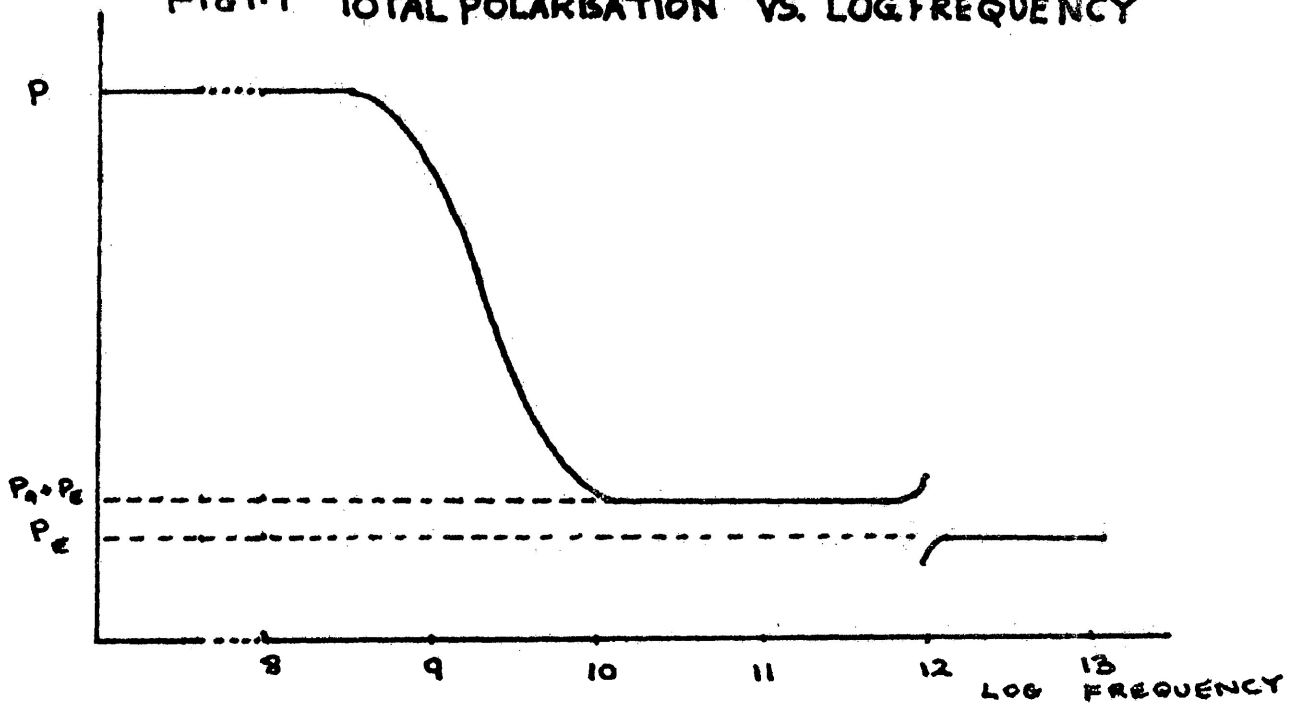
ε' AND ε'' AS A FUNCTION OF $\omega\gamma$
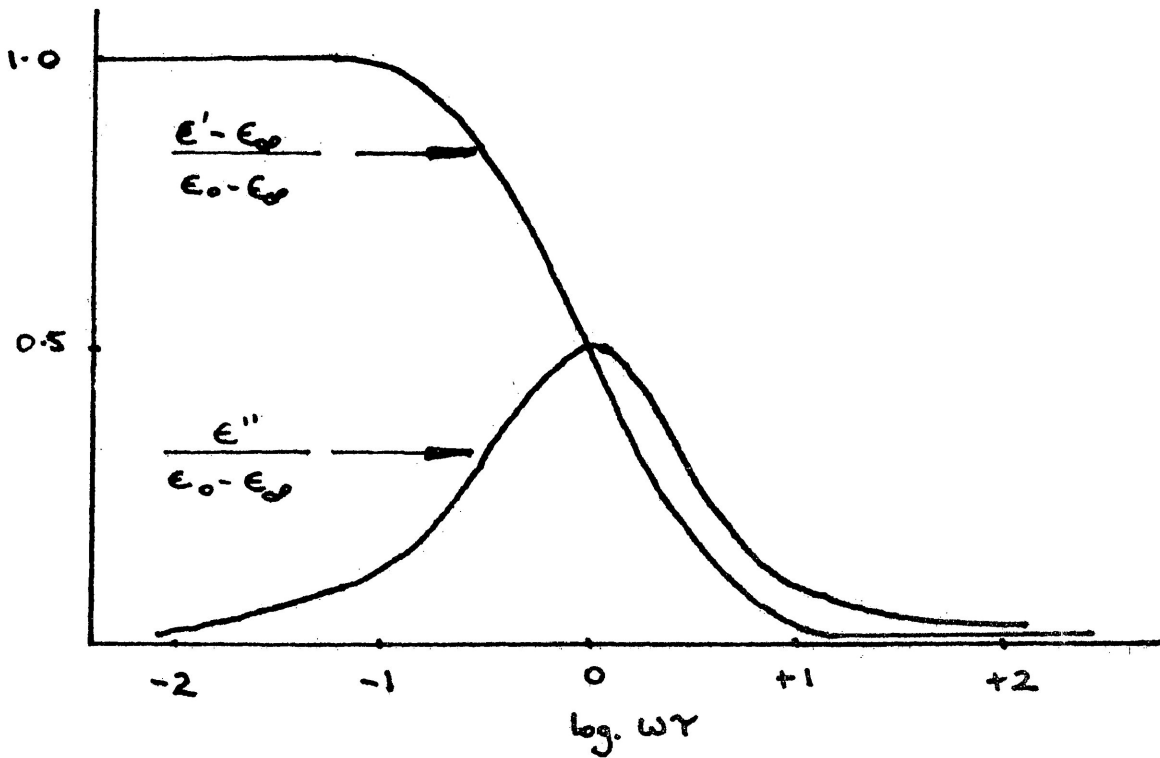
$$(\varepsilon' - \frac{\varepsilon_0 + \varepsilon_\infty}{2})^2 + (\varepsilon'')^2 = (\frac{\varepsilon_0 - \varepsilon_\infty}{2})^2 \qquad (1.8)$$

which is the equation of a circle. The locus of ε' and ε'' in an Argand diagram is a semi-circle of radius $\varepsilon_0 - \varepsilon_\infty/2$ and centre of co-ordinates $(\frac{\varepsilon_0 + \varepsilon_\infty}{2})$, 0. This is known as a Cole-Cole (71) plot and it is seen that the centre of the semi-circle lies on the axis of reals.

For many dielectric systems the Cole-Cole plot is found to be an arc which corresponds to a clockwise rotation of the semi-circle about the ε_∞ point. Hence the centre of the semi-circle is below the axis of reals, and the behaviour of ε^* is represented by:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + i\omega\tau_0)^{1-\alpha}} \qquad (1.9)$$

in which τ_0 is the most probable, or mean, relaxation time and corresponds to the reciprocal of the angular frequency at which ε'' is a maximum, and α, the so-called distribution coefficient, is a measure of the spread of relaxation times about τ_0 and has the range of values $1 > \alpha > 0$. When α is zero (1.9) reduces to (1.5).

Separation of (1.9) into real and imaginary parts yields:

$$\varepsilon' = \frac{\varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)[1 + (\omega\tau_0)^{1-\alpha} \sin(\alpha\frac{\pi}{2})]}{1 + 2(\omega\tau_0)^{1-\alpha} \sin(\alpha\pi/2) + \omega\tau_0^{2(1-\alpha)}} \qquad (1.10)$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)(\omega\tau_0)^{1-\alpha} \cos(\alpha\pi/2)}{1 + 2(\omega\tau_0)^{1-\alpha} \sin(\alpha\pi/2) + \omega\tau_0^{2(1-\alpha)}} \qquad (1.11)$$

For systems which are characterized by two independent relaxation times Budó (12) assumed that the complex dielectric constant could be represented by the superimposition of two overlapping Debye absorptions. Such behaviour is described by the equations:

$$\varepsilon' = \varepsilon_\infty + \varepsilon_0 - \varepsilon_\infty \left[\frac{C_1}{1 + \omega^2 \tau_1^2} + \frac{C_2}{1 + \omega^2 \tau_2^2} \right] \qquad (1.12)$$

$$\varepsilon'' = \left(\varepsilon_0 - \varepsilon_\infty \right) \left[\frac{C_1 \omega \tau_1}{1 + \omega^2 \tau_1^2} + \frac{C_2 \omega \tau_2}{1 + \omega^2 \tau_2^2} \right] \qquad (1.13)$$

$$C_1 + C_2 = 1 \qquad (1.14)$$

where τ_1 and τ_2 are the relaxation times of the two processes and C_1 and C_2 weight the importance of each contributing absorption.

D. Apparatus

(a) A bridge method, which has been previously described (73) was used for measuring dielectric constants and losses in the microwave region. The frequencies of measurement and errors in the parameters obtained are listed in table 1.1.

Table 1.1 frequencies of measurement and errors in parameters.

Band designation	operating frequency	errors	
	G.Hz.	ϵ'	ϵ''
C	6.98	± 0.003	± 0.003
X	9.313	± 0.003	± 0.002
P	16.20	± 0.006	± 0.003
K	23.98	± 0.003	± 0.003
Q	35.22	± 0.006	± 0.003

The errors involved in this method have been discussed by Magee (17).

(b) Measurements in the frequency region 0.9 to 2.0 G.Hz.

In this region dielectric absorption measurements are conveniently made using coaxial-line equipment. The apparatus to be discribed has been used previously by Grant et.al.(75), (76), (77), for determination of the dielectric parameters of medium and high loss liquids but does not seem to have been used for low loss media.

One of the advantages of this technique of measurement is that the electric field vector is sampled within the liquid under investigation. Thus, difficulties which arise from reflectionsfrom the air-liquid interface are not encountered.

A schematic diagram of the apparatus is shown in fig.1.2. Radiation from a signal generator enters the cell through a locking

Fig 1·2 Schematic Diagram of Coaxial Cell Circuit
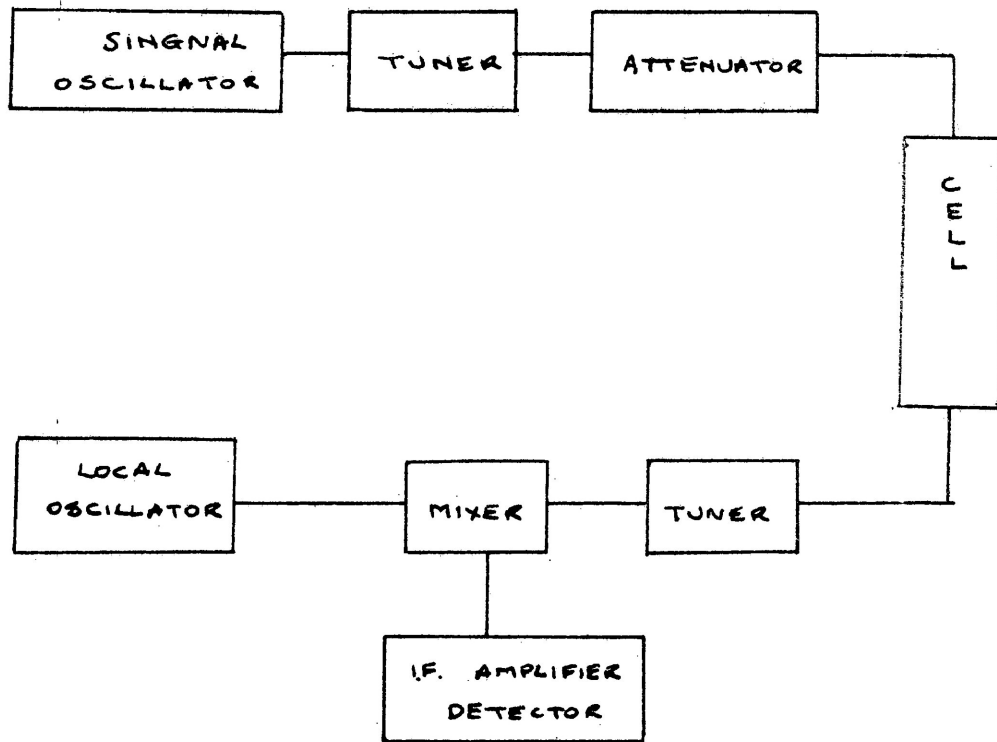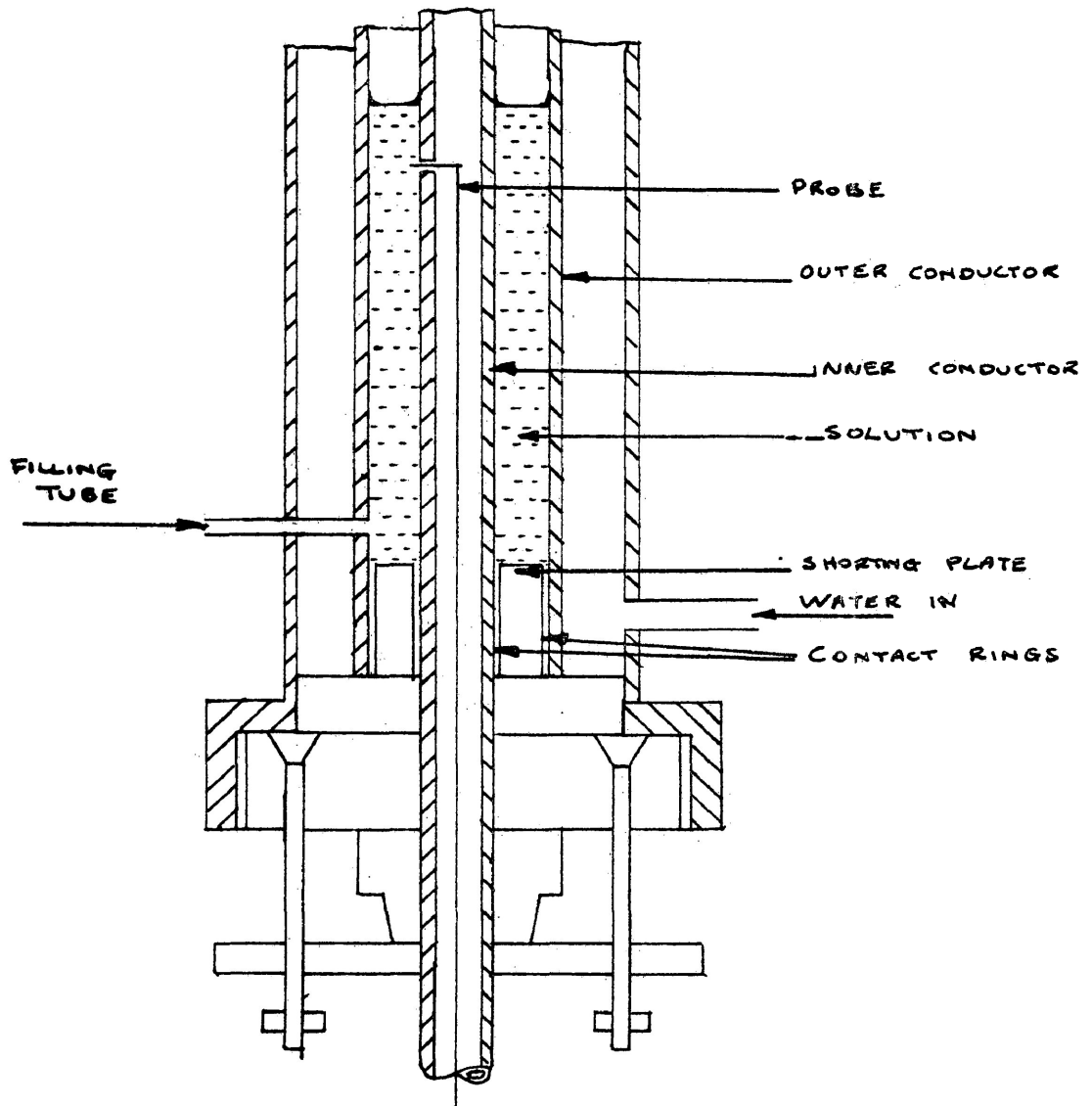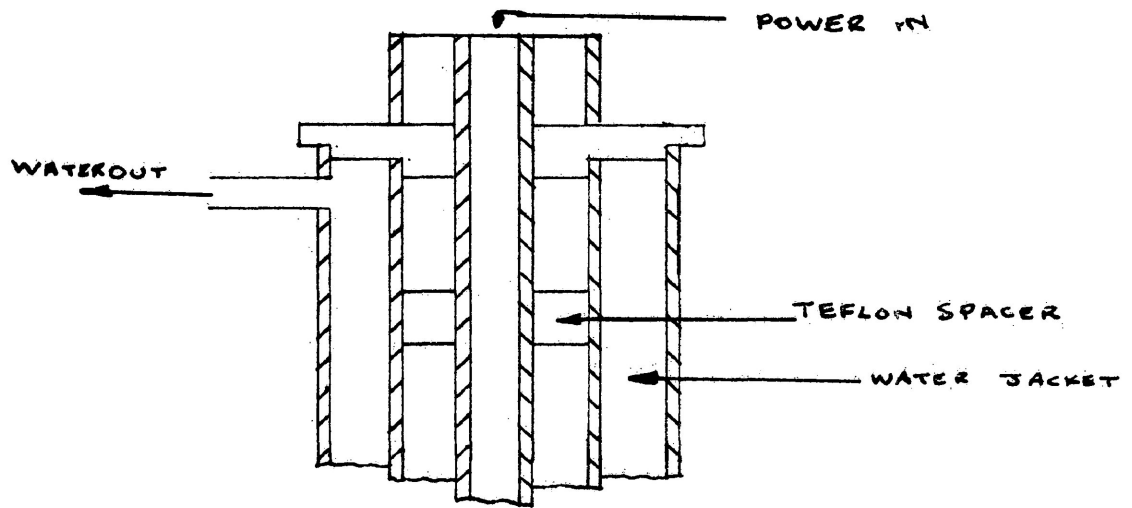
connector and is reflected from a silver short circuiting plate at the opposite end. The electric vector of the resulting standing wave pattern is sampled, within the liquid, by a probe which projects from the inner conductor of the coaxial cell. The output from the probe passes into a mixer where it meets with a signal from the local oscillator tuned to a frequency 30 MHz. away from the input signal. The resulting beat frequency is fed into an intermediate frequency amplifier which has a calibrated db. scale and allows the power level to be determined at the probe position.

The cell is hown in fig.1.3. It consists of a coaxial line made from a silver outer conductor of i.d. 14.3 mm. and a silver inner conductor of o.d. 4.1 mm. To ensure good electrical contact between the conductors and the shorting plate contact springs, made from silver collars, were inserted between both conductors and the short circuit. The centre conductor passes through a telescopic tube which ensures that it moves along the axis of the cell. Two teflon plugs hold the guide tube in position and its top, at the input end, which is connected to the centre contact of the input locking connector. The probe is the termination of the core of a length of coaxial cable which passes down the centre of the silver inner conductor. It is held in position by a plug of polyethylene which was melted within the centre conductor to provide a seal and eliminate the possibility of solution entering the tube. The position of the probe within the cell is measured on a vernier caliper which can be read to an accuracy of 0.02 m/m. The cell is filled through a small tube which passes through the water jacket into the centre conductor. The cell temperature could be controlled to $\pm$ 0.05°C. by circulating

FIG.1·3   THE COAXIAL CELL

POWER IN

WATER OUT

TEFLON SPACER

WATER JACKET

PROBE

OUTER CONDUCTOR

INNER CONDUCTOR

SOLUTION

FILLING TUBE

SHORTING PLATE

WATER IN

CONTACT RINGS

water from a thermostat bath through an outer jacket.

The frequency of the input radiation was measured using a Rodhe and Swartz U.H.F. Resonance Frequency meter type WAL. BN 4321/2.

A pad attenuator was inserted in the line between the oscillator and the cell to prevent pulling of the oscillator. Tuners were used in the line between the signal source and cell, and between the cell and mixer, to match the impedences of the circuit components. In order to eliminate harmonics generated by the source low pass filters, covering the appropriate measuring ranges, were inserted in the line between the oscillator and the cell. All connectors between components were General Radio Type QBL locking connectors to reduce reflections in the line and avoid any stray electromagnetic fields.

Table 1.2 lists the oscillators and components used in this apparatus.

Table 1.2

Component	Frequency Range G.Hz.	Supplier	Model
Oscillators	0.50 - 2.50	Rohde & Schwartz	SLRD
	0.90 - 2.00	General Radio	1218B
Low-Pass	<1.0 <2.0	General Radio	874 F1000L
Filters			874 F2000L
Tuners	0.90 - 2.0	General Radio	874LTL
		Microlab	S305N
Mixer	0.90 - 2.0	General Radio	MRAL

Table 1.2 continued.

Component	Frequency Range G.Hz.	Supplier	Model
I.F.Amplifier and db. meter	30 M.Hz	General Radio	1236

E. Determination of ϵ' and ϵ''

The variation of electric field strength of an electro-
magnetic plane wave, travelling through a medium, as a function
of time, t, and distance, x, is described (79) by the equation -

$$E = E_0 \exp. i\omega t \exp. - (\gamma x).$$ 1.15

where Eo is the amplitude of the electric vector, ω is the angular
frequency, and γ is known as the propagation coefficient defined
by the equation:

$$\gamma = \alpha + i\beta$$ 1.16

The significance of α and β is understood when 1.16 is re-
written in the form 1.17

$$E = [E_0 \exp. - (x\alpha)[\cos(\omega t - \beta x) + i\sin(\omega t - \beta x)]$$ 1.17

The first term on the right hand side is the amplitude of the wave
and it is seen that in travelling through a distance x the electric
vector has been reduced by a factor exp - (αx). Hence α is known
as the attenuation constant and is a measure of the diminution of
the electric field intensity of the wave per cm. of the medium. The
second term indicates that the phase of the wave has been reduced by
βx radians, hence, β is known as the phase constant.

When the incident wave, travelling in the +x direction, meets
the shorting plate it is reflected back towards the source. The
reflected wave returns to the -x direction and combines with the
incident wave to form a standing wave, the resultant field strength
of which is given by:

$$E = E_0 \exp. i\omega t \exp. -(\gamma x) + E_0 \exp i\omega t \exp (\gamma x). \qquad 1.18$$

i.e. $$E = E_0 \exp. i\omega t [\exp -(\gamma x) + \exp. (\gamma x)]. \qquad 1.19$$

Hence at any point x from the short circuit the amplitude of the

electric field is given by:

$$E = E_0 [2(\cosh 2\alpha x - \cos 2\beta x)]^{1/2} \qquad 1.20$$

From equation 1.20 it follows that the values of x at which

minima occur in the wave is given by

$$2\beta x = n\pi + (-1)^n \sin^{-1}[-\alpha/\beta \sinh 2\alpha x] \qquad 1.21$$

in which n is an even number integer.

For low loss solutions $\alpha << \beta$ hence, equation 1.21 gives β

as:

$$\beta = \frac{n\pi}{2x} \qquad 1.22$$

From equation 1.20 the ratio r of the amplitude at a minimum

position to that at a maximum, of the standing wave, is given by:

$$r^2 = \frac{|E_{min}|^2}{|E_{max}|^2} = \frac{(\cosh 2\alpha x_1 - 2\cos 2\beta x_1)}{(\cosh 2\alpha x_2 - 2\cos 2\beta x_2)} \qquad 1.23$$

$$\approx \frac{\sinh \alpha x_1}{\cosh \alpha x_2} \simeq \sinh \alpha x_1 \qquad 1.24$$

Where x_1 and x_2 are the distances of a minimum and maximum,

respectively, from the short circuit. For low loss solutions pairs

of positions of maxima and minima occur exactly at $x_1 = 2x_2$

hence, equation 1.24 reduces to

$$\alpha = \frac{r}{x_1} \qquad 1.25$$

β is determined by measuring the positions of the minima in

the liquid and α is determined by measuring the standing wave ratio

at each minimum. The latter was measured using the double minimum

method (78). In this procedure the electrical distance which

separates two points, on either side of a minimum, at which the

output is twice the minimum value, is measured. The s.w.r. is then given by the equation:

$$\frac{1}{r} = \frac{\lambda_m}{\pi \Delta x} \tag{1.27}$$

where λ_m is the length of the wave in the liquid, and Δx is the distance between 2 points on either side of the minimum separated by 3db.

α and β are related to ϵ' and ϵ' for coaxially propagated waves by:

$$\epsilon' = \frac{(\beta^2 - \alpha^2) \lambda_o^2}{4\pi^2} \tag{1.28}$$

and

$$\epsilon'' = \alpha\beta \frac{\lambda_o^2}{4\pi^2} \tag{1.29}$$

where, λ_o, is the free space length of the wave. Hence, by substituting values of α and β from equations (1.22) and (1.25) in (1.28) and (1.29) ϵ' and ϵ'' may be obtained.

The above theory was deduced on the assumption that the short circuit was perfectly reflecting and that the probe had no perturbing effect on the field. Buchanan and Grant showed that errors in α result if these two conditions are not fulfilled. Minimal errors in α, owing to reflections from the probe, are introduced when the length of the latter is 0.3 m/m or less. Thus, this was the optimum length selected for the probe. The above authors found that for a reflecting probe the apparent values of α increased as the distance from the short circuit increased, whereas if the short circuit is dissipative α decreases with increasing distance from the short circuit.

To test the efficiency of the short circuit and the suitability of the probe the cell was filled with acetone, which gave a large

number of minima, and α was measured at each minimum. The cell was found to be satisfactory up to a frequency of 2.5 G.Hz, at this value, however, α increased with increasing distance from the short which indicated errors due to reflections from the probe. Measurements were thus limited to an upper frequency of 2.0 G.Hz. It was found impossible to reduce the probe length, to extend the usable frequency range, since this resulted in a large decrease in the level of the detected power.

(c)   Assessment of the cell

Since the data obtained from the cell described forms a major part of the Cole - Cole plot the apparatus was evaluated by measuring the dielectric absorption of five dilute solutions of $\Delta^{3,5}$ Cholestadiene-7-one covering a range of concentration. The solvent used was p-xylene, and in addition to the above measurements the static dielectric constant, at 2 MHz, and the refractive index, at the frequency of the sodium D line, were measured for each solution. A Cole - Cole plot was constructed for each concentration and the data analysed using the Cole - Cole computer program.

It has been shown (80) that the dielectric parameters ϵ', ϵ'', ϵ_o, and ϵ_∞ can be represented as functions of concentration by the linear equations:

$$\epsilon'' = a'' w_2 \qquad\qquad (1.30)$$

$$\epsilon' = \epsilon_1 + a' w_2 \qquad\qquad (1.31)$$

$$\epsilon_o = \epsilon_1 + a_o w_2 \qquad\qquad (1.32)$$

$$\epsilon_\infty = \epsilon_1 + a_\infty w_2 \qquad\qquad (1.33)$$

Where α is the slope of the line, w_2 is the weight fraction of

the solute , and ϵ_1 is the dielectric constant of the solvent. From

the α values a Cole - Cole plot can be constructed and analysed to

give the required parameters τ_0, α, and ϵ_∞ . For each plot the

dipole moment was evaluated. The moment from the $a' - a''$ plot

was obtained from the equation.

$$\mu = \left[\frac{27 RT M(a_o - a_\infty)}{4\pi Nd (\epsilon_1 + 2)^2} \right]^{1/2} \qquad (1.34)$$

Hence, comparison of the data from each concentration plot with that

from the $a' - a''$ plot gives an assessment of the accuracy of the

method.   In addition the dipole moment was evaluated by the

Guggenheim method (55), to compare with the values obtained from the

plots.   Such a comparison is an invaluable aid as a check on the

analysed ϵ_∞ value, since errors in this parameter seriously affect

the relaxation time.

A typical Cole- Cole plot, at one concentration, and the $a' - a''$

plot, are shown in fig. 1.4.   The ϵ', and ϵ'' against concentration

plots are shown in figures 1.5 and 1.6 for the three frequencies at

which the cell was employed.   It is seen that the ϵ'' vs. concentra-

tion plots do not pass through the origin.   The intercept on the

ϵ'' axis at zero concentration was taken to be due to wall losses

within the cell.

The results of the analyses of the data are given in table 1.3.
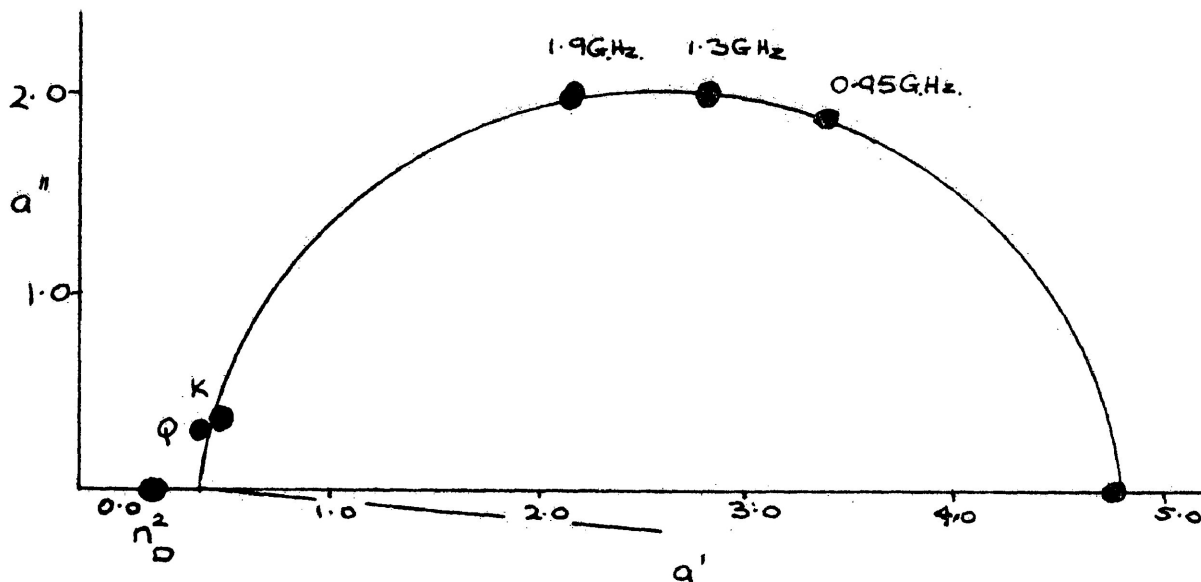
FIG 1.4a   a' - a" PLOT FOR   Δ-CHOLSTADIENE-7-ONE
IN   P-XYLENE.

Fig 1.4b. COLE-COLE PLOT FOR $^{3.5}$Δ-CHOLESTADIENE-7-ONE
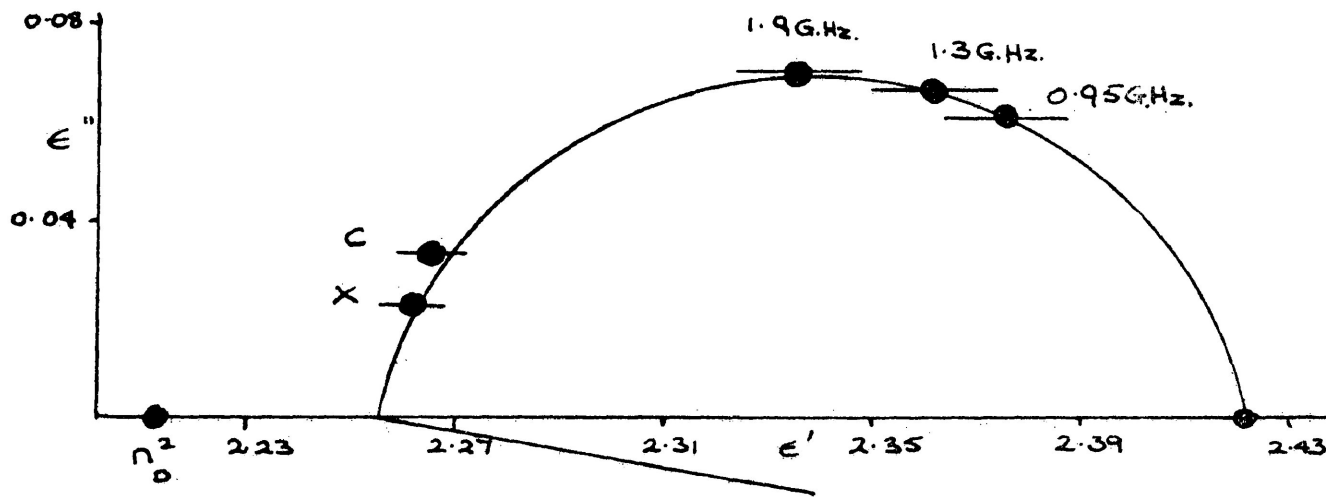
IN P-XYLENE T= 37.5°C $W_2 = 0.04044$.

FIG. 1.5 ϵ'-vs- WT. FRACTION FOR $\Delta^{3,5}$-CHOLESTADIENE-7-ONE IN P-XLENE

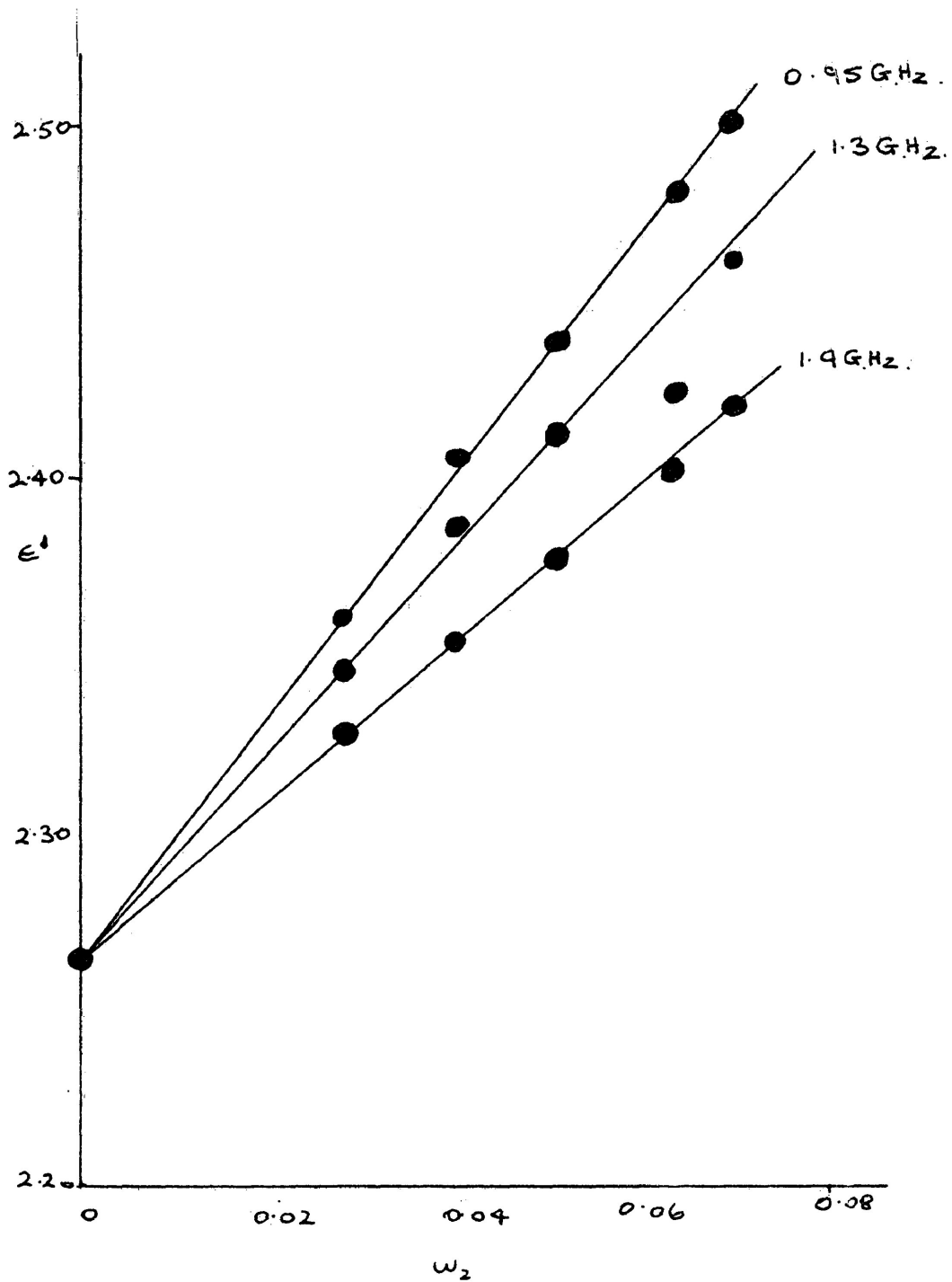FIG 1.6. $\mathcal{E}''$ -vs- WT. FRACTION FOR $\Delta^{3,5}$CHOLESTADIENE-7-ONE IN P-XYLENE
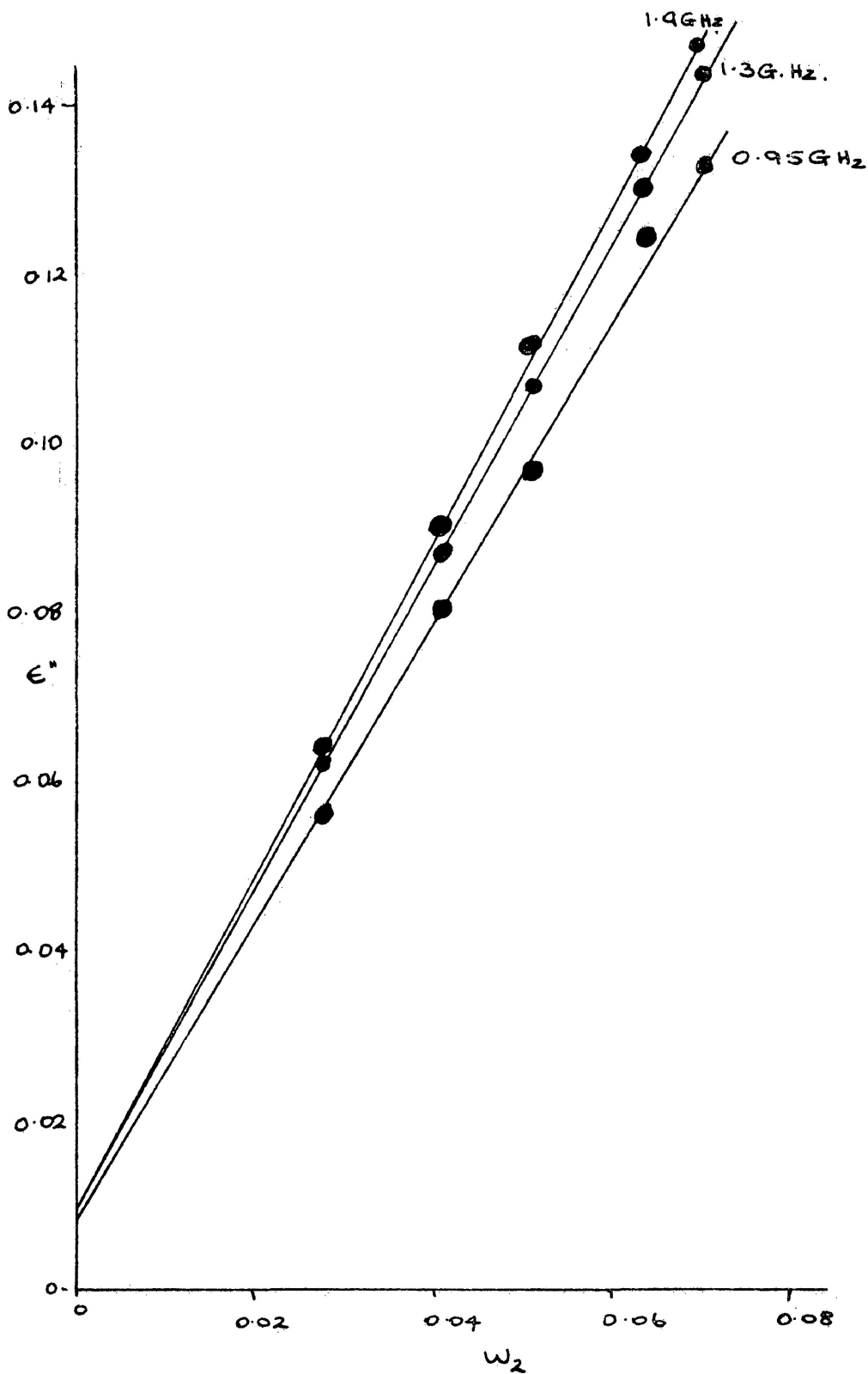
Table 1.3 comparison of data at different concentrations with the $a' - a''$ data

W_2	$T\,°C$	$\tau_0 \times 10^{-12}$ sec.	α	μ	μ Guggenheim
0.02798	25	108	0.11	4.03	
0.04071	25	108	0.08	4.03	
0.05089	25	103	0.09	4.02	4.09
0.06210	25	114	0.13	4.02	
0.06988	25	111	0.09	4.02	
$a' - a''$	25	102	0.08	4.06	

The agreement between the data from individual concentrations and the $a' - a''$ data is satisfactory and the moments compare satisfactorily with the Guggenheim value. Table 1.4 gives the measured and calculated values obtained from the analysis for the $a' - a''$ data. The microwave points show larger errors than those obtained from the coaxial equipment, which is to be expected, since the experimental error in the ϵ' points is larger than the total variation of this parameter over the whole concentration range. Similarly, ϵ'' does not exceed 0.02 and measurement of such small losses is subject to greater error than losses above 0.02.

Table 1.4 measured and calculated a' and a'', and percentage errors in each parameter.

ω rad sec^{-1}	a'meas.	a''meas.	a'calc.	a''calc.	% Error a'	a''
22.06×10^{10}	0.3889	0.3085	0.2397	0.2546	45.0	3.2
15.08×10^{10}	0.4878	0.3704	0.2671	0.3583	38.3	17.0
1.1939×10^{10}	2.1635	1.9930	2.1257	2.0014	1.7	0.4
8.163×10^{9}	2.8060	2.000	2.8365	2.0043	1.1	0.2
5.969×10^{9}	3.3962	1.8909	3.3781	1.8533	0.5	2.0
2×10^{6}	4.7872					

In view of the satisfactory agreement between the various parameters determined at individual concentrations, with one another and the $\alpha'-\alpha''$ data, future measurements were made at a single concentration.

Before making any measurements on any solutions the dielectric constant of cyclohexane was measured in order to check that the apparatus was working satisfactorily and to determine the short circuit position. The latter could not be measured directly since the vernier caliper was attached to the inner conductor at a position which prevented the probe from being damaged by contact with the shorting plate. Combined solvent and wall losses were measured and subtracted from the apparent loss of the solution. When there were sufficient minima, within a measured solution, the position of the short circuit was calculated from the minima positions and compared with that obtained from measuring cyclohexane. This provided an additional check on the accuracy of the determination of the minima positions. The loss factor was determined at each minimum and the average value used in the construction of the Cole - Cole arc.

F. Analysis of Results

(a) The mean, or most probable, relaxation time, τ_o .

The Cole - Cole plot (71) was used as the basis for the interpretation of the dielectric data. Values of α and ϵ_{∞} were estimated from the plot whereas τ_o was estimated from one of the linear plots. These estimates together with the measured value of ϵ' and ϵ'' at each frequency of measurement, and ϵ_o , were fed into an I.B.M. 360 computer programed to fit equations 1.10 and 1.11 to the experimetal data.

From the initial estimates of τ_o , α , and ϵ_{∞} the computer back calculates the values of ϵ' and ϵ'' at each frequency and, by an iterative procedure, the three parameters are sucessively varied until the square of the differences between measured and calculated values is a minimum. At this stage the best fit of the experimental data to the equations is obtained. The accuracy of the analysis was then judged from a comparison of the calculated and measured values when minimisation was complete.

(b) Graphical Methods of Analysis

τ_o may be obtained by plotting the function log $\frac{v}{u}$ against log ω , where v is the distance between an experimental point on the arc and ϵ_o , at a frequency ω , and u is the distance from the point to ϵ_{∞} .

It follows from the relation:

$$\frac{v}{u} = (\omega \tau_o)^{1-\alpha}$$

that when $\log \frac{\vee}{\overline{u}}$ is zero the frequency intercept corresponds to

that at which ϵ'' is a maximum, hence, τ_o is evaluated from this

frequency.

A number of other equations have been obtained by algebraic

manipulation of equations 1.6 and 1.7.

Elimination of ϵ_∞ from 1.6 and 1.7 gives:

$$\epsilon' = \epsilon_o - \tau \omega \epsilon'' \qquad (1.35)$$

and

$$\epsilon \quad \epsilon_\infty + \frac{\tau \epsilon''}{\omega} \qquad (1.36)$$

These equations are linear and τ can be obtained from the

slope by plotting ϵ' against either $\epsilon'' \omega$ or ϵ''/ω. Equation 1.35

has been employed by Purcell, Fish and Smyth (74) to give an

indication of a second relaxation process for systems showing a

non-zero distribution coefficient. For systems characterised by

Budó behaviour the plot is a curve, the limiting slopes of which

in the low and high frequency regions give the approximate values

of two relaxation times. This procedure tends to yield a higher

relaxation time which is too short, and a lower relaxation time

which is too long.

The plots of equation (1.35) for the three types of behaviour

according to equations (1.5), (1.9) and (1.12) and (1.13) are given in

fig. 1.7. The corresponding ϵ'' log ω plots are given in fig.1.8

and the Cole - Cole plots in fig.1.9.

Fig 1.7a ϵ'-vs $\epsilon''\omega$ plot for Debye Behavior.
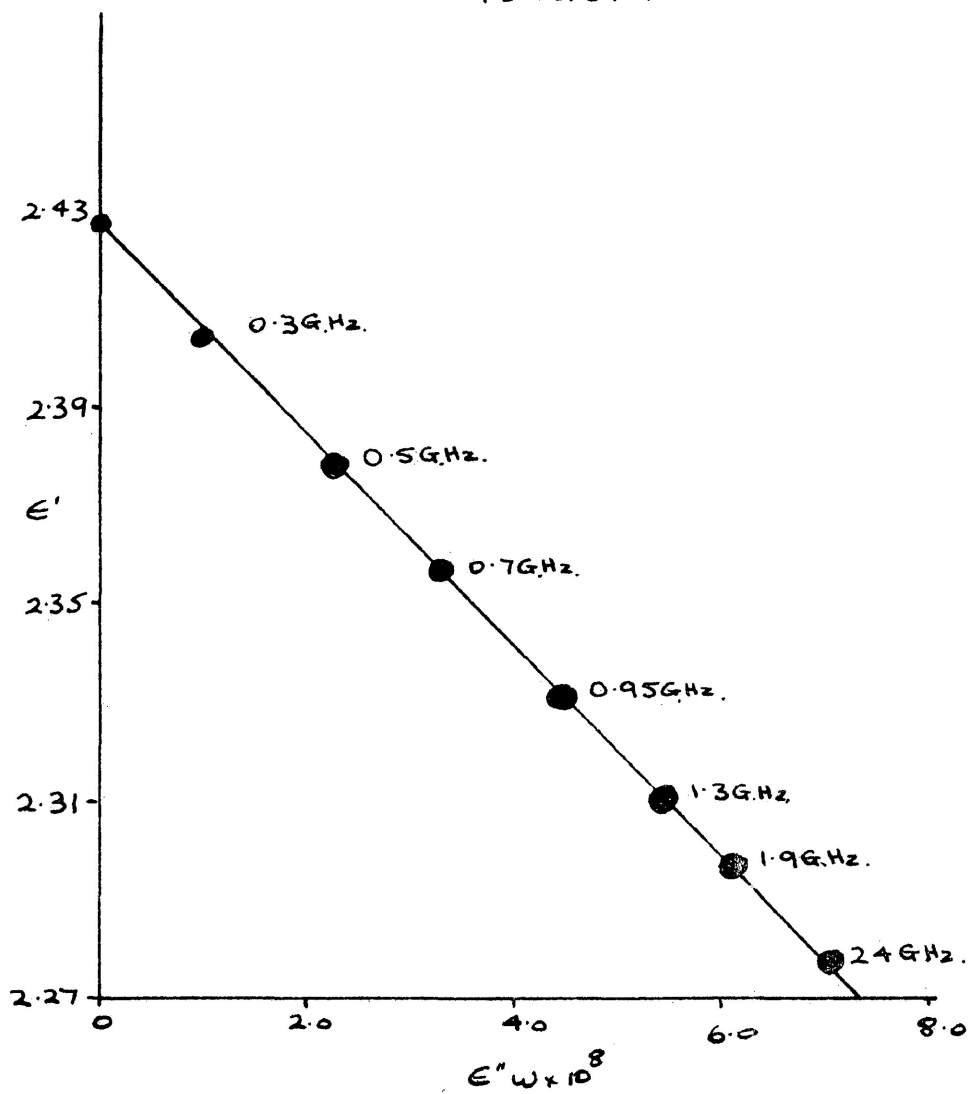
$\gamma = 216 \times 10^{-12}$ sec.

FIG 1.7b. ϵ'–vs $\epsilon''\omega$ PLOT FOR COLE-COLE

BEHAVIOR

$\tau_0 = 216 \times 10^{-12}$ sec. $\alpha = 0.15$
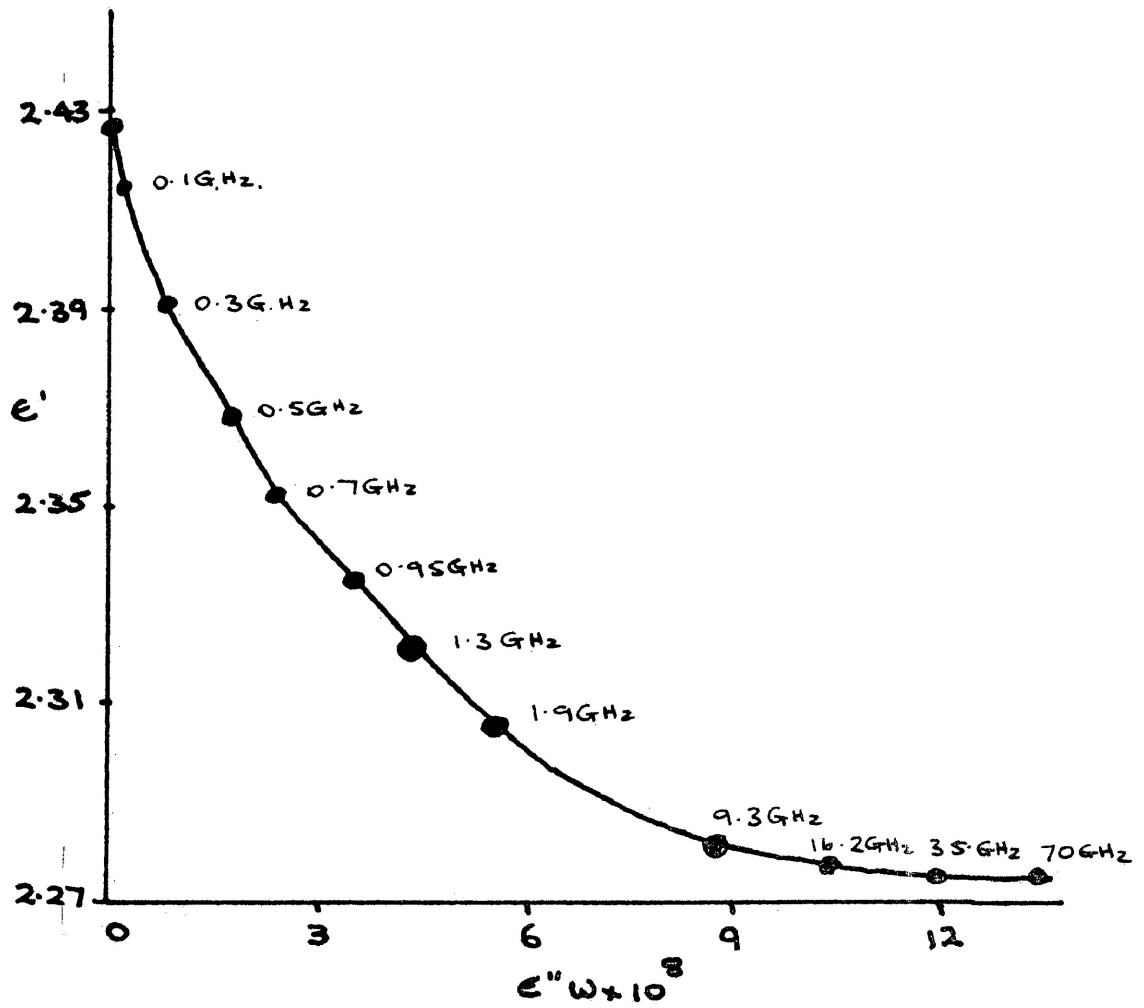
Fig 1.7c. ϵ'-vs-$\epsilon''\omega$ plot for Budó Behavior.

$\gamma_1 = 200 \times 10^{-12} sec.$

$\gamma_2 = 50 \times 10^{-12} sec.$
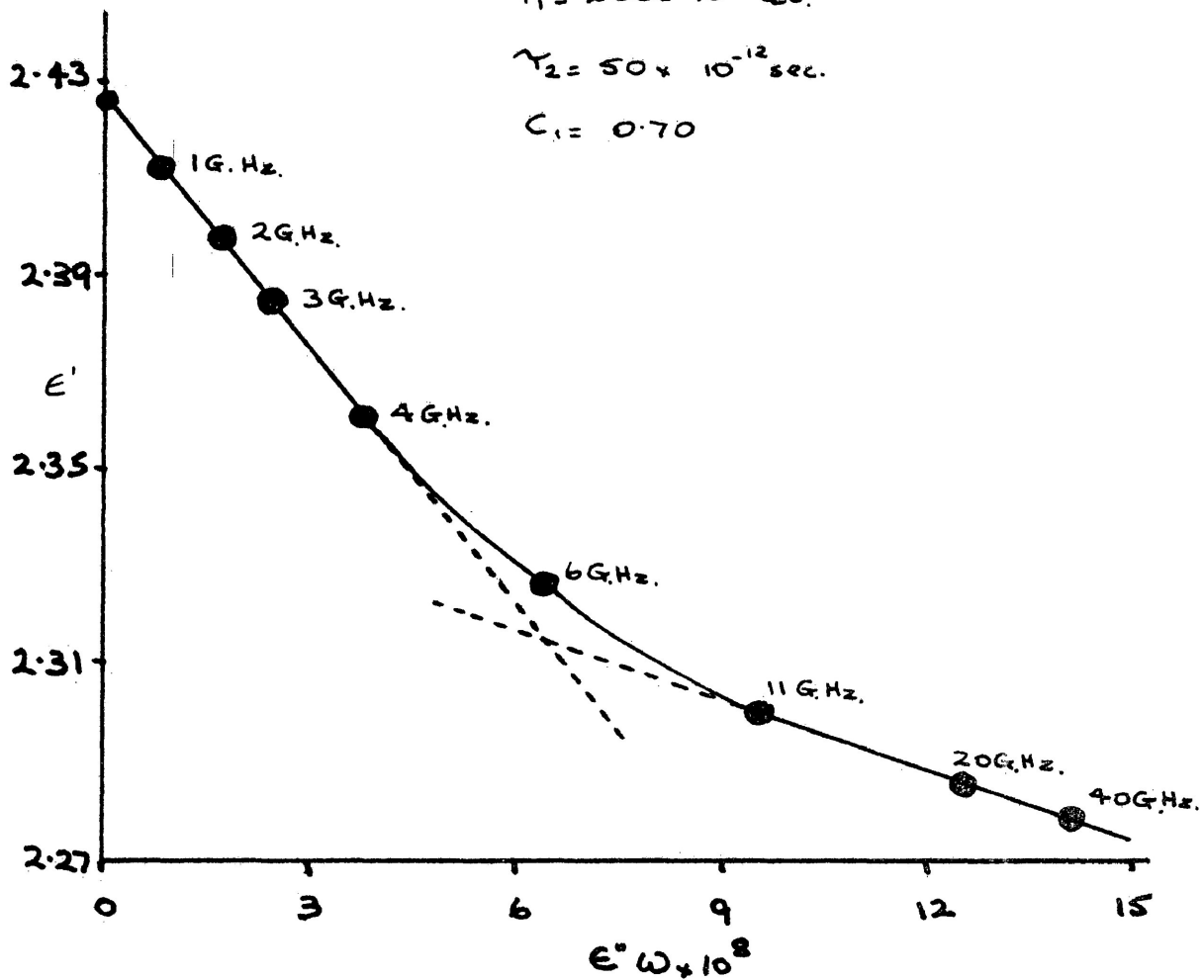
$C_1 = 0.70$

Fig 1·8a. ε''-log ω. plots for Debye and Cole-Cole Behavior
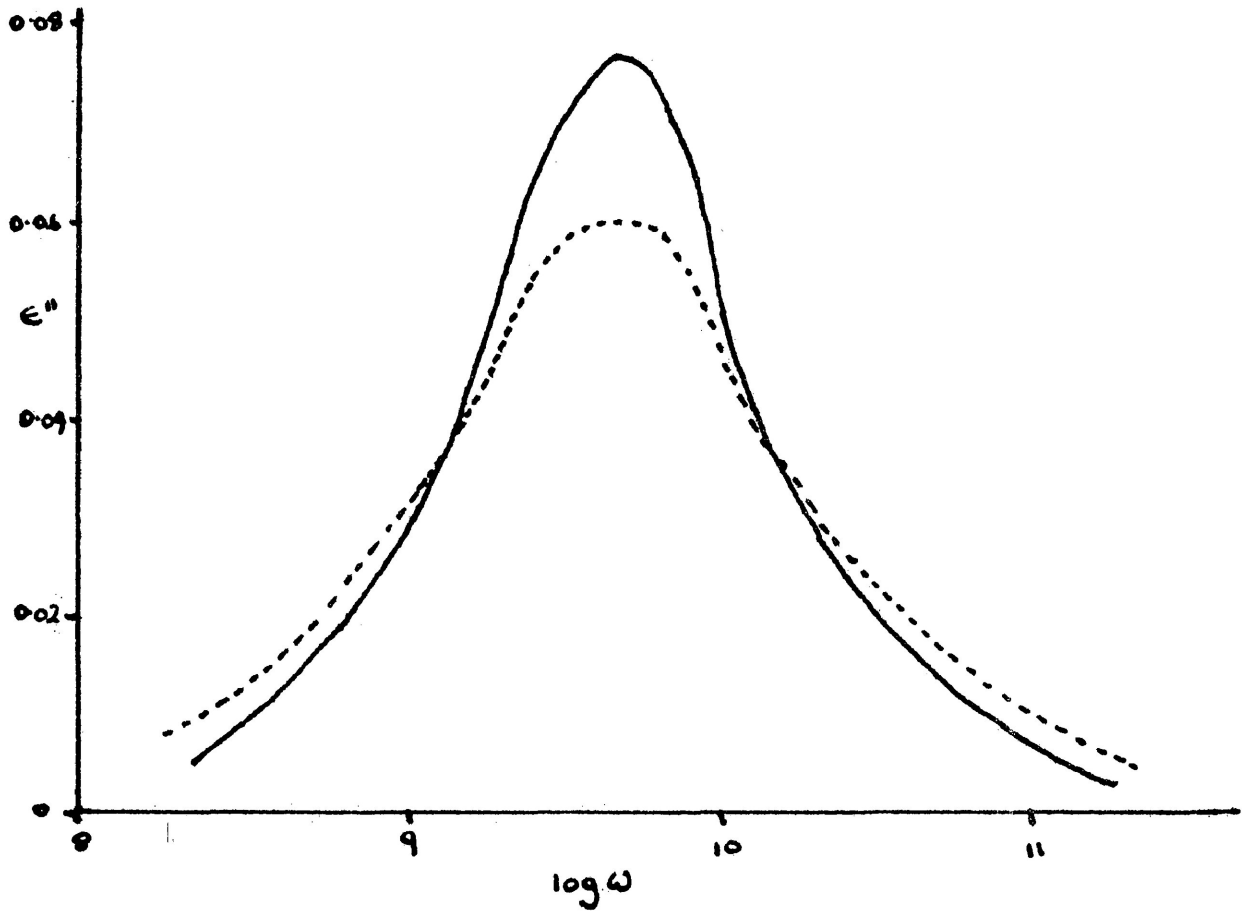
DEBYE $\tau = 216 \times 10^{-12}$ sec.

COLE-COLE $\tau_0 = 216 \times 10^{-12}$ sec. $\alpha = 0.15$

FIG. 1·8b ϵ''-$\log\omega$ PLOT FOR BUDÓ BEHAVIOR

$\gamma_1 = 200 \times 10^{-12}$ sec., $\gamma_2 = 50 \times 10^{-12}$, $C_1 = 0.70$
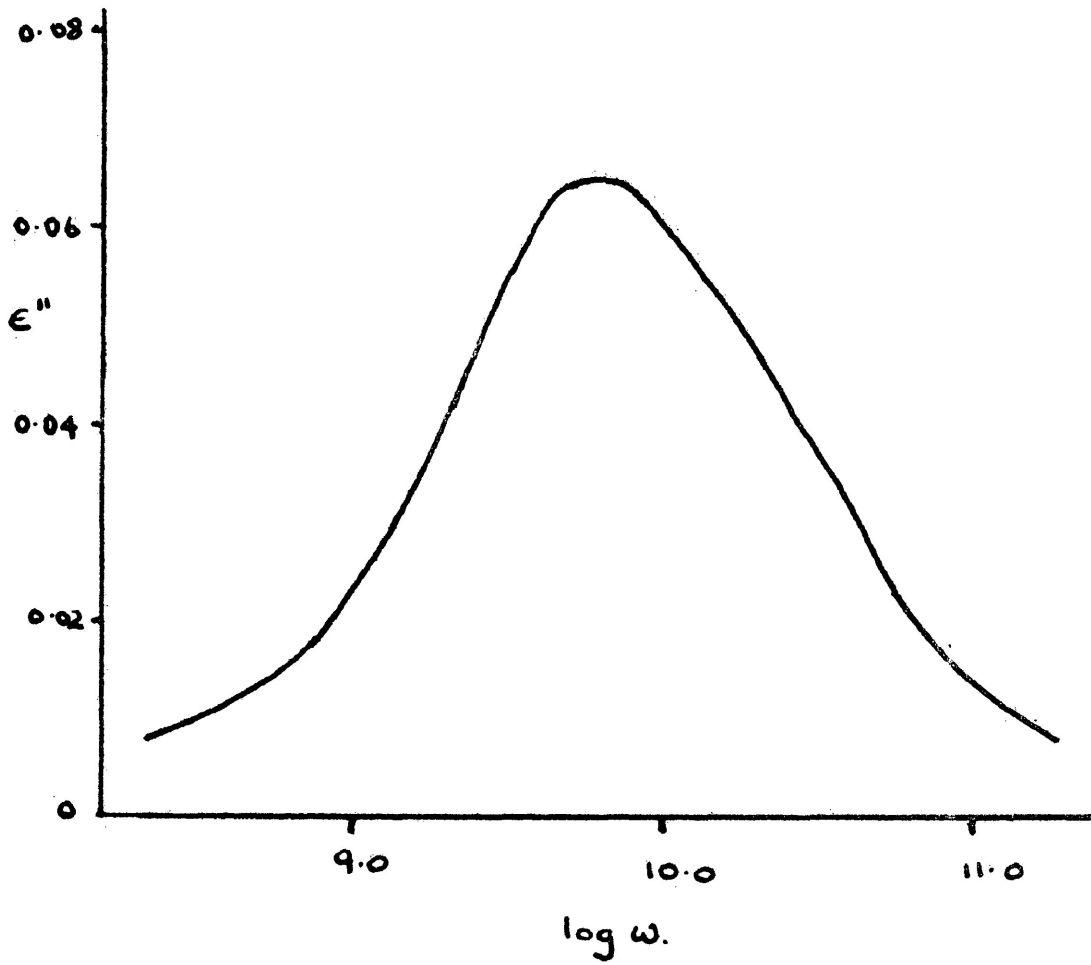
FIG 1.9a COLE-COLE FOR DEBYE BEHAVIOR

$$\Upsilon = 216 \times 10^{-12} \text{ sec.}$$
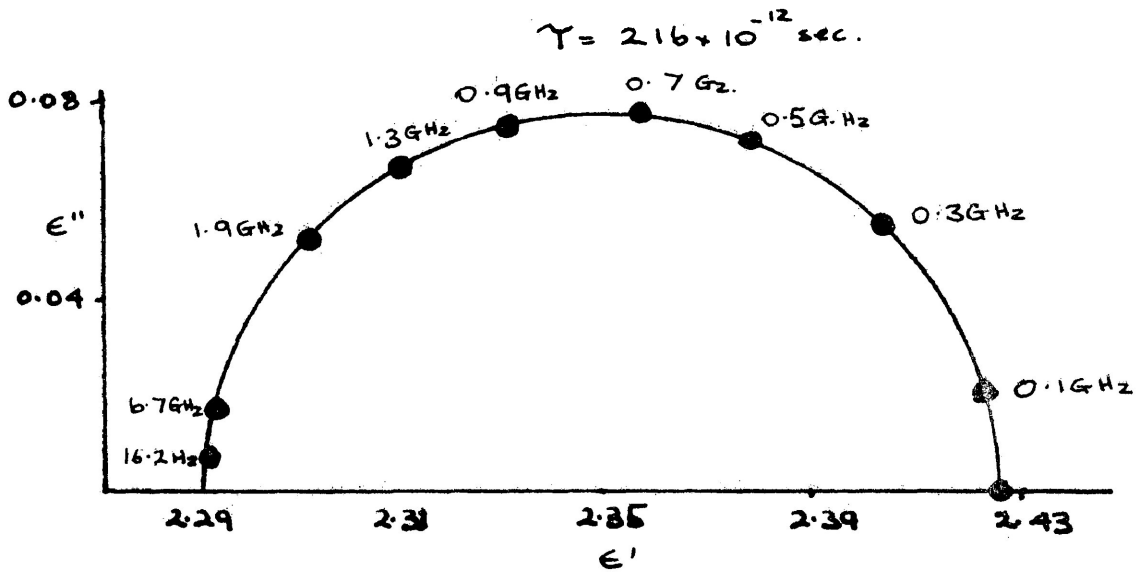
FIG 1.9b COLE -COLE BEHAVIOR

$$\Upsilon = 216 \times 10^{-12} \text{ sec.} \quad \alpha = 0.15$$
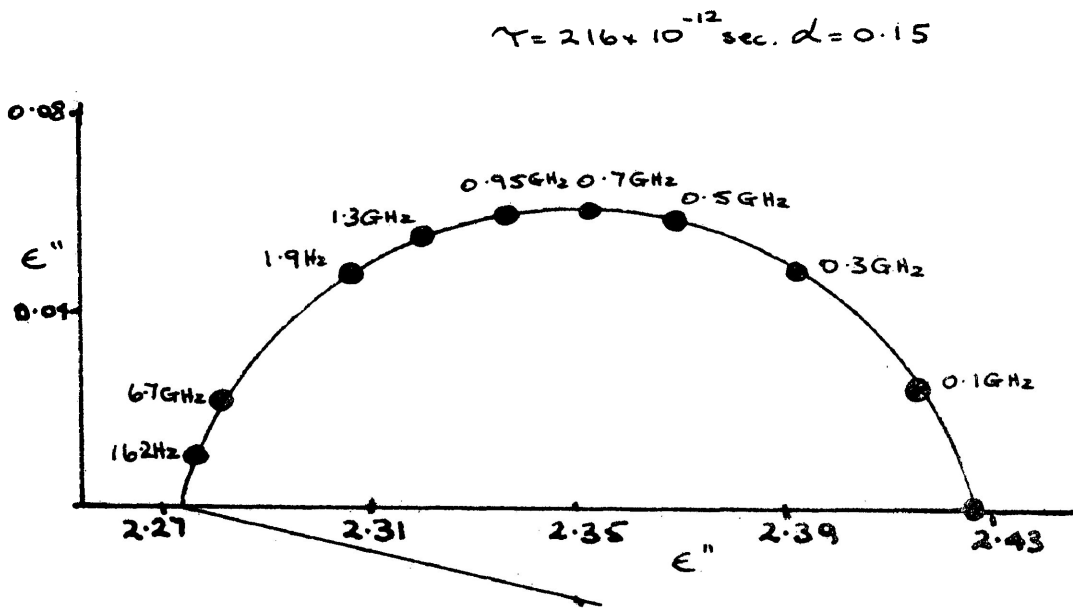
FIG. 1.9c. COLE-COLE PLOT FOR BUDÓ BEHAVIOR

$\tau_1 = 200 \times 10^{-12} sec., \tau_2 = 50 \times 10^{-12} sec, C_1 = 0.70.$
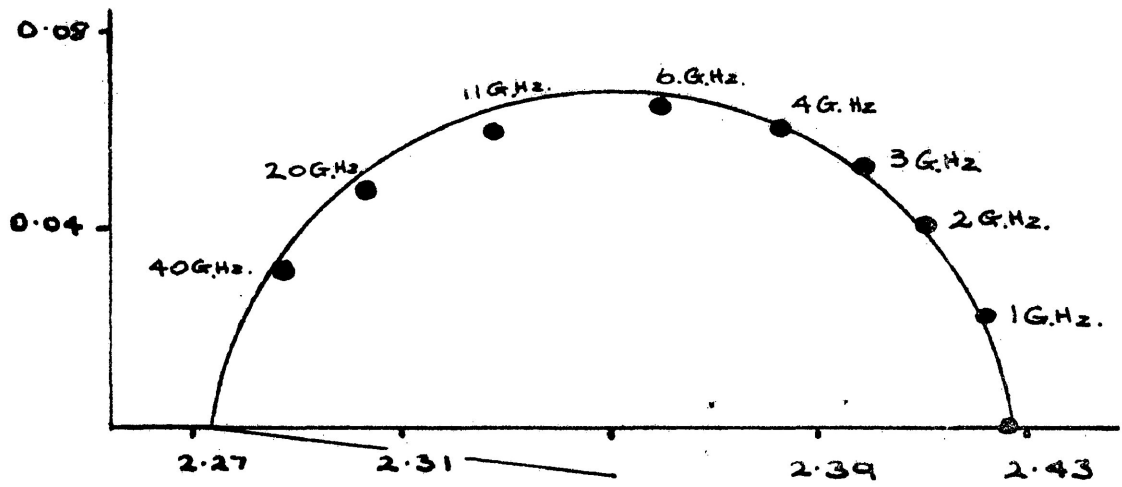
G. Dipole Moment Determination

The Debye equation gives the dipole moment of a polar solute

as

$$\mu = 0.01281 \, 2 \left[\frac{3T(\epsilon_o - \epsilon_\infty)M}{(\epsilon_o + 2)(\epsilon_\infty + 2) w_2 \, d_{12}} \right]^{1/2} \tag{1.37}$$

where M is the molecular weight of the solute, w_2 is the weight fraction of the solute, and d_{12} is the density of the solution. For dilute solutions this has been modified by extrapolation to infinite dilution to yield.

$$\mu = 0.01281 \, 2 \left[\frac{3T(\epsilon_o - \epsilon_\infty)M}{(\epsilon_1 + 2)^2 \, d_1 \, w_2} \right]^{1/2} \tag{1.38}$$

in which ϵ_1 is the dielectric constant of the solvent and d_1 is its density.

H. <u>Preparation and Purification of Materials</u>

1) Solvents

Cyclohexane and p-xylene were obtained from commercial

sources. The solvents were dried over, and refluxed from, sodium,

followed by distillation from sodium through a two foot column

packed with glass rings. The middle fraction was collected and

stored over sodium in stoppered amber bottles.

2) <u>Purification of Solutes</u>

With the exception of 5α -Androstan-3-one, which was used as

received, the sterioids were recrystalised from alcohol and dried

in a vacuum oven over P_2O_5 . Tetraphenylcyclopentadieneone was

recrystallized from cyclohexane and dried as above. After purifi-

cation the spectra of the materials were examined and compared with

literature data (81) (82) (83) (86). The melting points, the

supplier, and literature value of the melting point of the materials

is given in Table 1.4.

Table 1.4

Solute	Supplier	M.pt.^{o}C	lit.M.pt^{o}C	ref.
5α -Cholestan-3-one	B.D.H.	127-128	129	83
3,5Δ-Cholestadiene-7-one	K and K Lab. Inc.	106-107	107-108	86
5α-Androstan-3-one	Mann Research Laboratories	104-106	104.5-105.5	87
5α-Androstan-3:17-dione	Sigma Chem. Co.	131-133	132-133	88
4Δ-Androstᴇn-3:11:17-trione	K & K Lab. Inc.	220-222	222	89
Tetraphenyl cyclopentadien-eone	K & K Lab. Inc.	218-219	219-220	90

I. Additional Measurements

Static dielectric constants were measured on a heterodyne beat apparatus at 2 MHz. A Wiss-Tech-Werkstatten Dipolmeter type DM01, was used. Before each measurement the instrument was calibrated with, dry air, pure cyclohexane, pure p-xylene and for dielectric constants higher than 2.30, pure toluene. The value of ϵ_o was reproducible to $\pm$ 0.002.

Refractive indices were measured using an Abbe refractometer, type 58273 manufactured by Carl Zeiss, at the frequency of the sodium D line.

Densities were determined using a pyknometer of the type described by Cumper, Vogel and Walker (84)

J. Experimental Results

(a) Corrections

The solvents used in this study have been found to have a small absorption in the microwave region (85), (96). Hence, the measured dielectric parameters have been corrected using the equations:

$$\epsilon''_{corr.} = \epsilon''_{meas.} - \epsilon''_{solvent.}$$

$$\epsilon'_{corr.} = \epsilon'_{meas.} + \left[\epsilon'_{o\ solvent} - \epsilon'_{solvent} \right]$$

Corrections of this nature were only found to be necessary for K and Q band points.

(b) Presentation of Results

The static dielectric constant, high frequency dielectric constant, square of the refractive index, dipole moment, distribution coefficient, and mean relaxation time are listed for each compound measured in table 2.1 of chapter 2.

Measured and calculated dielectric constant and loss data, and parameters for determination of dipole moment by the Guggenheim method, are listed in an appendix at the end of the thesis.

Although the data obtained could not be analysed into contributions from two or more relaxation times the presence of more than one absorption mechanism, corresponding to different molecular reorientations, is inferred by comparing relaxation times of molecules of similar size and shape.

The data listed in table 1.5 are used to illustrate this point. The data were compiled by calculating ϵ' and ϵ'' at a number of frequencies using the Budó equations for various τ_1, τ_2 and C_1 values it was then fed into the Cole - Cole program to obtain the mean relaxation time and the distribution coefficient. It is seen that

α is not very sensitive as a means of detecting two processes, one of which has a weighting factor greater than 0.5, however, the mean relaxation time is sensitive and thus can be used to infer the presence of more than one process.

Table 1.5 Relationship between τ_1, τ_2, c_1, and τ_0, and α.

$\tau_1 = 200$, $\tau_2 = 180$			$\tau_1 = 200$, $\tau_2 = 150$			$\tau_1 = 200$ $\tau_2 = 100$		
c_1	τ_0	α	c_1	τ_0	α	c_1	τ_0	α
0.90	198	0	0.90	195	0	0.90	188	0.010
0.70	194	0	0.70	184	0	0.70	163	0.028
0.50	190	0	0.50	173	0	0.50	141	0.034
0.30	186	0	0.30	163	0	0.30	122	0.029
0.10	184	0	0.10	154	0	0.10	107	0.010

$\tau_1 = 200$, $\tau_2 = 80$			$\tau_1 = 200$, $\tau_2 = 50$		
c_1	τ_0	α	c_1	τ_0	α
0.90	185	0.016	0.90	181	0.029
0.70	155	0.042	0.70	142	0.066
0.50	127	0.054	0.50	102	0.109
0.30	104	0.050	0.30	72	0.107
0.10	86	0.027	0.10	55	0.047

All τ values in units of 10^{-12} sec.

CHAPTER TWO

THE DEBYE MODEL AND ITS

MODIFICATIONS

Introduction

Many attempts have been made to determine the parameters which govern the magnitude of the dielectric relaxation times of rigid polar molecules. Among the effects investigated are the viscosity of the medium, the size and shape of the polar molecule, and the direction of the dipole within the molecule.

A series of molecules which had a wide range of sizes was examined by Meakins using two or three solvents. This author compared the experimental relaxation times with those calculated from the equation:

$$\tau = \frac{3\upsilon\eta}{kT}$$

where υ is the volume of the molecule,

η is the viscosity of the solution of the polar molecules,

k is the Boltzmann constant,

T is the absolute temperature.

The result of this study prompted Meakins to conclude "*where the molecular volume of the solute is about three times that of the solvent, the calculated relaxation times are in reasonable agreement with the measured values.*" One of the molecules for which Meakins found this agreement was the steroid $^4\Delta$-cholestan-3-one. Such molecules which have a double bond at the 4-5 position, or steroids of the 5α series which have four trans-fused rings, have structures which are conformationally locked. As well as being rigid, the molecules are roughly ellipsoidal in shape. It then becomes

possible to take members of a particular steroid series and alter the position of the dipole with respect to the principal axes of the molecular ellipsoid. By choosing molecules with a rigid dipole, in this case the carbonyl group, no intramolecular processes are possible, hence, the measured relaxation times correspond to molecular motions.

In other systems of smaller molecules, alteration of the dipole position usually affects the overall shape of the molecules and in doing so varies two parameters. In the steroids, however, little change in shape occurs on alteration of the position of the dipole within the molecule.

Two basic steroid structures of differing elliplicity were examined in order that the effect of changing the axial ratios could be investigated, and for comparison the relaxation time of the disc-like ketone, tetraphenyl-cyclopentadieneone has been measured.

Discussion

Debye (41) proposed a model for the dielectric relaxation of rigid spherical polar molecules in which it was assumed that the molecule was of radius, a, and moved in a continuous fuid of viscosity, η. The fluid was considered to adhere to the surface of the sphere and the frictional coefficient, ξ, which it experienced during its rotation, was assumed to be given by Stokes' law as:

$$\xi = 8\Pi\eta a^3$$

The motion of the molecule was considered to be the rotational

analogue of Brownian translation motion, since changes in direction

of the molecule and fluctuations of its kinetic energy are frequent due to

collisions with the surrounding molecules of the liquid. In the presence

of an electric field the angular distribution of the dipoles is altered

very slightly such that there tends to be a small excess in the field

direction, and this is the origin of the dielectric polarisation. If the

induced moment in the field direction is M_F then the rate of change of

M_F with time is given by:

$$\frac{dM_F}{dt} = -\frac{M_F}{\tau} \pm \frac{2}{3} \frac{\mu^2 FN}{\xi}$$

where F is the field strength,

   μ is the moment of the dipole,

   τ is the relaxation time,

   N is the number of dipolar molecules.

The above equation is valid if the following conditions are satisfied:

   (i)   there is no interaction between the dipoles,

   (ii) in the short time interval, δt, the angle which the

         dipole makes with the field is altered only slightly.

This then leads to an exponential approach to an equilibrium distribution

of orientation of the dipoles, and hence to the Debye dispersion equation.

The relationship between the viscosity for solute rotation, the radius of

the sphere, and the relaxation time is given from this approach by the

equation:

$$\tau = \frac{4\pi\eta a^3}{kT} \dots\dots\dots\dots\dots\dots\dots\dots(2.1)$$

Frequent reference will be made to equation (2.1) during this chapter, so for the sake of clarity it will be referred to as the Debye-Stokes' equation.

Over the years equation (2.1) has been the subject of many investigations on dielectric behaviour, and although it is only applicable to molecules of spherical shape, it is often used to interpret the behaviour of molecules of lower symmetry.

One of the early investigations of the equation was made by Curtis, McGeer, Rathmann, and Smyth (42). Although few spherical molecules exist, these authors considered methylchloroform and tertiary butyl chloride to be of approximate spherical shape. They measured the dielectric relaxation times of these molecules in n-heptane, carbon tetrachloride and nujol solutions and in all cases it was found that the measured relaxation times were smaller than those predicted by the Debye-Stokes' equation. In fact, they found little parallelism between τ and the viscosity of the medium. For example, they found that the relaxation time of t-butyl chloride in nujol was only 2/3 greater than in heptane, although the viscosity of the former is $\sim$260 times that of the latter. Furthermore, the relaxation time for t-butyl chloride in the pure liquid state was found to be greater than for the nujol solution, but its viscosity was only 1/200th

of that of the oil.

Derivatives of benzene deviate somewhat from the ideal spheri-
cal shape but equation (2.1) has been applied to them (43). Pyridine
and fluorobenzene in the pure liquid state have nearly the same re-
laxation times, yet the measured viscosity of pyridine is 47% larger
than that of fluorobenzene. Clearly, the use of the measured vis-
cosity in equation (2.1) does not give satisfactory agreement between
measured and calculated values of relaxation time.

Because of the lack of dependence of relaxation time on
measured viscosity, the concept of inner friction or microscopic vis-
cosity was postulated (44). This quantity was calculated by using
the measured relaxation time and known molecular dimensions in equa-
tion (2.1), which was solved for η. The inner friction is a somewhat
vague parameter and it shows little parallelism with the macroscopic
viscosity (44). Indeed, the apparent microscopic viscosity of
pseudo-spherical molecules in the solid state may be less than that
for the pure liquid.

Fischer (45) found that the inner friction coefficient for
benzene solutions was of the order of one quarter of the solvent
viscosity. However, on changing the solvent, the apparent agreement
between theory and experiment was lost. In a comprehensive review of
dielectric relaxation, Illinger (46) concluded that only in the
limiting condition that the solvent medium surrounding an absorbing

polar molecule represents a uniform fluid is it possible to define a viscosity coefficient which is a property of the medium alone.

Hill (47) attempted to account for the frictional coefficient by a different approach. Based on the Andrade (48) model of the liquid state, she assumed that the torque produced in the loss of angular momentum, resulting from the collision of solute and solvent molecules, was equal and opposite to the torque applied by the field. The Hill equation includes a factor involving the moment of inertia of the molecules and a mutual viscosity parameter accounting for the interaction between the solvent and solute molecules.

Meakins (49) compared the calculated relaxation times obtained by the Hill and Debye-Stokes' equations and concluded that for small solute molecules, the former equation gave results closer to those experimentally determined. The agreement, however, with the Hill equation becomes poorer with deviation from approximate equality of size of solute and solvent (44)(50). In fact, Meakins found that, as the solute size increased, the system tended towards the hydrodynamic behaviour assumed as the basis for the Debye model.

The investigation of the effect of the molecular dimensions on the relaxation time of polar molecules has been more successful

than the viscosity approaches. It is observed that for molecules
of similar shape, which have the molecular dipole along the same
principal symmetry axis, that there is a regular increase of re-
laxation time with molecular size. Hassell (51) has observed such
a linear dependence of relaxation time on molecular volume for p-
xylene solutions of the halobenzenes. A more extensive investigation
was made by Eichhoff and Huffnagel(20). These workers found, for
a number of solutes in a given solvent, a linear relationship, when
log τ was plotted against an effective radius. The latter para-
meter was taken as the distance from the centre of mass to the
perifery of the molecule.

To account for deviations from spherical symmetry, Perrin(52)
modified the Debye-Stokes' equation for the general case of ellip-
soidal molecules. For a rigid molecule having a resultant moment μ,
composed of components μa, μb, and μc, along each of the three prin-
cipal axes of inertia, there are three corresponding relaxation times.

On the basis of the Perrin theory, the average moment M_F in
the field direction is given by :

$$M_F = \frac{Fe\ N}{3kT}\ iwt\left[\frac{\mu a^2}{1+iw\tau a} + \frac{\mu b^2}{1+iw\tau b} + \frac{\mu c^2}{1+iw\tau c}\right]$$

Where μa, μb, and μc are the moment components along the three
principal axes A,B, and C and τa, τb, and τc are the corresponding

relaxation times. In terms of the frictional coefficients, ξ, the relaxation times are given by:

$$\tau a = \frac{\xi bc}{2kT}$$

$$\tau b = \frac{\xi ac}{2kT}$$

$$\tau c = \frac{\xi ab}{2kT}$$

Where

$$\frac{2}{\xi_{bc}} = \frac{1}{\xi_b} + \frac{1}{\xi_c}$$

anologous expressions describe ξ_{ab} and ξ_{ac}. It is thus seen that the relaxation time for rotation about a particular axis depends on the frictional coefficients associated with the other two axes. When the molecular moment is directed along one of the principal axes of the molecule, then the theory predicts a single relaxation time, since two of the moment components are zero.

Fischer (45) expressed the Perrin theory in the form:

$$\tau z = \frac{4 \Pi f z}{kT} \eta abc$$

Where $z = a, b, c$ and fz is a factor which gives the ratio of the relaxation time about an ellipsoid axis to that of a sphere of equal volume; a,b, and c are the lengths of the semi-axes of the molecular ellipsoid. The form factor f_z has been tabulated in

terms of the axial ratios $\underline{b}$ and $\underline{c}$ by Budo, Fischer and Miyamoto (53). $\frac{b}{a}$ $\frac{c}{a}$
The mean relaxation time is then obtained from the Budo (54) re-
lationship:

$$\tau_0 = \sum_{\mu} \frac{\mu i^2}{\mu^2} \tau i$$

Where μi is a moment component in the direction of a symmetry
axis and τi is its corresponding relaxation time.

Although the Perrin theory predicts a single relaxation time
when the molecular dipole is parallel to a principal symmetry axis
it apparently neglects the fact that there are two axes perpendicular
to the dipole around which rotation is possible. Pitt and Smyth (37)
have drawn attention to this point. These authors measured the
dielectric relaxation times of two porphyrazine derivatives, the
structural formulae of which are shown in Fig. 2.2, which are disc-
like molecules and have a radius of approximately $10\overset{\circ}{A}$. One molecule,
heptaphenyl chlorophenylporphyrazine, VI, has its dipole in the
plane of the ring, the other, ferric octaphenyl porphyrazine chloride,
VII, has its dipole perpendicular to the ring plane. Rotation about
the two axes perpendicular to the moment in VII involves similar out-
of-plane molecular motions, however, in the other molecule one motion
is in the plane of the ring whereas the other is out of the plane.
It was observed that the relaxation time of VII was more than twice
that of VI but the Fischer formula predicted that the relaxation
time for the two molecules should be similar.

The observed large differences between the relaxation times was explained in terms of the volumes swept out by the molecules during their rotations. In the case of VII rotation involves a large displacement of the solvent molecules, it thus suffers considerable frictional resistance to its motion. For VI, however, rotation in the disc plane involves only a small displacement of solvent molecules, it thus suffers less resistance to this motion which results in a reduction of its mean relaxation time. The same authors also accounted for the behaviour of three, 3-ring, disc-shaped molecules using the same argument.

The results of the measurements on the large ketones are given in Table 2:1. Computer analysis of the data into two or more component relaxation times was not possible because of the sparcity and distribution of the points on the Cole-Cole arc. For all the systems measured ε' against $\varepsilon''\omega$ plots were constructed and it was found that generally two straight lines could be drawn through the experimental points. One line passed through the coaxial cell points, and C and X_{b} and bridge points when these could be measured; the other was of somewhat uncertain slope and passed through the high frequency bridge points of P, $Q_{,}$ and K bonds. In this latter region of the absorption of the molecules ε' varies little with frequency, so that the error in this parameter is larger than the change in its value observed when the frequency of measurement is

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Table 2.1 static dielectric constant, ε_0, high frequency dielectric constant, ε_∞, square of, refractive index, n_D^2, mean relaxation time, τ_0, distribution coefficient, α, dipole moment from Cole – Cole plot μ_{C-C} and Guggenheim moment μ_G for some large ketone molecules

Solute	Solvent	T°C	ε_0	ε_∞	n_D^2	τ_0 10^{-12} sec.	α	μ_{C-C}	μ_G	μ lit.
5α-Cholestan-3-one	p-xylene	15	2.452	2.289	2.244	252	0.16	3.01		
		25	2.427	2.276	2.230	216	0.15	2.99	3.04	3.01 (59)
		37.5	2.405	2.265	2.221	187	0.18	3.09		
		50	2.371	2.238	2.194	156	0.16	3.00		
3,5Δ-Cholestadiene-7-one	p-xylene	15	2.484	2.293	2.249	135	0.14	4.02		
		25	2.461	2.243	2.217	108	0.11	4.03	4.09	
		37.5	2.422	2.255	2.213	88	0.11	3.98		
		50	2.390	2.233	2.194	74	0.11	3.98		
5α- Androstan-3-one	p-xylene	15	2.419	2.298	2.248	87	0.01	2.92		
		25	2.399	2.288	2.233	69	0.0	2.92		
		37.5	2.371	2.266	2.214	58	0.0	2.89		
		50	2.345	2.255	2.194	47	0.0	2.90		

Table 2.1 continued

Solute	Solvent	T°C	ε_0	ε_∞	n_D^2	τ_0 10^{-12} sec.	α	μ_{c-c}	μ_G	μlit.
5α-Androstan-3:17-dione	p-xylene	15	2.451	2.298	2.244	62	0.04	2.92		
		25	2.925	2.281	2.234	52	0.05	2.91	3.05	2.94(56)3.1(58)
		37.5	2.394	2.258	2.215	41	0.06	2.92		
		50	2.361	2.236	2.196	34	0.06	2.89		
5α-Androstan-3:17-dione	p-xylene + napthalene	37.5	2.397	2.319	2.284	53	0.05	2.77		
4Δ-Androsten-3:11:17-trione	p-xylene + naphthalene	37.5	2.551	2.323	2.284	78	0.04	4.86		
Tetraphenylcyclo-pentadieneone (Tetracyclone)	p-xylene	37.5	2.328	2.251		140	0.04	3.53		
		50	2.301	2.231		122	0.03	2.49		3.5± 0.1(26)
		60	2.281	2.215		100	0.0	3.47		
		70	2.262	2.200		91	0.02	3.45		

changed. Furthermore, since ε'' is small and changes only slightly
with a large change of frequency, an apparent slope is to be ex-
pected in this region. The value of the relaxation time obtained
from the slope is of the order of 15 to 20×10^{-12} sec. and for a rigid
molecule this would correspond to a reorienting unit of about the
size of p-bromotoluene. Since no intramolecular process is possible
in these molecules, because of their rigidity, the second apparent
relaxation time was considered to have no physical meaning.

As an example to illustrate the type of plots obtained from the data
the Cole-Cole diagram, an ε' against $\varepsilon''\omega$ and an ε'' log ω plot is shown
in Fig. 2:1 for $^4\Delta$-Androsten-3:11:17-trione in a naphthalene p-
xylene solvent mixture at 37.5°C.

A valuable check on the analysis of the data is to compare
the dipole moment calculated from the difference, $\varepsilon_o - \varepsilon_\infty$, obtained
from the Cole-Cole program, with that obtained by another method.
Agreement between the two methods helps to verify the extrapolated
value of ε_∞ and gives support to the analysis of the Cole-Cole
parameters.

Dipole moments have been evaluated by the Guggenheim method (55)
for three of the compounds studied. For the remainder either in-
sufficient material or low solubility prevented determination of
the dipole moment, hence the microwave values have been compared
with literature data when available. In addition, the refractive
index, n_D, has been measured at the frequency of the sodium D line.

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FIG. 2·1a COLE-COLE PLOT FOR $^4\Delta$-ANDROSTEN-3:11:17-TRIONE
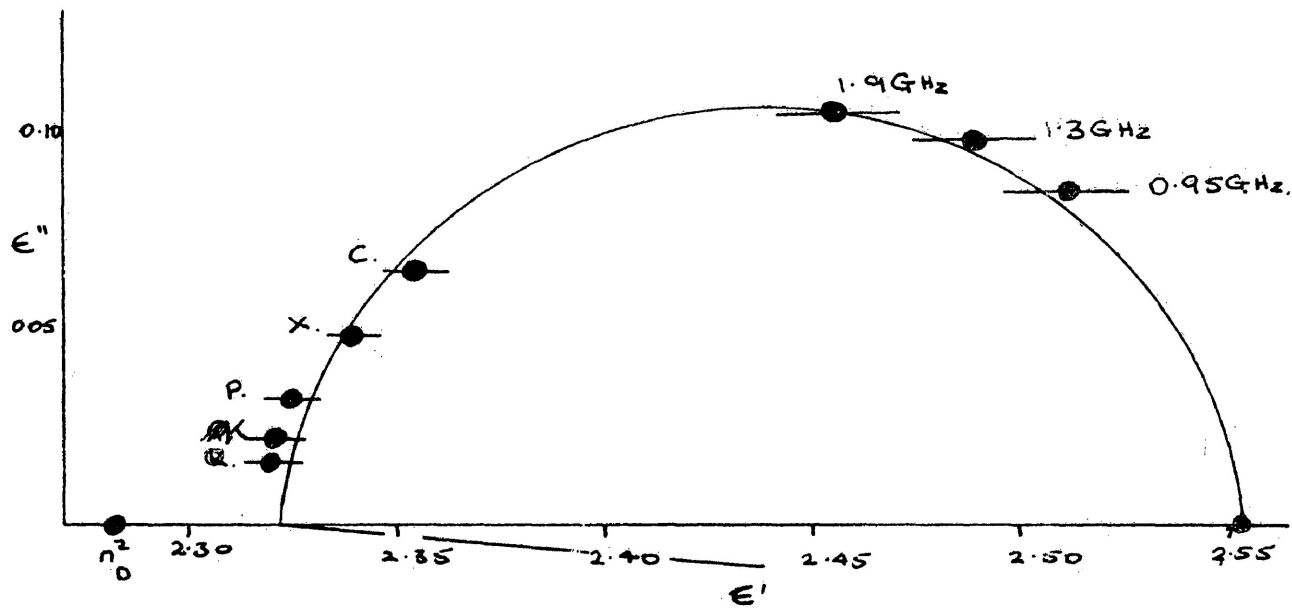

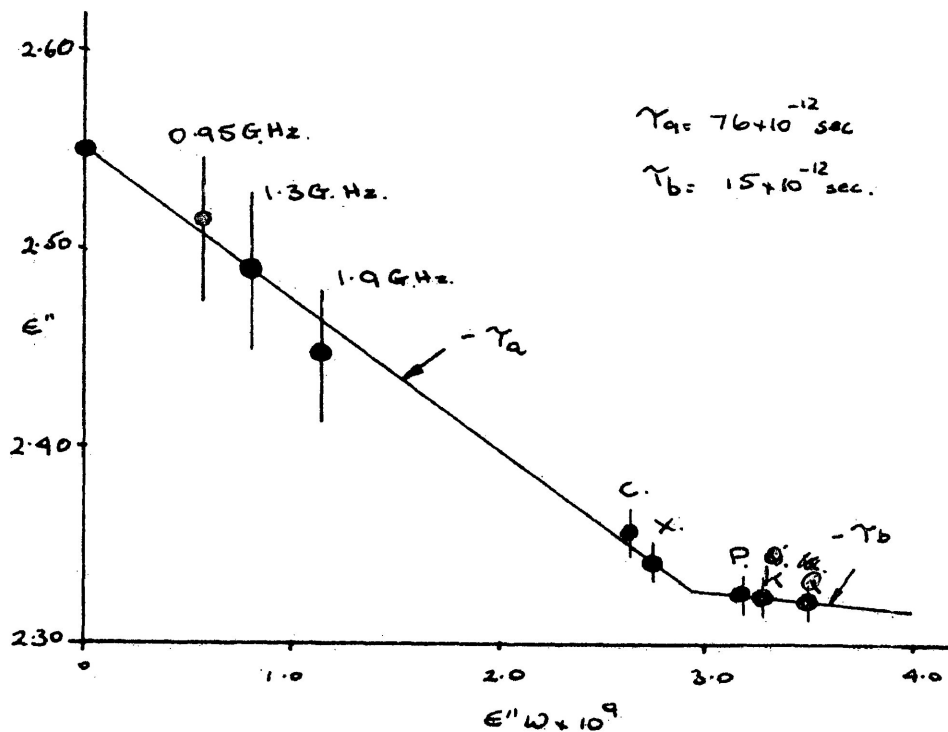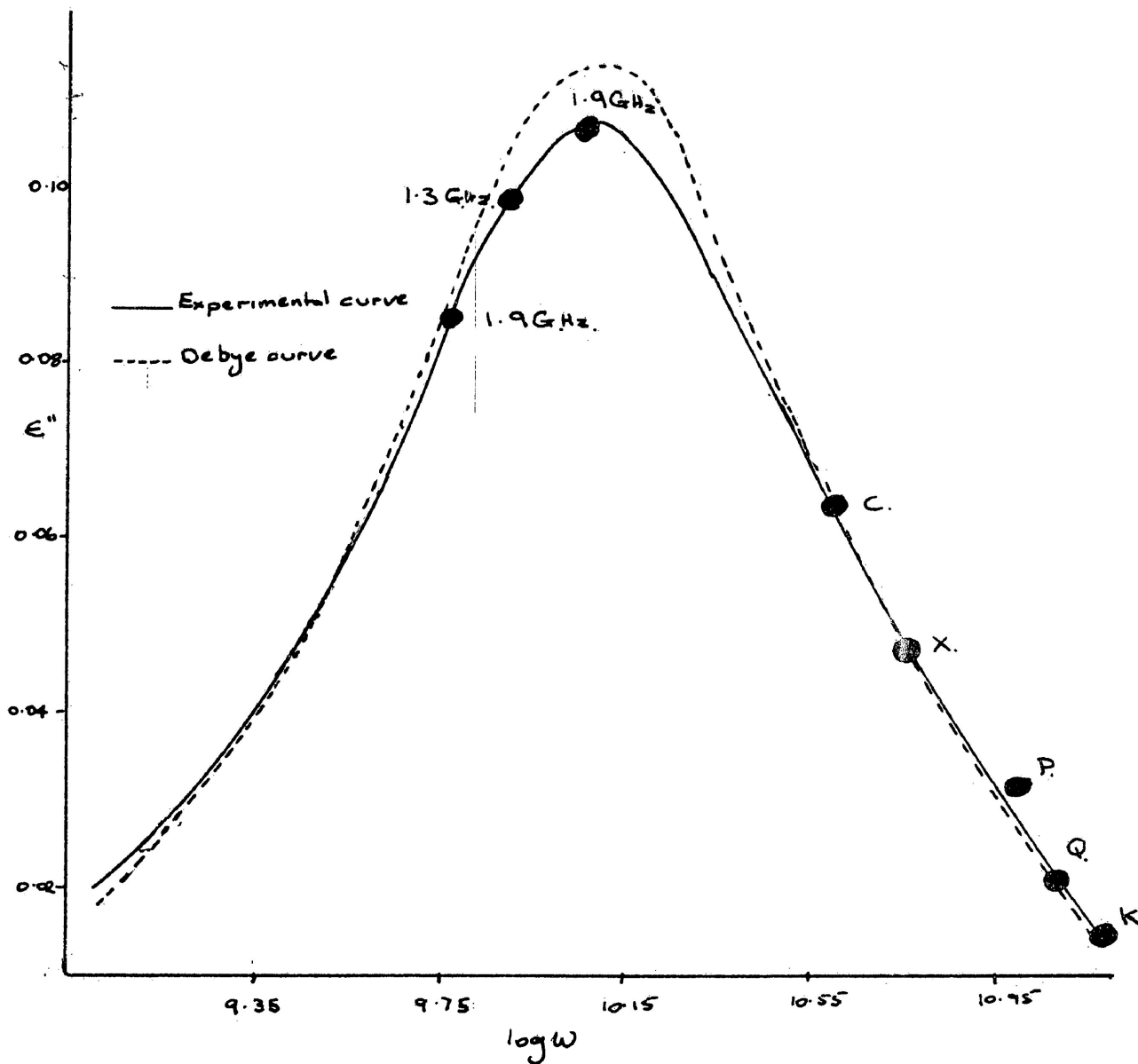FIG. 2·1b. ϵ'-$\epsilon''\omega$ PLOT FOR $^4\Delta$-ANDROSTEN-3:11:17-TRIONE.

$\tau_a = 76 + 10^{-12}$ sec

$\tau_b = 15 + 10^{-12}$ sec.

FIG 2·1c ϵ''-logW PLOT FOR $^4\Delta$-ANDROSTEN-3:11:17-TRIONE

The position of n_D^2, in relation to ε_∞, on the axis of reals

of the Argand diagram, provides additional support for the ε_∞

value. An agrement of ±0.10 between the Guggenheim moment and

that determined from the Cole-Cole plot was considered to be

satisfactory.

Fig. 2:2 shows the position of the molecular dipole in the

ellipsoidal steroid molecules, the corresponding axes about which

rotation is possible, and the structural formulae of the molecules

The molecular axes are designated A, B, and C and have

lengths which decrease in the order A>B>C; the semi-axes of the el-

lipsoid are designated a, b, and c. The molecular dipoles lie in

the A-B plane and the component moments parallel to these axes are

designated μ_a and μ_b, respectively, the relaxation times corres-

ponding to these moment components are termed τ_a and τ_b respectively.

5α-Cholestan-3-one, I, has been found to have a relaxation

time of 216 x 10^{-12} sec. at 25°C in p-xylene, this compares satis-

factorily with the value of 233 x 10^{-12} sec. obtained by Meakins (49)

for the similar molecule $^4\Delta$Cholesten-3-one in benzene at 20°C. The

dipole moment obtained for the molecule from the Cole-Cole arc

and by the Guggenheim method is in satisfactory agreement with the

literature value. As the dipole moment in the molecule is parallel

to the long axis, A, it should have a single relaxation time on

Fig 2·2a Representation of dipole direction and corresponding axes of rotation
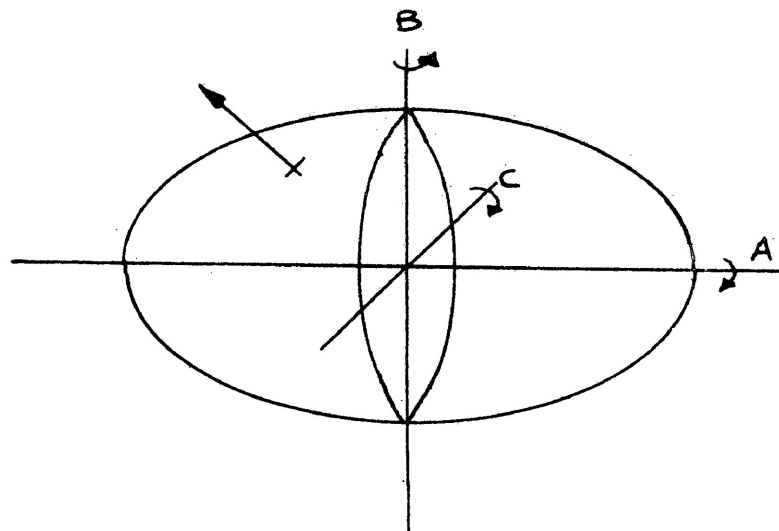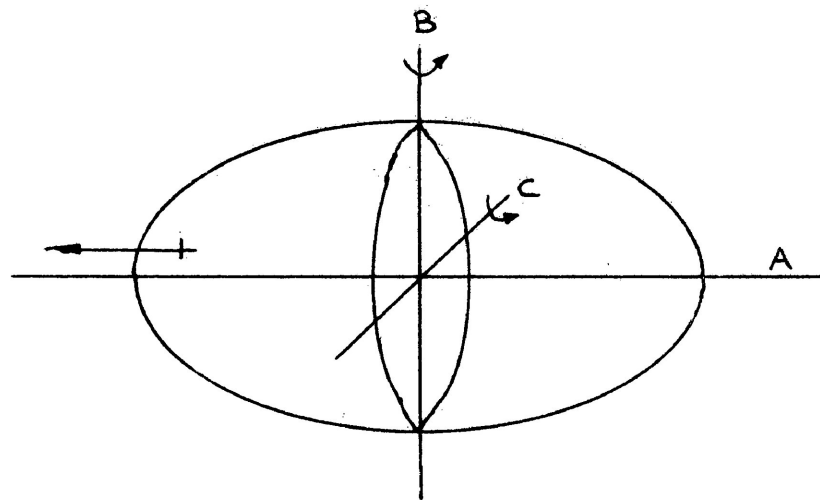
FIG 2.2b STRUCTURAL FORMULA OF MOLECULES DISCUSSED
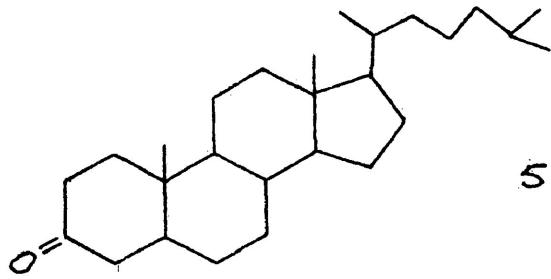
5α-CHOLESTAN-3-ONE   I
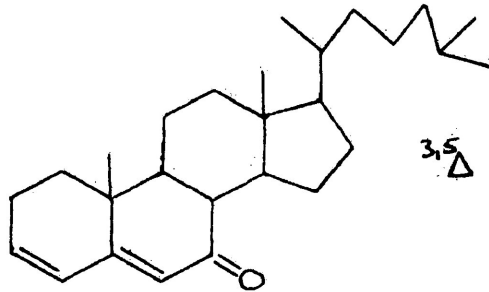
$\Delta^{3,5}$-CHOLESTADIENE-7-ONE   II
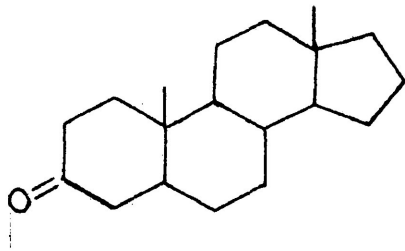
5α-ANDROSTAN-3-ONE   III
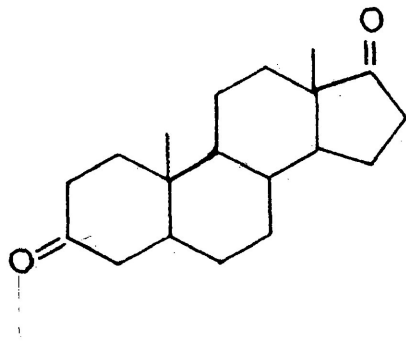
5α-ANDROSTAN-3:17-DIONE   IV
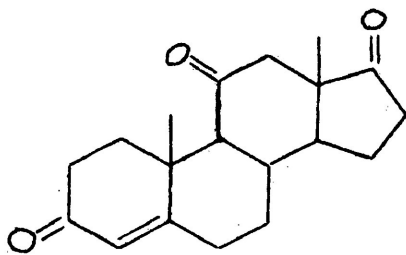
Δ^4-ANDROSTEN-3:11:17-TRIONE   V

FIG 2.2b. CONTINUED
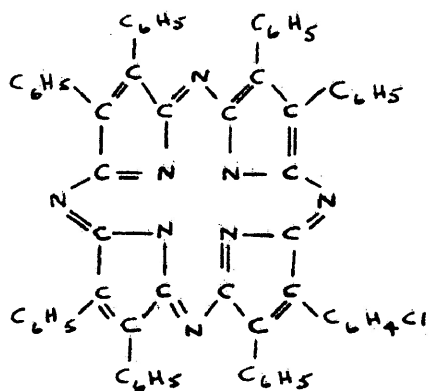
HEPTAPHENYCHLOROPHENYL PORPHYRAZINE $\underline{VI}$
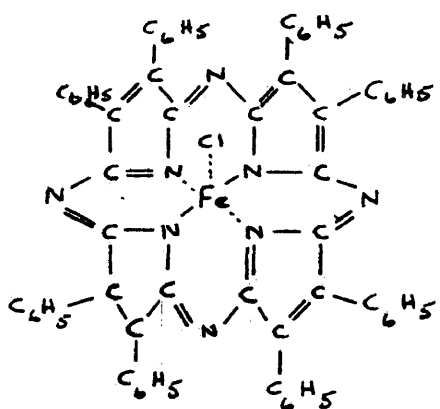
FERRIC OCTAPHENYLPORPHYRAZINE

CHLORIDE $\underline{VII}$
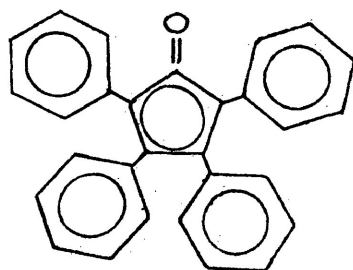
TETRAPHENYLCYCLOPENTADIENEONE $\underline{VIII}$

(TETRACYCLONE)

the basis of the Perrin theory, however, a large distribution coefficient has been observed. The $\varepsilon''\log w$ plot given by Meakins for his analogous molecule is of none-Debye form, which also indicates a distribution of relaxation times. As there are two axes, B, and C, perpendicular to the direction of the resultant moment, it would seem in principle that there are two axes about which this molecule can rotate. Examination of Table 1.5 in Chapter 1 shows that a large α is only observed when the two component relaxation times differ considerably and have equal weight in contributing to the dielectric absorption. In this case, however, rotation about either, or both, of the axes B, and C would involve similar motions. The molecule displaces a large amount of solvent during the course of these rotations and suffers considerable frictional resistance. Hence, a large difference between the two possible relaxation times would not be expected and cannot account for the large α.

A second possibility is that the flexible side chain is contributing to the absorption. However, the weight factor for this absorption would be very small since the dipole moment of the side chain would not be expected to exceed 0.4D and as:

$$C = \frac{\mu_i^2}{\mu^2} = \frac{0.4^2}{3^2} \backsim 0.02$$ any separate absorption by the side chain would not be detectable. The large ketone, lupenone,

measured by Meakins is the same shape as 5α-Cholestan-3-one and slightly longer, but instead of having a side chain it has an additional six membered ring. The molecule has its dipole along the A axis of the ellipsoid and the molecular absorption is characterised by a Debye-type ε" against logω curve. Furthermore, 5α-Androstan-3-one, III, measured in this study has a similarly located dipole and no side chain and shows no distribution of relaxation times. It would thus appear that the distribution observed in the case of 5α-Cholestan-3-one, I, is in some way associated with the flexible side chain, but the precise cause is not completely understood.

Hill (61) considered that a distribution of relaxation times is to be expected for molecules which show deviations from spherical symmetry. She found that when the moments of inertia of the molecule differ widely about different axes the distribution is broadened. As the side chain in the Cholestanes is flexible, it would seem possible that alteration of the conformation of this unit could give rise to a variation of the moment of inertia about the axes of rotation and contribute to the distribution of relaxation times. The moments of inertia about the axes B and C would show greater variation with side chain conformation than would the moment about the axis A, and since these are the axes

which are perpendicular to the molecular dipole moment, the effect would be expected to be greater than if the molecule rotated about the axis A.

For ^{3,5}Δ-Chloestadiene-7-one,II, there is a large component of the molecular moment which gives rise to rotation about the A axis. Hence, this molecule can rotate about all three of the perpendicular axes, yet, it has a smaller distribution coefficient than 5α-Cholestan-3-one,I, because its major component relaxation time involves rotation about the A axis and the moment of intertia about this axis is the least affected by changes in the conformation of the side chain. These initial effects can be used, tentatively, to explain the distribution parameters observed for the two cholestane derivatives. The other molecules measured which have the dipole inclined to a principal symmetry axis have small distributions of the order of what might be expected for rotation about two or more of the molecular axes.

The agreement between the microwave and Guggenheim moments for ^{3,5}Δ-Cholestadiene-7-one,II, is satisfactory and supports the computer assigned ε_∞ value. The precise angle which the dipole in this molecule makes with the long axis is difficult to determine, since the increase in the dipole moment of ID, relative to saturated monoketo steroids, indicates a flow of charge along the double

bonds conjugated to the carbonyl group. However, there is no doubt that there is an appreciable component of the molecular moment perpendicular to the long axis.

If it is assumed that the resultant moment is in the direction of the C=O bond, then this is inclined at an angle of approximately 65° to the long axis. One of the two possible motions which can be associated with the moment component parallel to the B axis is rotation around the long axis of the molecule. This causes little disturbance of the surrounding solvent molecules and the frictional resistance offered to the rotation is small. Hence, a reduction in the relaxation time would be expected, and is observed, for this molecule in comparison to 5α-Cholestan-3-one.

Similar effects are seen in the Androstane derivatives. The molecule with the keto group in the 3 position has the highest relaxation time since it executes similar motions to 5α-Cholestan-3-one,I. When the dipole is inclined to the A axis, rotation becomes possible around this axis and is accompanied by a reduction of the mean relaxation time.

Analogous behaviour has been observed for similar dipole orientation effects in the biphenyls and anthraquinones. For both systems it is found that when the dipole is parallel to the long

axis of the molecule the relaxation time is higher than
when the dipole is inclined to this axis. Thus, 2, 2 - di-
chlorobiphenyl has a relaxation time of 38.5×10^{-12} (60) at
20°C in cyclohexane, whereas 4-bromobiphenyl has a value of
62×10^{-12} sec. under the same conditions. Similarly, 2-
chloroanthraquinone has its dipole inclined to the long axis
and has a relaxation time, in benzene at 23°C, of 40×10^{-12}
sec.while 2,3 -dichloroanthraquinone has a value of 76×10^{-12}
sec. For both molecules which have the dipole parallel to the
long axis, some of the increase in their relaxation times, re-
lative to the molecule having the alternate dipole orientation,
must be attributed to the increased length of the molecule
caused by the position of the substituent.

When the steroid ring system is changed from the Choles-
tane series to the Androstanes the length of the major axis of
the ellipsoid is reduced by $\sim 6\overset{\circ}{A}$, this is attended by a re-
duction of the size of the relaxation time of compounds having
analogous dipole orientations in the two series.

5α-Androstan-3-one, III, has the major component of the
molecular dipole parallel to the long axis and has a longer re-
laxation time than 5α-Androstan-3:17-dione,IV. The molecular

dipole in this latter molecule is inclined at approximately 60°
to the long axis. Δ^4-Androsten-3:11:17-trione, V, was only soluble
in a naphthalene p-xylene solvent mixture, at a sufficient con-
centration for measurement, at a temperature of 37.5°C. The dione
was measured under the same conditions in order that the relaxation
times of the two molecules might be compared. The trione is longer
in both the A and B directions and vector diagrams indicate that
the inclination of the resultant moment to the long axis is approxi-
mately 50°. Hence, in this compound the relaxation time corres-
poinding to the moment component along the A axis will have a higher
weighting than for the dione. Further, since the component relax-
ation times will be larger, because of the increased molecular
dimensions, the trione would be expected to have the larger relax-
ation time.

A number of equations which have been developed for the cal-
culation of relaxation times of rigid molecules will now be examined
to see how they predict the values for the molecules measured in
this study.

The first relation to be examined is that due to Debye.
When this equation is used to calculate the relaxation times of
molecules which are not spherical, it is usual to rewrite it in

the form:

$$\tau = \frac{3V\eta}{kT}$$

Where V is the molecular volume. Thus the molecule is treated
as a sphere which has a volume equivalent to that of the non-spherical
molecule. In the literature there are two methods used to calculate
the molecular volume. One (51) assumes the molecule to be a regular
solid body, that is, it is spherical, ellipsoidal, or cylindrical,
etc., dimensions are then taken from molecular models and used in the
appropriate equation which describes the volume of the body. The
other approach is due to Edward (57) who calculated the van der
Waals volumes of the elements in various valency states. The
molecular volume is then computed as a summation of the volume of
the atoms making up the molecule. Neither method can be considered
to be completely satisfactory. The first approach suffers from the
fact that few molecules have a perfectly regular shape and the
Edwards' method is limited in that it gives no difference in
volume for various possible conformations of a molecule, or for
different isomeric forms.

Both methods have been used to calculate the molecule volume
in order that their effect on the calculated relaxation time can
be evaluated.

Table 2:2 gives the molecular dimensions of the compounds studied and the relaxation times calculated using the Debye-Stokes' equation. When the molecular volume has been calculated by Edwards' method, the relaxation time is designated τ_E, and when Courtauld model dimensions have been used the calculated τ is designated τ_c. In addition, the two large porphyrazine molecules measured by Pitt and Smyth have been included. Calculation of the volume of tetraphenylcyclopentadieneone from Courtauld models was not considered to be possible for the following reasons: the molecule is of a rather irregular shape, there are large spaces between the phenyl groups, and the angle between the cyclopentadienone ring and the phenyl groups is uncertain. The viscosity used in these calculations was that of the solvent given in Timmermans(62). For the p-xylene naphthalene solvent, the viscosity was measured using an Ubelöhde ? viscometer.

The only steroid which gives satisfactory agreement between measured and calculated relaxation times is 5α-Cholestan-3-one, I. The molecule of $\Delta^{3,5}$-Cholestadiene-7-one,II, has a slightly larger molecular volume calculated from Courtauld models, than by the additive method. However, the molecular

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Table 2.2 lengths of molecular axes A, B and C, observed relaxation times τobs. and relaxation times calculated according to the Debye equation using Edwards' volumes and Courtauld molecular volumes.

Solute	Dimensions $\overset{o}{A}$			T°C	Solvent	τobs $\times 10^{12}$sec.	τE $\times 10^{12}$sec.	τC $\times 10^{12}$sec.
	A	B	C					
5α-cholestan-3-one				15		252	213	212
	19.6	7.2	5.6	25	p-xylene	216	184	183
				37.5		187	151	150
				50		156	127	127
3,5Δ-Cholestadiene-7-one				15		135	205	233
				25	p-xylene	108	177	201
	19.1	8.1	5.6	37.5		87.5	145	164
				50		74	122	139
5α-Androstan-3-one				15		84	146	141
				25	p-xylene	75	126	121
	13.0	7.2	5.6	37.5		56	103	99
				50		48	87	84

Table 2.2 continued.

Solute	Dimensions A°			T°C	Solvent	τ_{obs} x10^{12} secs.	τ_E x10^{12} sec.	τ_C x10^{12} sec.
	A	B	C					
5α-Androstan-3:17-dione				15		62	148	144
	13.3	7.2	5.6	25	p-xylene	52	128	124
				37.5		41	105	102
				50		34	88	86
5α-Androstan-3:17-dione	13.3	7.2	5.6	37.5	p-xylene + naphthalene	53	137	134
4Δ-Androsten-3:11:17-trione	13.6	8.0	5.6	37.5	p-xylene + naphthalene	78	137	152
Tetraphenylcyclo-pentadieneone				37.5	p-xylene	140	134	
				50		122	113	
				60		100	102	
				70		91	93	

Table 2.2 continued.

Solute	Dimensions Å			$T^\circ C$	Solvent	τobs. $\times 10^{12}$ sec.	τ_E $\times 10^{12}$ sec.	τ_C $\times 10^{12}$ sec.
	A	B	C					
Heptaphenylchlor-ophenyl-Porphyrazine	20.3	19.0	6.25	20		302	424	912
				40	Benzene	212	309	665
				60		159	227	488
Ferric Octaphenyl-porphyrazine chloride	19	19	7.15	20		706	426	977
				40	Benzene	500	311	712
				60		367	228	522

volume is greater than three times the solvent volume, yet the
relaxation time is not predicted by the Debye-Stokes' equation.
On the basis of the Meakins' criteron, this is an unexpected
result. It would, therefore, appear that the effect of dipole
orientation within a molecule must be taken into account, before
any statement can be made about the applicability of the simple
Debye-Stokes' equation. The dipole must be positioned in a
molecule so that the molecular rotation involves considerable
displacement of the surrounding solvent molecules.

Although the simple Debye-Stokes' equation predicts, fairly
well, the observed relaxation time of 5α-Cholestan-3-one, it
gives too large a value for 5α-Androstan-3-one, III, the ratio$\frac{\tau calc}{\tau meas}$
being ∿1.7:1. This latter molecule has its dipole oriented so that its
rotation will displace surrounding solvent molecules, but the solute
solvent volume ratio is only 2.4:1 for the p-xylene solution.

Because of the similar molecular volume of the three an-
drostanes, the Debye equation predicts that they will have
similar molecular relaxation times; again it is not able to pre-
dict the effect of the angle of inclination of the dipole in the
molecule. It is interesting to note, however, that the increase
in relaxation time of 5α-Androstan-3:17-dione,IV, observed on
changing the solvent from p-xylene to the naphthalene p-xylene

mixture is proportional to the viscosity increase.

It is seen that for the steroids the two methods used to calculate the molecular volume are in reasonable agreement. In fact, the volumes calculated from the Courtauld models seem more sensitive to changes in the molecular shape than do the Edward's volumes.

The relaxation time of tetracyclone is in good agreement with the calculated values. Nelson and Smyth (63) have previously measured this molecule in four other solvents, at a single temperature, and obtained close correspondence between calculated and measured values when the solute-solvent ratio was greater than 3:1. The small distribution coefficient observed for this molecule is zero within the limits of experimental measurement. Again, this is in accord with the data of Nelson and Smyth.

The porphyrazine molecules have a solute solvent volume ratio of the order of 11:1 and would be expected to satisfy the Meakins' relative volume criterion. However, on comparison of the τ_E values, it is seen that neither compound shows very good agreement between calculated and measured data. The metal-free structure has a calculated τ which is too high by 40%, whereas the iron complex has a value which is too low by 66%. If Edward's volume is the correct function to be used for these molecules, then the

data indicate that the viscosity for solute rotation is greater than the liquid viscosity for the metal complex. Such a conclusion would seem improbable. When the volumes are calculated from the dimensions of Courtauld models, the situation is not improved. The metal-free complex has a calculated relaxation time which is three times the measured value; the iron complex has a relaxation time which is 40% too large. When the maximum lengths of the three axes measured from the models are used to calculate the volume, this leads to an overestimation of this parameter. Since, in the iron complex a chlorine atom protrudes above the plane of the great ring and in the metal-free complex one of the phenyl rings has a chlorine substituent. If the dimensions of the basic porphyrazine structure are taken for each molecule, then the calculated relaxation time will be 854×10^{-12} sec., at 20°C., for each molecule. This is still larger than the value observed for the metal complex.

It would seem that the only way in which agreement could be obtained between measured and calculated relaxation times for these two molecules is by using different frictional coefficients for each of the two types of molecular motion. In order that one of these coefficients is not larger than the solvent viscosity, Courtauld volumes would have to be used.

Although the empirical equation of Eichhoff and Huffnagel predicts the relaxation time of 9-bromophenanthrene, which has its dipole inclined to the principal symmetry axes of the molecule, it would fail to predict the effects of dipole inclination observed in the steroids. Calculation of the effective radius of the steroids would be difficult because of the large number of atoms and stereochemistry of the molecules. However, the effect of altering the position of the carbonyl group within the molecule would not be expected to have a large effect upon the centre of mass, and hence the effective radius would be similar for similar structures. ~~If it can be assumed that the~~ ~~centre of mass is at the centre of symmetry of the molecules,~~ ~~then~~ the effective radius is $_\wedge$ taken to be half the length of the long axis of the molecules. For p-xylene solutions the Eichhoff-Huffnagel equation is:

$$\tau = 1.66 \times 10^{-13} \exp (1.20 \times 10^{8} r_{eff.})$$

5α-Cholestan-3-one, I, and $\Delta^{3,5}$ - Cholestadiene-7-one, II, have effective radiii of 9.8 $\overset{o}{A}$ and 9.55 $\overset{o}{A}$ respectively, which gives corresponding calculated relaxation times of 2.1×10^{-8} sec. and 1.6×10^{-8} sec. for these two molecules, a result in error by two orders of magnitude. A similar situation is found with the androstane steroids. The equation predicts a relaxation time of

405×10^{-12} sec. for 5α-Androstan-3-one,III, and 495×10^{-12} sec.
for 5α-Androstan-3:17-dione,IV. In this case the relaxation times
are closer to the observed values but in the wrong order. For the
porphyrazine metal complex, which is completely symmetrical, the
centre of mass will be at the centre of symmetry of the molecule,
so there is no approximation in determining its effective radius.
The equation predicts a relaxation time of 1.5×10^{-9} sec. which is a
little over two times the observed value suggesting that the
equation is more suitable for predicting the relaxation times of
flat molecules. In the metal-free complex the presence of a chlorine
substituent will cause a slight shift of the centre of mass toward
the perifery of the ring. It will thus have the effect of increas-
ing the effective radius and increase the calculated relaxation time.
However, the measured value of τ for this compound, as has been seen,
is only one half that of the metal complex, hence the agreement in
the former case may be fortuitous.

Other empirical equations for the *a priori* calculation of re-
laxation time have been developed by LeFevre et al. Le Fevre and
Sullivan (64) noted an approximate correlation of τ with the mean
polarisability and the shape of a solute which led them to write
the equation:

$$\tau = \frac{4\Pi\eta\alpha_{mean}(exp\Delta_1)(exph^2)^2}{(\varepsilon_1+2)kT}$$

Where α_{mean} is the mean polarizability of the solute, Δ_0 is the mean depolarization factor of the solvent, ε_1 is the dielectric constant of the solvent, and $h(65)$ is defined by the relation:

$$h = [(A-B)^2 + (B-C)^2 + (C-A)^2]/(A+B+C)^2 ,$$

where A,B, and C are the axial lengths characterising the ellipsoid $A \geqslant B \geqslant C$. These authors found that $(\exp h^2)^2 \alpha_{mean}$ was numerically equivalent to $(ABC)/8$ and proposed the following simplified equation:

$$\tau = \frac{\pi}{2kT} \eta ABC(\exp.\Delta_1)(\varepsilon_1+2)^{-1}$$

Since, in this equation, the only properties of the solute are the lengths of the axes it will not predict variations of relaxation time resulting from a change in the position of the molecular dipole. It will predict a larger relaxation time for $\Delta^{3,5}$-Cholestadiene-7-one, II, than for 5α-Cholestan-3-one, I, and similarly it will give a higher relaxation time for 5α-Androstan-3:17-dione, IV, than for 5α-Androstan-3-one, III.

Wirtz and his co-workers (66)(67) derived an equation for the calculation of molecular relaxation times based on a system of spherical solute and solvent molecules. Because of the finite size of the solvent molecules they considered that the Stokes' law relation was not applicable and developed a microfrictional coefficient for rotation. This yielded the equation:

$$\tau = \frac{4\pi}{kT} \, \eta r^3 \, \frac{f}{2} \, _{rot}$$

Where f_{rot} is the microfriction factor defined by

$$f_{rot} = [(6r_1/r_2 + (1+r_1/r_2)^{-3}]^{-1}$$

The mean radii r_1 and r_2 of the solvent and solute molecules, respectively, are obtained from the molecular weights Mi and the densities d_i using the relation:

$$r = (0.556 \, M_i/\pi d_i N)^{1/3}$$

Although the equation is strictly only applicable to systems having spherical solute and solvent molecules, Pit and Smyth (36) obtained reasonable agreement between measured and calculated τ's for three ellipsoidal molecules which were of similar molecular size and had the molecular dipole directed along the same axis of symmetry. Density data is not available for the steroids measured but an estimate of the mean radii of the molecules may be obtained from calculated molecular volumes. However, it is obvious that since the molecular volumes for members of the steroids in each series is similar, the relaxation times predicted by the Wirtz equation will not be in agreement with experiment. As an alternative, it might seem feasible to consider the measured relaxation time to be the resultant of components corresponding to rotation about particular molecular axes, and to take the radii appropriate for each

motion. Using this procedure the relaxation time corresponding
to the moment components in the direction of the long axis for
5α-Cholestan-3-one, I, and 5α-Androstan-3-one,III, at 25°C, are
715×10^{-12} sec. and 152×10^{-12} sec. In all the molecules where the
dipole is inclined at an angle to the long axis, the radius to
be associated with the moment component perpendicular to this
axis, is the same. Hence, this approach would predict similar
relaxation times for this type of motion in all the molecules.
It is thus obvious that the Wirtz equation is not applicable to
such systems which deviate considerably from spherical form.

The Fischer formula, however, should be applicable to these
ellipsoidal steroid molecules, but because the f factor is always
greater than unity it will predict higher relaxation times than
the Debye-Stokes' equation. Although the relaxation time of 5α-
Cholestan-3-one,I, is predicted by this latter equation, the
Fischer formula will predict its value to be f times that ob-
served. In order to obtain agreement between measured and cal-
culated τ's for 5α-Cholestan-3-one,I, it then becomes necessary to
employ a frictional coefficient in the Fischer equation which is
less than the solvent viscosity.

Two approaches have been used to make evaluations using the
Fischer equation. In the first, the viscosity of the solvent was
taken and relaxation times were calculated corresponding to moment

components along the directions of the principal axes, with the aid of the f factors. The component relaxation times were used to compute a mean value with the aid of the equation.

$$\tau_o = \sqrt{\frac{\sum \mu_i^2 \tau_i}{\sum \mu_i^2}}$$

Magee and Walker (68) have shown that this simple equation gives reasonable values for τ_o when the ratio τ_a/τ_b is of the order of 2. The Fischer f factors give the ratio of the component relaxation times, and for the steroids the largest τ_a/τ_b ratio is 2.5:1, hence the above equation would be expected to give fairly reasonable mean relaxation times.

The form factors, obtained from the ellipsoid axial ratios, are given in table 2.3. The relaxation times corresponding to moment components along the principal axes are obtained by multiplying τ_c, given in table 2.2, by the appropriate f factor. The value of the mean relaxation time computed from the component values is given in column 8 of the table.

As was expected the mean relaxation times, calculated using the solvent viscosity, given in column 8 of table 2.3 are considerably higher than the experimentally observed values. However, the relaxation times are predicted to be in the correct order; the effect of altering the position of the molecular dipole within the

TABLE 2.3 FORM FACTORS f_a AND f_b, RELAXATION TIMES, τ_a and τ_b AND MEAN RELAXATION TIMES, τ_o, CALCULATED USING THE FISCHER EQUATION.

SOLUTE	SOLVENT	T°C	fa	fb	τa $\times 10^{-12}$ sec.	τb $\times 10^{-12}$ sec.	τo	$\tau o \times 10^{-12}$ sec. microscopic viscosity
5α-Cholestan-								
3-one	p-xylene	15			522	-	522	
		25	2.46	-	450	-	450	
		37.5			369	-	369	
		50			312	-	312	
$\Delta^{3,5}$-Choles-	p-xylene	15			533	280	326	169
tadiene-7-one		25	2.29	1.20	460	241	280	135
		37.5			376	197	229	116
		50			318	167	194	98
5α- Androstan-								
3-one	p-xylene	15			221	-	221	
		25	1.57	-	190	-	190	
		37.5			155	-	155	
		50			132	-	132	
5α-Androstan-								
3:17-dione	p-xylene	15			230	158	176	67
		25	1.60	1.10	198	136	152	59
		37.5			163	112	125	45

Table 2.3 continued.

SOLUTE	SOLVENT	T°C	fa	fb	τa x10^{-12} sec.	τb x10^{-12} sec.	τo	τox10^{-12} sec. microscopic viscosity
5α-Androstan-3:17-dione	p-xylene	50			138	95	106	38
5α-Androstan-3:17-dione + naphthalene	p-xylene	37.5	1.6	1.10	214	147	164	
Δ^4-Androsten-3:11:17-trione + naphthalene	p-xylene	37.5	1.56	1.20	237	182	214	

molecule is at least qualitatively correct. The f factors show
that rotation around the long axis of the ellipsoid gives rise to
relaxation times which are only slightly larger than would be
expected for a sphere having the volume of the ellipsoid. This
is understandable since the lengths of the two axes perpendicular
to the moment component, which give rise to the shorter relax-
ation time, are similar. Hence, the molecule does not displace
much solvent when undergoing this type of barrel motion and its
behaviour approaches that of a sphere. It can also be deduced
from the f factors that as the ellipticity decreases the differ-
ence in size of the two component relaxation times becomes smaller.

In an attempt to improve the agreement between measured and
calculated relaxation times the microscopic viscosities were ev-
aluated for 5α-Cholestan-3-one, I, and 5α-Androstan-3-one, III.
Since the Fischer equation predicts that these molecules should
have a single relaxation time their measured relaxation times
were equated with $\frac{4\pi abcf}{kT}$ to obtain the microscopic friction
coefficient. It was then assumed that this viscosity could be
used to calculate the component relaxation times of the molecules
in each of the two series. The resulting τ_0's are shown in
column 9 of table 2.3. Unfortunately, insufficient 5α-Androstan-3-
one, III, was available to measure its relaxation time in the p-
xylene naphthalene solvent mixture and hence evaluate the micros-
copic viscosity for this solvent.

It is seen that, in this case, the correspondence between measured and calculated values is considerably improved. The agreement for $\Delta^{3,5}$-Cholestadiene-7-one, II, is poorer than for 5α-Androstan-3:17-dione, IV, which may indicate that the viscosity coefficient for rotation around the long axis is smaller than the microscopic viscosity evaluated for 5α-Cholestan-3-one, I.

In conclusion, it would seem that the effect of dipole orientation within large molecules, with rigid dipoles, is to produce considerable changes in measured relaxation times.

The Fischer equation is ~~the only satisfactory~~ *an* expression which can be used to evaluate the mean relaxation time of an ellipsoidal molecule which has its dipole inclined to a principal symmetry axis.

Some difficulties arise when attempts are made to consider the conditions under which the simple Debye-Stokes' equation can be applied to non-spherical molecular systems. In some cases it appears to predict the measured relaxation time when the solute-solvent molecular volume ratio is greater than 3:1, and when Edward's volume and the solvent viscosity are used. In the case of the steroids the Debye-Stokes' equation is only satisfactory when the dipole is so positioned in the molecule that rotation occurs about an axis which involves considerable displacement of

solvent molecules.

When the solute molecule is disc-like in shape and the moment is situated in the plane of the disc,agreement is obtained between measured and calculated relaxation times. A moment so positioned gives rise to two extreme types of molecular motion. One involves a large displacement of solvent, corresponding to rotation out of the plane of the disc, the other, in-plane rotation, involves less solvent displacement. These two motions of a disc-like molecule resemble the behaviour of a steroid which has the dipole inclined to the main axis, but the Debye equation is unable to predict the relaxation time for the steroid.

If the disc-like molecule has a dipole perpendicular to the ring plane,its motions resemble that of a steroid with the dipole parallel to the long axis. It was seen for 5α-Cholestan-3-one, I, the relaxation time was predicted by the Debye-Stokes' equation. However, the two disc-like molecules ferric octaphenylporphyrazine chloride, and bis(diphenylmethyl) ether (63), both have the molecular dipole perpendicular to the molecular plane,yet the Debye-Stokes' equation predicts a relaxation time which is too small for the former, but of the correct order for the latter.

In order to obtain agreement of the experimental values with those calculated from the Fischer formula it was necessary to employ a frictional coefficient less than the solvent viscosity. Yet, for 5α-Cholestan-3-one, I, agreement was obtained using the Debye-Stokes' equation in which the solvent viscosity was used. Clearly the molecule can experience only one frictional coefficient and as the Fischer equation, but not the Debye-Stokes' equation, is appropriate for calculating the relaxation times of non-spherical molecules, it would appear that agreement with the latter equation is fortuitous.

CHAPTER THREE

DIELECTRIC RELAXATION AS A

RATE PROCESS

Introduction

The relaxation rate of a dielectric is found to be strongly dependent upon temperature. Such behaviour is significant in understanding the physical nature of the process involved, for by analogy with chemical kinetics, this observation indicates that the units undergoing change are forced to wait until they have acquired energy in excess of the average thermal energy available.

Kauzmann(1) considered that the dipole, upon thermal activation, jumped from one equilibrium position of orientation to another over an energy barrier, and the fact that the activation energy for dielectric relaxation processes is of the order of 5 to 10 kT for liquid systems led him to conclude that the dipoles change direction not continuously, but in a series of sudden jumps.

Although the mechanism of the dielectric relaxation process is understood, few attempts have been made at the quantitative interpretation of the activation parameters for dilute solutions of rigid molecules. It was thus thought that a closer examination of these quantitites might provide additional, useful information on the dielectric behaviour of polar molecules.

Discussion

In the literature there appear several rate expressions which may be used for the interpretation of dielectric behaviour. The most widely used of these is that due to Eyring (2). However, it is

often employed without due regard for its limitations and before a deeper examination of the dielectric rate process is carried out, the various rate equations available will be discussed.

Kauzmann showed that the transition probability for dipole reorientation is proportional to the Boltzmann factor $\exp(-\Delta E/RT)$. Furthermore it is known that any system undergoing a physical or chemical transformation, the rate of which depends on a factor of the type $\exp(-\alpha/T)$ can be treated in terms of absolute rate theory. Thus,Eyring (2)(3) recognized the similarity between dielectric relaxation and the rates of chemical reactions and suggested that dipole orientation could be treated by the statistical mechanical methods of absolute rate theory.

In the derivation of the Eyring equation it is assumed that a potential energy barrier of height ΔG^+ separates two equilibrium positions of dipole orientation as shown in figure (3.1). The top of the energy barrier is known as the activated state. It is supposed that the initial state is in thermodynamic equilibrium with the activated state, the equilibrium corresponding to librational oscillations which upon thermal activation undergo a libration-rotation transition. The activated state undergoes a transition at a definite rate the frequency of which is the reciprocal of the relaxation time τ. ~~The mean life time of the activated state is τ and~~ is equal to the length of the activated state divided by the average rate at which dipoles cross the barrier. This leads to the familiar

FIG. 3·1 POTENTIAL ENERGY BARRIER OPPOSING SOLUTE ROTATION

a) NO FIELD
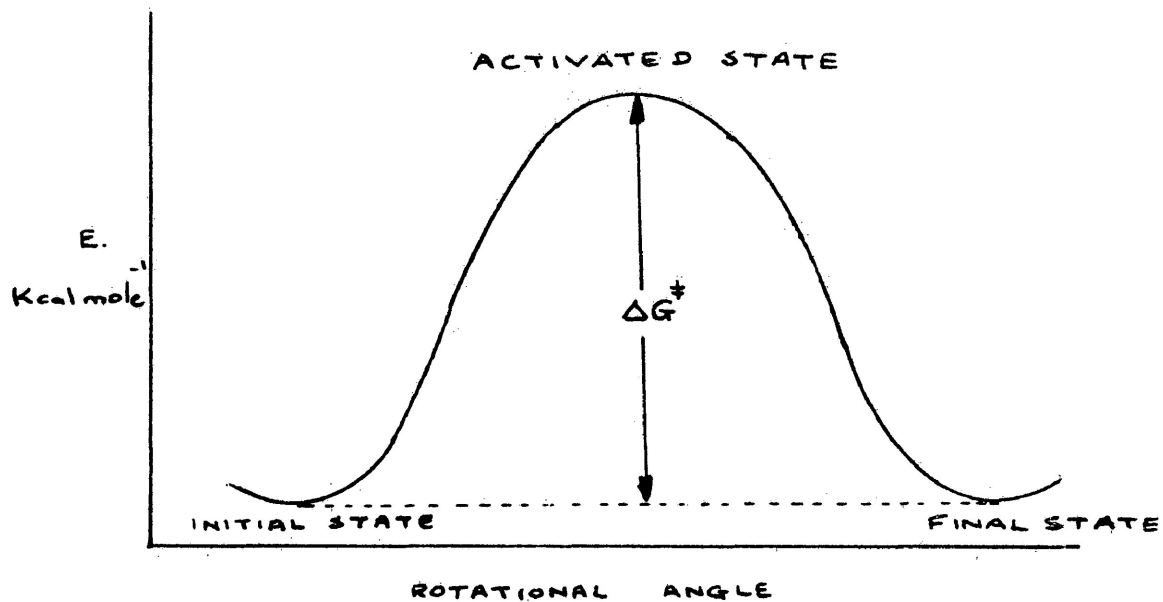
b) IN PRESENCE OF FIELD
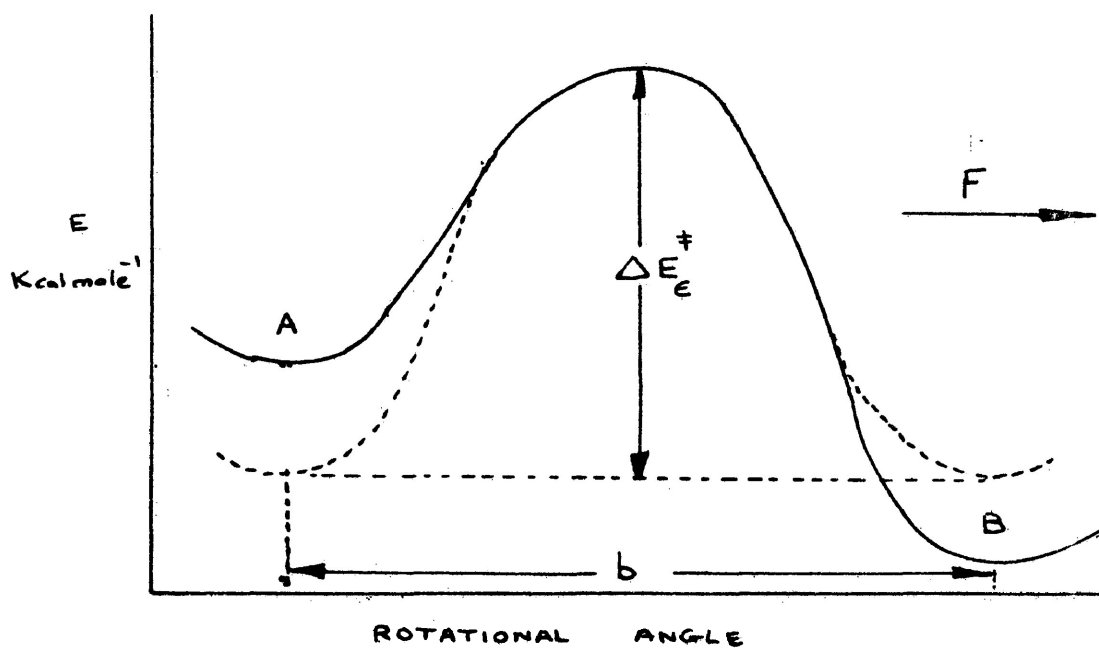
Eyring expression:

$$\tau = \frac{1}{K} = \alpha h e^{\Delta G^{\ddagger}/RT} \frac{}{kT} \qquad (3.1)$$

Where K = the dipole jump rate.

h = Planck's constant.

k = Boltzmann's constant.

$\Delta G^{\ddagger}$ = barrier height, the free energy of activation.

R = universal gas constant.

T = absolute temperature.

α = is a transmission coefficient normally taken

to be unity. It is the probability that, once

the dipole reaches the activated state, it

will continue to move in the same direction to

a new position of orientation.

Since $\Delta G = \Delta H - T\Delta S$, equation (1) can be rewritten in the form:

$$\tau = \frac{h}{kT} e^{(\Delta H^{\ddagger}/RT - \Delta S^{\ddagger}/R)} \qquad (3.2)$$

Hence, from equation (2) $\Delta G^{\ddagger}$ can be obtained from the re-lation:

$$\Delta G^{\ddagger} = RT.2.3026[\log \tau + \log kT/h], \text{and } \Delta H^{\ddagger} \text{ can be}$$

obtained from a study of the variation of relaxation time with

temperature from the slope of a log τT-vs-1/T plot.

Because of its simplicity, the Eyring expression has been

used to evaluate the thermodynamic activation parameters for

many dielectric systems. However, the proof of its validity is not established because of the difficulty of directly determining the activation terms. The use and limitations of the expression have, however, been discussed (4)(5).

It is observed (6) for dilute solutions of polar molecules in non-polar solvents that when $\Delta H^{\ddagger}$ is less than 3.6 kcal. mole^{-1} $\Delta S^{\ddagger}$ is negative, but for polymers $\Delta H^{\ddagger}$ is of the order of 50-100 Kcals, and $\Delta S^{\ddagger}$ is positive to the extent of 100 - 300 e.u.

Levi (5) explained the polymer data on the basis that the reorientation involves the motion of large molecular segments. Extensive local disorganization of the polymer gives rise to the large entropy: the energy expended in creating the disorganization accounted for the enthalpy change. In liquid systems the system is different. The lack of rigidity and weaker intermolecular interactions reduce $\Delta H^{\ddagger}$ to a small value. Bauer (5) explained the negative entropy on the basis that it represents merely a higher state of order in the activated state relative to the initial state, ~~since in the activated state the dipole is forced to adopt a particular configuration relative to the field direction, reducing the entropy relative to the initial state~~. The Eyring equation thus allows its user considerable flexibility in the interpretation of the experimental observations.

Davies and Clemett (4) have questioned the significance of the entropy term given by equation (3.2). When $\Delta H^{\ddagger}$ is written in the form of an Arrhenius expression:

$$\frac{1}{\tau} = A \exp(-\Delta H^{\ddagger}/RT)$$

and this is compared with equation (3.2), it is seen that the pre-exponential function becomes:

$$A = \frac{kT}{h} \exp(\Delta s^{\ddagger}/R)$$

$\Delta G^{\ddagger}$ calculated from equation (3.2) is then an arbitrary parameter which may be adjusted to fit the experimental data. Since $\Delta s^{\ddagger}$ is calculated from the difference between $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$, it must be assumed that the universal frequency factor of the Eyring expression is correct for $\Delta s^{\ddagger}$ to have any physical meaning.

Powles (9) has pointed out that the Eyring frequency factor kT/h is no more than the uncertainty principle time for the energy kT. Furthermore, it is the same for all molecules, whereas he favours a characteristic frequency factor for each molecule. Other rate expressions have different pre-exponential factors.

As an alternative to the Eyring expression, Clemett and Davies favour the equation of Bauer (7):

$$\frac{1}{\tau} = \sqrt{\frac{kT}{2\pi I}} \left[\frac{1}{\sigma_1} + \frac{1}{\sigma_2} \right] L e^{\frac{-\Delta H}{RT}}$$

The symbols as defined by Bauer (7) are:

$$I = \text{moment of inertia of the particle}$$

σ_1 and σ_2 = configuration partition functions

corresponding to the two equilibrium positions.

L = effective length of the potential barrier

Unfortunately, in order to calculate all the pre-exponential terms of the Bauer expression, detailed knowledge of the form of the potential energy surface is required. Hence, attempts to make evaluations of the activation terms, by using this expression, are hindered by its intractibility in comparison to the arbitrary nature of the Eyring expression.

For the systems which they studied Clemett and Davies found that the differences in enthalpy evaluated by the Eyring and Bauer expressions were no more than the experimental error. However, the entropies of activation were considerably different; the Eyring expression gave negative entropies, whereas the Bauer equation gave positive values.

Hoffman and Pfeiffer (8) treated theoretically the dielectric behaviour of a polar crystalline solid. The rate expression derived by these workers was of the general Arrhenius form of the previous expressions given above. However, they considered that the form of

the pre-exponential term was uncertain. In a later paper (9)
Hoffman states "there is some implication that the pre-
exponential factor is somewhat smaller than kT/h being nearer to
$$\frac{3}{2\pi}\left[\frac{kT}{I}\right]^{1/2}\text{ "}$$

Frohlich has treated dielectric relaxation as a rate process,
and a discussion of this approach would seem profitable. It is con-
sidered that the particle has two equilibrium positions which have
the same potential energy in the absence of a field. An energy bar-
rier $\Delta E^{\pm}$ separates the two positions A and B (Figure 3.1 (a)). In
equilibrium each of the sites is equally occupied with particles and
there is no net polarization. If $\Delta E^{\pm} > kT$ then the fraction of par-
ticles in either site, which has sufficient energy to cross the
barrier, in either direction, is given by the Boltzmann factor:

$$e^{-\Delta E^{\pm}/kT}$$

When an electric field is applied to the system, the potential
energy of the particles in the two equilibrium positions will be
changed. The potential energy of the particles in A is raised with
respect to B (Figure 1b). Jumps in the direction of the field then
become favoured, since they are to positions of lower potential en-
ergy, and the number of particles in position B will thus tend to
increase leading to a polarization of the medium in the field dir-
ection. For simplicity the particles are considered to have a charge,
e, and hence their interaction energy with the field will be

$\frac{1}{2}$ eFb where F is the field strength and b is the distance of separation of the equilibrium positions. A particle in site A is then separated from site B by an energy barrier:

$$\Delta E_A^{\ddagger} = \Delta E^{\ddagger} - \frac{1}{2} eFb \quad (3.3)$$

In site B the particle experiences an effective height:

$$\Delta E_B^{\ddagger} = \Delta E^{\ddagger} + \frac{1}{2} eFb \quad (3.4)$$

In the absence of a field it is assumed that the particles are librating about a mean position with a frequency Wo. The probability, P°_{AB}, that a particle will cross from A to B or from B to A is given by:

$$P^{\circ}_{AB} = Woe^{-\Delta E^{\ddagger}/kT} = P^{\circ}_{BA} \quad (3.5)$$

If a field is now applied, the particles in A facing a lower potential energy barrier have an increased probability, P_{AB}, of crossing to B given by:

$$P_{AB} = Woe^{-\Delta E_A^{\ddagger}/kT}$$
$$= Woe^{-\Delta E^{\ddagger}/kT} e^{\frac{eFb}{2kT}}$$

Hence, for eFb << kT

$$= P^{\circ}_{AB} \left[1 + \frac{eFb}{2kT} \right] \quad (3.6)$$

Similarly, the particles in B face a higher potential barrier and have a decreased probability of crossing to A given by:

$$P_{BA} = Woe^{-\Delta E_B^{\ddagger}/kT}$$

$$= Woe^{-\Delta E^{\ddagger}/kT} e^{-eFb/kT}$$

$$= P^{\circ}_{AB} \left[1 - \frac{eFb}{2kT} \right] \tag{3.7}$$

The net rate at which the number of particles in A is changing is determined by Boltzmann's equation.

Hence

$$\frac{dN_A}{dt} = - P_{AB} N_A + P_{BA} N_B \tag{3.8}$$

where N_A and N_B are the number of particles in sites A and B respectively. The number in site B is given by the analogous expressions:

$$\frac{dN_B}{dt} = -P_{BA} N_B + P_{AB} N_A \tag{3.9}$$

Adding (3.8) and (3.9)

$$\frac{d}{dT} (N_A + N_B) = 0$$

so that the total number of particles in both sites is constant with time, as must be so.

The difference in population numbers between the two sites is proportional to the induced polarization i.e.

$$\frac{d}{dt} (N_B - N_A) = -2P_{BA} N_B + 2P_{AB} N_A \qquad (3.10)$$

but from (3.6) and (3.7), (3.10) becomes

$$\frac{d}{dt} (N_B - N_A) = -2P^\circ_{AB} \left[1 - \frac{eFb}{2kT} \right] N_B + 2P^\circ_{AB} \left[1 + \frac{eFb}{2kT} \right] N_A$$

$$= 2P^\circ_{AB} \left[-(N_B - N_A) + \frac{eFb}{2kT} (N_A + N_B) \right]$$

But $N_A + N_B = N =$ total number of particles $=$ constant and

since $M = eb (N_B - N_A)$ (3.11)

where M is the total moment induced into the system by the

electric field, the equation for the variation of induced moment

with time is:

$$\frac{dM}{dt} = \frac{- 2P^\circ_{AB} M + e^2 b^2 FP^\circ_{AB} N}{kT} \qquad (3.12)$$

A solution to this equation exists which has the form:

$$M(t) = \alpha + \beta e^{-t/\tau} \qquad (3.13)$$

where α, β and τ are constants.

Differentating (3.13) with respect to t gives

$$\frac{dM}{dt} = - \frac{\beta}{\tau} [M(t) - \alpha]$$

$$= -\frac{1}{\tau} M(t) + \frac{\alpha}{\tau}$$

This is of the form of equation (3.12) provided

$$\frac{1}{\tau} = 2P^{\circ}_{AB}$$

$$\frac{\alpha}{\tau} = \frac{e^2 b^2 FP^{\circ}_{AB} N}{kT}$$

or $$\alpha = \frac{e^2 b^2 FN}{2kT}$$

Thus, a solution of 10 satisfying the initial condition, that M(o) = o at t=o, i.e. that there is no net total moment at t=o, is:

$$M(t) = \frac{e^2 b^2 FN}{2kT}\left[1 - e^{-t/\tau}\right]$$

The relaxation time is given in terms of the transition probability of the particle jumping the barrier by:

$$\tau = \frac{1}{2P^{\circ}_{AB}}$$

Now as t → ∞, $M(t) \to M(\infty) = \frac{e^2 b^2 FN}{2kT}$ which is the equilibrium moment induced into the medium. Hence:

$$M(t) = M(\infty)\left[1 - e^{-t/\tau}\right]$$

An exponential variation of the moment with time gives rise to Debye-type absorption for the dielectric. This mechanism is, then,

phenomonologically indistinguishable from the Brownian rotation diffusion model proposed by Debye, since the Debye dispersion equations follow from both approaches.

Since $\tau = \dfrac{1}{2P^{\circ}_{AB}}$

it follows that:

$$\tau = \frac{1}{2W_0} e^{\Delta E^{\ddagger}/kT}$$

This is the Fröhlich equation. The action of the field on the medium merely alters the relative energies of the two equilibrium positions. It is unable to lift the particle over the energy barrier, the energy required by the molecule to surmount the barrier being acquired by exchange of energy in collision processes with other molecules.

Fröhlich considered that the pre-exponential frequency factor could not be determined with accuracy but it may be considered to be of the order of 10^{12} to 10^{14} sec^{-1}.

It thus appears that, since the form of the pre-exponential factor cannot be fully justified, the entropy of activation determined by the Eyring expression has no absolute significance. In view of this it was decided to use the general equation:

$$\tau = \frac{A}{T} \exp (\Delta E^{\ddagger}_{\varepsilon}/RT) \qquad (3.14)$$

for the calculation of the experimental activation energy,

$\Delta E_\epsilon^{\ddagger}$, opposing the reorientation of the dipole. A ~~is a constant and~~ is considered to be a function of temperature and pressure (39).

When the dipole is fixed, as in a rigid molecule, then $\Delta E_\epsilon^{\ddagger}$ represents the energy barrier to rotation of the molecule as a whole.

An attempt will now be made to gain insight into the nature of the energy barrier opposing the rotation of rigid molecules.

Since the dipolar molecule is not rotating freely in solution, the barrier to its rotation can be regarded as the resistance produced by the neighbouring molecules of its environment. In order to reorient, then, the dipolar molecule displaces the molecules surrounding it and does work against the attractive forces of the liquid in going from an equilibrium position of orientation to the activated state.

To evaluate the work done, it is necessary to have knowledge of the forces acting between the molecules of a liquid, and for this the thermodynamic property known as internal pressure, which was taken by Hildebrand (11) to be a general measure of the intermolecular forces within a liquid, will be used. Internal pressure, Pi, or cohesion energy density, as it is also known, is defined by the relation

Pi $= \left(\dfrac{\partial u}{\partial v}\right)_T$ where ∂u is the charge of internal energy of the liquid resulting from a charge in volume, ∂v, at constant temperature.

When the dipolar molecular reorients in a liquid, it occupies space which was previously occupied by other molecules. Thus, the activated state can then be regarded as a process which involves a volume expansion within the liquid due to the reorienting molecule displacing its neighbours. An analogous situation has been observed in the solid state where the appearance or a rotator phase is often accompanied by a change from a brittle to a waxy state (12). Such behaviour has been attributed to a loosening of the lattice structure allowing a volume expansion accompanying the onset of molecular rotation, and has been observed for the symmetrically substituted methanes, e.g. $(CH_3)_3 CCl(13)$.

If a liquid is subjected to a volume charge, then work is done against its internal pressure. The work done is given by the expression

$$W = \left[\frac{\partial u}{\partial V} \right]_T dV$$

where dV is the volume change. The activation energy can then be regarded as the work done by the dipolar molecule reorienting whereby:

$$\Delta E_\epsilon^{\ddagger} = Pi \Delta v_\epsilon^{\ddagger} \qquad (3.15)$$

where $\Delta V_\epsilon^{\ddagger}$ is the activation volume and represents the volume swept out by the molecule in going from the intial to the activated state.

The internal pressure of a liquid may be estimated by the following methods. If it is assumed that the internal molar heat of vaporization, L, is a measure of the work done against the internal pressure in vaporizing one mole of liquid occupying a volume V, then

$$\left[\frac{\partial u}{\partial V}\right]_T V = L$$

but

$$\left[\frac{\partial u}{\partial V}\right]_T = Pi$$

hence $Pi = L/V$

Pi can also be obtained from the coefficients of cubic expansion α and compressibility β in the following manner:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

and

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

hence

$$\frac{\alpha}{\beta} = \left(\frac{\partial P}{\partial T}\right)_V$$

Using the therodynamic equation of state:

$$Pi = \left[\frac{\partial u}{\partial V}\right]_T = T\left[\frac{\partial P}{\partial T}\right]_V - P$$

since the external pressure, P, is small in comparison to Pi, which

is of the order of 2000 - 8000 atmospheres, then:

$$Pi = T\left[\frac{\partial P}{\partial T}\right]_V$$

from which it follows that

$$Pi = T\frac{\alpha}{\beta}$$

The assumption that the barrier to molecular reorientation, $\Delta E_\epsilon^{\ast}$ is equal to work done in creating the volume charge within the liquid can now be tested. By inserting $\Delta E_\epsilon^{\ast} = Pi\Delta V_\epsilon^{\ast}$ into equation (3.14), then:

$$\tau = \frac{A}{T}\exp\frac{Pi\Delta V_\epsilon^{\ast}}{RT}$$

The relationship between τ, Pi and $\Delta V^{\ast}$ can be studied by measuring τ for a particular solute in a number of solvents of differing internal pressure. Of the solvents commonly used in dielectric measurements decalin and nujol are not suitable for investigation of the effect of internal pressure, because, from the physical properties stated by various workers, decalin invariably appears to be a mixture of the cis and trans isomers, furthermore, nujol is also a mixture, and the internal pressures of these mixtures are not known.

Table (3.1) gives the internal pressures of a number of suitable solvents. These have been calculated from heat of vaporization data given in Hildebrand and Scott (14) or tables of physical constants by Dreisback (15).

TABLE 3.1

INTERNAL PRESSURES OF SOLVENTS

Solvent	Internal Pressure calcc^{-1}
iso-Octane	46.9
n-Hexane	51.8
n-Heptane	55.2
Methylcyclohexane	61.0
Cyclohexane	67.2
Carbon tetrachloride	74.3
p-Xylene	76.9
Benzene	83.9
1:4 Dioxane	96.0

A plot of log τ against internal pressure will give the relationship between τ, Pi and $\Delta E^{\ddagger}_{\varepsilon}$. $\Delta V^{\ddagger}_{\varepsilon}$ can be obtained from the slope, i.e.:

$$\ell n\tau = \ell n \frac{A}{T} + \frac{P_i \Delta V^+}{RT}\epsilon$$

and $\quad\quad \dfrac{\Delta V^{\ddagger}}{\epsilon} = 2.3026 \, RT \times slope.$

Figs. 2 to 11 are constructed from the work of Chau, Tardif and LeFèvre (15), Hasse (21), Chitoku and Higasi (16), Magee (17), and Eichhoff and Hufnagel (20). It can be seen that, in general, fairly good straight lines are obtained. It is conspicuous, however, that the relaxation times in carbon tetrachloride are higher than would be expected if internal pressure alone governed the relaxation time.

Higasi (18) has commented on the apparently anomolously high values of carbon tetrachloride solutions of polar molecules. He compared relaxation times of a number of solutes in the two solvents, cyclohexane and carbon tetrachloride, both of which have almost identical viscosity, but relaxation times were observed to be some 70% higher in carbon tetrachloride. The observation was explained by suggesting that molecules interacted with the carbon tetrachloride. In fact, molecular compound formation has been detected in some solutions in this solvent (19).

Table II gives the activation volumes obtained from the log τ-Pi plots in figures 2 to 9. They are compared with molar volumes calculated from the molecular weight and density, and the ratio molar volume/$\Delta V^{\pm}_{\epsilon}$ is given.

FIG 3.2 Log γ- Pi PLOT FOR PYRIDINE (ref. 21)
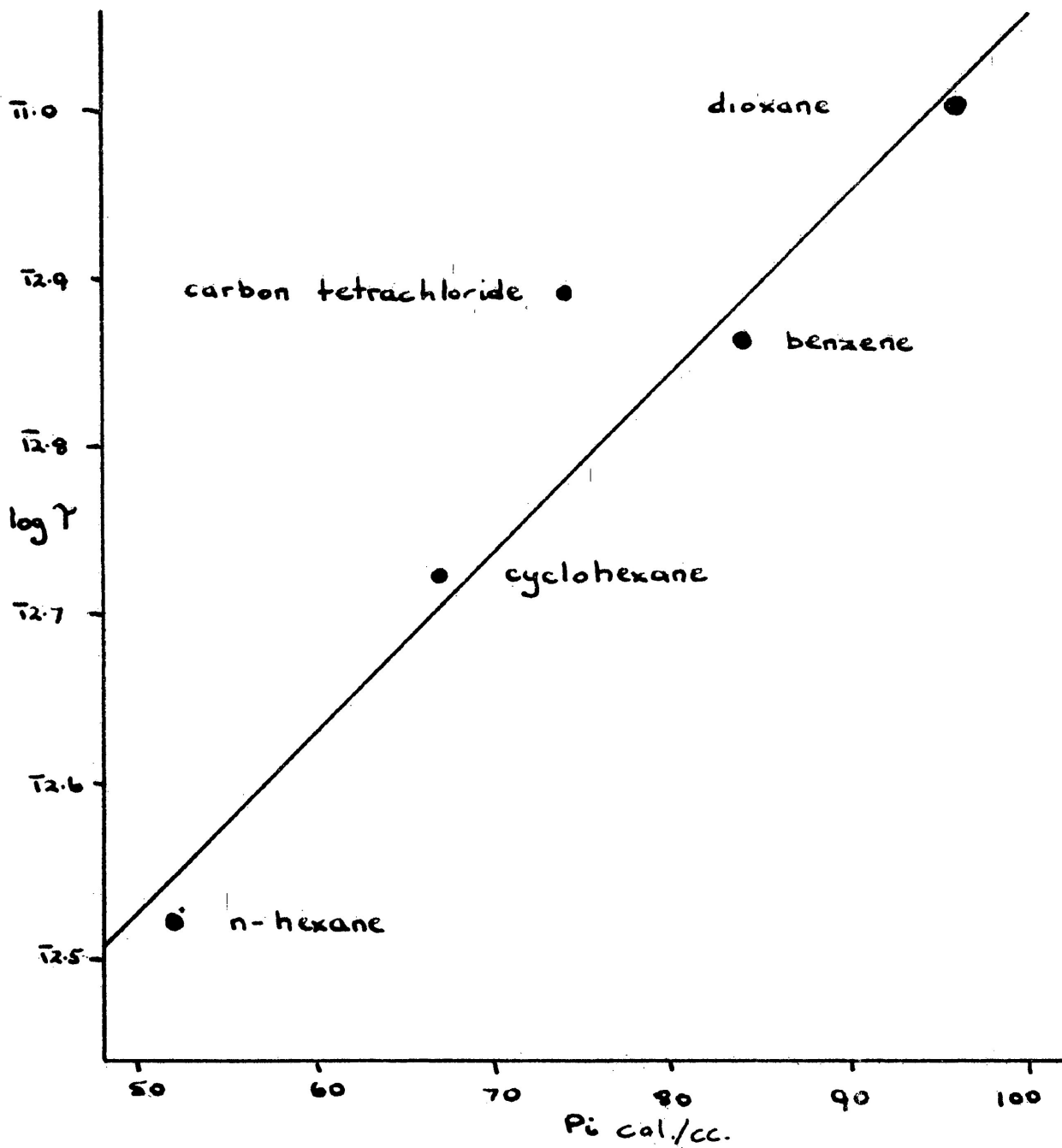
FIG 3.3 Log γ - P_L PLOT FOR o-NITROPHENOL (ref. 17).
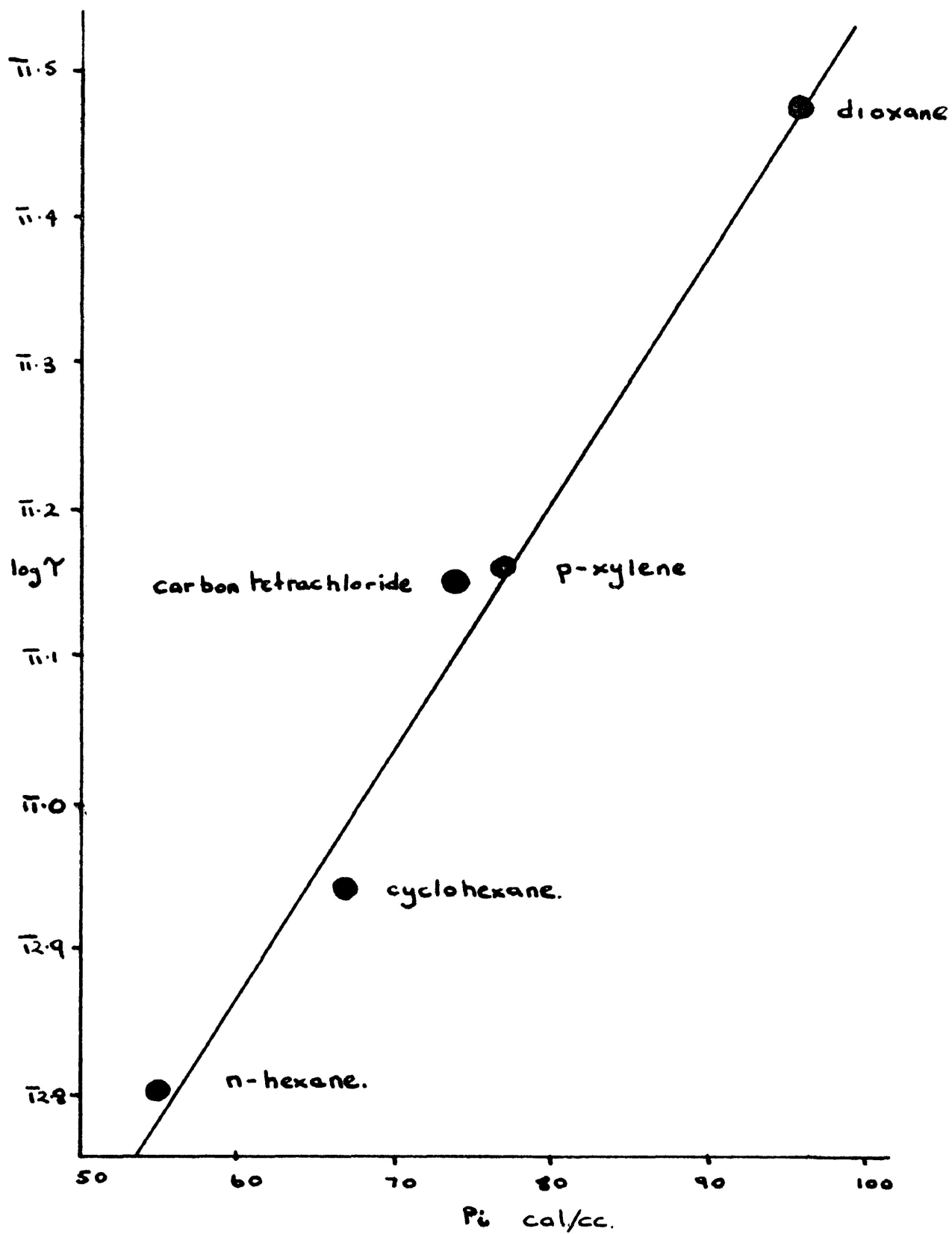
Fig. 3·4 Log γ - Pi PLOT FOR NITROBENZENE (ref. 21.).
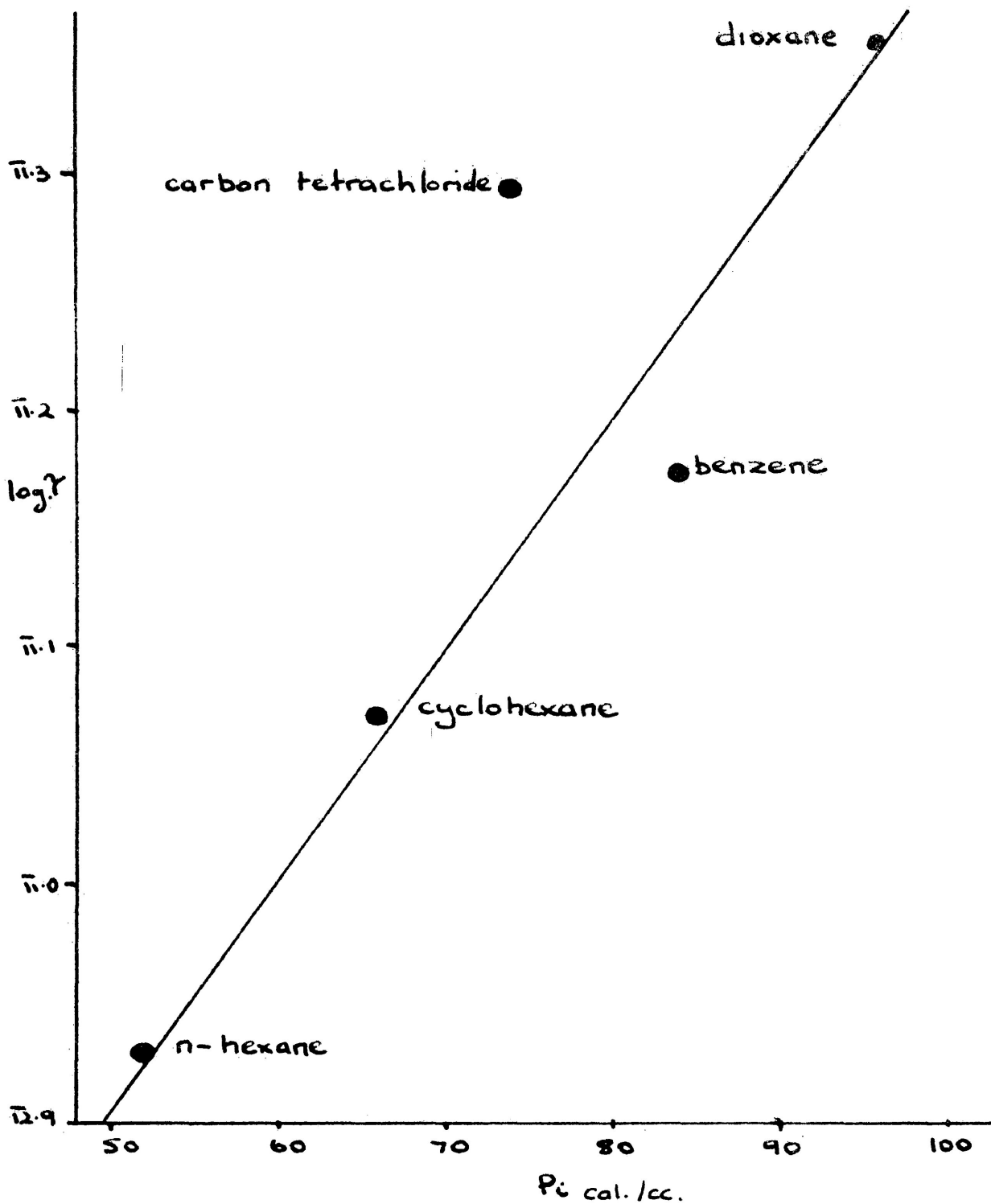
FIG. 3.5 Log γ - Pi PLOT FOR CHLOROBENZENE (ref. 21.)
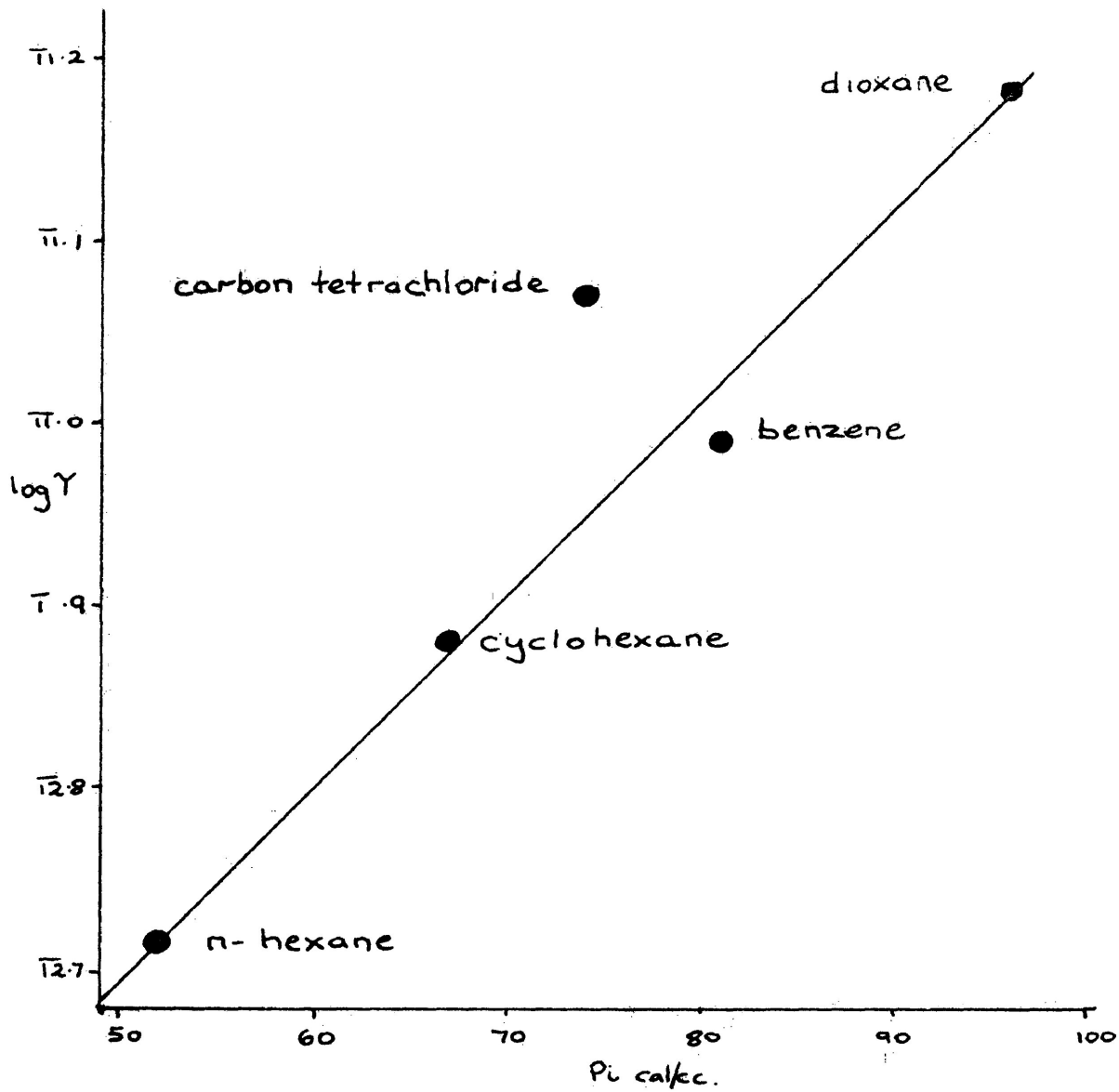
FIG. 3·6. Log. γ-Pi PLOT FOR P-NITROTOLUENE (ref. 16).
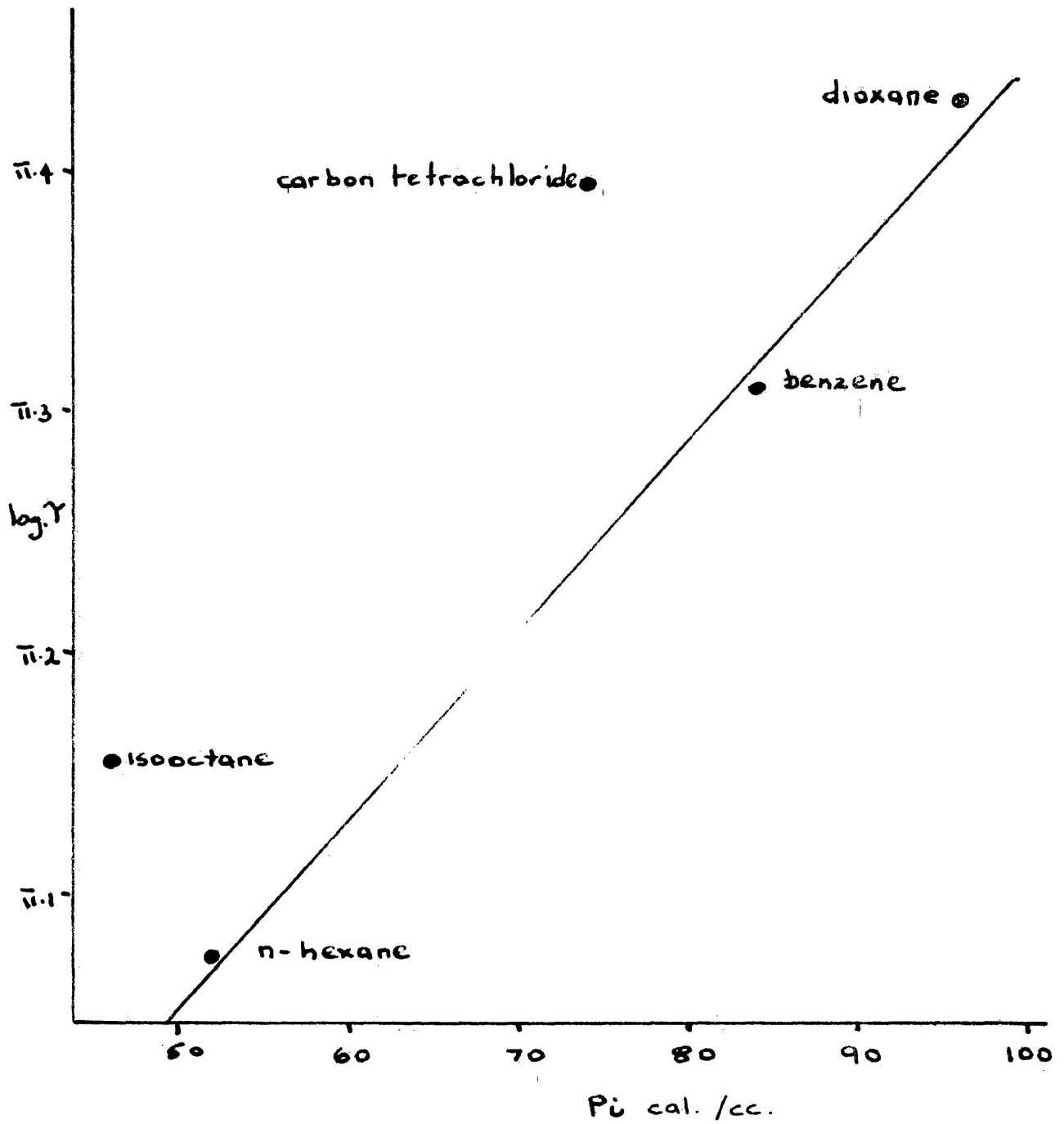
Fig 3.7 Log Υ- Pi PLOT FOR CYCLOHEXYLCHLORIDE (ref. 21).
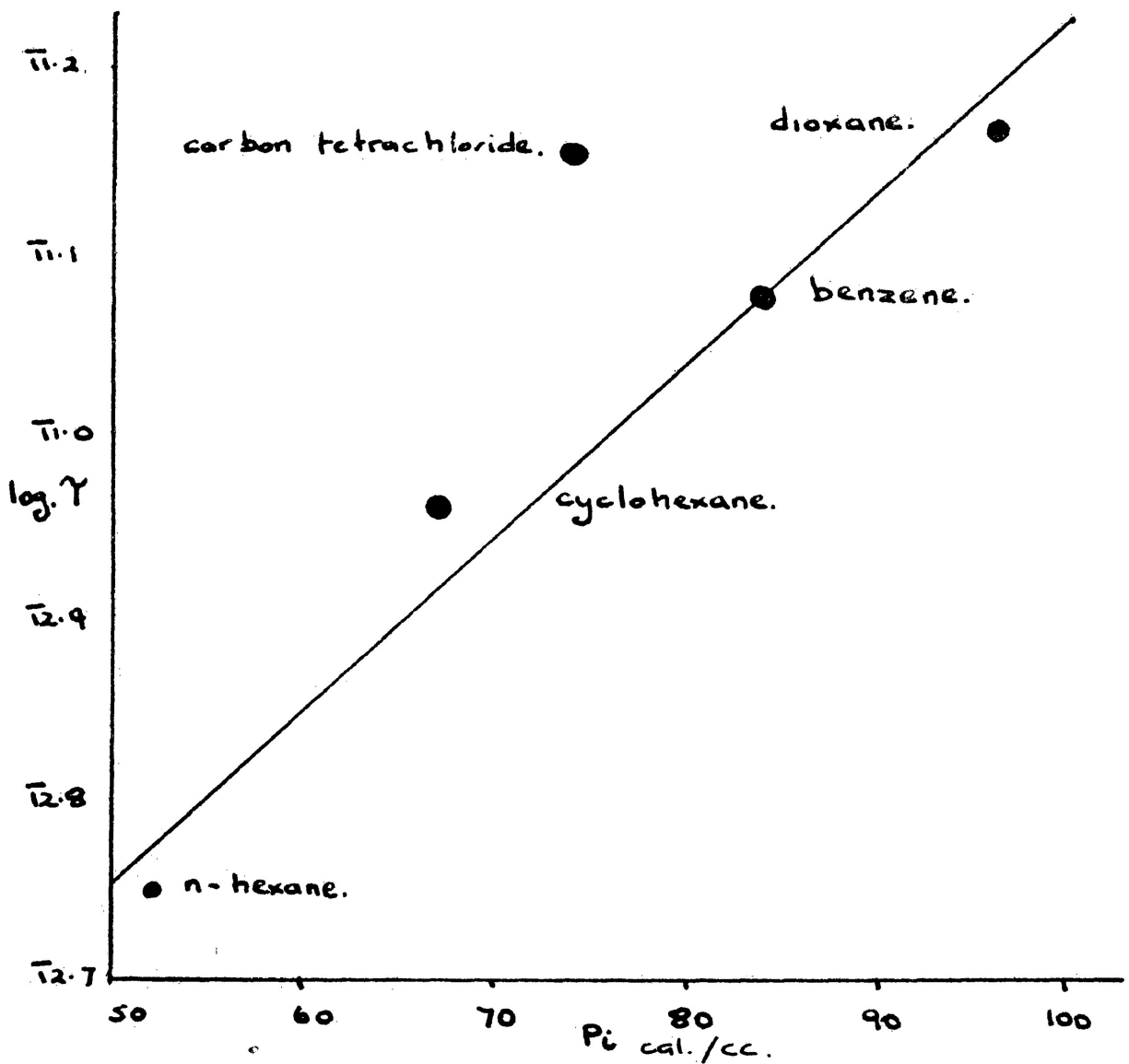
FiG. 3·8. Log ϒ- Pi PLOT FOR αNITRONAPHTHALENE
(ref. 15.)
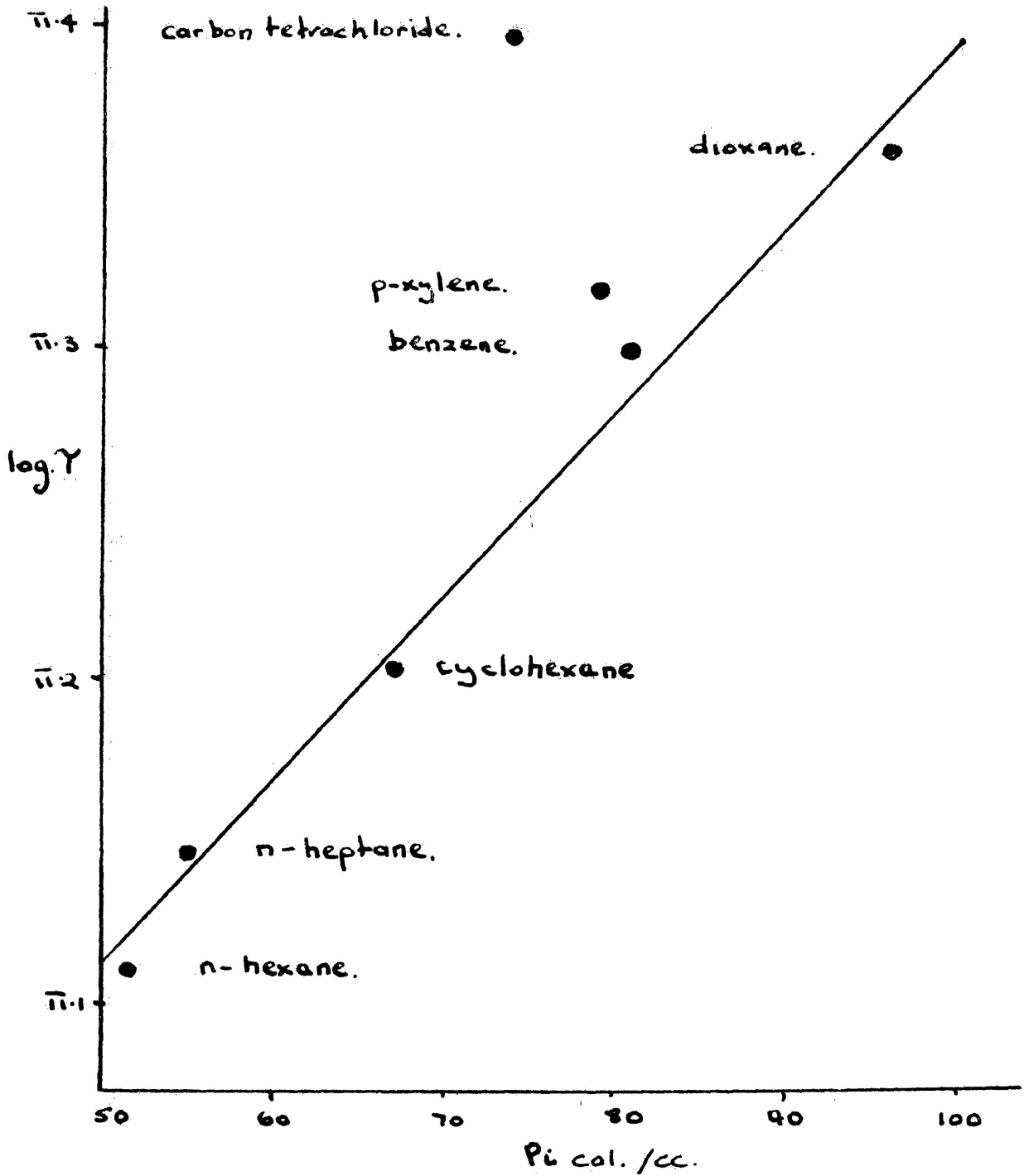
FIG 3.9 LOG $\gamma - P_c$ PLOT FOR 2,2 dichloropropane
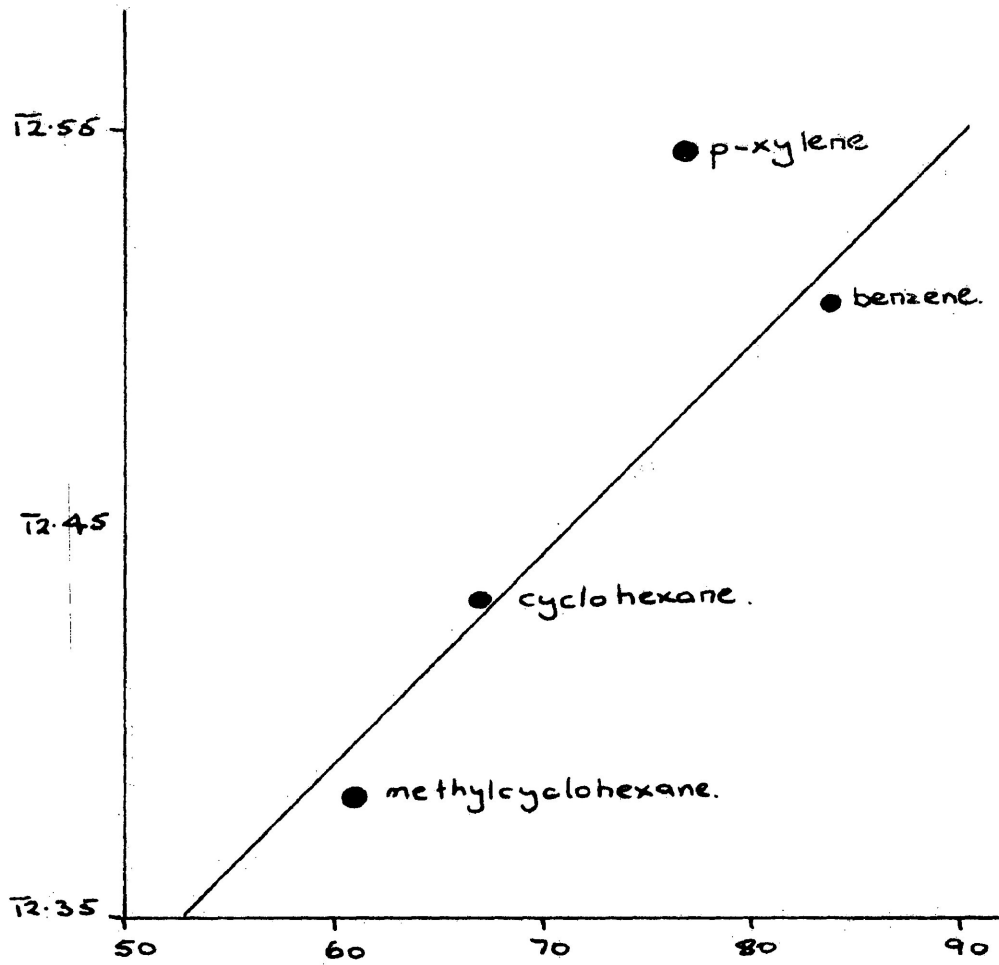
FIG. 3·10 LOG Υ-P_i PLOT FOR PYRIDINE (ref. 20.).
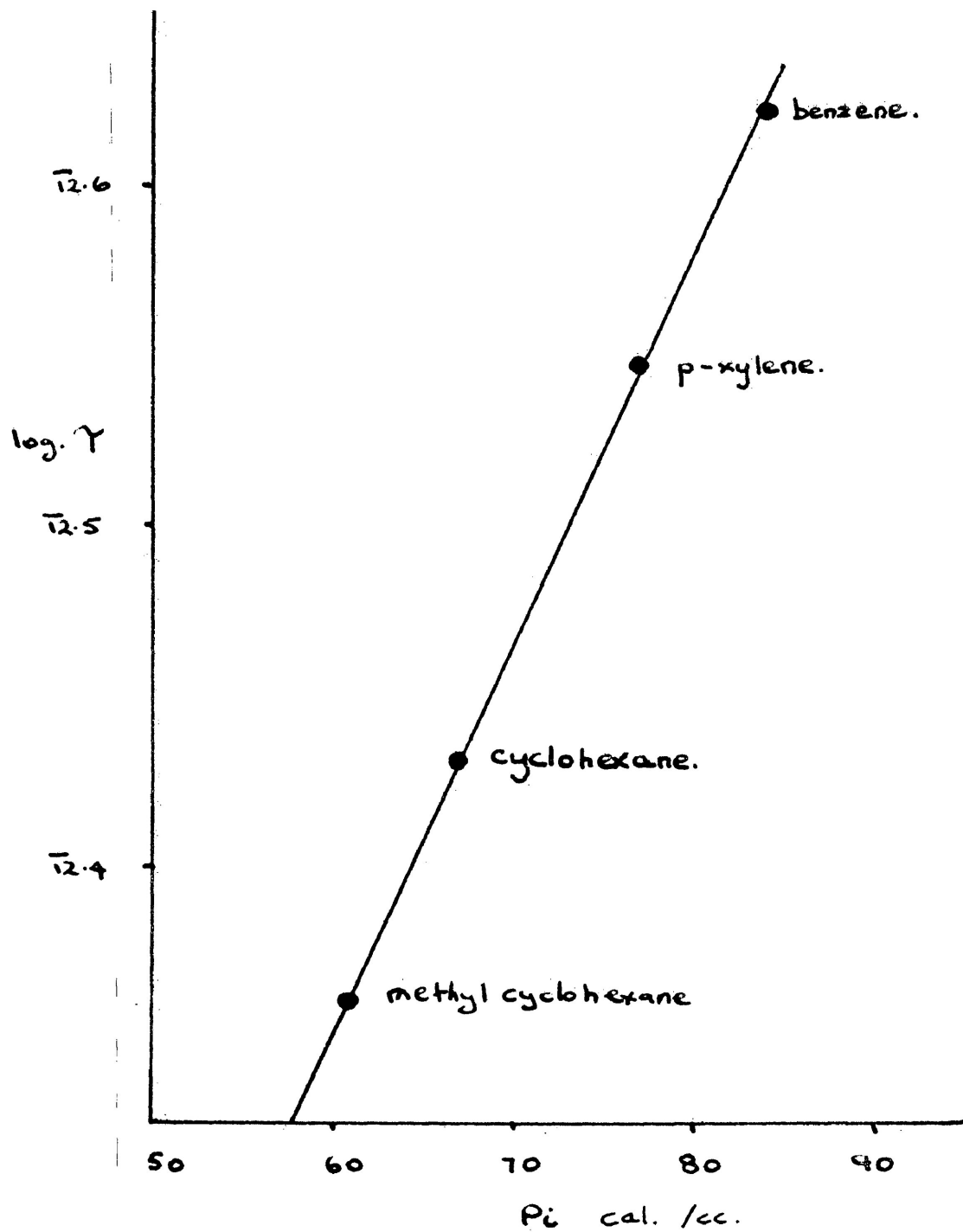
FIG. 3.11 Log γ-P$_i$ PLOT FOR NITROBENZENE (ref 20)
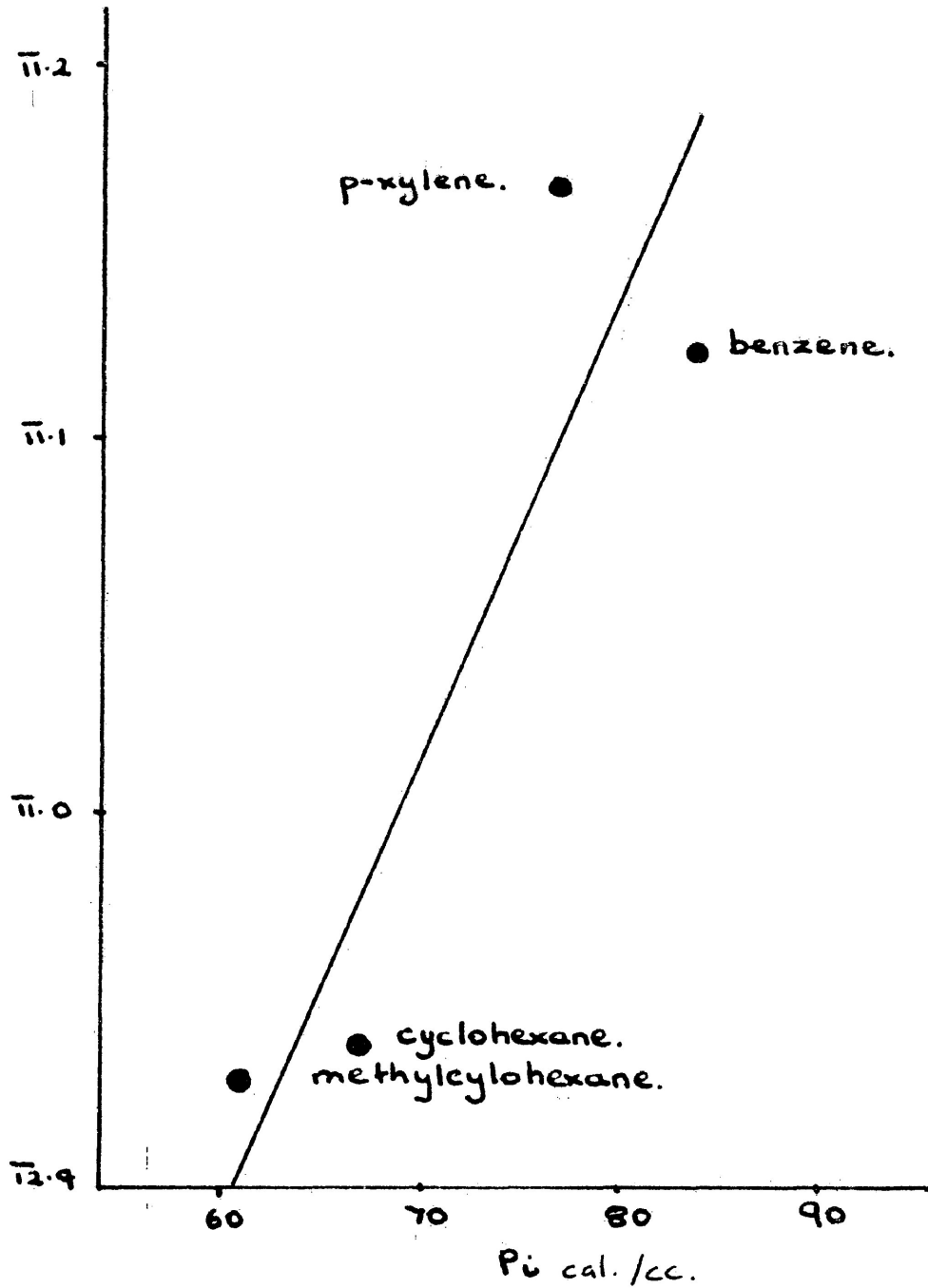
TABLE (3.2)

ACTIVATION VOLUMES $\Delta V_\epsilon^\ddagger$ OBTAINED FROM FIGURES 2 TO 9

Solute	Activation Volume -1 cc/mole	Molar Volume M -1 cc/mole 25°C	$\dfrac{M^\ddagger}{\Delta V_\epsilon}$
Pyridine	14.5	80.6	5.6
o-Nitrophenol	22.9	93.7 (14°C)	4.0
Chlorobenzene	12.6	100.3	8.0
Nitrobenzene	13.8	102.3	7.4
2:2 Dichoropropane	8.5	103.4	12.1
p-Nitrotoluene	10.9	105.5 (0°C)	9.7
Cyclohexyl chloride	13.2	118.6	9.0
α-Nitronaphthalene	7.7	130	16.9

The activation volume is seen to vary from 7.7 cc.mole^{-1}

for α-nitronaphthalene to 22.9 cc.mole^{-1} for o-nitrophenol, and in all

cases it is considerably less than the molar volume of the solute.

It appears from table 3.2 that the larger molecule, α-nitronaphthalene,

has a slightly smaller activation volume than the other solutes.

However, these volumes are subject to error, since the slopes of the

lines are of the order 0.006-0.01, and 2.303 RT, the factor

by which they are multiplied to obtain the volume has a value 1364.1

at 25°C. Thus, only a small error is needed in the slope to give a large error in the activation volume. Further, the values of relaxation time quoted by different authors (15)(16)(20)(21) for the same solute solvent system show variation.

A comparison is made in Table 3.3 of various values of the relaxation time quoted for pyridine and nitrobenzene; the author reference is shown in parenthesis. (See Table 3.3).

Although the values of Hasse appear to be larger than the more recently measured values (20)(22), they were used because they had the largest variation of internal pressure of the solvents. The data of Eichhoff and Hufnagel (20) for pyridine and nitrobenzene are shown in Figures 10 and 11 respectively for comparison with the Hasse data. The activation volumes obtained from these results, 15.4 and 14.4 ccMole^{-1} respectively, are in reasonable agreement with that from the Hasse data, suggesting that the relative relaxation times obtained by Hasse are correct.

The log τ-Pi plots are seen to predict the effect of solvent on relaxation time more accurately than the Debye equation in which the solvent viscosity is used for η.

Based solely on the solvent viscosity, the relaxation times for a particular solute in a variety of solvents would be expected to increase in the order: n-hexane < n-heptane < p-xylene $\sim$ benzene < methylcyclohexane < cyclohexane $\sim$ carbontetrachloride < dioxane.

TABLE 3.3

VALUES OF τ OBTAINED BY VARIOUS AUTHORS FOR NITROBENZENE AND
PYRIDINE IN DIFFERENT SOLVENTS.

Solvent	Pyridine $\tau \times 10^{-12}$ sec.	Nitrobenzene $\tau \times 10^{-12}$ sec.
Hexane	3.3(21) 3.8(16)	9.6(15) 8.5(21)
Cyclohexane	5.3(21) 2.7(20) 2.9(22)	11.8(21) 8.7(20)
Benzene	4.4(15) 7.3(21) 3.6(16) 4.2(20) 4.6(22)	11.0(16) 14.9(21) 13.3(20)
p-Xylene	3.4(20) 4.3(22)	14.7(20)
Carbontet-rachloride	7.2(15) 7.8(21) 4.4(16) 5.0(22)	14.1(16) 19.6(21)
Dioxane	10.5(21)	17.3(16) 22.6(21)
Methyl-cyclohaxane	2.3(20)	8.5(20)

The linearity of the log τPi plots, then, provides strong supporting evidence for the hypothesis that the barrier to rotation of the molecules is the work done by the solute in displacing the solvent molecules surrounding it.

The graph for 2:2-dichloropropane is not as good as for the other solutes, since, the value of the relaxation time in p-xylene in comparison to benzene appears to be anomolously high. A similar case has been observed by Chitoku and Higasi (23) for dichloroethane in these aromatic solvents which these authors attribute to the formation of a hydrogen bond between the solute and the solvent.

For the cases where the plots are linear for a number of solvents, as in figures 2,3,4,5,6,7and 8, it may be tentatively concluded that solute-solvent interaction does not contribute detectably to the activation energy.

To determine whether solute-solvent interaction energy is likely to contribute to the energy barrier to rotation, these terms will now be calculated for nitrobenzene and pyridine in a number of solvents.

Three general types of attractive interactions are known to exist between molecules. Dipole-dipole interactions operate between two molecules, each of which has a permanent dipole and come into being when two dipoles approach one another.When a molecule with a permanent dipole approaches a non-polar polarizable molecule, then a dipole is induced in the latter, which gives rise to an attractive interaction

known as the dipole-induced-dipole term. The third type of interaction arises from dispersion forces which were shown by London to act between all molecules and are always attractive.

For dilute solutions of polar molecules in non-polar solvents, provided hydrogen bonding or other specific interactions do not occur, the only interactions possible are those depending on the polarizability of the solute and solvent and the dipole moment of the solute.

Because of the low concentration of the polar molecules, inter-actions between the permanent dipoles of the solute can be ignored. Of the three general types of interaction discussed, only those due to London forces and dipole-induced-dipole forces need to be considered for dilute solutions.

The expressions for London dispersion energy, E_L, and dipole-induced-dipole interaction, E_D, are given by:

$$E_L = \frac{-3\alpha_1 \alpha_2 \ I_1 \ I_2}{2r^6 \ I_1 + I_2}$$

$$E_D = \frac{-1}{r^6} \ \alpha_1 \mu^2$$

where α_i is the mean molecular polarizability.

I_i is the first ionization potential.

r is the distance of separation of molecular centres.

and μ is the molecular permanent dipole moment.

Precise calculation of the attractive energy terms is difficult because of the nature of the liquid state, moreover, the distance of separation of the molecules is subject to variation with time and is not known with certainty. Therefore, as an approximation, it will be assumed that both solute and solvent molecules are spherical, the mean radii being determined from the molar volumes. The distance of separation of the molecules will be assumed to be the sum of their mean radii. For the calculation of E_D, only interactions between neighbouring pairs of molecules need to be considered. For dispersion energies, however, the attraction is between all molecules surrounding a central molecule and is the sum of all the pair interactions. It then becomes necessary to know the coordination number for the solute-solvent system. This parameter is unknown. Furthermore, it will be subject to variation with time. In view of this difficulty, the dispersion energy interaction is calculated only for neighbouring pair interactions. Table (3.4) gives the dispersion and dipole-induced-dipole energy interaction terms for pyridine and nitrobenze in a number of solvents. The polarizability data were taken from LeFevre (24)(15), the ionization potentials from Kiser (25), and dipole

moments from McClellen (26).

TABLE (3.4)

Solute-solvent Interaction Energies
for Pyridine and Nitrobenzene

	Pyridine				Nitrobenzene		
Solvent	r (Å)	E_L Kcal mole^{-1}	E_D Kcal mole^{-1}	Solvent	r (Å)	E_L Kcal mole^{-1}	E_D Kcal mole^{-1}
Dioxane	6.4	0.20	0.01	Dioxane	6.6	0.23	0.022
Benzene	6.5	0.20	0.01	Benzene	6.7	0.23	0.022
CCl$_4$	6.6	0.21	0.009	CCl$_4$	6.8	0.24	0.020
Cyclohexane	6.7	0.18	0.009	Cyclohexane	6.9	0.21	0.019
p-Xylene	6.8	0.20	0.10	p-Xylene	7.0	0.23	0.023
n-Heptane	6.7	0.19	0.009	n-Heptane	7.1	0.22	0.02
n-Hexane	7.1	0.14	0.007	n-Hexane	7.3	0.20	0.015

The dipole -induced-dipole terms are seen to be very small and
their contribution to the activation energy would not be detectable.[†]
That the carbon tetrachloride values are of the same size as the other
solvents suggests that the observed lengthening of relaxation times
in this solvent is due to more specific interactions. This is also
supported by the fact that carbon tetrachloride and cyclohexane have
similar mean polarizabilities.

It can also be seen that the dispersion energy terms for

† The tabulated energies would have to be multiplied
by the number of nearest neighbours if this information
were available.

neighbouring pair interactions do not vary appreciably from one solvent to another. Thus, provided the number of solvent molecules surrounding each solute does not change too greatly from one solvent to another, it may tentatively be concluded that the solute-solvent dispersion interaction energy does not change appreciably from solvent to solvent. The apparent constancy of the interaction energy terms, on the basis of the somewhat crude model used to calculate these terms, cannot account for the lengthening of the relaxation time observed to follow an increase in internal pressure of the solvent, but gives additional support to the postulate that the barrier to reorientation involves the displacement of solvent molecules by the solute.

If a change in the solute-solvent interaction energy, in going from the initial to the activated state, was contributing to the barrier to rotation, less regular log τ-Pi plots might be anticipated. Since it is unlikely that during the course of reorientation the solute and its immediate neighbour solvent molecules retain the same relative spacial orientations. Hence, if the general type of solute-solvent interactions calculated above were significant in determining the energy barrier, the solvents with greatest anisotropy of polarizability would produce changes in the interaction energy upon alteration of the relative positions of solute and solvent molecules. On this basis, benzene and p-xylene would be expected to show deviations on

the log τ-Pi plots. In these molecules the polarizability differs appreciably in the planes parallel and perpendicular to the carbon ring. Similarly, the aromatic solutes have a variation of molecular polarizability in the planes parallel and perpendicular to the ring, and by the same argument might be expected to exhibit similar behaviour.

Since the molecules in the liquid state are in continuous motion, owing to the Brownian movement, the approximation of treating them as spheres of mean polarizability may not be too serious. Effectively, each molecule experiences an averaged polarizability of its near neighbours owing to the flucutation of molecular positions with time. Thus, to a first approximation, the medium surrounding the polar molecule can be regarded as being of uniform polarizability. The log τ-Pi plots would then seem to indicate cases of specific interactions, i.e. hydrogen bonding or donor acceptor interactions and may prove valuable in studying molecular interaction.

In terms of equation (3.15) one interpretation of the linearity of the log τ-Pi plots is that the activation volume for solute reorientation does not change on changing the solvent. This assumes that the pre-exponential term, A, remains constant on variation of the solvent. Thus, if A can be assumed to remain constant for a

particular solute, then an explanation for the poor correlation between relaxation time and viscosity can be advanced.

Viscosity, like dielectric relaxation, has been treated as a rate process. The associated activation energy can be determined from a plot of log η against $1/T$ since Eyring (2) has shown that:

$$\eta = Be^{\Delta E^{\ddagger}_{vis}/RT}$$

where B is a constant and $\Delta E^{\ddagger}_{vis}$ is the activation energy for viscous flow.

Employing the concept of internal pressure Gee (27) has shown that the activation energy for viscous flow $\Delta E^{\ddagger}_{vis}$ is related to the activation volume $\Delta V^{\ddagger}_{vis}$ for the process by the following equation:

$$\frac{\Delta E^{\ddagger}_{vis}}{\Delta V^{\ddagger}} = \left[\frac{\partial u}{\partial v}\right]_T$$

It has been generally observed (28)(29) that activation energies for viscous flow are usually larger than the corresponding activation energies for dielectric relaxation. This holds both for dilute solutions of polar molecules in non-polar solvents and for pure liquids. The effect of the larger activation energy for the viscosity process is to increase the activation volume relative to that for dielectric relaxation in support of the suggestion that viscosity processes involve both translation and rotation of molecules, whereas

dielectric relaxation involves only rotational motions.

Sinha, Roy and Kastha (30) have measured the dielectric relaxation times and the viscosity of solutions of some rigid polar molecules in hexane, benzene, and carbon tetrachloride at a number of temperatures. From the data obtained, they calculated the activation energies for viscous flow and dielectric relaxation. The corresponding activation volumes have been evaluated from these data are given in Table (3.5) (See Table 3.5).

It is seen that in all cases the activation volume for viscous flow is greater than that for the dielectric relaxation process. The latter is seen to be approximately the same for solutions in benzene and carbon tetrachloride. For hexane solutions, however, bromobenzene and m-dichlorobenzene have higher activation volumes than in the other two solvents. Chlorobenzene, however, has the same activation volume in all three solvents. Since hexane has the smallest internal pressure of the three solvents, any small error in $\Delta E_{\varepsilon}^{\ddagger}$ will produce a correspondingly larger increase in $\Delta V_{\varepsilon}^{\ddagger}$ hence, the hexane volumes will be subject to larger errors which could account for the discrepancy.

When the activation volumes for the three monohalobenzenes in carbon tetrachloride solution in table 3.5 are compared, it is seen that $\Delta E_{\varepsilon}^{\ddagger}$ and $\Delta V_{\varepsilon}^{\ddagger}$ increase as the size of the molecule increases,

TABLE 3.5

ACTIVATION ENERGIES and VOLUMES FOR SOME RIGID MOLECULES.

Solute	Solvent	$\Delta E^{\ddagger}_{\varepsilon}$ (Kcal mole⁻¹)	$\Delta E^{\ddagger}_{vis}$ (Kcal mole⁻¹)	$\Delta V^{\ddagger}_{\varepsilon}$ (cc mole⁻¹)	$\Delta V^{\ddagger}_{vis}$ (cc mole⁻¹)
Fluorobenzene	CCl$_4$	0.7	2.4	10.4	32.9
Chlorobenzene	Hexane	0.6	1.8	12.2	35.5
"	Benzene	1.0	2.5	11.8	30.2
"	CCl$_4$	0.9	2.4	12.1	32.9
Bromobenzene	Hexane	1.5	1.8	29.7	35.5
"	Benzene	1.5	2.5	18.0	30.2
"	CCl$_4$	1.5	2.4	19.7	32.9
m-Dichlorobenzene	Hexane	1.7	1.8	32.4	35.5
"	Benzene	2.0	2.5	23.9	30.2
"	CCl$_4$	1.5	2.4	20.5	32.9

TABLE 3.5 continued.

Solute	Solvent	$\Delta E^{\ddagger}_{\varepsilon}$ Kcal mole^{-1}	$\Delta E^{\ddagger}_{vis}$ Kcal mole^{-1}	$\Delta V^{\ddagger}_{\varepsilon}$ cc mole^{-1}	$\Delta V^{\ddagger}_{vis}$ cc mole^{-1}
o-Dichlorobenzene	Benzene	1.8	2.5	21.6	30.2
	CCl$_4$	1.4	2.4	18.6	32.9
α-Chloronaphthalene	Benzene	1.4	2.5	15.7	30.2
"	CCl$_4$	1.4	2.4	19.2	32.9

indicating that the volumes swept out by the molecules in their re-
orientation process increase as the molecular size increases.

Davies and Edwards (21) have observed a similar linear relation-
ship between the activation energy for the reorientation process and
the volume swept out by the molecule for four polar molecules dispersed
in a polystyrene matrix. In view of this correlation, it was decided
to examine the relation between these two p$\overset{a}{\Lambda}$rameters for some dilute
solutions of rigid aromatic molecules in p-xylene measured by Hassell
(22), and Mountain (32), in this laboratory.

The volumes swept out by the dipole rotating through 180° about
the two axes perpendicular to the molecular moment, corresponding to
in-plane and out-of-plane rotations, were calculated. Since the point
about which the molecules rotate is unknown, volumes were calculated
for rotation about the centre of mass, the centre of symmetry, and the
centre of the aromatic ring, of the molecules. The volumes of re-
volution were assumed to be cylinders. For rotation about points
other than the centre of symmetry, the swept volume is composed of
two half-cylinders, the radii of which were taken to be the maximum
lengths of the molecule in each direction from the point of rotation,
and the cylinder lengths to be the length of the molecule in the
direction parallel to the axis of rotation (fig. 3.12). All di-
mensions used in these calculations were taken either from Courtauld

FIG 3.12 VOLUME SWEPT OUT BY A ROTATING MOLECULE.
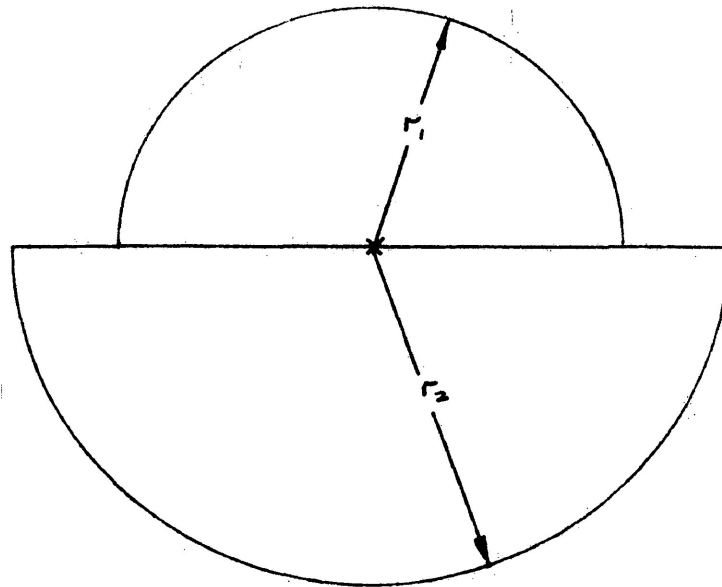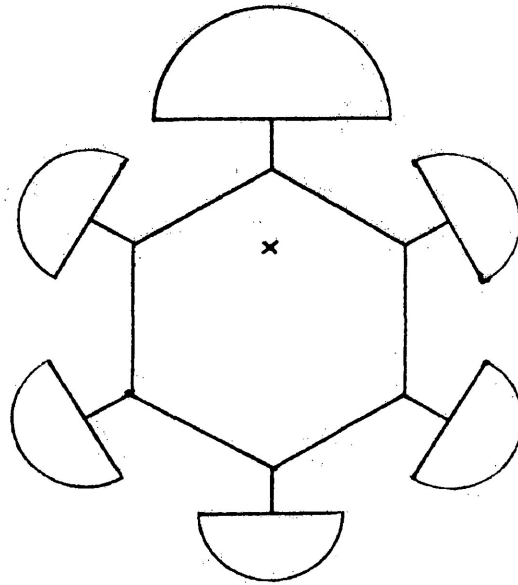
molecular models or scale drawings constructed from known bond

lengths and van der Waal's (91) radii. The volumes are not con-

sidered to be more accurate than $\pm$ 10%. Graphs were plotted of

activation energy against rotational volume about the X axis V_x,

the Y axis V_Y and the mean volume, $V_{mean} = V_x + V_Y/2$, for rotation

about the three centres. Activation energies are considered no

more accurate than ±0.3 kcal. mole^{-1}. Figs. 13, 14 and 15 show

V_{mean} again $\Delta E_\epsilon^{\ddagger}$ for rotation about the three points considered.

In all cases it was found that p-chlorotoluene fell off the plots.

As this molecule is intermediate in size, between iodobenzene and

p-bromotoluene, both of which fall on the plots, it will be assumed

that its activation energy is subject to a larger error. In general,

the plots for rotation about the X axis were not as satisfactory as

those for the mean volume and Y axis volume. For rotation of the

X axis about the three points, it was found in all cases that o-

diiobenzene and m-diiodobenzene fell off the plots in addition to

p-chlorotoluene. However, these two compounds fell on the plots for

the mean volume and Y axis rotational volume.

From the figures it can be seen that there is, within the limits

of measurement, a linear relationship between volume swept out and the

activation energy. This supports the hypothesis that the energy barrier

has its origins in the work done by the solute in displacing its

FIG 3.13 ACTIVATION ENERGY -VS- MEAN VOLUME SWEPT
OUT BY ROTATION ABOUT THE MOLECULAR
CENTRE OF SYMMETRY.
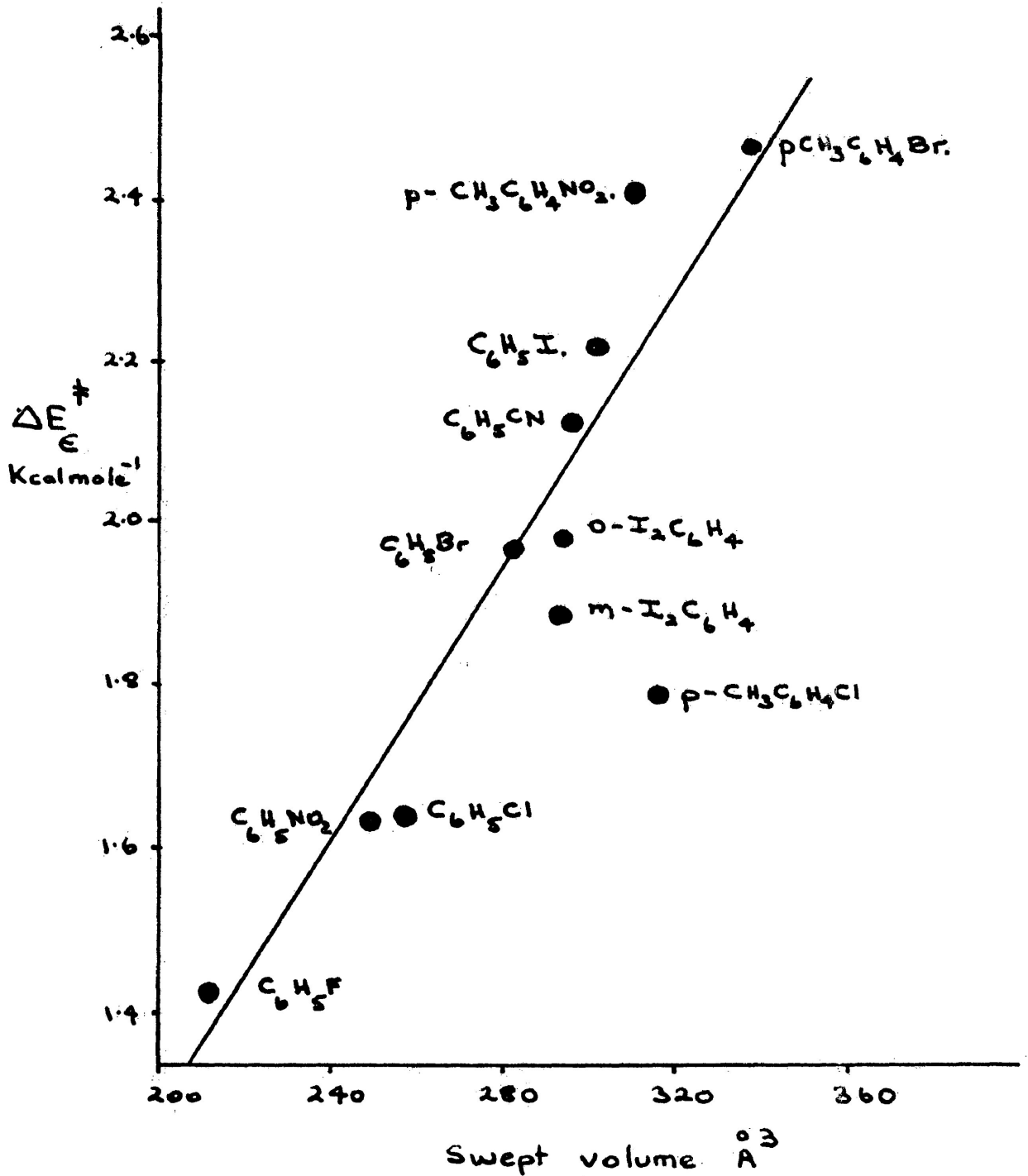
Fig 3.14. Activation energy -vs- mean volume swept out by rotation about the centre of the aromatic ring.
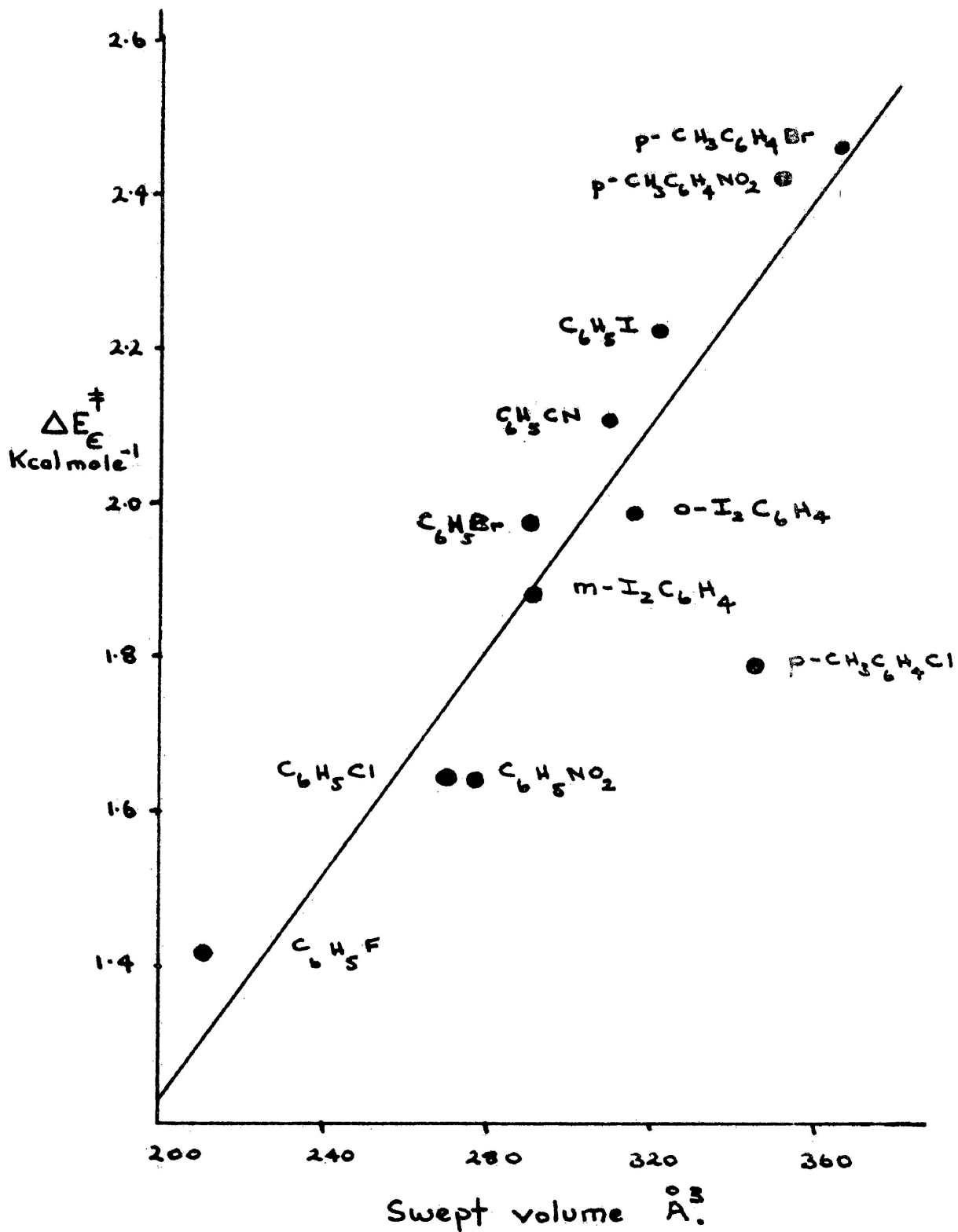
FIG 3.15 ACTIVATION ENERGY-VS- MEAN VOLUME SWEPT OUT BY ROTATION ABOUT THE MOLECULAR CENTRE OF MASS.
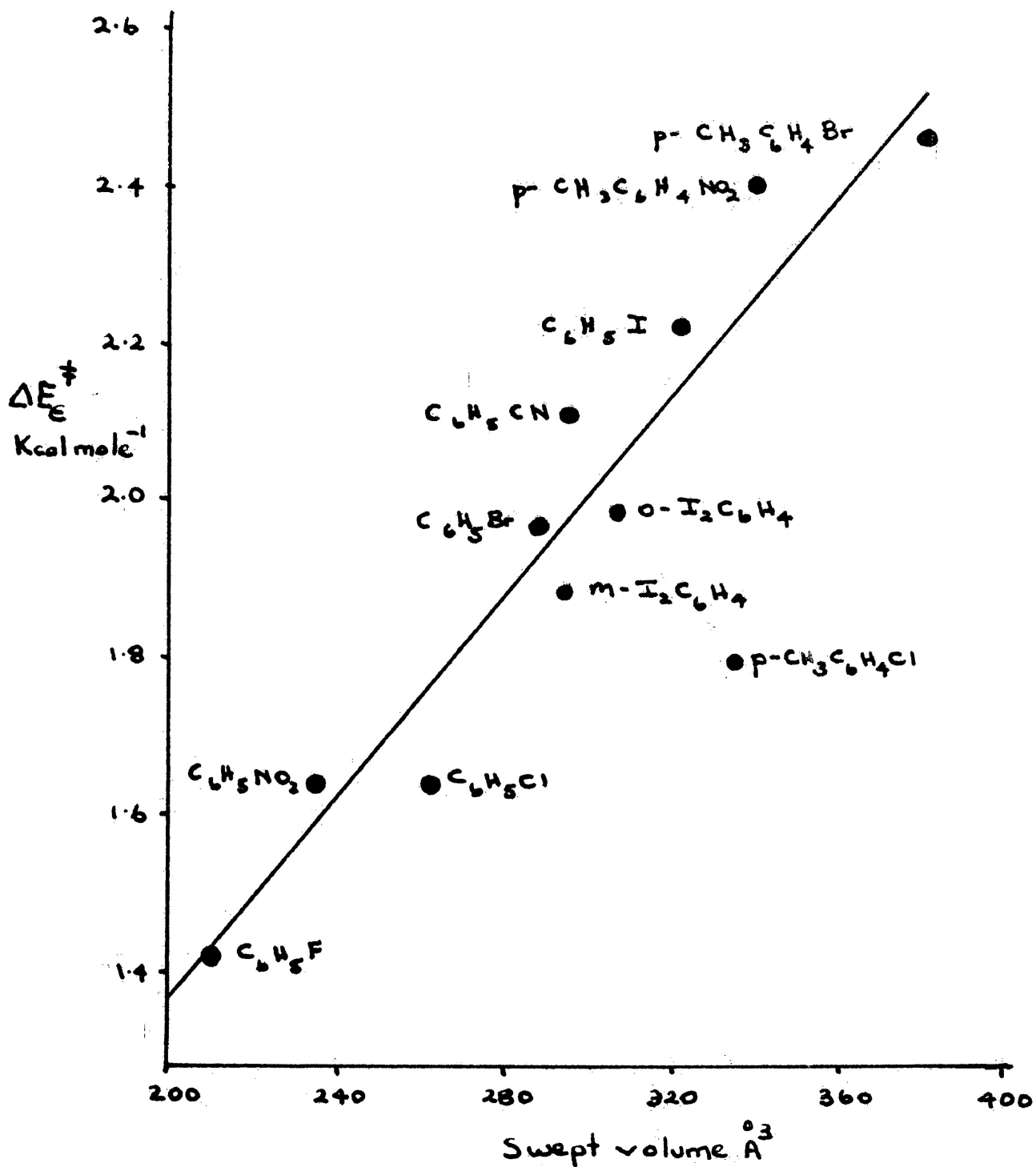
solvent environment. Based on this data alone, however, it is impossible to determine about which of the three centres the molecule rotates in solution. It is useful, however, to compare the activation volumes with the mean volumes swept out by the molecules rotating about the three centres. These data are given in table (3.6). (See Table (3.6)).

The activation volume is seen to be considerably smaller than the calculated volumes swept out. In fact, the average ratio $V_{swept\ out}/V_{\varepsilon}^{\ddagger}$ for rotation about three points considered is of the order 6.8 ± 1. As the swept volumes were calculated for rotation of the dipole through an angle of 180°, this ratio suggests that the molecules rotate through a relatively small angle during their re-orientation. It thus appears that when the molecule jumps from one equilibrium position of orientation to another, this involves a small change in the position of the molecule relative to the initial position.

^{r} Although table (3.6) shows the activation energy to increase as the size of the molecule increases in a particular series, it cannot be expected to increase beyond a certain limit, for, as the activation volume for a mole of solute approaches the molar volume of the solvent, the activation energy for the reorientation process will approach the heat of vaporization of the solvent.

The solvents commonly used in dielectric relaxation studies

TABLE (3.6)

COMPARISON OF ACTIVATION VOLUME WITH MEAN VOLUMES

SWEPT OUT ABOUT THE THREE CENTRES OF ROTATION.

Solute	Activation Energy $E_{\varepsilon}^{\ddagger}$ Kcal mole^{-1}	Activation Volume $\Delta V_{\varepsilon}^{\ddagger}$ cc mole	Mean Swept Volume cc mole^{-1}		
			Centre of mass V_{CM}	Centre of Symmetry V_{CS}	Centre of ring V_{CR}
Fluorobenzene	1.4	18.5	126.5	126.5	127.1
Chlorobenzene	1.6	21.3	158.4	154.8	162.6
Bromobenzene	2.0	25.6	173.5	169.8	175.3
Iodobenzene	2.2	28.9	193.9	181.9	194.0
Nitrobenzene	1.6	21.3	141.5	151.2	166.2
Benzonitrile	2.1	27.4	178.3	178.3	186.7
p-Chlorotoluene	1.8	23.3	202.4	190.3	208.4
p-Bromotoluene	2.5	32.0	229.5	203.0	220.4
p-Nitrotoluene	2.4	31.3	204.8	186.1	212.0
o-Diiodobenzene	1.9	25.8	184.9	176.5	190.3
m-Diiodobenzene	2.0	24.5	177.1	176.5	175.3

have heats of vaporization of the order of 8 - 10 Kcals.mole^{-1}.

Activation energies for the molecular reorientation process, however, rarely seem to exceed 3Kcal.mole^{-1} for dilute solutions. Again this would suggest that the activation volume is small compared to the volume of the solvent molecules. When the solvent is nujol, which is composed of a mixture of large molecules, the activation energies are often (33)(34) found to be much higher than those observed for the solvents having smaller-sized molecules.

Powell, Roseveare, and Eyring (38) have found that the heats of activation for viscous flow are of the order of 1/4 to 1/3 of the heat of vaporization of the liquid. For non-polar unassociated liquids, the molecules of which have approximate spherical symmetry, the ratio is close to 1/3, but for polar molecules, and others differing from spherical symmetry, e.g. long chain hydrocarbons, the factor is closer to 1/4. It then follows from this observation that the activation volume for viscous flow is of the order of 1/3 to 1/4 of the molar volume of the liquid.

No such simple relationship would seem to exist for dielectric relaxation activation energies for dilute solutions. From the data given in Table 3.6 it was seen that within the limited series examined the activation volume increased as the size of the solute

molecule increased. Consequently, the ratio of the heat of vapori-
zation of the solvent to the activation energy for dipole relaxation
decreases as the size of the solute increases.

A further comparison of dielectric activation parameters and
molecular volume functions is given in Table (3.7). The molecular
volumes were calculated by the method of Edward for an Avagadro number
of molecules; swept out volumes are mean values, as defined previously,
for rotation of the dipole about the molecular centre of symmetry
through an angle of 180°. (See Table 3.7).

Although the size of all these molecules is larger than the
benzene derivatives given in Table (3.6), it appears that the acti-
vation volumes and energies are similar. For the steroids the
androstane derivatives have smaller molecular volumes and smaller
volumes swept out in comparison to the cholestane derivatives. The
two steroids which have their dipoles inclined to the long axis of the
ellipsoid have the smaller volumes swept out because of the symmetry of
the molecules about this axis. Rotation about an axis perpendicular to
the long axis sweeps out a much larger volume than rotation about the
long axis. Activation energies for these compounds are not considered
to be more accurate than ± 0.5 Kcal mole^{-1} which gives an error of
± 7cc mole^{-1} in the activation volume. For these compounds the acti-
vation energy is then approximately constant. Similarly, the activation
volume shows little variation from one molecule to another, but the
volume swept out increases in the order 5α-androstan-3:17-dione <

TABLE 3.7

ACTIVATION ENERGIES, ACTIVATION VOLUMES, MOLECULAR VOLUMES

AND VOLUMES SWEPT OUT FOR A NUMBER OF RIGID MOLECULES.

Solute	Solvent	$\Delta E^{\ddagger}_{\epsilon}$ (Kcal mole⁻¹)	$\Delta V^{\ddagger}_{\epsilon}$ (cc mole⁻¹)	Molecular Volume (cc mole⁻¹)	Swept Volume (cc mole⁻¹)	Ref.
α-Fluoronaphthalene	Benzene	1.6	19.1	80.1	157	35
Anthrone	Benzene	2.1	25.0	109	186	36
Phenanthrene quinone	Benzene	2.6	31.0	113	227	36
Tetracyclone	P-xylene	2.4	31.0	223	725	This work
Heptaphenyl chlorophenyl porphyrazine	Benzene	2.5	30.0	530	1894	37
Ferric Octaphenyl porphyrazine chloride	Benzene	2.6	31.0	540	2163	37

TABLE 3.7 continued.

ACTIVATION ENERGIES, ACTIVATION VOLUMES, MOLECULAR VOLUMES AND VOLUMES SWEPT OUT FOR A NUMBER OF RIGID MOLECULES.

Solute	Solvent	$\Delta E^{\ddagger}_{\varepsilon}$ Kcal mole^{-1}	$\Delta V^{\ddagger}_{\varepsilon}$ cc mole^{-1}	Molecular Volume cc mole^{-1}	Swept Volume cc mole^{-1}	Ref.
5α-Androstan-3:17-dione	P-xylene	2.6	34.0	170	265	This work
5α-Androstan-3-one	P-xylene	2.7	35.0	166	341	=
Δ³,⁵ Cholestadiene-7-one	P-xylene	2.5	33.0	245	520	"
5α Cholestan-3-one	P-xylene	1.8	23.0	251	775	

5α-androstan-3-one $< {}^{3,5}\Delta$ cholestadiene-7-one $<$ 5α-cholestan-3-one.

These data indicate that the angle through which the dipole rotates decreases in the same-order as the volume swept out increases.

A similar situation is found for the first six molecules of the table which are flat and disc-like in shape. When the two ring naphthalene structure is compared to the three ring anthrone, both an increase in activation energy and volume swept out is observed. A similar increase is found for the two molecules, anthrone, and phenanthrene quinone. In this case, however, the molecular volume increases slightly, whereas the increase in the volume swept out is almost as large as going from α-fluoronaphthalene to anthrone. The three remaining disc-like molecules have similar activation volumes to phenanthrene quinone but considerably larger volume swept out. Thus, for these molecules, the activation volume becomes a decreasing fraction of the volume swept out and the size of the angle through which the dipole jumps appears to decrease in the order: fluoronaphthalene $\simeq$ anthrone $\simeq$ phenanthrene quinone $>$ tetracyclone $>$ heptaphenylchlorophenyl porphyrazine $>$ ferric octaphenylporphyrazine. chloride.

The ratio of activation volume to volume swept out by the molecule in rotating through 180° should give the approximate angle through which the molecule has jumped. This is shown in Table (3.8)

TABLE 3.8

APPARENT ROTATIONAL ANGLE OF VARIOUS MOLECULES.

Solute	Solvent	Apparent rotational Angle.
α-Fluoronaphthalene	Benzene	22°
Anthrone	Benzene	24°
Phenanthrenequinone	Benzene	26°
Tetracyclone	P-xylene	7.7°
5α-Androstan-3:17-dione	P-xylene	23°
5α-Androstan-3-one	P-xylene	18°
3,5-Δ-Cholestadiene-7-one	P-xylene	11.4°
5α-Cholestan-3-one	P-xylene	5.3°
Heptaphenylchlorophenyl porphyrazine	Benzene	2.9°
Ferric octaphenyl porphyrazine chloride	Benzene	2.6°

For the first ~~six~~ *five* molecules the apparent angle of rotation is approximately constant. However, when the molecular size increases and the volume swept out increases, the angle becomes very much less. For the last four molecules the angle is very small and similar to what might be expected for Brownian rotation diffusion. Hence, when the volume swept out becomes sufficiently large to make the apparent rotational angle small, the jump mechanism approaches the Brownian rotational diffusion model assumed by Debye.

In conclusion it would seem that dielectric relaxation processes can be best explained in terms of a model in which the dipole jumps over an energy barrier which separates two equilibrium positions of orientation. The energy of activation of the molecules, obtained by molecular collision, is expended in doing work against the internal pressure of the molecules surrounding the relaxing unit. Such a model is able to predict the effect of solvent on the relaxation time of a molecule, except when the solvent is carbon-tetrachloride. A study of the variation of relaxation time with the solvent and construction of a log τ-Pi plot can give useful information on the possible existence of specific solute-solvent interactions.

When the polar solute is sufficiently large and its dipole is located such that it sweeps out a large volume of solvent during the course of its rotation, then the apparent angle through which it jumps is small and its behaviour approaches that of the Brownian rotational diffusion model assumed by Debye.

CHAPTER   THREE

APPENDIX

Introduction

In view of the good correlation found between internal pressure and log γ for dilute solutions of polar molecules in non-polar solvents it was decided to examine this relationship for some pure liquids.

Discussion

It was found that compounds which constituted an homologous series all fell on the same line of the log γ -Pi plot. The plots are shown in figures 3A, 3B, 3C, and 3D.

Fig. 3A shows the plots for the n-alkylhalides. The non-linearity of these is not perhaps surprising in view of the complex behaviour of these molecules. It is seen that when the halogen atom is changed from chlorine to bromine to iodine different curves result. From Fig. 3B it is seen that the position of the halogen atom is changed or a methyl group is substituted into the side chain then such molecules deviate from the curve through the n-alkyl compounds. Hence, compounds only appear to fall on a particular line when they are chemically and structurally similar.

When the plot for the alkyl substituted aromatic compounds, Fig. 3C, is compared with that for the halogen derivatives, Fig.3D, it is seen that the slope of the former is negative. Similarly, except in the case of the n-alkyl chlorides, negative slopes are obtained for the alkyl halides. The apparent negative activation volume may indicate that in the activated state a decrease of the volume of the system occurs, indicating that the molecules are more closely packed in this state. However, the sign of the slope may be of no absolute significance since it merely indicates the relative rate at which molar volume and heat of vaporisation change within a series of compounds. Thus, if the molar volume increases , in a series, at a greater rate than the heat

FIG 3A log γ - Pi PLOT FOR n-ALKYL HALIDES IN THE PURE LIQUID STATE
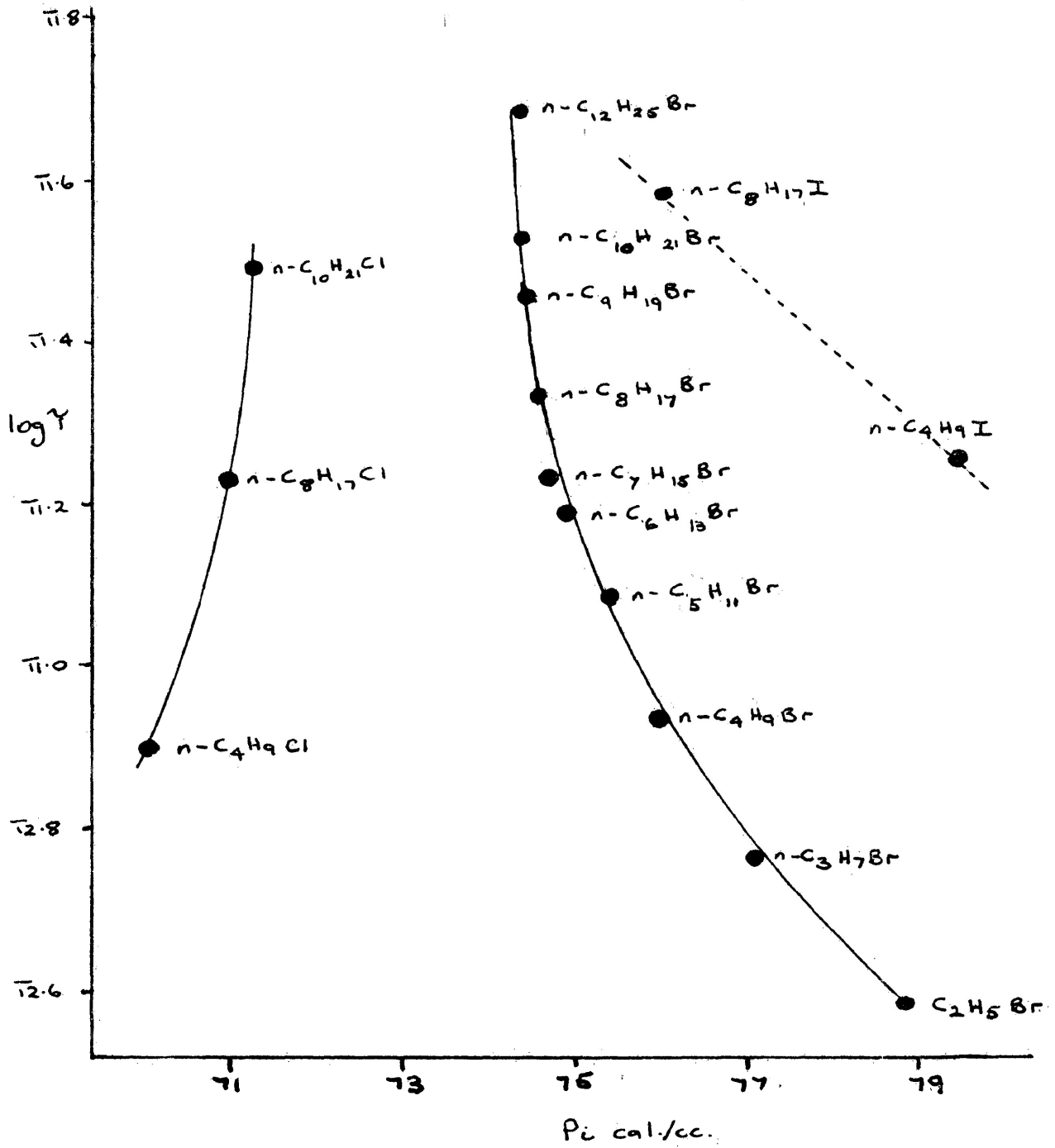
FIG 3B LOG γ - Pi PLOT FOR SOME ALIPHATIC HALOGENS IN THE PURE LIQUID STATE

n-alkyl bromides

C_{12}

$\bar{1}1.6$

C_8

C_{10}

C_{12}

C_9 n-alkyl iodides

$\bar{1}1.4$

n-alkyl chlorides

C_8

C_8

C_4

C_7

$\bar{1}1.2$

C_8

C_6

$\log \gamma$

C_5

$\bar{1}1.0$

Cl(CH$_2$)$_9$Cl

C_4

C_4

CH$_3$CH$_2$CCl(CH$_3$)$_2$

ClCH$_2$CH$_2$Cl

CH$_3$CBr(CH$_3$)$_2$

$\bar{1}2.8$

CH$_3$CCl$_2$CH$_3$

CBr$_3$F

C_3

CH$_3$CHBrCH$_3$

CH$_3$CCl(CH$_3$)$_2$

$\bar{1}2.6$

CBr$_2$Cl$_2$

CBrCl$_3$

$\bar{1}2.4$

CBr$_2$F$_2$

CCl$_3$F C_2

60   70   80   90   100

Pi cal./cc.
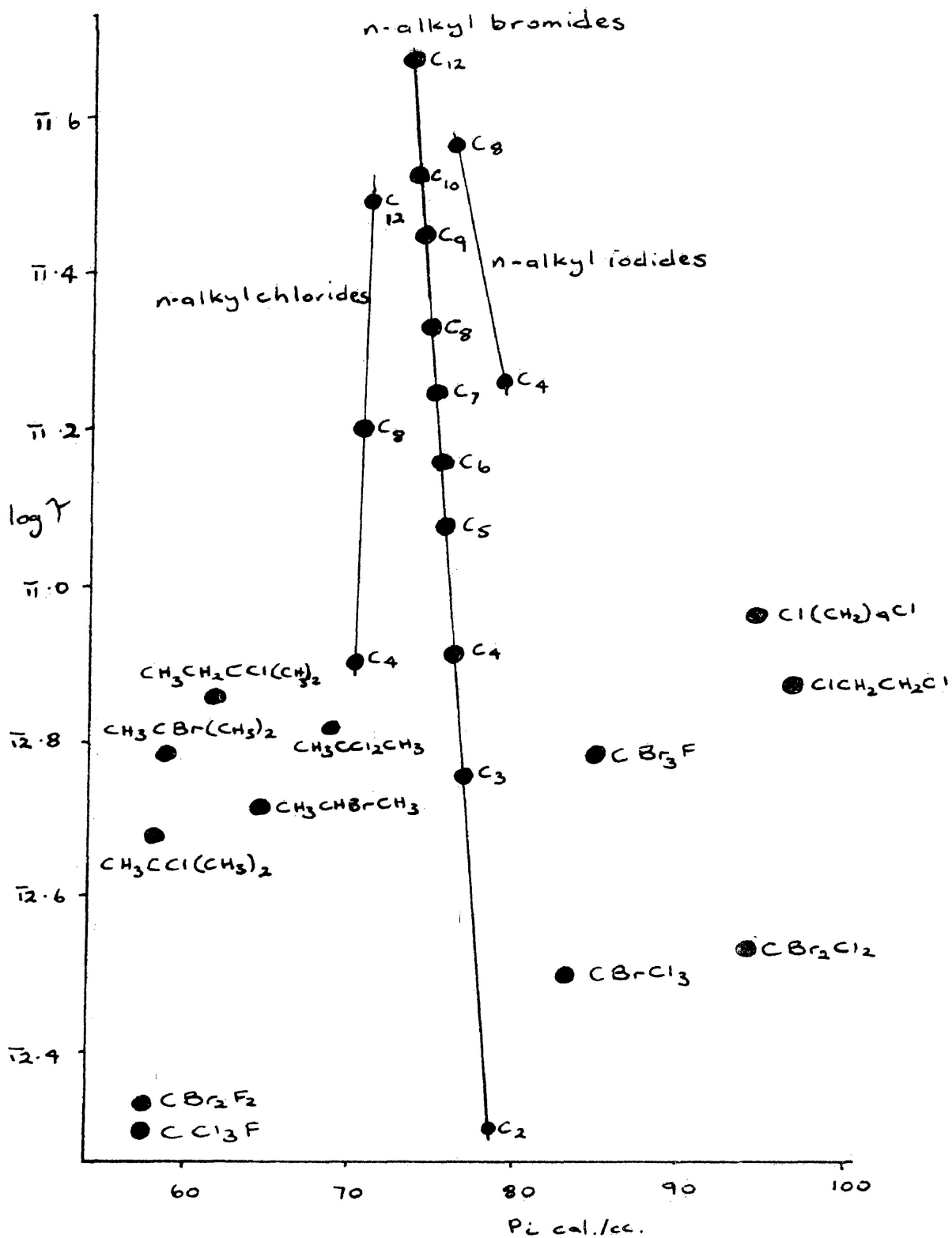
FIG 30 LOG γ-Pι PLOT FOR SOME SUBSTITUTED AROMATIC MOLECULES IN THE PURE LIQUID STATE
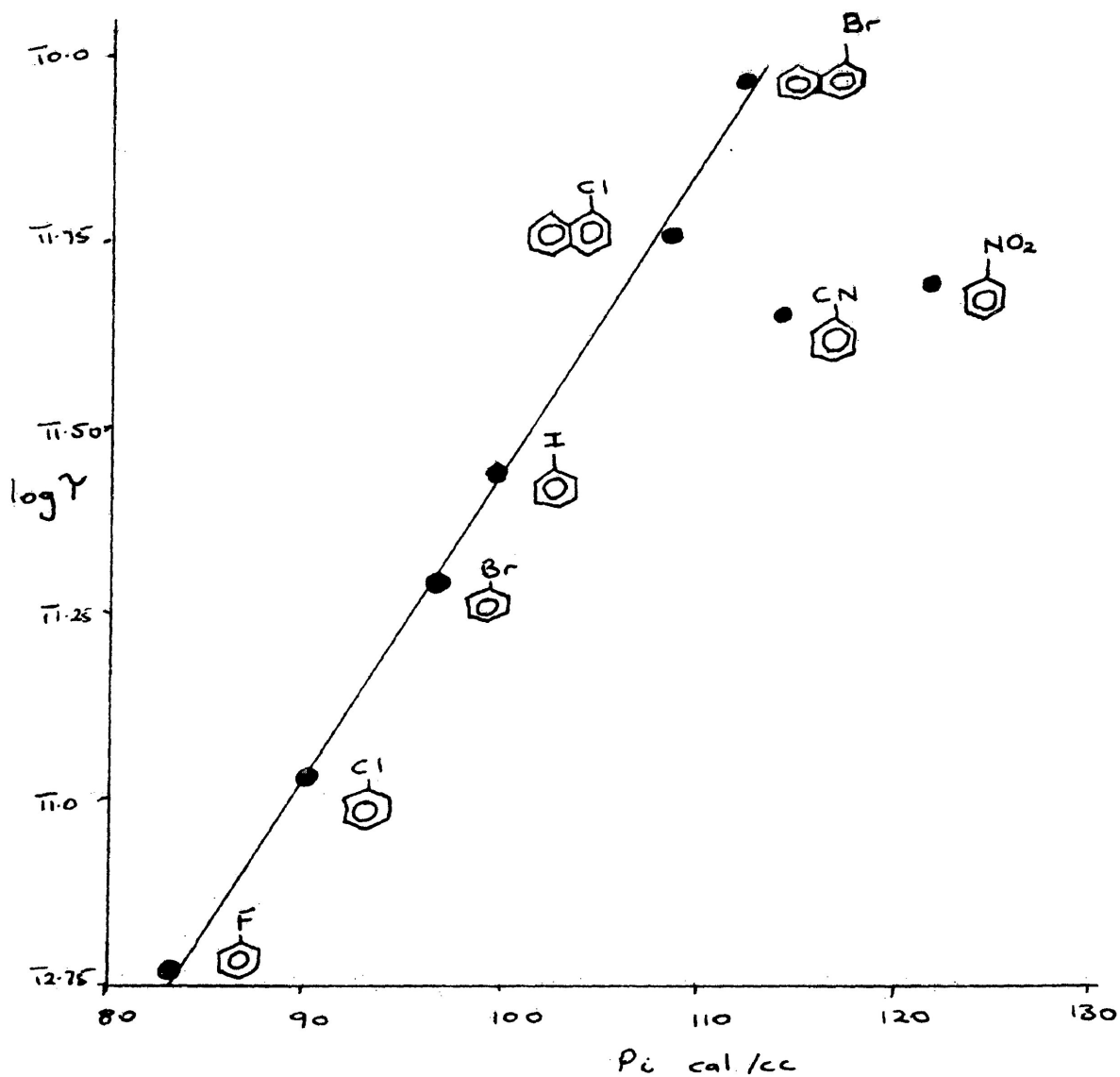
FIG 3c Log. γ-P_i PLOT FOR SOME AROMATIC HYROCARBONS IN THE PURE LIQUID STATE.
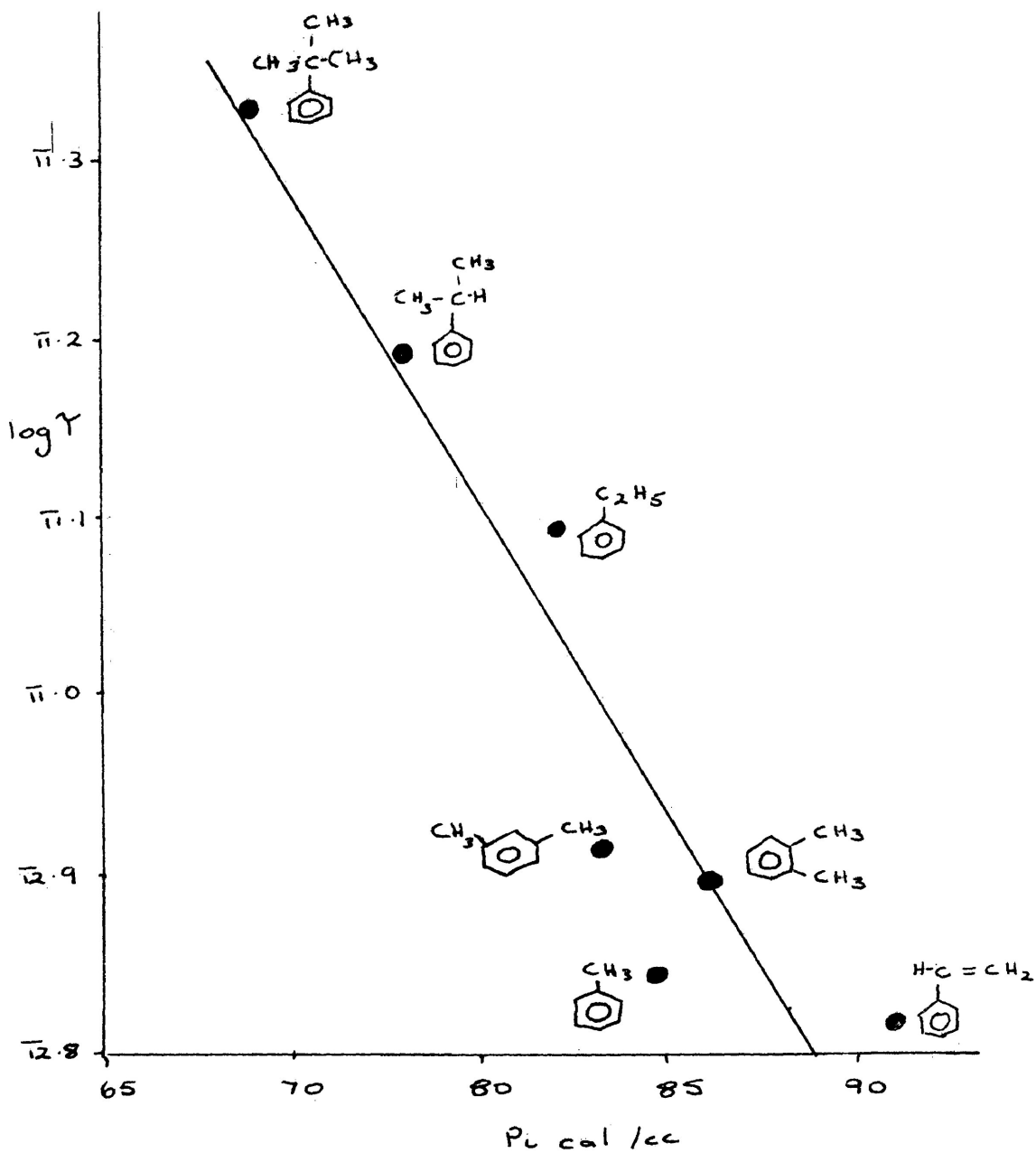
of vaporisation then the internal pressure decreases as the molecular

size increases, and a negative slope is obtained.

That such regular plots are obtained, for the pure liquids

examined, again supports the hypothesis that the barrier to the

rotation of the molecules is due to the work done against the internal

pressure of the medium.

Bhanumathi (40) measured the activation energies for dielectric

relaxation of a number of pure liquids and accounted for the energy

barriers in terms of dipole - dipole interactions. She considered

only Keesom and Debye forces and neglected any contribution from

dispersion forces.

Equations 3A and 3B give the interaction energies for Keesom

E_K and Debye, E_D, terms:

$$E_K = \frac{2}{3} \quad \frac{\mu^4}{r^6 kT} \qquad \text{3A}$$

$$E_D = -2 \quad \frac{\alpha \mu^2}{r^6} \qquad \text{3B}$$

the symbols have the same meaning as for the interaction terms

described previously. Bhanumathi determined the activation energy

from the slope of a log Υ T against 1/T plots. She found that such

plots were linear indicating $\Delta E_{\varepsilon}^{\ddagger}$ to be independent of temperature.

However, examination of the above equations for the interaction terms

shows that E_K is temperature dependent. Furthermore, r will be

expected to change with temperature hence, the agreement between the

measured and calculated values would seem to be somewhat fortuitous.

Both Keesom and Debye terms account for dipole - dipole

interactions , however, Fröhlich (10) has stated that if the dipolar

particles are interacting with one another that an exponential rate

of decay of polarisation will not be observed. This follows from equation

(3.8). If the particles are interacting with one another the transition

probability $W_{ij}^{P_{ij}}$ depends on the number of particles in the equilibrium

position Ni. Under such circumstances 3.8 is non-linear and cannot

be solved by exponential functions. A straight line relationship

between $\log \tau T$ and 1/T would not be observed when dipole - dipole inter-

action was present. As Bhanumathi obtained linear plots this refutes the

postulate that the energy barrier is due to the interaction which she

considered.

As the plots of $\log \tau$ against internal pressure are linear,

it would seem that a more reasonable explanation for the energy barrier

could be formulated in terms of the work done, by the reorienting unit,

against the internal pressure of the liquid.

Appendix

Experimental Results.

Dipole moment data

Solutions in p-xylene at 25°C

Solute	wt fraction	ε_o	n_D^2
$3,5\Delta$-Cholestadiene-7-one	0	2.263	2.229
	0.02798	2.401	2.2320
	0.04071	2.461	2.2350
	0.05089	2.509	2.2356
	0.06200	2.566	2.2372
	0.06988	2.602	2.2383
5α-Cholestan-3-one	0	2.263	2.2288
	0.01060	2.298	2.229
	0.02180	2.319	2.2293
	0.03184	2.344	2.2296
	0.04580	2.379	2.2302
	0.06246	2.425	2.2323
5α-Androstan-3:17-dione	0	2.263	2.2290
	0.01097	2.303	2.2299
	0.02142	2.337	2.2310
	0.03046	2.369	2.2320
	0.03726	2.393	2.2344
	0.04629	2.425	2.2344

Dielectric Constant and Loss Data

Solution	$T°C$	frequency GH_z	ε' meas.	ε'' meas.	ε' calc.	ε'' calc.
3,5Δ-Cholestadiene-7-one	25	35.22	2.275	0.008	2.270	0.008
p-xylene		23.98	2.259	0.011	2.271	0.010
$w_2 = 0.02798$		1.90	2.329	0.055	2.322	0.054
		1.30	2.345	0.056	2.341	0.055
		0.95	2.361	0.050	2.356	0.052
3,5Δ-Cholestadiene-7-one	25	35.22	2.279	0.012	2.285	0.007
p-xylene		23.98	2.175	0.016	2.285	0.011
$w_2 = 0.04071$		1.90	2.354	0.081	2.351	0.085
		1.30	2.385	0.080	2.384	0.087
		0.95	2.405	0.075	2.409	0.080
3,5Δ-Cholestadiene-7-one	25	35.22	2.273	0.016	2.278	0.013
p-xylene		23.98	2.285	0.019	2.279	0.019
$w_2 = 0.05089$		1.90	2.376	0.103	2.373	0.099
		1.30	2.411	0.099	2.408	0.100
		0.95	2.438	0.091	2.435	0.093

Solution	T°C	frequency GHz	ε' meas.	ε'' meas.	ε' calc.	ε'' calc.
$3,5_\Delta$-Cholestadiene-7-one	25	35.22	2.295	0.0198	2.276	0.017
p-xylene		23.98	2.225	0.022	2.278	0.023
$w_2 = 0.06210$		16.20	2.295	0.034	2.282	0.032
		1.90	2.401	0.116	2.386	0.116
		1.30	2.421	0.111	2.426	0.119
		0.95	2.482	0.119	2.458	0.114
$3,5_\Delta$-Cholestadiene-7-one	25	35.22	2.286	0.019	2.285	0.017
p-xylene		23.98	2.298	0.030	2.287	0.024
$w_2 = 0.06988$		1.90	2.420	0.138	2.406	0.134
		1.30	2.461	0.137	2.453	0.138
		0.95	2.501	0.128	2.491	0.131
$3,5_\Delta$-Cholestadiene-7-one	15	16.2	2.301	0.018	2.299	0.018
p-xylene		9.313	2.299	0.027	2.304	0.028
$w_2 = 0.04044$		1.90	2.354	0.074	2.357	0.072
		1.30	2.380	0.075	2.382	0.077
		0.95	2.401	0.076	2.403	0.076

Solution	T°C	frequency GHz	ε' meas.	ε'' meas.	ε' calc.	ε'' calc.
3,5$_\Delta$-Cholestadiene-7-one	37.5	16.2	2.262	0.023	2.262	0.022
p-xylene		9.313	2.265	0.033	2.269	0.034
w_2 = 0.04044		1.90	2.335	0.070	2.336	0.070
		1.30	2.362	0.067	2.359	0.067
		0.95	2.376	0.061	2.376	0.061
3,5$_\Delta$-Cholestadiene-7-one	50	16.20	2.244	0.025	2.241	0.024
p-xylene		9.313	2.248	0.035	2.249	0.036
w_2 = 0.04044		1.90	2.323	0.065	2.318	0.065
		1.30	2.340	0.061	2.340	0.061
		0.95	2.355	0.054	2.354	0.053
5α-Cholestan-3-one	15	35.22	2.283	0.007	2.291	0.005
p-xylene		16.20	2.298	0.013	2.292	0.010
w_2 = 0.06246		1.90	2.327	0.045	2.320	0.046
		1.30	2.344	0.056	2.334	0.054
		0.95	2.354	0.060	2.349	0.060

Solution	T°C	frequency GHz	ε' meas.	ε'' meas.	ε' calc.	ε'' calc.
5α-Cholestan-3-one	25	35.22	2.279	0.008	2.276	0.006
p-xylene		16.20	2.285	0.015	2.278	0.010
w$_2$ = 0.06246		9.313	2.280	0.019	2.281	0.016
		1.90	2.313	0.046	2.308	0.047
		1.30	2.329	0.055	2.323	0.054
		0.95	2.343	0.060	2.338	0.058
5α-Cholestan-3-one	37.5	35.22	2.257	0.008	2.254	0.007
p-xylene		16.20	2.263	0.015	2.256	0.012
w$_2$ = 0.06246		1.90	2.296	0.051	2.292	0.049
		1.30	2.307	0.053	2.308	0.055
		0.95	2.324	0.059	2.323	0.058
5α-Cholestan-3-one	50	35.22	2.239	0.008	2.238	0.007
p-xylene		16.20	2.245	0.014	2.240	0.012
w$_2$ = 0.06246		1.90	2.277	0.048	2.277	0.047
		1.30	2.297	0.050	2.293	0.051
		0.95	2.310	0.053	2.307	0.052

Solution	T°C	frequency GHz	ε' meas.	ε'' meas.	ε' calc.	ε'' calc.
5α-Androstan-3-one	37.5	35.22	2.270	0.011	2.267	0.008
p-xylene		23.98	2.271	0.017	2.267	0.012
$w_2 = 0.03460$		16.20	2.267	0.024	2.269	0.017
		1.90	2.338	0.052	2.337	0.049
		1.30	2.354	0.043	2.352	0.041
		0.95	2.362	0.036	2.360	0.033
5α-Androstan-3-one	50	35.22	2.248	0.010	2.255	0.009
p-xylene		23.98	2.249	0.014	2.256	0.012
$w_2 = 0.0346$		16.20	2.246	0.020	2.259	0.018
		1.90	2.320	0.043	2.323	0.039
		1.30	2.332	0.033	2.333	0.031
		0.95	2.338	0.028	2.338	0.024
5α-Androstan-3:17-dione	15	35.22	2.294	0.013	2.299	0.012
p-xylene		23.98	2.312	0.022	2.301	0.017
$w_2 = 0.04629$		16.20	2.317	0.026	2.303	0.025
		1.90	2.397	0.071	2.396	0.070

Solution	T°C	frequency GHz	ε' meas.	ε" meas.	ε' calc.	ε" calc.
		1.30	2.421	0.061	2.417	0.060
		0.95	2.430	0.050	2.430	0.049
5α-Androstan-3:17-dione	25	35.22	2.287	0.016	2.283	0.014
p-xylene		23.98	2.298	0.021	2.285	0.020
w₂ = 0.04629		16.20	2.302	0.028	2.289	0.028
		1.90	2.383	0.062	2.382	0.061
		1.30	2.403	0.052	2.399	0.050
		0.95	2.410	0.043	2.409	0.041
Tetracyclone	60	9.313	2.217	0.011	2.217	0.011
p-xylene		6.98	2.221	0.015	2.218	0.015
w₂ = 0.0236		1.90	2.244	0.033	2.420	0.033
		1.30	2.256	0.032	2.255	0.033
		1.10	2.263	0.031	2.260	0.031
		0.95	2.265	0.029	2.265	0.028

Solution	T°C	frequency GHz	ϵ' meas.	ϵ'' meas.	ϵ' calc.	ϵ'' calc.
Tetracyclone	50	9.313	2.234	0.010	2.233	0.010
p-xylene		6.98	2.234	0.014	2.235	0.013
$w_2 = 0.02360$		1.90	2.255	0.031	2.255	0.031
		1.30	2.269	0.033	2.266	0.033
		0.95	2.279	0.032	2.278	0.031
5α-Androstan-3-one	15	35.22	2.302	0.008	2.298	0.007
p-xylene		23.98	2.304	0.010	2.299	0.010
$w_2 = 0.03460$		16.20	2.297	0.0140	2.300	0.014
		1.90	2.357	0.056	2.356	0.059
		1.30	2.378	0.056	2.378	0.056
		0.95	2.395	0.049	2.392	0.049
5α-Androstan-3-one	25	35.22	2.290	0.010	2.289	0.007
p-xylene		23.98	2.297	0.015	2.289	0.011
$w_2 = 0.03460$		16.20	2.285	0.024	2.290	0.015
		1.90	2.349	0.056	2.354	0.055
		1.30	2.366	0.050	2.372	0.048
		0.95	2.379	0.045	2.383	0.039

Solution	T°C	frequency GHz	ϵ' meas.	ϵ'' meas.	ϵ' calc.	ϵ'' calc.
5α-Androstan-3:17-dione	37.5	35.22	2.272	0.020	2.263	0.018
p-xylene		23.98	2.275	0.023	2.266	0.024
w_2 = 0.04629		16.20	2.281	0.034	2.272	0.032
		1.90	2.361	0.050	2.361	0.049
		1.30	2.378	0.043	2.373	0.040
		0.95	2.384	0.034	2.380	0.032
5α-Androstan-3:17-dione	50	35.22	2.249	0.018	2.241	0.018
p-xylene		23.98	2.260	0.027	2.244	0.025
w_2 = 0.04629		16.20	2.259	0.035	2.250	0.034
		1.90	2.331	0.044	2.337	0.042
		1.30	2.335	0.034	2.346	0.033
		0.95	2.344	0.027	2.351	0.026
5α-Androstan-3:17-dione	37.5	35.22	2.317	0.008	2.320	0.007
naphthalene p-xylene		23.98	2.320	0.011	2.321	0.010
w naphthalene = 0.2035		16.20	2.317	0.014	2.323	0.015
w_2 = 0.02725		1.90	2.378	0.033	2.373	0.033

Solution	T°C	frequency GHz	ε' meas.	ε'' meas.	ε' calc.	ε'' calc.
d = 0.8829 gcm.$^{-3}$		1.30	2.382	0.027	2.383	0.028
η = 0.681 C.P.		0.95	2.386	0.023	2.388	0.022
4_Δ-Androsten-3:11:17-trione	37.5	35.22	2.317	0.008	2.320	0.007
naphthalene-p-xylene		23.98	2.320	0.011	2.321	0.010
w naphthalene = 0.2035		16.20	2.317	0.014	2.323	0.015
w_2 = 0.0272		1.90	2.378	0.033	2.373	0.033
d = 0.8829 gcm.$^{-3}$		1.30	2.382	0.027	2.383	0.028
η = 0.681 C.P.		0.95	2.386	0.023	2.388	0.022
Tetracyclone	37.5	16.20	2.255	0.008	2.252	0.006
p-xylene		9.313	2.255	0.010	2.253	0.010
w_2 = 0.02360		1.90	2.271	0.032	2.273	0.032
		1.30	2.285	0.035	2.285	0.035
		0.95	2.295	0.036	2.297	0.035

Solution	T°C	frequency GHz	ϵ' meas.	ϵ'' meas.	ϵ' calc.	ϵ'' calc.
Tetracyclone	70	1.90	2.229	0.030	2.228	0.030
p-xylene		1.75	2.234	0.030	2.231	0.030
$w_2 = 0.0236$		1.60	2.239	0.030	2.234	0.030
		1.10	2.244	0.028	2.244	0.027
		0.90	2.248	0.025	2.248	0.025

Suggestions for Further Work

The dependence of relaxation time on internal pressure for a particular solute in a number of solvents was examined only for small solvent molecules. It would seem that further examination of this relationship for a wider range of solute and solvent sizes would be of value. In particular it would be valuable to study the relaxation times of solutes dissolved in the two decalin isomers. The number of large solvent molecules which are liquid at reasonable temperatures is not extensive but it may be practical to make measurements in liquid naphthalene and biphenyl.

When a sufficiently large frequency range becomes available it would be valuable to measure the steroids in other solvents. Measurements on solutions of these molecules in n-hexane, cyclohexane, methylcyclohexane, p-xylene, benzene and dioxane would give a reasonable range of internal pressure variation.

Little work seems to have been done in the solvent carbon disulfide, probably because of the objectionable nature of the compound, but, it has an internal pressure of the order of 100 cal cc^{-1}, and since the molecule is small such measurements may yield useful information.

No use has been made in this thesis of the intercepts of the $\log \Upsilon$ vs. Pi plots or the $\log \Upsilon T$ vs. $1/T$ plots. The reasons for this being this being that in the former case the absolute magnitudes of the relaxation times were in doubt and in the latter case greater coverage of the absorption range of the molecules would have been necessary in order to obtain more accurate Υ values. However, a comparison of the A factors from both the pressure and temperature plots would seem worthwhile and may provide valuable information on the

behaviour of molecules.

As several of the rate expressions discussed in Chapter 2 involve the moment of inertia in the pre-exponential factor accurate evaluation of the log plot intercepts, and attempts to correlate this with moments of inertia would seem to be of value. In this laboratory Mountain has found a correlation between the relaxation time and $\sqrt{I}$ which is suggestive.

If a relationship between A and the molecular moments of inertia can be found then information may be obtained on the axis about which the molecules rotate. Large molecules, with considerable differences in moments of inertia about different axes, would be suitable for such a study. The biphenyls would seem useful/ systems, since the position of the molecular moment can be varied, to cause rotation about different axes, and the moments of inertia should be considerably different for rotation about the long and short axes. All these factors, which contribute towards understanding the nature of the pre-exponential term of the rate equations, would assist in the understanding of the dielectric behaviour of polar molecules.

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